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EXPLORATORY AND MECHANISTIC PHENYLALLENE PHOTOCHEMISTRY:
PROTIC SOLVENT ADDITIONS, ISOMERIZATIONS, AND REACTIONS OF
PHOTOGENERATED RADICAL CATIONS

Iowa State University

Ph.D. 1986

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Exploratory and mechanistic phenylallene photochemistry:
Protic solvent additions, isomerizations,
and reactions of photogenerated radical cations

by

Michael W. Klett

A Dissertation Submitted to the
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Ames, Iowa

1986

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DEDICATION

To Barbara, my loving wife and toots

OVERALL INTRODUCTION

The photochemistry of allenes or 1,2-propadienes has received surprisingly little attention. This is despite the extensive study on the photoreactions of simple alkenes and 1,3-dienes. The objective of the present work was to explore the photoreactions of allenes in protic and aprotic solvents. A systematic study from which generalities could be deduced and used to predict the reaction of other allenes, required a fundamental series of allene substrates. The substrate chosen for this study consisted of tetraphenyl-, triphenyl-, diphenyl- and phenyl-allene; their reactions in protic and aprotic solvents are detailed in Chapters I and II, respectively. Reactions and mechanistic studies of photogenerated radical cations of allenes and propyne are presented in Chapter III.

CHAPTER I: PHOTOPROTONATION OF PHENYLALLENES

Introduction

The photochemistry of alkenes and 1,3-dienes have been extensively investigated during the past three decades, and comprehensive reviews of this subject are available (1). It has long been recognized that alkene excited states have a potential surface minimum in the vicinity of 90° twisting (Figure 1). Due to an avoided state crossing, the minimum is poised above a ground state surface minimum, thus providing a mechanism for radiationless decay and cis-trans isomerization. Photochemists had once regarded this excited state minimum as a biradical.

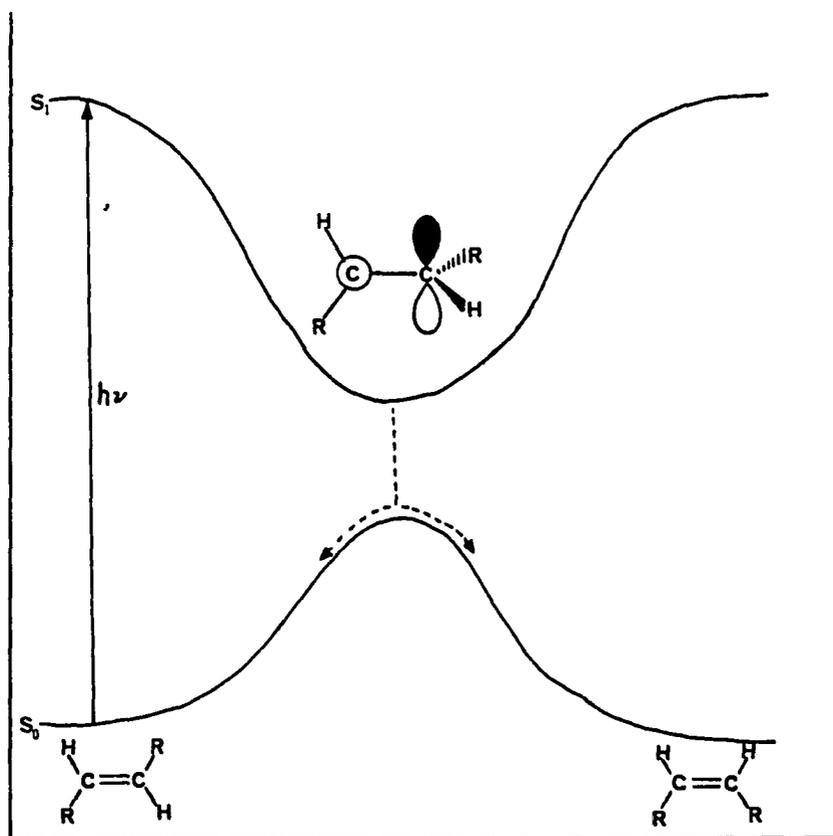
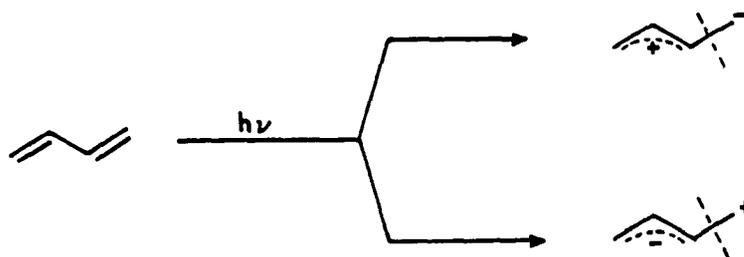


Figure 1. Singlet potential surface for twisting and bending in ethylene

Recent theoretical calculations by Salem (2), however, showed that singlet excited states of polyenes may rotate to a strongly polarized species (Scheme 1). This followed an earlier suggestion of Wulfman and Kumei (3). Salem had initially termed this phenomenon as "sudden polarization" because of its apparently instantaneous onset as a 90° twist is approached. Many theoretical studies (4) since then have



Scheme 1.

confirmed the existence of suddenly polarized species in singlet excited states of ethylenes, dienes and trienes. "Suddenly polarized" excited states have been invoked in a wide variety of photoreactions, including electrocyclizations (5), alcohol additions to alkenes (6) and dienes (7), cis - trans isomerization (8) and molecular rearrangements (9).

In contrast to simple alkenes, the excited state characteristics and photoreactions of allenes have received relatively little attention. Johnson (10) has recently surveyed the known photochemical reactions of allenes in a comprehensive review. Singlet excited allenes undergo isomerization to cyclopropenes, alkynes and indenenes in aprotic solvents, whereas triplet states are either unreactive or yield products which may arise from triplet cyclopropylidenes (Scheme 2). This latter process is

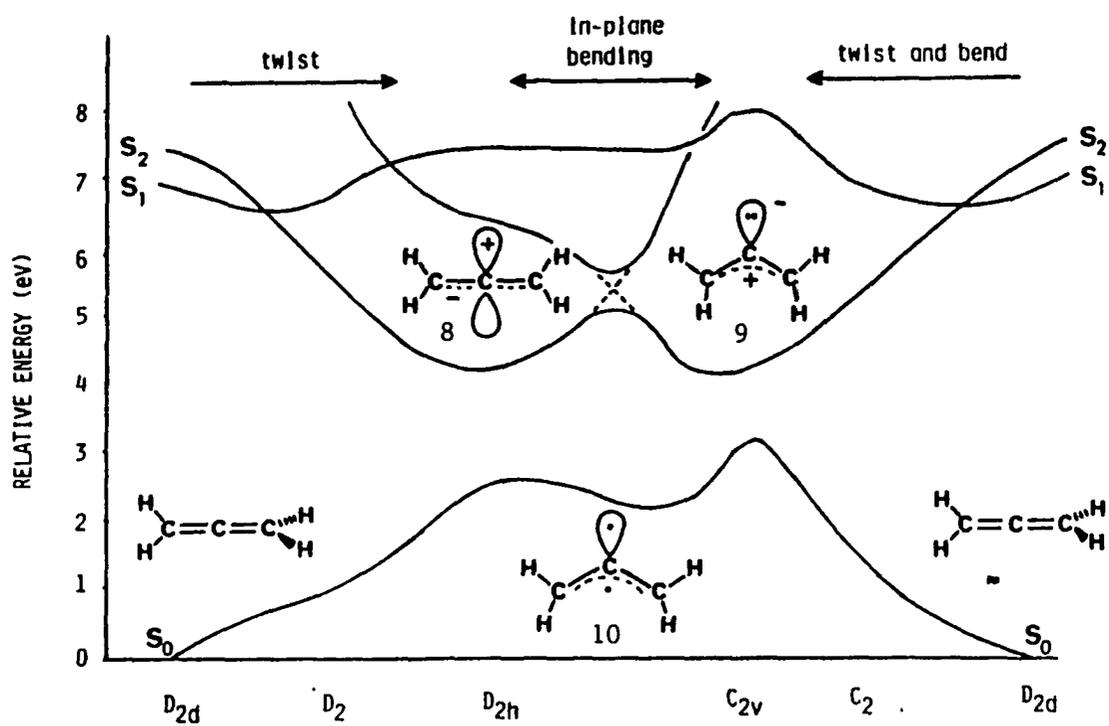
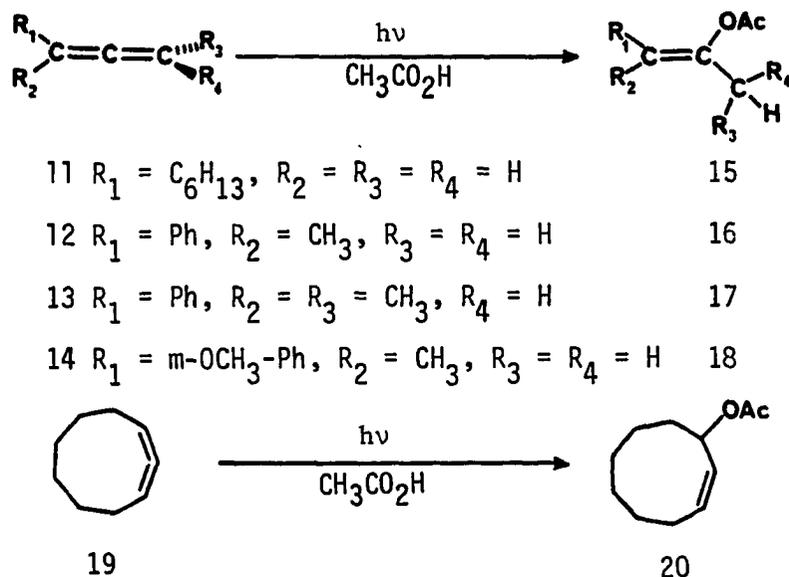


Figure 2. Singlet potential surfaces for twisting and bending in allene

affords the allylic acetate **20** under identical conditions (Scheme 3). The authors suggested a triplet mechanism, based upon observations that sensitization with xanthone gave identical results (13).

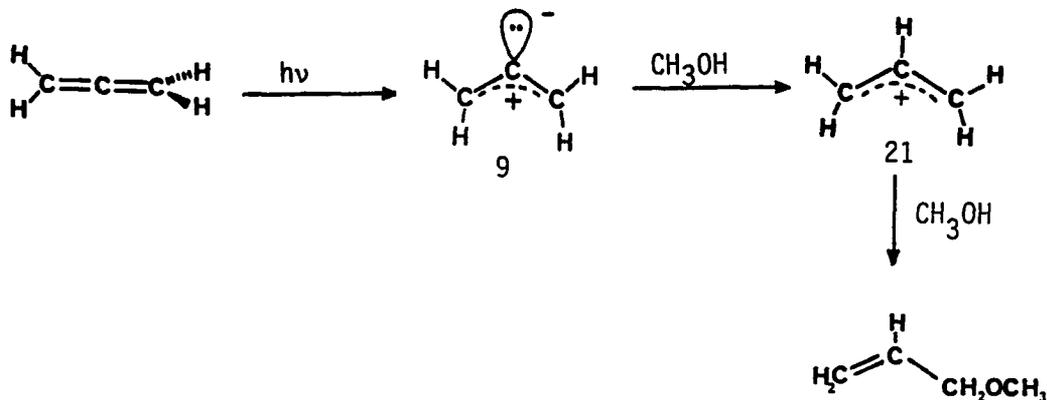


Scheme 3.

In 1983, we reported in preliminary form the photochemical addition of methanol to tetra-, tri-, and 1,3-diphenylallenes to yield allylic methyl ethers (14). A general mechanism proposed for this reaction involves initial protonation of a polarized singlet excited state **9** to yield an allyl cation **21**. Subsequent trapping by methoxide completes the process (Scheme 4). The mechanistic details of this reaction will be addressed in sections below.

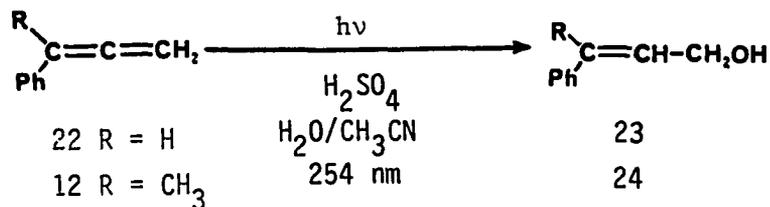
More recently, Rafizadeh and Yates (15) have studied the photohydration of phenylallene and some simple derivatives in 20% aqueous sulfuric acid - acetonitrile. Allenes **22** and **12** yielded cinnamyl alcohols **23** and **24** (Scheme 5) with regiochemistry opposite to that

observed by Fujita *et al.* (13). These results, however, are in accord with the regiochemistry reported by Klett and Johnson (14b).



Scheme 4.

Triplet sensitization of allenes 12 and 22 proved ineffective, thus implicating a singlet excited state mechanism. The efficiency of singlet photohydration of phenylallene 22 and quenching of its fluorescent intensity both showed sigmoid dependence on pH. The authors

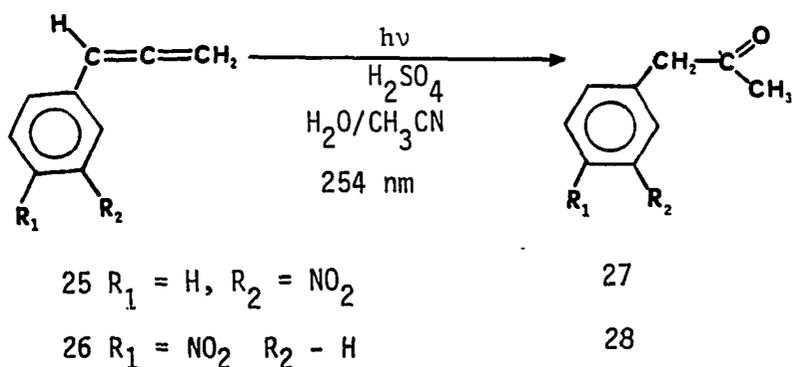


Scheme 5.

suggested that protonation of S₁ leads to both product formation and fluorescence quenching as the rate determining step. A polarized allene excited state was proposed to precede protonation.

Irradiation of nitro derivatives 25 and 26 afforded ketones 27 and 28 (Scheme 6). This rather dramatic change in regiochemistry was postulated to result from a triplet state reaction, since triplet sensitization yielded identical results.

Photohydration efficiency of *p*-nitrophenylallene 25 again showed sigmoid dependence on pH, while reaction of the *m*-nitro derivative 26, was not acid dependent and even occurred in water. The authors suggested a polarized triplet intermediate, which protonates at C₁ or C₂ to give a vinyl cation. Nucleophilic trapping by water, loss of a proton, and subsequent tautomerization account for the observed products.



Scheme 6.

Nucleophilic trapping at C₂ may be better explained by an ejection to solvent which would generate a solvated electron and allene radical cation. This has precedent in photonucleophilic aromatic substitution. Although nitro derivatives have been reported to undergo efficient intersystem crossing (16), electron ejection to solvent can occur from either singlet or triplet excited states (17). Nucleophilic

trapping of allene radical cations is known (14, 18) to occur exclusively at C₂, an aspect which will be discussed in Chapter 3.

Goals of This Research

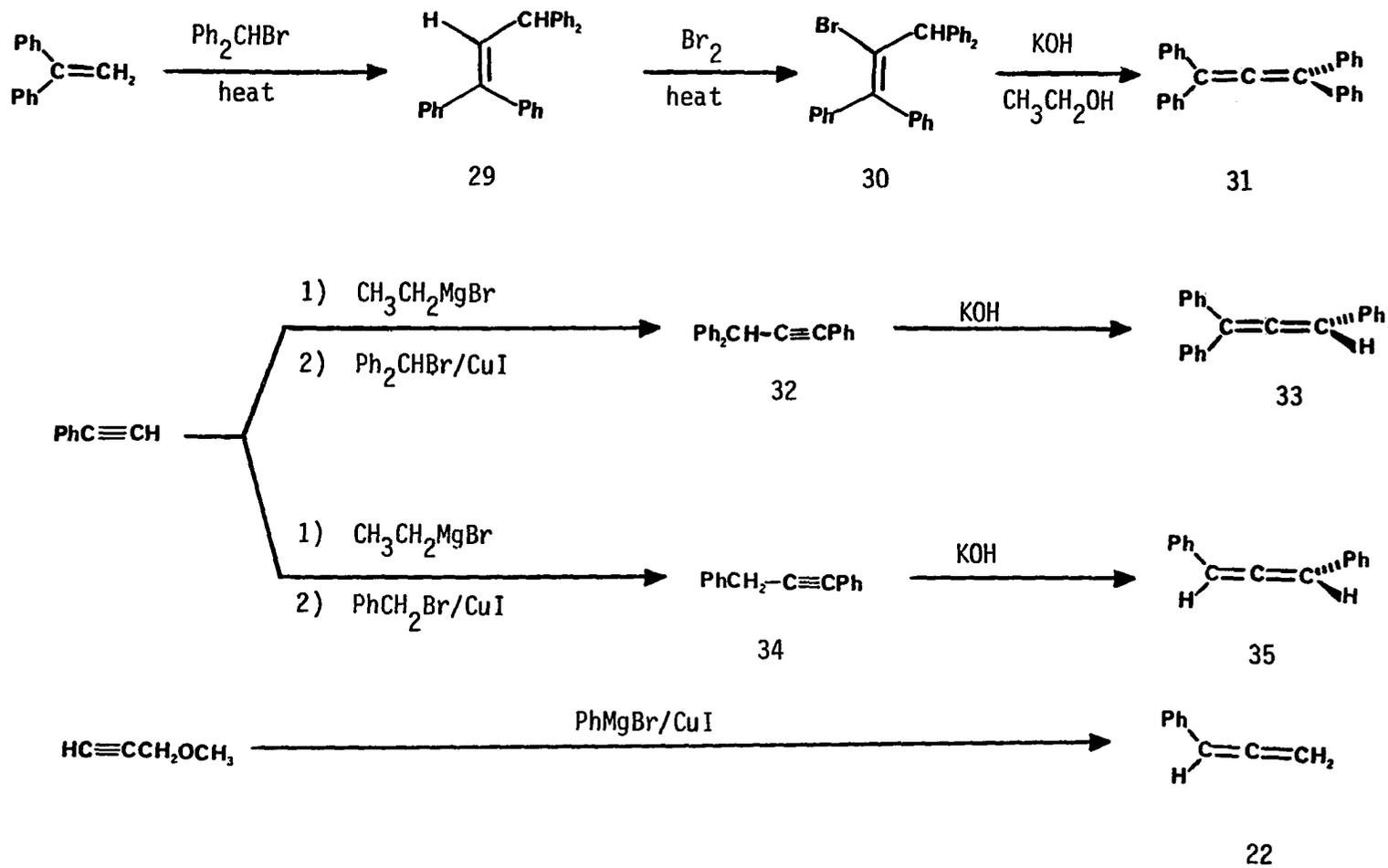
The goal of research described in this chapter was to seek experimental evidence for the "sudden polarization" effect in phenylallene excited states. Theory predicts that allene singlet excited states should be strongly polarized. In principle, these could be trapped by methanol. Analogous alcohol photoadditions to styrenes and butadienes are known to occur and, in allenes, offered the potential to distinguish between the two possible polarizations.

Systematic structure variation is a useful technique in understanding photochemical and ground state reactions. Sequential substitution of allene by phenyl is expected to effectively stabilize a polarized intermediate. The phenylallenes employed in the present study comprise such a fundamental series from which mechanistic implications could be deduced.

Exploratory Phenylallene Photochemistry

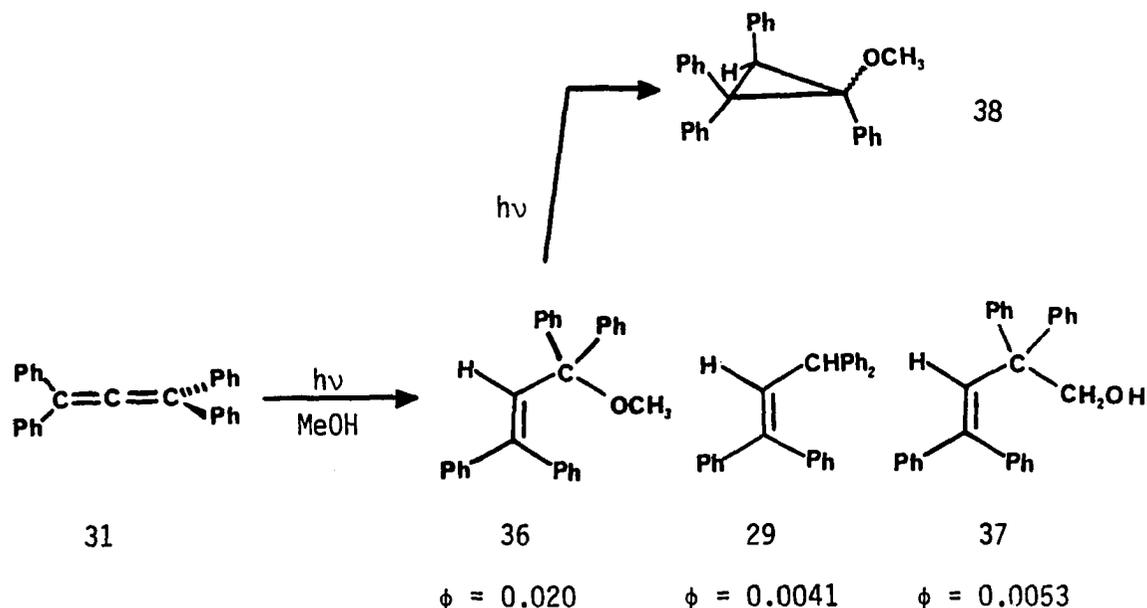
Allenes used in this study were prepared according to literature procedures as outlined in Scheme 7. Purification procedures are detailed in the experimental section.

Direct irradiation of dilute methanol solutions of 31 through Corex ($\lambda > 260$ nm) or Pyrex ($\lambda > 290$ nm) cut-off filters yielded



Scheme 7.

photoproducts 29, 36 and 37 (Scheme 8). At conversions > 10%, 1-methoxy-1,2,2,3-tetraphenylcyclopropane 38 was consistently



Scheme 8.

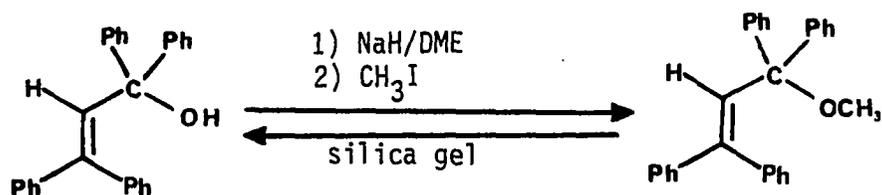
observed by ^1H NMR as a minor product; this is the expected photoproduct from 36 via a di- π -methane rearrangement, as previously reported by Brophy and Griffin (19). All photoproducts were isolated by chromatography and were unambiguously identified by comparison to authentic samples, prepared as outlined below.

Ether 36 was prepared from 1,1,3,3-tetraphenylpropenol 39 via Williamson ether synthesis. Pure samples of 36 were obtained by flash chromatography over neutral alumina, as silica gel chromatography invariably led to ether cleavage to yield 39 (Scheme 9).

2,2,4,4-tetraphenyl-3-butanol 37 was obtained in moderate yield by a sequence of steps shown in Scheme 10. This followed the procedure previously described by Zimmerman and co-workers (20) involving carbon

dioxide quenching of tetraphenylallene radical anion to 2,2,4,4-tetraphenyl-3-butenoic acid 40, and subsequent reduction.

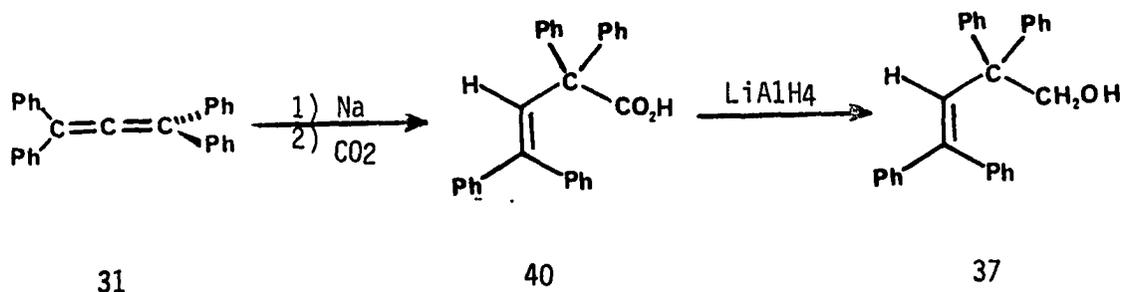
Quantum yields for photoproducts were measured on an optical bench, with potassium ferrioxalate actinometry. Product analyses at low



Scheme 9. 39

36

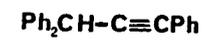
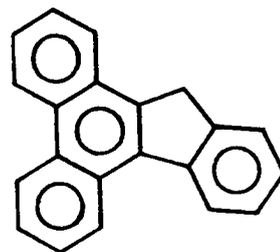
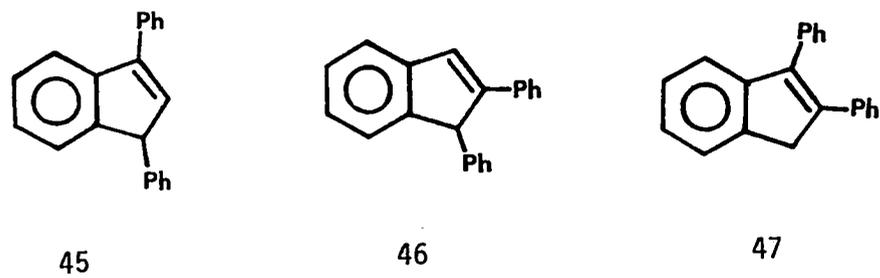
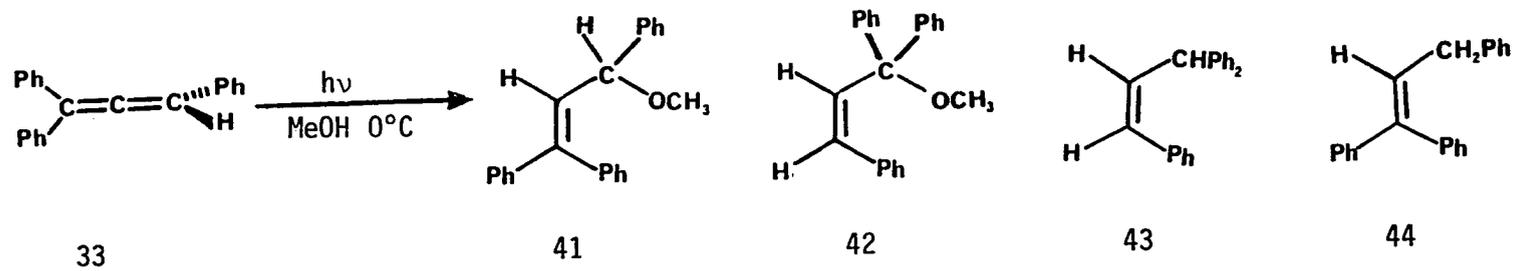
conversions (0.1 - 13%) were accomplished by 300 MHz ^1H NMR integration relative to added internal standard and are summarized in Scheme 8.



Scheme 10.

Photoreactions of triphenylallene 33 were best conducted at -10°C in a specially constructed Pyrex vessel (experimental) in order to minimize thermal dimerization (21) of this sensitive molecule.

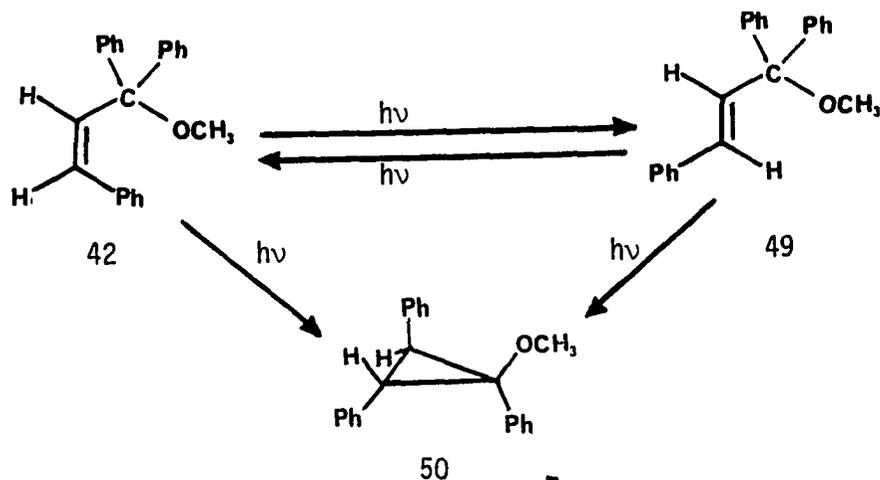
Direct irradiation (300 nm lamps) of 33 yielded a plethora of photoproducts, as depicted in Scheme 11. All were isolated by chromatography in sufficient purity for unambiguous identification. Major products were 41 - 44.



32

Scheme 11.

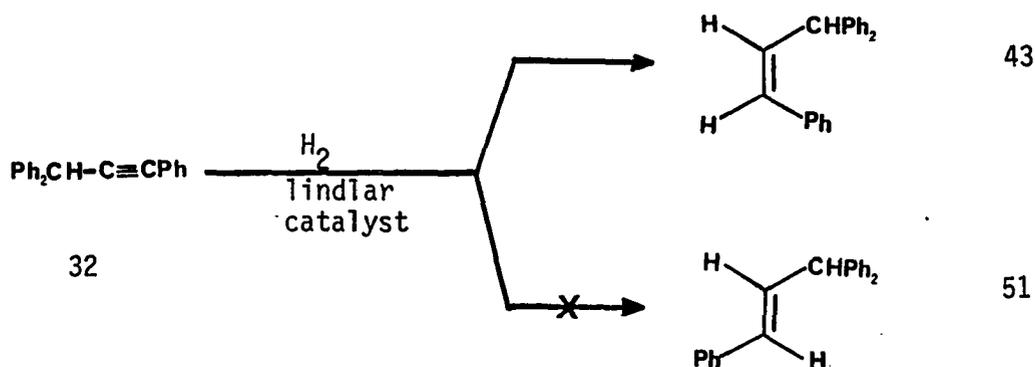
Prolonged irradiation experiments invariably resulted in cis - trans isomerization of 42 to 49 and rearrangement to trans-1-methoxy-1,2,3-triphenylcyclopropane 50 (Scheme 11). This was verified by independent irradiation (300 nm lamps) of methanol solutions of 42.



Scheme 12.

Authentic samples of 42 and 50 were prepared by Williamson ether synthesis from the corresponding known alcohols; trans isomer - 49, was not detected (HPLC and ¹H NMR) in the low conversion irradiations. These ethers, especially 42, did not prove stable to slow elution over silica gel. Pure samples were best obtained by flash chromatography over neutral alumina.

Catalytic hydrogenation (Lindlar catalyst) of triphenylpropene 32 yielded (Z)-1,3,3-triphenylpropene 43 as a colorless oil (Scheme 13). The ¹H NMR of 43 displays two doublets at 5.20 and 6.61 ppm (J = 10.4 and 10.9 Hz) and a triplet at 6.13 ppm. By comparison, the trans isomer 51 displays two doublets at 4.85 and 6.30 ppm and a doublet



Scheme 13.

of doublets at 6.71 ppm. (22); this was not observed in the reaction mixture at any conversion examined.

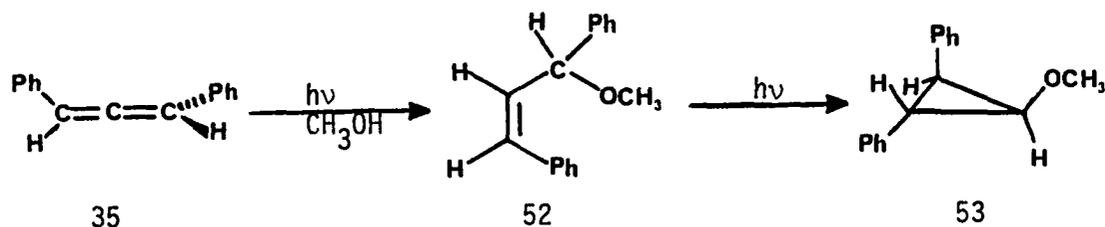
1,1,3-triphenylpropene 44 was identified by spectral data alone; this molecule displays a characteristic doublet ($J = 7.5$ Hz) at 3.47 ppm and a triplet at 6.27 ppm, identical with an authentic sample (22).

Synthesis and spectral data for hydrocarbons 45-48 are described in Chapter 2. These, and 32, are the photoproducts which are observed in aprotic solvents.

Quantitative product analysis was best performed by 300 MHz ^1H NMR integration of appropriate resonances. Normal phase (silica, hexane elution) HPLC analysis was not suitable, as ethers 41 and 42 proved unstable towards silica, and reverse phase (C_{18} /u-porasil; aqueous methanol elution) conditions did not provide adequate separation. The photoproduct ratios of 41:42:43:44 were 1.0:0.33:0.50:0.24, respectively, between 2 and 13% conversion. Hydrocarbons 32 and 45-48 represent a maximum of 10% of the photoproduct mixture.

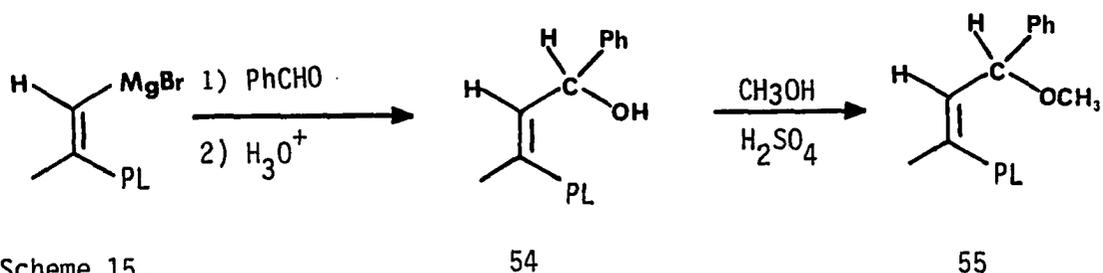
Direct irradiation (254 or 300 nm lamps) of 1,3-diphenylallene 35

in methanol very slowly yielded 52 and its expected di- π -methane photoproduct 53 (Scheme 14). These were isolated by repetitive preparative TLC, and found to be identical to authentic samples.



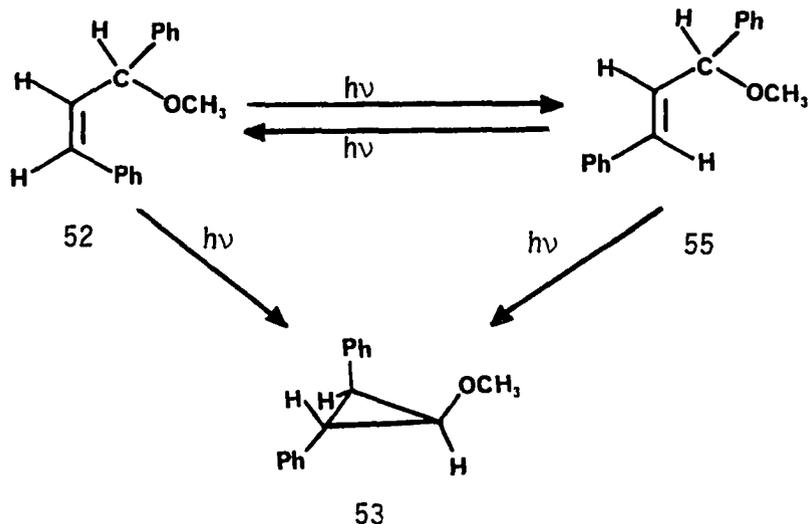
Scheme 14.

Ether 52 was prepared from the known cis-alcohol 54 via Williamson ether synthesis (Scheme 15). (E)-1,3-diphenyl-3-methoxypropene 55 was also prepared for comparison purposes; this was not observed (capillary GLC) in the photomixture, even at low conversions (< 1%).



Scheme 15.

The photochemistry of allylic ethers 52 and 55 was briefly investigated (Scheme 16). Independent irradiation (300 nm lamps) of 52 or 55 afforded 53. Interestingly, 52 did not appear (GLC analysis) to undergo any significant photochemical cis - trans isomerization.



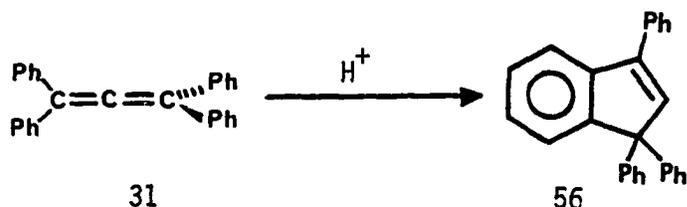
Scheme 16.

The structure of the previously unknown cyclopropane 53, derives from its spectral data, which included ^1H NMR resonances at 2.39 (t, 7.7 Hz), 2.55 and 3.69 (dd, 6.7 and 3.8 Hz), 3.28 (methoxy singlet) and aromatic hydrogens in a respective ratio of 1:1:1:3:10.

Preliminary irradiations (> 260 nm) of phenylallene 22 in methanol showed no discernible photoproducts by ^1H NMR or GLC analysis, even upon prolonged (28 hours) irradiation. Very small amounts of what appeared to be oxidation products (23), however, were consistently observed when the allene was exposed to air; these were not identified.

Mechanistic Studies and Discussion

Dark control experiments with tetraphenylallene 31 with and without acid, showed that 29, 36 and 37 are truly photoproducts. Reactions of 31 in slightly acidic (10^{-3}M HCl) methanol or benzene solutions very slowly yielded 1,1,3-triphenylindene (56) (Scheme 17).



Scheme 17.

Rearrangement of **31** to **56** was facilitated by heating or use of stronger acids, consistent with previous reports (24).

To verify the absence of adventitious acid catalysis, methanol solutions of **31** ($2.9 \times 10^{-3}M$), with and without sodium methoxide ($4.6 \times 10^{-2}M$), were irradiated simultaneously at 300 nm in a merry-go-round apparatus. Within experimental error, no difference was observed for the formation of methylether **36**.

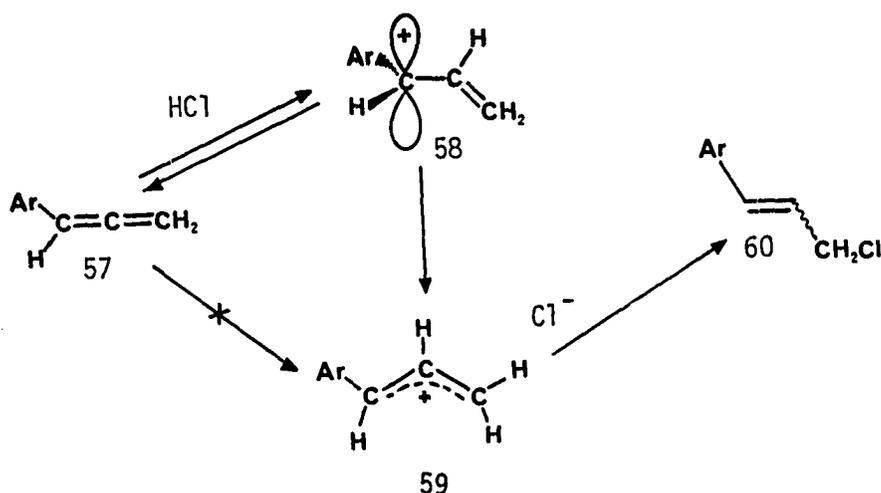
Quantitatively, the reactivity of phenylallenes decreased in the sequence **31** > **33** > **35** >> **22**. Phenylallene **22** yielded no ether photo-products in neutral methanol but is reported to yield cinnamyl alcohols in acidic (20% H₂SO₄) acetonitrile solutions (15).

Triplet sensitization of tetraphenylallene **31** with 4-phenylbenzophenone ($E_T = 60.7$ kcal/mol) or triphenylene ($E_T = 67.2$ kcal/mol) in methanol gave no reaction. The triplet energy of **31** has been previously estimated by Ullman and Henderson (25) from energy transfer experiments to be < 57.4 kcal/mol, thus energy transfer from triphenylene or 4-phenylbenzophenone should be efficient, and triplets of **31** are simply unreactive.

No detectable fluorescence emission was observed for dilute methanol or cyclohexane solutions of **31**, **33** or **35** at ambient

Ground state acid catalysis is not involved for the phenylallenes examined in the present work since irradiation of neutral and basic methanol solutions of tetraphenylallene **31** resulted in identical amounts of methyl ether **36**. Additionally, phenylallenes are subject to isomerization to form indene derivatives in the presence of acids (24).

Similar regiochemistry has been reported for ground state electrophilic additions. Hydrochlorination of aryl allenes was reported by Okuyama *et al.* to yield exclusively cinnamyl chloride **60** (26). A mechanism shown in Scheme 20 was supported by substituent effect studies and relative reaction rates. The rate determining step involves initial protonation to yield the benzyl cation **58**, in which the alkene π bond is orthogonal to the empty p-orbital. Subsequent rapid C-C bond rotation yields the conjugated allyl cation **59**, which is trapped by chloride ion. In the photochemical reaction, π bond rotation probably precedes



Scheme 20.

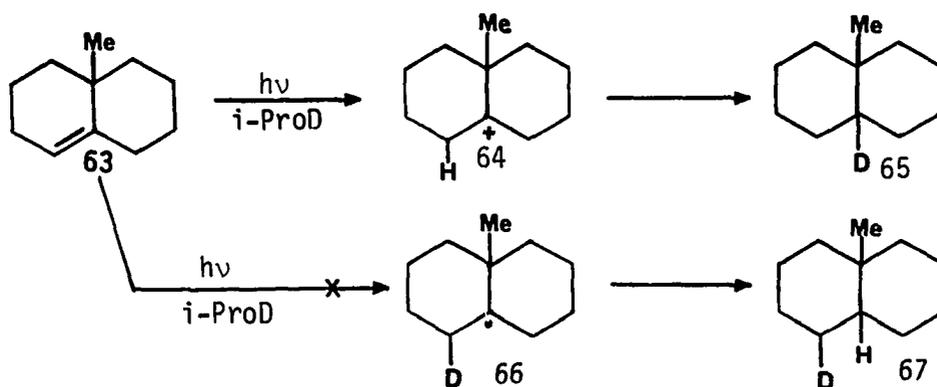
protonation. The deuterium isotope effect ($\phi_H/\phi_D = 2.9$) which is observed for ether **36** formation provides convincing evidence that protonation (deuteration) is the rate determining step in the photochemical process as well.

The remarkably clean cis stereoselectivity observed in photoaddition products **42**, **43** and **52** has little precedent. This result implies that planar allyl cations are not discrete intermediates in these reactions, since more random stereochemistry would be expected. Similarly, planar excited state species seem unlikely progenitors of cis products. Nevertheless, the preponderance of results argue that addition is ionic in character, especially since both ethers and reduction products incorporate deuterium at C₂ from irradiation in methanol-0-d. The most straightforward explanation is that polar excited state character and photoaddition occur quite early along the reaction coordinate. This is consistent with previous predictions (11) that polarization in allene singlet excited state is not "sudden" but develops gradually along a twisting and bending coordinate. Since the allene is surrounded by solvent molecules, diffusion is unnecessary and initial proton transfer might occur on a sub-picosecond time scale.

Simple representations of both modes of solvent addition appear in Figure 4. In geometry **61**, methanol adds across the less hindered side of allene (i.e., away from the C₁ substituent) in an effectively concerted fashion. Thus, "free" methoxide or a planar allyl cation are never generated. This formally is a symmetry allowed [$\pi 2s + \sigma 2s$]



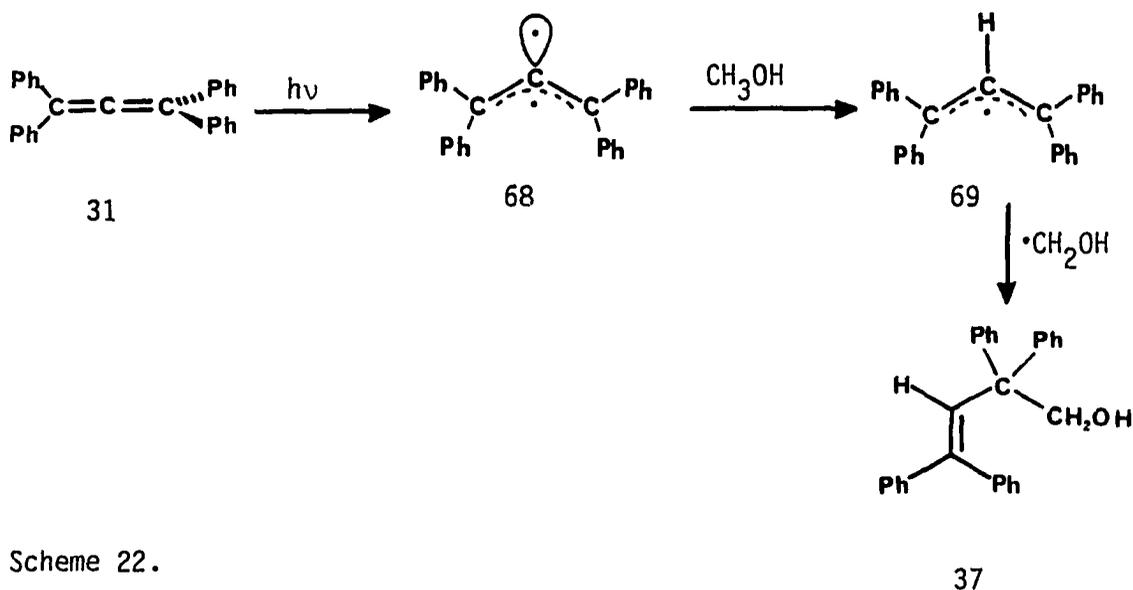
Figure 4. Potential geometries for allene photoprotonation process. Geometry 62 leads to reduction products. Sequential or concerted proton and hydride transfer effectively oxidizes methanol to formaldehyde. Once again, preferential addition occurs opposite to the C_3 substituent, and no formal allyl cation or methoxide intermediates are engendered. Photoreduction might first appear to be a radical process resulting from sequential hydrogen abstractions. However, this is inconsistent with the C_2 deuteration observed in reduction products of allenes 31 and 33. An ionic mechanism seems mandated. Reaction by an ionic mechanism does have precedent, although the stereochemistry was previously unknown. Marshall and Hockstetter (27) reported the photoreduction of 10-methyl- $\Delta^{1(9)}$ -octalene 63.



Scheme 21.

These authors found that irradiation of 63 in 2-propanol-2-d yielded 65 with deuterium exclusively at the tertiary center (Scheme 21). A radical mechanism was expected to yield 67, which was not observed. Similar observations are due to Hixson (6e) and Kropp *et al.* (28).

Formation of tetraphenylbutenol 37 deserves special comment, as this is expected to result from a radical process. The radical hydrogen abstraction and radical combination sequence shown in Scheme 22 could, in principle, account for 37. Singlet excited states of olefins have been reported to add $\cdot\text{CH}_2\text{OH}$ in a parallel fashion (1). The deuterium incorporation (ca. 60% at C_3) observed upon irradiation of tetraphenylallene 31 in methanol-0-d, however, would suggest a "mixed" mechanism. Deuteration at C_3 of 37 is consistent with an ionic process analogous to methyl ether formation or photoreduction. This would, however, involve rather unusual bond reorganization. Present



Scheme 22.

data do not allow for a satisfactory interpretation of deuterium incorporation in 37.

Conclusions

Phenylallene singlet excited states add methanol in an ionic fashion to yield allylic methylethers as the major products. Varying amounts of phenylpropenes formed in these reactions, also appear to result from an ionic mechanism. Stabilization due to phenyl substitution (6g) appears to increase the "basicity" of allene excited states, thus greater phenyl substitution increases reactivity. The high stereoselectivity and deuterium isotope effect observed for ether formation strongly argue for rate determining protonation and fast methoxide trapping in an effectively concerted manner, but one which does not involve planar allene. In a general sense, these reactions, parallel the alcohol additions to singlet excited states of styrenes and phenylbutadienes (6,7). Stereoselective methanol additions to acyclic alkene excited states, however, have never before been observed. The present results are in accord with theoretical calculations (11) which predict that bond twisting and bending of allene results in strong polarization. Singlet excitation of allenes is also predicted by theory to be a $\pi - \pi^*$ transition rather than Rydberg ($\pi, R(3s)$), thus avoiding much of the controversy engendered for ethylene (29). The present findings, taken together with theory, strongly argue for the role of "sudden polarization" in allene singlet excited states.

Experimental

General

All ^1H NMR spectra were measured on a Nicolet 300 or a Varian HA-100 MHz spectrometer, with CDCl_3 as solvent and TMS as reference. IR spectra were measured on a Beckman 4250 spectrometer. All UV spectra were measured on a Perkin-Elmer 320 instrument. HPLC analyses employed a Waters Associates M-45 pump and 440A detection system at 254 nm. Normal phase analyses were performed with a Water Associates u-porasil column (4.6 x 250 mm). A Dupont Zorbax ODS (4.6 x 250 mm) column was employed for reverse phase analysis. Gas chromatographic analyses were performed with a Hewlett-Packard 5793A instrument. A 25m SE-30 capillary column at 195°C was used for all analyses. GLC peak areas were measured by a Hewlett-Packard model 3390A integrator. Melting points are uncorrected.

Preparative chromatographic separations were performed with quartz columns that were slurry packed with Grace grade 62 silica containing added green phosphor (Sylvania #2282). Flash chromatography experiments employed quartz columns dry packed with preparative TLC silica gel 60 PF-254 (EM Laboratories, Inc.). Progress of component elution was monitored with an ultraviolet hand lamp.

Preparative photochemical experiments employed a standard immersion-well apparatus, equipped with 450 W Canrad-Hanovia lamp and sleeve filters, or a Rayonett RPR-100 reactor. For sub-ambient temperature irradiations in the Rayonett, quartz or Pyrex vessels with external

dewar jackets were constructed. Temperature was controlled with an internal cooling coil and a Lauda RC3 refrigerated recirculating bath.

Quantum yield measurements were made on an optical bench which is similar to that described by Zimmerman and co-workers (30). This consists of a 200 W high pressure Hg lamp, a Bausch and Lomb high intensity monochromator, a beam splitter, and an integrating electronic actinometer, which is calibrated vs. potassium ferrioxalate. Monochromator entrance and exit slits were set at 3.4 and 1.9 mm, respectively, to give a bandpass of 12.4 nm.

In all photochemical experiments, spectroquality solvents were used. Argon was bubbled through solutions prior to and during irradiation.

Bromodiphenylmethane

Bromodiphenylmethane was prepared in 73% yield by the method of Norris, Thomas and Brown (31): bp 130-132°C at 0.6 torr (literature 183°C, 23 torr); ^1H NMR (CDCl_3) δ 6.24 (s, 1H), 7.14-7.46 (m, 10H).

1,1-Diphenylethylene

1,1-Diphenylethylene was prepared in 69% yield by the method of Allen and Converse (32): bp 107-108°C at 0.08 torr (literature 123-125°C, 5 torr); ^1H NMR (CDCl_3) δ 5.40 (s, 2H), 7.2-7.3 (m, 10H).

1,1,3,3-Tetraphenylpropene 29

1,1,3,3-Tetraphenylpropene was prepared in 80% yield from condensation of 1,1-diphenylethylene and bromodiphenylmethane according to the

procedure of Tadros, Salka and Helmy (33): mp 127-128°C (literature 127°C); ^1H NMR (CDCl_3) δ 4.82 (d, 1H, $J = 10$ Hz), 6.54 (d, 1H), 7.16-7.32 (m, 20H).

2-Bromo-1,1,3,3-tetraphenylpropene 30

2-Bromo-1,1,3,3-tetraphenylpropene was prepared in 82% yield by the method of Tadros, Salka and Helmy (33): mp 123-124°C (literature 124°C); ^1H NMR (CDCl_3) δ 5.52 (s, 1H), 7.20 (s, 10H), 7.24 (s, 10H).

Tetraphenylallene 31

Tetraphenylallene was prepared according to the procedure of Tadros, Salka and Helmy (33). 2-Bromo-1,1,3,3-tetraphenylpropene (11.1g, 26.1 mmol) and potassium hydroxide (22g, 0.40 mol) in 300 mL of 95% ethanol were heated to reflux for 2 hours. The solution was cooled to room temperature and diluted with 500 mL of water to afford a white precipitate. The crystals were collected, washed with water until the filtrate was neutral to litmus. Recrystallization from methylenechloride-ethanol gave 7.6g (84%) of colorless needles melting at 166.5-167.0°C (literature mp 165°C); ^1H NMR (CDCl_3) δ 7.25-7.37 (m, 12H), 7.38-7.44 (m, 8H).

1,3,3-Triphenylpropyne 32

A modification of the method of Wieland and Kloss (34) was employed. Ethyl grignard prepared from ethylbromide (8.90 mL, 13.0g, 0.120 mol) and magnesium metal (2.90g, 0.120 mol) in ethyl ether (100

mL) was heated to reflux, and to this was slowly added phenylacetylene (14.6 mL, 13.6g, 0.130 mol) in ethyl ether (50 mL). The reflux was maintained for 18 hours and then CuI (500 mg) was added. After 1.0 hour, bromodiphenylmethane (29.6g, 0.120 mol) in ethyl ether (50 mL) was added dropwise to the mixture and reflux maintained for another 18 hours. The reaction mixture was cooled to room temperature, quenched with 10% aqueous hydrochloric acid (100 mL) and a yellow insoluble material was filtered away. The organic portion of the filtrate was decanted and the aqueous layer was extracted with ethyl ether (4 x 20 mL). Extracts were combined with the organic phase, dried over magnesium sulfate and concentrated in vacuo affording a red-brown residue. The crude product was taken up in 95% ethanol, Norite was added, and the mixture was heated to reflux for 0.5 hours, then filtered through celite. The filtrate was cooled and 15.7g (49%) of lightly tan colored needles was collected. An analytical sample of the propyne was obtained by flash chromatography with hexane elution to yield colorless crystals that melted at 79-80°C (literature 79°C); ^1H NMR (CDCl_3) δ 5.21 (s, 1H), 7.2-7.3 (m, 6H), 7.4-7.5 (m, 9H).

Triphenylallene 33

Triphenylallene was prepared according to the procedure of Jacobs and Danker (35). 1,3,3-Triphenylpropyne (5.00g, 18.6 mmol) in 300 mL of ethyl ether-hexane (1:1) was stirred over potassium hydroxide pellets (20g) under nitrogen and at room temperature for 24 hours. The inorganics were filtered away and the filtrate was concentrated in vacuo to afford a bright yellow colored residue. Chromatography (3.0 x 60 cm)

of the residue with hexane elution gave 4.8g of yellow colored crystals. Washing with cold pentane (-78°C) gave 1.87g (37%) of white crystals melting at 77.5-79.0°C (literature 77.5-79°C). Concentration of the filtrate to half volume, with cooling (0°C), gave 1.58g (32%) of slightly yellow crystals melting at 76.5-79°C. Another 0.60g (12%) of bright yellow colored crystals was collected upon further concentration of the filtrate, mp 75-79°C; ^1H NMR (CDCl_3) δ 6.70 (s, 1H), 7.2-7.4 (m, 15H). Pure triphenylallene was also obtained by flash chromatography with hexane elution.

1,3-Diphenylpropyne 34

A modification of the method of Jacobs and Danker was employed (36). Ethyl grignard prepared from ethylbromide (41.0 mL, 59.9g, 0.55 mol) and magnesium metal (13.4g, 0.56 mol) in ethyl ether (250 mL) was heated to reflux and to this was slowly added under nitrogen, phenylacetylene (55.0 mL, 51.2g, 0.500 mol) in ethyl ether (100 mL). The reflux was maintained for 18 hours and then copper (I) iodide (2.0g) was added. After 1.0 hour, benzylbromide (60.0 mL, 86.3g, 0.500 mol) in ethyl ether (100 mL) was added dropwise to the mixture and reflux was maintained for 24 The reaction mixture was cooled to room temperature, quenched with 10% aqueous hydrochloric acid (100 mL), and a yellow insoluble material was filtered. The organic portion of the filtrate was decanted and the aqueous layer was extracted with ethyl ether (4 x 20 mL). Extracts were combined with the organic phase, dried over magnesium sulfate, and then concentrated in vacuo. Distillation

afforded 20.7g of benzylbromide and 49.8g (50%) of a lightly yellow colored oil: bp 107-114°C, 0.25 torr (literature bp 140-145°C, 3.0 torr); ^1H NMR (CDCl_3) 3.87 (s, 2H), 7.2-7.4 (m, 10H).

1,3-Diphenylallene 35

A modification of the procedure by Jacobs and Danker was employed (36). 1,3-Diphenylpropyne (5.5g, 28.6 mmol) in pentane (200 mL) was stirred over potassium hydroxide pellets (20g) under nitrogen and at room temperature for 30 hours. The inorganics were filtered and the crude allene was subjected to flash chromatography (3.0 x 40 cm), with pentane elution. The pentane eluant was concentrated in vacuo at 0°C to afford 4.2g (77%) of white crystals melting at 56-58°C (literature 49-51°C). ^1H NMR (CDCl_3) δ 6.60 (s, 2H), 7.1-7.4 (m, 10H).

Phenylallene 22

Phenylallene was prepared according to the procedure of Moreau and Gaudemar (37). Phenyl grignard prepared from bromobenzene (10.9 mL, 16.2g, 0.100 mol) and magnesium metal (2.52g, 0.105 mol) in ethyl ether (100 ml) was slowly added under nitrogen to a stirring suspension of methylpropargylether (11.2 mL, 9.30g, 0.133 mol) and copper (I) iodide (1.6g, 8.4 mmol) in ethyl ether (100 mL). After 10 minutes of stirring, the reaction became exothermic and required water bath cooling to suppress the reflux. The mixture was stirred for 2.0 hours, cooled to 0°C and quenched with aqueous ammonium chloride (50 mL). The reaction mixture was extracted with ethyl ether (3 x 20 mL), washed with water and then with brine. The combined extracts were dried over magnesium

sulfate and concentrated in vacuo at 0°C. Distillation afforded 10.0g (65%) of a colorless oil, bp 67-69°C, 16 torr (literature bp 64-65°C, 11 torr). ^1H NMR (CDCl_3) δ 5.13 (d, 2H, 6.6 Hz), 6.15 (s, 1H), 7.18-7.30 (m, 5 H).

Direct irradiation of tetraphenylallene 31

Allene 31 (505 mg) dissolved in methanol (600 mL) was irradiated for 6 hours and 45 minutes through pyrex (> 290 nm). The reaction mixture was concentrated under reduced pressure and the residue was subjected to chromatography on a silica column (2.0 x 85 cm), slurry packed with 0.5% ether-hexane. Elution was with hexane in 50 mL fractions: 1-14, nil; 15-18, 34 mg of allene (31). Continued elution with 0.5% ether-hexane: 19-22, 51 mg of 31, tetraphenylpropene 29 and 1-methoxy-1,2,2,3-triphenylcyclopropane 38, ca. 1:3:0.01. Continued elution with 1.0% ether-hexane: 23-30, 44 mg of 29; 39-40, 13 mg of 1-methoxy-1,1,3,3-tetraphenylpropene (36). Continued elution was with 1.5% ether-hexane: 41-56, 338 mg of tetraphenylpropenol 39. Elution was continued with 5% ether-hexane: 57-76, nil; 77-84, 57 mg of 2,2,4,4-tetraphenyl-3-butenol 37. Mass balance $> 90\%$.

Quantum yield determination for tetraphenylallene 31

A 1.86×10^{-3} M methanol solution of allene 31 (50 mL) in a quartz cell was irradiated on the optical bench for periods of 10 to 165 hours. Internal standard (1,3,3-triphenylpropyne) was added and the mixture was analyzed by 300 MHz ^1H NMR integration. Four separate runs at 0.1% - 13% conversion yielded the following quantum efficiencies

for product formation: 3-methoxy-1,1,3,3-tetraphenylpropene 36, 0.020 ± 0.002 ; 1,1,3,3-tetraphenylpropene 29, 0.0041 ± 0.0002 ; 2,2,4,4-tetraphenyl-3-butenol 37, 0.0053 ± 0.0012 .

1,1,3,3-Tetraphenylpropenol 39

1,1-Diphenylethylene grignard was prepared from magnesium metal (0.37g, 15.4 mmol) and 2-bromo-1,1-diphenylethylene (4.0g, 15.4 mmol) in tetrahydrofuran (50 mL) under nitrogen. Benzophenone (2.80g, 15.4 mmol) in tetrahydrofuran (20 mL) was added dropwise to the cold (0°C) stirring grignard solution over a 3 hour period. After an additional 18 hours of stirring at room temperature, the mixture was quenched with ammonium chloride, extracted with ethyl ether (3 x 25 mL), and dried over magnesium sulfate. The solvent was removed under reduced pressure to afford an oily mass which was taken up in methylene chloride and triturated with hexane to yield 3.93g (70%) of white crystals that melted at 141-142°C (literature (38) 138-139°C); ^1H NMR (CDCl_3) δ 2.46 (s, 1H, OH), 6.86 (s, 1H), 7.0-7.5 (mult, 20H).

1-Methoxy-1,1,3,3-tetraphenylpropene 36

The general procedure of Diner, Sweet and Brown was followed (39). 1,1,3,3-Tetraphenylpropen-1-ol (500 mg, 1.38 mmol) in dry dimethoxyethane (15 mL) was added dropwise under nitrogen to a cold (0°C) stirring slurry of sodium hydride (200 mg, 4.2 mmol, 50% in oil, prewashed with hexane) in the same solvent. After 1.0 hour of stirring, methyl iodide (0.26 mL, 588 mg, 4.1 mmol) was added and stirring was continued for several hours at room temperature. The reaction mixture

was quenched with water, extracted with ether (3 x 15 mL) and dried over sodium carbonate. Flash chromatography over neutral alumina with hexanes afforded 485 mg (93% yield) of a colorless oil which crystallized upon cooling; mp 66-69°C; ^1H NMR (CDCl_3) δ 2.95 (s, 3H), 6.92 (s, 1H), 7.08-7.40 (m, 20H); IR (KBr) 3080, 3045, 3020, 2835, 2805, 1593, 1485, 1442, 1180, 1072, 950, 755 and 690 cm^{-1} ; high resolution MS, m/e 376.18275 (ca. error < 0.1 ppm).

2,2,4,4-Tetraphenyl-3-butenic acid 40

2,2,4,4-Tetraphenyl-3-butenic acid was prepared in 81% yield from tetraphenylallene radical anion and carbon dioxide by the procedure of Zimmerman *et al.* (20) mp 165-167°C (literature 181-182°C); ^1H NMR δ (CDCl_3) 6.38-7.10 (m, 21H), 11.4 (s, 1H).

2,2,4,4-Tetraphenyl-3-butenol 37

2,2,4,4-Tetraphenyl-3-butenic acid (100 mg, 0.257 mmol) in ethyl ether (15 mL) was added dropwise to a stirring slurry of lithium aluminum hydride (0.5g, 13.2 mmol in ethyl ether (15 mL). After 1 hour of stirring, the mixture was quenched with water (5 mL) then treated with sodium sulfate (1.0g) and Celite (1.0g). The reaction mixture was filtered after 12 hours of additional stirring, then dried over magnesium sulfate. The solvent was removed under reduced pressure to yield an oil. Recrystallization from ether-hexane yielded 30 mg (31%) of white crystals: mp 96-97°C (literature (20) 98-98.5°C); ^1H NMR (CDCl_3) δ 0.86 (bs, 1H, -OH), 3.94 (d, 2H, J = 6.3 Hz), 6.75-6.78 (m, 2H), 6.87 (s, 1H), 7.06-7.25 (m, 18H).

Irradiation of triphenylallene 33

Allene 33 (250 mg) dissolved in methanol (200 mL) at -10°C was irradiated with the 300 nm lamps for 6 hours. The solvent was removed by vacuum distillation at 0°C and the residue was subjected to flash chromatography (1.8 x 22 cm) with hexane elution in 25 mL fractions: 1-8, nil; 9-14, 90 mg of allene 33; 15-18, 31 mg of 33 and 1,1,3-triphenylpropene 44, ca. 30:1; 19-20, 1 mg of 44; 21-23, 2 mg of 44, 1,3-diphenylindene 45, 2,3-diphenylindene 46, indenophenanthrene 48 and (Z)-1,3,3-triphenylpropene 43, ca. 1.0:0.74:0.08:0.12:0.64; 24-28, 5 mg of 44 and 43, ca. 0.28:1.0; 29-30, 1 mg of predominantly 43. Continued elution with 0.1% ether-hexane: 31-42, 2 mg of triphenylpropyne 32; 43-54, nil. Continued elution with 0.5% ether-hexane: 55-64, nil; 70, 29 mg of dimer; 71-78, nil; 79-86, 2 mg of unidentified material; 87-101, 12 mg of 3-methoxy-1,1,3-triphenylpropene 41; 102-117, nil. Continued elution with 5% ether-hexane: 118-133, nil; 134-145, 3 mg of 1,3,3-triphenyl-2-propenol.

In other experiments, (Z)-3-methoxy-1,3,3-triphenylpropene 42 was isolated by rapid elution with 1.0% ether-hexane.

Spectral data of 44 were as follows: ^1H NMR (CDCl_3) δ 3.48 (d, 2H, $J = 7.6$ Hz), 6.27 (t, 1H), 7.18-7.33 (m, 15H).

Cis- β -Bromostyrene

Cis- β -bromostyrene was prepared in 66% overall yield from bromination and dehydrobromination of trans-cinnamic acid by the procedure of Cristol and Norris (40); bp $33-34^{\circ}\text{C}$ at 0.075 torr; ^1H NMR (CDCl_3) δ

6.41 (d, 2H, J = 8.2 Hz), 7.06 (d, 2H), 7.35-7.50 (m, 3H), 7.67 (d, 2H, J = 5.9 Hz).

(Z)-1,1,3-Triphenyl-2-propenol

Cis- -bromostyrene (530 mg, 2.73 mmol) in ethyl ether (10 mL) under nitrogen was cooled to -78°C then treated with tertiary-butyllithium (3.4 mL, 1.7 M, 5.80 mmol). After 1 hour of stirring, benzophenone (500 mg, 2.75 mmol) in ethyl ether (10 mL) was added dropwise. Stirring at -78°C was continued for 0.5 hours followed by gradual warming to room temperature (1 hour). The reaction mixture was quenched with water, extracted with ethyl ether (3 x 10 mL) and dried over magnesium sulfate. Solvent was removed under reduced pressure to afford a white residue. Recrystallization from ether-hexane yielded 650 mg (83%) of colorless needles, mp $90-91^{\circ}\text{C}$ (literature (41) $106-107^{\circ}\text{C}$); ^1H NMR (CDCl_3) δ 2.67 (s, 1H), 6.39 (d, 1H, J = 12.5 Hz), 6.73 (d, 1H), 7.20-7.34 (m, 17H), 7.46 (d, 2H, J = 7.4 Hz); IR(KBr) 3580, 3070, 3050, 3018, 1592, 1480, 1440, 1150, 1055, 960, 915, 890, 760, 745, 740, 680 cm^{-1} ; MS, m/e 286.13587 (ca. error +0.3 ppm).

(Z)-3-Methoxy-1,3,3-triphenylpropene 42

(Z)-3-Methoxy-1,3,3-triphenylpropene was prepared in 95% yield from (Z)-1,1,3-triphenyl-2-propenol by the methylation procedure described above; mp $128-129^{\circ}\text{C}$; ^1H NMR (CDCl_3) δ 3.02 (s, 3H), 6.41 (d, 1H, J = 12.9 Hz), 6.83 (d, 1H), 7.09-7.14 (m, 5H), 7.20-7.25 (t, 4H, J = 7.3 Hz), 7.30-7.33 (m, 2H), 7.48 (d, 4H, 7.3 Hz); IR(KBr) 3020, 2820, 1595, 1490, 1445, 1170, 1095, 1070, 1029, 690 cm^{-1} ; MS, m/e 300.15185 (ca. error +1.4 ppm).

(Z)-1,3,3-Triphenylpropene 43

The general hydrogenation procedure of Lindlar and Dubuis was employed (42). A mixture of triphenylpropyne (10 mg, 0.037 mmol), Lindlar's catalyst [5% Pd on BaSO₄] (0.5 mg) and quinoline (1 drop) in ethyl ether (10 mL) was stirred under hydrogen for 10 minutes. The solvent was removed under reduced pressure and the residue was filtered through a pipette containing alumina to yield 10 mg (99%) of a colorless liquid: ¹H NMR (CDCl₃) δ 5.20 (d, 1H, J = 10.4 Hz), 6.13 (t, 1H, J = 10.9 Hz), 6.61 (d, 1H), 7.2-7.4 (m, 15H); IR(film) 3080, 3060, 3025, 2920, 1600, 1490, 1445, 730, 690 cm⁻¹; MS, m/e 270.1407 (ca. error -0.4 ppm).

(E)-1,1,3-Triphenyl-2-propenol

(E)-1,1,3-Triphenyl-2-propenol was prepared in 80% yield from (E)-bromostyrene grignard and benzophenone following the procedure for 1,1,3,3-tetraphenylpropenol: mp 103-105°C (literature (43) 109-110°C); ¹H NMR (CDCl₃) δ 2.38 (s, 1H, -OH), 6.65 (d, 1H, J = 16 Hz), 6.83 (d, 1H), 7.16-7.45 (m, 15H).

(E)-3-Methoxy-1,3,3-triphenylpropene 50

(E)-3-Methoxy-1,3,3-triphenylpropene was prepared in 85% yield by the methylation procedure described above: mp 94-96°C (literature (43) 97-98°C); ¹H NMR (CDCl₃) δ 3.22 (s, 3H), 6.52 (d, 1H, J = 16.1 Hz), 6.81 (d, 1H), 7.23-7.42 (m, 15H).

1,3,3-Triphenyl-2-propenol

1,3,3-Triphenyl-2-propenol was prepared in 32% yield from 1-bromo-2,2-diphenylethylene grignard and benzaldehyde following the procedure for 1,1,3,3-tetraphenylpropenol: mp 76-77°C (literature (44) 77-78°C); ^1H NMR (CDCl_3) δ 2.20 (bs, 1H), 5.27 (d, 1H, $J = 9.4$ Hz), 6.30 (d, 1H), 7.23-7.44 (m, 15H).

1-Methoxy-1,3,3-triphenylpropene 41

1-Methoxy-1,3,3-triphenylpropene was prepared in 90% yield by the methylation procedure described above: mp 98-100°C (literature (44) 97-98°C); ^1H NMR (CDCl_3) δ 3.26 (s, 3H), 4.71 (d, 1H, $J = 9.4$ Hz), 6.25 (d, 1H), 7.20-7.45 (m, 15H).

Irradiation of 1,3-diphenylallene 35

Allene 35 (186 mg) dissolved in methanol (140 mL) was irradiated with 254 nm lamps for 6.5 hours. Concentration of the solution under reduced pressure and subsequent repetitive preparative TLC (silica plates, 1% ether-hexane development) yielded 111 mg of 35, 26 mg of dimers and 17 mg of a mixture consisting of (Z)-3-methoxy-1,3-diphenylpropene 52 and 1-methoxy-trans-2,3-diphenylcyclopropene 53, ca. 1.0:0.9. In other experiments, at lower conversion, reaction was followed by capillary GLC (SE-30; 25 meter, 195°C) and 300 MHz ^1H NMR. (Z)-3-methoxy-1,3-diphenylpropene 52 was observed to be the predominant primary photoproduct; little, if any, (E)-3-methoxy-1,3-diphenylpropene 55 was detectable.

(Z)-1,3-Diphenyl-2-propenol 54

(Z)-1,3-Diphenyl-2-propenol was prepared in 98% yield from *cis*- β -bromostyrene and benzaldehyde by the low temperature alkylation procedure described above; viscous oil (literature mp 57-58°C); ^1H NMR (CDCl_3) δ 2.57 (m, 1H, -OH), 5.59 (d, 1H, $J = 9.2$ Hz), 5.89 (dd, 1H), 6.64 (d, 1H, $J = 11.5$ Hz), 7.24-7.41 (m, 10H); IR(film) 3540, 3320, 3080, 3050, 3020, 2920, 1595, 1488, 1440, 1020, 990, 905, 845, 690 cm^{-1} ; MS, m/e 210.10412 (ca. error -1.7 ppm).

(Z)-1,3-Diphenyl-3-methoxypropene 52

(Z)-1,3-diphenyl-2-propenol (155 mg, 0.738 mmol) in dimethoxyethane (10 mL) was slowly added under nitrogen to a cold (-40°C) slurry of sodium hydride (200 mg, 4.2 mmol, 50% in oil, prewashed with hexane) and methyl iodide (2.0 mL, 4.56g, 32.1 mmol) in dimethoxyethane. After 0.5 hours of stirring at -40°C, the reaction mixture was slowly warmed to room temperature (1 hour). The reaction was slowly quenched with water, extracted with ethyl ether (3 x 10 mL) and dried over magnesium sulfate. Flash chromatography over neutral alumina with hexane afforded 164 mg (99% yield) of a colorless oil. ^1H NMR (CDCl_3) δ 3.27 (s, 3H), 5.07 (d, 1H, $J = 9.4$ Hz), 5.87 (dd, 1H), 6.74 (d, 1H, $J = 11.7$ Hz), 7.24-7.41 (m, 10H); IR(film) 3080, 3060, 3024, 2980, 2930, 2845, 2820, 1599, 1490, 1440, 1185, 1080, 950, 850, 690 cm^{-1} ; MS, m/e 224.1209 (ca. error +0.3 ppm).

(E)-1,3-Diphenyl-2-propenol 54

(E)-1,3-Diphenyl-2-propenol was prepared in 66% yield from cinnamaldehyde and phenyl grignard by the method of Nomura (45); mp 57-58°C

(literature 57.5-58°C); 100 MHz ^1H NMR (CDCl_3) δ 2.14 (bs, 1H, -OH), 5.36 (d, 1H, $J = 8.0$ Hz), 6.35 (dd, 1H), 6.68 (d, 1H, $J = 16$ Hz), 7.2-7.4 (m, 10H).

(E)-1,3-Diphenyl-3-methoxypropene 55

(E)-1,3-Diphenyl-3-methoxypropene was prepared in 96% yield from sulfuric acid catalyzed methanol addition to (E)1,3-diphenyl-2-propenol by the method of Bergman and Ukai (46); bp 125-134°C at 0.15 torr (literature 180-181°C at 11 torr); ^1H NMR (CDCl_3) δ 3.38 (s, 3H), 4.79 (d, 1H, $J = 6.9$ Hz), 6.28 (dd, 1H), 6.63 (d, 1H, $J = 16.0$ Hz), 7.21-7.40 (m, 10H).

Trans-1,2-Diphenyl-3-methoxycyclopropane 53

Methylether 54 (200 mg) dissolved in methanol (50 mL) was irradiated at 300 nm for 72 hours. The reaction mixture was concentrated under reduced pressure and the residue was subjected to flash chromatography (1.8 x 10 cm) over alumina. Elution with hexane afforded 100 mg (50%) of white crystals that melted at 71-72°C; ^1H NMR (CDCl_3) δ 2.39 (t, 1H, $J = 7.7$ Hz), 2.55 (dd, 1H, $J = 6.7$ Hz and 3.3 Hz), 3.28 (s, 3H), 3.69 (dd, 1H, $J = 6.7$ Hz and 3.8 Hz), 7.14-7.36 (m, 10H); IR(KBr) 3085, 3065, 3055, 3030, 2980, 2940, 2820, 1595, 1490, 1445, 1196, 1110, 1100, 740 and 690 cm^{-1} ; MS, m/e 224.11996 (ca. error -0.7 ppm).

Irradiation of (E) and (Z)-3-methoxy-1,3-diphenylpropene

Pyrex tubes containing methanol solutions of E-55 and Z-52 isomers ($6.25 \times 10^{-3}\text{M}$) were irradiated side by side in a Rayonett

merry-go-round apparatus for 4 hours. Aliquots were removed at designated times and analyzed by capillary GLC (SE-30, 25 M, 195°C) to yield the following results.

Table 1. Irradiation of E-55

Time (h)	52(%)	53(%)	% Conversion
1.0	6	11	17
1.5	5	21	26
2.0	1	31	32
4.0	1	68	69

Table 2. Irradiation of Z-52

Time (h)	55(%)	53(%)	% Conversion
1.0	15	10'	25
4.0	44	55	99

Direct irradiation of tetraphenylallene 31 in methanol-0-d

A quartz test tube containing tetraphenylallene 31 (250 mg) and methanol-0-d (20 mL) was positioned 5.0 cm from a Hanovia well. Irradiation was through a Pyrex filter ($\lambda > 280$ nm) for 8 hours. The reaction mixture was concentrated under reduced pressure and the residue was subjected to flash chromatography (2.0 x 12 cm) with hexane elution in 100 mL fractions: 1-5, nil; 6-7, mostly allene 31 and tetraphenylpropene 29-d. Continued elution with 0.5% ether-hexane: 8-10,

3-methoxy,1,1,3,3-tetraphenylpropene 36-d; 11-15, nil. Continued elution with 10% ether-hexane: 16-17, 2,2,4,4-tetraphenyl-3-butenol 37.

Fractions 6-7 were separated by repetitive preparative TLC (silica gel, hexane development) to yield a pure sample of tetraphenylpropene 29-d.

Spectral data are as follows:

Methylether 36-d: ^1H NMR (CDCl_3) δ 2.95 (s, 3H, $-\text{OCH}_3$), no definitive vinyl singlet at 6.92 was observed.

Tetraphenylpropene 29-d: recrystallized from ethanol, mp 127-128°C; ^1H NMR (CDCl_3) δ 4.81 (s, 1H), 7.1-7.4 (m, 20H). A small doublet at 6.54 was observed; this corresponds to the fully protonated compound 29 and constituted $\leq 10\%$.

Tetraphenylbutenol 37: ^1H NMR (CDCl_3) δ 3.95 (bs, 2H), 6.77 (d, 2H, $J = 7$ Hz), 6.87 (s, 0.2 H, vinyl), 7.0-7.4 (m, 18H).

Irradiation of tetraphenylallene 31 in basic methanol

Pyrex test tubes containing methanol solutions of tetraphenylallene 31 (10 mL, $2.91 \times 10^{-3}\text{M}$) with and without added sodium methoxide (25 mg, 0.46 mmol, 0.046 M) were irradiated (300 nm lamps) simultaneously in a Rayonett merry-go-round apparatus for 15 and 30 minute periods. Internal standard ([4,4'-dimethoxy]-1,1-diphenylethylene) was added and the solutions were evaporated to dryness. Photomixtures containing sodium methoxide were quenched with water (10 mL) then extracted with ethyl ether (3 x 5 mL), dried over sodium carbonate and concentrated in vacuo. Analysis was by 300 MHz ^1H NMR integration relative

to internal standard. Two separate runs at 10% and 20% conversion showed identical amounts of 3-methoxy-1,1,3,3-tetraphenylpropene **36** in runs with and without added sodium methoxide.

Measurement of deuterium isotope effect for tetraphenylallene **31**

Quartz test tubes containing methanol and methanol- D solutions (10 mL) of tetraphenylallene **31** ($2.90 \times 10^{-3} M$) were placed in a merry-go-round apparatus which was centered around a Hanovia well. Irradiation was through a corex filter ($\lambda > 260 \text{ nm}$) for 9 and 10 minutes. Internal standard (1,3,3-triphenylpropyne) was added and solutions were concentrated under reduced pressure. Product analysis was by 300 MHz 1H NMR integration. Two separate runs at 30-40% conversion yielded the following results for k_H/k_D (standard deviations shown): 3-methoxy-1,1,3,3-tetraphenylpropene **36-d**, 2.9 ± 0.1 ; tetraphenylpropene **29-d**, 5.4 ± 1.5 ; 2,2,4,4-tetraphenyl-3-butenol **37**, 6.0 ± 0.8 .

Sensitized irradiation of tetraphenylallene **31**

Allene **31** (350 mg) and 4-benzoylbiphenyl (1.00 g) dissolved in 150 mL of methanol-benzene (1:5) was irradiated through a uranium filter ($\lambda > 330 \text{ nm}$) for 24 hours. Concentration of the solution and subsequent chromatography gave 289 mg (83%) of unreacted **31**, 2.5 mg of adducts, and 945 mg (94%) of recovered sensitizer.

In a similar experiment, allene **31** (203 mg) and triphenylene (203 mg) dissolved in methanol-benzene (2:1) was irradiated for 72 hours through a uranium filter. Solvent removal and subsequent chromatography

gave 188 mg (93%) of unreacted 31 and 208 mg (102%) of recovered sensitizer.

Irradiation of triphenylallene 23 in methanol-0-d

Allene 23 (200 mg) in methanol-0-d (150 mL) at -10°C was irradiated at 300 nm for 5 hours. The solvent was removed by vacuum distillation at 0°C and the residue was subjected to flash chromatography (2.2 x 24 cm). Elution was with 1.0% ether-hexane in 25 mL fractions: 1-8, nil; 9-13, 190 mg of a mixture containing allene 23, propenes 43-d and 44-d, methyl ether 42-d and hydrocarbons 45-48 and 32; 14-18, nil; 19-27, 7 mg of 3-methoxy-1,1,3-triphenylpropene 41-d.

Fractions 9-13 were rechromatographed (flash, 1.5 x 32 cm) with hexane elution in 30 mL fractions: 1-7, nil; 8-15, overlap; 16-20, mixture of (Z)-1,3,3-triphenylpropene 43-d and 1,1,3-triphenylpropene 44-d, ca. 1.0:0.06; 21-30,

Spectral data are as follows:

41-d: ^1H NMR (CDCl_3) δ 3.26 (s, 3H), 4.70 (s, 1H), 7.2-7.6 (m, 15H);

43-d: ^1H NMR (CDCl_3) δ 5.20 (bs, 1H), 6.67 (bs, 1H), 7.19-7.37 (m, 15H)

44-d: ^1H NMR (CDCl_3) δ 3.47 (bs), no vinyl resonances were observed.

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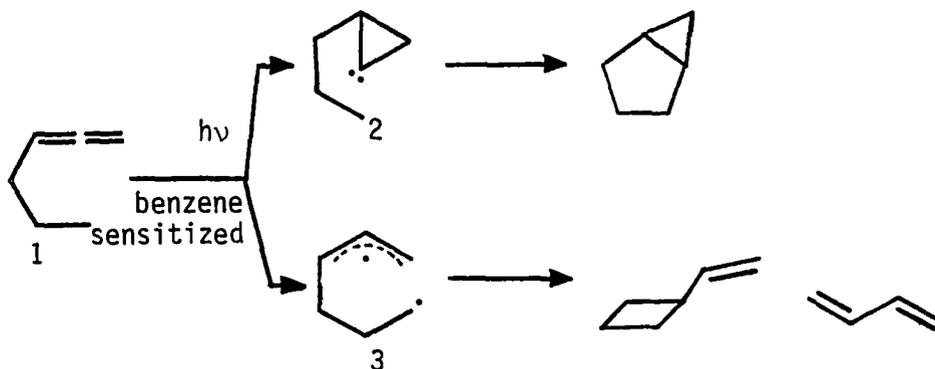
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CHAPTER II: PHOTOISOMERIZATION OF PHENYLALLENES

Introduction

The photoreactions of simple alkenes and 1,3-dienes have been intensively studied for many years and comprehensive reviews of this subject are available (1). By contrast, the photochemistry of allenes has received relatively little attention. Johnson (2) has recently surveyed allene photoreactions in a comprehensive review of which a substantial portion of this work is reported. Appropriate examples of allene photochemistry pertinent to the present work are described below.

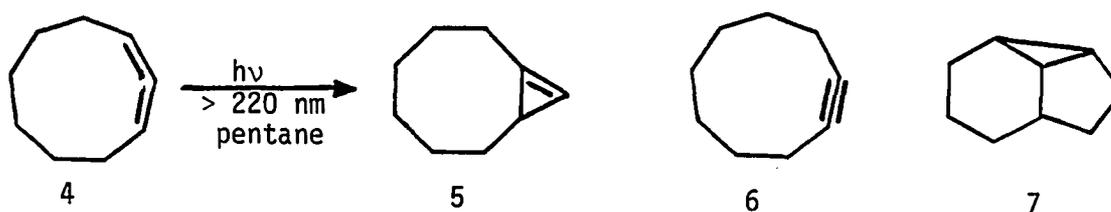
The earliest comprehensive study of allene photochemistry is due to Ward and Karafiath (3) who described the benzene sensitized vapor phase irradiation of several acyclic and cyclic allenes. The major products from these reactions were interpreted as arising from triplets of cyclopropylidene 2 and diradical 3. The isomerization of 1,2-hexadiene 1 (Scheme 1) is representative of their work. Karan has reported similar results for the benzene sensitized vapor phase irradiation of 1,2,6-octatriene (4). The solution phase photochemistry, however, was not carefully investigated.



Scheme 1.

More recently, the solution phase photochemistry of 1,2-cyclononadiene **4** has been extensively investigated by Stierman and Johnson (5,6).

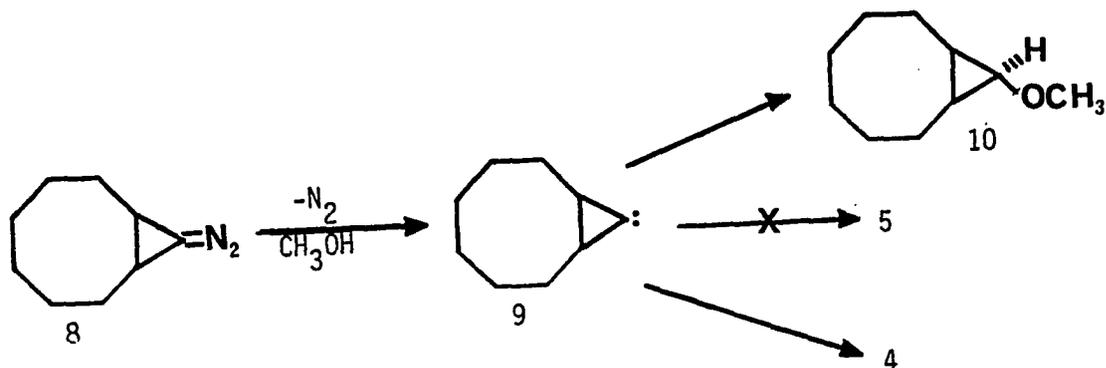
Direct irradiation ($\lambda > 220$ nm) of **4** in pentane afforded bicyclo-[6.1.0]-non-1(9)-ene **5**, cyclononyne **6**, and tricyclo-[4.3.0.0^{2,9}] nonane **7** in a ratio of 94:3:3, respectively (Scheme 2).



Scheme 2.

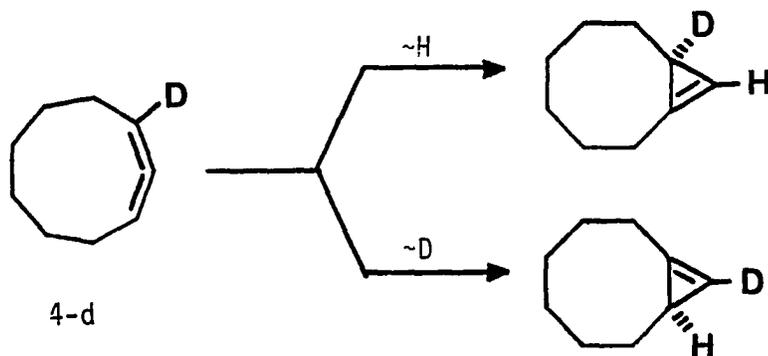
Kirmse (7) has previously observed that generation of cyclopropylidene **9** (presumably singlet) in methanol yields predominantly allene **4** (Scheme 3). This mitigates against singlet **9** as an intermediate in direct irradiation of **4**. The **8** - **4** rearrangement probably is significantly faster than intramolecular 1,2-H shift as cyclopropene **5** was not observed. Chapman (8) and Jones *et al.* (9) have observed similar reactivity from independently generated cyclopropylidenes. Additionally, extensive *ab initio* calculations by Honjou *et al.* (10), predict that the energy barrier for 1,2-H migration in cyclopropylidene is higher than ring opening to allene.

Isomerization of **4** to **5** could, in principle, involve hydrogen or carbon migration to vinylcarbenes **11** and **14**, with subsequent cyclization. Monodeuterated **4** (Scheme 4) displayed a kinetic isotope effect of



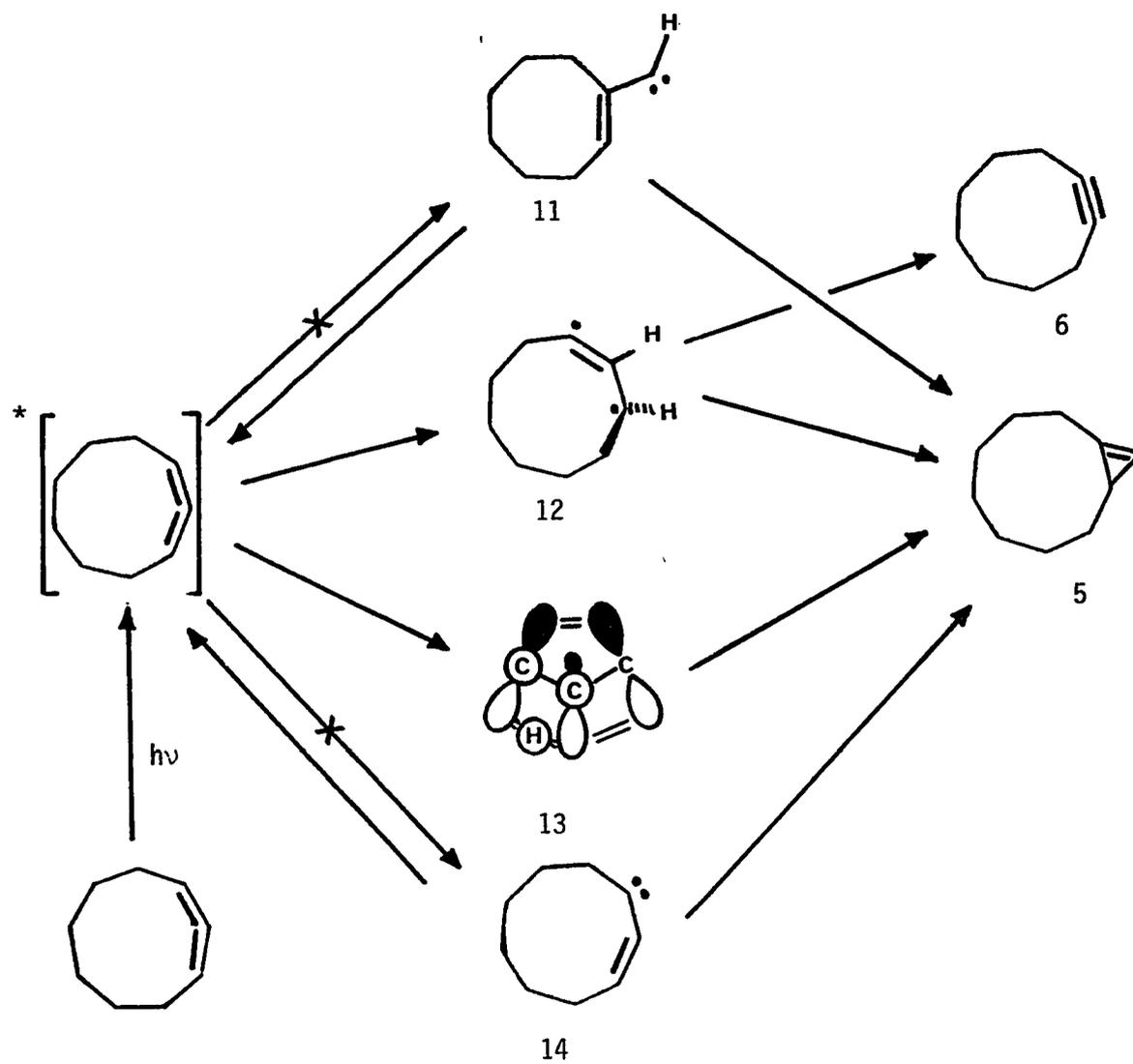
Scheme 3.

$k_{\text{H}}/k_{\text{D}} = 1.30 \pm 0.06$, thus suggesting that hydrogen rather than carbon migration was occurring.



Scheme 4.

The involvement of discrete vinylcarbene intermediates in singlet reactions of **4**, however, was rejected, since independent generation of **11** and **14** from diazo precursors yielded a plethora of products not observed from **4**. The authors proposed a concerted mechanism which proceeds through a $[\sigma_{2a} + \pi_{2a}]$ Hückel transition state (**13**), illustrated in Scheme 5, to account for **5**. A stepwise mechanism proceeding through diradical **12**, however, was not excluded since this best accounted



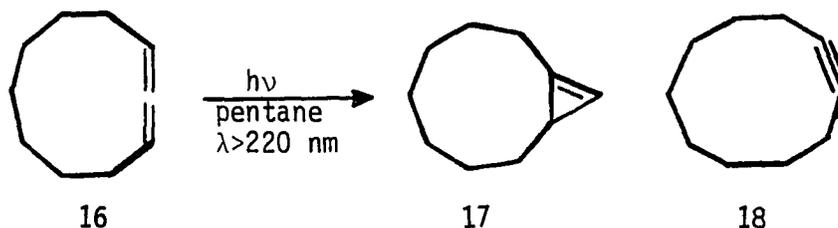
Scheme 5.

for **6** (Scheme 5). Tricyclic **7** was suggested to arise from diradical **15** (Scheme 6). Price and Johnson (11) have observed similar results for 1,2-cyclodecadiene **16** (Scheme 7).



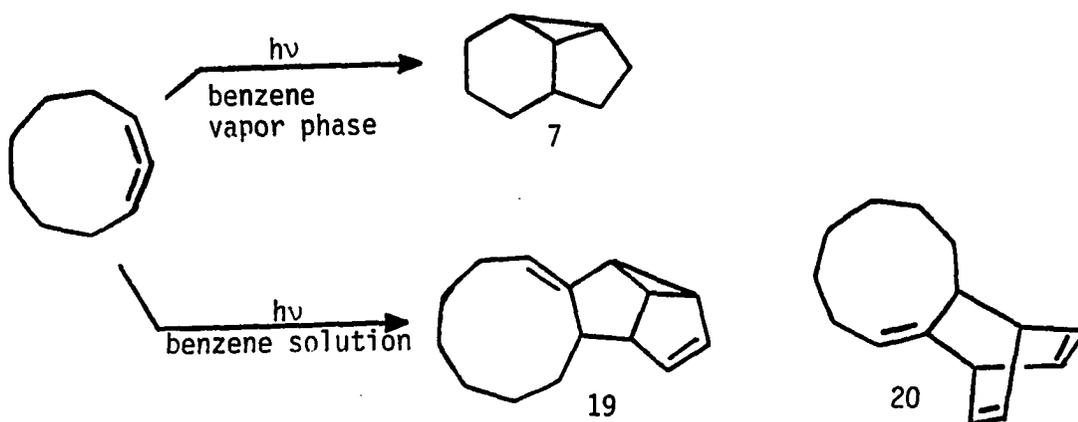
Scheme 6.

Triplet sensitization of **4** in the vapor phase and in solution has been reported (6, 12) to yield products significantly different from



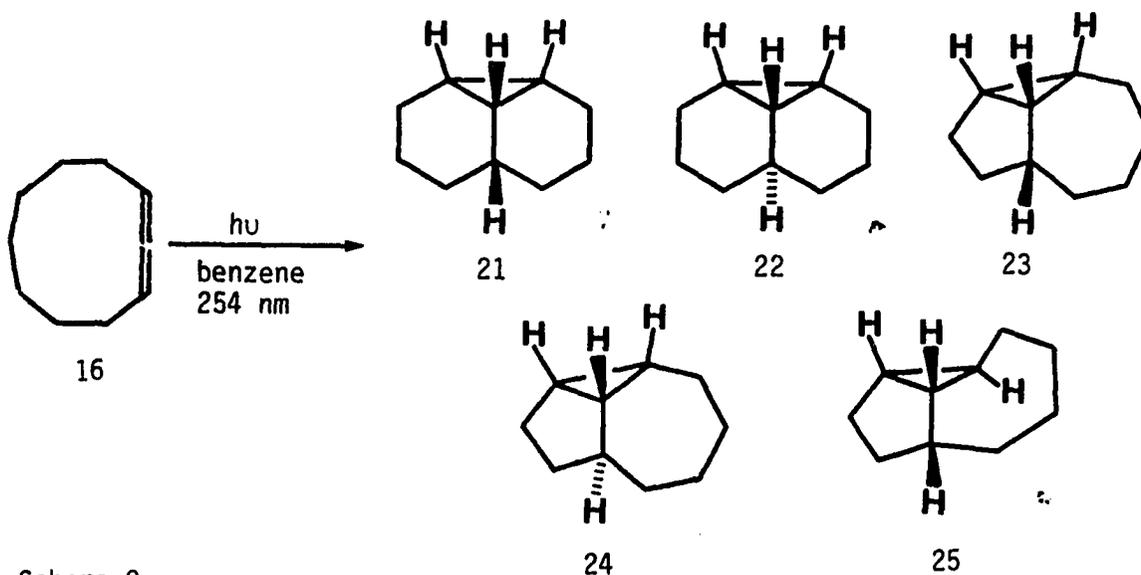
Scheme 7.

the singlet reaction. Irradiation of **4** in benzene solution afforded meta cycloadduct **19** and para cycloadduct **20** (Scheme 8). The benzene sensitized vapor phase irradiation of **4** yielded **7** as the predominant (94%) product, presumably via **26** (Figure 1). By contrast, benzene solution or benzene sensitized vapor phase irradiation of **16** (11) yielded tricyclics **21 - 25** (Scheme 9). The tricyclics were postulated to arise from two stereoisomeric triplet cyclopropylidenes **27** and **28** (Figure 1). No ready explanation is apparent for the differences in benzene solution phase photochemistry of **4** and **16**.



Scheme 8.

We were the first to report the solution phase photochemistry of linear acyclic allenes (13). The photoreactions of tetra- and triphenylallenes in hydrocarbon solvents yielded products which are explicable in terms of discrete vinylcarbene intermediates. This work forms the substances of much of the present dissertation.

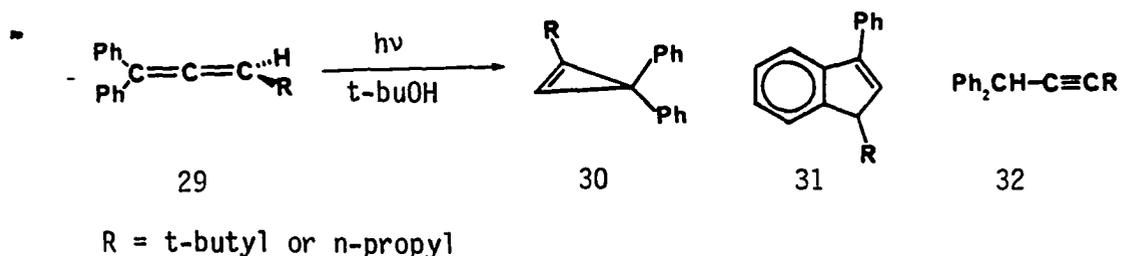


Scheme 9.



Figure 1. Cyclopropylidene intermediates

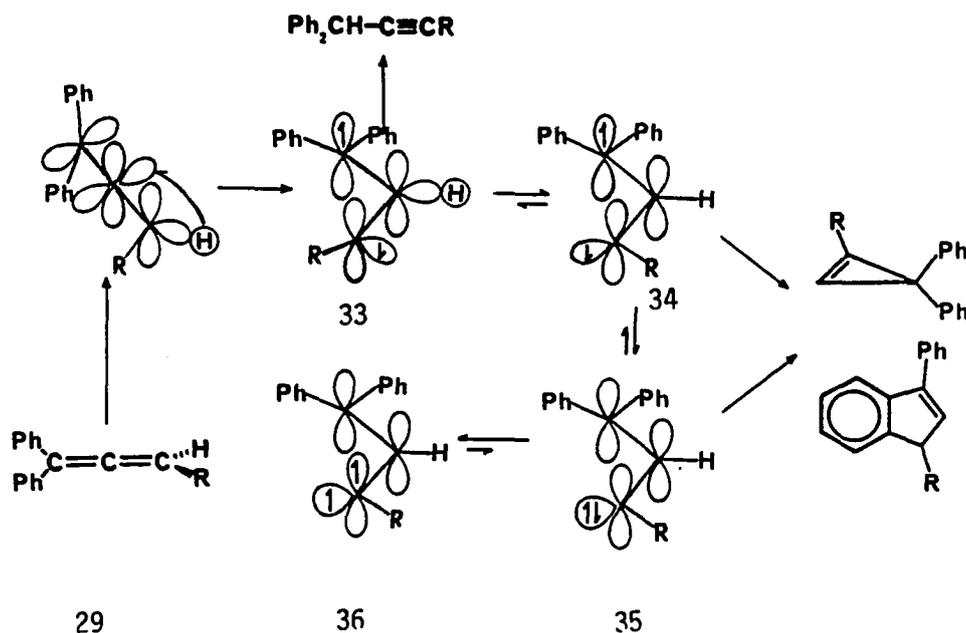
Photoreactions of 1,1,-diphenyl-3-alkylallenes, studied by Steinmetz *et al.* (14), yielded similar results. Direct irradiation of **29** in *t*-butanol afforded cyclopropene **30**, indene **31**, and propyne **32** as the primary products (Scheme 10). Triplet sensitization of **29** proved ineffective, thus implicating a singlet excited state mechanism.



Scheme 10.

These authors postulated a rather complex mechanistic scheme involving state-selective and conformation-selective behavior, as depicted in Scheme 11. Propyne formation is argued to arise exclusively from excited vinyl carbene ($^1A''$) **33** in a specific *syn* conformation, with a subsequent 1,2-H-migration. Stereoisomerization of *syn*-**33** to *anti*-**34** due to unfavorable steric interactions provides a geometry suitable for cyclopropene **30** and indene **31** formation. An additional pathway to **30**

and 31 is suggested to arise from the $^1A'$ electronic state 35, after equilibration.

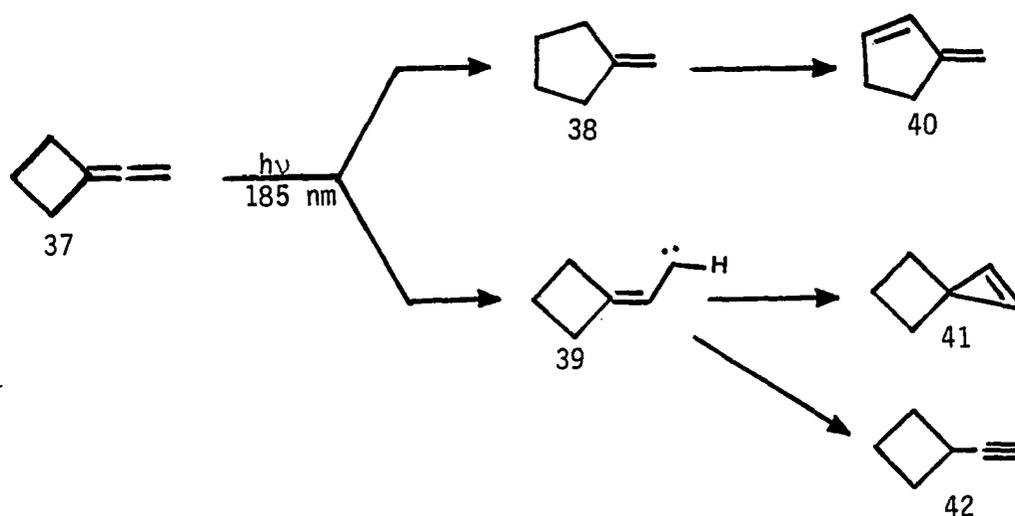


Scheme 11.

Photolysis of vinyl diazo compounds and cyclopropenes strongly suggested vinylcarbenes as precursors to cyclopropene and indene. Vinylcarbenes, however, do not appear to be progenitors of propynes. The premise of vinylcarbene state selective chemistry for propyne formation, as proposed by Steinmetz *et al.* (15), rests solely on previous theoretical calculations which predict the potential existence of an excited vinylcarbene ($^1A''$) (15). State and conformationally selective reactivity of vinylcarbenes, however, lacks experimental and theoretical support. A more detailed analysis of this aspect will be discussed later.

Steinmetz *et al.* (16) have provided the first example of competitive 1,2-H and 1,2-alkyl migrations in allene photochemistry. Direct

irradiation ($\lambda = 185\text{nm}$) of vinylidenecyclobutane **37** in pentane solution afforded **40** - **42** as primary photoproducts (Scheme 12). In contrast to their earlier interpretation, the authors proposed that propyne **42** and photoproducts **40** and **41** are formed directly from a $^1A'$ vinylcarbene electronic state. The authors, however, failed to provide any experimental support for their proposed mechanism.



Scheme 12.

Goals of This Research

The intention of the research in this chapter was to explore the reactivity of allene excited states in aprotic solvents. The effect of solvents on electronically excited states is well known. The photoreactions of ethylenes have been described to arise from an initially formed polarized species which may be trapped by nucleophilic solvents (17). In

a similar fashion, polarized intermediates have been implicated for singlet excited states of phenylallenes (13c,18). In nonnucleophilic media, simple olefins undergo photochemical isomerizations via carbene intermediates (1a), however, parallel studies with allenes were unknown at the outset of the present work.

Phenylallenes are among the oldest known and least studied allenes. This is despite their ready synthetic availability and well characterized chemistry of allenic structural isomers. The structural simplicity and extended chromophores of phenylallenes made these ideal candidates for exploratory photochemical studies.

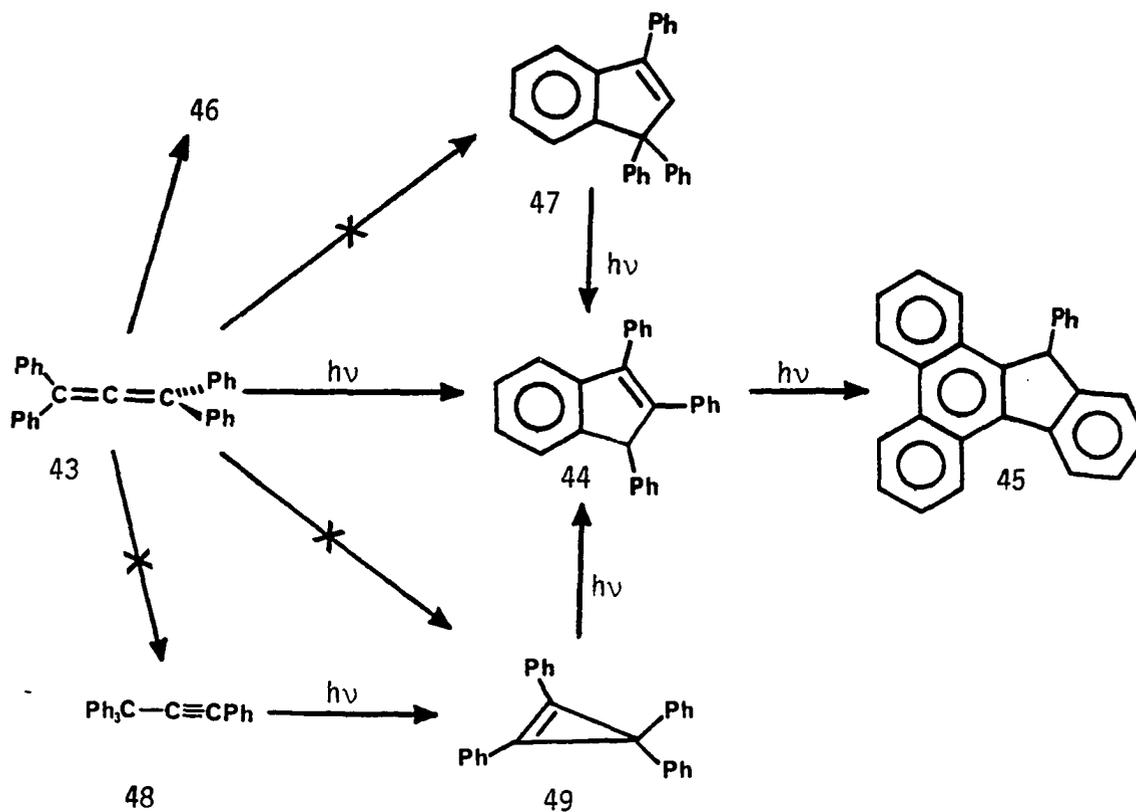
Phenylallene singlet excited states have the capacity to form vinylcarbene intermediates by either phenyl or hydrogen migration, thus providing another entry onto the cyclopropene excited state potential surface. The commonality of vinylcarbene intermediates is strongly suggested from the photolysis of phenylallenes, phenylcyclopropenes and corresponding vinyl diazo compounds, as will be discussed.

Exploratory Tetraphenylallene Photochemistry

Tetraphenylallene **43** was prepared and purified as described in Chapter 1.

Direct irradiation of dilute cyclohexane solutions of **43** at > 280 nm (Pyrex filter), 254 nm, or > 220 nm (Vycor filter), very slowly yielded 1,2,3-triphenylindene **44** and its known phenanthrene photoproduct **45** (19), along with one other very minor component **46** (Scheme 13).

Authentic samples of **44** and **45** were prepared for comparison, according to literature procedures (experimental).



Scheme 13.

Secondary **44** - **45** conversion was substantially more rapid than primary reaction of **43** and, even at < 5% conversion, only small amounts of **44** were observable. Photocyclization across the stilbene moiety of **44** and subsequent oxidation accounts for **45**; this is a well-known reaction (20). The intermediacy of **44** was verified by monitoring the photoreaction by 300 MHz ^1H NMR and HPLC analysis at very low conversions.

Tetraphenylcyclopropene **49**, 1,3,3-triphenylindene **47**, and tetraphenylpropyne **48** were independently synthesized according to literature procedures (experimental) for comparison to **46**, and to determine their presence in the reaction mixture. The unidentified component (**46**) displayed an HPLC retention time on silica columns which was identical to **47** and **49**, both of which are known photochemical precursors (**19**) to **44**. Analysis by reverse phase HPLC eliminated this possibility. Preparative isolation of **46** was achieved by tedious column chromatography and repetitive TLC.

The ^1H NMR spectrum of **46** revealed doublets at 8.78 and 8.80 ppm, suggestive of H_4 and H_5 of a phenanthrene skeleton (Figure 2). The lack of a sufficient quantity of pure material, however, precluded a definitive structural assignment.

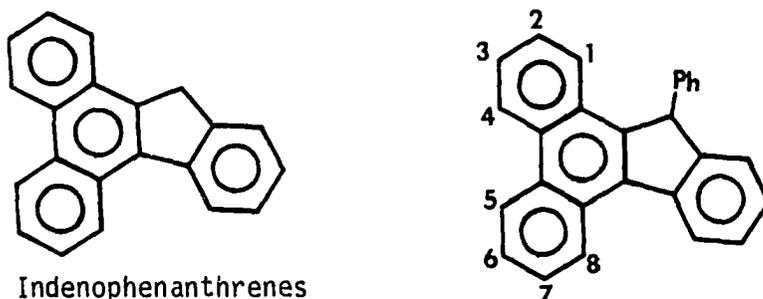
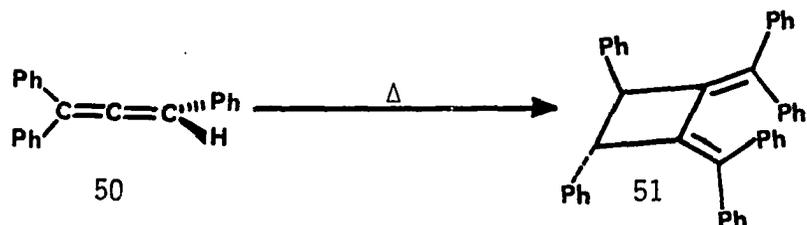


Figure 2. Indenophenanthrenes

Exploratory Triphenylallene Photochemistry

Triphenylallene **50** was prepared as described in Chapter 1, and was rigorously purified. Irradiation of **50** was best conducted at 254 nm in a specially constructed quartz vessel (see experimental). Dilute pentane solutions of **50** were maintained at -10°C to minimize thermal dimerization of this sensitive molecule. At ambient temperatures, solutions of **50** were found to yield **51** (Scheme 14). Equilibration

of **51** to other [2 + 2] dimers is known to occur at higher temperatures (21).

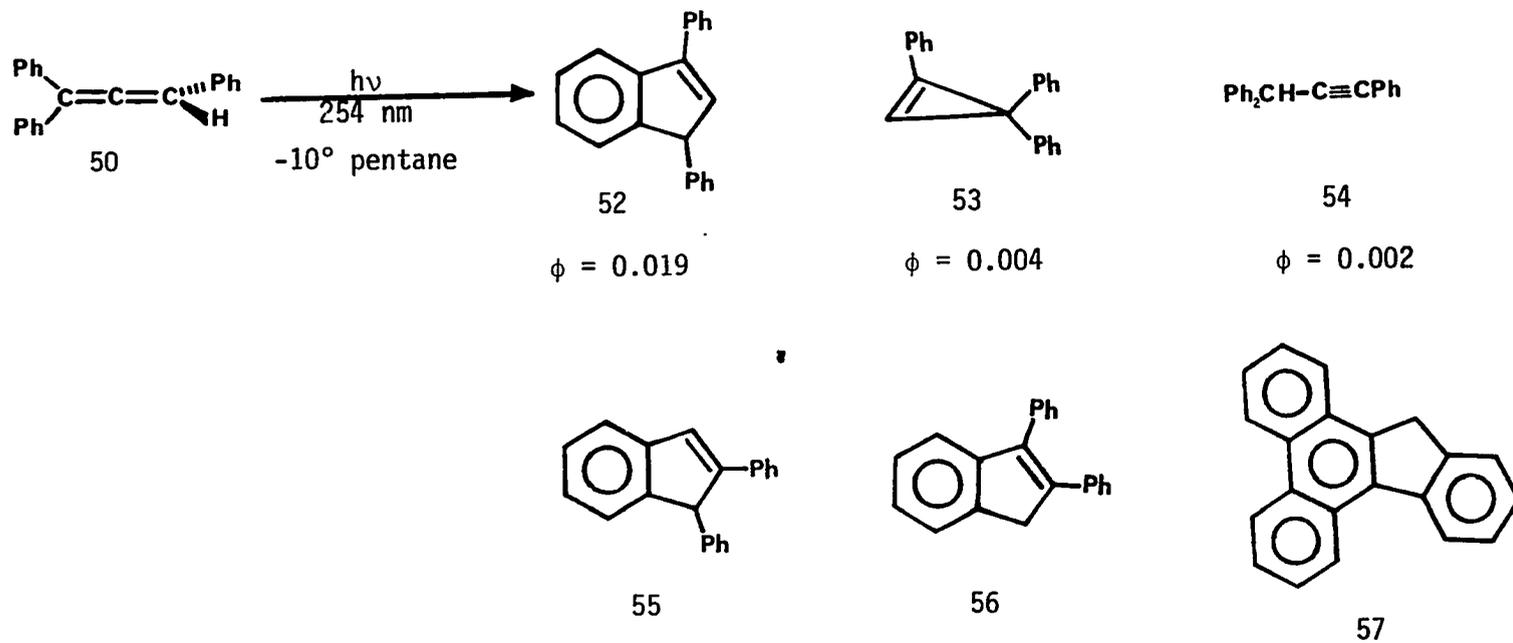


Scheme 14.

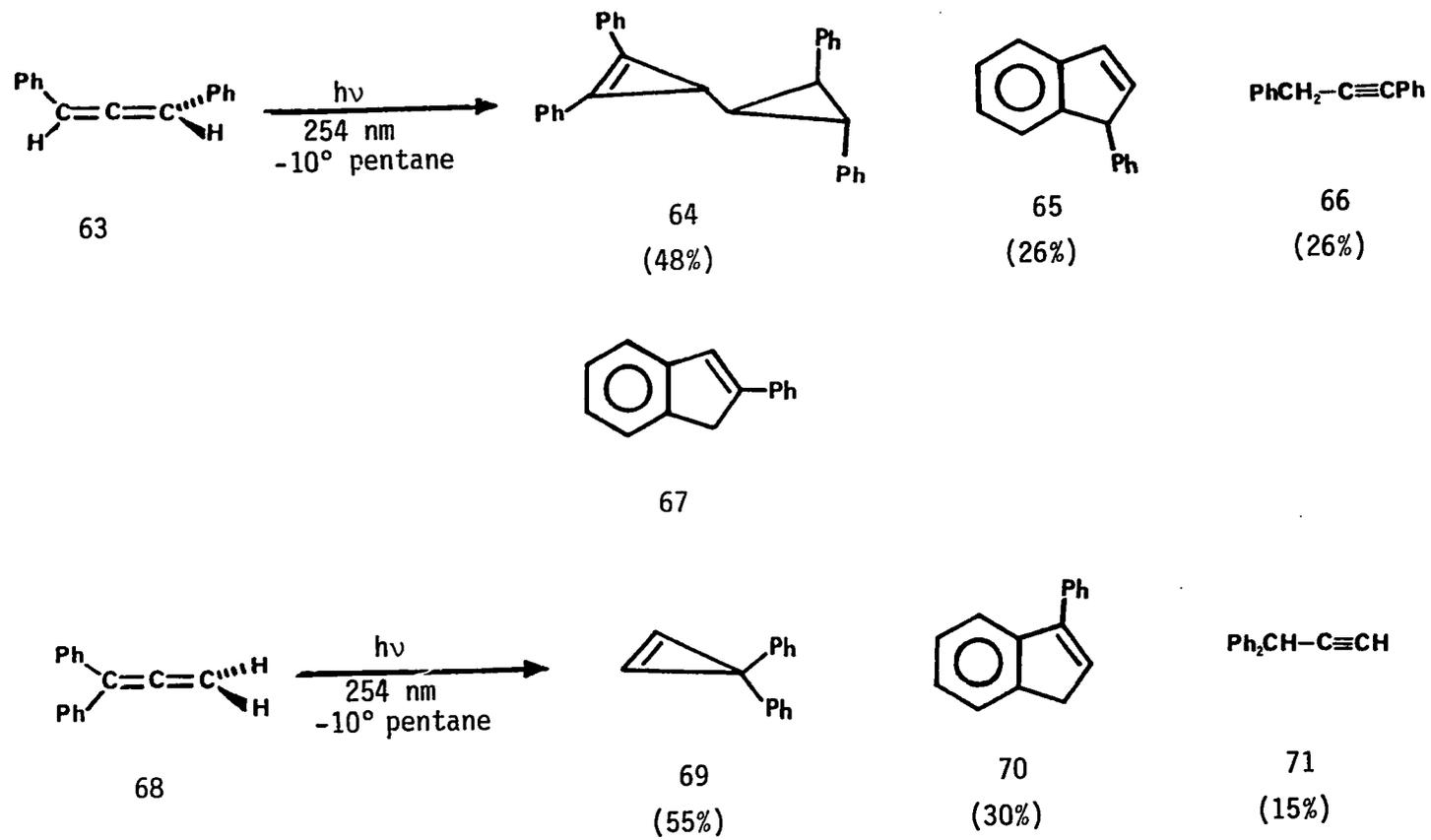
Direct irradiation of **50** under the conditions described above yielded photoproducts **52** - **57**, as shown in Scheme 15. All were isolated by chromatography in sufficient purity for unambiguous identification by comparison to authentic samples.

The previously unknown cyclopropene **53**, was prepared by the vinylcarbene route illustrated in Scheme 16. Cyclopropene **53** displays a distinct vinyl proton at 7.51 ppm and an infrared stretch at 1758 cm^{-1} , consistent with its assigned structure. The remaining photoproducts were synthesized according to literature procedures; these are detailed in the experimental section.

Progress of photochemical experiments was monitored by HPLC and 300 MHz ^1H NMR spectroscopy. At low conversion, **52** - **54** were found to be primary photoproducts, with **55** - **57** resulting from secondary rearrangements. At high conversion, the major isolated product was phenanthrene **57**, one of the ultimate photochemical "sinks" among triphenyl C_3 isomers.



Scheme 15.



Scheme 17.

Quantum yields for primary products were measured on an optical bench with potassium ferrioxalate actinometry. Product analysis at low conversion (0.5 - 1.0%) was accomplished by HPLC, relative to internal standard. Results are summarized in Scheme 15.

Exploratory 1,3-Diphenylallene Photochemistry

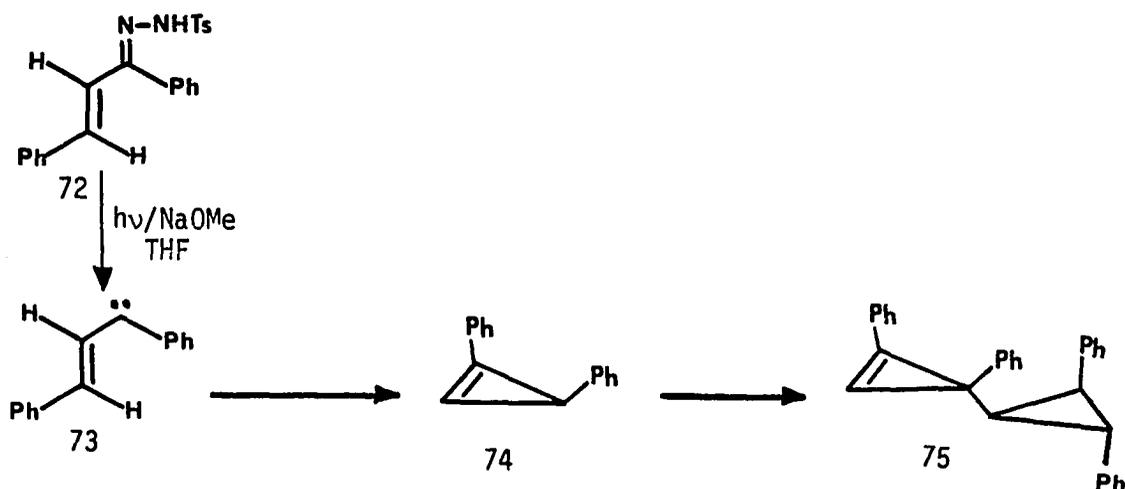
Preparation and purification of 1,3-diphenylallene **63** was described in Chapter 1. Photoreactions of **63** also were conducted at -10°C in order to preclude complications arising from thermal dimerization (**22**).

Direct irradiation of dilute pentane solutions of **63** at 254 nm yielded photoproducts **64** - **67** (Scheme 17), all of which were isolated by flash chromatography and identified by comparison to authentic samples. Independent synthesis of **64** - **67** were accomplished according to literature procedures and are detailed in the experimental section.

Irradiations carried out at greater than 20 - 30% conversion resulted in complex mixtures due to photocycloaddition of **63** with the photoproducts. These cycloadducts were not isolated, however, they compared well to a ^1H NMR spectrum from irradiation of a mixture of **63** and **67**.

Progress of the photoreaction of **63** was best analyzed by ^1H NMR, as HPLC detection at 254 nm did not prove adequate. Concentration versus time plots indicated **64** - **66** as primary, with **67** being a secondary photoproduct. The ratio of **64:65:66** at low conversion was 1.8:1.0:1.0.

Cyclopropene dimer **64** was identical in all respects with material which was isolated from vinylcarbene generations (vide infra).



Scheme 18.

Durr (23) had originally reported that carbene 73 yielded 75 via dimerization of 74 (Scheme 18). The spectral data obtained for this material, however, were entirely inconsistent with structure 75. The dimer displays intense UV absorptions at 337, 319, 290 and 230 nm, characteristic of a 1,2-diphenylcyclopropene chromophore. By comparison, 1,2-diphenylcyclopropene and tetraphenylcyclopropene exhibit UV absorptions at 336, 318, 308 and 234 nm and 336, 318, 314 and 230 nm, respectively. The UV spectrum of 1,3,3-triphenylcyclopropene, on the other hand, exhibits only one long wavelength absorption at 258 nm.

^1H NMR analysis of dimer 64 shows both aliphatic and aromatic resonances in a ratio of 1:5. The aliphatic hydrogen resonances appear as doublets at 2.49 and 2.48, and a doublet of doublets at 1.99 ppm, in a ratio of 1:2:1, respectively.

It is noteworthy that H_c appears as a doublet, thus indicating the symmetrical cis stereochemistry. An analogous structural assignment was reported by Breslow and Dowd (24) for dimers 76 and 77 (Figure 3).

The aliphatic hydrogens of *cis* 76 appear as an unsplit ^1H NMR resonance while an AB quartet is observed for *trans* 77.

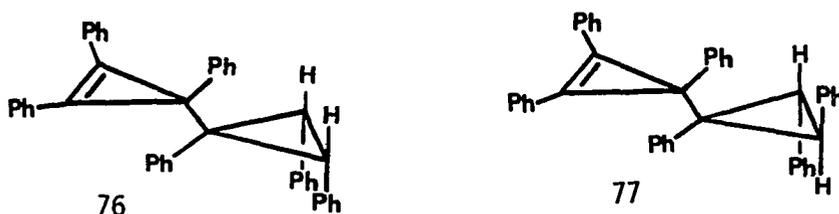
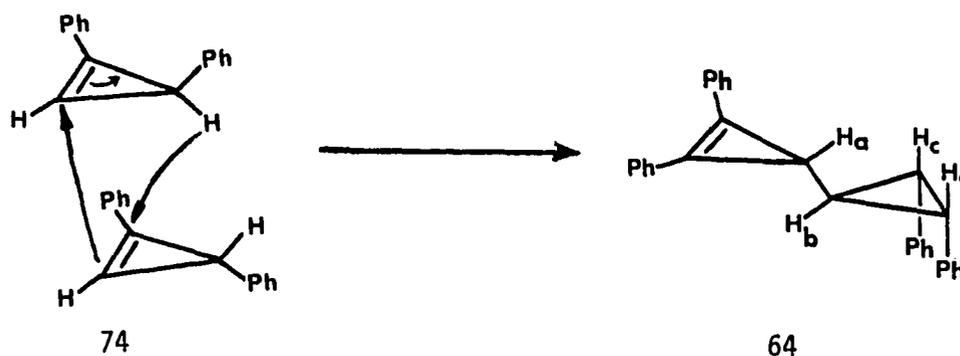


Figure 3. Cyclopropylcyclopropenes

Thermal dimerization of 1,3-diphenylcyclopropene 74 shown in Scheme 19 best rationalizes formation of 64. Cyclopropenes containing at least one hydrogen substituent at C-3 are known (24,25) to undergo extraordinarily facile thermal dimerization to cyclopropylcyclopropenes. A six-electron process analogous to the "ene-reaction" was postulated for this thermal dimerization, which benefits from strain release.

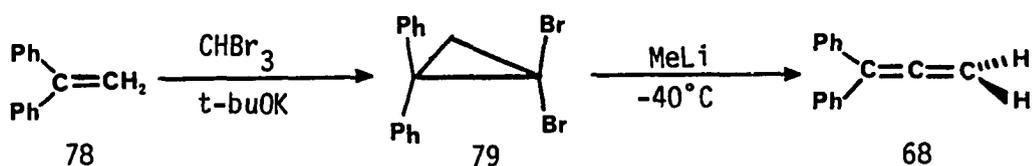


Scheme 19.

The *cis* relationship of the cyclopropyl hydrogen to the cyclopropene linkage at C₃ of 64 is consistent with the steric requirements for the "ene" dimerization mechanism.

Exploratory 1,1-Diphenylallene Photochemistry

1,1-Diphenylallene 68 was prepared in 52% yield from 1,1-diphenylethylene, according to the procedure of Skattebol (26) shown in Scheme 20. Purification (> 99%) was achieved by flash chromatography with pentane elution. A trace (< 0.5%) impurity, consistently present, was isolated and identified as 1,1-diphenylethylene 78.



Scheme 20.

Direct irradiation of dilute pentane solutions of 68 at 254 nm yielded photoproducts 69 - 71 (Scheme 17). All were isolated by flash chromatography and identified by comparison to authentic samples.

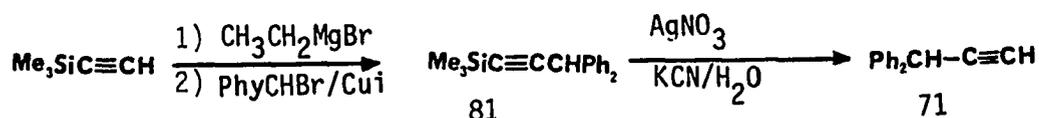
Kuznetrov and Libman (27a,b) have previously reported that dehydrohalogenation of 2,2-dichloro-1,1-diphenylpropane 80 afforded a 7% yield of 71 as an oil (Scheme 21); no spectral data were given.



Scheme 21.

An authentic sample of 71 was prepared in 35% overall yield as outlined in Scheme 22. Spectral data for 71 that support this structure, are ^1H NMR doublets at 2.38 and 4.91 ppm ($J = 2.6$ Hz) and infrared bands at 3300

and 2160 cm^{-1} . Cyclopropene 69 and indene 71 were prepared according to literature procedures (experimental).



Scheme 22.

Allene 68 and its photoproducts are thermally stable and its photoreactions were best monitored by GLC analysis, relative to 78 as internal standard. Under the conditions of irradiation, 78 proved to be inert. Concentration versus time plots of photoproducts gave a ratio of 1.8:1.0:0.5 for 69, 70, 71, respectively, at low conversion. At higher conversions, adduct 82 was formed from secondary photocycloaddition reactions (Figure 4).

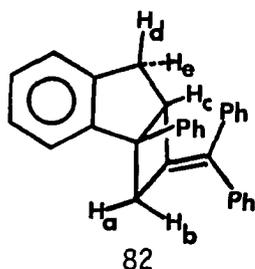


Figure 4. [2 + 2] Adduct of 1,1-diphenylallene and 3-phenylindene

The spectral data of 82 were identical with those obtained by photocyclization of 68 and 70. The assigned stereochemistry is consistent with the two distinct proton doublets (17 Hz) observed for H_d and H_e and the three sets of doublets (16, 8 and 3 Hz) for H_a , H_b and H_c .

Exploratory Phenylallene Photochemistry

Irradiation of dilute cold (-10°C) pentane solutions of phenylallene **83** yielded no isomeric products, as ascertained by ^1H NMR (300 MHz) and HPLC analysis during the course of the irradiation. Subsequent chromatography afforded a mass balance of only 18%, thus suggesting that allene **83** had undergone oligomerization. This was not investigated further.

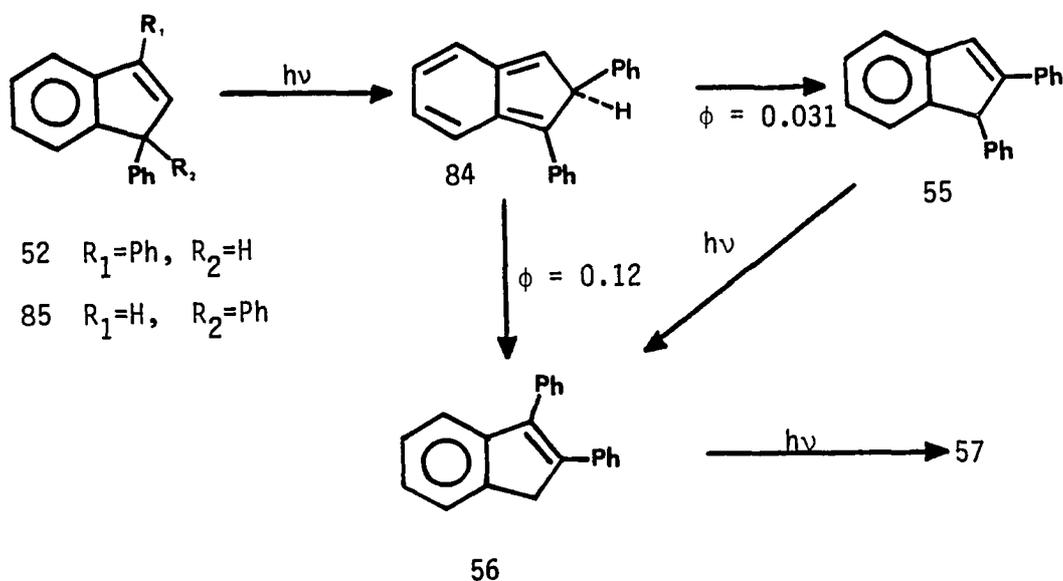
Exploratory Phenylpropyne Photochemistry

Phenylalkynes are reported to undergo photochemical dimerization to naphthalene and azulene derivatives (28). The mechanism of this process is not well understood. By contrast, Griffin and co-workers (19) found that tetraphenylpropyne **48** yields tetraphenylcyclopropene **49** and 1,2,3-triphenylindene **44** as the primary photoproducts upon direct irradiation. The authors also report that 1,3-diphenylpropyne **66** was photochemically inert. A primary concern during the present work was the potential isomerization reaction of triphenylpropyne **54** to cyclopropene and indene derivatives. Thus, a brief examination of the photochemistry of **54** was warranted. Direct irradiation ($\lambda = 254 \text{ nm}$) of a cold pentane solution of **54** did not yield evidence for isomers **52**, **53**, **55**, **56** and **57**, as ascertained by HPLC and ^1H NMR analysis. Subsequent chromatography yielded a both colorless and blue colored (presumably an azulene derivative) materials; these were not further characterized.

Exploratory Phenylindene Photochemistry

The photorearrangements of phenyl and alkyl substituted indenenes have been the subject of several previous reviews (29). In the present work, the observation of facile secondary indene photorearrangements during studies on phenylallenes prompted a brief examination of the isomeric phenylindene photochemistry.

Direct irradiation of 1,3-diphenylindene 52 yielded 55 and 56 in a ratio of 1:3 at low conversion. Quantum yields were measured on an optical bench, with potassium ferrioxalate actinometry. Analysis by ^1H NMR integration of appropriate resonances, relative to added internal standard is summarized in Scheme 23. McCullough (30a) and Manning *et al.*

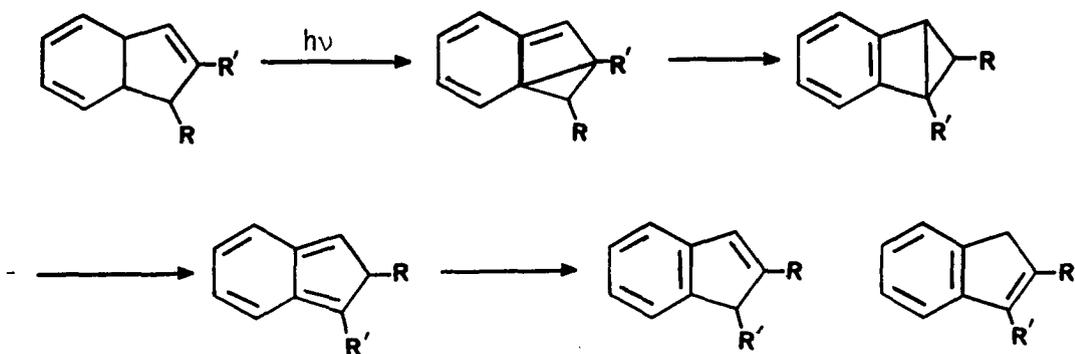


Scheme 23.

(30b) have reported an identical product mixture from irradiation of isomer 85, which argues for the common intermediacy of isoindene 84. Subsequent thermal 1,5-H migrations yield the observed products.

Formation of 56 and 57 from 52 was first reported by Padwa *et al.* (31); isomer 55 was not reported as a product in this work.

Irradiation of 1,2-diphenylindene 55 slowly yielded 56, 57 and a mixture of [2+2] dimers, presumably of 55. The dimerization products were not further investigated. Isomerization of 55 to 56 may be viewed as a photochemically allowed 1,3-H migration or a skeletal rearrangement, as depicted in Scheme 24. The photoisomerization of alkyl substituted indenenes, previously reported by Morrison and co-workers (32a,b), has



Scheme 24.

been suggested to proceed by this latter mechanism. The present experiments do not allow distinction between the two pathways.

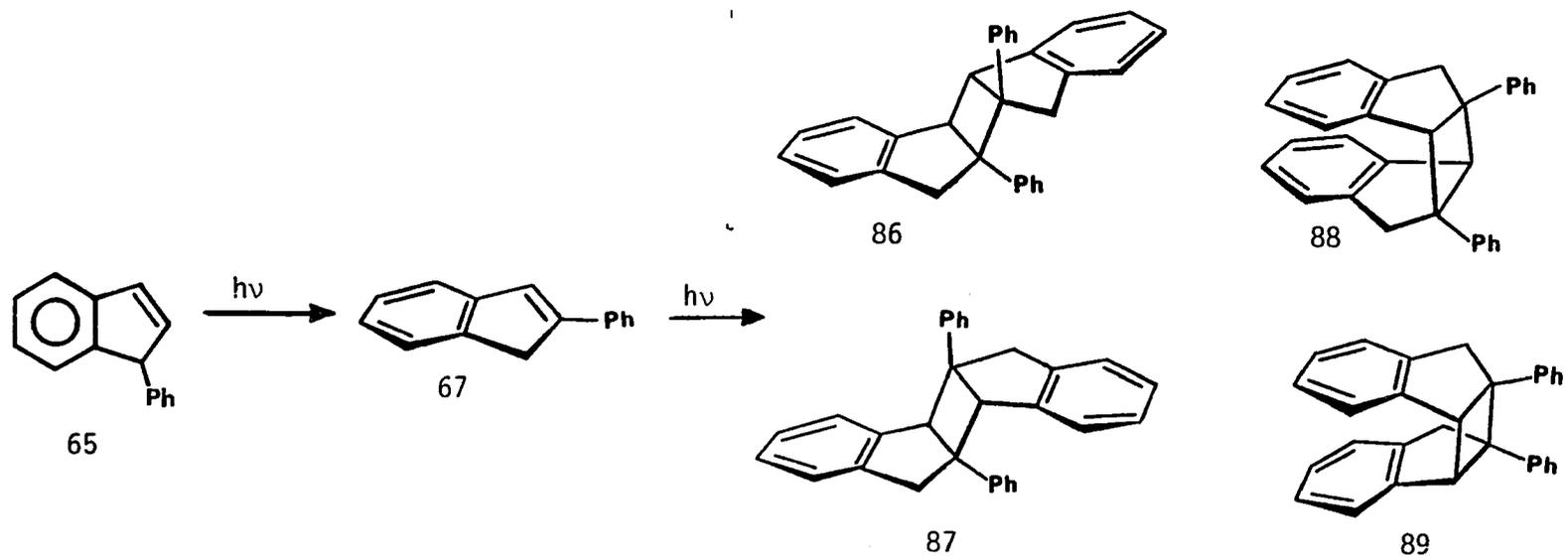
The photoreactions of phenylindenenes 65, 67 and 70 have never been reported. Direct irradiation of 65 at 254 nm proceeds smoothly to 67. The isomerization of 65 - 67 presumably involves a 1,2-phenyl migration to an isoindene intermediate, however, Morrison's skeletal rearrangement mechanism cannot be ruled out. By contrast, direct irradiation of 3-phenylindene 70 did not yield any of the isomeric

products even after prolonged irradiation. A small amount of a polycyclic aromatic compound was isolated, but this was not characterized.

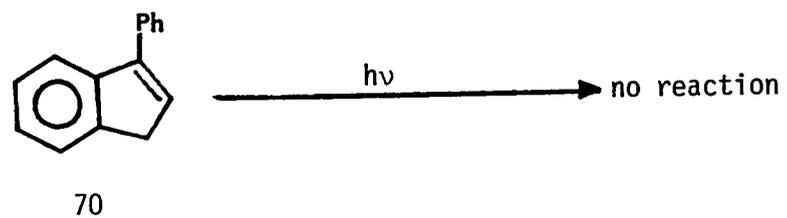
Irradiation of **67** at 300 nm yielded only [2+2] dimers (Scheme 25). These proved to be surprisingly well resolved by conventional column chromatography, with hexane elution. The four dimers were tentatively assigned structures **86** - **89**, based on physical and spectral properties.

Mass spectral and ^{13}C NMR data confirmed these compounds as dimers. ^1H NMR analysis showed 4 distinct resonances: two sets of doublets ($J \sim 17$ Hz), a benzylic singlet and aromatic hydrogens in a ratio of 1:1:1:9.

The significant benzene ring anisotropy effects permitted further structural assignments for these isomers. The endo dimers **88** and **89**, display similar aromatic proton resonances, which are distinctly different from those observed for **86** and **87**. The orientation of the phenyl and fused benzene rings of **86** and **87** are such that the anisotropy effects result in a relative upfield shift for the aromatic hydrogens. Molecular models of the dimers indicate that the phenyl rings of **89** are the most rigidly locked due to steric constraints. Consequently, the methylene hydrogens experience a strong anisotropy effect and are significantly shifted upfield. Molecular models also revealed that steric congestion causes the phenyl rings of **86** to be more rigid than those of **87**, resulting in a downfield shift for methine and upfield shift for methylene hydrogens.



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Scheme 25.

Additional support for the above structural assignments derives from column chromatography elution order. For a constant stationary phase and eluant, adsorption chromatography theory (33) predicts that elution order of similar molecules is dependent on their surface areas. The endo configuration of dimers 88 and 89 possess relatively less surface area than dimers 86 and 87, and therefore the former should elute faster. The observed elution order from a silica packed column was 88 > 89 > 86 > 87.

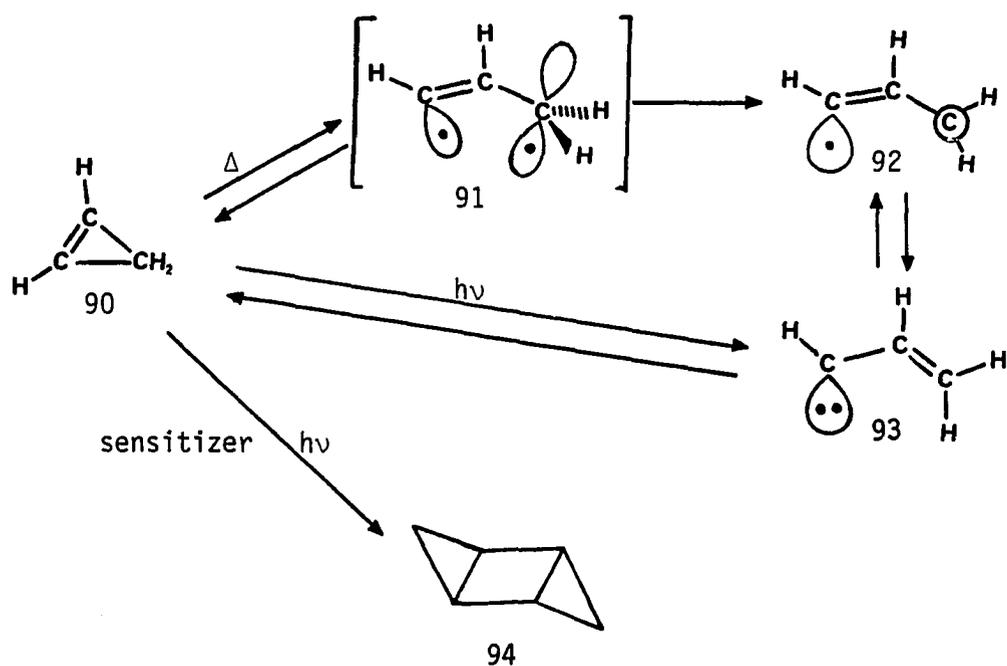
Exploratory Phenylcyclopropene Photochemistry

The photochemistry of the isomeric phenylcyclopropenes were also examined because of their intimate relationship with phenylallene photoisomerizations. The thermal and photochemistry of cyclopropenes is well documented (34).

Thermolysis of cyclopropenes is postulated (15, 34b) to result in σ -bond cleavage and subsequently rapid C₂-C₃ bond rotation to diradical 92, shown in Scheme 26. Decay of 92 to vinylcarbene 93 accounts for the observed products (35). By contrast, photolysis (15,34) is believed to cause σ -bond cleavage, with simultaneous C₂-C₃ rotation to 93.

The facile thermal (36) and photochemical (37) racemizations which are observed for optically active cyclopropenes argue that the major pathway of vinylcarbenes is return to cyclopropene.

Surprisingly, triplet sensitization of cyclopropenes does not result in ring opening reactions, despite sufficient energy to do so. Instead, efficient [2+2] dimerization to tricyclohexanes 94 is noted (34a).



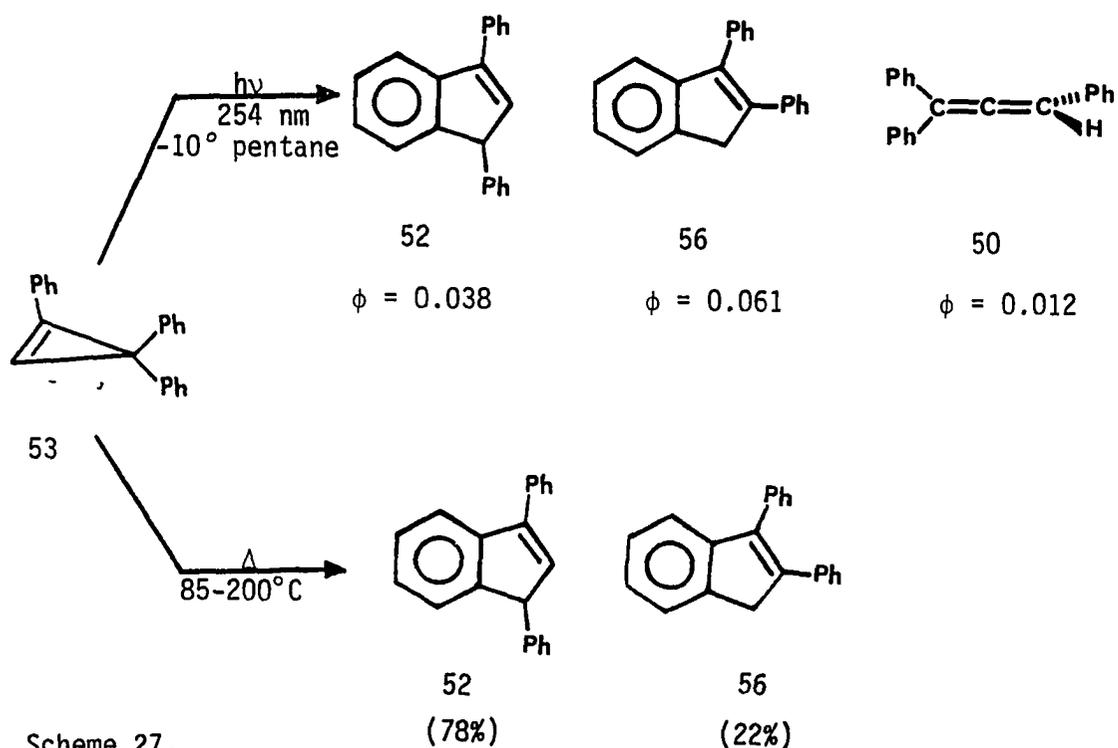
Scheme 26.

1,3,3-Triphenylcyclopropene **53** was prepared as described earlier (Scheme 16). Analytical samples of **53**, used in all experiments, were purified by flash chromatography, with subsequent recrystallization from hexane.

Direct irradiation of **53** at 254 nm yielded indenenes **52** and **56**, in addition to allene **50** (Scheme 27). Triphenylallene was isolated from the reaction mixture by chromatography and was identified spectroscopically. Indenenes **52** and **56** exhibit identical retention times by normal and reverse phase chromatography and thus were not separable. The structural assignments of **52** and **56** were based on their characteristic ¹H NMR signals.

Quantum yields for product formation were constant between 1 to 10% conversion. Analyses were performed by 300 MHz ^1H NMR, relative to added internal standard. Results are summarized in Scheme 27.

Photochemical ring opening of 53 to carbenes 95 and 96, with subsequent insertion into the aromatic ring, accounts for indenenes 54 and 50 respectively (Scheme 28). Triphenylallene presumably arises by either 1,2-phenyl or hydrogen shift from 95 and 96, respectively.



Scheme 27.

The preference of photochemical a-bond cleavage to vinylcarbene 95 is as expected; independent vinylcarbene generations (*vide infra*) support this. Thermolysis of 1,3,3-triphenylcyclopropene 52 at $85^\circ\text{--}200^\circ\text{C}$ yielded indenenes 52 and 56 (ca. 3:1), thus indicating preferential b-bond cleavage (29).

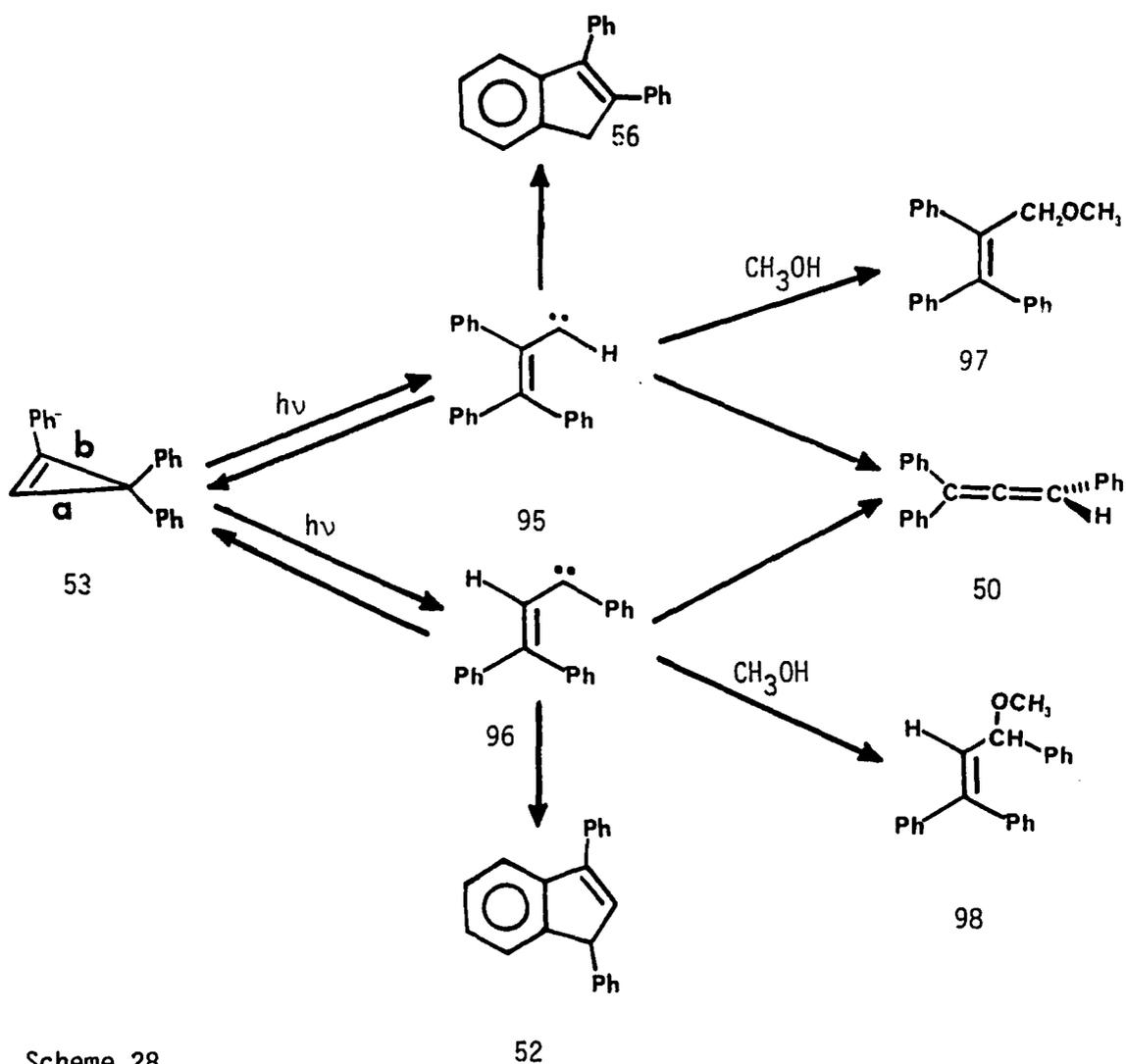
Padwa (34a) and Zimmerman and Bunce (38) have argued that ground state selectivity follows the relative stability of incipient vinylcarbenes, while excited state selectivity is a consequence of closer approach of ground and excited state surfaces along the reaction coordinate toward the less stable carbene. An alternative possibility is that ground and excited state bond orders for the two cyclopropene σ -bonds are reversed.

The substitution pattern of cyclopropenes is well-known (39) to play a significant role in ring opening and subsequent reactions. The effect of solvent on cyclopropene excited states, however, is not well understood. Photolysis of cyclopropenes in the presence of methanol (40) have been reported to yield variable amounts of allylic methyl ethers derived from intramolecular trapping by vinylcarbene intermediates. In a similar fashion, **53** yields the expected methylether, **97** and **98** (shown in Scheme 28) (ca. 0.8 and 0.5% yield at 60% conversion). Ethers **97** and **98** were identified by 300 MHz ^1H NMR analysis of the product mixture, with comparison to authentic samples (Chapter 1). The effect of solvent and rates for product formation were measured in hexane and methanol. Methanol and hexane solutions of **53** of identical concentration, were simultaneously irradiated at 254 nm in a merry-go-round apparatus with product analysis by 300 MHz ^1H NMR integration relative to internal standard. The intramolecular reaction products were calculated to be 74 times faster than intermolecular trapping by methanol, with no significant solvent effect for cyclopropene ring opening.

Formation of allenes from cyclopropenes has not been widely recognized; only recently have several examples of this rearrangement

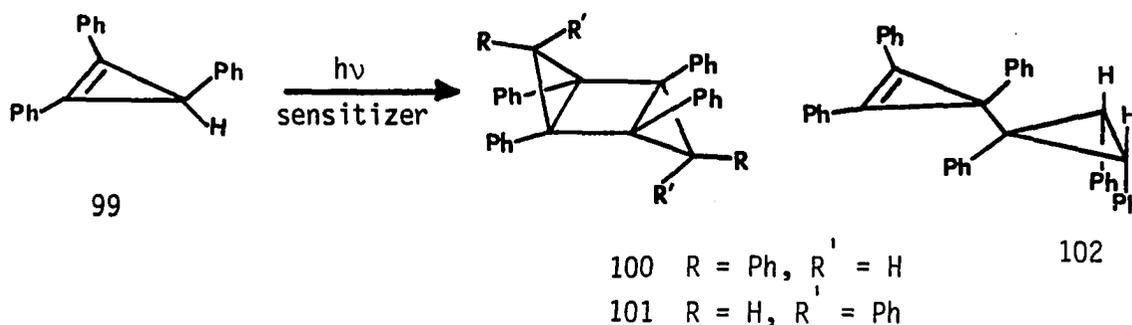
been reported (5,13b,14,41,42). The generality of cyclopropene to allene isomerization was therefore examined for the isomeric phenylcyclopropenes.

Photoreactions of 99 have been previously reported by several groups, with distinctly conflicting results. DeBoer *et al.* (43a) and DeBoer and Breslow (43b) initially reported "no reactions of quantum



yields greater than 10^{-2} on direct irradiation, but triplet sensitization yielded dimers **101** and **102** (Scheme 29). Subsequently Durr (44) reported that indene **55** and dimers **104** and **105** were formed.

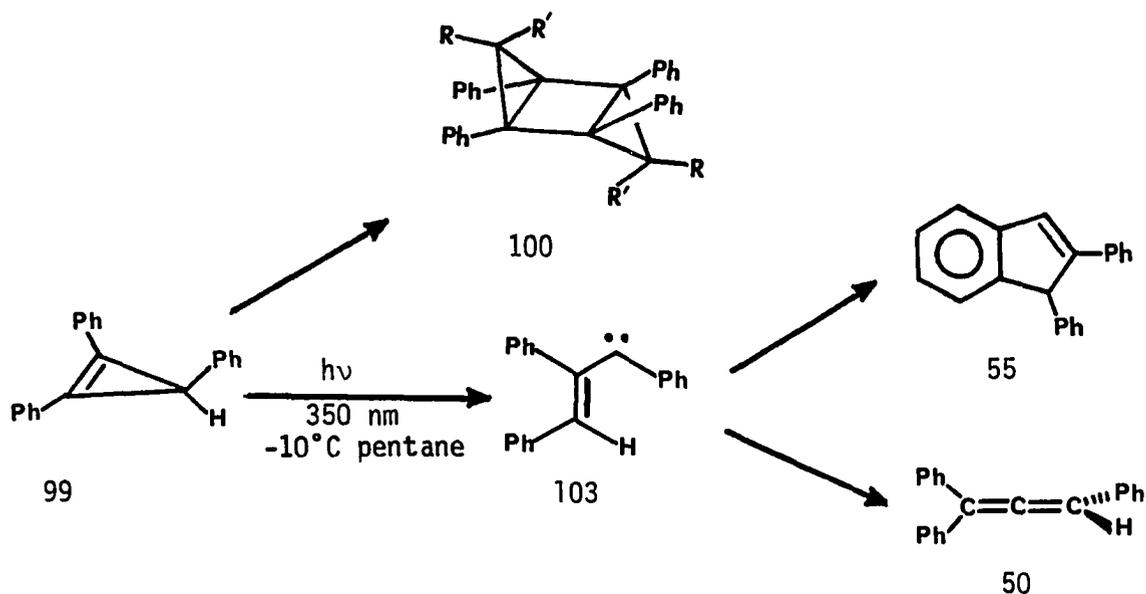
1,2,3-triphenylcyclopropene **99** was prepared according to literature procedure (experimental) and purified by flash chromatography with pentane elution, and subsequent recrystallization.



Scheme 29.

Low temperature (-10°C) irradiation of dilute pentane solutions of **99** at 350 nm yielded dimer **100**, 1,2-diphenylindene **55** and triphenylallene **56** in a ratio of 18:6:1 (Scheme 30). Analysis of the reaction mixture by HPLC showed a constant indene/allene ratio up to 83% conversion. Thus, allene is indeed formed, albeit inefficiently. Dimers **101** and **102** were not detected in the photomixture.

Formation of **100** is characteristic of the triplet excited state of cyclopropenes (34a). The predominance of **100** suggests that intersystem crossing of the singlet excited state competes favorably with ring opening to vinylcarbene **103**.

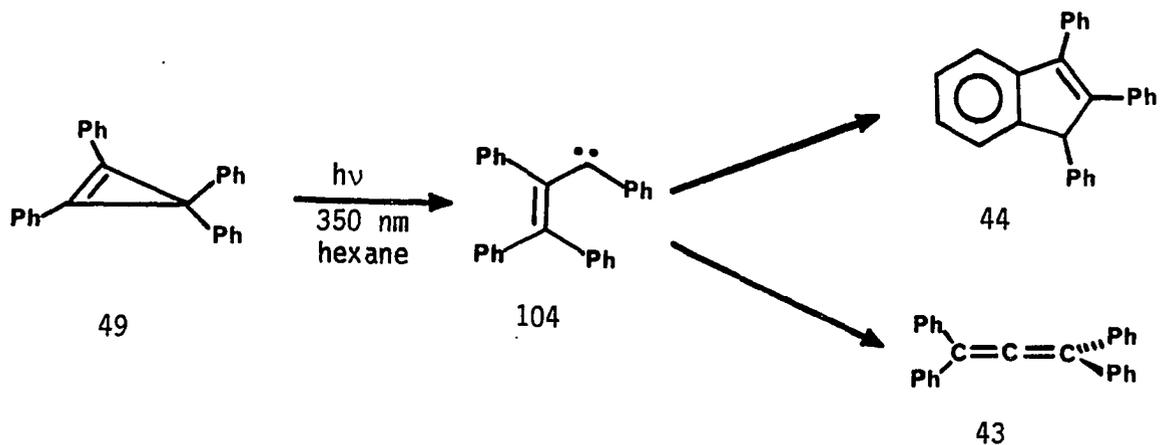


Scheme 30.

In a like manner, irradiation of tetraphenylcyclopropene 49 previously reported (19) to give only indene 44, was found by careful analysis and isolation to yield 4% of tetraphenylallene 43. This presumably involves ring opening to vinylcarbene 104 and subsequent phenyl migration (Scheme 31).

DeBoer *et al.* (43a) have previously reported that 1,2-diphenyl cyclopropene 105 yields the tricyclohexane derivative 106 upon triplet sensitization. Rearrangement of 106 to 1,2,4,5-tetraphenyl-1,4-cyclohexadiene 107 was observed to occur at temperatures greater than -30°C (Scheme 32). The singlet chemistry of 105, however, was not reported.

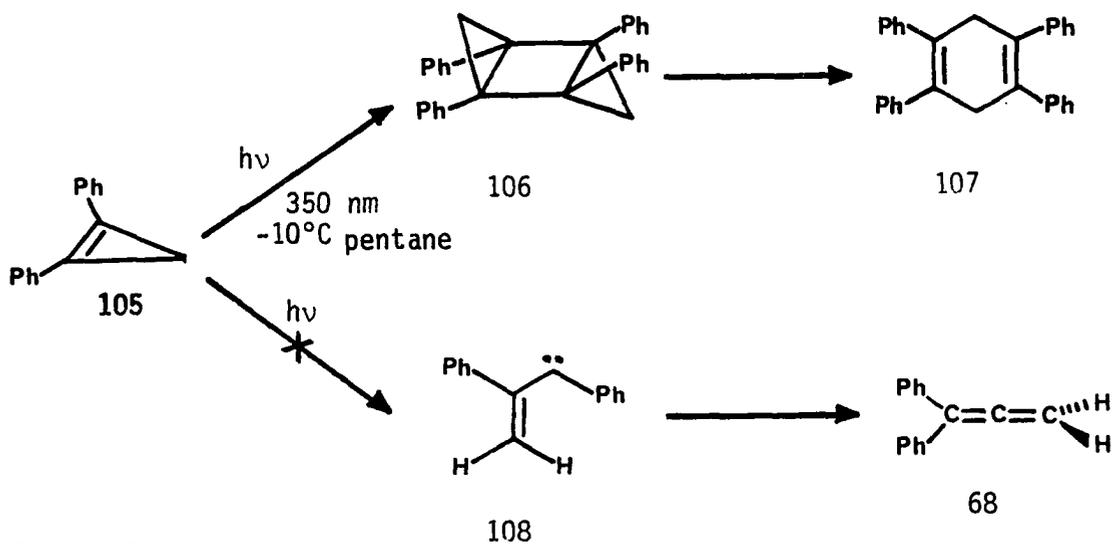
By analogy to other cyclopropenes, 105 has the capacity to ring open to carbene 108. In principle, this carbene might undergo reclosure to 105, or phenyl migration to allene 68. The UV characteristics of



Scheme 31.

105 and 68 are such to permit exclusive excitation of 105 at long wavelengths.

1,2-Diphenylcyclopropene 105 was prepared according to literature procedure (experimental), and purified by flash chromatography with pentane elution.

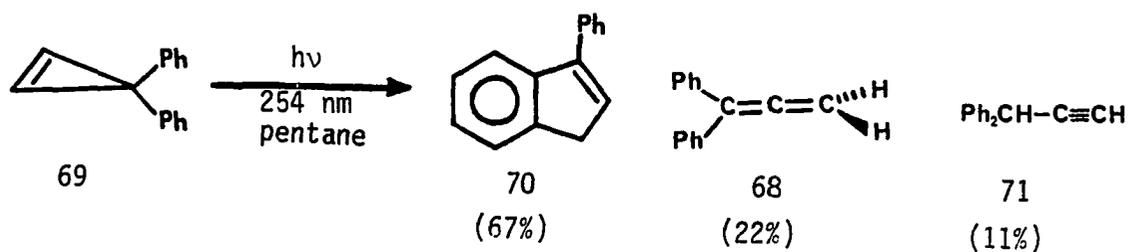


Scheme 32.

Direct irradiations of dilute and cold (-10°C) pentane solutions of 105 at 350 nm were monitored to completion by HPLC analysis. No isomeric photoproducts were observed. Analysis of the photomixture by 300 MHz ^1H NMR showed only the resonances of 107. These results, taken together with the known triplet reactivity of cyclopropenes, indicate that ring opening of 105 and subsequent phenyl migration is much slower than intersystem crossing.

3,3-Diphenylcyclopropene 69 was prepared by the vinylcarbene route (*vide infra*). Flash chromatography with pentane elution yielded a pure sample of 69 as a colorless oil.

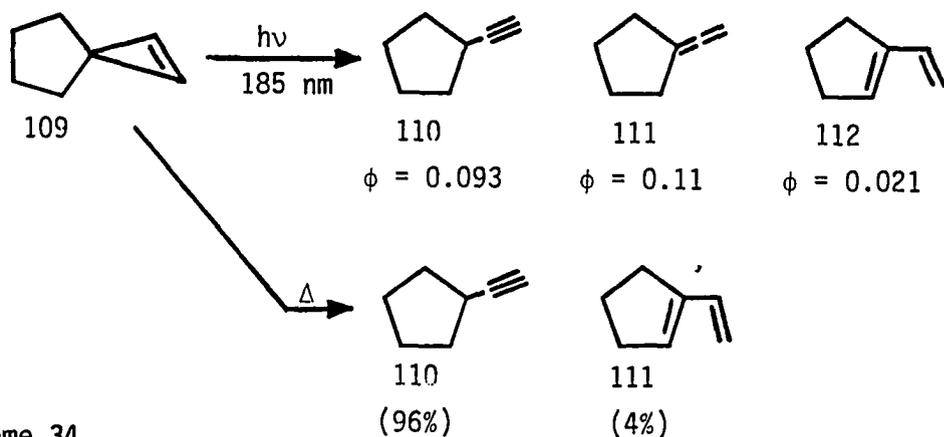
Direct irradiation of dilute pentane solutions of 73 at 254 nm afforded photoproducts 70, 68 and 71 (Scheme 33); these were isolated by flash chromatography in sufficient purity for unambiguous identification. Analysis of the reaction mixture by capillary GLC and ^1H NMR spectroscopy yielded a ratio of 3.1:1.0:0.5 for 70, 68, and 71, respectively, that was invariant up to 60% conversion.



Scheme 33.

Although thermal cyclopropene to propyne conversions are well-known, only two such photochemically induced isomerizations have been reported. Steinmetz *et al.* (42) have studied the thermal and photochemistry of

spiro[2.4]hept-1-ene **109**. Direct irradiation of **109** afforded **110** - **112** in 26, 34 and 8% yields, respectively (Scheme 34). In contrast, thermolysis afforded predominantly **110** and a small amount of **112**. The authors concluded that the difference between ground and excited state product distributions is attributable to state selective behavior. Photochemical ring opening of **109** yields an $^1A''$ vinylcarbene electronic state which undergoes subsequent radiationless decay to a maxima on the ground state surface corresponding to a transition state in cyclopropene thermolysis.

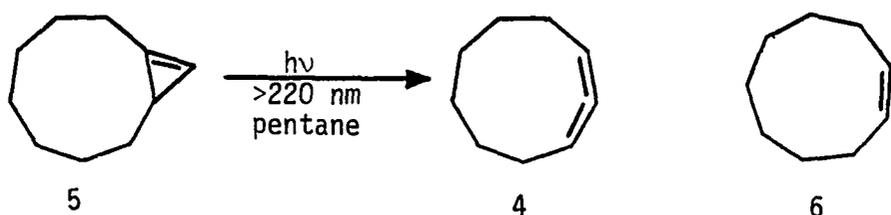


Scheme 34.

The intermediacy of discrete $^1A''$ vinylcarbenes, as proposed by Steinmetz et al., was based upon previous theoretical calculations (14). More recent, extensive ab initio calculations by Honjou et al. (10) and Feller et al. (45), however, predict that the $^1A''$ vinylcarbene may not be a stable species on the potential surface connecting cyclopropene and propyne. The disparity of the computational studies is due to the geometries employed for the potential intermediates. Honjou et al. predicted nonplanar allylic structures for vinylcarbene intermediates, based on MCSCF and CI calculations. Previous calculations had assumed

planar geometries. Additionally, independent vinylcarbene generations (vide infra) do not yield alkynes.

The first example of a cyclopropene to propyne photorearrangement is due to Stierman and Johnson (5). Irradiation of bicyclo[6.1.0]non-1(9)-ene 5 was reported to afford 7% of 6, 22% of 4 and a number of "characteristic" carbene derived products (Scheme 35). These authors postulated that 6 is formed by internal conversion of excited cyclopropene to a ground state geometry which approximates a bisected vinyl biradical 12 (Scheme 5). Subsequent 1,2-hydrogen migration prior to C₂-C₃ rotation accounts for alkyne formation.

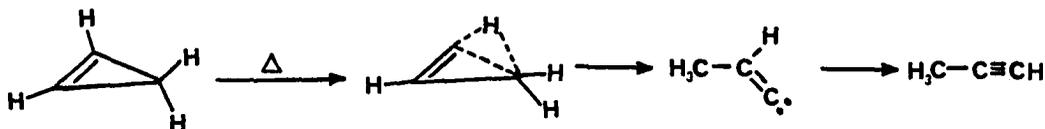


Scheme 35.

The differences in the excited state and ground state cyclopropene to propyne rearrangement may be due to two entirely different mechanisms rather than state selective carbene chemistry as proposed by Steinmetz et al.

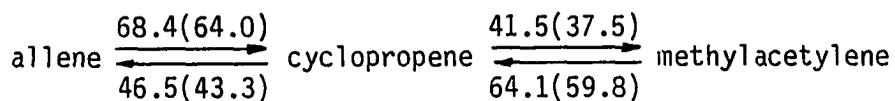
Based on extensive ab initio calculations, Honjou et al. (10) have proposed a novel thermal cyclopropene-propyne isomerization (Scheme 36) involving cyclopropene ring cleavage with simultaneous hydrogen migration to a vinylidene intermediate. Subsequent 1,2-hydrogen shift yields

propyne. Alkyne formation from independent vinylidene generation has been experimentally observed (46).



Scheme 36.

The activation energies calculated for this process are in excellent agreement with experimental results for pyrolysis of the parent cyclopropene, reported by Hopf *et al.* (47). Calculated activation energies in kcal/mol, with experimental energies in parentheses, are summarized below:



One final point in cyclopropene ring opening reactions is that allenes, albeit in small amounts, are always present from photolyses. The four examples investigated in this research and those of Stierman and Johnson (5), Steinmetz *et al.* (14,42), and Zimmerman and Kreil (41), argue for the generality of photochemical cyclopropene to allene isomerization. The small amount of allenes usually formed from these reactions may have prevented their detection in earlier studies.

Allenes are generally not observed in the thermal ring opening of cyclopropenes. Several exceptions include the high temperature pyrolysis of the parent cyclopropene (48), 1-methyl (49) and 1,3-diethyl (36) derivatives. In these examples, however, the thermal isomerization of alkyne to allene is reversible. The exclusion of allenes from other cyclopropene thermolyses may have been an oversight, or, the allenes

formed were destroyed under the thermolysis conditions. Pyrolysis of spiro[2.4]hept-1-ene 109, reported by Steinmetz et al. (42) (Scheme 33), would suggest otherwise, since allene 111 is stable under the pyrolysis conditions employed.

The E_{act} for allene formation which is calculated from pyrolysis of the parent cyclopropene (48) was 6 kcal/mol higher than that for propyne formation. Extensive ab initio calculations by Honjou et al. (10) concur with this result. The potential energy surface for interconversion of allene, cyclopropene and propyne calculated by the authors is depicted in Figure 5. Thus, the larger E_{act} for allene formation probably prevents this pathway on the ground state potential surface of cyclopropene ring opening, in favor of other lower energy pathways to thermodynamically stable products. Cyclopropene photolysis, however, probably results in close approach of the excited state potential surface to a ground state transition for allene formation. Subsequent radiationless decay accounts for allene in the photochemical reactions.

Mechanistic Studies: Triplet Sensitization

Triplet sensitization of 43 with xanthone (50) in benzene led to nearly quantitative recovery of 43 and sensitizer. The triplet energy of 43 has been previously estimated from energy transfer experiments by Ullman and Henderson (51) to be < 57.4 kcal/mol, thus energy transfer from xanthone ($E_T = 74$ kcal/mol) should be efficient

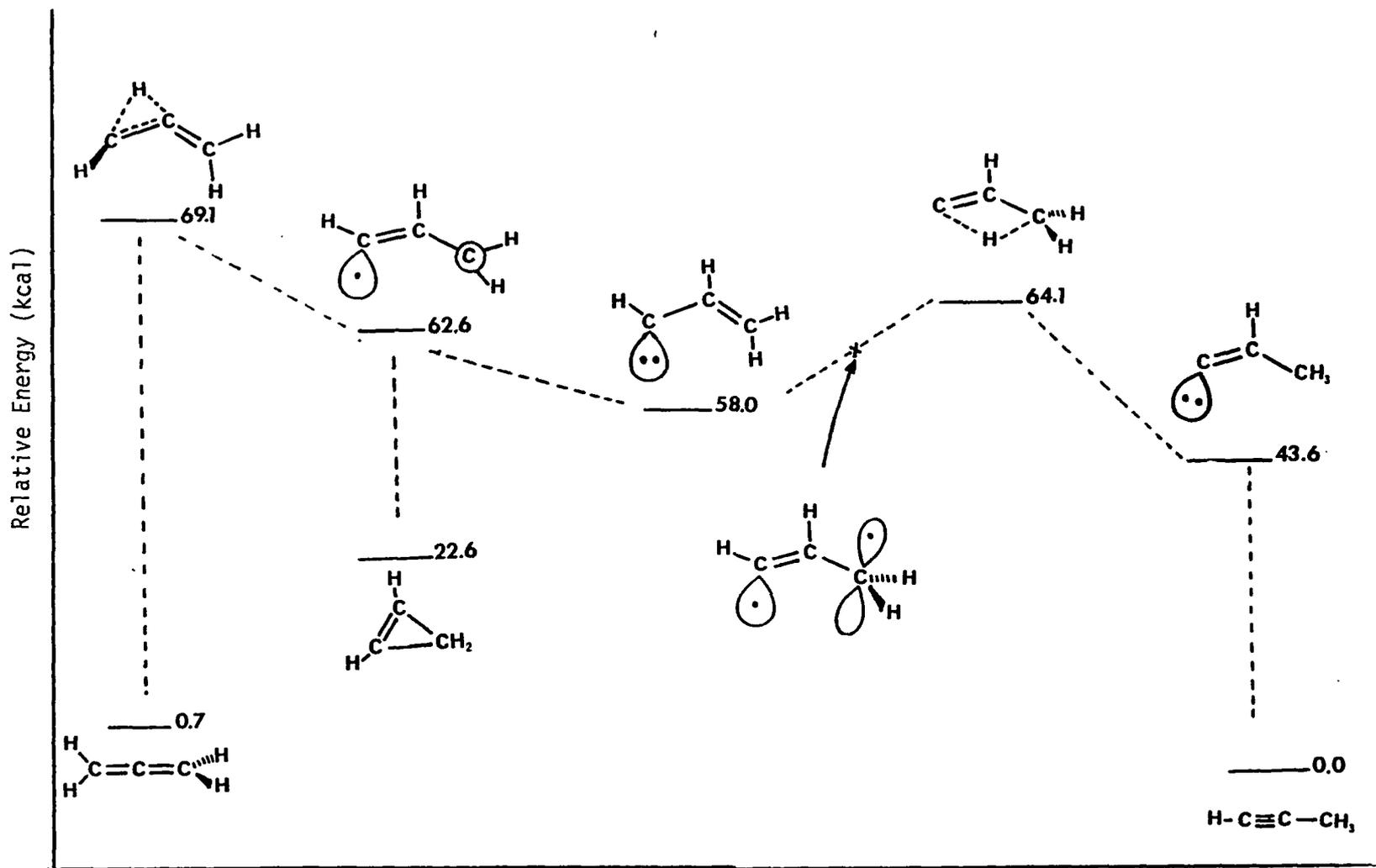


Figure 5. Potential energy surface for interconversion of allene, cyclopropene and propyne

and triplets of **43** are simply unreactive. The triplets of **50** and **63** should not be significantly higher than that of tetraphenylallene and, as expected, did not yield any observable reaction upon triplet sensitization with xanthone.

Allenes **43**, **50** and **63** showed no detectable fluorescence emission at ambient temperature in hydrocarbon solvents.

Mechanistic Studies: Vinylcarbene Generation

Experimental results from allenes **43**, **50**, **63** and **68** all suggested the common intermediacy of isomeric vinylcarbenes.

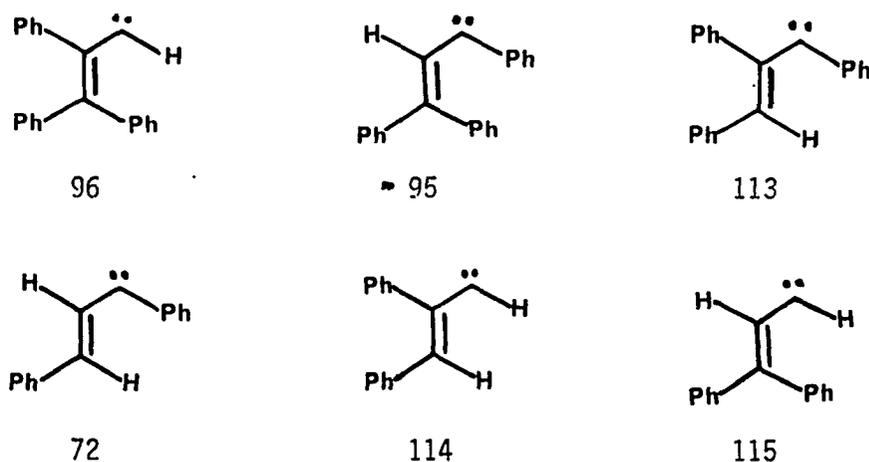
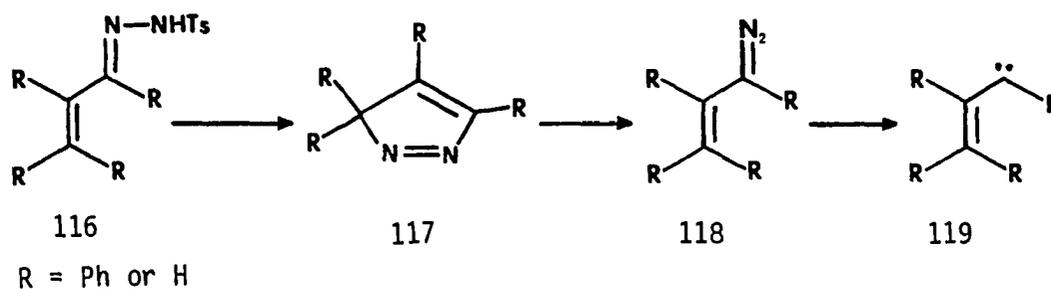


Figure 6. Potential vinylcarbene intermediates

Potential vinylcarbene intermediates depicted in Figure 6 were generated by photolysis of tosylhydrazone sodium salts in THF solution. Irradiations were conducted with a uranium glass filter ($\lambda > 330\text{nm}$), which precluded secondary rearrangements. Addition of sodium methoxide to the tosylhydrazone yielded a yellow colored solution. A pink

coloration was generally observed only after very short irradiation times. The sequence of intermediates associated with the color changes is probably due to the 3H-pyrazole 117 and diazo compound 118, respectively, (52) as shown in Scheme 37.

Preparations of enone and enal precursors not yet mentioned are detailed in the experimental section. The corresponding tosylhydrazone derivatives were obtained in good yields by heating acidic alcohol solutions of the enone or enal with p-toluenesulfonylhydrazide.

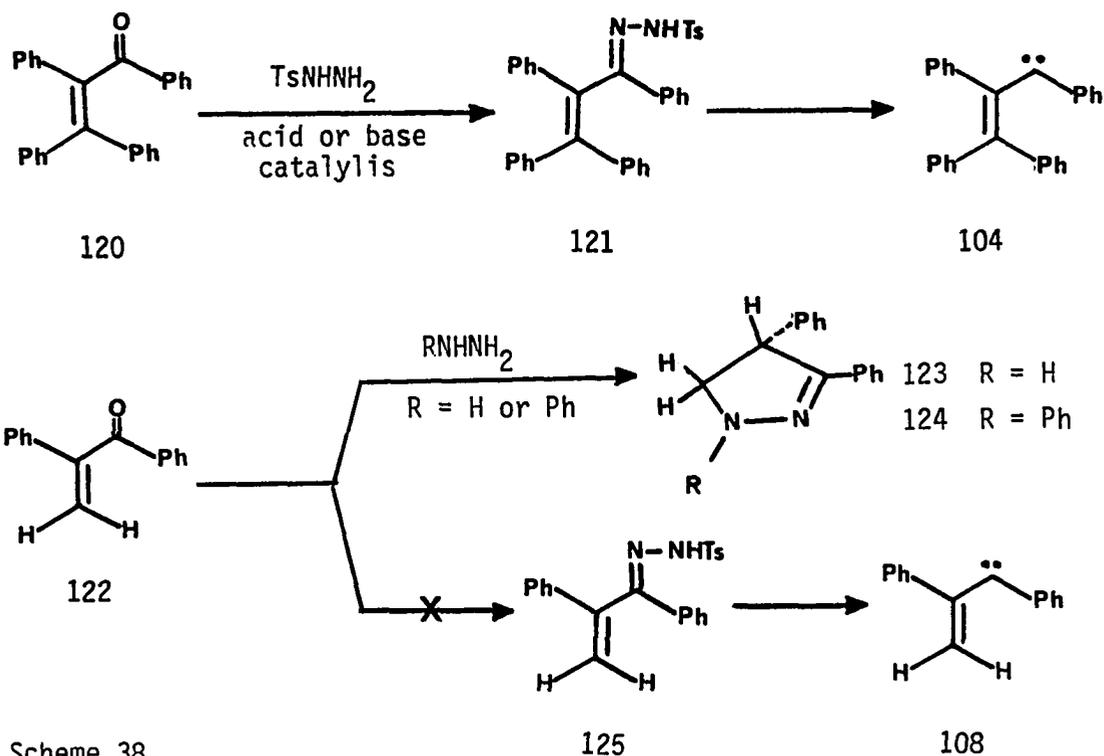


Scheme 37.

Numerous attempts to prepare the tetraphenylpropenone tosylhydrazone 121 were unsuccessful, probably because of steric effects (53).

Previous attempts to prepare hydrazone derivatives of 2,3-diphenylpropenone 122 were reported (49) to yield only pyrazole derivatives (Scheme 38), thus independent generation of 108 was omitted in the present study.

Results of carbene generations are depicted in Schemes 39 and 40. Hydrocarbon product ratios are summarized in Tables 1 and 2. Durr (23) first reported generation of carbenes 95, 113, 72 and 115. The present results parallel those of Durr's with few exceptions. These are: isolation of 49 from 126, formation of dimer 59 and not 67, and the

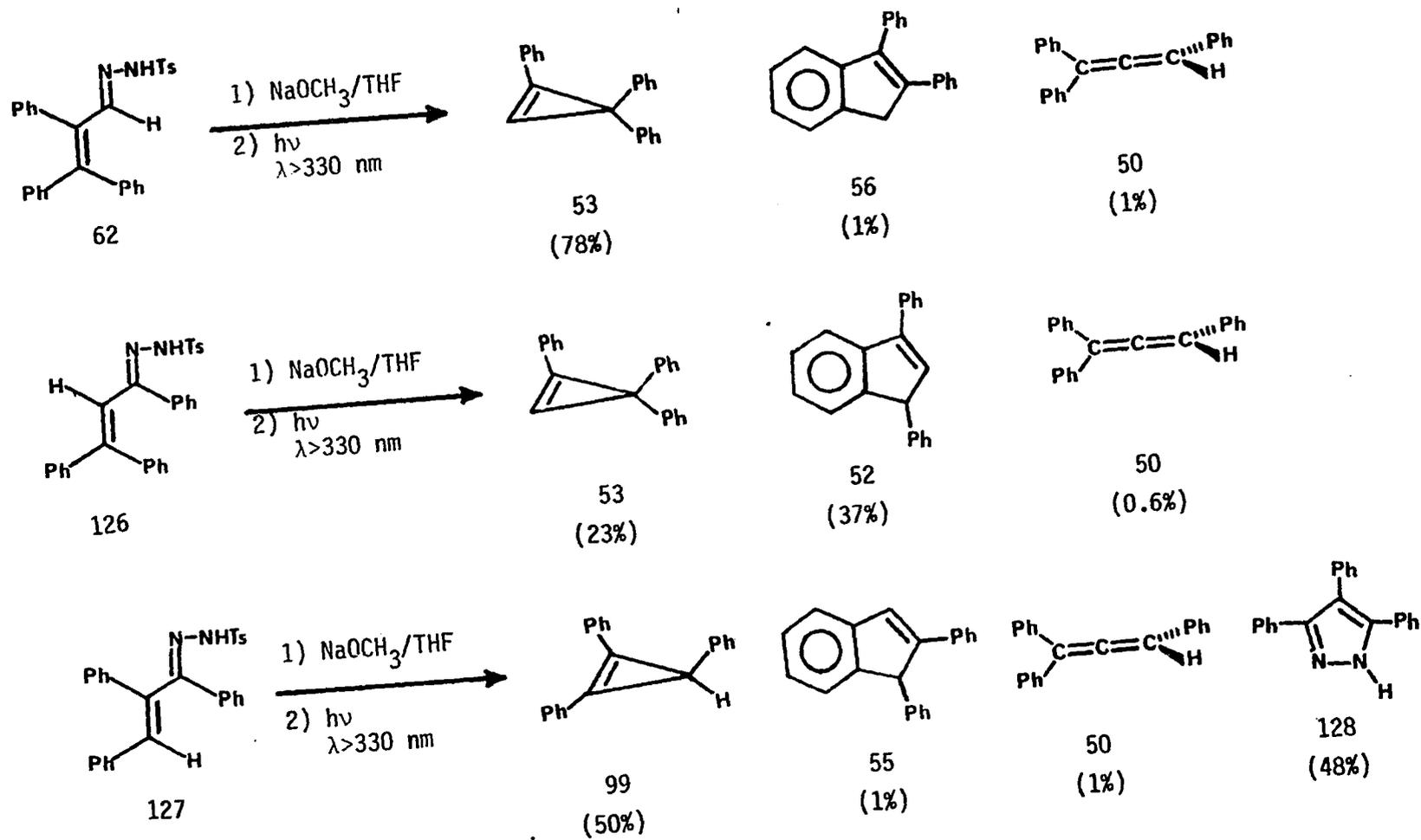


Scheme 38.

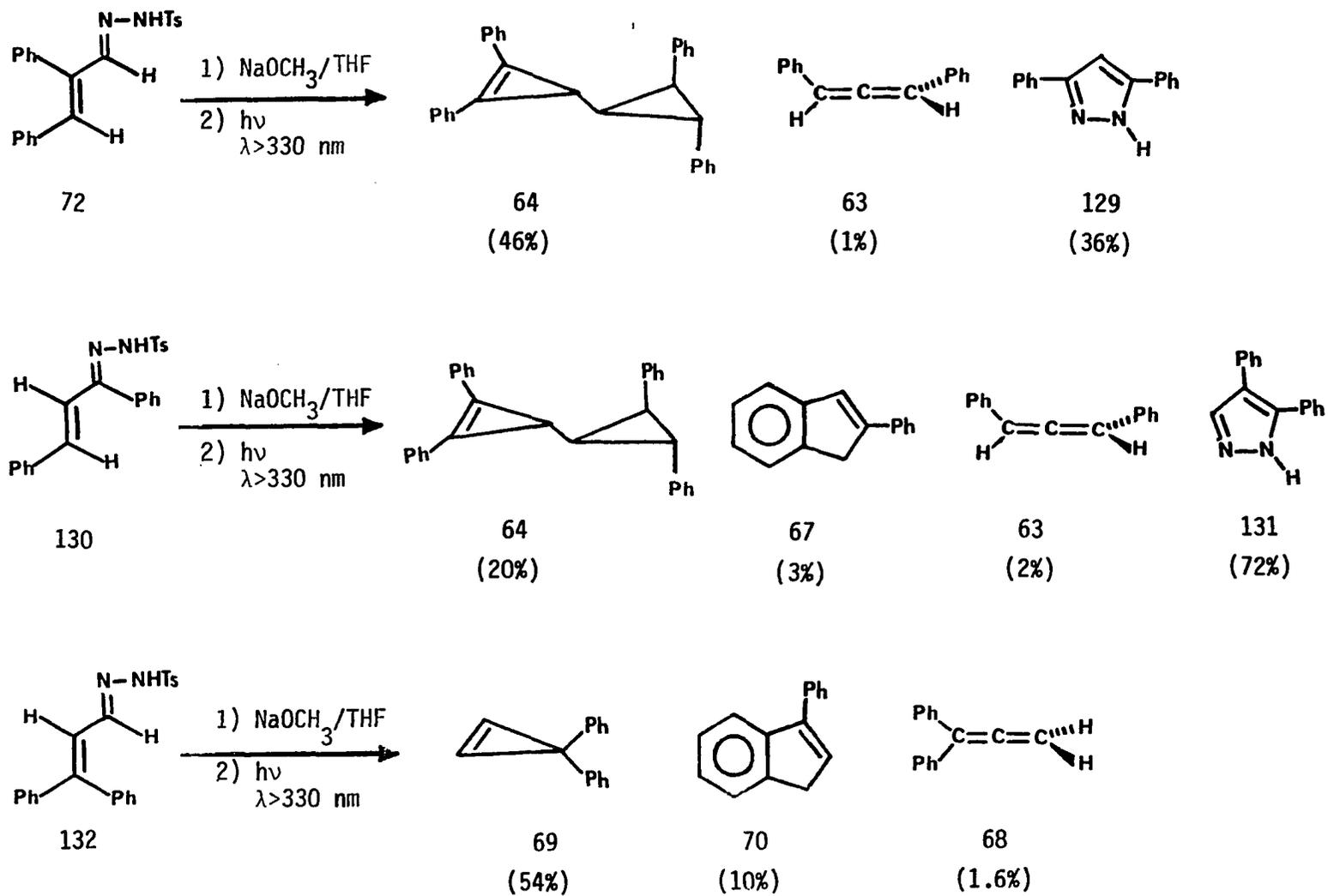
isolation of small quantities of allenes from each carbene. Cyclopropene 49 and allenes 23, 24 and 25 are quite photolabile and may have been destroyed under the reaction conditions employed by Durr. Reassignment of the structure of dimer 59 was discussed earlier.

The vinylcarbenes examined in this work, whether formed from photolysis of diazo compounds or cyclopropenes, consistently yielded small amounts of allenes. Similar observations recently reported by other investigators provide argument for the generality of this reaction.

The significance of independent vinylcarbene generations and their relationship to allene photoisomerizations is seen in the product distributions (Tables 1-3). These results indicate that photoisomerization of allenes 23, 24 and 25 proceeds through initial hydrogen migration to



Scheme 39.



Scheme 40.

Table 1. Hydrocarbon product yield from triphenyl C₃ vinylcarbenes

Vinylcarbene	50	53	52	55	56	99
96	1.2	97.6	---	---	1.2	---
95	1.1	31.3	67.6	---	---	---
113	0.2	---	---	0.2	---	99.6

Table 2. Hydrocarbon product yields from diphenyl C₃ vinylcarbenes

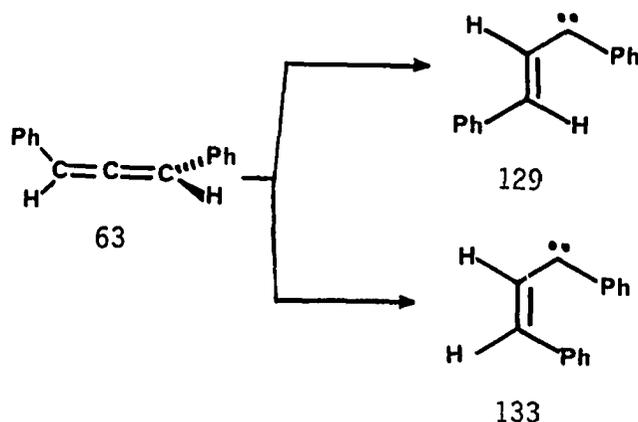
Vinylcarbene	68	63	64	69	65	67	70
72	---	3	97	---	---	---	---
114	---	8	80	---	---	12	---
115	2.4	---	---	82.4	---	---	15.2

Table 3. Comparison of cyclopropene/indene ratios from allene irradiation and corresponding carbene generations

cyclopropene/indene from allene		cyclopropene/indene from carbene
49/44 < 100	(43)	49/44 not available
53/52 = 0.21	(50)	53/52 = 0.46 (95)
72/65 = 1.8	(63)	72/65 > 100 (73)
69/70 = 1.8	(68)	69/70 = 5.4 (115)

carbenes 96, 72 and 115, respectively. With the exception of carbene 96, cyclopropenes are the predominant products from independent carbene generation or allene irradiations. The reversal of the cyclopropene/indene ratio observed for 96 relative to photoisomerization of 50 probably reflects the close proximity of the carbene carbon to the ortho-carbon of the β -phenyl ring. Extrapolation of these results would suggest that 1,2,3-triphenylindene 44 should be the predominant if not exclusive, photoproduct from allene 43, as was experimentally observed. Unfortunately, product analysis from 104 is not available for comparison.

Allene 63 has the capacity to undergo photochemical 1,2-hydrogen migration to cis and trans vinylcarbenes 72 and 133 (Scheme 41).

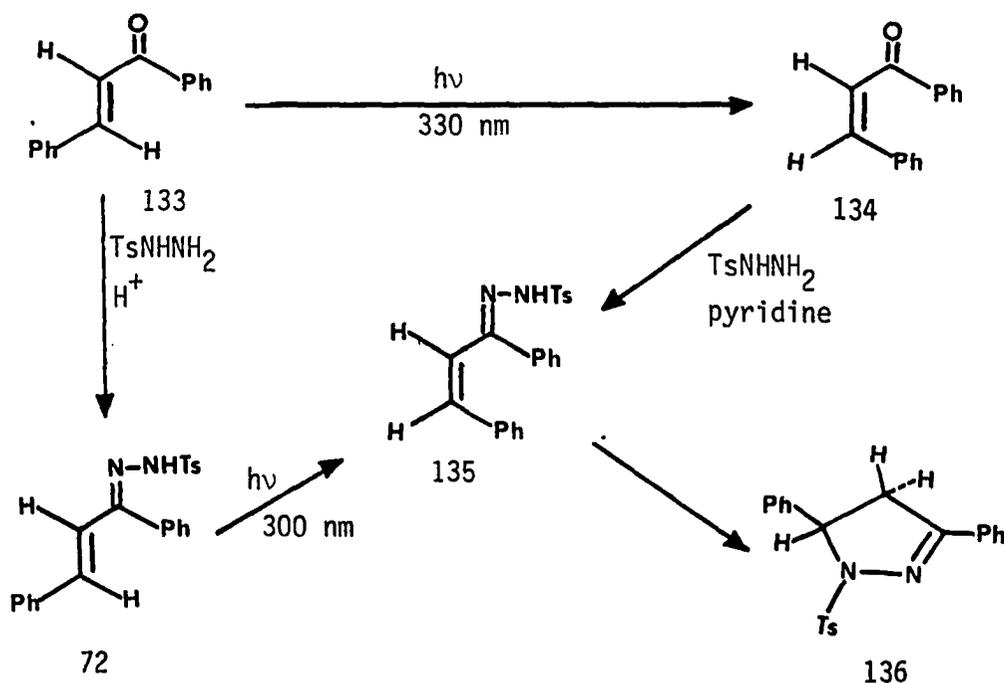


Scheme 41.

The observed product distribution from allene 63 is consistent with reaction from both stereoisomers. Independent generation of (E)-73 from (E)-tosylhydrazone 72 affords cyclopropene dimer 64 and allene 63; no 1-phenylindene 65, expected from the (Z)-vinylcarbene 133, was observed. Similar observations for the cis isomers of vinylcarbenes 113 and 117

suggest that cis - trans isomerization for these vinylcarbenes is not significant. Carbene reactivity from E and Z stereoisomers has never been addressed and, because of their potential involvement in allene photochemistry, a closer examination of this intriguing aspect was warranted.

Synthesis of (Z)-1,3-diphenylpropenone tosylhydrazone 135 was attempted as shown in Scheme 42. Photochemical cis - trans isomerization of (Z)-72 or direct tosylhydrazone formation from (E)-134 under mildly basic conditions (to prevent isomerization) afforded a substance which was identified as 2,3-diphenyl-N-tosylpyrazoline 136.

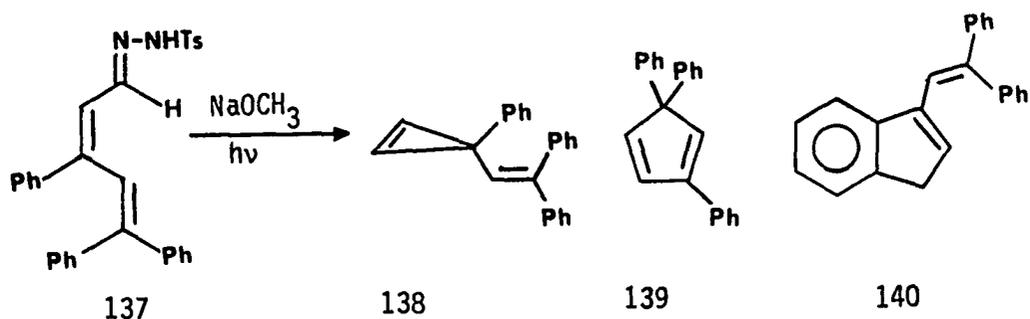


Scheme 42.

The ¹H NMR of 136 displays a methyl singlet (2.93 ppm) and three hydrogen resonances as doublets of doublets at 3.93, 4.11 and 4.91

ppm ($J = 3.6, 9.7$ and 17.8 Hz) in addition to fourteen aromatic hydrogens. By comparison, the three ring hydrogens of 2,3,5-triphenylpyrazoline 121 (Scheme 38) appear as doublets of doublets at 3.83, 4.18 and 4.72 ppm (54). Infrared and mass spectral data (experimental) of 136 are also consistent with this structure. The apparently more reactive C-C double bond of Z-135 precluded further attempts to prepare a diazo precursor.

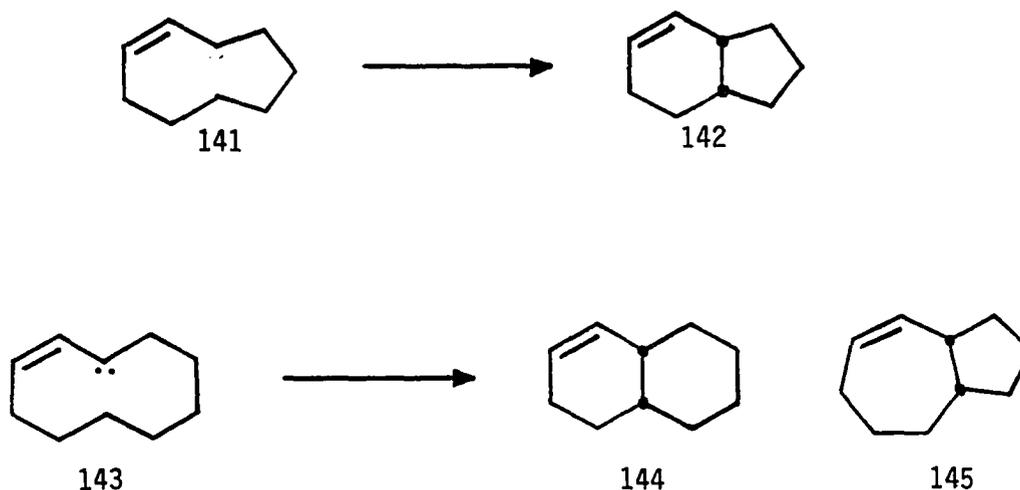
Zimmerman and Kreil (41) have recently described the photolysis of E-tosylhydrazone 137 to yield products explicable from both E and Z vinylcarbene stereoisomers (Scheme 43). No attempt to prepare the Z vinylcarbene, however, was reported. Thus, cis - trans isomerization of the vinylcarbenes 72, 113, 114, observed in the present study, may be precluded by more rapid cyclization or insertion reactions.



Scheme 43.

Although products presumably arise from the more reactive singlet carbene ($^1A'$) (55), equilibration to the ground state triplet ($^3A''$) and subsequent reaction cannot be rigorously excluded. ESR studies (56) demonstrate a triplet ground state for vinyl methylene, consisting of syn and anti conformers. Theoretical calculations (10,15) at various levels

of sophistication also predict a triplet ground state lying 8-16 kcal/mol below the singlet carbene. Conservation of spin requirements and energetic considerations, however, preclude direct cyclopropene and indene formation from triplet vinylcarbenes. The observation (5,11) of stereospecific formation of cis fused bicyclics from 141 and 143 (Scheme 44) argues for reaction from a singlet vinylcarbene.

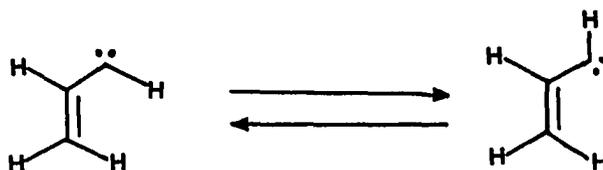


Scheme 44.

The suggestion of conformationally selective behavior of vinylcarbenes by Steinmetz et al. (14) warrants comment. The syn and anti conformers of singlet vinylmethylene were calculated by Honjou et al. (10) to be isoenergetic, with a potential energy barrier of approximately 10 kcal/mol between them. Similarly, syn and anti conformations of triplet vinylmethylene were predicted by theory (10,45) to be isoenergetic, with an energy barrier of 6.5 kcal/mol for interconversion. These findings are in excellent agreement with ESR studies by Hutton et al.

(56). In light of the thermally accessible (12 kcal/mol) triplet to singlet vinylcarbene transition (55,57), conformationally selective behavior is likely to constitute a significant effect in solution (Scheme 45).

One additional and pertinent observation from the independent vinylcarbene generations is that propynes are not formed. In contrast, the photochemistry of every acyclic or cyclic allene reported to date

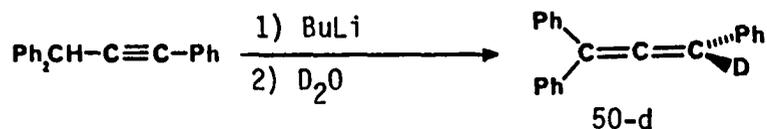


Scheme 45.

yields alkynes. The absence of propynes from vinyl diazo compounds indicates that vinylcarbenes are not the exclusive intermediates in allene photoisomerizations. A kinetic deuterium isotope was used to explore this aspect further.

Mechanistic Studies: Deuterium Isotope Effect

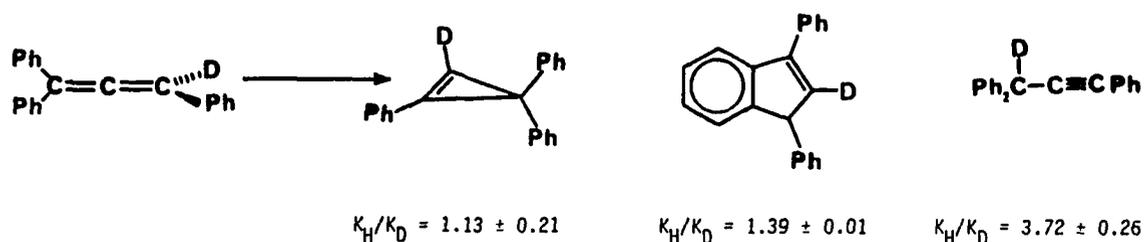
3-Deuteriotriphenylallene 50-d was prepared from triphenylpropyne by treatment with n-BuLi/THF and subsequent quenching with D₂O



Scheme 46.

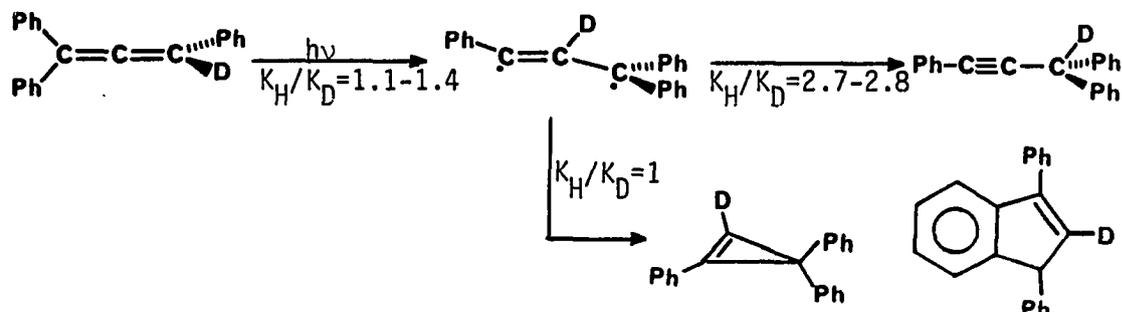
(Scheme 46). Pentane solutions of 50 and 50-d of identical concentration were cooled to -10°C and simultaneously irradiated to low conversion in a

merry-go-round apparatus at 254 nm. Products were analyzed with HPLC, relative to internal standard; resultant values for ϕ_H/ϕ_D and observed standard deviations are summarized in Scheme 47. The value for 52-d is subject to the greatest error due to rapid secondary conversions. The location of deuterium in products was determined by ^1H and ^2H NMR to be on the vinyl position in 52-d and 53-d and the propargylic position in 54-d.



Scheme 47.

Although the effect of deuterium on excited state lifetimes is well-known (58), relatively little is known about kinetic isotope effects in photoreactions. The ϕ_H/ϕ_D values for 52, 53 and 54 suggest a common excited state 1,2-H(D) shift, with a second H(D) shift affording 54. Consistent with this is the observation that values for 52 and 53 (1.13 and 1.39) are similar within experimental error, while that for 54 is much larger (3.72). Parallel studies by Stierman and Johnson (6) report a $k_H/k_D = 1.30 \pm 0.06$ for cyclonadiene to cyclopropene conversion. Assuming the isotope effects for each hydrogen migration step to be approximately multiplicative, Scheme 48 is obtained.



Scheme 48.

In principle, this scheme should lead to a reverse isotope effect in formation of 52-d and 53-d, however, since 54-d is only a minor product, the magnitude is too small to be observable.

Kinetic isotope effects of the magnitude observed here normally are ascribed to strongly bent transition states, with C-H-C angles of 60-90°. Based on the classic More-O'Ferrall relationship (59), the observed $\phi_\text{H}/\phi_\text{D}$ values are not inconsistent with the approximate geometries predicted from *ab initio* calculations that will be discussed later. The transition state for the first 1,2-H shift 146 is predicted to be symmetrical while that for propyne formation 147 is quite early and unsymmetrical, due to its greater exothermicity (Figure 7). Theoretical studies by Honjou *et al.* (10) show geometry 145 to be a transition

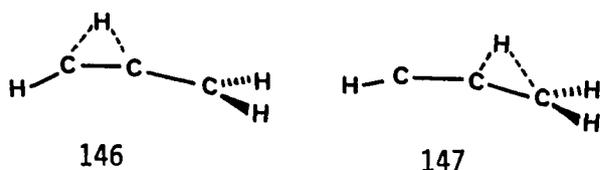


Figure 7. Potential transition states for 1,2-hydrogen shifts in allene

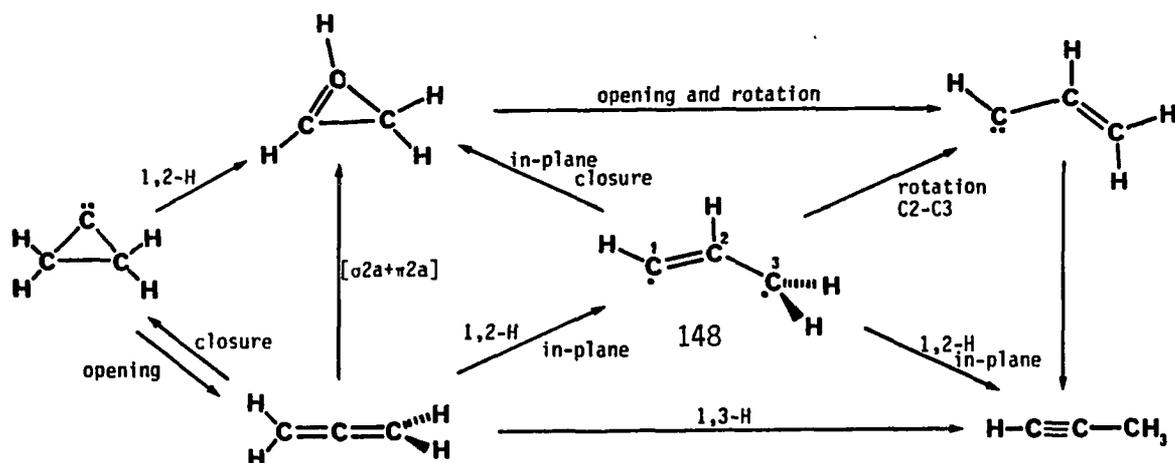
state on the ground state pathway from allene to propyne. In the photoreaction, this provides an approach of ground and excited state surfaces and the second hydrogen migration may occur simultaneously with internal conversion from S_1 to S_0 . Thus, the observed isotope effect probably is not due to a simple ground state process.

Reaction Mechanisms: Allene Photoreactions

The congruence of product identities, especially indenenes, from photolysis of phenylallenes, phenylcyclopropenes and appropriate tosylhydrazone sodium salts, strongly implicates the common intermediacy of vinylcarbenes. An important exception is phenylpropyne formation, which is not observed from vinylcarbenes. Cyclopropene and indene formation require a single hydrogen migration step, while propyne formation probably involves two separate steps. This is consistent with the kinetic isotope effect observed for 23-d; i.e., ϕ_H/ϕ_D (propyne) $>$ ϕ_H/ϕ_D (cyclopropene) = ϕ_H/ϕ_D (indene).

Scheme 49 shows a framework for analysis of C_3H_4 reaction mechanisms. Central to this is bisected vinylbiradical 148; this is related along C_s reaction coordinates to allene and propyne through in-plane 1,2-H migrations to cyclopropene through in-plane closure, and to vinylcarbenes through simple σ -bond rotation. This geometry seems the most likely precursor to alkyne. Ab initio calculations (vide infra) support this possibility.

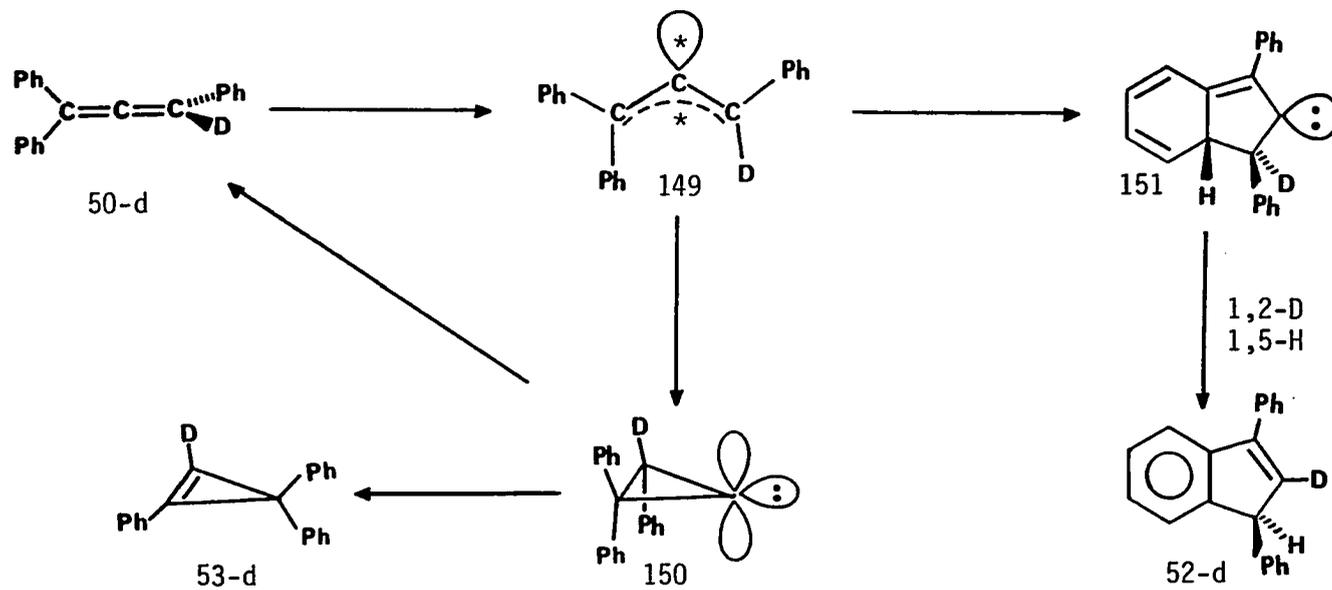
One alternative hydrogen migration mechanism bears brief consideration; this is outlined in Scheme 50 for 50-d. Excited state π -bond twisting in S_1 may afford a diradical 149 or a "suddenly polarized"



Scheme 49.

species represented by 149 (60), which could close to singlet cyclopropylidene 150 or carbene 151. 1,2-Deuterium shift in 150, or sequential 1,2-D and 1,2-H shifts in 151 would give the observed products. Perhaps the most cogent argument against this mechanism is that 1,2-D shift in singlet cyclopropylidene 150 would be expected to be uncompetitive with ring opening to 50-d (10). Consistent with this are observations (7-9) of facile ring opening of singlet cyclopropylidene to yield exclusively allenes. In addition, the similar small isotope effects observed for cyclopropene and indene formation argue for a common preceding step, as would occur in Scheme 49. In protic solvents (e.g., CH_3OH) efficient solvent addition occurs for phenylallenes from zwitterion 149, while rearrangements are kinetically uncompetitive (see Chapter 1).

Hydrogen migration in phenylallenes occurs more efficiently than phenyl migration, a conclusion supported by the observation of exclusive

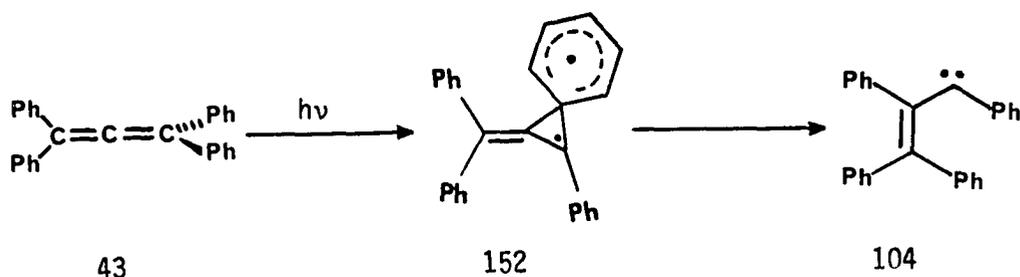


Scheme 50.

hydrogen migration in 50, 63, and 68 and lower relative reactivity of 43. This is perhaps surprising, given the number of well-known photochemical phenyl migrations (61).

A straightforward phenyl migration mechanism is shown in Scheme 51. Bridging and subsequent rotation about the bridged bond would yield biradical 152 which could open to planar vinylcarbene 104.

Inefficient reaction of 43 probably reflects both inefficient bridging and rapid competitive radiationless decay through π bond rotation. Allenes are excellent "free-rotors", (62) as demonstrated by



Scheme 51.

their lack of fluorescence and the observation of facile photoracemization with optically active allenes (5b).

Stierman and Johnson (5) favor a concerted process involving a $[\sigma 2a + \pi 2a]$ transition state for cyclononadiene 4 to cyclopropene 5 conversion. This requires 1,2-hydrogen migration and simultaneous 1,3-bonding. Ab initio CI calculations for such a process vide infra show the expected pericyclic minimum due to approach of ground and

excited states. Constraints imposed by the carbocyclic ring are probably crucial in preventing rotation to vinylcarbenes.

The mechanistic schemes for photoisomerization of allene proposed by Steinmetz *et al.* (16) seem unlikely for reasons discussed earlier.

Thus, two mechanistic extremes are envisioned as the most likely route from vertically-excited allene to products: (a) in-plane hydrogen migrations along a C_s reaction coordinate, which can readily afford both cyclopropene and propyne, or (b) hydrogen migration and rotation to discrete vinylcarbene intermediates, precursors to cyclopropene and indene products.

Theoretical Studies: C_s Potential Surfaces

Calculation of ground and excited state potential surfaces often provides substantial mechanistic insight. However, even for C_3H_4 , characterization of multidimensional surfaces is a formidable task, and we consider here only those C_s pathways outlined in Scheme 6. In recent studies, Honjou has mapped much of the ground state surface (10).

Minimal basis set (STO-3G) configuration interaction (CI) calculations were performed along C_s reaction coordinates connecting allene with propyne and cyclopropene. Experimental geometries were used for allene, cyclopropene, and propyne. Geometries at intermediate points were extrapolated or partially optimized at the CI level. The CI space (946 configurations) was generated from all single and double excitations from the six highest occupied MOs (closed shell reference configuration) to the lowest seven virtuals (63). Results of calculations are shown in

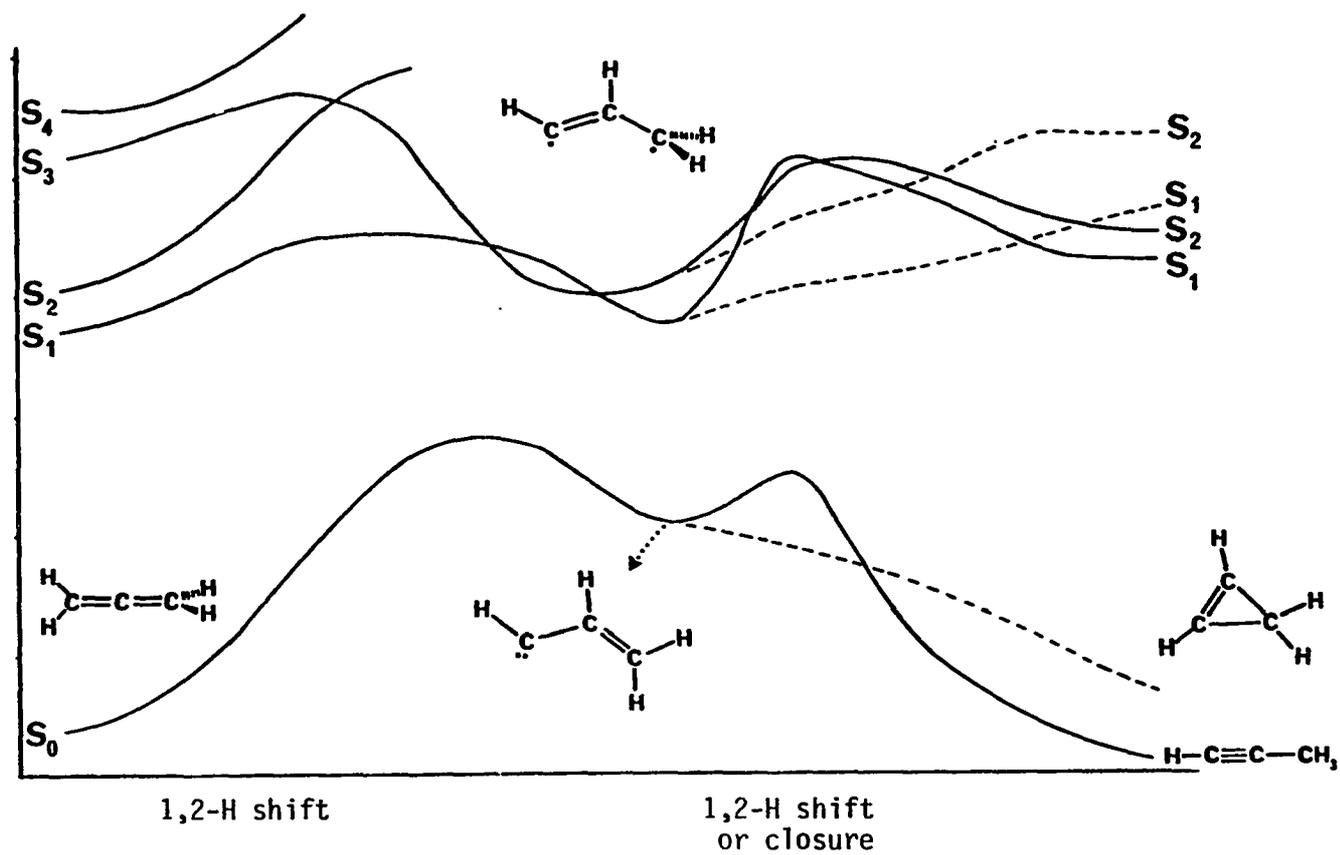


Figure 8. Excited and ground state potential surface

Figure 8. Solid lines correlate states between allene, vinylbiradical 148 (Scheme 6), and propyne. Dashed lines correlate the vinylbiradical with cyclopropene. These calculations should significantly overestimate barrier heights and excitation energies but are expected to be qualitatively useful in correlating valence states. Comparable level calculations have proved useful in understanding other aspects of C_3H_4 photochemistry (64).

Allene S_1 and S_2 valence states arise from in-phase and out-of-phase combination of out-of-plane excitations; i.e.,

$$[\pi_x \rightarrow \pi_y^* \pm \pi_y \rightarrow \pi_x^*].$$

Along a C_s reaction coordinate, these correlate with states of $^1A'$ symmetry, due to $\sigma - \pi^*$ or $\pi - \sigma^*$ excitations. Here, σ and π refer to local symmetry, i.e., σ is in the plane of hydrogen migration and π is out of plane. Thus, S_1 of allene correlates directly with the lowest $\sigma - \pi^*$ state of cyclopropene. By contrast, S_3 and S_4

(neglecting Rydberg states) are due to in-plane excitations; i.e.,

$$[\pi_x \rightarrow \pi_x^* \pm \pi_y \rightarrow \pi_y^* \text{ and thus correlate with } ^1A' \text{ states which are}$$

$\sigma \rightarrow \sigma^*$ or $\pi \rightarrow \pi^*$. Both A' and A'' states have minima along the C_s coordinate. Inspection of MO's shows orbital crossings for each migration step.

In-plane hydrogen migration leads over a small barrier--undoubtedly exaggerated by our calculations--to either of two excited minima. The first of these corresponds to the expected pericyclic minimum for concerted [$\sigma 2a + \pi 2a$] formation of cyclopropene. Internal conversion at

this geometry might lead to cyclopropene, or, through σ bond rotation, to intermediate vinylcarbene. Molecular constraints, such as exist in a cyclic allene, might prevent rotation, and yield cyclopropene directly, in an effectively concerted reaction. Out-of-plane hydrogen migration paths were not explored and thus cannot be ruled out. However, the in-plane path provides the most straightforward route to cyclopropene and propyne.

The second minimum seems more closely poised above the ground transition state to propyne and the second hydrogen migration may occur on a ground state surface, over a small barrier, or during the crossing back to ground state. At this point on the ground state surface, hydrogen shift and σ -bond rotation to vinylcarbene are competitive. The precise molecular dynamics will be highly structure dependent and Figure 8 is, at best, a crude model for reaction of phenylallenes. High temperature ($> 200^\circ\text{C}$) interconversion of allene and propyne is well-documented (34b). Deuterium labelling and kinetic studies have provided argument for the intermediacy of cyclopropene (47). The major process competing with hydrogen migration in allenes will be simple bond rotation in vertically excited allene. Low efficiencies for reaction of phenylallenes and lack of observable fluorescence argue that these molecules are efficient free rotors (62). Such σ bond rotation leads to strongly polarized species (60), which may be trapped in polar solvents (14a,c). It is conceivable that in-plane hydrogen (migration 29 to 30) might offer a path to vinylcarbene. This would be exothermic by > 20 kcal/mol (10,45,60), but seems a rather unusual mechanism. Some support

is found in ab initio calculations by Evleth and Sevin (64), which show that in-plane 1,2-hydrogen migration in twisted (C_S) ethylene can lead to ethylidene, through an adiabatic process. However, since 29 is already an excited surface minimum, it seems unlikely that this hydrogen shift could compete with internal conversion to ground state.

Two mechanistic extremes are envisioned as the most likely route from vertically-excited allene to products: (a) in-plane hydrogen migrations along a C_S reaction coordinate, which can readily afford both cyclopropene and propyne, or (b) hydrogen migration and rotation to discrete vinylcarbene intermediates, precursors to cyclopropene and indene products.

Conclusions

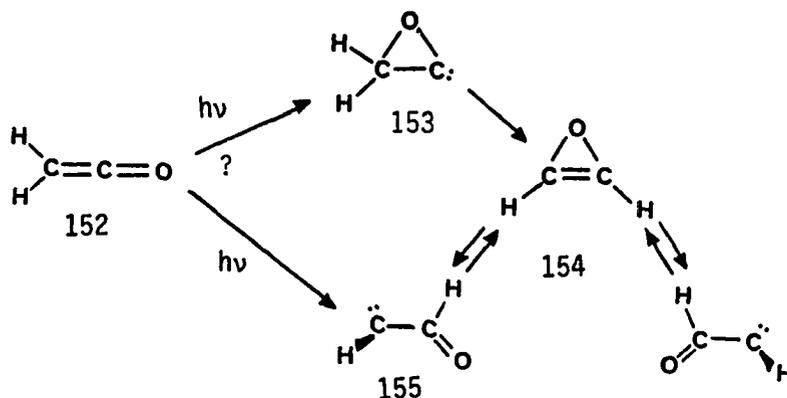
Singlet photorearrangement of simple alkenes to carbenes via 1,2-hydrogen or alkyl shifts is a well-known process (1). Kropp has advocated the intermediacy of Rydberg states ($\pi \rightarrow 3s$) (1a), although evidence for this is inconclusive. In allenes, current evidence indicates the lowest excited state to be valence ($\pi - \pi^*$) (65). Triplet states are unreactive. 1,2-Shifts can lead to vinylcarbenes as discrete intermediates, or along closely related pathways which lead directly to cyclopropene and propyne. Present evidence suggests that the mechanism is quite dependent upon structure. For the linear phenylallenes described here (13) and those studied by Steinmetz et al. (14), vinylcarbenes are likely precursors to cyclopropene and indene photo-products, whereas in 1,2-cyclononadiene, ring constraints may favor an

effectively concerted process (5). Ab initio calculations show that hydrogen migration in S_1 of allene can lead to points on the excited state surface which, through internal conversion or rotation, provide routes to vinylcarbenes, cyclopropene or propyne. The exact pathway and partitioning among these various outcomes will be highly structure dependent, however, augmentation by phenyl does not significantly alter allene photochemistry. Along the route to propyne, the first 1,2-H shift is believed to occur in the excited state, and the second after (or perhaps during) crossing to the ground state.

Isotope effects observed here and in reactions of 1,2-cyclononadiene (5) have little precedent, but the immediate interpretation seems little different from that which usually is given for ground state processes. Unfortunately, phenylallenes are nonfluorescent, thus it is not possible to measure the effect of deuterium on the singlet lifetime, or absolute rates for rearrangement.

The photoreactions of allene have some interesting, and perhaps surprising, parallels with those of ketene (Scheme 52). In addition to the well-known photodissociation, Russell and Rowland (66a) observed carbon scrambling in irradiated ketene. This was suggested to occur as a result of closure to oxacyclopropylidene (153), 1,2-hydrogen shift to oxirene (154), and equilibration through formylmethylenes (66b). However, ab initio calculations predict (66c) a large barrier for 1,2-H shift in 153, relative to that for ring opening. To account for the observed photochemical scrambling, Radom has suggested a 1,2-H shift to

formylmethylene (155) in a ketene excited state (66c). This behavior is paralleled in reactions of allene.



Scheme 52.

Experimental

General

All ^1H (^{13}C) NMR spectra were measured on a Nicolet 300 MHz (76 MHz) spectrometer, with CDCl_3 as solvent and TMS as reference. IR spectra were measured on a Beckman 4250 spectrometer. All UV spectra were measured on a Perkin-Elmer 320 instrument. HPLC analyses employed a Waters Associates M-45 pump and 440A detection system at 254nm. Normal phase analyses were performed with a Water Associates μ -porasil column (4.6 x 250 mm). A Dupont Zorbax ODS (4.6 x 250 mm) column was employed for reverse phase analysis. Gas chromatographic analyses were performed with a Hewlett-Packard 5793A instrument. A 10m SE-30 capillary column at 150°C was used for all analyses. HPLC and GLC peak areas were measured

by a Hewlett-Packard model 3390A integrator. Melting points are uncorrected.

Preparative chromatographic separations were performed with quartz columns that were slurry packed with Grace grade 62 silica containing added green phosphor (Sylvania #2282). Flash chromatography experiments employed quartz columns dry packed with preparative TLC silica gel 60 PF-254 (EM Laboratories, Inc.). Progress of component elution was monitored with an ultraviolet hand lamp.

Preparative photochemical experiments employed a standard immersion-well apparatus, equipped with 450 W Canrad-Hanovia lamp and sleeve filters, or a Rayonett RPR-100 reactor. For sub-ambient temperature irradiations in the Rayonett, quartz or Pyrex vessels with external dewar jackets were constructed. Temperature was controlled with an internal cooling coil and a Lauda RC3 refrigerated recirculating bath.

Quantum yield measurements were made on an optical bench which is similar to that described by Zimmerman and co-workers (67). This consists of a 200 W high pressure Hg lamp, a Bausch and Lomb high intensity monochromator, a beam splitter, and an integrating electronic actinometer, which is calibrated vs. potassium ferrioxalate. Monochromator entrance and exit slits were set at 3.4 and 1.9 mm, respectively, to give a bandpass of 12.4 nm.

In all photochemical experiments, spectroquality solvents were used. Argon was bubbled through solutions prior to and during irradiation.

Direct irradiation of tetraphenylallene 43

Allene **43** (288 mg) dissolved in cyclohexane (180 mL) was irradiated through a Vycor filter ($\lambda > 220$ nm) for 17.5 hours. The solution was concentrated under reduced pressure and chromatographed (2.0 x 75 cm). Elution was with 1% ether-hexane in 50 mL fractions: 1-5, nil; 6-9, 186 mg of **43**, 10-11, 37 mg of **45**. Mass balance was 80%.

In other experiments at lower conversion and at 254 nm, reaction was followed by HPLC (μ -Porasil, hexane elution) and 300 MHz NMR. Both **45** and its precursor **44** were consistently observed. One very minor product could not be isolated in sufficient quantity for identification. 1,1,3-Triphenylindene (**47**) was shown not to be present.

1,1,3-Triphenylindene 47

1,1,3-Triphenylindene was prepared in 98% yield from tetraphenylallene by the method of Vorander and Siebert (68): mp 139-140°C (literature 135-136°C); ^1H NMR (CDCl_3) δ 6.82 (s, 1H), 7.21-7.30 (m, 12H), 7.39-7.57 (m, 4H).

1,2,3-Triphenylindene 44

1,2,3-Triphenylindene was prepared in 82% yield from 1,1,3-triphenylindene by the method of Hodgkins and Hughes (69): mp 133-134°C (literature 132-134°C); ^1H NMR (CDCl_3) δ 5.11 (s, 1H), 7.04-7.19 (m, 15H), 7.25 (d, 2H, $J = 8.0$ Hz), 7.42 (d, 2H, $J = 4.5$ Hz).

Phenylindenophenanthrene 45

1,1,3-Triphenylindene (54 mg, 0.20 mmol) in cyclohexane (20 mL) was irradiated at 300 nm for 70 hours. Chromatography (1.2 x 10 cm) with

hexane elution gave 37 mg (68%) of white crystals. Recrystallization from 95% ethanol yielded colorless needles melting at 200.5-201°C (literature (19) 213-215°C); ^1H NMR (CDCl_3) δ 5.40 (s, 1H), 7.13-7.25 (m, 6H), 7.39-7.57 (m, 3H), 7.59 (t, 1H, $J = 7.7$ Hz), 7.74-7.82 (m, 3H), 8.43 (d, 1H, $J = 7.7$ Hz), 8.73 (d, 1H, $J = 8.5$ Hz), 8.86 (d, 1H, $J = 7.7$ Hz), 8.96 (d, 1H, $J = 7.8$ Hz).

1,2,3-Triphenylcyclopropenium bromide

1,2,3-Triphenylcyclopropenium bromide was prepared in 80% yield according to the method of Breslow and Chang (70): mp 105-108°C (literature 105-106°C).

Tetraphenylcyclopropene 49

Tetraphenylcyclopropene was provided by Dr. R. P. Johnson. This material was prepared from 1,2,3-triphenylcyclopropenium bromide according to the procedure of Stoffer and Bohanon: mp 177-178°C (literature (71) 176-177°C); ^1H NMR (CDCl_3) δ 7.15-7.26 (m, 6H), 7.34-7.45 (m, 10H), 7.52 (d, 4H, $J = 7.5$ Hz).

Tetraphenylpropyne 48

Tetraphenylpropyne was prepared in 30% yield from phenylacetylene and tritylchloride by the method of Wieland and Closs (72): mp 139-140°C (literature 139°C); ^1H NMR (CDCl_3) δ 7.23-7.49 (m, 10H), 7.50-7.52 (m, 1H).

Direct irradiation of triphenylallene 50

Allene 50 (250 mg) in pentane (200 mL) at -10°C was irradiated with 254 nm lamps for 2 hours. The solution was concentrated under reduced pressure and chromatographed (2 x 65 cm). Elution was with hexane in 50 mL fractions: 1-8, nil; 9-14, 122 mg of essentially pure triphenylallene (50); 15-20, 79 mg of a mixture of 50, 53, 52, 56, and 57 in the ratio 3.0:0.5:1.3:1.0:0.1; 21-24, 16 mg of a mixture of 53, 52, 56, and 57 in the ratio 0.6:1.2:1.0:0.2; 25-28, 8 mg of 54, 53, 52, and 56, in the ratio 1:2.6:1.4:1.0; 29-31, 5 mg of 54 and 53, ratio 1:0.4; 32-35, 5 mg of 53, 54 and 55, ratio 0.1:1:0.35; 36-40, 3 mg of 54 and 55, ratio 1:2.1; 49-61, 2 mg of pure 1,2-diphenylindene (55). Mass balance was 97%.

Fractions 21-28 were rechromatographed (1.2 x 80 cm). Elution with hexane in 20 mL fractions yielded: 1-10, nil; 11-13, 5 mg of 50; 14-18, 23 mg of overlap; 19, 2 mg of pure 1,3,3-triphenylcyclopropene 53; 20-22, 8 mg of overlap; 23-26, 7 mg of pure 1,3,3-triphenylpropyne 54.

In other experiments at lower conversion, reaction was followed by HPLC (μ -Porasil, hexane elution) and 300 MHz NMR. Triphenylcyclopropene 53, 1,3-diphenylindene 52 and triphenylpropyne 54 were observed to be primary, with the remaining products secondary.

Quantum yield determination for triphenylallene 50

A $1.54 \times 10^{-3}\text{M}$ isooctane solution of 50 (50 mL) in a quartz cell was irradiated on the optical bench for periods of 40 minutes to 3

hours. Internal standard (1,1,3,3-tetraphenylpropene) was added and the mixture was analyzed by HPLC. Four separate runs at 0.1%-1.0% conversion yielded the following quantum yields for product formation. Cyclopropene 53, 0.004 ± 0.0006 ; 1,3-diphenylindene 52, 0.019 ± 0.004 ; 1,3,3-triphenylpropyne 54, 0.002 ± 0.0005 .

1,3-Diphenylindene 52

1,3-Diphenylindene was prepared in 65% yield from triphenylallene by the method of Greibrokk (73): mp 84.5-85.5°C (literature 68-69°C); ^1H NMR (CDCl_3) δ 4.70 (d, 1H, $J = 2.0$ Hz), 6.34 (d, 1H), 7.16-7.46 (m, 11H), 7.58 (d, 1H, $J = 8.4$ Hz), 7.64 (d, 2H, $J = 0.98$ Hz).

1,2-Diphenylindene 55

1,2-Diphenylindene was prepared in 51% yield from 2,3-diphenylindene by the method of Pettit and Wilson (74): mp 177-179°C (literature 175-177°C); ^1H NMR (CDCl_3) δ 4.97 (s, 1H), 7.10-7.27 (m, 11H), 7.36 (s, 1H, vinyl), 7.41 (d, 1H, $J = 2.4$ Hz), 7.50 (d, 2H, $J = 7.4$ Hz).

2,3-Diphenylindene

2,3-Diphenylindene was prepared in 57% yield from 1,2-diphenylindene by the method of McCullough (30a): mp 108-109°C (literature 108-109°C); ^1H NMR (CDCl_3) δ 3.91 (s, 2H), 7.11-7.29 (m, 8H), 7.34-7.41 (m, 5H), 7.21 (d, 1H, $J = 7.0$ Hz).

α,α -Diphenylacetophenone

α,α -Diphenylacetophenone was prepared in 62% yield from benzoin by the method of Curtin and Harwitz (75): mp 132-133°C (literature 133-135°C).

1,1,2-Triphenylpropene 58

1,1,2-triphenylpropene was prepared in 77% overall yield from α,α -diphenylacetophenone by the method of Schlenk and Bergman (76): mp 85-86°C (literature 90°C); ^1H NMR (CDCl_3) δ 2.08 (s, 1H), 6.92-7.24 (m, 15H).

3-Bromo-1,1,2-triphenylpropene 59

A modification of the procedure by Norman and Thomas (77) was employed. Benzoyl peroxide (100 mg) was added to 1,1,3-triphenylpropene (5.0g, 18.5 mmol) and N-bromosuccinamide (3.3g, 18.5 mmol) in carbon tetrachloride (150 mL) under nitrogen. The mixture was heated to reflux for 10 minutes and then externally cooled in an ice bath. The resulting succinimide was filtered away. Concentration of the filtrate under reduced pressure gave 6.3g (97%) of an off-white residue melting at 115-117°C (literature 125-127°C); ^1H NMR (CDCl_3) δ 4.33 (s, 2H), 6.96 (s, 5H), 7.16 (s, 5H), 7.36 (s, 5H).

2,3,3-Triphenyl-2-propenol 60

Silver nitrate (6.3g, 37.1 mmol) and 3-bromo-1,1,2-triphenylpropene (6.3g, 18.1 mmol) in aqueous acetone (200 mL, 25% water) was heated to

reflux for 30 minutes. The reaction mixture was cooled to room temperature and then extracted with ethyl ether (3 x 20 mL). The combined ether extracts were dried over magnesium sulfate and concentrated under reduced pressure to yield a yellow colored residue. Recrystallization from hexane gave 4.0g (97%) of colorless needles that melted at 127-128°C (literature (78) 126-128°C). $^1\text{H NMR}$ (CDCl_3) δ 4.50 (s, 2H), 5.27 (s, 1H, OH), 7.03 (s, 5H), 7.23 (s, 5H), 7.37 (s, 5H).

2,3,3-Triphenylpropenal 61

The general procedure of Carpino was employed (79). A slurry of 2,3,3-triphenylpropenol (4.00g, 14.0 mmol) and an excess of activated MnO_2 (6.0g) in benzene (200 mL) was stirred under nitrogen for 4 hours. The mixture was filtered through Celite and concentrated under reduced pressure to yield a yellow colored residue. Recrystallization from ethanol gave 3.86g (97%) of slightly yellow colored crystals that melted at 175-177°C (literature (80) 177-178°C); $^1\text{H NMR}$ (CDCl_3) δ 6.9-7.6 (m, 15H), 9.78 (s, 1H).

2,3,3-Triphenylpropenal tosylhydrazone 62

Propenal 61 (5.00g, 17.6 mmol) and *p*-toluenesulfonylhydrazide (4.47g, 24.0 mmol) in methanol (50 mL) was treated with H_2SO_4 (3 drops) and heated to reflux for 20 minutes. The mixture was cooled in ice and 3.80g (80%) of 62 was collected. Recrystallization from ethanol gave white crystals that melted at 141-142°C; $^1\text{H NMR}$ (CDCl_3) 2.46 (s, 3H), 6.81-7.62 (m, 21H); I.R. (KBr) 3200, 3045, 3022, 2820,

1595, 1486, 1440, 1360, 1315, 1164, 1050, 935, 885, 775, 765 and 695 cm^{-1} . MS, no M^+ , m/e 296.13120 (m-Tosyl H; ca. 296.13135).

Photolysis of 2,3,3-triphenylpropenal tosylhydrazone sodium salt

Sodium methoxide (2.30g, 42.6 mmol) was added to 62 (4.80g, 10.6 mmol) in dry THF (280 mL) and then irradiated through a uranium filter for 3.3 hours. The photolysis mixture was filtered through Celite concentrated under reduced pressure and chromatographed (2.8 x 54 cm). Elution was with hexane in 200 mL fractions: 1-3, nil; 4-5, 703 mg of 50, 56, and 53, ratio 1:1:40; 6, 581 mg of 50, 56, and 53, ratio 1:0.5:62; 7-10, 899 mg of pure 53. Continued elution with 0.5% ether-hexane: 11-15, 129 mg of pure 10; 16, nil; 17-19, 131 mg of hexatriene dimers. Mass balance was 87%.

1,3,3-Triphenylcyclopropene 53

1,3,3-triphenylcyclopropene was recrystallized from pentane, mp 88-89°C; ^1H NMR (CDCl_3) δ 7.16-7.38 (m, 13H), 7.51 (s, 1H, vinyl), 7.62 (d, 2H, $J = 7.3$ Hz); ^{13}C NMR (CDCl_3) δ 146.2, 131.0, 129.5, 129.3, 128.8, 128.1, 127.7, 127.2, 125.7, 122.6, 106.5, 35.2; I.R. (KBr) 3120, 3080, 3055, 3020, 1758, 1595, 1488, 1442, 780, 756 and 695 cm^{-1} ; UV (cyclohexane) λ_{max} 258 (ϵ 18000); MS, m/e 268.12492 (ca. 268.12520).

Direct irradiation of 1,3-diphenylallene 63

Allene 63 (200 mg) dissolved in pentane (200 mL) at -10°C was irradiated for 6.5 hours at 254 nm. The reaction mixture was

concentrated under reduced pressure at 0°C and residue subjected to flash chromatography (1.5 x 35 cm). Elution was with pentane in 25 mL fractions: 1-4, nil; 5-6, 122 mg of 63; 7, 18 mg of 63 and 65, ca. 1.0:0.1; 8, 4 mg of 63 and 65, ca. 0.5:1.0; 9, 2 mg of 63, 66, 65 and 67, ca. 0.36:1.1:0.36:1.0; 10-13, 3 mg of 66. Continued elution with hexanes: 14-25, nil; 26-33, 3 mg of adducts; 34-49, 14 mg of mostly 64 and some adducts; elution with 1.0% ether-hexane, 50-57, 7 mg of adducts. Mass balance was 86%.

Quantitative ^1H NMR analysis of 1,3-diphenylallene 63 irradiation

Allene 63 (100 mg) in pentane (200 mL) at -10°C was irradiated at 254 nm. The reaction mixture was concentrated under reduced pressure at 0°C. Analysis was by ^1H NMR integration relative to internal standard (bibenzyl). The allene used in all runs contained 0.25% of bibenzyl as an impurity. The percentage of bibenzyl was determined by ^1H NMR integration relative to added internal standard (1,1,3,3-tetraphenylpropene) and did not vary under the irradiation conditions. Five separate runs at 0.3-10% conversion yielded the following percent photoproduct composition: cyclopropene dimer 64, 27% \pm 1.0%; diphenylpropyne 66, 26% \pm 2.0%; 1-phenylindene, 65 47% \pm 4.0%.

1-Phenylindene 65

1-Phenylindene was prepared in 44% overall yield from hydrocinnamic acid by the method of Friedrich and Taggart (81): mp 36.5-37.5°C

(literature bp 111-114°C, 0.9 torr); ^1H NMR (CDCl_3) δ 4.60 (bs, 1H), 6.59 (dd, 1H, $J = 5.4$ and 1.9 Hz), 6.90 (dd, 1H), 7.1-7.4 (m, 9H).

2-Phenylindene 67

2-Phenylindene was prepared in 27% overall yield from 2-indanone by the method of Bordwell and Drucker (82): mp 166-167°C (literature 167.5-168°C); ^1H NMR (CDCl_3) δ 3.80 (s, 2H), 7.18-7.30 (m, 5H), 7.38 (t, 2H, $J = 8.9$ Hz), 7.48 (d, 1H, $J = 7.2$ Hz), 7.64 (d, 2H, $J = 7.1$ Hz).

(E)-1,3-Diphenylpropenone 133

1,3-Diphenylpropenone was prepared from acetophenone and benzaldehyde by the undergraduate organic laboratory class of 1981 following the procedure of Vogel (83): mp 55-57°C (literature 56-57°C).

(E)-1,3-Diphenylpropenone tosylhydrazone 72

1,3-Diphenylpropenone tosylhydrazone was prepared in 80% yield by the method of Durr (23): mp 170-171°C (literature 171-172°C).

Photolysis of 1,3-diphenylpropenone tosylhydrazone sodium salt

Sodium methoxide (1.96g, 35 mmol) was added to 1,3-diphenylpropenone tosylhydrazone 72 (2.50g, 6.65 mmol) in dry THF (300 mL) 15 minutes prior to irradiation. The solution was irradiated through a Uranium filter for 46 minutes. The photolysis mixture was filtered through celite and chromatographed (2.8 x 52 cm). Elution was with hexane in 200 mL fractions: 1-2, nil; 3-5, 20 mg of 63; 6-7, nil; elution with 1.0% ether-hexane: 8-11, nil; 12-13, 585 mg of 64; 14, nil; elution

with 20% ethyl acetate-hexane: 15-20, 186 mg of oligomeric material; 21, nil; 22-23, 534 mg of 3,5-diphenylpyrazole 129.

1,2-Diphenyl-3-[trans-2,3-diphenylcyclopropyl]cyclopropene 64 was recrystallized from hexane, mp 138-139°C (literature (23) 139-140°C); ^1H NMR (CDCl_3) δ 1.99 (q, 1H, $J = 5.6$ Hz), 2.48 (d, 2H), 2.49 (d, 1H, $J = 5.2$ Hz), 6.88 (d, 4H, $J = 7.9$ Hz), 7.0-7.1 (m, 6H), 7.36 (t, 2H, $J = 7.4$ Hz), 7.48 (t, 4H, $J = 7.5$ Hz), 7.78 (d, 4H, $J = 7.3$ Hz); UV (cyclohexane) λ_{max} 230 (ϵ 32310), λ_{sh} 290 (ϵ 25540), λ_{max} 319 (ϵ 31700), λ_{max} 337 (ϵ 24850).

3,5-Diphenylpyrazole 129 was recrystallized from ether-hexane, mp 199-200°C (literature (23) 198-200°C); ^1H NMR (CDCl_3) δ 6.80 (s, 1H), 7.2-7.4 (m, 5H), 7.5-7.8 (m, 5H).

1,1,-Dibromo-2,2-diphenylcyclopropane 79

1,1,-Dibromo-2,2-diphenylcyclopropane was prepared in 58% yield from 1,1-diphenylethylene by the method of Skattebol (26): mp 153-155°C (literature 154-156°C); ^1H NMR (CDCl_3) δ 2.47 (s, 2H), 7.2-7.3 (m, 6H), 7.51 (d, 4H, $J = 7.3$ Hz).

1,1-Diphenylallene 68

1,1-Diphenylallene was prepared by the method of Skattelbol (26). To a cold (-40°C) stirring suspension of 1,1-dibromo-2,2-diphenylcyclopropane (400 mg, 1.14 mmol) in ethyl ether (5 mL) was added dropwise 2.1 mL of 1.5M methyllithium (3.2 mmol) under nitrogen. The reaction mixture was stirred for an additional 20 minutes at -30°C and then slowly quenched with 10% aqueous hydrochloric acid (5 mL) and extracted with

ethyl ether (3 x 5 mL). The combined ether extracts were dried over magnesium sulfate, and concentrated in vacuo. Flash chromatography (2.0 x 10 cm) with pentane elution gave 199 mg (90%) of a colorless liquid that rapidly turned yellow upon standing. ^1H NMR (CDCl_3) δ 5.26 (s, 2H), 7.1-7.4 (m, 10H). Other spectral data (IR, UV) were as reported.

GC analysis showed the allene to contain 0.65% 1,1-diphenylethylene.

Direct irradiation of 1,1-diphenylallene 68

Allene 68 (353 mg) dissolved in pentane (300 mL) at 0°C was irradiated through a corex filter for 31 hours. The reaction mixture was concentrated under reduced pressure at 0°C and residue subjected to chromatography (1.8 x 49 cm). Elution was with hexane in 50 mL fractions: 1-3, nil; 4-5, 109 mg of 68 and 1,1-diphenylethylene 78, ca. 1.0:0.04; 6-9, 77 mg of 68 and 70 (trace); 10, nil; 11-12, 5 mg of 69 and 71, ca. 1.0:0.06; 13-14, 6 mg of 69 and 71, ca. 1.0:0.4; 15-17, 7 mg of uncharacterized material; 18-19, nil; 20-34, 66 mg of 82; 35-38, nil; 39-46, 11 mg of polymeric material. Mass balance was greater than 74%.

Diphenylethylene was unambiguously characterized by GC-MS and ^1H NMR.

Quantitative GLC analysis of 1,1-diphenylallene 68 irradiation

Allene 68 (172 mg) in pentane (200 mL) at -10°C was irradiated at 254 nm for 10 hours. The allene used contained 0.65% of 1,1-diphenylethylene as an impurity. The percentage of 1,1-diphenylethylene was invariant under the reaction conditions and was used as the internal

standard. Aliquots (2 mL) were removed after 1, 2, 3, 4, 5 and 10 hours and concentrated to one-fourth the volume. Analysis by capillary GLC (flow rate 2.5 mL/min.; 10 meter SE-30, 150°C) relative to internal standard gave the following points on the graph shown in Figure 8.

3-Phenylindene 70

3-Phenylindene was prepared in 65% overall yield from 1-indenone by the method of Bordwell and Drucker (82). An analytical sample was obtained by flash chromatography with pentane elution: bp 112-120°C, 0.6 torr (literature bp 100-108°C, 0.2 torr); ^1H NMR (CDCl_3) δ 3.51 (d, 2H, J = 2.0 Hz), 6.58 (t, 1H), 7.2-7.7 (m, 9H).

Trimethylsilyl-3,3-diphenylpropyne 81

Trimethylsilylacetylene (1.45 mL, 1.01g, 10.3 mmol) was slowly added under nitrogen to a stirring solution of ethyl grignard (1.29g, 9.69 mmol) in ethyl ether (15 mL). After 4 hours of stirring, copper (I) iodide (100 mg) was added and the reaction mixture was heated to reflux for 1.0 hour. Bromodiphenylmethane (2.48g, 9.58 mmol) in ethyl ether (10 mL) was then added and the reaction mixture was heated to reflux for 48 hours. Chromatography (2.8 x 18.5 cm) with hexane elution yielded 867 mg (35%) of a colorless liquid. ^1H NMR (CDCl_3) δ 0.199 (s, 9H), 5.01 (s, 1H), 7.2-7.4 (m, 10H); IR (film) 3080, 3060, 3025, 2955, 2160, 1595, 1480, 1450, 1245, 1035, 1015, 845, 835, 750 and 690 cm^{-1} .

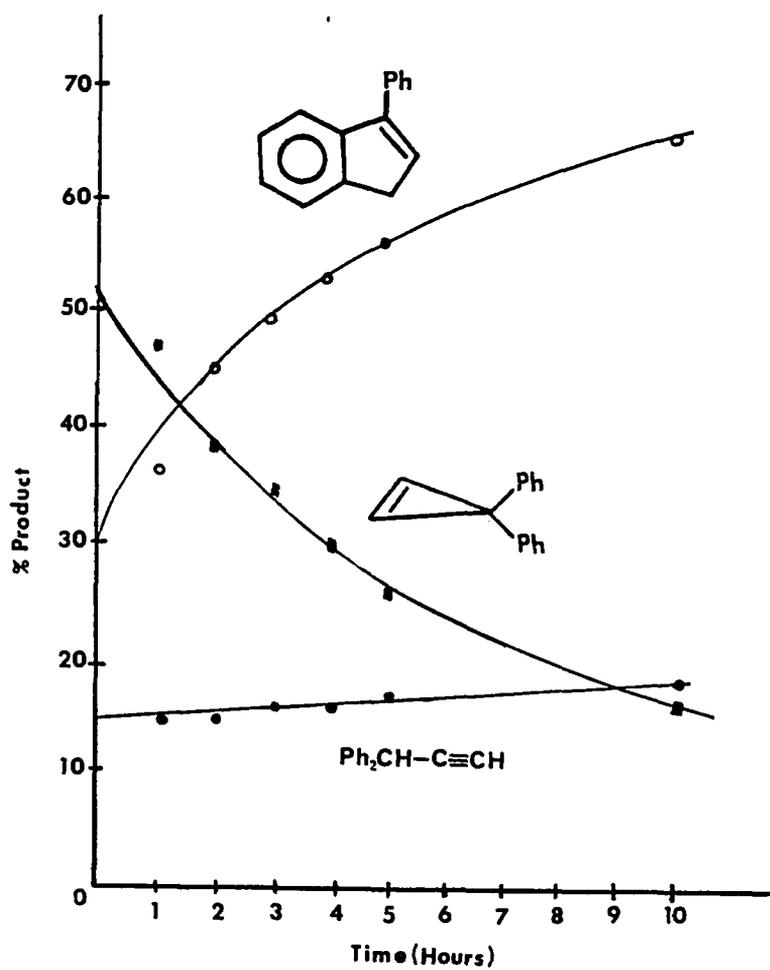


Figure 9. Photorearrangement of 1,1-diphenylallene: photoproduct percentage versus time

3,3-Diphenylpropyne

The general deprotection procedure of Engel was employed (84). Silver nitrate (136 mg, 0.800 mmol) in 3 mL of ethanol-water (2:1) was added with stirring to trimethylsilyl-3,3-diphenylpropyne (212 mg, 0.800 mmol) in 7 mL of ethyl ether-ethanol (4:3) resulting in the formation of a white precipitate. After 10 minutes of additional stirring, 2.0 mL of a 2.0M aqueous solution of potassium cyanide (262 mg, 4.04 mmol) was added and the precipitate disappeared. The reaction mixture was extracted with hexane (3 x 10 mL) and washed with brine. The combined hexane extracts were dried over magnesium sulfate and concentrated under reduced pressure to yield 152 mg (99%) of a colorless liquid which crystallized upon cooling: mp 49-51°C; ^1H NMR (CDCl_3) δ 2.38 (d, 1H, $J = 2.6$ Hz), 4.91 (d, 1H), 7.2-7.3 (m, 10H); IR (film) 3300, 3080, 3060, 2950, 2160, 1595, 1490, 1445, 845, 830 and 685 cm^{-1} ; MS m/e 192.0934 (ca. error - 2.6 ppm).

3,3-Diphenylpropenal

3,3-Diphenylpropenal was provided by Dr. R. P. Johnson. This material was prepared according to the procedure for 3,3-diphenyl-p-tolylacrolein by the method of Zimmerman, Armesto, Amezua, Garnett and Johnson (85): mp 45-46°C (literature (86) 46-47°C).

3,3-Diphenylpropenal tosylhydrazone 132

3,3-Diphenylpropenal tosylhydrazone was prepared in 87% yield by the method of Durr (23): mp 162-166°C (literature 169-170°C).

Photolysis of 3,3-diphenylpropenal tosylhydrazone sodium salt

Sodium methoxide (1.7g, 32 mmol) was added to 3,3-diphenylpropenal tosylhydrazone 132 (3.0g, 8.0 mmol) in dry THF (300 mL) and the solution was irradiated through a uranium filter for 1.5 hours. Interruption of the photolysis after 0.5 hours of irradiation revealed a red colored solution characteristic of a diazo compound. The photolysis mixture was filtered through Celite and chromatographed (2.8 x 40 cm). Elution was with hexane in 100 mL fractions: 1-2, nil; 3-6, 577 mg of 68, 70, and 69, ca. 0.16:1.0:2.6; 7-13, 437 mg of 69. Continued elution with 1.0% ether-hexane: 14-16, nil; 17-22, 91 mg of oligomeric material. Continued elution with 10% ether-hexane: 66 mg of oligomeric material; 25, nil. Continued elution with 20% ether-hexane: 26-29, 242 mg of a substance tentatively characterized as 1,1,6,6-tetraphenylhexatriene isomers.

3,3-Diphenylcyclopropene 69 was obtained as a colorless oil; ^1H NMR (CDCl_3) δ 7.16-7.19 (m, 5H), 7.20-7.30 (m, 5H), 7.48 (s, 1H).

1-Phenyl-2,3-dibenzo-6-diphenylethylene [3.2.0] heptene 82

1,1-diphenylallene 68 (120 mg, 0.625 mmol) and 3-phenylindene 70 (130 mg, 0.677 mmol) in pentane (300 mL) at 0°C was irradiated through a corex filter for 10 hours and 40 minutes. The reaction mixture was concentrated under reduced pressure and the residue subjected to flash chromatography (2.0 x 18.5 cm). Elution was with pentane in 200 mL fractions: 1, 50 mg of 68; 2-6, nil. Continued elution with hexane: 7-11, 141 mg of (58%) as a viscous yellow oil. Recrystallization from

ethanol gave white crystals melting at 110-111°C. ^1H NMR (CDCl_3) δ 2.81 (d, 1H, $J = 17$ Hz), 3.26 (dd, 1H, $J = 17$ and 8.0 Hz), 3.40 (dd, 1H, $J = 16$ and 3.0 Hz), 3.67 (d, 1H, $J = 16$ Hz), 4.22 (dd, 1H, $J = 8.0$ and 3.0 Hz), 7.1-7.3 (m, 19H); ^{13}C NMR (CDCl_3) 149.7, 146.8, 143.5, 140.6, 140.5, 138.9, 136.7, 129.1, 128.8, 128.3, 128.2, 128.1, 128.0, 127.1, 127.0, 126.9, 126.7, 126.6, 126.4, 126.1, 126.0, 125.2, 125.1, 124.9, 56.1, 55.6, 45.3, 45.2, 36.7. IR (film) 3030, 3010, 2940, 2915, 2840, 1592, 1488, 1470, 1449, 1436, 750 and 695 cm^{-1} ; MS m/e 384.18781 (ca. error -1.0 ppm).

Direct irradiation of phenylallene 83

Allene 83 (300 mg) dissolved in pentane (300 mL) at 0°C was irradiated for 28 hours through a Corex filter. Aliquots (10 mL) were removed after 0.5, 3.0, 16 and 28 hours of irradiation. ^1H NMR analysis of the aliquots showed no discernible isomeric products. HPLC analysis showed the presence of more than 17 very minor uncharacterized products. The Corex filter was removed, replaced with a Vycor filter and irradiation continued for another 24 hours. ^1H NMR and HPLC analysis showed no discernible isomeric products. Low temperature (-10°C) chromatography (2.2 x 24 cm) with pentane elution gave only 53 mg of phenylallene. Mass balance was 18%.

Direct irradiation of 1,3-diphenylindene 52

Indene 52 (200 mg) dissolved in pentane (200 mL) at 0°C was irradiated at 254 nm for 2.5 hours. The solution was concentrated under

reduced pressure and chromatographed (1.8 x 48 cm). Elution was with hexane in 100 mL fractions: 1-5, nil; 6-10, 152 mg of 52, 56 and 57, ratio 0.16:1.0:3.6; 11, 5 mg of 56 and 57, ratio 0.15:1.0; 12-17, 29 mg of 55. Mass balance was 93%.

Quantum yield determination of 1,3-diphenylindene 52

A quartz cell containing 52 (25 mg) and isooctane (50 mL) was irradiated on the optical bench for 2 to 9 hours. Internal standard (bibenzyl) was added and the solution was concentrated under reduced pressure. Products were analyzed by 300 MHz NMR integration. Five separate runs at 0.5-20% conversion yielded the following quantum efficiencies for product formation: 2,3-Diphenylindene (56), 0.12 ± 0.01 ; 1,2-diphenylindene (55), 0.031 ± 0.004 .

Direct irradiation of 1,2-diphenylindene 55

Indene 55 (100 mg) in pentane (200 mL) at 0°C was irradiated at 254 nm for 10.5 hours. The solution was concentrated under reduced pressure and chromatographed (1.8 x 48 cm). Elution was with hexane in 100 mL fractions: 1-4, nil; 5-8, 4 mg of 57; 9-16, 47 mg of 55. Continued elution with 5% ether-hexane: 17, nil; 18-19, 5% 34 mg of dimers. Mass balance was 85%.

Direct irradiation of 1-phenylindene 65

Indene 65 (250 mg) in pentane (200 mL) at -10°C was irradiated at 254 nm for 30 minutes. Aliquots (10 mL) of the irradiation solution

were removed after 6, 15 and 30 minutes. HPLC and 300 MHz ^1H NMR analysis of the aliquots showed the formation of 67. The reaction mixture was concentrated under reduced pressure at 0°C. Chromatography (2.2 x 56 cm) with hexane elution gave 117 mg of 65, 52 mg of 67 and 56 mg of oligomeric material. Mass balance was 87%.

Direct irradiation of 3-phenylindene 70

Indene 70 (200 mg) in pentane (200 mL) at -10°C was irradiated at 254 nm for 3 hours. Aliquots (4.0 mL) of the irradiation solution were removed after 2, 6, 12, 30, 60 and 180 minutes. HPLC and 300 MHz ^1H NMR analysis of the aliquots showed no isomeric products. The reaction mixture was concentrated under reduced pressure at 0°C. Chromatography (1.8 x 17 cm) with hexane elution gave 172 mg of 70, 6 mg of a polycyclic aromatic photoproduct and 6 mg of oligomeric material. Mass balance was 92%.

Direct irradiation of 2-phenylindene 67

Indene 67 (201 mg) in pentane (200 mL) at 0°C was irradiated at 300 nm for 2.5 hours. Aliquots (6 mL) of the irradiation solution were removed after 12, 30 and 90 minutes of irradiation. ^1H NMR analysis of the aliquots showed only dimeric products. The reaction mixture was concentrated under reduced pressure and chromatographed (1.8 x 43 cm). Elution was with hexane in 100 mL (1-12) then 200 mL fractions: 1-2, nil; 3-4, 20 mg of 67; 5-6, 11 mg of uncharacterized material; 7-9, 25 mg of dimer 88; 10-13, 40 mg of dimer 89; 14-17, 56 mg of

dimers 86 and 87, ca. 3.4:1.0; 18-19, 29 mg of dimers 86 and 87, ca. 1.0:20. Mass balance was 90%.

Dimer 88 was recrystallized from hexane, mp 205-205.5°C; ^1H NMR (CDCl_3) δ 3.09 (d, 2H, J = 15 Hz), 3.29 (d, 2H, J = 15 Hz), 4.12 (s, 2H), 6.93 (d, 2H, J = 7.5 Hz), 7.10-7.27 (m, 14H), 7.42 (d, 2H, J = 7.5 Hz); ^{13}C NMR (CDCl_3) δ 146.4, 145.5, 143.8, 128.0, 127.1, 126.9, 126.8, 126.0, 124.4, 123.8, 59.4, 55.3, 46.4

Dimer 89 was recrystallized from hexane, mp 198.5-201.5°C; ^1H NMR (CDCl_3) δ 2.78 (d, 2H, J = 17.3 Hz), 3.16 (d, 2H, J = 17.3 Hz), 4.61 (s, 2H), 6.86 (d, 2H, J = 7.4 Hz), 7.1-7.4 (m, 16H); ^{13}C NMR (CDCl_3) δ 150.3, 145.5, 142.4, 128.5, 127.1, 126.3, 125.4, 125.3, 124.5, 60.4, 53.2, 44.7.

Dimer 86 was recrystallized from hexane, mp 191-192°C; ^1H NMR (CDCl_3) δ 3.30 (d, 2H, J = 17 Hz), 3.81 (d, 2H, J = 17 Hz), 4.68 (s, 2H), 6.8-7.2 (m, 18H); ^{13}C NMR (CDCl_3) δ 146.4, 142.3, 127.7, 127.5, 127.2, 127.0, 126.6, 126.5, 125.8, 125.4, 125.1, 123.8, 52.5, 50.6, 44.6.

Dimer 87 was recrystallized from hexane, mp 239-240.5°C; ^1H NMR (CDCl_3) δ 3.41 (d, 2H, J = 16.6 Hz), 3.76 (d, 2H, J = 16.6 Hz), 4.47 (s, 2H), 7.0-7.2 (m, 18H); ^{13}C NMR (CDCl_3) δ 144.9, 143.2, 127.7, 127.0, 126.6, 126.5, 125.8, 125.4, 124.3, 59.4, 55.9, 50.6.

Direct irradiation of 1,3,3-triphenylcyclopropene 53

Cyclopropene 53 (128 mg) dissolved in pentane (200 mL) at -10°C was irradiated at 254 nm for 16 minutes. Chromatography (2.1 x 74 cm)

with hexane elution in 25 mL fractions yielded the following: 1-47, nil; 48-56, 5 mg of triphenylallene 50, 57-60, 6 mg of 50, 52, 56 and 57, ratio 1:2:8:1.5; 61-63, 13 mg of 52, 56 and 57, ratio 1:2.5:0.1; 64-76, 48 mg of 52, 56, 57 and 53, ratio 1:2:0.1:9; 77-102, 30 mg of pure 55; 103-112, 2 mg of pure 12. Mass balance was 81%.

Other experiments monitored by HPLC and 300 MHz NMR showed 50, 52, and 56 to be primary (ratio 0.38:1.0:1.6 at 4% conversion).

Quantum yield determination for 1,3,3-triphenylcyclopropene 53

A quartz cell containing cyclopropene 53 (30 mg) and isooctane (50 mL) was irradiated on the optical bench for 7.5 to 14 hours. Internal standard (bibenzyl) was added and the solution was concentrated in vacuo. The product was analyzed by 300 MHz ^1H NMR integration. Five separate runs at 1-10% conversion yielded the following quantum efficiencies for products: triphenylallene (50), 0.012 ± 0.003 ; 2,3-diphenylindene (56), 0.061 ± 0.01 ; 1,3-diphenylindene (52), 0.034 ± 0.006 .

Rates and trapping of 1,3,3-triphenylcyclopropene 53 ring opening

Quartz test tubes were charged with either 10 mL aliquots of 1,3,3-triphenylcyclopropene 53 stock solutions (2.66×10^{-4} M) in methanol and hexane. The tubes were cooled to -15°C placed in merry-go-round apparatus of Rayonett and irradiated at 254 nm for 15 and 30 minutes. Internal standard (bibenzyl) was added and solvents were concentrated under reduced pressure.

Analysis by 300 MHz ^1H NMR relative to internal standard gave the following percentages at 60% conversion (30 min.): triphenylallene 50 (4%), 1,3-diphenylindene 52 (8%), 1,2-diphenylindene 55 (4%), 2,3-diphenylindene 56 (59%), indenophenanthrene 57 (24%). 3-Methoxy-1,1,3-triphenylpropene 98 (0.8%) and 3-methoxy-1,1,2-triphenylpropene 97 (0.5%) were observed in the methanol run. The relative ratio of hydrocarbon products (50, 52, 55, 56 and 57) to ether photoproducts (98 and 97) was ca. to be 74. A similar value was obtained from the lower conversion (15 min.) experiment.

3-Methoxy-1,1,2-triphenylpropene 97

3-Methoxy-1,1,2-triphenylpropene was prepared in 95% yield from 3-bromo-1,1,2-triphenylpropene by the method of Norman and Thomas (77): mp 132-133°C (literature 132-133°C); ^1H NMR (CDCl_3) δ 3.24 (s, 3H), 4.22 (s, 2H), 6.92 - 7.35 (m, 15H).

1,2,3-Triphenylcyclopropene 99

1,2,3-Triphenylcyclopropene was prepared in 54% yield from triphenylcyclopropenium bromide by the method of Breslow and Chang (70): mp 112-113°C (literature 112-113°C); ^1H NMR (CDCl_3) δ 3.26 (s, 1H), 7.11-7.16 (m, 1H), 7.22-7.24 (m, 4H), 7.33 (t, 2H, $J = 7.2$ Hz), 7.42 (t, 4H, $J = 7.5$ Hz), 7.68 (d, 4H, $J = 7.5$ Hz).

Direct irradiation of 1,2,3-triphenylcyclopropene 99

Cyclopropene 99 (152 mg) dissolved in pentane (200 mL) at -10°C was irradiated at 350 nm for 9 hours. The solvent was decanted from a

white precipitate which had formed during irradiation. Chromatography (1.8 x 45 cm) with hexane elution in 100 mL fractions yielded the following: 1-5, nil; 6, 5 mg of a mixture of triphenylallene (50) and 99, ratio 1:1; 7-10, 25 mg of a mixture of 50 and 99, ratio 1:16; 11-16, 27 mg of pure 1,2-diphenylindene (55). Continued elution with 5% ether-hexane: nil; 18-21, 46 mg of oligomeric material, from which 4 mg of 100 was obtained by trituration with hexane. The precipitate in the reaction vessel was removed with methylene chloride to yield another 38 mg of dimer 100. Mass balance was 93%.

The dimer 100 was recrystallized from hexane. It melted at 214°C, then crystallized between 216-220°C (literature mp 330-350°C with phase change 200°C); ^1H NMR (CDCl_3) δ 4.10 (s, 1H), 6.7-7.1 (m, 5H), 7.26 (s, 10H).

Direct irradiation of tetraphenylcyclopropene 49

Cyclopropene 49 (100 mg) dissolved in cyclohexane (100 mL) was irradiated at 350 nm. After 15 minutes, 44 and 43 were observed (HPLC analysis; μ -Porasil) in a ratio 26:1. Continued irradiation yielded increasing amounts of phenanthrene 45. Concentration of the solution and subsequent repetitive preparative TLC (silica plates, hexane development) yielded pure samples of 43, 44, and 45, identical with authentic material.

1,2-Diphenylcyclopropanone

1,2-Diphenylcyclopropanone was prepared in 45% overall yield from dibenzylketone by the method of Breslow, Eicher, Krebs, Peterson and Posner (87) mp 119-120°C (literature 119-120°C).

1,2-Diphenylcyclopropene 105

1,2-diphenylcyclopropene was prepared in 31% yield from diphenylcyclopropane by the method of Perkins and Wadsworth (88): mp 45-46°C (literature 44-47°C); ^1H NMR δ 1.53 (s, 1H), 7.2-7.4 (m, 5H).

Direct irradiation of 1,2-diphenylcyclopropene 105

Cyclopropene 105 (53 mg) in pentane (200 mL) at -10°C was irradiated at 350 nm for 2 hours. Aliquots (0.5 mL) of the irradiation solution removed after 1.0, 7.0, 30, 60 and 120 minutes of irradiation. HPLC analysis of the aliquots showed no isomeric products. The reaction mixture was concentrated under reduced pressure at 0°C. Analysis by 300 MHz ^1H NMR showed only 1,2,4,5-tetraphenylcyclohexa-1,4-diene 107 as previously reported.

Direct irradiation of 3,3-diphenylcyclopropene 69

Cyclopropene 69 (65 mg) dissolved in pentane at -10°C was irradiated for 30 minutes at 254 nm. The reaction mixture was concentrated under reduced pressure at 0°C and subjected to flash chromatography (1.8 x 34 cm) with pentane elution in 25 mL fractions: 1-8, nil; 9, 11 mg 68; 10, 9 mg of 70 + 68, ca. 3:1; 11-13, 12 mg 70;

14-17, 15 mg of 69; 18-20, 2 mg of 69 + 71, ca. 10:1; 21-24, 7 mg, 69 and 71 ca. 3:2; 25-28, 2 mg of 71. Mass balance was 89%.

Quantitative GLC analysis of 3,3-diphenylcyclopropene 69 irradiation

Cyclopropene 69 (20 mg) dissolved in pentane (20 mL) was cooled to -15°C and irradiated at 254 nm. Aliquots (2 mL) were removed after 5, 8, 10, 16 and 20 minutes then analyzed by capillary GLC (flow rate 2.5 mL/min.; 10m SE-30, 150°C). The product ratio of 70:68:71 was 3.1:1.0:0.5 and was invariant up to 60% conversion.

Thermolysis of 1,3,3-triphenylcyclopropene 53

Samples of cyclopropene 53 (16 mg) in toluene (10 mL) were degassed with three freeze-pump-thaw cycles, sealed, then thermolyzed at constant temperature. Internal standard (bibenzyl) was added and solution was concentrated under reduced pressure. Products were analyzed by 300 MHz ¹H NMR integration. Three separate runs yielded the following results:

Temperature	Time	% 52	% 56	Conversion
196°	1 hour	78	22	100%
132°	0.5 hours	78	22	100%
85°	0.5 hours	75	25	6%

Sensitized irradiation of tetraphenylallene 43

Allene 43 (405 mg) and xanthone (1.18g) dissolved in benzene (150 mL) was irradiated through a uranium filter for 18 hours.

Concentration of the solution and subsequent chromatography gave 393 mg (97%) of unreacted 43 and 1.16g (98%) of sensitizer.

Sensitized irradiation of triphenylallene 50

Allene 50 (442 mg) and xanthone (1.20g) dissolved in benzene (150 mL) was cooled at 10°C and irradiated through uranium for 24 hours. Concentration of the solution at reduced pressure and subsequent chromatography yielded 450 mg (102%) of unreacted 50 and 1.18g (97%) of recovered sensitizer.

Sensitized irradiation of 1,1-diphenylallene 68

Allene 68 (175 mg) and xanthone (1.00g) dissolved in 160 mL of benzene-hexane (1:2) was irradiated through uranium for 14 hours. Concentration of the solution at reduced pressure and subsequent chromatography yielded 164 mg (95%) of allene 68 and 712 mg (71%) xanthone plus 175 mg of unidentified adducts. No isomeric products were detected by ^1H NMR or HPLC analysis.

1,2,3-Triphenylpropenone

The general procedure of Buckles and Brener was employed (89). 2,3-Diphenylpropenoic acid (7.00g, 31.2 mmol) was added portion-wise at 0°C to phenyllithium (5.44g, 64.8 mmol) in ethyl ether (50 mL). After 0.5 hours of stirring, the reaction mixture was quenched with 10% aqueous hydrochloric acid and extracted with ethyl ether (3 x 15 mL). The combined ether extracts were dried over magnesium sulfate and concentrated under reduced pressure to yield a brown oil. This was taken

up in ethyl ether and triturated with hexane to separate a brown tar. The solution was decanted from the tar and 4.7g (56%) of lightly yellow colored crystals were collected, mp 99-100°C (literature 100°C).

1,2,3-Triphenylpropenone tosylhydrazone 127

1,2,3-Triphenylpropenone tosylhydrazone was prepared in 40% yield as described by Durr (23): mp 169-171°C (literature 171-172°C).

Diphenyl-oxy-propiofenone

Diphenyl-oxy-propiofenone was prepared in 13% yield from diethylmalonate and phenylgrignard by the method of Vorander (90): mp 119-120°C (literature 118-119°C); ^1H NMR (CDCl_3) δ 5.20 (d, 1H, 10.6 Hz), 6.73 (d, 1H), 7.1-7.6 (m, 12H), 7.8-8.1 (m, 3H).

1,3,3-Triphenylpropenone

1,3,3-Triphenylpropenone was prepared in 87% yield from diphenyl-oxy-propiofenone by the method of Clemo, Raper and Robson (91): mp 86-87°C (literature 85-87°C).

1,3,3-Triphenylpropenone tosylhydrazone 126

1,3,3-Triphenylpropenone tosylhydrazone was prepared in 70% yield as described by Durr (23): mp 172-173°C (literature 173-174°C).

1,2,3,3-Tetraphenylpropenone 120

1,2,3,3-Tetraphenylpropenone was prepared in 46% overall yield from 1,2,3-triphenylpropenone by the method of Kohler and Nygaard (92): mp

150-151°C (literature 150-151.5°C); IR (CCl₄) 3080, 3060, 3030, 1665, 1540, 1440, 1225, 1220 and 1000 cm⁻¹.

(E)-2,3-Diphenylpropenal

(E)-2,3-Diphenylpropenal was prepared in 19% yield from benzaldehyde and phenylacetaldehyde by the method of Payne and Williams (93): mp 97-99°C (literature 94-95°C).

(E)-2,3-Diphenylpropenal tosylhydrazone 130

(E)-2,3-Diphenylpropenal tosylhydrazone was prepared in 80% yield according to the general procedure of Durr (23): mp 152-153°C; ¹H NMR (CDCl₃) δ 2.41 (s, 3H), 6.74 (s, 1H), 6.9-7.4 (m, 14H), 7.60 (d, 1H, J = 8.2 Hz), 7.70 (s, 1H); IR (KBr) 3465, 3170, 3085, 3040, 2985, 2830, 2740, 1590, 1486, 1440, 1350, 1320, 1160, 1050, 1015, 925, 810, 695 and 680 cm⁻¹; MS m/e 220.10025 (ca. error +1.0 ppm).

Photolysis of 1,2,3-triphenylpropenone tosylhydrazone sodium salt

Sodium methoxide (1.10g, 20.4 mmol) was added to 127 (2.20g, 4.87 mmol) in dry THF (280 mL) and then irradiated through a uranium filter for 0.5 hours. The photolysis mixture was concentrated under reduced pressure then filtered through silica with hexane to yield 675 mg of 50, 99 and 55, ratio 0.2:99.6:0.2 by ¹H NMR analysis. Hot ethyl acetate washing of the silica gel gave 434 mg of 3,4,5-Triphenyl pyrazole 128. Mass balance was 102%.

Photolysis of 1,3,3-triphenylpropenone tosylhydrazone sodium salt

Sodium methoxide (1.00g, 18.5 mmol) was added to 126 (1.95g, 4.31 mmol) in dry THF (280 mL) and then irradiated through a uranium filter for 1.5 hours. The photolysis mixture was filtered through Celite, concentrated under reduced pressure and chromatographed (2.8 x 54 cm). Elution was with hexane in 100 mL fractions: 1-10, nil; 11-12, 45 mg of 50 and 52, ratio 1:10; 13-14, 169 mg of 50, 52 and 53, ratio 1:96:3; 15-18, 298 mg of 52 and 53, ratio 7:3; 19-24, 129 mg of 52 and 53, ratio 4:6; 25-26, 23 mg of 52 and 53. Continued elution with 1% ether-hexane: 39-42, 210 mg of oligomeric material. Continued elution with 5.0% ether-hexane: 43-44, ether-hexane, nil; 45-52, 17 mg of oligomeric material. Continued elution with 10% ether-hexane: 53-60, 45 mg of hexatriene dimers; 61-62, nil; 63-69, 62 mg of 126.

Photolysis of 2,3-diphenylpropenal tosylhydrazone sodium salt

Sodium methoxide (1.80g, 32 mmol) was added to 2,3-diphenylpropenal tosylhydrazone 130 (3.0g, 8.0 mmol) in dry THF (300 mL) and the solution was irradiated through a Uranium filter for 50 minutes. The photolysis mixture was filtered through celite and chromatographed (2.8 x 50 cm). Elution was with hexane in 50 mL fractions: 1-6, nil; 7-11, 31 mg of 63; 12-14, 28 mg of 63 and 67, ca. 1:14; 15-24, 200 mg of 67; 25-44, nil. Continued elution with 1.0% ether-hexane in 200 mL fractions: 45-47, nil; 48-50, 303 mg of 64. Continued elution with 25% ether-hexane in 500 mL fractions: 51-52, 82 mg of oligomeric material; 53-56, 1.16g of 4,5-diphenylpyrazole 131.

4,5-Diphenylpyrazole 131 was recrystallized from ether, mp 152-154°C (literature (94) 154-155°C); ^1H NMR (CDCl_3) δ 7.43 (s, 7H), 7.50 (s, 3H), 7.78 (s, 1H).

Direct irradiation of 1,3-diphenylpropenone tosylhydrazone 72

Tosylhydrazone 72 (100 mg) in 60 mL of cyclohexane-benzene (1:1) was irradiated for 45 minutes with the 254 nm lamps. The solvent was removed under reduced pressure. The yellow residue was taken up in 10 mL of warm ethanol (95%) and cooled to give 30 mg of 2,3-diphenyl-n-tosylpyrazoline (136). ^1H NMR analysis of mother liquor showed only the presence of 72.

Spectral data for 136 are as follows: mp 149-150°C; ^1H NMR (CDCl_3) δ 2.39 (s, 3H), 3.93 (dd, 1H, $J = 9.7$ and 17.8 Hz), 4.11 (dd, 1H, $J = 3.6$ and 17.8 Hz), 4.91 (dd, 1H, $J = 3.6$ and 9.7 Hz), 7.1-7.5 (m, 12H), 7.94 (d, 2H, $J = 7.2$ Hz); IR (KBr) 3035, 2950, 1670, 1585, 1575, 1250, 1070, 1010, 780 cm^{-1} ; MS m/e 376.12320 (ca. error -3.6 ppm).

Photochemical isomerization of (E)-1,3-diphenylpropenone 133

Propenone 133 (300 mg, 1.44 mmol) in benzene (70 mL) was irradiated with the 300 nm lamps for 1.0 hour. The reaction mixture was concentrated under reduced pressure to yield an oily yellow residue. ^1H NMR analysis showed both E and Z isomers (ca. 1.0:1.2). No attempt was made to separate the isomers. ^1H NMR of Z-134 isomer was obtained by a subtracting routine of the Nicolet 300 MHz instrument and was as follows: ^1H NMR (CDCl_3) δ 6.58 (d, 1H, $J = 12.9$ Hz), 6.97 (d, 1H),

7.21-7.25 (m, 3H), 7.40-7.49 (m, 4H), 7.51 (t, 1H, J = 7.2 Hz), 7.96 (d, 2H, J = 7.2 Hz).

(E)-133 isomer: (CDCl₃) δ 7.40-7.66 (m, 9H), 7.81 (d, 1H, J = 15.7 Hz), 8.02 (d, 2H, J = 7.0 Hz).

Reaction of (Z)-1,3-diphenylpropenone with p-tosylhydrazide

The mixture of (E)-133 and (Z)-134 enones obtained from above isomerization (300 mg, 1.44 mmol) and p-toluenesulfonylhydrazide (268 mg, 1.44 mmol) in methanol (5.0 mL) was treated with pyridine (3 drops) and heated to reflux for 5 hours. The reaction mixture was concentrated to one-half volume and 100 mg (15%) of 136 was collected. The mother liquor was analyzed by ¹H NMR and revealed only starting materials.

3-Deuterio-triphenylallene 50-d

Triphenylpropyne 54 (1.00g, 3.73 mmol) in THF (10 mL) was treated with 1.84 mL of a 2.4M n-butyllithium (283 mg, 4.42 mmol) at 0°C. The resultant red solution was quenched with D₂O (2.0 mL). The organic layer was separated, dried over magnesium sulfate and concentrated under reduced pressure at 0°C. Chromatography with hexane elution gave 560 mg (56%) of white crystals that melted at 76-78°C. The ¹H NMR showed no vinyl resonance. HPLC showed no detectable propyne. MS m/e 269.13158 (ca. 269.13148).

Direct irradiation of 3-deuteriotriphenylallene 50-d

Allene 50-d (100 mg) dissolved in pentane (200 mL) was cooled to -10°C , irradiated with 254 nm lamps for 1.0 hour, and then was concentrated under reduced pressure. ^1H NMR analysis showed singlets at δ 4.70 (allylic proton of 52), broad singlets at 4.25, 3.90 and 4.97 (corresponding to 56, 57 and 55, respectively). No signals at 5.21 (propyne 54) or 6.67 (vinyl proton of 52) were observed.

Measurement of deuterium isotope effect

Quartz tubes containing solutions of 50 and 50-d (10.0 mg each) were purged with N_2 , cooled to -20°C and irradiated side by side in a Rayonett merry-go-round apparatus for 1-2 minutes. Internal standard (1,1,3,3-tetraphenylpropene) was added and the mixture was analyzed by HPLC. Three separate runs at 0.5-1% conversion yielded (HPLC analysis) the following results for $\phi_{\text{H}}/\phi_{\text{D}}$ (standard deviations shown); 1,3-diphenylindene (52), 1.13 ± 0.21 ; 1,3,3-triphenylcyclopropene (53), 1.39 ± 0.01 ; 1,3,3-triphenylpropyne (54), 3.72 ± 0.26 .

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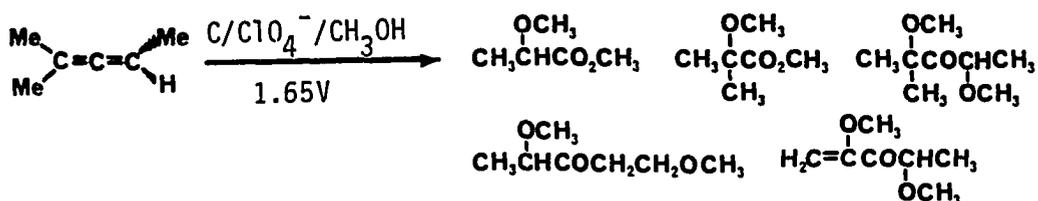
CHAPTER III: PHOTOGENERATION OF TETRAPHENYL AND TRIPHENYL C₃ RADICAL IONS

Introduction

The solution-phase chemistry of radical cations is an area of fundamental interest and importance (1). Radical cations may be efficiently generated through photochemically induced single electron transfer (SET) to an appropriate sensitizer (2). The energetics of this electron transfer are described approximately by the Weller relationship (3). Recent studies have shown an amazing diversity of electron transfer photoreactions (2), as might be anticipated from the diversity of reactive intermediates which can be generated.

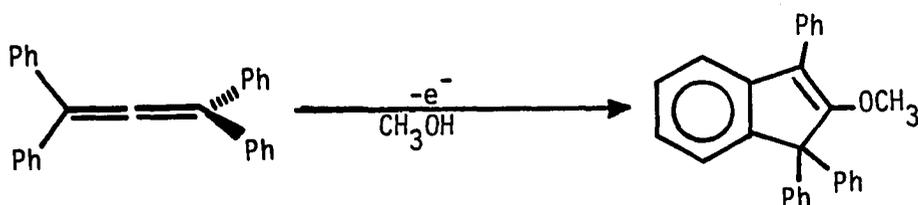
Allene radical cations have been studied by mass (4), photoelectron (5-8), and electron spin resonance (9,10) spectroscopic techniques. Molecular orbital calculations on allene radical cation (8,9,11-13) predict a twisted structure of D₂ symmetry, consistent with evidence from experiment (5,6,9). Solution phase allene radical cation chemistry is, however, poorly characterized. Becker and Zinger have reported on the anodic oxidation of simple allene derivatives in methanol (14a) and in acetonitrile (14b). Multiple-electron oxidation resulted in the isolation of a complex mixture of products. The oxidation of trimethylallene in methanol (Scheme 1) is representative of their work. The authors suggested that addition of nucleophile to the initially formed radical cation would occur at C₂ (Scheme 1).

Schlegel and Schaefer recently described (15) the electrochemical oxidation and reduction of several simple allenes. The radical cation



Scheme 1.

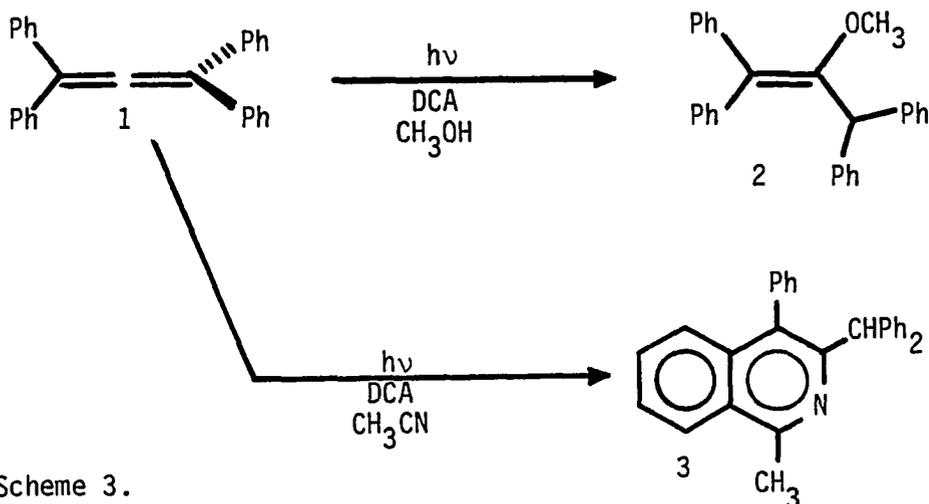
of tetraphenylallene (1, oxidation potential 1.25 V) was suggested to undergo cyclization to an indene structure (Scheme 2).



Scheme 2.

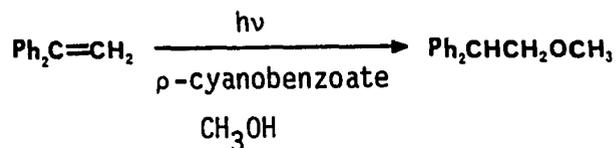
In the first example of photochemical SET reactions of allenes, we (16) and Johnson *et al.* (17) have reported that tetraphenylallene may be photooxidized by irradiation with xanthone or 9,10-dicyanoanthracene. In methanol, this afforded a high yield of vinyl ether 2 (16) while in acetonitrile, an isoquinoline derivative 3 was obtained (Scheme 3). These reactions and others constitute the present work and will be addressed shortly. Trapping of radical cations of 1 by methanol parallels behavior of 1,1-diphenylethylene, which was reported by Neunteufel and Arnold (18) to yield 1,1-diphenyl-2-methoxyethane (Scheme 4).

During the course of the present work, Somekawa *et al.* reported that 2-phenyl-1-pyrrolinium perchlorate will easily photooxidize



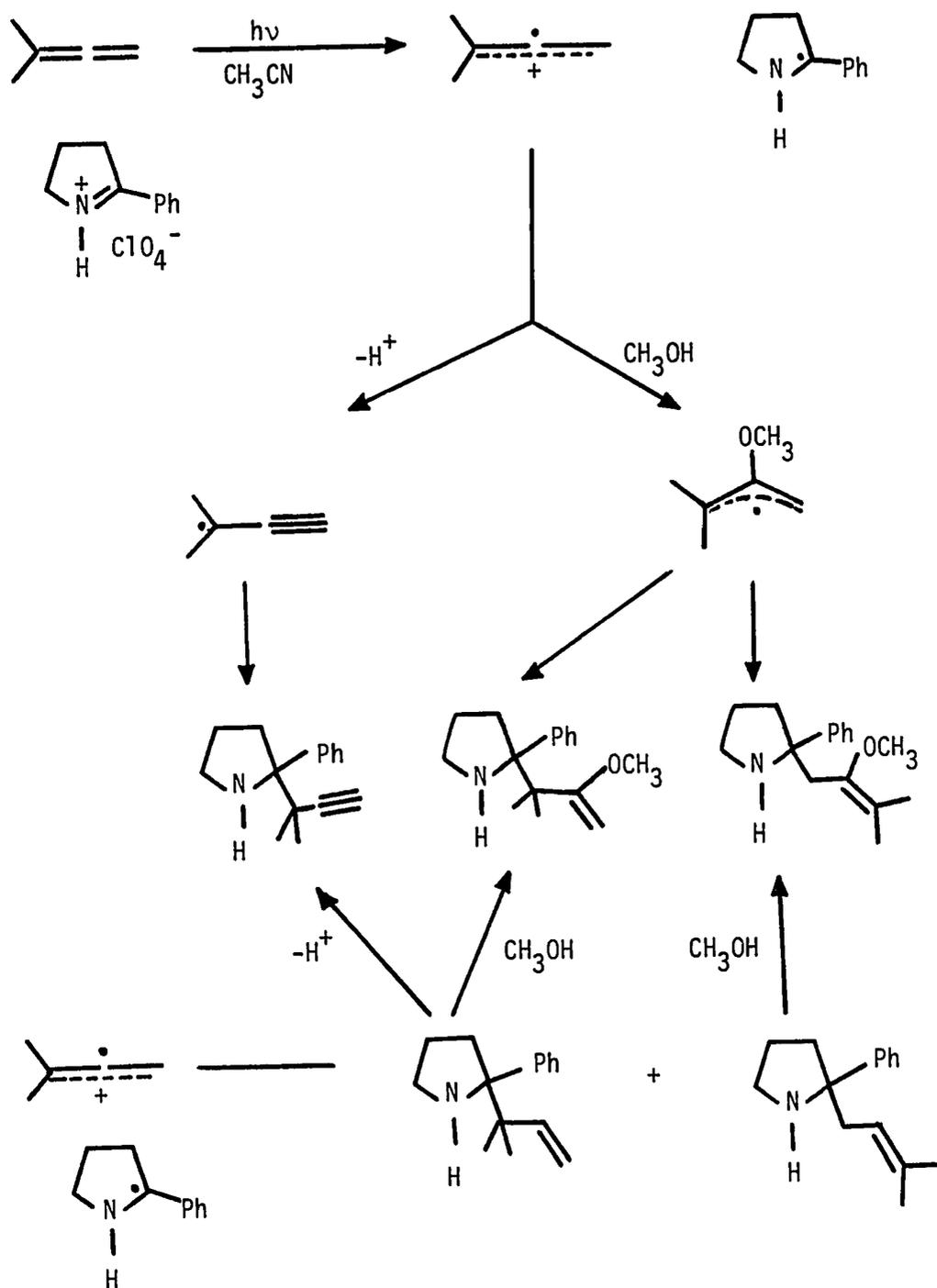
Scheme 3.

allenes (12). Radical coupling in the resultant radical cation-radical pair was suggested to precede nucleophilic addition or deprotonation (Scheme 5). *Ab initio* UHF calculations provided arguments that partial localization of positive charge character at C₂ was the source of regioselective nucleophilic addition at this site (19).



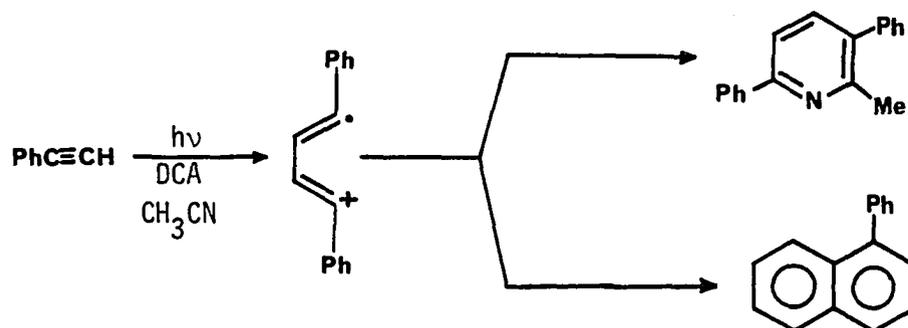
Scheme 4.

Propyne radical cations have received similar attention from mass spectroscopists (4). Theoretical studies (11,13) and photoelectron spectroscopy (14) suggest that the geometry of propyne radical cation should be similar to that of the neutral species. Both experiment (4b) and theory (11) show that the radical cation of propyne is ca. 0.6eV less stable than that of allene. Simple alkyne radical cations may be generated photochemically (20) or electrochemically (21). Mattes and



Scheme 5.

Farid have reported on the electron transfer photooxidation of diphenylacetylene (20) to yield a naphthalene and pyridine derivative shown in Scheme 6.



Scheme 6.

Goals of This Research

The present work was undertaken as an exploratory investigation of the comparative solution phase behavior of substituted allene and propyne radical cations. Tetraphenyl allene (1), triphenylallene (4) and triphenylpropyne (5), depicted in Figure 1, were chosen as substrates because of their isomeric nature, structural simplicity, and anticipated ease of photochemical oxidation (vide infra).

Interconversion of allene and propyne radical cations in the vapor phase has been the subject of some debate (4,11b) and one question was whether triphenylallene and triphenylpropyne radical cations would undergo solution phase isomerizations. A second major point of interest was the competition between nucleophilic addition, and deprotonation of $4\cdot^+$ and $5\cdot^+$ to a common radical species.



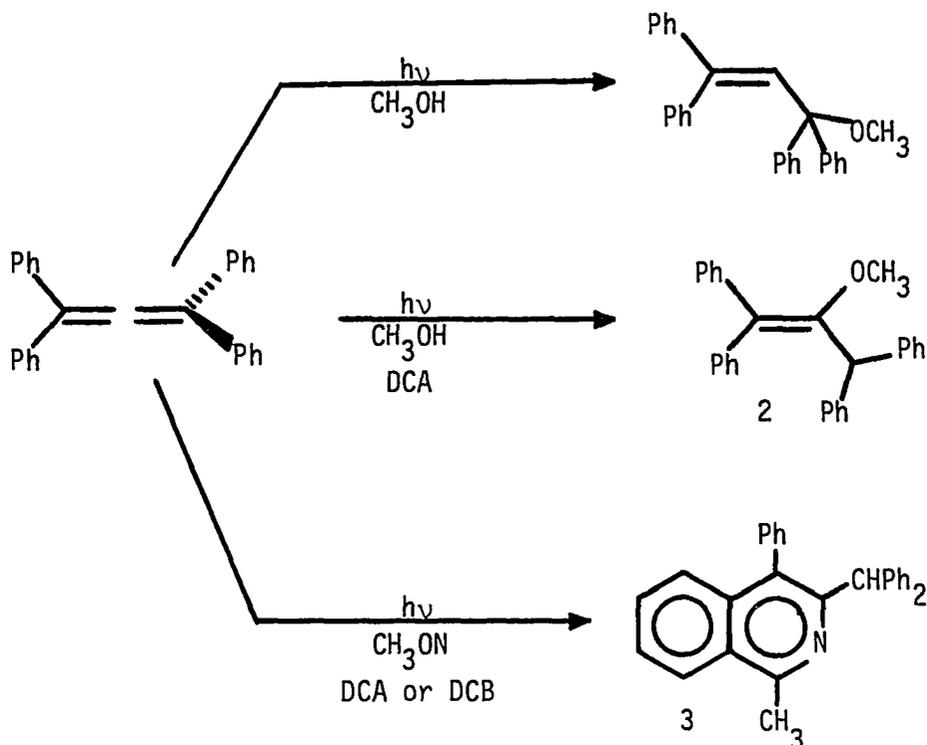
Figure 1. Triphenylallene and triphenylpropyne

The previous chapters describe exploration of the singlet photoreactions of phenylallenes in protic and aprotic solvents. Methanol addition to singlet excited states of allenes affords allylic methylethers, whereas in aprotic solvents, hydrogen or phenyl migration yields photoproducts which are characteristic of vinylcarbenes and biradical intermediates (22).

Exploratory Studies

Tetraphenylallene **1** was prepared according to literature procedure, as detailed in Chapter 1. Preparative irradiations were conducted on solutions of **1** in methanol, with 9,10-dicyanoanthracene (DCA) or xanthone (X) as sensitizer. A uranium glass filter ($\lambda > 330\text{nm}$) was employed to ensure that only the sensitizer absorbed light. Irradiation of **1** with DCA in methanol yielded 2-methoxy-1,1,3,3-tetraphenylpropene **2** as the exclusive product. The structure of **2** derives from its spectral data and acid hydrolysis to 1,1,3,3-tetraphenylacetone. By contrast, direct irradiation without sensitizer afforded 3-methoxy-1,1,3,3-tetraphenylpropene as the predominant product (Scheme 7).

An electron transfer process is mandated since the triplet energy of DCA ($E_T < 33 \text{ kcal/mol}$) (2a) is much lower than that of **1** ($E_T < 57.4 \text{ kcal/mol}$) (23). Additionally, employment of higher triplet energy sensitizers gave no reaction.



Scheme 7.

The free energy change (ΔG) involved in an electron-transfer process is given by the Weller Relationship (3):

$$\Delta G = 23.06 \text{ kcal/mol} [E(D/D^+) - E(A^-/A) - e_0^2/a - E_{0,0}]$$

Here, $E(D/D^+)$ is the oxidation potential of the donor (D), $E(A^-/A)$ is the reduction potential of the acceptor (A) or sensitizer, e_0^2/a is the energy (ca. 0.06 kcal/mol) gained by bringing the two radical ions to the encounter distance (a) in a solvent of dielectric constant ϵ , and $E_{0,0}$ is the electronic excitation energy of the acceptor.

Substitution of the oxidation potential of 1 ($E_{1/2}^{\text{ox}} = 1.25\text{V}$)

(16) and appropriate values for DCA ($E_{1/2}^{\text{ox}} = +0.89 \text{ V}$, $E_{0,0} = 2.88 \text{ V}$) (2a)

gives a value of $\Delta G = -18.4$ kcal/mol. Thus, electron transfer is thermodynamically quite feasible.

Utilizing xanthone (X) as a sensitizer gave identical results, *i.e.*, exclusive formation of 2. Xanthone, traditionally considered a triplet energy sensitizer, is however, a strong enough oxidizing agent to oxidize tetraphenylallene 1 (vide infra). Balzani and co-workers (23) have noted that when both energy transfer and electron transfer are thermodynamically allowed, electron transfer predominates. Incorporation of the reduction potential ($E_{1/2}^{\text{red}} = -1.63$ V) (24a) and triplet energy ($E_{0,0} = 3.08$ V) (24b) of xanthone into the Weller equation gives a ΔG of -6.0 kcal/mol.

Irradiation of 1 with DCA or 1,4-dicyanobenzene in acetonitrile yielded a product tentatively identified as the isoquinoline derivative 3. The structure of 3 derives from its spectral data (experimental) and expected regiochemistry of acetonitrile addition to the radical cation of 1 (vide infra).

Formation of 2 and 3 is envisioned to arise by initial solvent trapping at C₂ of tetraphenylallene radical cation, as shown in Scheme 8. Back electron-transfer from radical anion of sensitizer affords an allylic cation which may be protonated to yield methyl ether 2 or undergo cyclization to the isoquinoline derivative 3. Isoquinoline 3 formation is analogous to the reaction of acetonitrile with phenylacetylene radical cation to form a pyridine derivative, as previously reported (Scheme 6) by Mattes and Farid (20a,b).

Triphenylallene (4) and triphenylpropyne (5) were synthesized according to literature methods detailed in Chapter 1. It is significant in the present context that allene 4 is prepared by base treatment of 5 (25). Preparative irradiations were conducted on solutions of 4 or 5 in methanol, with DCA or 1,4-dicyanonaphthalene (DCN) as sensitizers. Filtered light (pyrex or uranium) was employed to ensure that only the sensitizer absorbed light. Experiments were carried to low conversion in order to minimize secondary processes and products were isolated by flash chromatography over silica gel. Product mixtures were analyzed by high pressure liquid chromatography, and by 300 MHz ^1H NMR.

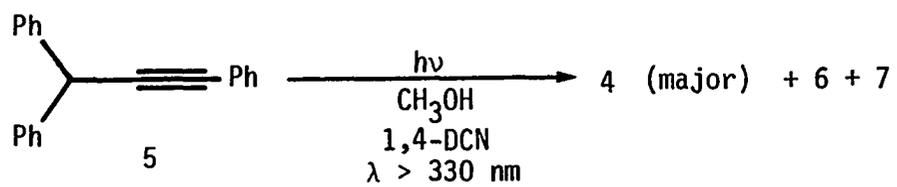
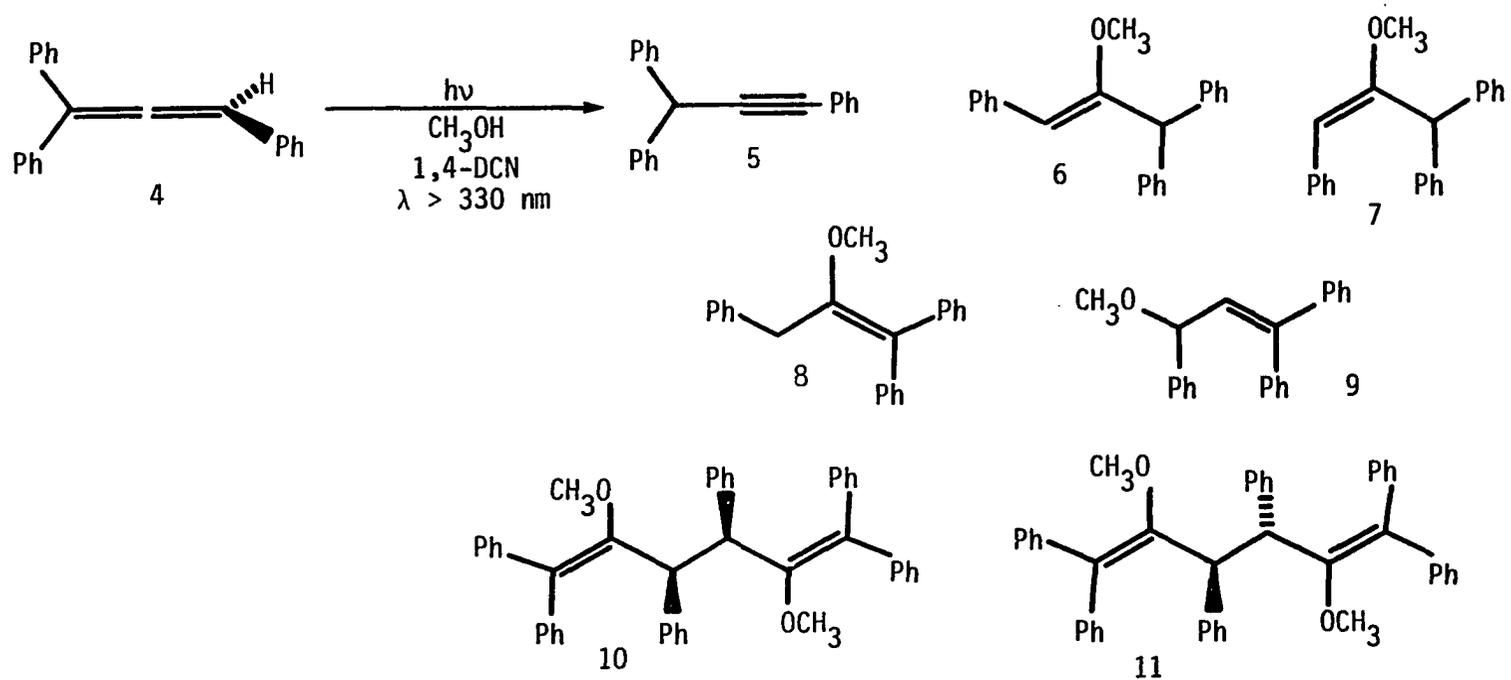
Irradiation of triphenylallene with DCA or DCN in methanol reproducibly yielded the ensemble of photoproducts shown in Scheme 9. Other isomers of 4 and 5 such as indenenes (26) were not detected. Product composition in low conversion photochemical experiments (HPLC analysis) is given in Table 1. Ethers 6-9 were isolated by flash chromatography, and were identified by spectral data and by comparison with samples prepared through independent synthesis (illustrated in Scheme 10). Stereochemical assignment for (Z) and (E) 2-methoxy ethers 6 and 7 is based upon ultraviolet spectra; the (E) isomer shows a more intense absorption band at longer wavelength. A priori, methanol may have been added to 5 with the opposite regiochemistry; samples of (E) and (Z)-1-methoxy-1,3,3-triphenylpropene, 12 and 13, were prepared by alkoxymercuration of 5 (Scheme 11); these were not detectable as photoproducts. Small amounts (1-2%) of allylic ether 9 also could

Table 1. Product composition from electron transfer sensitized irradiations in methanol

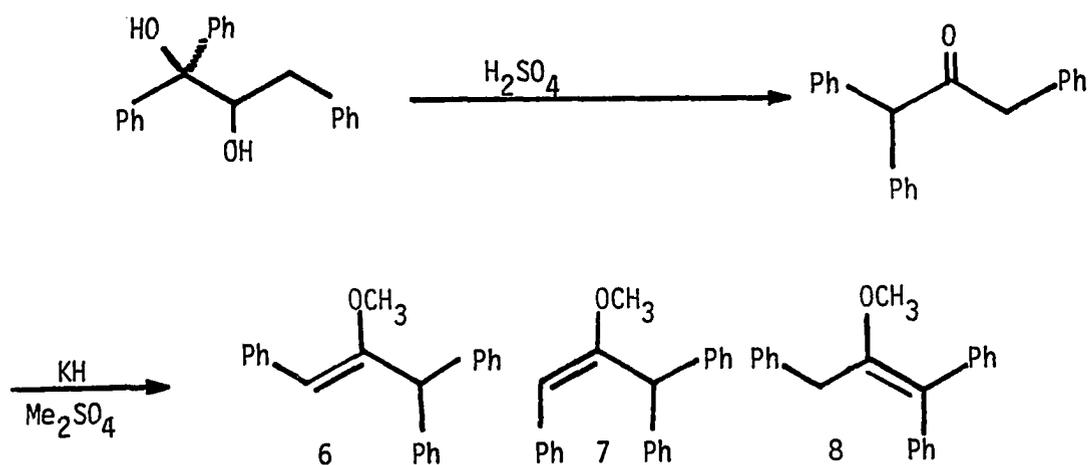
Substrate	Sensitizer	Products (%) ^{a,b}						
		4	5	6	7	8	10	11
triphenylallene (4)	DCN	--	1.5	49	9.0	36	0.84	2.0
triphenylallene (4)	DCA	--	3.0	18	6.0	5.0	21	48
triphenylpropyne (5)	DCN	92	--	8	<1	0	0	0

^aAll analyses by HPLC at low conversion.

^bSmall amounts (<2%) of ether 9 are also formed from irradiation of 4, but could not be reliably analyzed by HPLC.

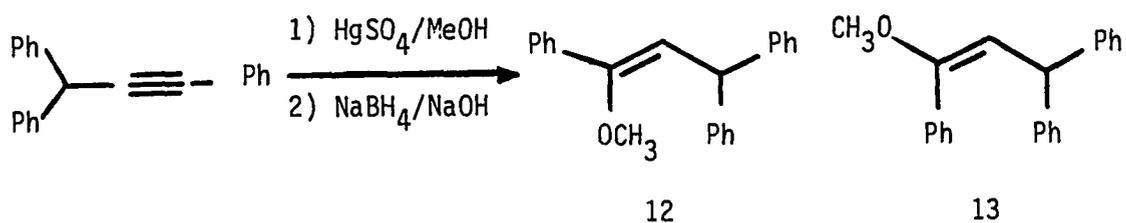


Scheme 9.



Scheme 10.

be isolated by rapid chromatography. This compound proved somewhat unstable to silica gel and it could not be analyzed satisfactorily by HPLC.



Scheme 11.

Dimers 10 and 11 were isolated by chromatography. Neither stereoisomer showed a significant parent molecular ion by mass spectrometry. Their characterization as ethers followed from infrared and ^1H NMR data (methyl singlets at 3.18 and 2.93, respectively); a dimeric

structure was suggested by the high melting points (174-175°C for 10; 265-268° for 11). The structure of erythro isomer 11 (major dimer) was unambiguously determined by single crystal x-ray analysis. The resultant geometry is shown in Figure 2.

Two differences were noted in comparison of DCN and DCA as sensitizers. First, the proportion of dimers from 4 was much higher with DCA than DCN. Second, although DCN was generally recovered in good yield from experiments which were carried to moderate conversion, DCA recovery was poor and small amounts of apparent adducts to solvent and to substrate invariably were isolated. Their structures were not investigated. Preliminary experiments showed that xanthone gives results similar to DCA.

Initial irradiations of triphenylpropyne (5) with DCN in methanol led to isolation of triphenylallene and ethers 6-8 as products but no dimers 10 and 11. Irradiation of 5 in methanol without DCN yielded a complex product mixture which contained ca. 1% of 4, but no detectable 6, 7 or 8. Formation of 8 in SET reactions seemed a puzzling result, since no allyl-type intermediates (vide infra) were anticipated in this reaction. Concentration versus time plots (2 - 17% conversion) of the photoreaction showed that the major primary photoproduct was triphenylallene (4; 92% at 2% conversion), with ether 8 entirely a secondary product of 4. Thus, the major product of SET generated triphenylpropyne radical cation in methanol is its isomer triphenylallene, with ethers 6 and 7 comprising only ca. 10% of primary

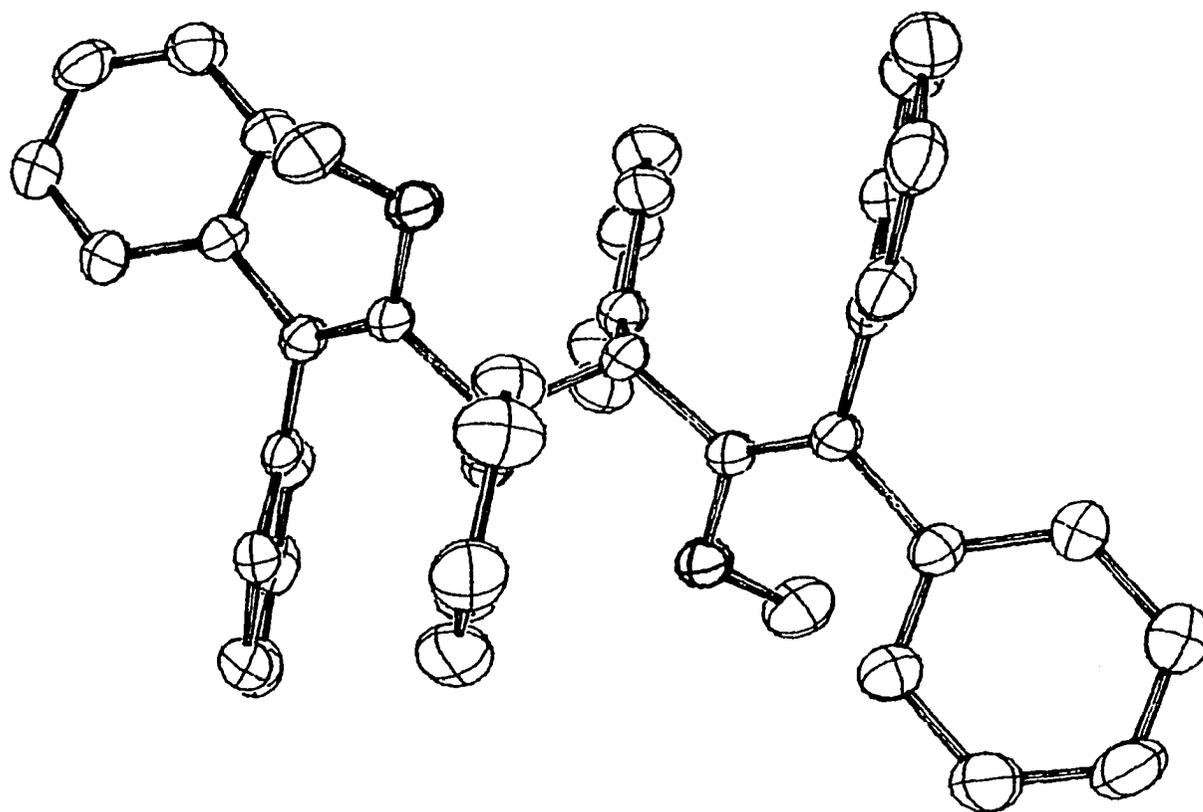
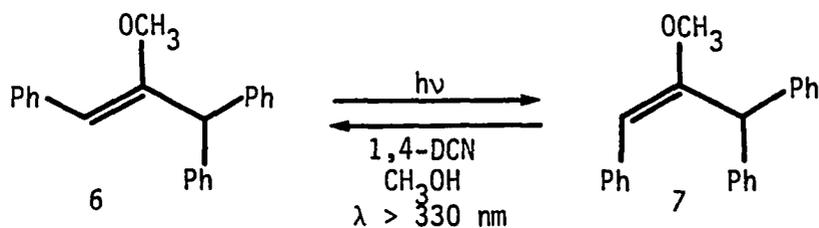


Figure 2. X-ray crystal structure of meso-2,5-dimethoxy-1,1,3,4,6,6-hexaphenyl-1,5-hexadiene

products. The mechanism for this novel and efficient alkyne to allene photoconversion will be considered below.

Irradiation of triphenylpropyne (5) with DCA resulted in an extremely slow reaction. This is consistent with an estimated G for electron transfer from 5 to excited DCA. Although the oxidation potential for triphenylpropyne has not been measured, it may be approximated by the value for phenylacetylene ($E_{1/2}^{OX} = 2.04$ V) (21). Substitution into the Weller equation yields the free energies of -0.23 and -4.38 kcal/mol for sensitization by DCA and DCN respectively.

Irradiation of isomeric vinyl ethers 6, 7 and 8 was briefly explored in order to estimate potential secondary reactions (Scheme 12). (E)-(Z)-isomers 7 and 6, were interconverted by sensitized irradiation with DCN or DCA in methanol. Equilibrium strongly favored (ca. 4:1) (Z) isomer 6. Ether 8 proved to be inert under these conditions. Irradiation of 8 in CH_3OD did not lead (1H NMR analysis) to incorporation of measurable deuterium at the allylic position.

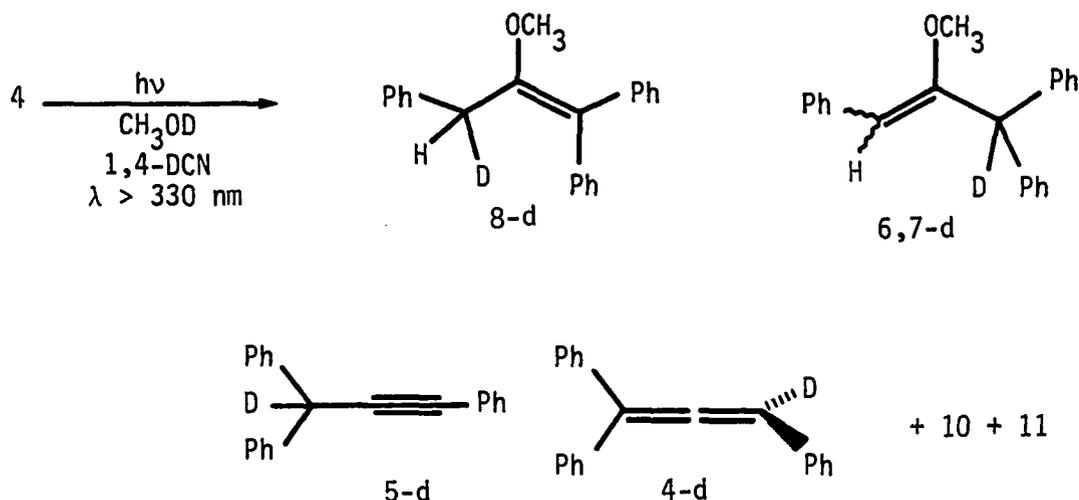


Scheme 12.

Mechanistic Studies: SET Sensitized Irradiations in CH_3OD

Deuterium labelling offered a straightforward means of probing reaction mechanisms, especially the potential intramolecularity of the

5 to 4 conversion. Irradiation of triphenylallene with DCA or DCN in CH_3OD (Scheme 13) resulted in no significant change in product distribution, relative to experiments in CH_3OH . These experiments afforded

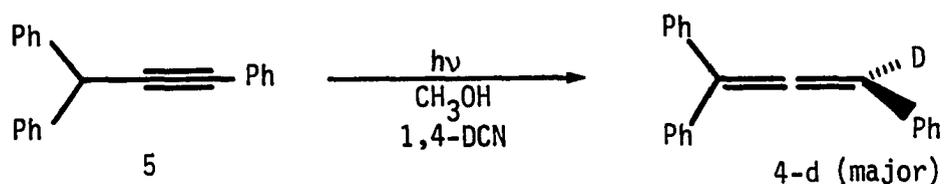


Scheme 13.

ether photoproducts 6d-8d which had cleanly incorporated one allylic deuterium. The extent of deuteration was assessed by 300 MHz ^1H NMR integration of appropriate resonances versus the methoxy singlet, following chromatographic isolation of photoproducts. The small amount of propyne 5 which was isolated proved to be 100% d_1 (MS or ^1H NMR analysis). Dimers 10 and 11, isolated from irradiation with DCA as sensitizer, were undeuterated within limits of detection by NMR. Recovered allene 4 was 18% d_1 (MS analysis) in an experiment which was carried to 30% conversion.

Irradiation of triphenylpropyne in CH_3OD (Scheme 14) led to photoproducts in which deuteration varied with conversion, a result

anticipated from the rapid secondary reactions. HPLC analyses again showed the major primary photoproduct to be triphenylallene, with ether 8 entirely a secondary product. Not surprisingly, isomer 8, isolated from these experiments, was ca. 90% dideuterated, while the deuterium



Scheme 14.

content in 6 and 7 varied with conversion. At the lowest conversion studied (8%), major ether 6 was 100% d_1 , with deuterium 87% in the vinylic position. Allene 4, isolated as a photoproduct of 5, was ca. 80% d_1 (MS or ^1H NMR analysis). This incomplete deuteration of 4 was observed in three separate experiments and proved to be independent of conversion. Recovered propyne 5 had not incorporated measurable (MS analysis) deuterium, even at 84% conversion.

C_3H_3 Intermediates

In the ensuing discussion, the structure of liner $\text{C}_3\text{R}_3\cdot$ ($\text{R} = \text{H}, \text{Ph}$) and C_3R_3^- intermediates is of considerable relevance. In principle, each of these may exist in allenic or propargylic forms (Figure 3). For the anion, both theoretical (27) and experimental studies (28,29) have concluded that the allenic structure (14a) is preferred. Oakes and Ellison have summarized previous work, and

reported the photoelectron spectrum of 14a (28). They concluded that the equilibrium geometry of $C_3H_3^-$ is quite different from that of $C_3H_3\cdot$. This result concurs with studies on the radical, which indicates a propargylic structure 15p (29). One recent theoretical study concluded that 15a is not an energy minimum, while 15p may be the most stable $C_3H_3\cdot$ structure (30).

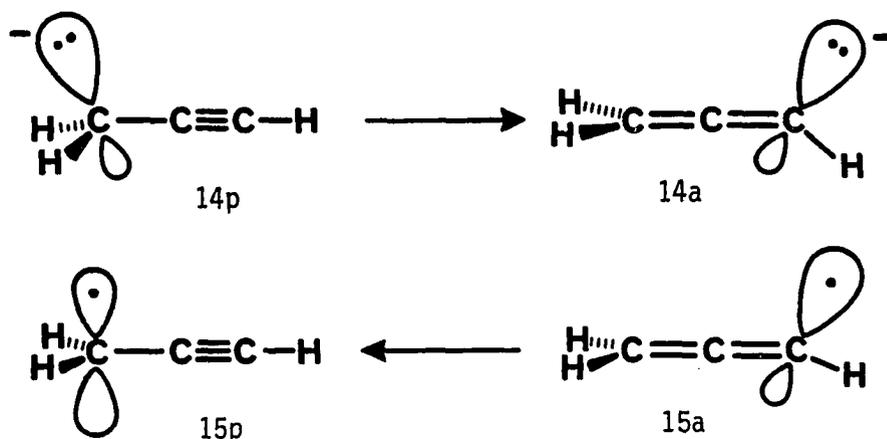
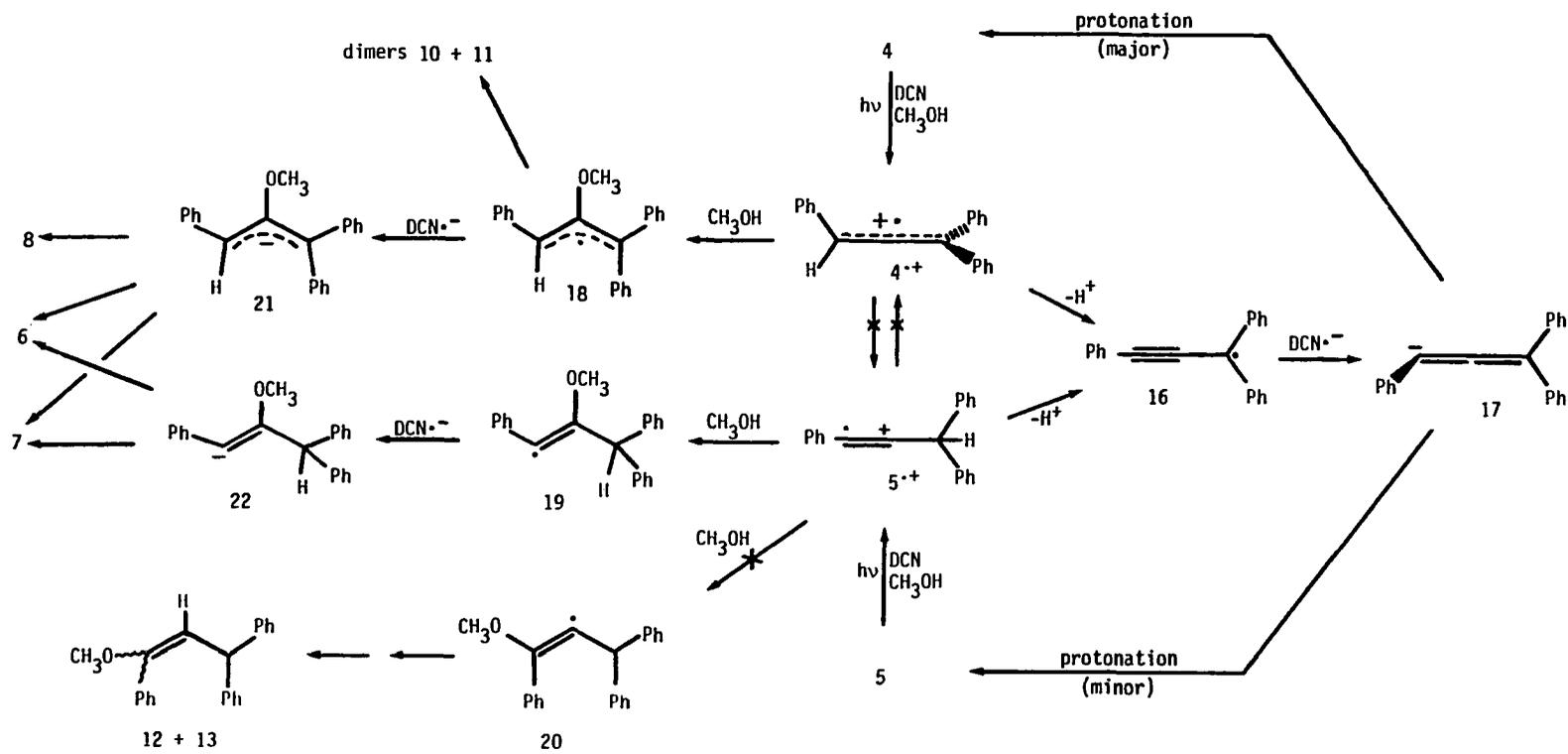


Figure 3. Triphenyl C_3 radicals and anions

Current evidence thus indicates that linear $C_3H_3^-$ and $C_3H_3\cdot$ exist as allenic and propargylic structures 14a and 15p, respectively.

Reaction Mechanisms

Scheme 15 summarizes mechanisms which are consistent with results of both exploratory studies and deuterium labeling experiments. Initial electron transfer from 4 or 5 to excited sensitizer will result in a contact radical cation-radical anion pair (2a). At this juncture, dominant competitive pathways for the radical cation are deprotonation to



Scheme 15.

radical 16, or trapping by nucleophile; these will be considered separately.

Loss of a proton from $4\cdot^+$ or $5\cdot^+$ to solvent should, in either case, yield radical 16, assumed here to have a propargylic structure. Subsequent back electron transfer from sensitizer radical anion affords triphenyl C_3 anion 17. Kinetic protonation of 17 under these conditions yields predominantly, but not exclusively, triphenylallene. This multi-step process readily explains the significant incorporation of deuterium in samples of allene 4 which are recovered from irradiation of 4 in CH_3OD , as well as the remarkably facile photoconversion of propyne 5 to allene 4. Protonation (or deuteration) of 17 to yield propyne 5 (or 5-d) must be a minor pathway, however, since 5 is a minor product (1-3%) of 4. Deprotonation must be the dominant pathway (> 90%) for $5\cdot^+$. By contrast, for $4\cdot^+$, the observed ratio of 4-d to ether products in CH_3OD indicates a ca. 2:1 preference for nucleophilic attack rather than deprotonation.

Differences in behavior of $4\cdot^+$ and $5\cdot^+$ are ascribed to several cooperative factors. Based on data for the parent hydrocarbon (4b), $4\cdot^+$ should be more thermodynamically stable than $5\cdot^+$, hence less acidic. This is reinforced by the relative stability which is anticipated for radicals generated by nucleophilic trapping: i.e., allyl radical 18 > vinyl radical 19.

Irradiation of triphenylpropyne with DCN in CH_3OD reproducibly yielded allene 4 which was ca. 80% d_1 , in agreement with dominance of the above mechanism; i.e. $5\cdot^+$ to 16 to 17 to 4-d. The origin

of protium (ca. 20%) in this material can be rationalized through several routes: (a) intramolecular 1,3-shift; (b) homolytic hydrogen abstraction from CH_3OH by 16; (c) a "conducted tour" type mechanism (26b).

Theoretical studies of path (a) suggest this to have a high (> 30 kcal/mol) activation energy (11b), as might be expected from the linear geometries for allene and propyne radical cations. Intramolecular hydrogen transfer requires substantial bending. Parr and co-workers have suggested (4c,d) substantial isomerization of allene to propyne radical cation, although results of Wiersig et al. (4a) and of Wagner et al. (4b) argue against this. Path (b), hydrogen abstraction by a propargyl radical to yield an allene, does have precedent. For example, reduction of 3-chloropropyne with $(\text{nBu})_3\text{SnH}$ yields propyne and allene in a ratio of 5.9:1 (31). Path (c) might be similar to the "conducted tour" mechanism for base catalyzed isomerization of 5-d to 4-d, which was reported some years ago by Cram and co-workers (26b). Treatment of 5-d with $\text{CH}_3\text{OH}/\text{CH}_3\text{ONa}$ yielded allene which retained 18% of deuterium. A higher degree of intramolecularity was observed under other conditions. In the present case, the contact radical ion pair $\text{DCN}^{\cdot-} \text{5}^{\cdot+}$ loses a proton to afford an effectively termolecular complex with CH_3OHD^+ . If back electron transfer from $\text{DCN}^{\cdot-}$ is sufficiently rapid, which seems likely in view of its efficiency, then reprotonation by the same CH_3OHD^+ molecule might compete with diffusion. This transfer benefits from an isotope effect, since CH_3OHD^+ should preferentially transfer H^+ rather than D^+ .

Present data do not allow discrimination among these mechanisms. In principle, irradiation of 5-d in CH₃OH might distinguish the latter two possibilities. However, the sequential isotope effects which would be expected for dedeuteration, or redeuteration in a "conducted tour" mechanism perturb the reaction to a degree where comparison may be inappropriate.

A second pathway for the photogenerated radical ions is nucleophilic trapping by solvent. In the case of 4^{•+}, the observed regiochemistry is in accord with previous studies on allene radical cations; i.e., addition occurs to the central carbon (13,17). One can make arguments based upon charge density (13), but the simplest explanation for this result is formation of a very stable allyl radical. A small quantity of allylic ether 9 is isolated (Scheme 9), which shows that nucleophilic addition is not entirely regiospecific. To complete the sequence, back electron transfer from sensitizer radical anion to allyl radical 18 yields an allyl anion 21 which, upon kinetic protonation, affords ethers 6-8. Deuterium labeling experiments with 4 in CH₃OD support this straightforward mechanism.

When DCA is used as a sensitizer for 4, dimers 10 and 11 are the major isolated products, and recovery of sensitizer is poor. Our interpretation of these results is that back electron transfer from DCA^{•-} to 18 is quenched by some other process, possibly separation of the contact radical ion pair, or protonation of DCA^{•-} by solvent. The resultant radical 18 is sufficiently long-lived that it can dimerize to 10 and 11. With DCN as sensitizer, this is a minor process.

Nucleophilic addition to $5\cdot^+$ proceeds regioselectively at C-2 to yield vinyl ethers 6 and 7, with 19 and 22 the presumed intermediates. Addition at C-1 would yield a similar vinyl radical 20, which would lead to ethers 12 and 13; these are not observed. Several factors probably favor this regiochemical outcome. Coefficients (MNDO) of the singly occupied MO of phenylpropyne radical cation are illustrated in Figure 4. The MNDO (32) optimized geometry of this species ($H_f = 253.8$ kcal/mol) is essentially linear (179°) and is little changed from that for neutral phenylpropyne (MNDO $H_f = 56.7$ kcal/mol). Addition at C_2 is favored by perturbation arguments, as well as benzylic

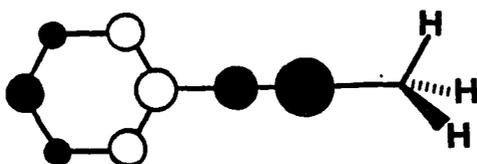


Figure 4. Molecular orbital coefficients for singly occupied phenylpropyne

stabilization of the incipient vinyl radical. Previous HMO calculations led to similar conclusions (21).

Conclusions

Isomeric radical cations of triphenylallene (4) and triphenylpropyne (5) are readily photogenerated by single electron transfer to an appropriate sensitizer. Interconversion of triphenylpropyne and triphenylallene radical cations does not appear to be a major pathway, consistent with results of earlier vapor-phase experiments (4a,b). In

methanol, the ensuing chemistry derives from a competition between radical cation acidity, and propensity for reaction with nucleophile. The major reaction of $5\cdot^+$ is proton loss, while $4\cdot^+$ is more readily trapped by nucleophile. Nucleophilic addition to $4\cdot^+$ or $5\cdot^+$ occurs with high regioselectivity at the central carbon. Proton loss from $4\cdot^+$ or $5\cdot^+$ apparently gives the same propargyl radical 16 (Scheme 15) which, upon back electron transfer and protonation, yields predominantly allene 4. This succession of intermediates, radical cation to radical to anion, provides a novel alkyne to allene photochemical conversion.

These experiments and recent work of Somekawa et al. (12) demonstrate both the diversity and interrelationship of allene and propyne radical cation chemistry.

Experimental

General: ^1H NMR spectra were measured on a Nicolet 300 MHz spectrometer, with CDCl_3 as solvent. HPLC analyses employed a Waters Associates instrument, with detection at 254 nm. A Hewlett-Packard 3390A integrator was used to measure HPLC peak areas.

Spectroquality methanol was used in all photochemical experiments. Methanol- 0-d (Aldrich, $>99\%$ d_1) was distilled. Argon was bubbled through solutions prior to and during irradiation. Preparative photochemical experiments employed a standard immersion-well apparatus equipped with a 450 W Hg lamp. Quantitative photochemical experiments employed a Rayonett RPR-100 reactor. External cooling was employed to maintain solutions at 0° to -10°C .

1,4-Dicyanonaphthalene (DCN) was prepared by reaction of 1,4-dibromonaphthalene with CuCN following the procedure described for 1-cyanonaphthalene (33). 9,10-Dicyanoanthracene (Eastman) was recrystallized from acetone.

Flash chromatography experiments employed quartz columns dry packed with preparative TLC Silica gel 60 PF-254 (EM Laboratories, Inc.). Progress of component elution was monitored with an ultraviolet hand lamp.

Xanthone sensitized irradiation of tetraphenylallene 1 in methanol

Allene 1 (654 mg) and xanthone (1.15g) in 170 mL of benzene-methanol (1:4) was irradiated through a uranium filter for 9 hours. Solvent removal in vacuo afforded a white residue which was taken up in methylene-chloride, and triturated with hexane to precipitate 723 mg of xanthone. The mother liquor was then subjected to chromatography (2.0 x 100 cm) with hexane elution in 100mL fractions: 1-14, nil; 15-30, 241 mg of 1; elution with 1.0% ether-hexane: 31-37, nil; 38-39, 382 mg of 2; elution with 2% ether-hexane: 40-45, nil; elution with 5% ether-hexane: 46-54, 390 mg of xanthone.

Spectral data of 2 are as follows: mp 156-157°C; ^1H NMR (CDCl_3) δ 3.14 (s, 3H), 5.06 (s, 1H), 7.2-7.4 (m, 20H); ^{13}C NMR (CDCl_3) δ 53.6, 61.0, 125.9, 126.4, 126.6, 126.9, 128.2, 128.4, 129.1, 130.0, 130.3, 140.5, 142.0, 142.2, 157.3. IR (CCl_4 soln.) 3080, 3060, 3020, 2930, 2830, 1620, 1595, 1490, 1440, 1205, 1020 and 690 cm^{-1} ; UV (cyclohexane) λ_{max} 258(ϵ 26530); MS m/e 376.1826 (ca. for $\text{C}_{28}\text{H}_{24}\text{O}$, 376.1827).

Hydrolysis of 2-methoxy-1,1,3,3-tetraphenylpropene 2

The vinyl ether 2 (57 mg) in 6 mL of 95% ethanol and aqueous HCl (1.5 mL) was allowed to reflux for 4 hours. Upon cooling, 36 mg of tetraphenylacetone was collected.

Spectral data of tetraphenylacetone are as follows: mp 131-133°C (lit. mp 131-133°C) (34); ^1H NMR (CDCl_3) δ 5.26 (s, 1H), 7.1-7.3 (m, 10H); IR (CCl_4 soln.) 3080, 3060, 3020, 1725, 1590, 1480, 1445, 1070, 1050, 1025 and 695 cm^{-1} .

Exploratory DCB sensitized irradiation of tetraphenylallene 1 in acetonitrile

Allene 1 (500 mg) and DCB (524 mg) in acetonitrile (600 mL) was irradiated through a pyrex filter for 8 hours. The solution was concentrated in vacuo and residue was subjected to chromatography (2.0 x 80 cm) with 0.5% ether-hexane elution in 100 mL fractions: 1-8, nil; elution with 1.0% ether-hexane: 9-12, 380 mg of 1; elution with 2% ether-hexane: 13-14, nil; 15-16, 49 mg of 3; 17-18, nil; 19-22, 14 mg of an unidentified fluorescent product.

Spectral data of 3 are as follows: mp 171-173°C; ^1H NMR (CDCl_3) δ 2.94 (s, 3H), 5.42 (s, 1H), 7.1-7.5 (m, 19H); IR(KBr) 3060, 3017, 2960, 1655, 1595, 1555, 1490, 1430, 1381, 1070, 1028, 761, 737, 696 cm^{-1} ; MS m/e 384.17567 (ca. for $\text{C}_{29}\text{H}_{22}\text{N}$, 384.17523).

Synthesis of potential vinyl ether photoproducts

1,1,3-triphenylacetone was prepared by the method of Orehoff (35): mp 82-83°C (lit. 82-83°C); ^1H NMR (CDCl_3) δ 3.79 (s, 2H), 5.22 (s, 1H), 7.14-7.31 (m, 15H).

Triphenylacetone (500 mg, 1.75 mmol) in dry DMF (10 mL) was added dropwise to a cold (0°C) stirring slurry of potassium hydride (1.8 mmol) in DMF (10 mL). After 2 hours, dimethyl sulfate (0.25 mL, 2.64 mmol) was added. The mixture was quenched with water and extracted with ether (3 x 25 mL). Combined extracts were washed successively with aqueous ammonia and brine, dried (MgSO_4) and concentrated. Chromatography over silica gel, eluted with 0.1% ether-hexane, yielded 251 mg (48%) of a mixture of ethers 6, 7, and 8 (ratio 1.5:1:5.8 by ^1H NMR).

Analytical samples of each ether were obtained by preparative TLC (silica gel; 0.25% ether-hexane development). Spectral data were as follows:

6: (Z)-2-methoxy-1,3,3-triphenylpropene: mp 89-90°C; ^1H NMR (CDCl_3) δ 3.68 (s, 3H), 5.36 (s, 1H), 5.86 (s, 1H), 7.2-7.3 (m, 15H); IR(KBr) 3045, 3015, 2985, 2945, 2925, 2825, 1635, 1595, 1488, 1440, 1260, 1216, 1185, 1157, 1034, 1020 and 690 cm^{-1} , UV(isooctane) λ_{max} 253 (14,000); high resolution MS, m/e 300.1509 (error -1.7 ppm).

7: (E)-2-methoxy-1,3,3-triphenylpropene: mp 111-113°C; ^1H NMR (CDCl_3) δ 3.58 (s, 3H), 5.16 (s, 1H), 5.19 (s, 1H), 7.07 (d, 1H, J = 7.8 Hz), 7.2-7.3 (m, 12H), 7.49 (d, 2H, J = 7.5 Hz); IR(KBr) 3060,

3030, 3000, 2975, 2940, 2820, 1643, 1592, 1487, 1446, 1441, 1350, 1195, 1118, 1075, 1035, 1022, 700 and 690 cm^{-1} , UV(isooctane) $\lambda_{\text{max}}^{260}$ (ϵ 24,000); MS, m/e 300.1513 (error -0.3 ppm).

8: 2-methoxy-1,1,3-triphenylpropene: mp 63-66°C; ^1H NMR (CDCl_3) δ 3.44 (s, 3H), 3.67 (s, 2H), 7.2-7.3 (m, 15H); IR(film) 3080, 3060, 3020, 2920, 2825, 1620, 1592, 1484, 1444, 1432, 1240, 1140, 1045, 1020, 750 and 685 cm^{-1} , UV(isooctane) $\lambda_{\text{max}}^{258}$ (ϵ 14,800); MS, m/e 300.1512 (error -0.7 ppm).

(Z) and (E)-1-Methoxy-1,3,3-triphenylpropenes (12 and 13) were prepared as follows: Triphenylpropyne (5, 100 mg, 0.373 mmol) and mercuric acetate (120 mg, 0.376 mmol) in methanol (5 mL) was heated at reflux for 19 hours. The mixture was cooled and treated with NaBH_4 (40 mg) and 3N aqueous NaOH (2 mL), then extracted with ether (3 x 15 mL). Silica gel chromatography afforded 66 mg (50%) of a colorless oil, characterized as a mixture (1:1.3) of 12 and 13. No attempt was made to separate the two isomers. Spectral data for the mixture were as follows: ^1H NMR (CDCl_3), (minor isomer) δ 3.49 (s, 3H), 5.39 (d, 1H, $J = 10.5$ Hz), 5.77 (d, 1H); major isomer 3.71 (s, 3H), 4.75 (d, 1H, $J = 9.8$ Hz), 5.19 (d, 1H), 7.1-7.5 (mult.). IR(film) 1650, 1602, 1200, 1116 cm^{-1} . MS, m/e 300.1515 (error 4.7 ppm).

DCN sensitized irradiation of triphenylallene 4

Allene 4 (500 mg) and DCN (150 mg) in methanol (300 mL) at 0°C was irradiated through a uranium filter for 5.0 hours. Methanol was

removed under vacuum and the residue was subjected to flash chromatography (2.0 x 30 cm) with hexane in 50 mL fractions: 1-4, nil; 5-12, 356 mg of 4; 13-18, nil; 19-22, 10 mg of 5; 23-40, nil; 41-51, 36 mg of 6; 52-58, 8 mg of 6 and 7, ca. 0.8:1.0; 59-64, 3 mg of 17; 65-70, nil; elution with 0.1% ether-hexane: 71-103, 43 mg of 8; 104-107, nil; 108-111, 17 mg of 10 and 11, ca. 1.0:1.4; elution with 10% ether-hexane: 112-115, nil; 116-119, 10 mg of DCN adducts; 120-127, 140 mg of DCN.

Spectral data for dimers 10 and 11 are as follows:

10: threo-2,5-dimethoxy-1,1,3,4,6,6-hexaphenyl-1,5-hexadiene: mp 174-176°C; ^1H NMR (CDCl_3) δ 3.18 (s, 3H), 4.27 (s, 1H), 6.94 (dd, 4H, $J = 7.9$ and 11.0 Hz), 7.2-7.4 (m, 11H); IR(KBr) 3050, 3018, 2965, 2930, 2830, 1610, 1595, 1490, 1450, 1440, 1380, 1225, 1190, 1030, 695, and 690 cm^{-1} ; MS shows very weak parent ion of m/e 598 and strong m/e 299 ($\text{M}^+ - 299$).

11: erythro isomer: mp 265-268°C; ^1H NMR (CDCl_3) δ 2.93 (s, 3H), 4.28 (s, 1H), 6.54 (d, 2H, $J = 7.7$ Hz), 6.84 (d, 2H), 7.01-7.03 (m, 3H), 7.2-7.3 (m, 8H); ^{13}C NMR (acetone- d_6) δ 51.6, 60.7, 125.4, 126.0, 126.3, 127.6, 127.9, 129.3, 129.8, 131.0, 141.9, 156.5; IR(KBr) 3095, 3070, 3040, 2945, 2845, 1620, 1604, 1496, 1450, 1200, 1025 and 690 cm^{-1} ; MS no M^+ but a strong m/e 299 ($\text{M}^+ - 299$).

Crystal structure for meso dimer 11

The structure was solved using MULTAN 76. X-ray data: Crystals were triclinic; space group $\text{P}\bar{1}$; $Z = 2$; cell constants: $a = 12.955(4)$ Å,

$b = 13.558(5) \text{ \AA}$, $c = 10.623(4) \text{ \AA}$, $\alpha = 105.03(4)^\circ$, $\beta = 108.34(3)^\circ$, $\gamma = 75.78(3)^\circ$. 5281 reflections were measured with Mo $K\alpha$ radiation ($\gamma = 0.70926$): 3124 reflections were observed $F_0 > 1.8\sigma F_0$; 3124 reflections $2\theta < 50^\circ$ were used in the final refinement, which included hydrogen atoms. Present $R = 7.2\%$; $R_w = 9.9\%$. Atomic coordinates and thermal parameters are listed in Table 2.

DCA sensitized irradiation of triphenylallene 4

Allene 4 (502 mg) and DCA (152 mg) in methanol (300 mL) at 0°C was irradiated through a uranium filter for 2.5 hours. The methanol was removed under vacuum and residue subjected to flash chromatography (2.0 x 30 cm) with hexane elution in 100 mL fractions: 1-2, nil; 3-6, 243 mg of 4; 7-8, nil; 9-10, 3 mg of 5; 11-24, nil; 25-32, 15 mg of 6; 33-35, 4 mg of 6 and 7, ca. 1.0:1.7; 36-41, 26 mg of 6 and 7, ca. 1.0:1.0; 42-49, 4 mg of 7; elution with 0.05% ether-hexane: 50-56, nil; 57-68, 59 mg of 8; 69-73, nil; 74-76, 15 mg predominantly 10; 77-80, 22 mg of 10 and 11, ca. 1:5; 81-84, 11 mg of 11; 85-86, 3 mg of 11 and a substance tentatively characterized as 9,10-dihydro-9,10-dimethoxyanthracene (23), ca. 3:1; 87-96, 8 mg of 23. In other experiments, 3-methoxy-1,1,3-triphenylpropene (9) was also isolated (1-2% yield by column chromatography when more polar elution and shorter column retention times were maintained. This material elutes off between 11 and 23. Hydrolysis to the corresponding alcohol occurs on silica gel. NMR analysis of crude photoproduct mixtures confirmed that this is only a very minor product.

Table 2. Atomic and thermal parameters for dimer 11
meso-2,5-dimethoxy-1,1,3,4,6,6-hexaphenyl-1,5-hexadiene

Atom	X	Y	Z	U(ave)
O1	4608.(4)	1052.(4)	3217.(5)	62.
C11	6569.(6)	864.(6)	4211.(8)	46.
C12	5546.(6)	836.(6)	4268.(8)	45.
C13	5274.(6)	500.(6)	5324.(8)	49.
C14	4387.(7)	2017.(6)	2841.(9)	78.
C111	7547.(6)	725.(6)	5379.(8)	52.
C112	7621.(8)	1351.(7)	6644.(9)	60.
C113	8576.(8)	1180.(8)	7733.(9)	76.
C114	9436.(8)	413.(8)	7550.(10)	86.
C115	9398.(7)	-202.(8)	6258.(11)	79.
C116	8458.(7)	-49.(8)	5185.(10)	66.
C121	6780.(6)	999.(6)	2929.(8)	49.
C122	6347.(7)	439.(7)	1709.(8)	61.
C123	6576.(8)	603.(8)	599.(8)	79.
C124	7223.(7)	1278.(8)	704.(9)	82.
C125	7672.(8)	1815.(8)	1918.(9)	75.
C126	7453.(7)	1685.(7)	3086.(9)	60.
C131	4537.(7)	1352.(7)	6079.(8)	53.
C132	3439.(7)	1730.(7)	5435.(9)	71.
C133	2826.(8)	2505.(7)	6167.(11)	99.
C134	3213.(10)	2886.(9)	7411.(13)	99.
C135	4271.(10)	2542.(9)	8088.(10)	111.
H13	5847.(65)	358.(61)	5904.(78)	50.7(0)
H116	8454.(64)	-441.(62)	4364.(78)	50.7(0)
H123	6087.(64)	206.(61)	-629.(80)	50.7(0)
H235	12221.(66)	1320.(61)	9298.(77)	50.7(0)
H226	6181.(64)	3816.(61)	6001.(79)	50.7(0)
H122	5812.(65)	-11.(61)	1627.(78)	50.7(0)
H236	11175.(65)	2815.(61)	8339.(78)	50.7(0)
H115	9823.(65)	-656.(62)	5916.(76)	50.7(0)
H223	4841.(64)	6555.(60)	8683.(77)	50.7(0)
H126	7616.(65)	2167.(62)	3870.(78)	50.7(0)
H124	7367.(65)	1417.(62)	-92.(78)	50.7(0)
H112	7071.(64)	2025.(62)	6909.(77)	50.7(0)
H215	8649.(65)	5357.(61)	4252.(77)	50.7(0)
H23	10093.(65)	4491.(61)	8674.(79)	50.7(0)
H232	9990.(66)	3893.(62)	11816.(79)	50.7(0)
H141	4831.(66)	2478.(61)	3883.(77)	50.7(0)
H132	2903.(64)	1567.(61)	4409.(76)	50.7(0)
H113	8649.(64)	1517.(62)	8482.(77)	50.7(0)
H233	10857.(64)	2214.(61)	12379.(77)	50.7(0)
H241	7845.(65)	3266.(62)	9799.(78)	50.7(0)
H214	9608.(64)	3567.(61)	3744.(77)	50.7(0)
H142	4552.(66)	1775.(62)	1430.(78)	50.7(0)
H212	9298.(65)	2658.(62)	7218.(77)	50.7(0)

DCN sensitized irradiation of triphenylpropyne 5

Propyne 5 (500 mg) and DCN (215 mg) in methanol (300 mL) at 0°C was irradiated through a pyrex filter for 3.0 hours. The methanol was removed under vacuum and the residue was subjected to flash chromatography (2.0 x 26 cm) with hexane elution in 50 mL fractions: 1-4, nil; 5-9, 56 mg of 4; 10, nil; 11-19, 210 mg of 5; 20-27, nil; 28-47, 98 mg of 6; 48-51, 10 mg of 6 and 7, ca. 1.0:4.0; 52-64, 26 mg of 7; elution with 0.5% ether-hexane: 65-68, nil; 69-70, 43 mg of 8; elution with 10% ether-hexane: 71-73, 40 mg of DCN-adducts; 74-77, 170 mg of DCN.

DCN sensitized irradiation of (E)-2-methoxy-1,3,3-triphenylpropene 6

Vinyl ether 6 (10 mg) and DCN (3 mg) in methanol (10 mL) was irradiated through pyrex with 300 nm lamps for 2 hours. Both 6 and 7 were observed (ca. 4:1) by HPLC and ^1H NMR analysis. Sensitization with DCA (350 nm irradiation) for 24 hours gave identical results.

Irradiation in CH_3OD under identical conditions afforded 6 and 7 without detectable (300 MHz ^1H NMR analysis) deuterium incorporation.

DCN sensitized irradiation of (Z)-2-methoxy-1,3,3-triphenylpropene 7

Vinyl ether 7 (9 mg) and DCN (3 mg) in methanol (10 mL) was irradiated through pyrex with 350 nm lamps for 19 hours. Both 6 and 7 are observed (ca. 4:1) by HPLC and ^1H NMR analysis.

DCN sensitized irradiation of 2-methoxy-1,1,3-triphenylpropene 8

Vinyl ether 8 (10 mg) and DCN (3 mg) in methanol (10 mL) was irradiated through pyrex with 350 nm lamps for 18 hours. Analysis by

HPLC and ^1H NMR showed only unreacted 8. No deuterium incorporation was detected in 8 when irradiation was performed in CH_3OD .

DCA sensitized irradiation of triphenylallene 4 in methanol- O-d

Allene 4 (500 mg) and DCA (60 mg) in methanol- O-d (170 mL) at 0°C was irradiated through a uranium filter for 4 hours. The solvent was removed by vacuum distillation at 0°C and the residue was subjected to flash chromatography (2.0 x 31 cm) with hexane elution in 100 mL fractions: 1-2, nil; 3-9, 353 mg of 4; 10-11, 2 mg of 5; elution with 0.1% ether-hexane: 12-25, nil; 26-30, 31 mg of 6, 7 and 8; 31-35, nil; 36-47, 24 mg of 10 and 11.

Recovered allene 4 was recrystallized from pentane and determined to be 18% deuterated by mass spectroscopic analyses. Propyne 5 was further purified by HPLC; the ^1H NMR spectrum showed no detectable propargylic resonance. Vinyl ethers 6, 7 and 8 were separated by preparative TLC. ^1H NMR analysis showed each to be 100%- d_1 within experimental error, with deuterium exclusively at the allylic positions. Dimers 10 and 11 were undeuterated within limits of detection.

DCN sensitized irradiation of triphenylpropyne 5 in methanol- O-d

Propyne 5 (500 mg) and DCN (150 mg) in methanol- O-d (170 mL) at 0°C was irradiated through a pyrex filter for 4 hours. The solvent was removed by vacuum distillation at 0°C and the residue was subjected to flash chromatography (2.0 x 31 cm) with hexane elution in 100 mL fractions: 1-5, nil; 6-7, 24 mg of 4; 8-13, 81 mg of 5; 14-19, nil; 20-32, 149 mg of 6; 33-34, nil; 35-50, 46 mg of 7; elution with 1.0%

ether-hexane: 51-52, 10 mg of 7 and 8, ca. 1.0:0.8; 53-54, 78 mg of 8; elution with 10% ether-hexane: 55-56, 60 mg of DCN adducts; 57-60, 100 mg of DCN.

Deuterium distribution in products with runs at 8, 30 and 84% conversion was determined by integration vs. the methoxy singlet. Results are described below.

Table 3. Percent deuterium incorporation

% Conversion	4 ^a	5 ^a	6 ^b	7 ^b	8 ^b
8	80	0	50	50	90
30	80	0	60	60	90
84	80	0	70	70	90

^aDetermined by mass spectroscopy.

^bDetermined by ¹H NMR integration of total allylic and vinylic protons relative to methoxy protons.

Table 4. Deuterium distribution by ¹H NMR integration

% Conversion	6 (vinylic : allylic)	7 (vinylic : allylic)
8	1.0:6.6	1.0:2.4
30	1.0:4.6	1.0:2.4
84	1.0:2.0	1.0:2.0

Quantitative HPLC analysis of sensitized reactions

Irradiations were conducted at -10°C. Aliquots (5 mL) of the reaction solution were removed at intervals during the irradiation and

analyzed as follows: Internal standard ([4,4'-dimethoxy]-1,1-diphenylethylene) and reaction solution (2 mL) were combined, concentrated in vacuo and extracted with 20% ether-hexane (1.0 mL). The extract was filtered through a plug of alumina (1.5 cm) and then analyzed by HPLC (0.25% ether-hexane, μ -Porasil). Results in Table 1 are the average of five determinations. Representative HPLC retention times were as follows: 4 (3.3 min), 5 (3.8 min), 6 (6.5 min), 7 (9.3 min), 8 (11.1 min), 10 (12.5 min), 11 (14.2 min).

Quantitative DCA sensitized irradiation of triphenylallene 4

Allene 4 (200 mg) and DCA (54 mg) in methanol (200 mL) at -10°C was irradiated with 350 nm lamps for 5 hours. At this time, significant quantities of precipitated dimers 10 and 11 were observed.

Quantitative DCN sensitized irradiation of triphenylallene 4

Allene 4 (200 mg) and DCN (100 mg) in methanol at -10°C was irradiated with the 300 nm lamps for 3 hours.

Quantitative DCN sensitized irradiation of triphenylpropyne 5

Propyne 4 (200 mg) and DCN (56 mg) in methanol (200 mL) at -10°C was irradiated with 300 nm lamps for 4 hours. The photoproduct (%) versus conversion (%) graph obtained is shown in Figure 5.

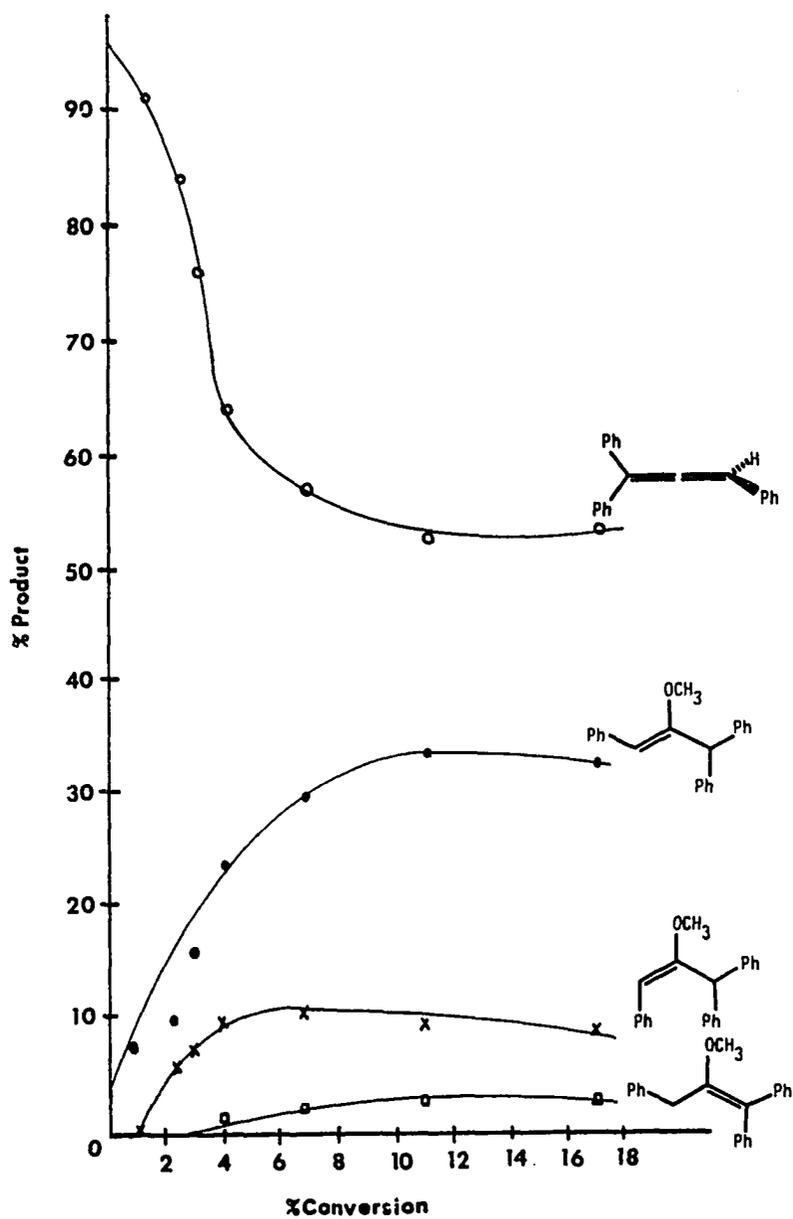


Figure 5. Reaction of triphenylpropyne radical cation: concentration versus percent conversion graph

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OVERALL CONCLUSION

The foregoing work represents the first comprehensive and systematic study of allene photoreactions in both protic and aprotic solvents. These reactions are generalized in the conclusion of each respective chapter. The reactions of photogenerated radical cations of allene and propyne were also described for the first time.

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