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Macias, James Robert

I. DIRECT OBSERVATION OF O-XYLYLENE (O-QUINODIMETHANE) IN SOLUTION. DIMERIZATION KINETICS OF SOME O-QUINODIMETHANES. II. KINETIC AND PRODUCT STUDIES ON THE DIMERIZATION OF ALPHA-METHYL-SUBSTITUTED O-QUINODIMETHANES. III. DIRECT OBSERVATION OF 1,2-NAPTHOQUINODIMETHANE AND 9,10-PHENANTHROQUINODIMETHANE. DIMERIZATION KINETICS OF RESONANCE-STABILIZED O-QUINODIMETHANES

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- I. Direct observation of o-xylylene (o-quinodimethane) in solution. Dimerization kinetics of some o-quinodimethanes
- II. Kinetic and product studies on the dimerization of o-methyl-substituted o-quinodimethanes
- III. Direct observation of 1,2-naphthoquinodimethane and 9,10-phenanthroquinodimethane. Dimerization kinetics of resonance-stabilized o-quinodimethanes

by

James Robert Macias

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GENERAL INTRODUCTION

For several years, work in Trahanovsky's group has focused on the study of reactive organic molecules. Of particular interest has been the o-quinodimethane class of reactive molecules. This dissertation is divided into three parts, all of which involve the study of the parent benzenoid o-quinodimethane, o-xylylene (1), and its derivatives.

Part I describes the direct observation of 1 in solution by UV-visible spectroscopy. Part I also describes the dimerization kinetics of 1 and some ring-alkylated derivatives of 1.

Part II describes a kinetic study of the dimerization of α -methyl-substituted derivatives of 1. This study provides evidence for a stepwise mechanism in the dimerization of benzenoid o-quinodimethanes.

In Part III, the first reported direct observation of 1,2-naphthoquinodimethane (2) is presented. The first ^1H NMR of an o-quinodimethane, 9,10-phenanthroquinodimethane (3), not substituted in the exo-methylene positions is presented. Dimerization kinetics of 2 and 3 are also described.

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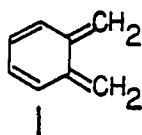
Each part is in the form of a full paper, suitable for publication in a professional journal. As such, each part has

its own numbering system and each part's references follow it.
The research described in the Results and Experimental
sections was done by the author.

PART I. DIRECT OBSERVATION OF o-XYLYLENE (o-QUINODIMETHANE)
IN SOLUTION. DIMERIZATION KINETICS
OF SOME o-QUINODIMETHANES

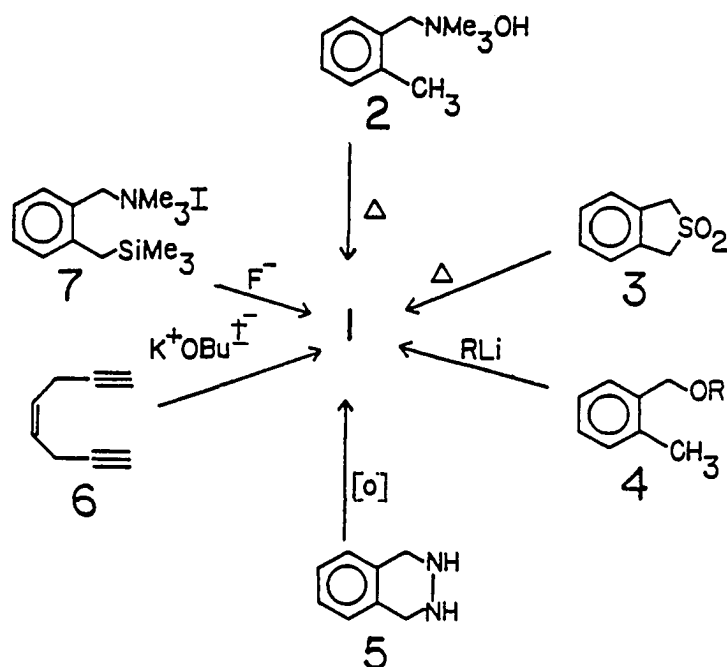
INTRODUCTION

o-Xylylene (1),¹ also called o-quinodimethane, was first postulated as a reactive intermediate by Cava and Napier in 1957.² Since that time 1 and its derivatives have been the subject of considerable interest from the standpoint of theoretical,^{3,4} physical organic,^{5,6} and synthetic organic chemistry.^{7,8,9}



In the time following Cava's work on the debromination of $\alpha, \alpha, \alpha', \alpha'$ -tetrabromo-o-xylene,² a number of methods for generating o-quinodimethanes (o-QDMs) have been developed. Some reactions which presumably proceed via 1 are Hoffman degradation of *o*-(methylbenzyl)trimethylammonium iodide (2),¹⁰ chelotropic desulfurization of 1,3-dihydrobenzo[c]thiophene-2,2-dioxide (3),¹¹ base induced 1,4-elimination from o-methylbenzyl ethers (4),¹² oxidation of 1,2,3,4-tetrahydroptthalazine (5) at 0°C,¹³ treatment of cis-4-octene-1,7-diyne (6) with potassium t-butoxide¹⁴ and fluoride ion induced 1,4-elimination from [o-[α -(trimethylsilyl)methyl]benzyl]-trimethylammonium iodide (7)⁹ (Scheme 1).

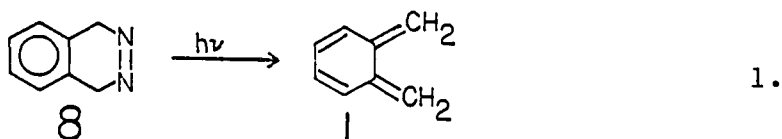
Scheme 1



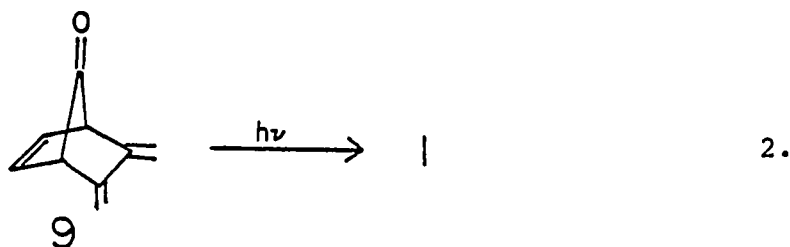
Although the high reactivity of $\underline{1}$ has precluded its characterization by ^1H NMR spectroscopy, some direct evidence for its existence has been reported. It has been observed directly by UV-visible spectroscopy both in solution¹⁵ and in a low temperature matrix,¹⁶ and by IR, Raman, fluorescence and fluorescence excitation spectroscopy in a low temperature matrix.¹⁶ The UV-photoelectron spectrum of $\underline{1}$ in the gas phase has also been published.¹⁷

Michl and Flynn have reported the UV-visible spectrum of $\underline{1}$ in a low temperature matrix by irradiation of 1,4-dihydro-

pthalazine (8)⁵ (reaction 1). Michl reported a λ_{max} of 373 nm and a ϵ_{max} of >3000 for 1.



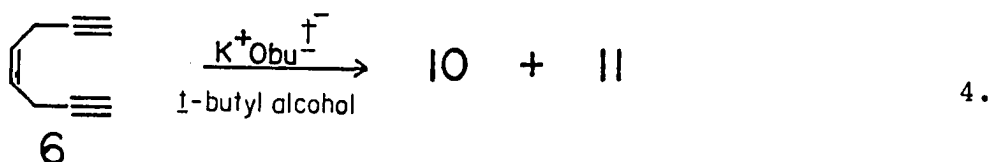
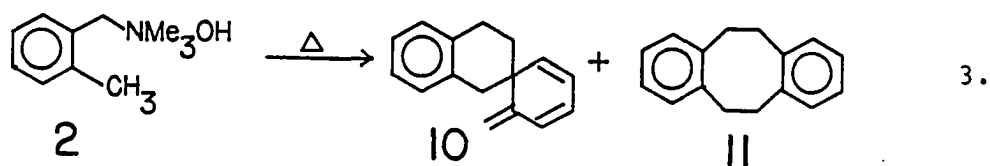
Roth generated 1 in solution by flash photolysis of 5,6-dimethylenebicyclo[2.2.1]hept-2-en-7-one (9)¹⁵ (reaction 2). Using Michl's estimated λ_{max} value of 3000 for 1 Roth calculated a second-order rate constant of $9.85 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$ for the dimerization of 1 at 22°C.



The major dimer produced when 1 is generated at low temperatures (-78 to 250°C) is spiro[6.6]8,9-benz-5-methylenundeca-1,3-diene (spiro-di-o-xylylene) (10).¹⁰ When 2 is allowed to decompose at 200-250°C in a low pressure flow apparatus 10 is the major dimeric product along with

5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (11) in a 3 to 1 ratio, respectively (reaction 3).

This ratio appears to increase when 1 is generated at temperatures closer to ambient. When 6 is treated with potassium t-butoxide in t-butyl alcohol at 60-65°C,¹⁴ the ratio of 10 to 11 formed is 12.5 to 1 (reaction 4).

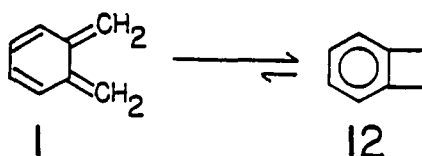


Aside from Roth's kinetic data for 1 little is known about the details of its dimerization. One of the foremost obstacles to studying the dimerization of 1 and its derivatives is the lack of suitable precursors.

When 1 is generated at high temperatures (>300°C) it does not dimerize but rather closes to form benzocyclobutene (12) (Scheme 2), a thermodynamically more stable valence

tautomer.^{18,6} The Eact for this process is significant and was reported by Roth to be 26 kcal mol⁻¹.

Scheme 2



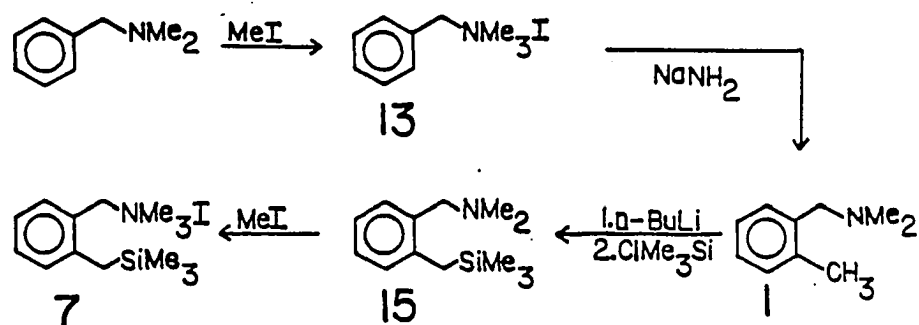
Lower temperature methods which lead predominantly to 10 and 11 are not suitable for studying these dimerization reactions for a number of reasons. First, compounds such as 9 are difficult to prepare and difficult to derivatize. Second, if the decay of 1 is to be monitored directly, it must be generated very rapidly. Given the extreme reactivity of 1, the reaction leading to 1 must occur much faster than the expected dimerization reaction. Third, the method chosen must allow kinetic measurements to be taken. That is, it must be amenable to some type of spectroscopy.

After examining the literature it became obvious that there existed no general method for generating o-QDMs for the purpose of spectroscopic investigation. Therefore, this study was undertaken to develop a general method for generating and observing o-QDMs by UV-visible spectroscopy. This work has been briefly described in a communication.¹⁹

RESULTS

[o-[(Trimethylsilyl)methyl]benzyl]trimethylammonium iodide (7) was prepared according to the procedure of Ito, Nakatsuka, and Saegusa,⁹ as outlined in Scheme 3. The key steps in the synthesis are Sommelet-Hauser rearrangement of benzyltri-methylammonium iodide (13) followed by lithiation of the resultant tertiary amine (14) and quenching with chlorotri-methylsilane.

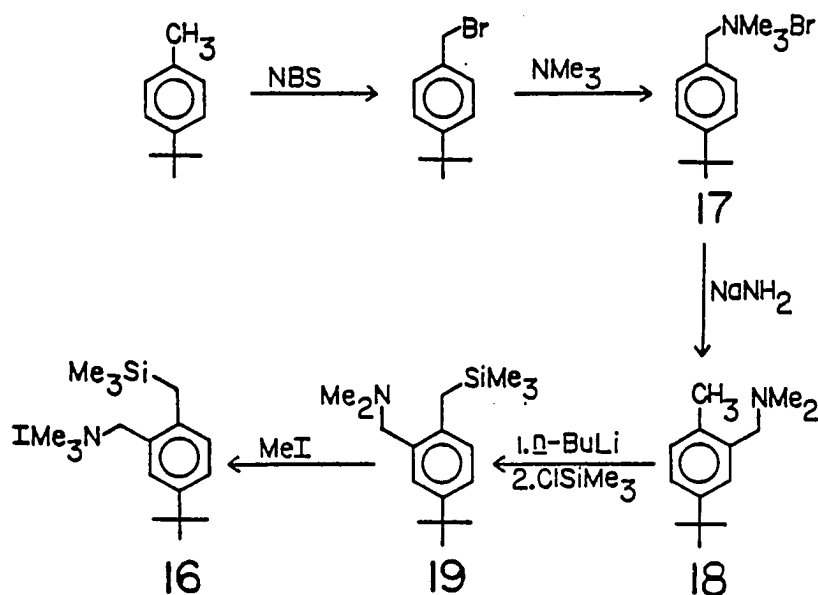
Scheme 3



[2-((Trimethylsilyl)methyl)-5-t-butylbenzyl]trimethyl-ammonium iodide (16) was prepared from (p-t-butylbenzyl)tri-methylammonium bromide (17) in a manner analogous to that used for the parent system. The synthesis is outlined in Scheme 4.

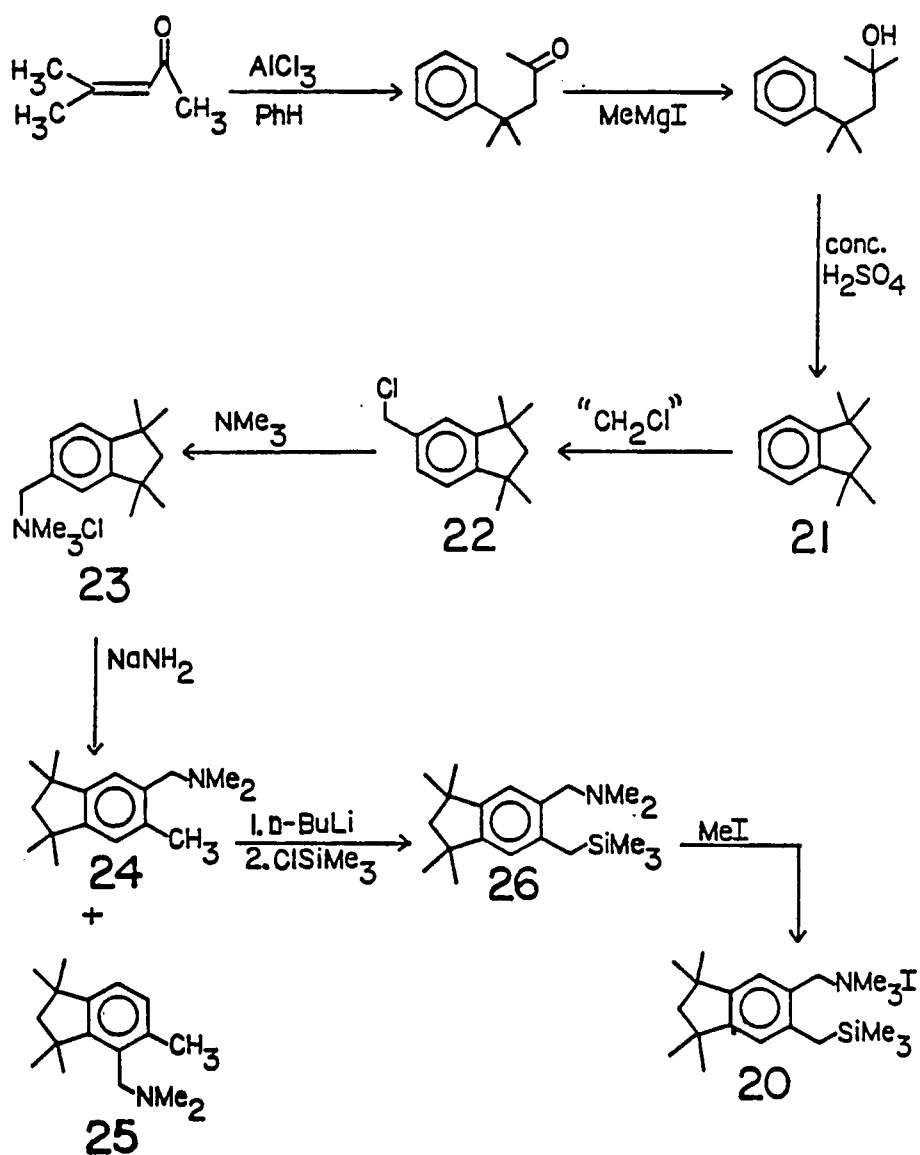
[(2-((Trimethylsilyl)methyl))-4,5-(1,1,3,3-tetramethyl-trimethylene)benzyl]trimethylammonium iodide (20) was prepared as follows. Sommelet-Hauser rearrangement of [3,4-(1,1,3,3-tetramethyltrimethylene)benzyl]trimethylammonium chloride

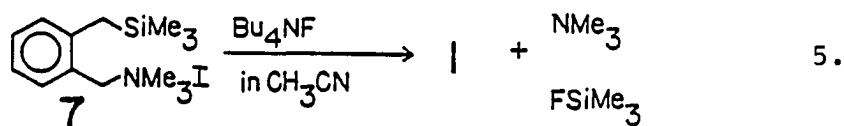
Scheme 4



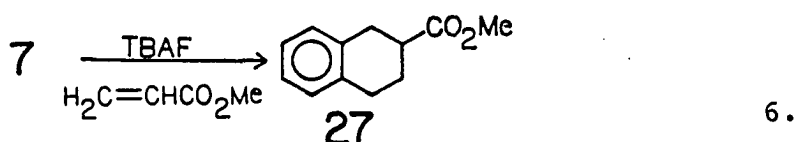
(23) produced two (pentamethylindanyl)dimethylamines (24) and (25) which were separated on silica gel. Interestingly, 25 was the major isomer formed being favored by a 3 to 1 ratio. Conversion of 24 to 20 was analogous to the sequence used for the parent system (Scheme 5).

When an acetonitrile solution of 7 (10^{-3} M) was treated with an acetonitrile solution of tetra-*n*-butylammonium fluoride (TBAF, 10^{-1} M) at room temperature in a UV-visible cell, a species with a λ_{max} of 367 nm was produced which rapidly decayed following second order kinetics (reaction 5). These observations are consistent with very rapid formation of *o*-xylylene (1).^{6,15} The value of the λ_{max} of the reactive species is similar to the reported λ_{max} of 1 in a rigid glass (373 nm)⁶ and in benzene (369 nm).¹⁵ Further support for the

Scheme 5



rapid formation of 1 under the conditions used in the UV-visible spectroscopy experiments was obtained by product studies under these conditions and under conditions which differed only by the presence of an excess of methyl acrylate. In the absence of methyl acrylate the known¹⁰ [4+2] (10) and [4+4] (11) dimers were produced in a ratio of 11:1. However, with added excess methyl acrylate, the Diels-Alder adduct of 1 and methyl acrylate (27) was obtained instead of dimers 10 and 11 (reaction 6).



The very rapid formation of 1 under the conditions used in the UV-visible spectroscopy experiments allows the rate of dimerization of 1 and other reactive o-QDMs to be measured using the stopped flow technique (see Appendix). Since the

rate of dimerization is a second-order process, measurement of the rate constant requires knowledge of the concentration of I_2 and this can be obtained by knowing the ϵ_{max} of I_2 . We have determined the ϵ_{max} for I_2 in the following manner. Several runs were carried out in which the concentration of I_2 was kept constant but the fluoride ion concentration was varied from 5×10^{-3} to 1 M. As the concentration of fluoride ion increased, the maximum absorbance of the intermediate did not continue to increase but leveled off at a fluoride ion concentration of 0.025 M. Thus it was assumed that when the fluoride ion concentration was at least 0.025 M, I_2 was converted quantitatively to I_2^- before much of I_2 had dimerized. Knowing the concentration of I_2 , the ϵ_{max} was calculated to be 3015.

Rate constants, k 's, for the dimerization of I_2 were determined from the second-order rate law of a single reactant. A plot of $[\text{I}_2]^{-1}$ versus time was found to be linear with a slope equal to k_1 . In Figure 1, the scaled UV-visible plot ($\lambda_{\text{max}} = 367 \text{ nm}$) of absorbance versus time for the generation and decay (dimerization) of I_2 at 25°C is presented. In Figure 2, a plot of the reciprocal of I_2 , $[\text{I}_2]^{-1}$, versus time is presented. The slope of the straight line, obtained from a least-squares fit calculation, gives the value of k_1 ; the value in this run is $8.95 \pm 0.32 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$.

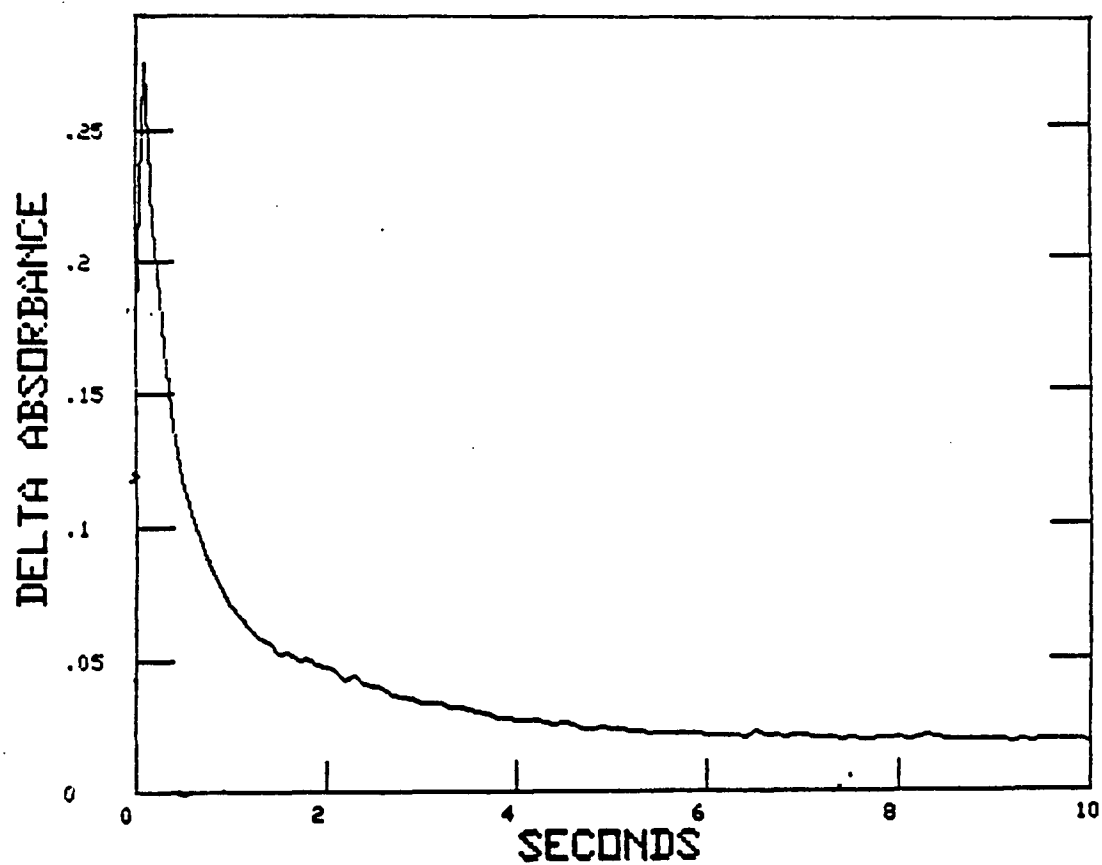


Figure 1. Scaled UV-visible plot ($\lambda_{\text{max}} = 367 \text{ nm}$) of absorbance versus time for the generation and decay (dimerization) of o-xylylene (1) at 25°C.

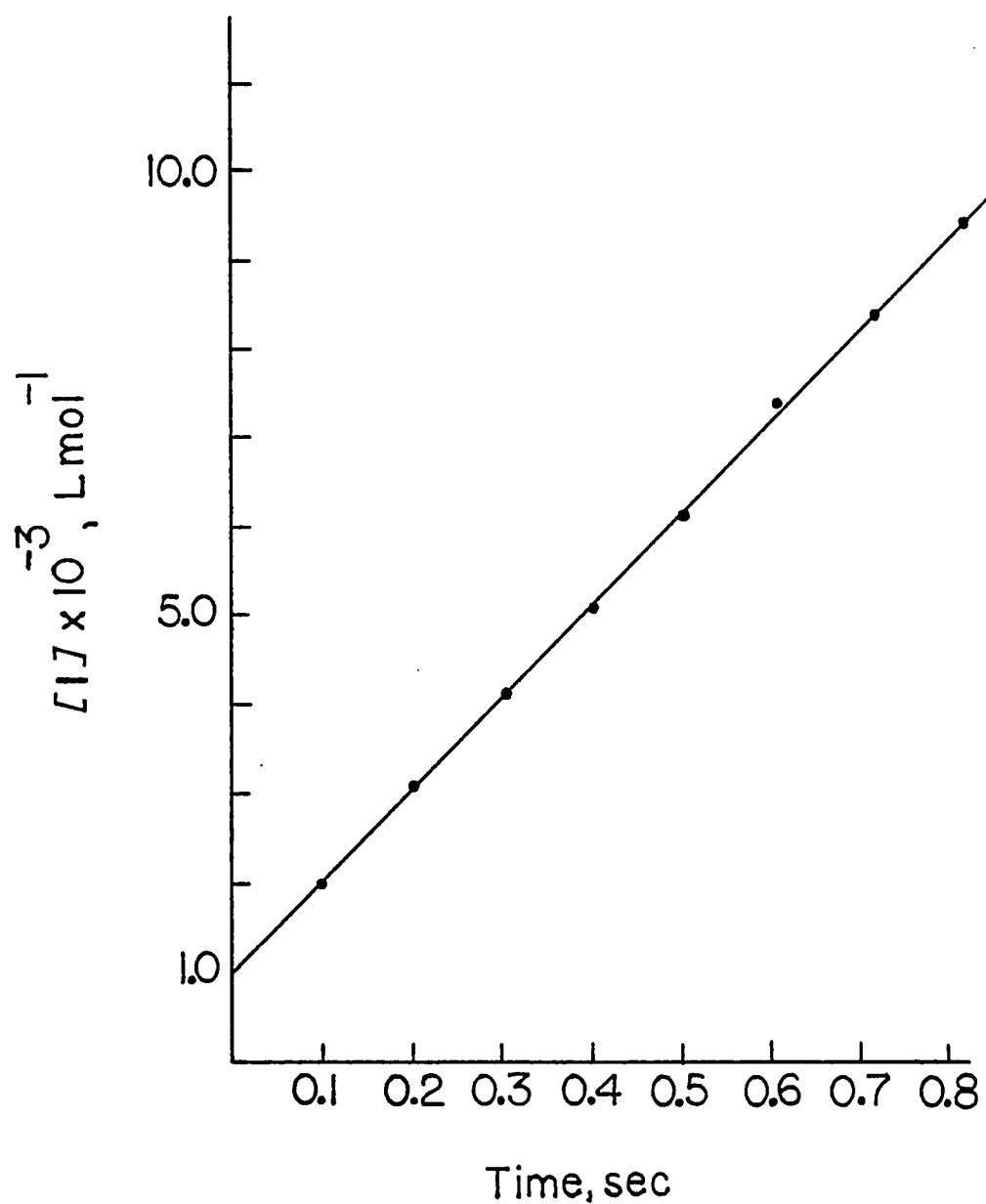


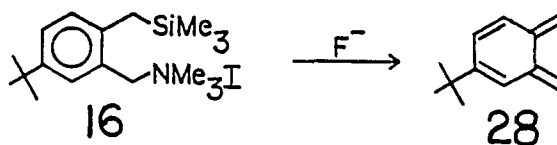
Figure 2. Plot of reciprocal of o-xylene (I), $[I]^{-1}$ versus time at 25°C in CH_3CN (the slope of the straight line = $k_1 = 8.95 \pm 0.32 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$)

Rate constants for the dimerization of 1 from 25 to 45°C were measured and these are reported in Table 1.

Kinetic Study of the Effects of Ring Substitution
on the Dimerization Rate of o-Xylylene (1)

When iodides 16 and 20 were treated with fluoride ion in CH₃CN (Schemes 6 and 7), o-QDMs 28 and 29, respectively, were generated. UV-visible data for 1, 28, and 29 are listed in Table 2.

Scheme 6



Scheme 7

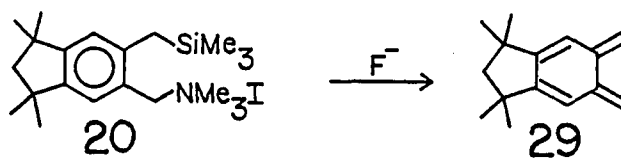


Table 1. Second-order rate constants for the dimerization of o-xylylene (1) in CH₃CN^a

Temp °C	k_1 , L mol ⁻¹ s ⁻¹
25	$9.94 \pm 0.32 \times 10^3$
35	$12.1 \pm 0.41 \times 10^3$
45	$15.4 \pm 0.51 \times 10^3$

^aFor all reactions the concentration of TBAF was 5.00×10^{-2} M and the concentration of 1 was 5.00×10^{-4} M. Rate constants were obtained from an average of at least nine kinetic runs.

Table 2. UV-visible data for o-xylylene (1), 4-t-butyl-1,2-xylylene (28), and 3,4-(1,1,3,3-tetramethyltri-methylene)-1,2-xylylene (29) obtained in CH₃CN

<u>o</u> -QDM	λ_{\max} nm	ϵ_{\max}
<u>1</u>	367	3015
<u>28</u>	381	2120
<u>29</u>	378	2390

A kinetic study of the dimerization of 28 and 29 was carried out in the same fashion as that of o-xylylene (1). Rate constants for the dimerization of 1, 28, and 29 are listed in Table 3.

As can be seen from Table 3 the differences in rate constants for the dimerization of 1, 28, and 29 are small, with $k_1/k_{28} = 2.5$ and $k_1/k_{29} = 1.8$ at 25°C.

Activation parameters for the dimerization of 1, 28, and 29 were obtained from Arrhenius^{20,21} plots and are listed in Table 4. The activation enthalpies, ΔH^\ddagger , (at 25°C) for the three reactions are in the vicinity of 4 kcal mol⁻¹ and the activation entropies, ΔS^\ddagger , are about -27 entropy units.

Dimerization of 28 and 29 produced [4+2] and [4+4] dimers of these o-QDMs.

Dimerization of 28 produced four major dimers (30a-d) in nearly equal amounts (reaction 7) as indicated by capillary GC. The ¹H NMR resonances observed at δ 5.03 and 5.23 for this mixture are characteristic of the exomethylene protons of [4+2] dimers of benzenoid o-QDMs.¹⁰

The dimer mixture 30a-d was converted to a 1:1 mixture of 2,8- and 2,9-di-t-butyl-5,6,11,12-tetrahydrodibenzo[a,e]-cyclooctene (31) and (32) by subjecting it to flash vacuum pyrolysis (FVP)²² conditions (reaction 8). Comparison of the ¹H NMR spectra of the [4+2] mixture 30a-d (Figure 3a) and the [4+4] mixture 31 and 32 (Figure 3b) indicates that small

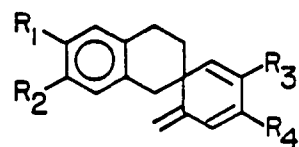
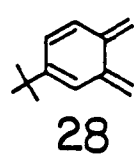
Table 3. Second-order rate constants for the dimerization of o-xylylene (1), 4-t-butyl-1,2-xylylene (28), and 3,4-(1,1,3,3-tetramethyltrimethylene)-1,2-xylylene (29) in CH₃CN^a

Temp °C	$k_1 \times 10^{-3}$, L mol ⁻¹ s ⁻¹	$k_{28} \times 10^{-3}$, L mol ⁻¹ s ⁻¹	$k_{29} \times 10^{-3}$, L mol ⁻¹ s ⁻¹
25	9.94 ± 0.32	3.90 ± 0.15	5.59 ± 0.21
35	12.1 ± 0.41	5.24 ± 0.18	7.89 ± 0.30
45	15.4 ± 0.51	6.78 ± 0.24	10.1 ± 0.38

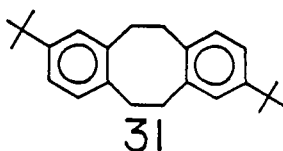
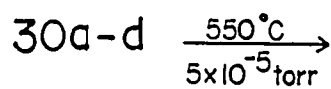
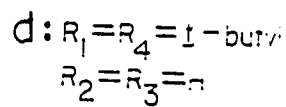
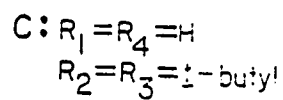
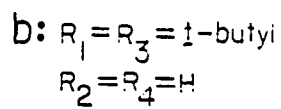
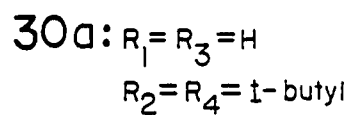
^aFor all reactants the concentration of TBAF was 5.00 x 10⁻² M and the concentration of 1, 16, or 20 was 5.00 x 10⁻⁴ M. Rate constants were obtained from an average of at least nine kinetic runs.

Table 4. Activation parameters for the dimerization of o-xylylene (1), 4-t-butyl-1,2-xylylene (28), and 3,4-(1,1,3,3-tetramethyltrimethylene)-1,2-xylylene (29)

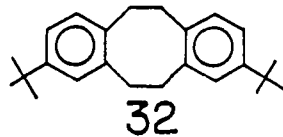
<u>o</u> -QDM	ΔH^\ddagger , at 25°C, kcal mol ⁻¹	ΔS^\ddagger , at 25°C, cal k ⁻¹ mol ⁻¹
<u>1</u>	3.5 ± 0.13	-29 ± 1.1
<u>28</u>	4.8 ± 0.17	-26 ± 1.0
<u>29</u>	4.9 ± 0.20	-25 ± 1.0



7.

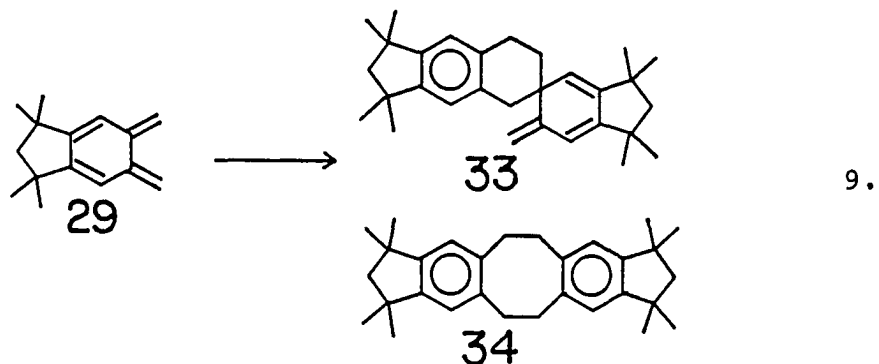


8.



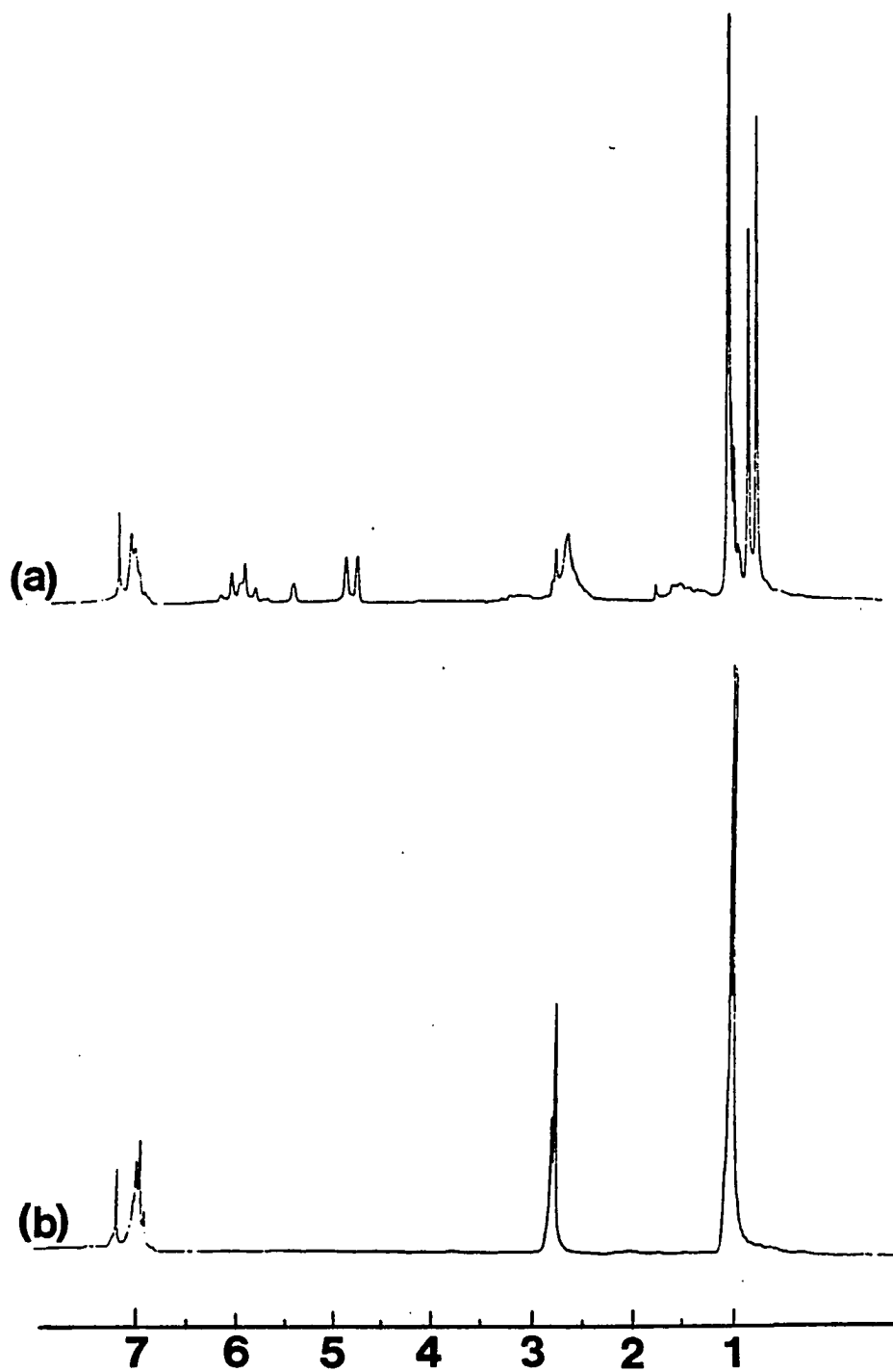
amounts of 31 and 32 are present in the [4+2] mixture. The ratio of [4+2] to [4+4] dimers could not be accurately determined either by ^1H NMR or GC but was estimated at >10:1.

Dimerization of 29 produced a [4+2] dimer (33) and a [4+4] dimer (34) (reaction 9) in a ratio of 11.5:1 as determined by ^1H NMR. The signal for the four aromatic protons of 34, which



occurred at δ 6.84, was integrated versus the aromatic signals for 33, which occurred at 6.97 and 6.90. The mixture of 34 and 33 was converted exclusively to 34 by FVP.

Figure 3. ^1H NMR spectrum (90 MHz) of (a) mixture of [4+2] and [4+4] dimers $\underline{30a-d}$, $\underline{31}$ and $\underline{32}$ of 4-t-butyl-1,2-xylylene ($\underline{29}$) and (b) [4+4] dimers $\underline{31}$ and $\underline{32}$ of $\underline{28}$



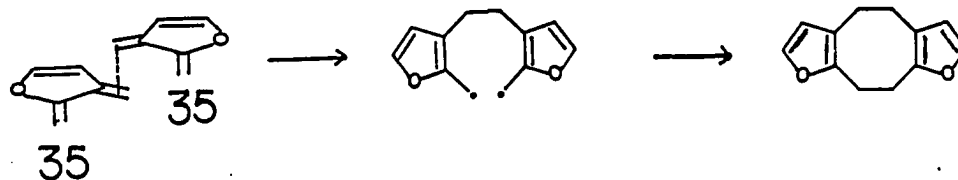
DISCUSSION

As Figure 1 indicates, the formation of *o*-xylylene (1) by the fluoride ion induced elimination from 7 is very rapid. The formation of 1 is much more rapid than the subsequent dimerization reaction. The very rapid formation of 1 under the conditions used in the UV-visible spectroscopy experiments allows the rate of dimerization of 1 and other reactive *o*-QDMs to be measured using the stopped flow technique. Both the values of the k_1 's (Table 1) and the temperature dependence (Table 4) of the reaction are in good agreement with Roth's data: $k_1 = 9.85 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ at 22.3°C , $\Delta H^\ddagger = 5.3 \text{ kcal/mol}$, and $\Delta S^\ddagger = -24.3 \text{ entropy units}$.¹⁵

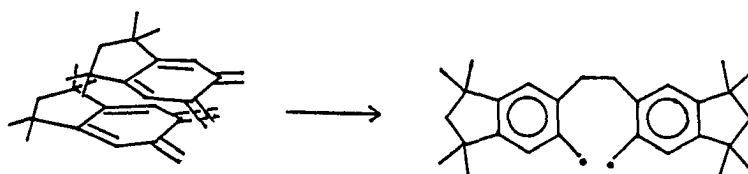
The 1,4-elimination from precursors such as 7, 16, and 20 seems well suited for generating *o*-QDMs for the purpose of spectroscopic investigation. This method makes it possible to study many substituted *o*-QDMs, the precursors of which are readily prepared from simple starting materials.

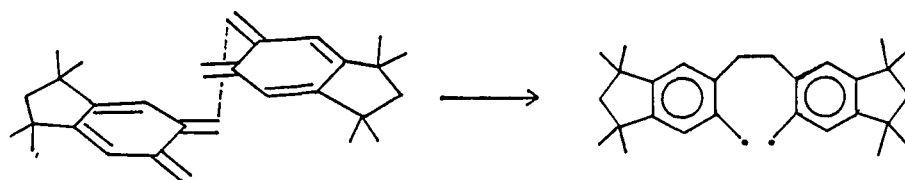
Some previous work in our laboratory on the corresponding 2,3-dimethylene-2,3-dihydrofuran (35) suggests that *o*-QDM dimerizations proceed via a stepwise mechanism involving a diradical intermediate. It is believed that in forming the diradical intermediate, the *o*-QDM monomers prefer a non-endo approach (Scheme 8).²³

o-QDMs such as 28 and 29 contain alkyl substituents which introduce steric bulk on the ring without significantly

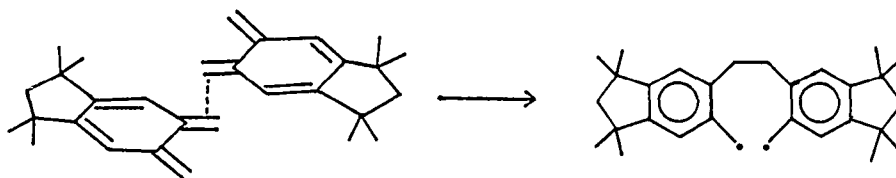
Scheme 8

changing the electronic nature of the molecule. If, o-QDM monomers prefer an endo approach when undergoing dimerization, the bulky substituents on 28 and 29 would be expected to cause severe steric interactions, resulting in significantly reduced rates of dimerization for these o-QDMs. Alternatively, if a non-endo approach is preferred, one would expect similar rates of dimerization for 1, 28, and 29.

Endo Approach

Non-Endo Approach

OR



From Table 3 it can clearly be seen that the differences in rate constants for the dimerization of 1, 28, and 29 are small and this supports the non-endo approach of monomers.

EXPERIMENTAL

General Procedure

Some general methods have been described.²⁴ GLC analyses were performed using a Hewlett-Packard HP 5840A gas chromatograph equipped with a 30 meter, DB-1 or DB-1701 capillary column from J & W Scientific. UV-visible spectra were recorded on Perkin-Elmer 7000 Lambda-array or Canterbury SF3A spectrophotometers. Elemental analyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, Michigan. The vacuum pyrolysis apparatus has been previously described²⁰ and is available from Kontes. Tetra-n-butylammonium fluoride was prepared by modifying the procedure of Ito, Nakatsuka, and Saegusa.⁹ Water was removed by azeotropic distillation with 1:1 benzeneacetonitrile at reduced pressure. The resultant white solid was further dried under vacuum (10^{-2} mmHg, 25°C) for 48 h. The acetonitrile used was HPLC grade and was distilled from CaH₂ under nitrogen prior to use. Acetonitrile-d₃ was purchased from Stohler Isotope Chemicals. *n*-BuLi and chlorotrimethylsilane were purchased from Aldrich Chemical Co.

[o-((Trimethylsilyl)methyl)benzyl]trimethylammonium iodide (7)

A 10.0 g (74.1 mmol) quantity of *N,N*-dimethylbenzylamine was converted to [o-((trimethylsilyl)methyl)benzyl]dimethylamine (15) in 84% yield by the three step procedure of

Ito, Nakatsuka, and Saegusa.⁹ A 2.04 g (9.23 mmol) quantity of 15 was converted to 7 in >90% yield as previously described by Ito et al.:⁹ mp 188–189°C [lit.⁹ 189.5–190.5°C]; ¹H NMR (CD₃CN) δ 7.10–6.50 (m, 4 H), 4.35 (s, 2 H), 2.85 (s, 9 H), 2.08 (s, 2 H), –0.30 (s, 9 H) [lit.⁹ NMR (CD₃CN) δ 7.31–6.60 (m, 4 H), 4.36 (s, 2 H), 2.85 (s, 9 H), 2.07 (s, 2 H), –0.32 (s, 9 H)].

[2-((Trimethylsilyl)methyl)-5-t-butylbenzyl]dimethylamine (19)

p-t-Butyltoluene (3.00 g, 20.3 mmol), N-bromosuccinimide (4.30 g, 24.3 mmol), and benzoyl peroxide (0.25 g) were combined in 50 mL of CCl₄ and the mixture was heated to reflux for 2 h. The reaction mixture was cooled to room temperature and then cooled in an ice-bath. The succinimide crystals were removed by filtration and the solvent was removed under reduced pressure. The residue was distilled [bp 134–140°C (15 mmHg) [lit.²⁵ bp 133°C (17 mmHg)]] affording 2.81 g of α-bromo-p-t-butyltoluene as a colorless oil (61%): ¹H NMR (CDCl₃) δ 7.34 (s, 4 H), 4.57 (s, 2 H), 1.28 (s, 9 H). The bromide (2.81, 12.4 mmole) was combined with 7 mL of a 20% solution of trimethylamine in methanol and the mixture was heated to reflux for 5 h. The solvent was removed under reduced pressure and the solid residue was purified by boiling in hexanes which afforded 3.23 g (11.3 mmole) of 4-t-butylbenzyltrimethylammonium bromide (17) (91%): ¹H NMR (D₂O) δ 7.78–7.50 (m, 4 H), 4.50 (s, 2 H), 3.15 (s, 9 H), 1.36 (s, 9

H). The ammonium salt 17 was converted to 2-methyl-4-t-butylbenzyl dimethylamine (18) in 75% yield using the procedure described for the synthesis of 14:²⁶ ^1H NMR (CDCl_3) δ 7.38-7.05 (m, 3 H), 3.37 (s, 2 H), 2.32 (s, 3 H), 2.25 (s, 6 H), 1.33 (s, 9 H). A 970 mg (4.73 mmol) quantity of 18 was converted to 19 in 91% yield by the procedure of Ito, Nakatsuka, and Saegusa⁹ for the preparation of 15: bp 89-91°C (0.5 mmHg); ^1H NMR (CDCl_3) δ 7.32-6.96 (m, 3 H), 3.34 (s, 2 H), 2.26 (s, 6 H), 2.23 (s, 2 H), 1.32 (s, 9 H), 0.05 (s, 9 H).

[2-((Trimethylsilyl)methyl)-5-t-butylbenzyl]trimethylammonium iodide (20)

A 484 mg (1.12 mmol) quantity of 19 was converted to 20 in >90% yield in the usual manner:⁹ mp. 205-206°C (Recrystallized from 1:1, ethyl acetate-acetone); IR (KBr disk) 2987, 2940, 1470, 1482, 1495, 1280, 1150, 837 cm^{-1} ; ^1H NMR (CD_3CN) δ 7.60-7.20 (m, 3 H), 4.43 (s, 2 H), 3.06 (s, 9 H), 2.30 (s, 2 H), 1.33 (s, 9 H), -0.05 (s, 9 H); ^{13}C NMR (CD_3CN) δ 147.06, 139.34, 131.02, 130.09, 127.27, 124.01, 66.00, 52.24, 34.06, 30.31, 23.00, -0.03; Anal. calcd for $\text{C}_{18}\text{H}_{34}\text{INSi}$: C, 51.54; H, 8.17; N, 3.34. Found: C, 51.62; H, 8.22; N, 3.27.

[2-((Trimethylsilyl)methyl)-4,5-(1,1,3,3-tetramethyl)trimethylene]benzyl]dimethylamine (26)

1,1,3,3-Tetramethylindane (21) was prepared in 73% yield according to the two step procedure of Carpenter, Easter, and

Wood:²⁷ bp 42-45°C (1.6 mmHg) [lit.²⁷ bp 47°C (1.5 mmHg)]; ¹H NMR (CDCl₃) δ 7.21-7.06 (m, 4 H), 1.91 (s, 2 H), 1.33 (s, 12 H). 5-Chloromethyl-1,1,3,3-tetramethylindane (22) was prepared in 75% yield from 21 according to the procedure of Arnold for the preparation of 5-chloromethylindane:²⁸ ¹H NMR (CDCl₃) δ 7.25-7.02 (m, 3 H), 4.32 (s, 2 H), 1.90 (s, 2 H), 1.31 (br s, 12 H). A 185 mg (0.83 mmol) quantity of 22 was dissolved in 2.0 mL of a 25% solution of trimethylene in methanol and the reaction mixture was heated to reflux for 5 h. Methanol was removed under reduced pressure leaving behind a white solid which was recrystallized from ethyl acetate-acetone yielding 204 mg (0.76 mmol) of [3,4-(1,1,3,3-tetramethyltrimethylene)benzyl]trimethylammonium chloride (23) (91%). The ammonium salt 23 was converted to [2-methyl-4,5-(1,1,3,3-tetramethyltrimethylene)benzyl]dimethylamine (24) in 14% yield using the procedure described for the synthesis of 14:²⁶ ¹H NMR (CDCl₃) δ 6.98 (s, 1 H), 6.86 (s, 1 H), 3.33 (s, 2 H), 2.31 (s, 3 H), 2.22 (s, 6 H), 1.86 (s, 2 H), 1.29 (s, 12 H). The major product, obtained in 41% yield was identified as [6-methyl-2,3-(1,1,3,3-tetramethyltrimethylene)benzyl]-dimethylamine (25):¹ ¹H NMR (CDCl₃) δ 6.93 (br s, 2 H), 3.52 (s, 2 H), 2.37 (s, 3 H), 2.19 (s, 6 H), 1.86 (s, 2 H), 1.44 (s, 6 H), 1.24 (s, 6 H). Amines 24 and 25 were separated by column chromatography (silica gel, 10% ether in hexanes elution). A 145 mg (0.59 mmol) quantity of 24 was converted

to 26, following the procedure previously described for the preparation of 15,⁹ in 79% yield (149 mg, 0.47 mmol): bp 92-94°C (0.4 mmHg); ¹H NMR (CDCl₃) δ 6.94 (s, 1 H), 6.69 (s, 1 H), 3.27 (s, 2 H), 2.20 (s, 6 H), 2.16 (s, 2 H), 1.83 (s, 2 H), 1.27 (s, 12 H), -0.05 (s, 9 H).

[2-((Trimethylsilylmethyl)-4,5-(1,1,3,3)-tetramethyltrimethylene)benzyl]trimethylammonium iodide (20)

[2-((Trimethylsilyl)methyl)-4,5-(1,1,3,3-tetramethyltrimethylene)benzyl]dimethylamine (26) was converted to 20 in 91% yield in the usual manner:⁹ mp. 204-205°C; IR (KBr disk) 2940, 1484, 1460, 1240 cm⁻¹; ¹H NMR (CD₃CN) 7.20 (s, 1 H), 6.96 (s, 1 H), 4.40 (s, 2 H), 3.04 (s, 9 H), 2.31 (s, 2 H), 1.91 (s, 2 H), 1.31 (s, 12 H), -0.03 (s, 9 H); ¹³C NMR (CD₃CN) δ 155.04, 148.99, 141.87, 129.22, 125.53, 123.48, 67.25, 57.43, 58.30, 53.38, 43.26, 31.77, 31.53, 24.78, 1.58; Anal. calcd for C₂₁H₃₈INSi: C, 54.88; H, 8.33; N, 3.05. Found: C, 54.81; H, 8.35; N, 3.01.

Spiro[6.6]8,9-benz-5-methyleneundeca-1,3-diene (10) and tetrahydrodibenzo[a,e]cyclooctene (11)

Preparative conditions To a solution of [2-((trimethylsilyl)methyl)benzyl]trimethylammonium iodide (7) (34 mg, 0.094 mmol) in 3 mL of CH₃CN was added a solution of TBAF (34 mg, 0.13 mmol) in 1 mL of CH₃CN under nitrogen. The reaction mixture was allowed to stir at room temperature for 1 h after which the solution was concentrated and triturated with 1:1

ether-hexanes precipitating a white material from solution. The precipitate was removed by filtration and the solvent was evaporated. The residue was purified by passing it through a short column of silica gel (hexanes elution). A mixture of 10 and 11 was obtained in 83% combined yield. The ratio of 10 to 11 produced was 11:1, respectively, as determined by GC and ^1H NMR integration. 10: ^1H NMR (CDCl_3) δ 7.23-7.07 (m, 4 H), 6.30-5.72 (m, 4 H), 5.09 (s, 1 H), 5.00 (s, 1 H), 2.99-2.67 (m, 4 H), 1.98-1.58 (s, 2 H), [lit.¹⁰ NMR (CDCl_3) δ 7.00, 5.80, 4.93, 2.80, 1.90]; 11: ^1H NMR (CDCl_3) δ 6.99 (s, 8 H), 3.07 (s, 8 H) [lit.¹⁰ NMR (CDCl_3) δ 6.90, 3.03].

Dilute conditions To a solution of 7 (18.4 mg, 0.051 mmol) in 30 mL of CH_3CN was added a solution of TBAF (179 mg, 0.69 mmol) in 250 mL of CH_3CN all at once. The reaction mixture was allowed to stand for 5 min after which 200 mL of H_2O was added and the organic products were extracted continuously with pentane for 72 h. The extract was then concentrated and analyzed by GC. The two products obtained by this method had the same GC retention times as the dimers (10 and 11) produced in method A, and were produced in the same ratio (combined yield 79% based upon an internal standard of biphenyl). Analysis of the reaction mixture by GC/MS gave the expected m/e of 214 for dimers of o-xylylene.

Diels-Alder reaction of *o*-xylylene (1) with methyl acrylate

To a solution of [*o*-((trimethylsilyl)methyl)benzyl]trimethylammonium iodide (7) (22.6 mg, 0.062 mmol) in 30 mL of CH₃CN was added a solution of TBAF (128.2 mg, 0.49 mmol) and methyl acrylate (1.91 g, 22.2 mmol) in 240 mL of CH₃CN all at once. Water (300 mL) was added and the mixture was extracted continuously with pentane for 60 h. GC and GC/MS analyses showed that dimers 16 and 17 were not produced in detectable amounts. A new peak appeared in the GC trace with a longer retention time than that for 10 or 11 and had a m/e of 190. Without further analysis this compound was assigned the structure 2-carbomethoxy-1,2,3,4-tetrahydronaphthalene (27) (65% yield, based upon internal standard of biphenyl): GC/MS (70 eV) m/e (% base peak) 190.94 (2.80), 189.92 (22.43), 131.00 (31.71), 130.00 (100.00), 129.00 (30.41), 128.00 (12.21), 114.98 (17.73), 91.00 (18.16), 64.64 (16.12).

2,8- and 2,9-di-*t*-butyl-5,6,11,12-tetrahydrodibenzo[a,e]-cyclooctene (31) and (32)

To a solution of 16 (371 mg, 0.885 mmol) in 5 mL of CH₃CN was added a solution of TBAF (254 mg, 0.97 mmol) in 5 mL of CH₃CN dropwise over a period of 20 min. The reaction mixture was allowed to stir at room temperature for 1 h after which the solution was concentrated and triturated with ether. The precipitate which formed was removed by filtration, the solvent was evaporated, and the residue was purified by

passing it through a short column of silica gel (hexanes elution). GC and GC/MS analyses of the products showed four major dimeric products with molecular ion peaks equal to 320 m/e (80% combined yield): ^1H NMR (Figure 3a) (CDCl_3) δ 5.03 (s, 1 H), 5.23 (s, 1 H) -exomethylene resonances from a mixture of [4+2] dimers (30a-d). The dimer mixture (83.5 mg, 0.71 mmol) was pyrolyzed at 550°C in a FVP system (5.0×10^{-5} mmHg). The sample head was heated to 40°C. The pyrolysis was complete after 1.5 h. After warming a colorless oil was collected from the liquid nitrogen trap with ether. The ether was removed yielding 38.4 mg (0.33 mmol) of a mixture of 2,8- and 2,9-di-*t*-butyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (31) and (32) (46%). The ratio of 31 to 32 was essentially 1:1 as determined by GC: ^1H NMR (Figure 3b) (CDCl_3) δ 6.99-6.90 (m, 6 H), 2.98 (s, 4 H), 2.95 (s, 4 H), 1.26 (s, 9 H), 1.23 (s, 9 H); GC/MS (70 eV) m/e (% base peak) 320.10 (2.83), 305.06 (10.28), 263.04 (7.48), 207.02 (10.18), 145.18 (17.23), 131.18 (12.55), 119.04 (25.60), 117.04 (19.69), 91.02 (12.04), 57.08 (100.00), 41.02 (20.31), and 320.10 (5.01), 305.06 (10.26), 263.04 (6.24), 207.02 (7.31), 145.06 (17.88), 131.16 (14.76), 119.06 (18.21), 117.04 (25.18), 105.04 (8.48), 91.02 (13.87), 57.08 (100.00), 41.02 (19.74).

Preparation of spiro[6.6]8,9-(1,1,3,3-tetramethylindan)-5-methylene-2,3-(1,1,3,3-tetramethyltrimethylene)-undeca-1,3-diene (33) and 2,3-8,9-bis(1,1,3,3-tetramethyltrimethylene)-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (34)

To a solution of [2-((trimethylsilylmethyl)-4,5-(1,1,3,3-tetramethyl)trimethylene)benzyl]trimethylammonium iodide (20) (190 mg, 0.41 mmol) in 2 mL of CH₃CN was added TBAF (129 mg, 0.49 mmol) in 4 mL of CH₃CN over a 15 min period. The reaction mixture was allowed to stir at room temperature for 1.5 h after which the solution was concentrated and triturated with ether. The precipitate which had formed during the trituration was removed by filtration and the solvent was evaporated. The residue was purified by passing it through a short column of silica gel (hexanes elution). A mixture of dimers 33 and 34 was obtained in 77% combined yield. The ratio of 33 to 34 produced was 11.5:1, as determined by GC and ¹H NMR integration. 33: ¹H NMR (C₆D₆) δ 6.97 (s, 1 H), 6.90 (s, 1 H), 6.02 (s, 1 H), 5.70 (s, 1 H), 5.10 (s, 1 H), 5.03 (s, 1 H), 3.07 (d, J = 12.0 Hz, 1 H), 2.95 (d, J = 12.0 Hz, 1 H), 2.91-2.73 (m, 2 H), 2.14 (s, 2 H), 1.87 (s, 2 H), 1.79-1.62 (m, 2 H), 1.58 (s, 2 H), 1.40 (s, 3 H), 1.37 (s, 3 H), 1.32 (s, 6 H), 1.10 (s, 6 H), 1.04 (s, 3 H), 0.95 (s, 3 H). The mixture of 33 and 34 (63.1 mg, 0.32 mmol) was pyrolyzed at 560°C in a FVP system (5.0 x 10⁻⁵ mmHg). The sample chamber of the pyrolysis unit was heated slowly to 140°C. The pyrolysis was discontinued after 4 h. A white

solid material, which had deposited just outside of the hot zone of the FVP apparatus, was collected by dissolving it in toluene. The solvent was removed yielding 27.8 mg (0.070 mmol) (44%) of the dimer 34 which was >96% pure by GC: mp. 271°C dec; ^1H NMR (C_6D_6) δ 6.84 (s, 4 H), 2.96 (s, 8 H), 1.82 (s, 4 H), 1.31 (s, 24 H); ^{13}C NMR (CD_3Cl) δ 148.97, 123.43, 57.57, 42.16, 35.67, 31.55; high resolution mass spectrum, calcd for $\text{C}_{30}\text{H}_{40}$: 440.6460 measured: 440.6468.

General Procedure for Determining the λ_{max} of
o-Xylylene (1) and Derivatives

The λ_{max} 's of o-QDMs 1, 28, and 29 were determined with use of a Perkin-Elmer 7000 Lambda-array UV-visible spectrophotometer. A 1.00 cm x 1.00 cm quartz cuvette was charged with 2.00 ml of CH_3CN and .50 ml of a solution of TBAF (10^{-1} M) in CH_3CN . To this mixture was added .50 ml of a solution of 7, 16 or 20 (10^{-3} M) in CH_3CN . The cuvette was shaken once and placed into the optical path of the spectrophotometer. Spectra were recorded every 0.2 sec in the spectral range from 350 to 410 nm. A cursor routine (see Appendix), contained within the software of the instrument, was used to find the wavelength of maximum absorbance.

General Procedure for Measuring Rate
Constants Using the Stopped-Flow Method

Kinetic experiments involving o-QDMs 1, 28, and 29 were monitored with use of a Canterbury SF3A stopped-flow²⁹

UV-visible spectrometer equipped with an OLIS model 3820 computer. The temperature for each run was controlled to within $\pm 0.2^\circ\text{C}$ and was monitored with a Cole-Palmer 8502-20 Celsius thermometer.

A typical kinetic run was carried out by filling one of the drive syringes with a solution of TBAF in CH_3CN (ca 10^{-3} M) and the other syringe with a solution of 7, 16, or 20 in CH_3CN (ca 10^{-3} M). The drive pistons were pushed forward manually propelling the reactants through the mixing chamber and into the observation cell. With the monochromator set at a selected wavelength, the absorbance curve for the formation and decay of the intermediate was recorded. Kinetic runs were rejected if their absorbance curves were judged to contain excessive noise.

Rate constants for the dimerization of 1, 28, and 29 were determined using a least-squares method³⁰. The resultant rate constants are the average of at least nine kinetic runs and were linear over three half-lives.

Determination of the ϵ_{max} of o-Xylylene (1)

The ϵ_{max} of 1 was determined using the stopped-flow technique. Several runs were carried out in which the concentration of 7 was held constant (5.00×10^{-4} M in CH_3CN) but the fluoride ion concentration (TBAF in CH_3CN) was varied from 5.0×10^{-3} to 1.0 M. The maximum absorbance of the intermediate was recorded for each run. The maximum

absorbance of λ increased up to a fluoride ion concentration of 0.025 M at which point it leveled off. Assuming quantitative conversion of λ to λ , and knowing the path length of the optical cell (0.200 cm), the ϵ_{max} of λ was determined using Beer's Law. The ϵ_{max} for λ determined in this manner was found to be 3015.

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APPENDIX

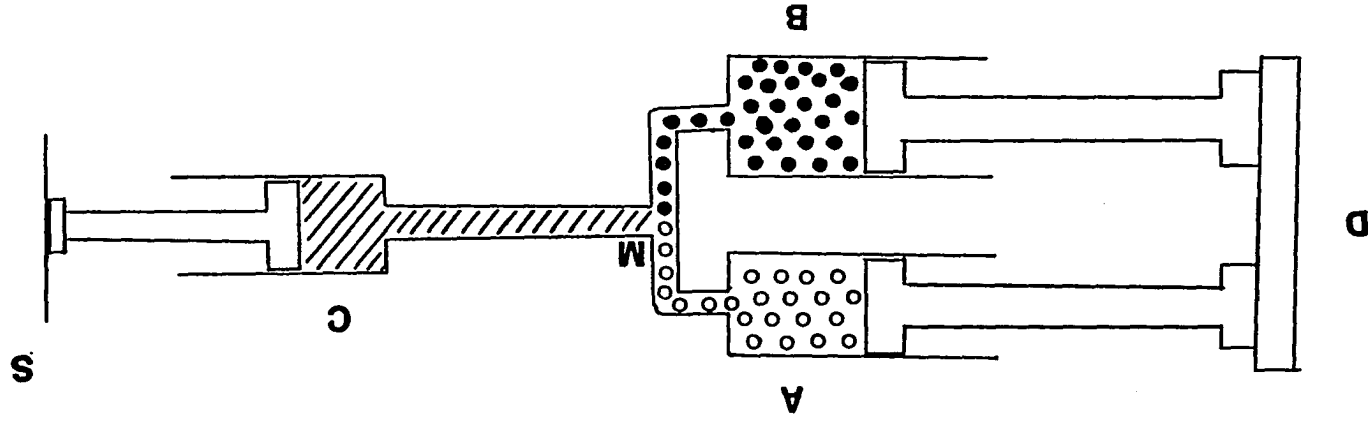
Stopped-flow UV-visible Spectroscopy

Kinetic experiments involving o-QDMs were carried out using the stopped-flow technique.^{28,29} A schematic diagram of the flow-unit is shown in Figure 1. Syringes A and B were filled with the appropriate o-QDM precursor in CH₃CN, and TBAF in CH₃CN, respectively. The common drive mechanism, a manually driven piston D, forced the solutions into the mixing chamber M and then into the stopping syringe C, whose plunger came to rest against fixed stop S. That action triggered the recording device which, in this study, consisted of an electronic transient recorder equipped with a computer for processing of data. The method of detection was UV-visible spectroscopy. The percent transmittance, as a function of time, was recorded for the formation and decay of the o-QDM. Each spectrum was then processed into a scaled plot of absorbance versus time.

Maximum Wavelength Determinations

The λ_{max} 's of the o-QDMs in this study were determined with use of a Perkin-Elmer 7000 Lambda-array UV-visible spectrophotometer. After generation of the appropriate o-QDM (see Experimental) spectra were recorded every 0.2 sec in the spectral range from 350 to 410 nm. A vertical line (cursor) of 0.1 nm width was then adjusted horizontally on the screen

Figure 1. Schematic of the flow unit of the stopped-flow UV-visible spectrophotometer (letters are defined in the text of this appendix)



until it rested on the wavelength of high absorbance, as read digitally. This value was then rounded to the nearest 1 nm.

Kinetic Data

Table A-1. Rate of disappearance of o-xylylene (1) measured at 25.0°C in CH₃CN

Time, sec	[<u>1</u>] x 10 ⁴ , mol L ⁻¹	[<u>1</u>] ⁻¹ x 10 ⁻³ , L mol ⁻¹
0.1	4.24	2.36
0.2	3.22	3.10
0.3	2.44	4.10
0.4	1.96	5.10
0.5	1.63	6.14
0.6	1.36	7.34
0.7	1.21	8.25
0.8	1.06	9.39
0.9	0.950	10.5
1.0	0.836	12.0
$k_1 = 10.5 \pm 0.32 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-2. Rate of disappearance of o-xylylene (\tilde{l}) measured at 35.0°C in CH_3CN

Time, sec	$[\tilde{l}] \times 10^4,$ mol L ⁻¹	$[\tilde{l}]^{-1} \times 10^{-3},$ L mol ⁻¹
0.1	4.27	2.34
0.2	2.86	3.50
0.3	2.14	4.67
0.4	1.71	5.84
0.5	1.41	7.10
0.6	1.21	8.30
0.7	1.05	9.52
0.8	0.929	10.8
0.9	0.817	12.2
1.0	0.744	13.4
$k_1 = 12.1 \pm 0.41 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-3. Rate of disappearance of o-xylylene ($\tilde{1}$) measured at 45.0°C in CH₃CN

Time, sec	$[\tilde{1}] \times 10^4,$ mol L ⁻¹	$[\tilde{1}]^{-1} \times 10^{-3},$ L mol ⁻¹
0.1	3.27	3.06
0.2	2.24	4.46
0.3	1.66	6.02
0.4	1.33	7.50
0.5	1.10	9.07
0.6	0.942	10.6
0.7	0.816	12.3
0.8	0.706	14.2
0.9	0.630	15.9
1.0	0.568	17.6
$k_1 = 15.3 \pm 0.51 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-4. Rate of disappearance of 4-*t*-butyl-1,2-xylene
(28) measured at 25.0°C in CH₃CN

Time, min	[28] x 10 ⁴ , mol L ⁻¹	[28] ⁻¹ x 10 ⁻³ , mol L ⁻¹
0.3	4.67	2.14
0.4	4.06	2.47
0.5	3.54	2.83
0.6	3.11	3.21
0.7	2.78	3.59
0.8	2.50	4.00
0.9	2.27	4.41
1.0	2.08	4.81
$k_{28} = 3.84 \pm 15 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-5. Rate of disappearance of 4-t-butyl-1,2-xylene
(28) measured at 35.0°C in $\overline{\text{CH}_3\text{CN}}$

Time, sec	$[\text{28}] \times 10^4,$ mol L ⁻¹	$[\text{28}] \times 10^{-3},$ mol L ⁻¹
0.1	5.28	1.89
0.2	4.29	2.33
0.3	3.58	2.79
0.4	3.04	3.29
0.5	2.64	3.79
0.6	2.33	4.29
0.7	2.07	4.83
0.8	1.86	5.38
0.9	1.68	5.95
1.0	1.54	6.51
$k_{28} = 5.24 \pm 0.18 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-6. Rate of disappearance of 4-*t*-butyl-1,2-xylylene
(28) measured at 45.0°C in CH_3CN

Time, sec	$[\text{28}] \times 10^4,$ mol L^{-1}	$[\text{28}]^{-1} \times 10^{-3},$ L mol^{-1}
0.1	4.95	2.02
0.2	3.82	2.62
0.3	3.09	3.24
0.4	2.57	3.89
0.5	2.20	4.54
0.6	1.92	5.22
0.7	1.69	5.93
0.8	1.51	6.64
0.9	1.36	7.36
1.0	1.23	8.14
$k_{28} = 6.79 \pm 0.24 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-7. Rate of disappearance of 2,3-(1,1,3,3-tetramethyltrimethylene)-1,2-xylene ($\sim\sim$) measured at 25.0°C in CH_3CN

Time, sec	$[\sim\sim] \times 10^4,$ mol L^{-1}	$[\sim\sim]^{-1} \times 10^{-3},$ L mol $^{-1}$
0.2	4.26	2.35
0.3	3.70	2.71
0.4	3.11	3.21
0.5	2.65	3.77
0.6	2.30	4.35
0.7	2.03	4.92
0.8	1.80	5.55
0.9	1.62	6.18
1.0	1.46	6.83
$k_{29} = 5.69 \pm 0.21 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-8. Rate of disappearance of 3,4-(1,1,3,3-tetramethyltrimethylene)-1,2-xylylene ($\sim\sim 29$) measured at 35.0°C in CH_3CN

Time, sec	$[\sim\sim 29] \times 10^4,$ mol L ⁻¹	$[\sim\sim 29]^{-1} \times 10^{-3},$ L mol ⁻¹
0.1	6.01	1.66
0.2	4.57	2.19
0.3	3.47	2.89
0.4	2.76	3.63
0.5	2.30	4.35
0.6	1.94	5.15
0.7	1.68	5.95
0.8	1.48	6.78
0.9	1.31	7.61
1.0	1.17	8.52
$k_{29} = 7.89 \pm 0.30 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-9. Rate of disappearance of 3,4-(1,1,3,3-tetramethyltrimethylene)-1,2-xylene ($\sim\sim$) measured at 45.0°C in CH_3CN

Time, sec	$[\sim\sim] \times 10^4,$ mol L^{-1}	$[\sim\sim]^{-1} \times 10^{-3},$ L mol $^{-1}$
0.1	5.87	1.70
0.2	3.88	2.58
0.3	2.84	3.52
0.4	2.23	4.48
0.5	1.83	5.46
0.6	1.54	6.50
0.7	1.33	7.52
0.8	1.16	8.60
0.9	1.03	9.70
1.0	0.927	10.8
$k_{29} = 10.2 \pm 0.38 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

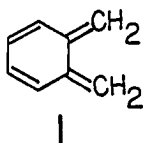
PART II. KINETIC AND PRODUCT STUDIES ON THE
DIMERIZATION OF α -METHYL-SUBSTITUTED
o-QUINODIMETHANES

INTRODUCTION

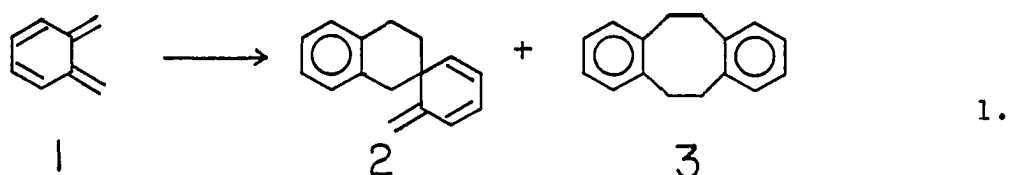
The mechanism of the Diels-Alder¹ (DA) reaction has been the subject of major interest for the past 60 years. Evidence for both concerted²⁻⁶ and stepwise^{5,6,7} mechanisms has been reported. Many [4+2]-cycloadditions are best described in terms of a symmetry-allowed one-step mechanism.⁶ In principle, however, a two-step mechanism cannot be ignored. The stereospecificity of many DA reactions suggest that they are concerted. However, it has been pointed out that the same would be true for a two-step mechanism if the intermediate biradicals or zwitterions collapse to the product faster than they isomerize by internal rotation.⁶

In addition to the "normal" and "reverse" DA reaction is the case in which the combination of two identical substrates leads to a DA-type dimer.⁶ For [4+2] dimerizations of this type, "neutral" DA reactions, a two-step reaction via a biradical intermediate should become energetically compatible.⁶ This expectation is due to the large HOMO-LUMO separation for the reactants of DA reactions of this type. A large HOMO-LUMO separation does not, however, guarantee a two-step mechanism.⁸

Our interest, within the context of this discussion, stems from our work with the dimerization of o-xylylene (1) and related systems.⁹ The dimerization of o-xylylene (1) at

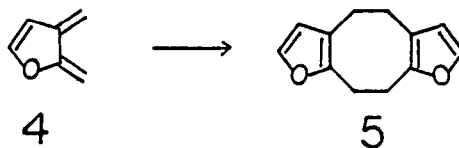


25.0°C in CH₃CN leads primarily to [4+2] dimer (2) (Reaction 1). This dimerization has been shown to occur very fast,



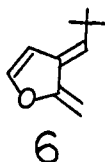
following second-order kinetics.^{9,10} A kinetic study on ring-substituted derivatives of 1 has shown that when undergoing dimerization the o-quinodimethane (o-QDM) monomers prefer a non-endo approach.⁹

It has also been shown that the [4+4] dimerization of 2,3-dihydro-2,3-dimethylenefuran (4), the furan analogue of 1, proceeds in a stepwise manner via a diradical intermediate (Reaction 2).¹¹ Detailed studies have shown that dimerization of 4 occurs slowly when bulky substituents are placed in the 3-exo-methylene position. The t-butyl derivative 6 is quite unreactive relative to 4. Solutions of 6 are stable for weeks



2.

at 10°C. However, bulky substituents on the 2-exo-methylene position do not significantly affect the dimerization rate of 4.¹² The rate determining step in the [4+4] dimerization of



4, then, clearly involves greater bond making in the 3-exo-methylene positions than in the 2-exo-methylene positions.

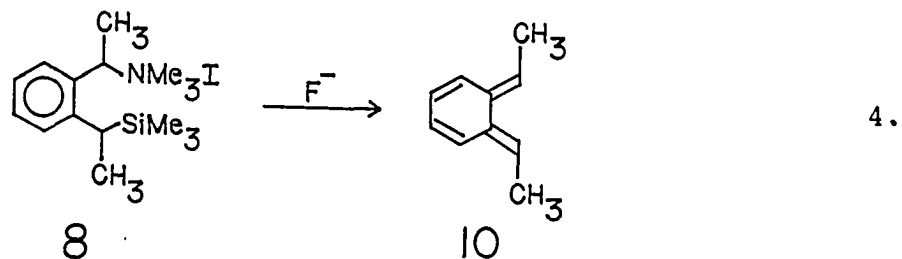
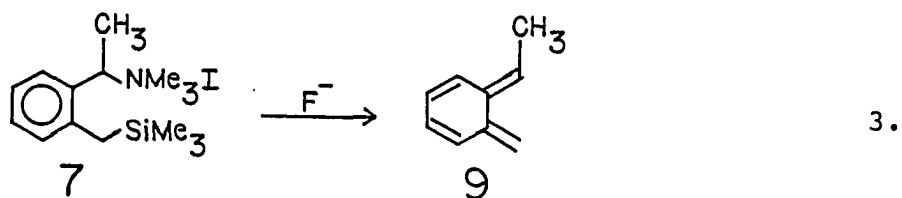
We were interested in obtaining similar information for the dimerization of o-xylylene (1). That is, what is the effect of placing alkyl substituents on the exo-methylene positions of 1? What will be the effect on the dimerization rate? What types of dimers will be isolated? And finally, could we obtain evidence for either a concerted or stepwise

mechanism for the dimerization of 1. Therefore, a kinetic study of the dimerization of α -methyl-substituted derivatives of 1 was undertaken.

RESULTS

[α -[α -((Trimethylsilyl)methyl)phenyl]ethyl]trimethylammonium iodide (**7**) and [α -[α -[α -(trimethylsilyl)ethyl]-phenyl]ethyl]trimethylammonium iodide (**8**) were prepared according to the procedure of Ito, Nakatsuka, and Saegusa.¹³ Iodide **8** existed as a 3:2 mixture of diastereomers.¹⁴

Treatment of CH₃CN solutions of **7** and **8** with tetra-*n*-butylammonium fluoride (CH₃CN solution), in a manner analogous to that described for α -xylylene (**1**),^{9,15} generated 5-ethylidene-6-methylene-1,3-cyclohexadiene (**9**) and 5,6-bis-(ethylidene)-1,3-cyclohexadiene (**10**), respectively (reactions 3 and 4). Using trapping experiments Ito et al. have shown



that α -alkyl and α,α' -dialkyl \underline{o} -QDMs exist exclusively in the (E)- $\underline{\alpha}$ and (E,E)- $\underline{\alpha},\underline{\alpha}'$ stereochemistry, respectively.¹³

McCullough and co-workers have shown that \underline{o} -QDMs with α -methyl groups oriented inward do not lead to dimers but rather decay by a facile 1,5-hydrogen shift.¹⁶ The λ_{max} and ϵ_{max} values for $\underline{9}$ and $\underline{10}$ were determined as previously described for \underline{o} -xylylene ($\underline{1}$)¹⁵ and these data are reported in Table 1.

Kinetic Study of the Effect of α -Methyl Substitution on the Dimerization Rate of \underline{o} -Xylylene ($\underline{1}$)

Rate constants, k 's, for the dimerization of $\underline{9}$ and $\underline{10}$ were determined from the second-order rate law of a single reactant. Kinetic experiments involving \underline{o} -QDMs $\underline{9}$ and $\underline{10}$ were carried out using the stopped-flow technique^{15,17} as previously described for \underline{o} -xylylene ($\underline{1}$). In Figure 1, a scaled UV-visible plot ($\lambda = 377$ nm) of absorbance versus time for the generation and decay (dimerization) of $\underline{9}$ at 25°C is presented. Figure 2 shows a similar plot ($\lambda = 381$ nm) for $\underline{10}$.

Rate constants for the dimerization of $\underline{9}$ from 27.8 to 45.0°C, and for $\underline{10}$ from 45.0°C to 60.6°C were measured and these are reported in Table 2, along with rate constants previously determined for the dimerization of $\underline{1}$.⁹ Kinetic experiments involving $\underline{10}$ were carried out at elevated temperatures because it was found that reaction 4 did not occur rapidly at 25°C. However, above 40°C this reaction was well-behaved.

Table 1. UV-visible data for 5-ethylidene-6-methylene-1,3-cyclohexadiene (9) and 5,6-bis(ethylidene)-1,3-cyclohexadiene (10) at 25.0°C in CH₃CN

<u>o</u> -QDM	λ_{max} , nm	ϵ_{max}
<u>9</u>	377	3020
<u>10</u>	384	2600

Table 2. Second-order rate constants for the dimerization of o-xylylene (1), 5-ethylidene-6-methylene-1,3-cyclohexadiene (9), and 5,6-bis(ethylidene)-1,3-cyclohexadiene (10) in CH₃CN^a

Temp, °C	$k_1 \times 10^{-3}$, $\text{L mol}^{-1} \text{s}^{-1}$	$k_9 \times 10^{-3}$, $\text{L mol}^{-1} \text{s}^{-1}$	$k_{10} \times 10^{-3}$, $\text{L mol}^{-1} \text{s}^{-1}$
25.0	9.94±0.32	(5.85±0.15)	(0.158±0.004)
27.8	-	6.05±0.15	-
34.9	-	8.90±0.19	-
35.0	12.1±0.41	-	-
45.0	15.4±0.51	10.8±0.15	6.02±0.17
53.3	-	-	8.73±0.22
60.6	-	-	14.2±0.18

^aFor all reactions the concentration of TBAF was 5.00×10^{-2} M and the concentration of 1, 9, or 10 was 5.00×10^{-4} M. Rate constants were obtained from an average of at least five kinetic runs (calculated values).

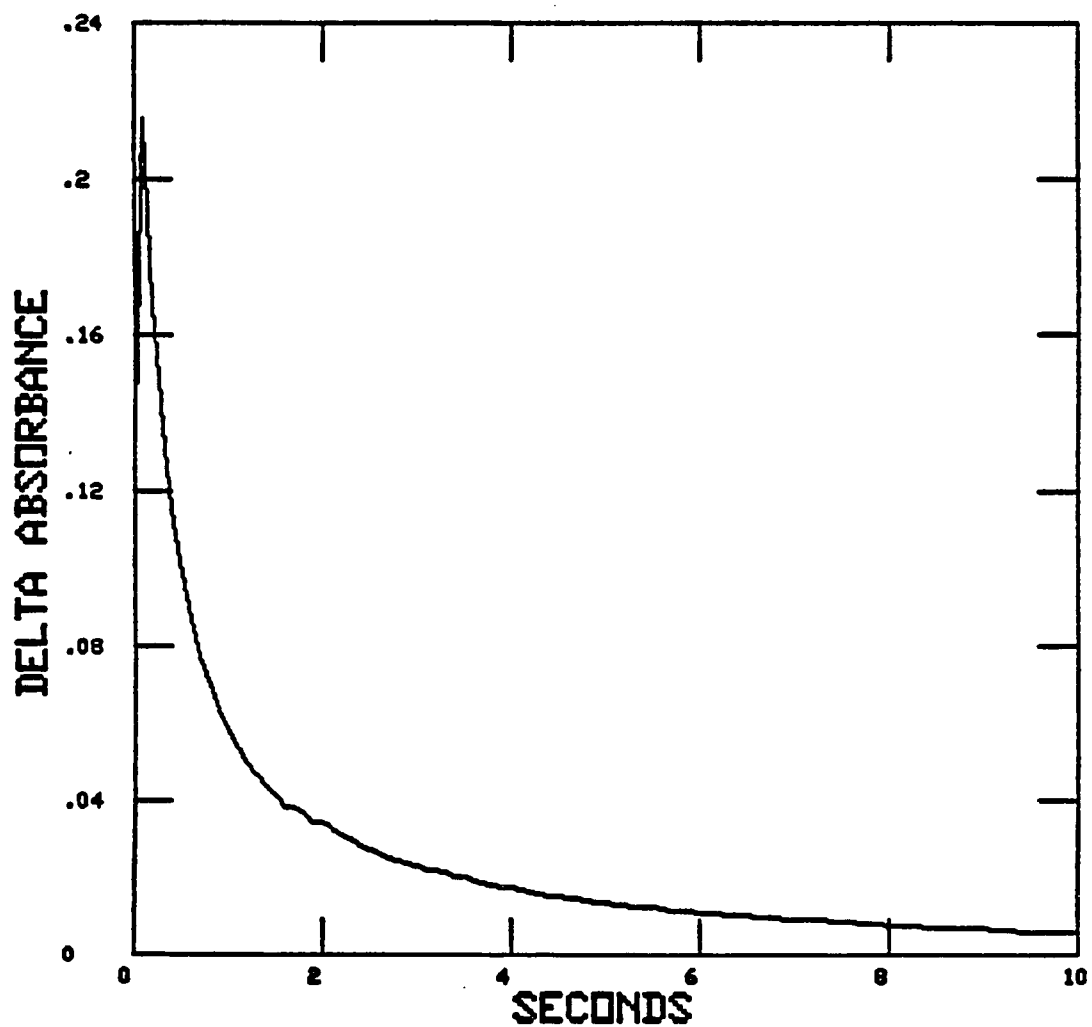


Figure 1. Scaled UV-visible plot ($\lambda = 377$ nm) of absorbance versus time for the generation and decay (dimerization) of 5-ethylidene-6-methylene-1,3-cyclohexadiene (9) at 27.8°C

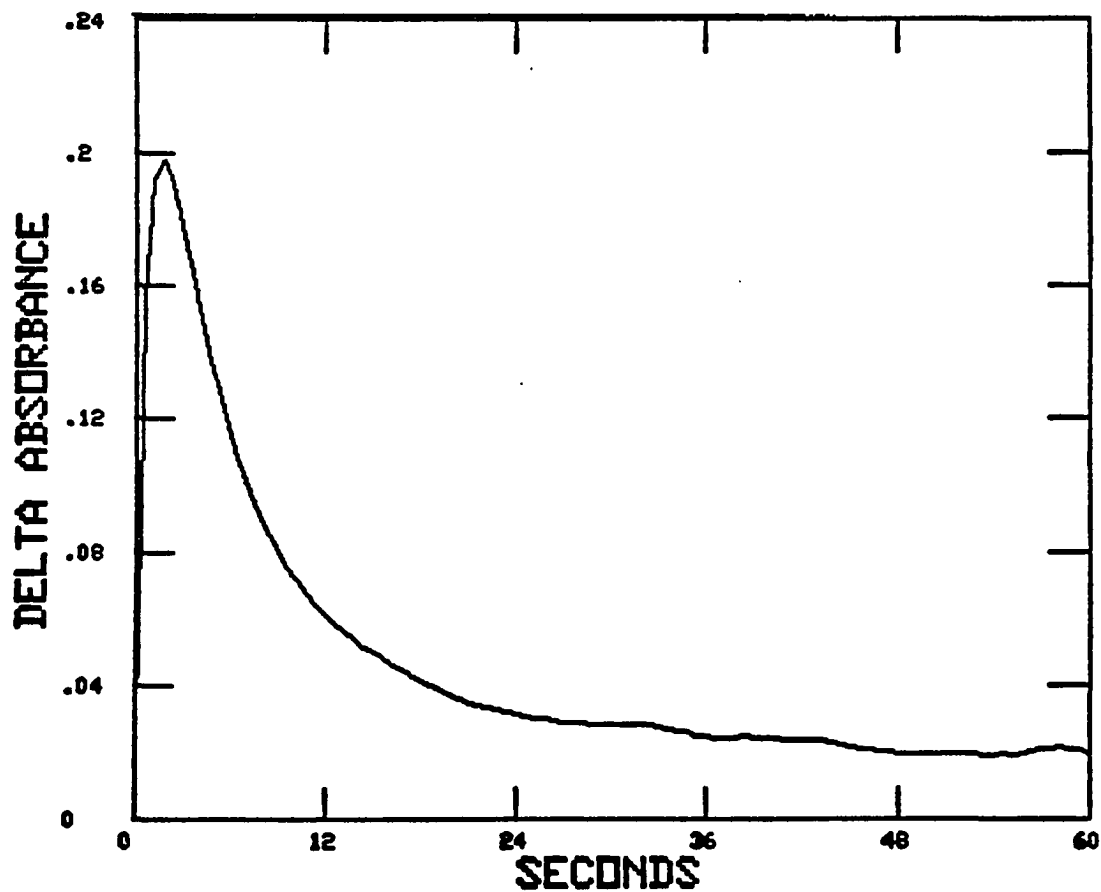


Figure 2. Scaled UV-visible plot ($\lambda = 381$ nm) of absorbance versus time for the generation and decay (dimerization) of 5,6-bis(methylene)-1,3-cyclohexadiene (10) at 45°C

Enthalpies of activation, ΔH^\ddagger 's for the dimerization of 9 and 10 were determined by their relation to the corresponding E_a 's ($\Delta H^\ddagger = E_a - RT$) which were obtained from Arrhenius plots.¹⁷ Entropies of activation, ΔS^\ddagger 's, were determined using the Eyring equation.¹⁷ These data are listed in Table 3 along with data previously determined for o-xylylene (1).⁹

Dimerization of 9 produced a complex mixture of dimers as evidenced by GC and GC/MS analyses. The instability of these dimers made it difficult to analyze the mixture fully. However, the ¹H NMR (Appendix, Figure 1) showed that the dimerization of 9 led predominantly to one [4+2] stereoisomer (11) of a possible 16 (each a racemate). The "E" stereochemistry of 9 should result in a [4+2] dimer of 9 with "E" stereochemistry about the exo-methylene double bond reducing this number to eight (each a racemate). We have determined that 11 has the constitution shown below based on the

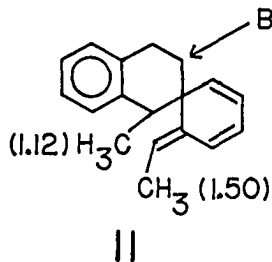


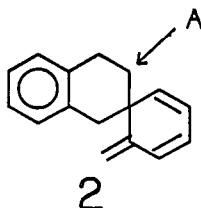
Table 3. Activation parameters^a for the dimerization of o-xylylene (1), 5-ethylidene-6-methylene-1,3-cyclohexadiene (9), and 5,6-bis(ethylidene)-1,3-cyclohexadiene (10)

<u>o</u> -QDM	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal k ⁻¹ mol ⁻¹
<u>1</u>	3.5±0.13	-29±1.1
<u>9</u>	5.4±0.24	-23±1.0
<u>10</u>	10.7±0.47	-13.8±0.69

^aAll values calculated at 25°C.

following. Firstly, irradiation of a doublet at δ 1.50 caused a quartet centered at 5.08 to collapse to a singlet (Appendix, Figure 2). Irradiation of the quartet at 5.08 caused the doublet at 1.50 to collapse to a singlet (Appendix, Figure 3). These results establish that the major dimer (11) has a methyl group on its exo-methylene carbon. Secondly, irradiation of a doublet at 1.12 caused a multiplet from 2.81 to 2.55 to simplify to a singlet and a multiplet (Appendix, Figure 4). This establishes that dimer 11 has a methyl group on the methylene bridge of its central ring.

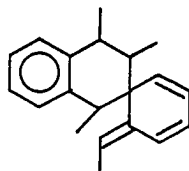
A comparison with the ¹H NMR spectrum (Appendix, Figure 5) of the known¹⁸ [4+2] dimer (2) of o-xylylene (1) corroborates these results. The non-benzylic protons of the central ring of 2 (marked "A") appear as separate multiplets. The upfield proton can clearly be resolved into eight peaks which result



from coupling with three different protons. The non-benzylic protons of the central ring of 11 (marked "B") also exist as separate multiplets. In this case the downfield proton can clearly be resolved into eight peaks. This observation is consistent with this proton being coupled to three different protons, as was observed for 2. This would not be the case if there existed a methyl group on or adjacent to the "B" protons.

Dimerization of 10 led also to a complex mixture of dimers as indicated by GC and GC/MS analyses. The ^1H NMR of this dimer mixture (Appendix, Figures 6-8) indicated the formation of predominantly one [4+2] stereoisomer (12) of a possible 16 (each a racemate). Again, fixing "E" stereochemistry about the exo-methylene double bond reduces this to eight possible dl pairs.

^1H NMR integrations indicate that 11 and 12 comprise between 65-80% of their respective dimer mixtures. In neither



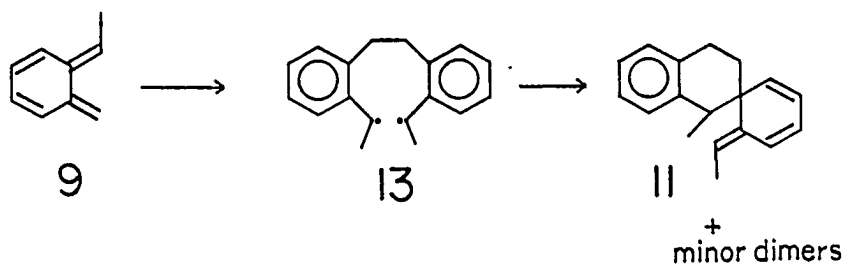
12

case were [4+4] dimers identified. However, because of the complexity of the ^1H NMRs of 11 and 12, [4+4] dimer yields of less than 5-10% would be difficult to identify.

DISCUSSION

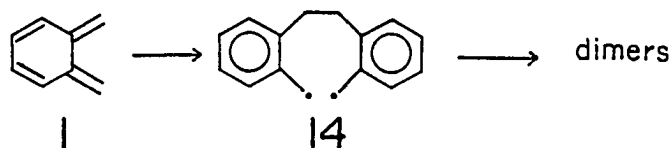
The dimerization rate of 5-ethylidene-6-methylene-1,3-cyclohexadiene (9) is very similar to that of o-xylylene (1), with $k_9/k_1 = 0.59$ at 25.0°C. The dimerization rate of 5,6-bis(ethylidene)-1,3-cyclohexadiene (10) is much slower than that observed either for 1 or 9, with $k_{10}/k_1 = 0.016$ at 25.0°C. This would appear to be evidence for a two-step mechanism. Consider the following analysis. The dimerization rate of 9 being similar to that of 1 is consistent with the formation of diradical 13 in the rate determining step (Scheme 1). The formation of diradical 13 is analogous to the formation of diradical 14 (Scheme 2) in that two unsubstituted exo-methylene carbons couple to form a diradical. These two processes should and do have similar rate constants and activation parameters (see Tables 2 and 3). The rate constant

Scheme 1



for the dimerization of 9 includes a probability factor of 1/4 relative to 1. This factor arises from the fact that 9 has one reactive site while 1 can dimerize by initial bond-formation at either of two exo-methylene carbons. When this factor is considered the rate constant for dimerization of 9 at 25.0°C is actually larger than that for 1. This may be due to a slight rate enhancement for the dimerization of 9 resulting from additional delocalization of diradical 13 relative 14.

Scheme 2



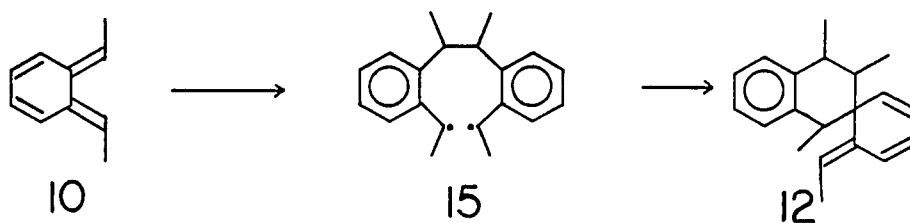
Either of the concerted modes shown below (reactions 5 and 6) would have one methyl group attached to a bond-making site in the transition state which would be expected to retard the dimerization rate of 9 relative to 1. Furthermore, dimer 11, which is the major product derived from the dimerization of 9, must arise either from diradical 13 or from the concerted mode



shown in reaction 6. It is not clear that this mode is favored to any significant extent over the one shown in reaction 5, which would lead to a dimer with a constitution other than that of 11.

It is not surprising that the dimerization rate of $\underline{10}$ is much slower than that of $\underline{1}$ or $\underline{9}$, since in going to diradical $\underline{15}$, steric repulsions between two methyl groups at the initial bond-making site are inevitable (Scheme 3). Indeed, this is reflected in the higher ΔH^\ddagger observed for the dimerization of $\underline{10}$ relative to $\underline{1}$ or $\underline{9}$.

Overall, the data seem to indicate that a stepwise mechanism for the dimerization of benzenoid o-QDMs is

Scheme 3

operating. However, a concerted mechanism cannot be rigorously ruled out.

EXPERIMENTAL

General

Some general methods have been described.^{9,15} UV-visible spectra were recorded on Perkin-Elmer 7000 Lambda-array or Canterbury SF3A spectrophotometers. *n*-BuLi, methyl iodide, and chlorotrimethylsilane were purchased from Aldrich Chemical Co. Benzene-d₆ was purchased from Stohler Isotope Chemicals.

[α -[*o*-((Trimethylsilyl)methyl)phenyl]ethyl]trimethylammonium iodide (7)

A 10.4 g (87 mmol) quantity of *o*-tolualdehyde was converted to 7 in 50% overall yield by the five step procedure of Ito, Nakatsuka, and Saegusa¹³: mp 167.5-170°C [lit.¹³ mp 168-170°C dec]; ¹H NMR (CD₃CN) δ 7.25-6.68 (m, 4 H), 4.62 (q, 1 H, *J* = 6.6 Hz), 2.72 (s, 9 H), 2.12 (AB quartet, 2H, *J* = 12.9 Hz), 1.51 and 1.41 (dt, 3 H, *J* = 6.9 Hz, 1.6 Hz), -0.18 (s, 9 H) [lit.¹³ NMR (CD₃CN) δ 7.3-6.7 (m, 4 H), 4.64 (q, 1 H, *J* = 6.7 Hz), 2.74 (s, 9 H), 2.12 (dd, AA' type, 2 H), 1.52 and 1.41 (dt, 3 H, *J* = 3.8 Hz), -0.21 (s, 9 H)].

[α -[*o*-[α -(Trimethylsilyl)ethyl]phenyl]trimethylammonium iodide (8)

A 1.25 g (5.32 mmol) quantity of [α -[*o*-((trimethylsilyl)methyl)phenyl]ethyl]dimethylamine was converted to 8 in two steps (43% yield) by the procedure of Ito, Nakatsuka, and Saegusa¹³: mp 172-181°C dec [lit.¹³ 174-182°C dec]; ¹H NMR

(CDCl₃) (3:2 diastereomeric mixture) δ 7.27-6.62 (m, 4 H), 5.13-4.37 (m, 1 H), 2.65 (br s, 9 H), 2.60-2.05 (m, 1 H), 1.61-1.33 (m, 3 H), 1.10 and 0.92 (d, 3 H, $J = 7.2$ Hz), -0.10 and -0.22 (s, 9 H) [lit.¹³ NMR (CD₃CN) (SiMe₄ as an external reference) (3:2 diastereomeric mixture) δ 7.3-6.6 (m, 4 H), 5.1-4.4 (m, 1 H), 2.67 (br s, 9 H), 2.6-2.0 (m, 1 H), 1.6-1.3 (m, 3 H), 1.10 and 0.90 (d, 3 H, $J = 7.2$ Hz), -0.09 and -0.27 (s, 9 H).

Dimers obtained from 5-ethylidene-6-methylene-1,3-cyclohexadiene (9)

To a solution of 7 (126 mg, 0.33 mmol) in 2 mL of CH₃CN was added a solution of TBAF (150 mg, 0.57 mmol) in 4 mL of CH₃CN. The reaction mixture was allowed to stir at room temperature for 1 h. Excess CH₃CN was removed under reduced pressure and the residue was triturated with ether, precipitating a white solid. The precipitate was removed by filtration and the organic product mixture was purified by passing it through a short column of silica gel (ether elution). The solvent was removed yielding 31.5 mg (0.13 mmol) of a mixture of dimers dominated by one major component (81%): ¹H NMR (C₆D₆) (Appendix, Figure 1) (major dimer) δ 7.15-6.95 (m, 4 H), 6.35 (d, 1 H, $J = 9$ Hz), 5.88-5.74 (m, 3 H), 5.08 (q, 1 H, $J = 7.5$ Hz), 2.81-2.55 (m, 3 H), 1.84-1.95 (m, 1 H), 1.66-1.57 (m, 1 H), 1.50 (d, 3 H, $J = 7.5$ Hz), 1.12 (d, 3 H, $J = 7.5$ Hz); GC/MS (70 eV) (% base peak) 236.10

(33.85), 130.04 (100.00), 119.06 (52.95), 117.04 (93.03),
115.02 (36.80), 91.02 (43.24).

Dimers obtained from 5,6-bis(ethylidene)-1,3-cyclohexadiene
(10)

A 110 mg (0.28 mmol) quantity of [α -[α -[α -(trimethylsilyl)ethyl]phenyl]ethyl]trimethylammonium iodide (8) was converted to a mixture of dimers of 10 (30.7 mg, 0.11 mmol, 83%) in a manner analogous to that used for the preparation of dimers of 5-ethylidene-6-methylene-1,3-cyclohexadiene (9): ^1H NMR (CD_3Cl) (Appendix, Figures 6-8) (major dimer) δ 7.47-6.92 (m, 4 H), 6.48 (br d, 1 H, $J = 9.6$ Hz), 5.96-5.84 (m, 2 H), 5.76-5.68 (br d, 1 H, $J = 10.5$ Hz), 5.39 (q, 1 H, $J = 7.5$ Hz), 2.79-2.66 (m, 2 H), 1.90 (d, 3 H, $J = 7.5$ Hz), 1.48 (d, 3 H, $J = 7.3$ Hz), 1.03 (d, 3 H, $J = 7.5$ Hz), 0.97 (d, 3 H, $J = 7.3$ Hz); GC/MS (70 eV) m/e (% base peak) 264.14 (7.80), 235.06 (27.55), 193.04 (16.18), 133.06 (78.18), 132.06 (50.09), 131.04 (57.00), 117.04 (100.00), 115.04 (31.50), 105.02 (16.89), 91.02 (38.64).

Determination of rate constants, k 's, for the dimerization of
5-ethylidene-6-methylene-1,3-cyclohexadiene (9) and
5,6-bis(ethylidene)-1,3-cyclohexadiene (10)

Kinetic experiments involving α -QDMs 9 and 10 were carried out in a manner analogous to that described for α -xylylene^{9,15} (see Experimental, Part I, of this thesis.¹⁵

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15. See Experimental, Part I of this thesis for λ_{max} determination procedure and Appendix, Part I for ϵ_{max} determination procedure.
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APPENDIX

Figure 1. ^1H NMR (300 MHz) spectrum (C_6D_6) of the major [4+2] dimer 11 (and minor dimers) of 5-ethylidene-6-methylene-1,3-cyclohexadiene (9) ⁶⁶

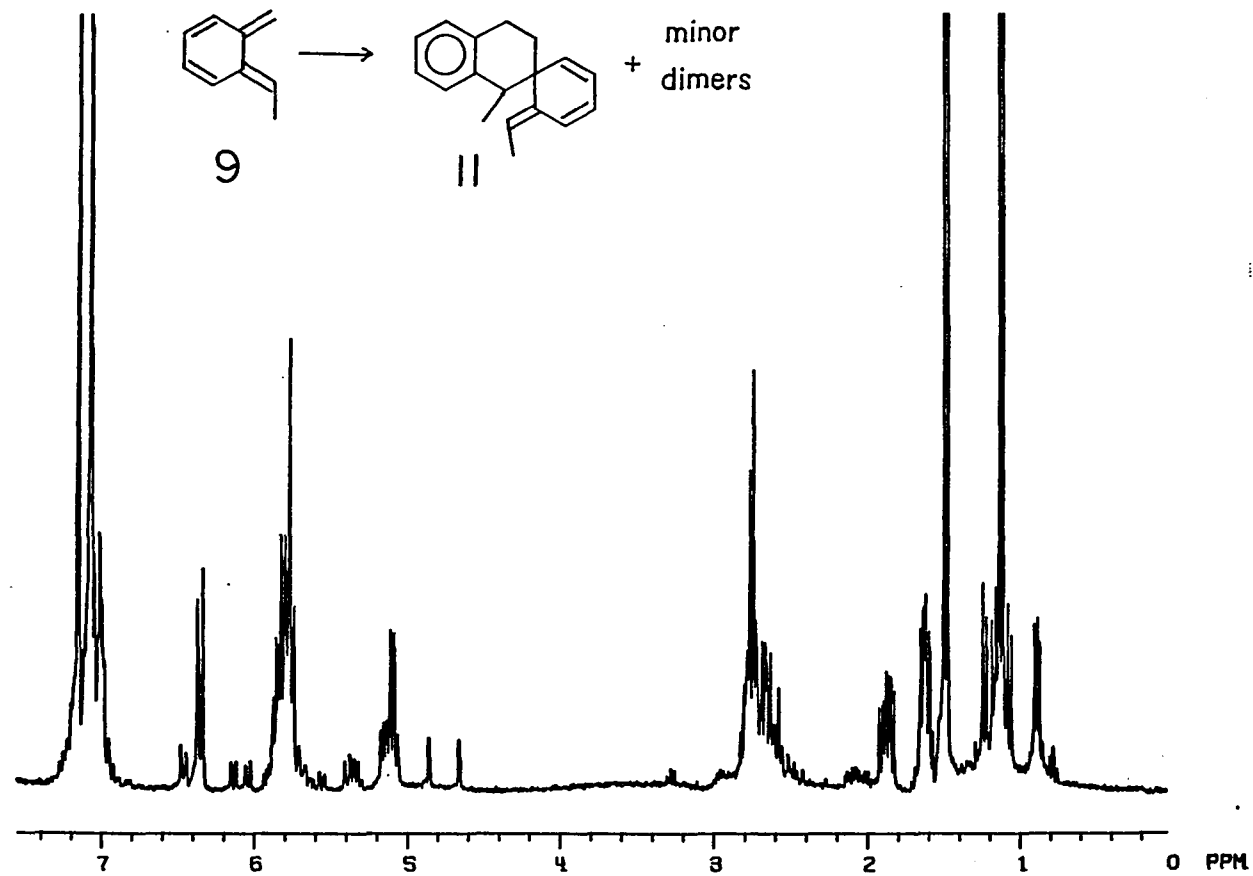


Figure 2. Closeup of the olefinic region of the ^1H NMR (300 MHz) spectrum (C_6D_6) of the major [4+2] dimer 11 (and minor dimers)⁶ obtained from 5-ethylidene-8-methylene-1,3-cyclohexadiene (9): a) spin-spin decoupled with irradiation at $\delta = 1.50$, b) normal

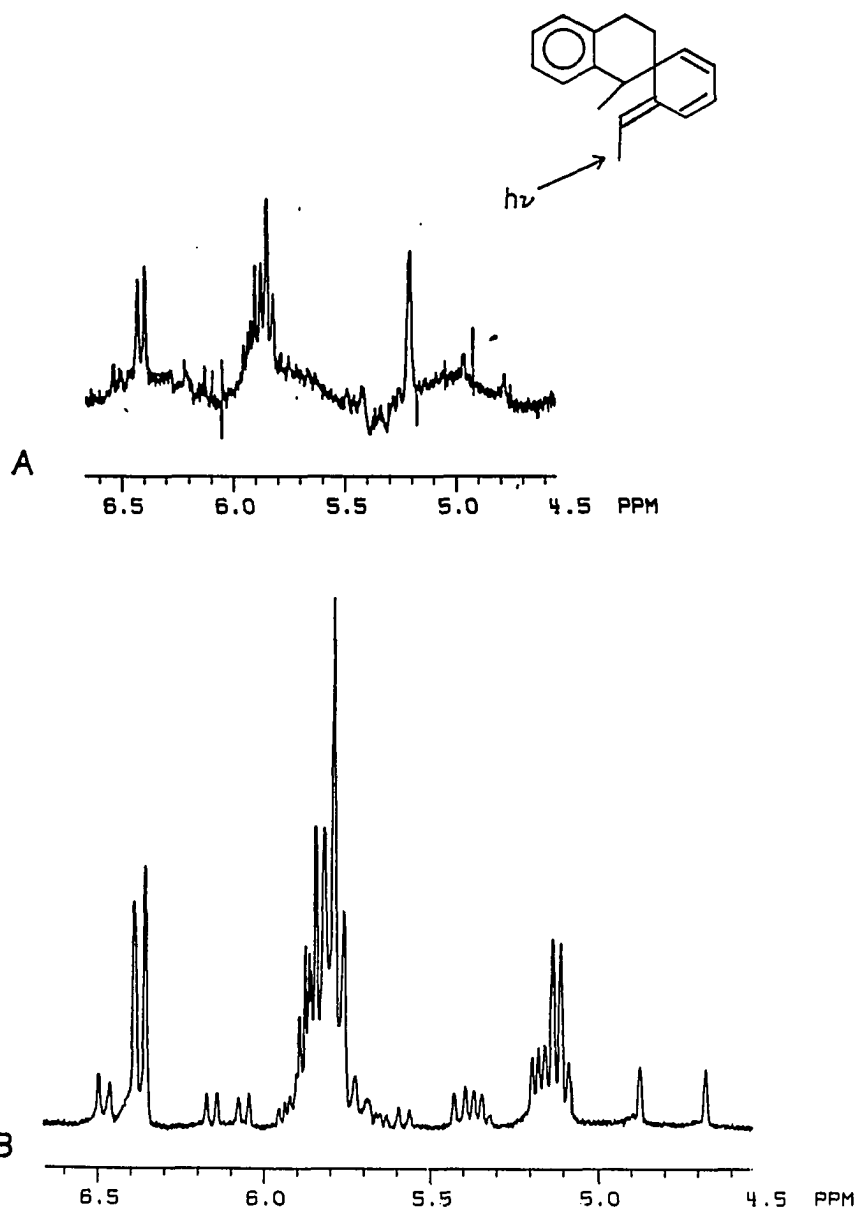


Figure 3. Closeup of the aliphatic region of the ^1H NMR (300 MHz) spectrum (C_6D_6) of the major [4+2] dimer 11 (and minor dimers) of 5-ethylidene-6-methylene-1,3-cyclohexadiene (9): a) spin-spin decoupled with irradiation at $\delta = 5.08$, b) normal

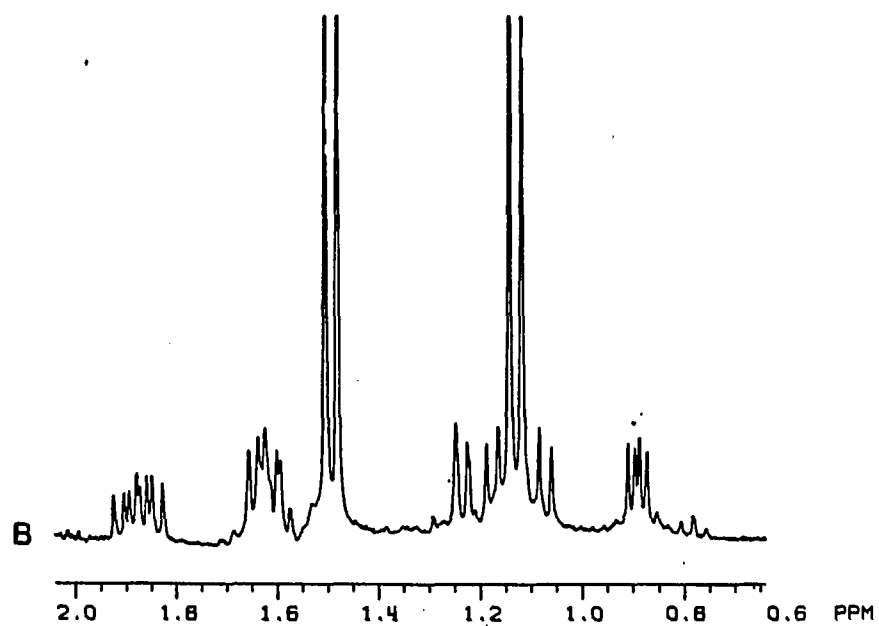
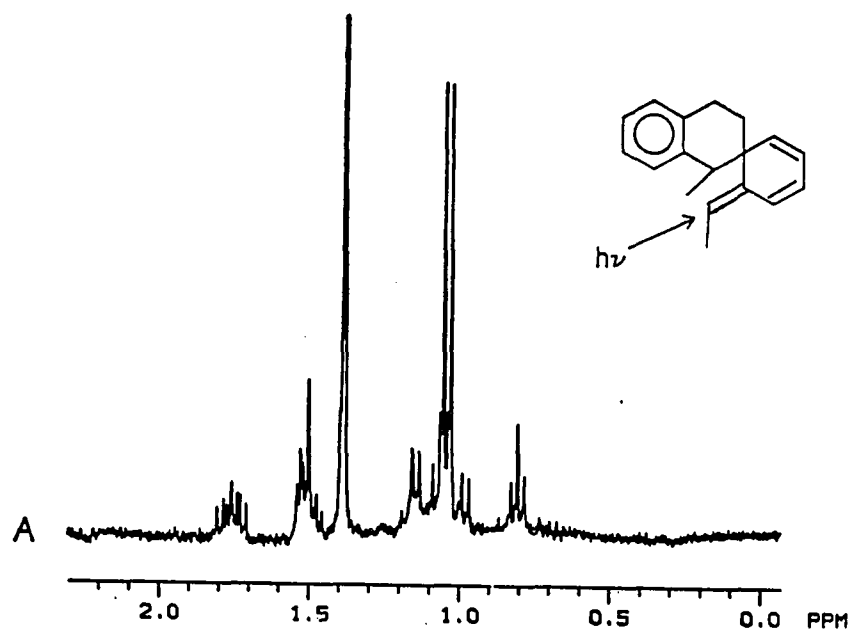


Figure 4. Closeup of the benzylic region of the ^1H NMR (300 MHz) spectrum (C_6D_6) of the major [4+2] dimer 11 (and minor dimer 8) obtained from 5-ethylidene-2-methylene-1,3-cyclohexadiene (9): a) spin-spin decoupled with irradiation at $\delta = 1.12$, b) normal

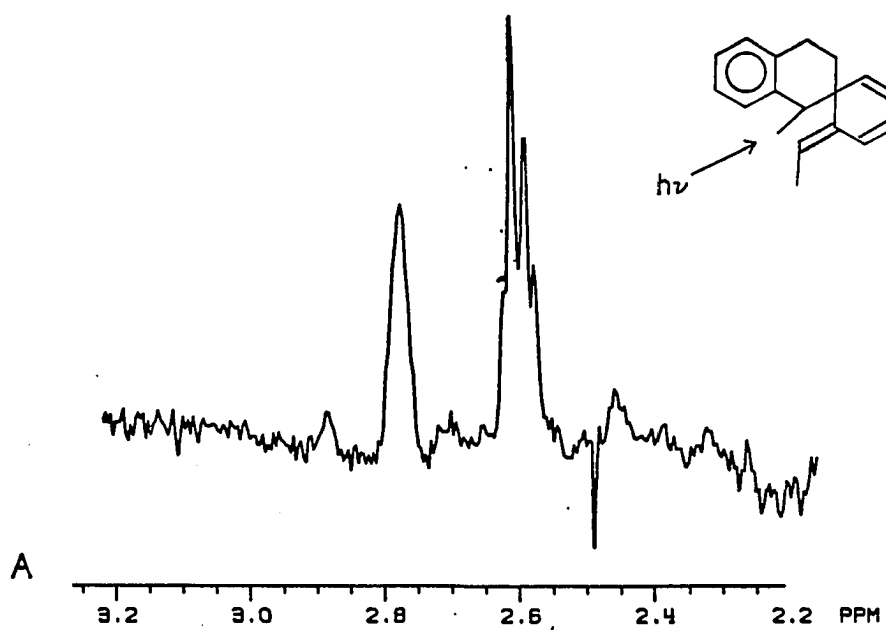


Figure 5. ^1H NMR (300 MHz) spectrum (C_6D_6) of spiro-(5,5)-2,3-benz-o-methylene-undeca-7,9-diene (2) and tetrahydrodibenzo[a,3]cyclooctene (3) (* = 3)

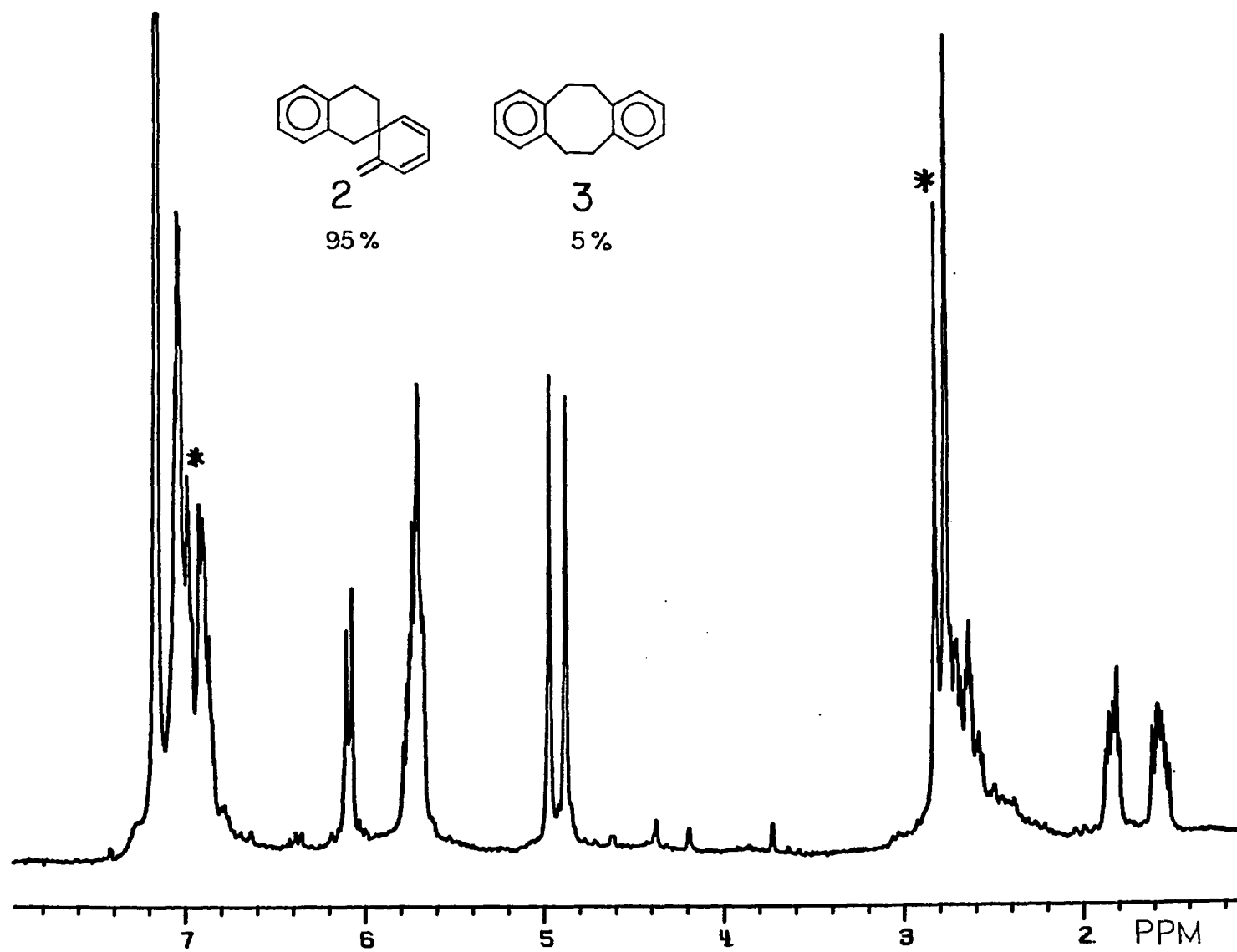


Figure 6. ^1H NMR (300 MHz) spectrum (CDCl_3) of the major [4+2] dimer 12 (and minor dimers) of 5,6-bis(ethylidene)-1,3-cyclohexadiene (10)

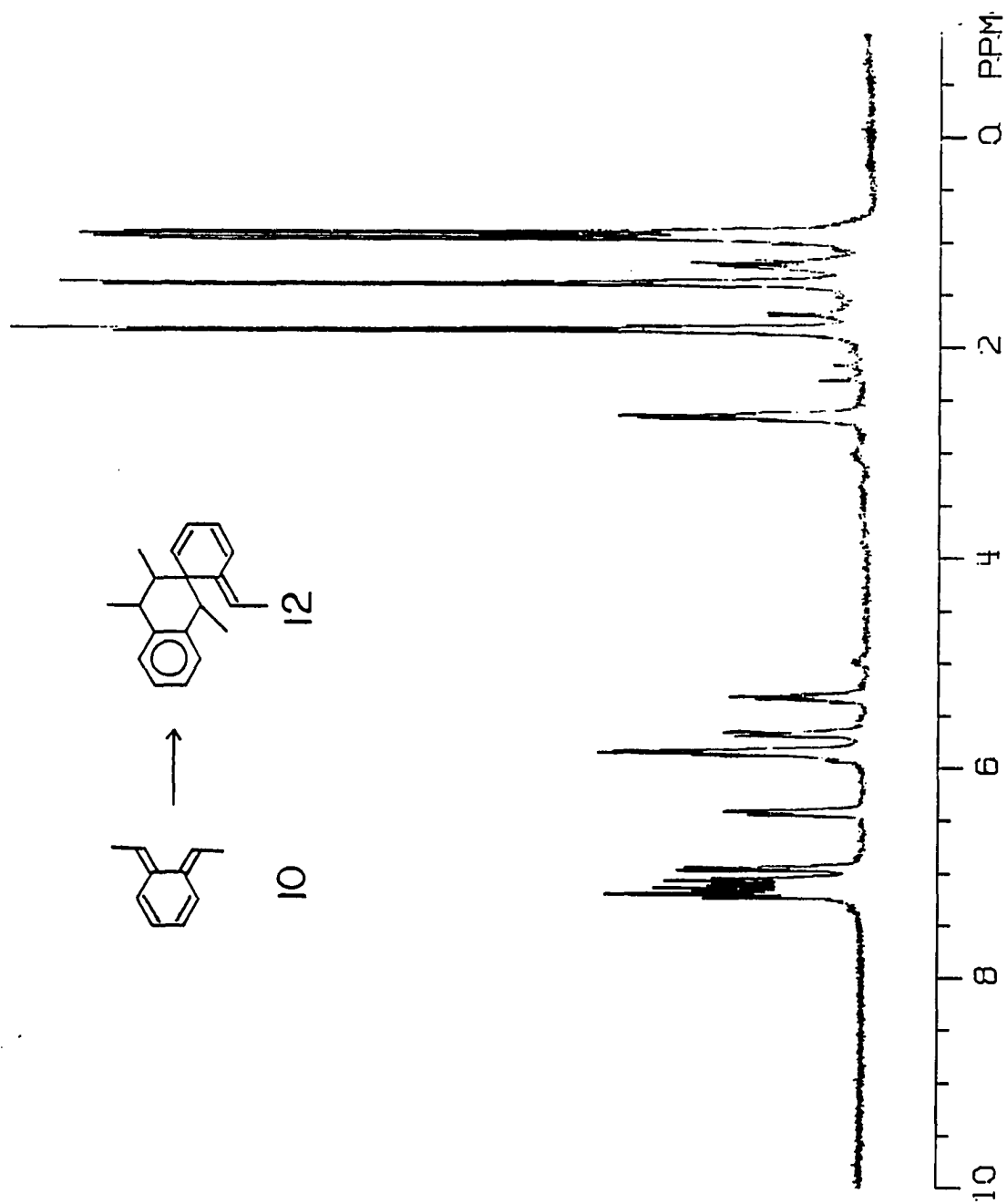


Figure 7. Closeup of the aliphatic region of the ^1H NMR (300 MHz) spectrum (CDCl_3) of the major [4+2] dimer 12 (and minor dimers) of 5-ethylidene-6-methylene-1,3-cyclohexadiene (10)

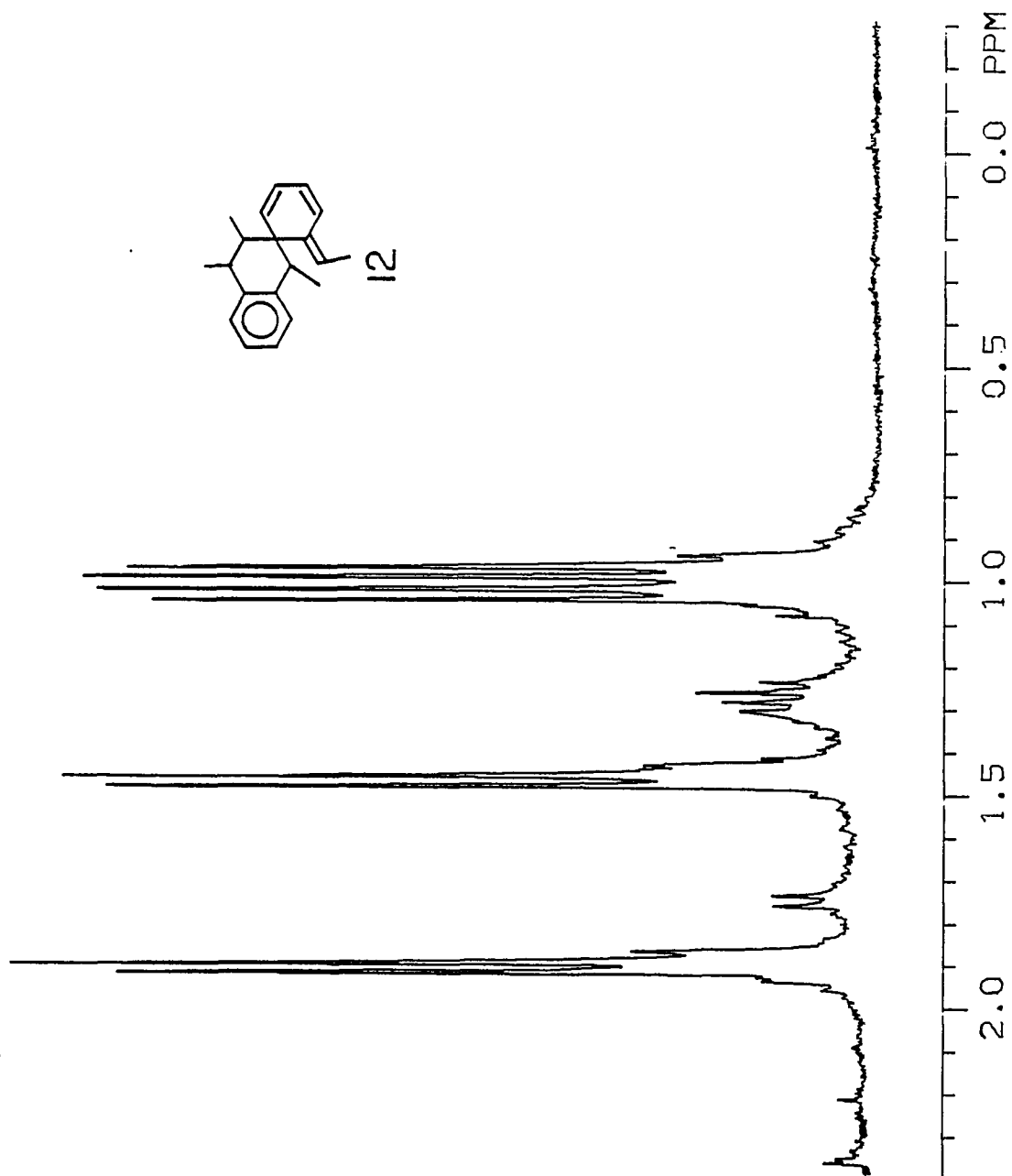
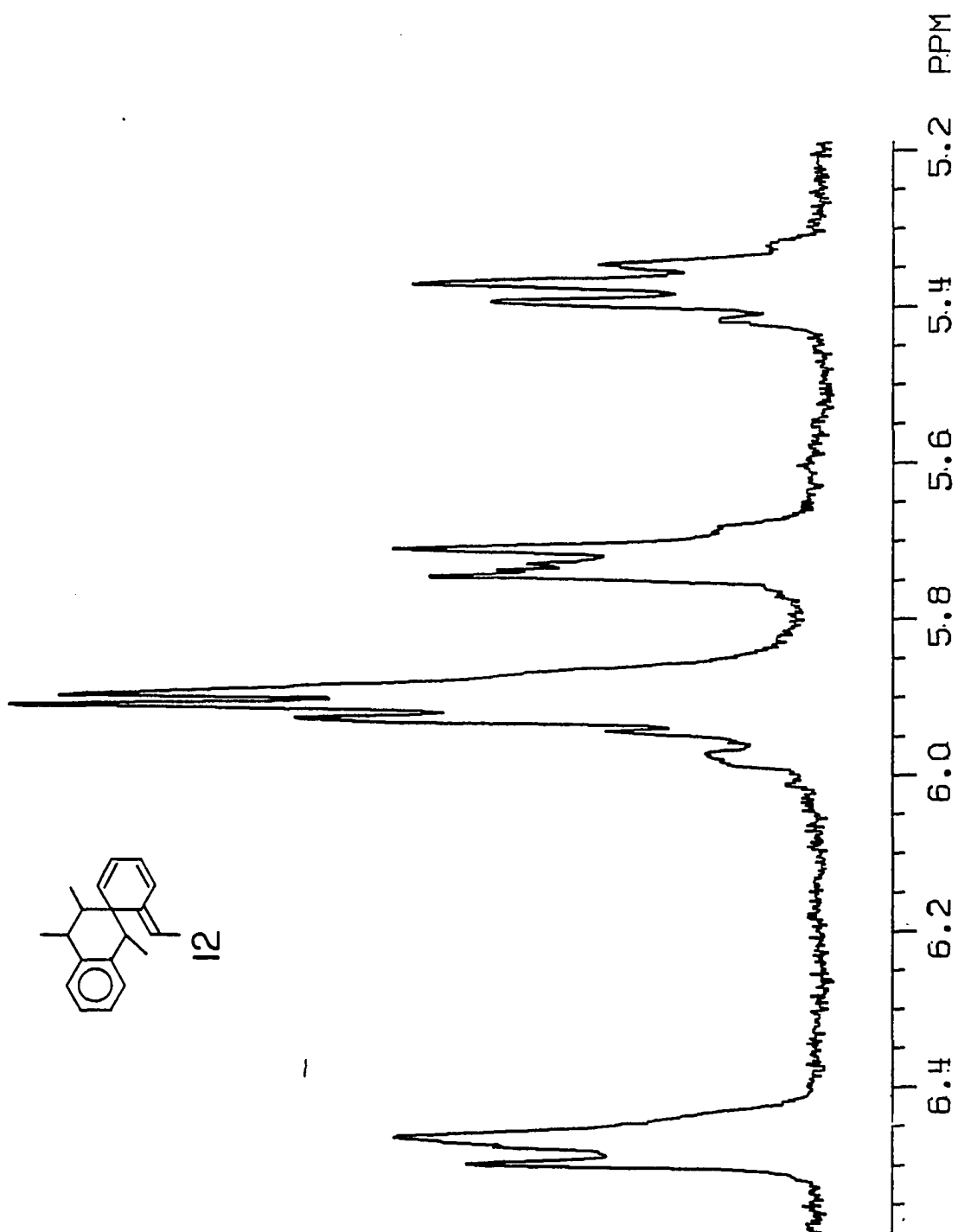


Figure 8. Closeup of the olefinic region of the ^1H NMR (300 MHz) spectrum (CDCl_3) of the major [4+2] dimer $\underline{12}$ (and minor dimers) of 5,6-bis(ethylidene)- $\underline{10}$ 1,3-cyclohexadiene ($\underline{10}$)



Data of Kinetic Study

Table A-1. Rate of disappearance of 5-ethylidene-6-methylene-1,3-cyclohexadiene ($\bar{9}$) measured at 27.8°C in CH₃CN

Time, min	$[\bar{9}] \times 10^4,$ mol L ⁻¹	$[\bar{9}]^{-1} \times 10^{-3},$ L mol ⁻¹
0.1	4.08	2.45
0.2	3.39	2.95
0.3	2.76	3.62
0.4	2.35	4.26
0.5	2.03	4.91
0.6	1.81	5.54
0.7	1.62	6.16
0.8	1.48	6.77
0.9	1.35	7.38
$k = 6.26 \pm 0.15 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-2. Rate of disappearance of 5-ethylidene-6-methylene-1,3-cyclohexadiene ($\tilde{9}$) measured at 34.9°C in CH_3CN

Time, min	$[\tilde{9}] \times 10^4,$ mol L^{-1}	$[\tilde{9}]^{-1} \times 10^{-3},$ L mol^{-1}
0.1	4.12	2.43
0.2	3.10	3.23
0.3	2.49	4.01
0.4	2.09	4.79
0.5	1.81	5.54
0.6	1.60	6.26
0.7	1.42	7.02
0.8	1.30	7.71
0.9	1.19	8.40
$k = 7.47 \pm 0.19 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-3. Rate of disappearance of 5-ethylidene-6-methylene-1,3-cyclohexadiene (η) measured at 45.0°C in CH_3CN

Time, min	$[\eta] \times 10^4,$ mol L^{-1}	$[\eta]^{-1} \times 10^{-3},$ L mol
0.1	3.97	2.52
0.2	2.85	3.51
0.3	2.22	4.50
0.4	1.82	5.50
0.5	1.54	6.47
0.6	1.34	7.46
0.7	1.19	8.42
0.8	1.07	8.34
0.9	0.970	10.3
$k = 19.9 \pm 0.15 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-4. Rate of disappearance of 5,6-bis(ethylidene)-1,3-cyclohexadiene ($\sim\sim$) measured at 45.0°C in CH_3CN

Time, min	$[\sim\sim] \times 10^4,$ mol L ⁻¹	$[\sim\sim]^{-1} \times 10^{-3},$ L mol
3.0	3.32	3.01
3.6	3.05	3.27
4.2	2.78	3.60
4.8	2.54	3.93
5.4	2.33	4.30
6.0	2.13	4.70
6.6	1.96	5.09
7.2	1.81	5.52
7.8	1.67	5.96
$k = 6.19 \pm 0.17 \times 10^2 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-5. Rate of disappearance of 5,6-bis(ethylidene)-1,3-cyclohexadiene ($\sim\sim$) measured at 53.3°C in CH_3CN

Time, min	$[\sim\sim] \times 10^4,$ mol L ⁻¹	$[\sim\sim]^{-1} \times 10^{-3},$ L mol ⁻¹
1.8	3.92	2.55
2.4	3.32	3.01
3.0	2.83	3.54
3.6	2.44	4.09
4.2	2.14	4.67
4.8	1.91	5.23
5.4	1.73	5.78
6.0	1.58	6.31
6.6	1.46	6.84
$k = 9.01 \pm 0.22 \times 10^2 \text{ L mol}^{-1} \text{ sec}^{-1}$		

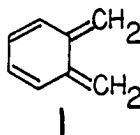
Table A-6. Rate of disappearance of 5,6-bis(ethylidene)-1,3-cyclohexadiene ($\sim\sim$) measured at 60.6°C in CH_3CN

Time min	$[\sim\sim] \times 10^4,$ mol L^{-1}	$[\sim\sim]^{-1} \times 10^{-3},$ L mol $^{-1}$
0.6	5.14	1.94
1.2	3.83	2.61
1.8	2.85	3.51
2.4	2.23	4.49
3.0	1.82	5.49
3.6	1.54	6.50
4.2	1.33	7.55
4.8	1.16	8.60
5.4	1.03	9.70
$k = 1.40 \pm 0.08 \times 10^3 \text{ L mol}^{-1} \text{ sec}^{-1}$		

PART III. DIRECT OBSERVATION OF 1,2-NAPTHOQUINODIMETHANE
AND 9,10-PHENANTHROQUINODIMETHANE. DIMERIZATION
KINETICS OF RESONANCE STABILIZED o-QUINODIMETHANES

INTRODUCTION

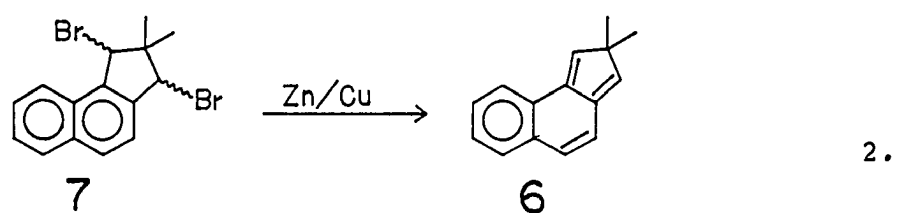
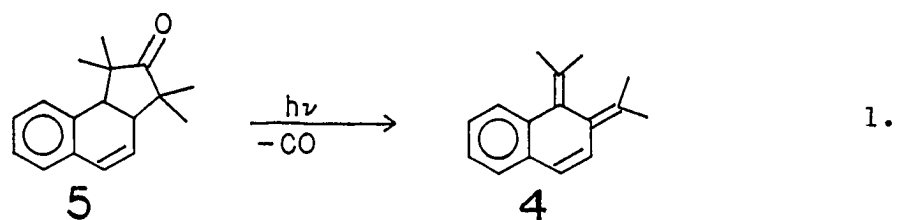
The study of o-quinodimethane-(o-QDM) type reactive molecules continues to be an active area of organic chemistry. Our own interest in the parent o-QDM, o-xylylene (1), has stimulated us to examine other systems of this type.¹ We were particularly interested in the effect of annulating benzene rings onto the parent structure.



Species such as 1,2-naphthoquinodimethane (2), and 9,10-phenanthroquinodimethane (3) are expected to be stabilized relative to 1 because of increased resonance energy.^{2,3,4} Gleicher and co-workers have reported, using SCF molecular orbital calculations, that 1 should be slightly antiaromatic, 2 should possess one-half the resonance energy of benzene, and 3 should show a delocalization approximately equal to twice that of benzene.³

Direct observation of 2 has not been reported⁵ although some derivatives of 2 have been observed. McCullough and co-workers have reported UV-visible data for 11,11,12,12-

tetramethyl-1,2-naphthoquinodimethane (4), generated by the photolysis of 1,1,3,3-tetramethyl-4,4-benzindan-2-one (5) (reaction 1).⁶

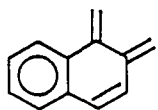
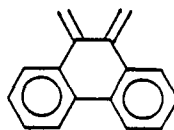


Dolbier generated 2,2-dimethyl-2H-benz[e]indene (6) by the debromination of 1,3-dibromo-2,3-dihydro-2,2-dimethyl-1H-benz[e]indene (7) (Reaction 2).⁷ o-QDM 6 was characterized by ^1H NMR.

9,10-Phenanthroquinodimethane (3) has been observed by UV-visible spectroscopy.⁸ The existence of 3 has also been

inferred from trapping experiments, and from isolation of the [4+2] dimer of 3.^{9,10,11}

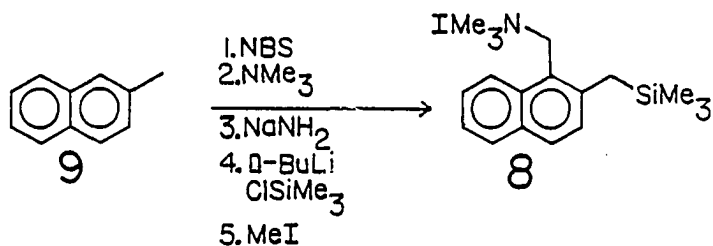
Given the predicted stabilities of 2 and especially of 3 it is surprising that the characterization of these species is

**2****3**

not more complete. Our recent success in the direct observation of o-xylylene (1) by a fluoride ion induced 1,4-elimination¹ led us to pursue the generation and observation of 2 and 3 using this methodology.

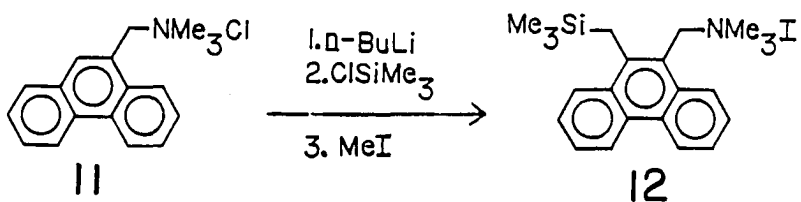
RESULTS

[2-(Trimethylsilylmethyl)]trimethyl-(1-naphthylmethyl)-
ammonium iodide (8) was synthesized in five steps from
2-methylnaphthalene (9) (Scheme 1). Trimethyl(10-trimethyl-
silylmethyl-9-phenanthrylmethyl)ammonium iodide (10) was
Scheme 1

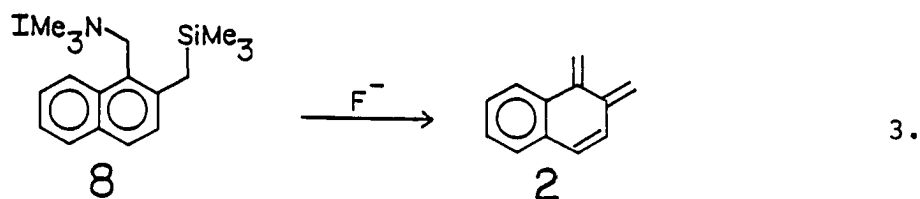


prepared in three steps from trimethyl(9-phenanthrylmethyl)-
ammonium chloride (11) (Scheme 2).

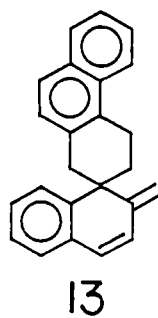
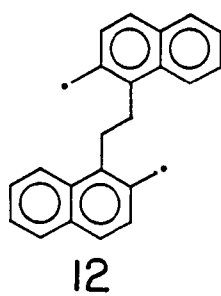
Scheme 2



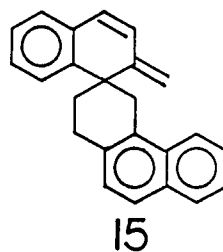
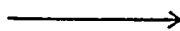
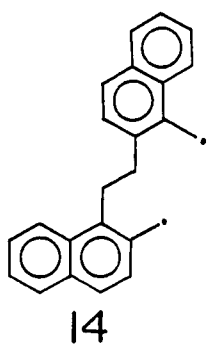
Treatment of an acetonitrile solution of **8** (10^{-3} M) with TBAF (CH_3CN solution, 10^{-1} M) generated 1,2-dimethylene-1,2-dihydronaphthalene (1,2-napthoquinodimethane) (**2**) (reaction 3).



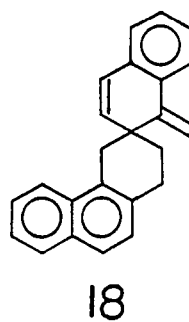
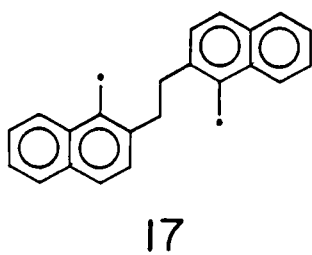
The decay of **2** leads to a complex mixture of [4+2] dimers as indicated by GC, GC/MS, and ^1H NMR (see Appendix, Figure 1). Analyses by GC and GC/MS indicated that at least three dimers were present. The thermal instability of these compounds made it impossible to determine relative dimer ratios. There are four conceivable [4+2] dimers (each a racemate) which may arise from dimerization of **2**, as shown below (reactions 4-6). No [4+4] dimers were observed for this system, as indicated by GC and GC/MS analyses. Diradicals **12**, **14**, and **17** would result from three different modes of coupling of the monomer **2**.¹² The ^1H NMR of the dimer mixture from **2** (Appendix, Figure 1) contains resonances in the region from δ 5.2 to 4.7, an area usually attributable to exo-methylene protons.¹⁰ When this dimer mixture was subjected to flash vacuum pyrolysis (FVP)¹³ conditions it was converted to a 1:1



4.

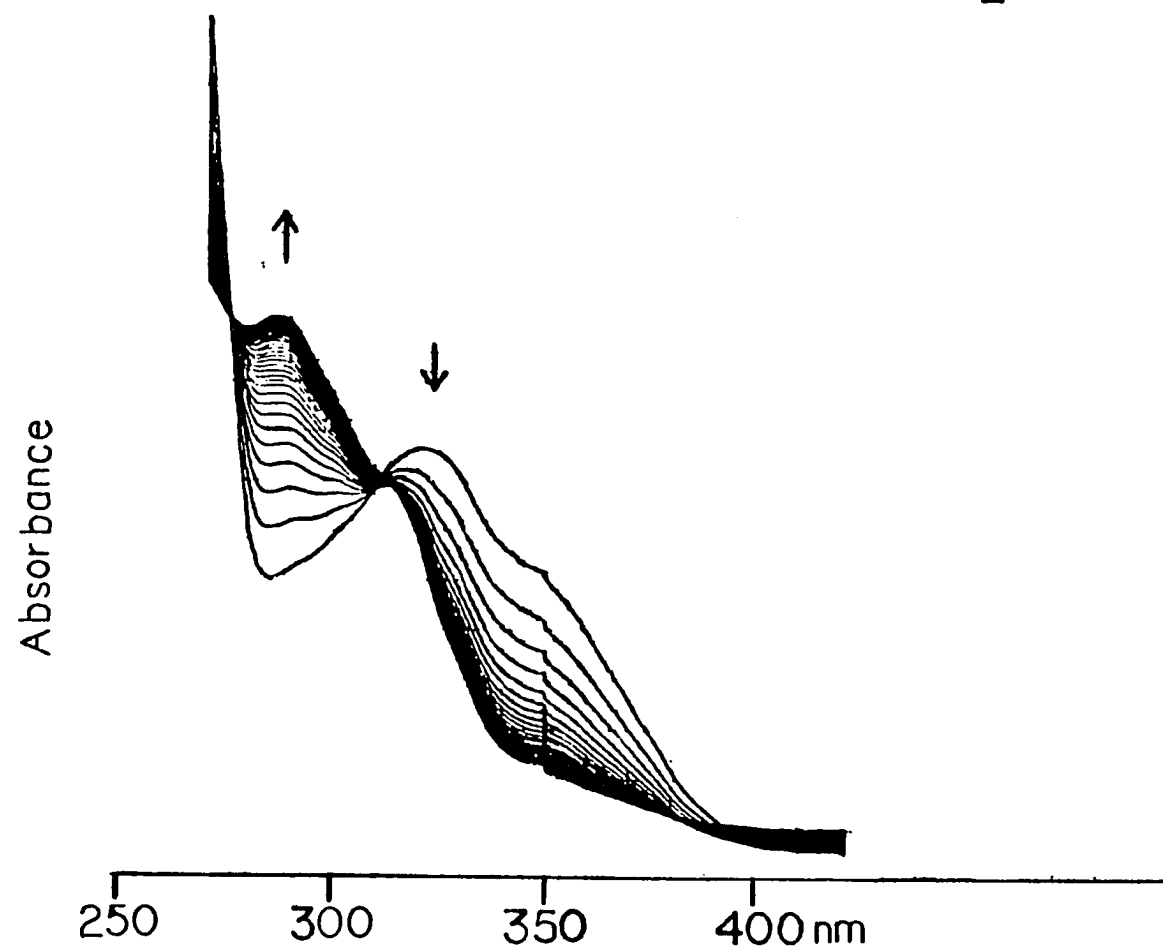
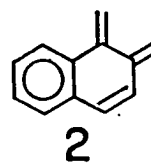


5.

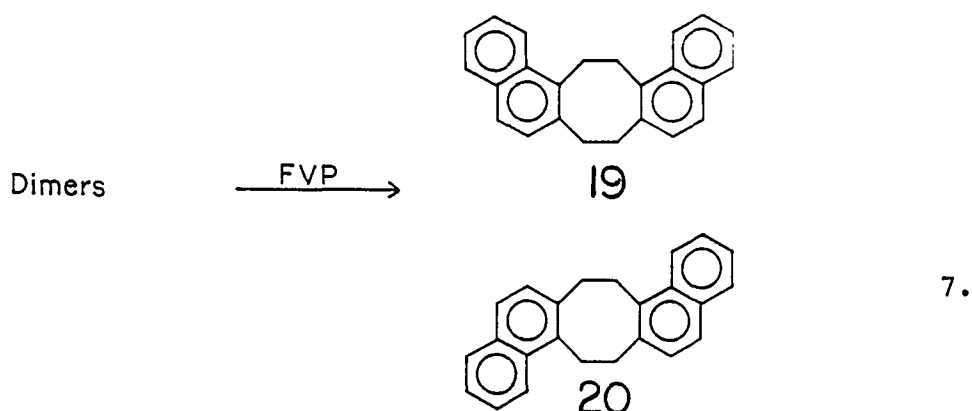


6.

Figure 1. UV-visible spectra of 1,2-napthoquinodimethane (2) and its subsequent dimerization at 25.0°C in CH₃CN (arrows up (+) indicate an increase of absorbance with time and arrows down (-) indicate a decrease of absorbance with time)

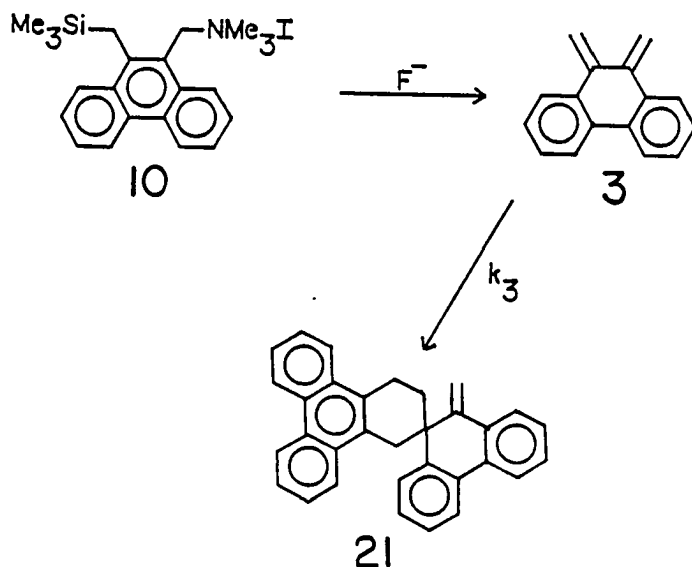


mixture of 1,2,7,8- and 1,2,9,10-dibenzo-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (19 and 20) (reaction 7) (^1H NMR: Appendix, Figures 2 and 3).



Treatment of a suspension of trimethyl(10-trimethylsilylmethyl-9-phenanthrylmethyl)ammonium iodide (10) in CD_3CN with TBAF (CD_3CN solution) in a NMR tube generated a species with ^1H NMR resonances (singlets) at δ 5.61 and 5.52. The aromatic region showed doublets at δ 7.97 and 7.74, and triplets at δ 7.42 and 7.34 (^1H NMR: Appendix, Figure 4). This species slowly disappeared ($t_{1/2} \sim 1$ h) giving way to the known [4+2] dimer (21) of 9,10-phenanthroquinodimethane (3) (^1H NMR: Appendix, Figures 5 and 6). These results are consistent with the formation and dimerization of 3 (Scheme 3).

Scheme 3



Dimerization Kinetics of 2 and 3

Both the dimerization of 2 and 3 were found to follow second-order kinetics. The dimerization of 2 was monitored by UV-visible spectroscopy at 360 nm. Rate constants for the dimerization of 2 were measured from 24.7 to 44.0°C and these are listed in Table 1. The $t_{1/2}$ of 2 under these conditions is about 1.5 min.

The dimerization rate of 3 is considerably slower than that for 2 ($t_{1/2} \sim 1$ h). This enabled us to measure the dimerization rate for 3 using 1H NMR spectroscopy. Figure 2 shows 1H NMR spectra for the dimerization of 3 at 22.0°C. The concentrations of 3 were calculated by comparing the 1H NMR peaks of 3 at 5.61 and 5.52 to that of the internal standard

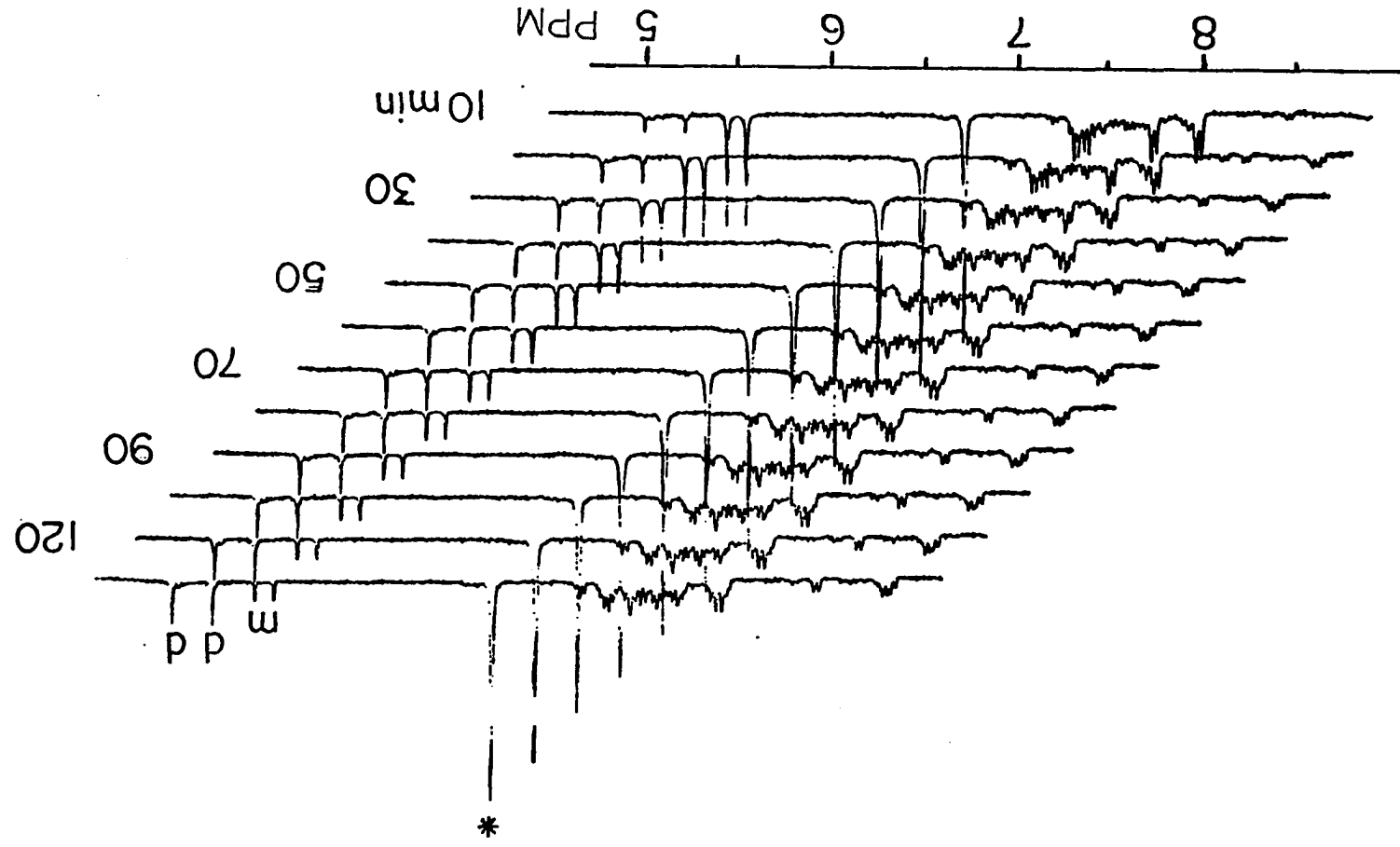
Table 1. Second-order rate constants for the dimerization of o-xylylene (1), 1,2-napthoquinodimethane (2), and 9,10-phenanthroquinodimethane (3) in CH_3CN ^a

temp, °C	$k_1 \times 10^{-3},$ $\text{L mol}^{-1} \text{ s}^{-1}$	$k_2,$ $\text{L mol}^{-1} \text{ s}^{-1}$	$k_3 \times 10^2,$ $\text{L mol}^{-1} \text{ s}^{-1}$
22.0	-	-	1.42 ± 0.07
24.7	-	61.7 ± 2.0	-
25.0	9.94 ± 0.32	$(62.0 \pm 2.1)^b$	$(1.68 \pm 0.10)^b$
34.5	-	73.4 ± 3.9	-
35.0	12.1 ± 0.41	-	-
44.0	-	95.4 ± 3.6	-
45.0	15.4 ± 0.51	-	-
52.0	-	-	7.54 ± 0.37
72.0	-	-	24.5 ± 1.22

^aFor reactions involving 1 and 2 the concentration of 1 or 2 was 5.00×10^{-4} M and the concentration of TBAF was 5.00×10^{-2} M. For reactions involving 3 the concentration of 3 was 0.060 M and the concentration of TBAF was 0.30 M.

^bCalculated values.

Figure 2. ^1H NMR (300 MHz) spectra of the dimerization of 9,10-phenanthroquinodimethane (3) at 52.0°C in CD_3CN (* = mesitylene, internal standard; m = 3; d = 2-methylene-3,4,5,6-dibenzo-3',4'-(9,10-phenanthro)-spirocyclohexane (21))



(mesitylene). Rate constants for the dimerization of 3 from 22.0 to 72.0°C were measured and these are reported in Table 1 along with data previously reported for o-xylylene (1).¹

Enthalpies of activation, ΔH^\ddagger 's, for the dimerization of 2 and 3 were determined by their relation to the corresponding E_a 's ($\Delta H^\ddagger = E_a - RT$) which were obtained from Arrhenius plots.¹⁴ Entropies of activation, ΔS^\ddagger 's, were determined using the Eyring equation.¹⁴ These data are listed in Table 2 along with data previously determined for o-xylylene (1).¹

Table 2. Activation parameters for the dimerization of o-xylylene (1),^a 1,2-naphthoquinodimethane (2),^b and 9,10-phenanthroquinodimethane (3)^c

<u>o</u> -QDM	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal k ⁻¹ mol ⁻¹
<u>1</u>	3.5 \pm 0.13	-29 \pm 1.1
<u>2</u>	3.6 \pm 0.20	-38 \pm 1.8
<u>3</u>	10.8 \pm 0.50	-30 \pm 1.5

^aFor 1, ΔH^\ddagger and ΔS^\ddagger are at 25.0°C.

^bFor 2, ΔH^\ddagger and ΔS^\ddagger are at 24.7°C.

^cFor 3, ΔH^\ddagger and ΔS^\ddagger are at 22.0°C.

DISCUSSION

The UV-visible spectrum (Figure 1) of 1,2-naphthoquinodimethane (2) is the first reported direct observation of this species.⁵ The ¹H NMR spectrum (Appendix, Figure 4) of 9,10-phenanthroquinodimethane (3) is the first reported ¹H NMR spectrum of a benzenoid o-QDM not substituted in the terminal methylene positions.⁵

The effect of annulating benzenoid units onto the parent system, o-xylylene (1), is dramatic. Table 3 shows rate constants for the dimerization of 1, 2, and 3 calculated at 25.0°C.¹⁵ At this temperature $k_1/k_2 = 163$ and $k_1/k_3 = 5.90 \times 10^5$.

The possible antiaromatic character of the quinodimethide portion of 2 still appears to be felt since its instability toward dimerization precluded its characterization by ¹H NMR spectroscopy.⁵

The stability of 3 is comparable to that of 2,3-dimethylene-2,3-dihydrofuran (22). o-QDM 22 has been shown to dimerize following second-order kinetics.¹⁶ In addition, the dimerization of 22 has been shown conclusively to proceed via diradical 23 (Scheme 4).^{16,17}

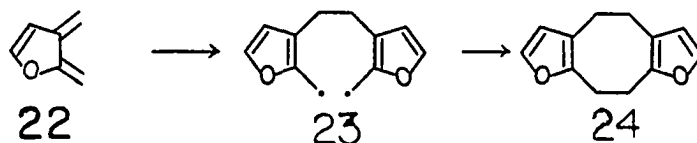
The rate constant for the dimerization of 22, measured in 1:1 CDCl₃/CS₂, is $4.05 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ at 25.0°C. It was also observed that there is little solvent effect on this

Table 3. Second-order rate constants for the dimerization of *o*-xylylene (1), 1,2-naphthoquinodimethane (2),^a and 9,10-phenanthroquinodimethane (3)^a calculated at 25.0°C

$k_1,$ $\text{L mol}^{-1} \text{ s}^{-1}$	$k_2,$ $\text{L mol}^{-1} \text{ s}^{-1}$	$k_3,$ $\text{L mol}^{-1} \text{ s}^{-1}$
$9.94 \pm 0.32 \times 10^3$	60.9 ± 2.0	$1.69 \pm 0.07 \times 10^{-2}$

^aRate constants determined by linear estimation of corresponding Arrhenius plots.¹⁵

Scheme 4

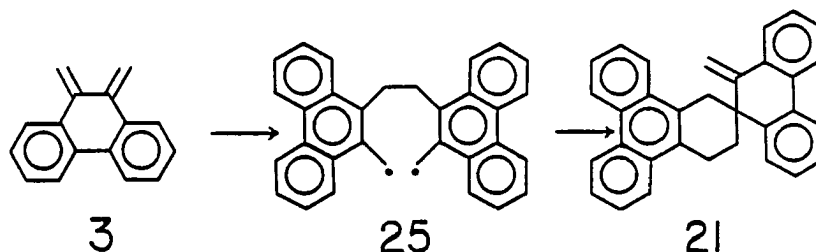


dimerization rate.¹⁶ The dimerization rate of 3, k_3 , is $1.69 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ at 25.0°C.

Activation parameters for the dimerization of 3 and 22 are also very similar. At 25.0°C ΔH^\ddagger_3 and ΔS^\ddagger_3 are equal to 10.8 kcal mol⁻¹ and -30.3 eu, respectively. At 25.0°C ΔH^\ddagger_{22} and ΔS^\ddagger_{22} are equal to 10.2 kcal mol⁻¹ and -30.9 eu,

respectively.¹⁶ Because of these striking similarities we believe it is likely that the dimerization of 3 includes diradical 25 (Scheme 5).

Scheme 5



The reason why 3 leads to [4+2] dimer and 22 leads to [4+4] dimer is not immediately obvious. However, it is possible that the products ([4+2] or [4+4] dimers) are determined by the specific conformations of the diradicals, which are determined by the orientation of the monomers as they react to form diradicals.¹⁸ A concerted mechanism cannot, however, be rigorously excluded.

The complex mixture of [4+2] dimers obtained in the dimerization of 2 was difficult to analyze, due in part to the instability of these dimers. Vacuum pyrolysis of dimers 13 and 18 should lead only to [4+4] dimer 19 (proceeding through either biradical 13 or 18). Vacuum pyrolysis of dimers 15 and

16 should lead only to [4+4] dimer 20¹⁹ (proceeding through diradical 14). The fact that a nearly 1:1 mixture of these dimers is obtained indicates that there is no one preferred mode of dimerization.

The low ΔH^\ddagger for the dimerization of 2, 3.6 kcal mol⁻¹ at 25.0°C, is very similar to that observed for o-xylylene (1).¹ This observation is consistent with the instability of the quinodimethide portions predicted for 1 and 2.³ The lower reactivity of 2 must then be reflected in the large negative ΔS^\ddagger observed in the dimerization of 2. Large negative ΔS^\ddagger values (in the range of about -40 to -30 eu), observed in many Diels-Alder reactions, have been interpreted in terms of a concerted mechanism.^{20,21} That is, a highly ordered transition state, required by the simultaneous bond formation in [4+2] cycloadditions, is consistent with these data. These data are usually reinforced with favorable stereochemical results.²⁰ It is not clear, however, that large negative ΔS^\ddagger values in themselves constitute evidence for simultaneous bond formation in [4+2] cycloadditions. Indeed, the previously mentioned dimerization of furan system 22 itself proceeds with a ΔS^\ddagger of -30.9 eu.¹⁶ We believe that the dimerization of 2 most likely proceeds via a biradical intermediate (as we do in general for all o-QDMs). However, more experimentation will be necessary to clarify the mechanism.

The fluoride ion induced 1,4-elimination reaction, which led to the formation of o-xylylene (1),¹ worked extremely well in the generation of 1,2-napthoquinodimethane (2) and 9,10-phenanthroquinodimethane (3). The second-order kinetics observed in the dimerization of 2 and 3 is in keeping with that previously observed for other o-QDM systems.^{1,16}

EXPERIMENTAL

General Procedure

Some general methods have been described.^{1,16} GLC analyses were performed using a Hewlett-Packard HP5840A gas chromatograph equipped with a 30 meter DB-1 or DB-1701 capillary column from J & W Scientific. UV-visible spectra were recorded on Perkin-Elmer 7000 Lambda-array, Canterbury SF3A, or Varian Cary 219 spectrophotometers. Elemental analyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, Michigan. The vacuum pyrolysis apparatus has been previously described¹⁴ and is available from Kontes. The preparation of tetra-*n*-butylammonium fluoride has been described.²² Acetonitrile, *n*-BuLi, phenanthrene, and chlorotrimethylsilane were purchased from Aldrich Chemical Co. Acetonitrile-*d*₃ was purchased from Stohler Isotope Chemicals.

[2-(Trimethylsilylmethyl)]trimethyl(1-naphthylmethyl)ammonium iodide (8)

2-Methylnapthalene (9) (9.94 gm, 0.070 moles) was converted to 2-bromomethylnapthalene (26) in 80% yield according to the procedure of McHale, Green, and Mamalis.²³ The bromide (26) (12.4 g, 0.056 moles) was dissolved in 60 mL of a 25% solution of trimethylamile in methanol and the mixture was heated to reflux for 6 h. After cooling to room temperature the reaction mixture was triturated with ether

which precipitated a white solid, (2-naphthylmethyl)trimethylammonium bromide (27) (recrystallized from acetone >85%): mp 203–205°C [lit.²⁴ mp 205–206°C]. A 4.90 g (18.4 mmol) quantity of 27 was converted to 8 in 44% yield following a three step procedure of Ito, Nakatsuka, and Saegusa for the preparation of [o-((trimethylsilyl)methyl)benzyl]trimethylammonium iodide:²⁵ mp 185–187°C dec (recrystallized from 40% ethyl acetate in acetone); IR (KBr disk) 3025, 2975, 1607, 1470, 1228, 1175, 1117, 955 cm⁻¹; ¹H NMR (CDCl₃) δ 8.49 (d, 1 H, J = 8.7 Hz), 7.87–7.19 (m, 5 H), 5.54 (d, 1 H, J = 13.7 Hz), 5.13 (d, 1 H, J = 13.7 Hz), 3.48 (s, 9 H), 2.92 (d, 1 H, J = 13.5 Hz), 2.43 (d, 1 H, J = 13.5 Hz), 0.021 (s, 9 H); ¹³C NMR (CD₃CN) δ 145.3, 135.2, 133.2, 132.1, 130.4, 130.1, 128.4, 126.2, 125.2, 119.6, 62.6, 54.73, 27.7, -1.20; Anal. calcd for C₁₈H₂₈INSi: C, 52.30; H, 6.83; N, 3.39. Found: C, 52.41; H, 6.89; N, 3.42.

Trimethyl(10-trimethylsilylmethyl-9-phenanthrylmethyl)ammonium iodide (10)

A 5.00 g (18.5 mmol) quantity of trimethyl(9-phenanthrylmethyl)ammonium chloride (11)⁹ was converted to 9-methyl-10-dimethylaminomethylphenanthrene (28) in 71% yield according to the procedure of Hauser and Brasen for the preparation of o-methyl-N,N-dimethylbenzylamine.²⁶ To a solution of 28 (1.08 g, 4.34 mmol) in 20 mL of ether was added n-BuLi (8.67 mmol) at 0°C. The resultant dark brown solution was allowed to stir

at room temperature for 18 h. The reaction mixture was cooled to 0°C and then quenched with a mixture of chlorotrimethylsilane (1.22 g, 11.3 mmol) and triethylamine (0.10 mL). The reaction mixture was allowed to stir at room temperature for 24 h followed by treatment with cold 5% NaHCO₃ (5 mL). The organic product was extracted with ether (2 x 25 mL). The ether layer was washed with water, and dried (MgSO₄). The solvent was evaporated and the residue distilled (Kughelrohr; 165°C, 0.03 mmHg) affording 808 mg (2.51 mmol) of 9-trimethylaminomethyl-10-trimethylsilylmethylphenanthrene (29) as a viscous oil (58%): ¹H NMR (CD₃CN) δ 8.76-7.44 (m, 8 H), 3.89 (s, 2 H), 2.90 (s, 2 H), 2.25 (s, 9 H), -0.04 (s, 9 H); IR (thin film) 3080, 2953, 2856, 1448, 1259, 1022 cm⁻¹.

Silylamine 29 was converted to [(10-trimethylsilylmethyl)]-trimethyl(9-phenanthrylmethyl)ammonium iodide (10) in the usual manner (>90%):²⁵ mp 210-212°C (recrystallized from acetone-ethyl acetate); IR (thin film) 3074, 3001, 2949, 1483, 1246, 847 cm⁻¹; ¹H NMR (CD₃CN) δ 8.90-8.71 (m, 2 H), 8.49-8.26 (m, 2 H), 7.80-7.57 (m, 4 H), 5.35 (d, 1 H, J = 13.3 Hz), 5.01 (d, 1 H, J = 13.3 Hz), 3.25 (d, 1 H, J = 12.8 Hz), 3.13 (s, 9 H), 2.90 (d, 1 H, J = 12.8 Hz), -0.11 (s, 9 H); ¹³C NMR (CD₃CN) δ 144.00, 132.61, 132.59, 132.50, 131.75, 130.26, 129.52, 128.58, 128.41, 127.96, 127.16, 125.82, 124.73, 124.28, 62.74, 54.65, 23.33, -0.74. Anal. calcd for

$C_{22}H_{30}NSi$: C, 57.01; H, 6.52; N, 3.02. Found: C, 57.11; H, 6.55; N, 3.05.

1,2,7,8- and 1,2,9,10-Dibenzo-5,6,11,12-tetrahydrodibenzo-[a,e]cyclooctene (19 and 20)

To a solution of 8 (500 mg, 1.21 mmol) in 10 mL of CH_3CN was added a solution of TBAF (474 mg, 1.82 mmol) in 5 mL of CH_3CN dropwise. The mixture was allowed to stir at room temperature for 5 h. The mixture was then concentrated and triturated with ether. After removing the precipitate by filtration the ether was removed and the residue was subjected to FVP conditions (temperature $660^\circ C$, pressure 5.0×10^{-5} mmHg). The sample chamber of the FVP apparatus was heated to $120^\circ C$. After 2 h the pyrolysis was complete. A white solid material was collected from the area just outside of the hot zone by dissolving it in toluene. GC analysis showed a 49:51 ratio of isomers (98 mg, 53%): 1H NMR ($CDCl_3$) δ 8.20 6.70 (m, 24 H), 3.40 (s, 4 H), 3.37-3.32 (t, 4 H, $J = 7.5$ Hz), 3.19-3.12 (t, 4 H, $J = 7.5$ Hz), 3.05 (s, 4 H) [lit.²⁷ NMR ($CDCl_3$) δ 8.2-6.7 (m, 12 H), 3.7-1.9 (m, 8 H)].

2-Methylene-3,4,5,6-dibenzo-3',4'-(9,10-phenanthro)spiro-bicyclohexane (21)

To a solution of 10 (108 mg, 0.23 mmol) in 5 mL of CH_3CN was added a solution of TBAF (121 mg, 0.47 mmol) in 2 mL of CH_3CN . The mixture was allowed to stir at room temperature for 6 h. The solvent was removed under reduced pressure and

the residue was purified by flash chromatography (1% ether in hexanes elution). The eluent was removed affording 33.1 mg (0.09 mmol) of 21 as a white solid (79%): mp 248–250°C dec [lit.¹⁰ mp 252–253°C]; ¹H NMR (C₆D₆) δ 8.60–8.47 (m, 2 H), 8.15 (br d, 1 H), 7.75–6.95 (m, 13 H), 5.16 (s, 1 H), 4.95 (s, 1 H), 3.67 (AB quartet, 2 H, J = 18.0 Hz), 2.81–2.60 (m, 2 H), 1.78 (t, 2 H, J = 7 Hz) [lit.¹⁰ NMR (CDCl₃) δ 5.24 (s, 1 H), 5.02 (s, 1 H), 3.84 (s, 2 H), 2.83 (t, 2 H), 1.90 (t, 2 H), (only peaks reported)].

UV-visible spectrum and ϵ_{max} determination of 1,2-naphtho-quinodimethane (2)

A 1 cm x 1 cm cuvette was charged with 2.00 mL CH₃CN and 0.50 mL of a 1.00×10^{-1} M solution of TBAF in CH₃CN. To this mixture was added 0.50 mL of a 1.00×10^{-3} M solution of 8 in CH₃CN. The cuvette was shaken once and then placed into a Cary 219 spectrophotometer. Spectra were recorded every 35 seconds, from 420 to 270 nm. The maximum wavelength absorbance (λ_{max}) was observed at 321 nm. Isobestic points were observed at 312 and 276 nm. A wavelength of 360 nm was chosen for kinetic experiments and the ϵ value at this wavelength was determined as previously described for o-xylylene (1).¹

Procedure for measuring rate constants for the dimerization of 1,2-naphthoquinodimethane (2)

A typical kinetic run was carried out as follows. A 1 cm x 1 cm UV-visible cell was charged with 2.00 mL of CH_3CN and 0.50 mL of a solution of TBAF in CH_3CN (1.00×10^{-1} M). This mixture and a stock solution of 8 in acetonitrile (1.00×10^{-3} M) were thermostatted at the reaction temperature for at least 20 min prior to each run. To the solution of TBAF in CH_3CN was added 0.50 mL of the stock solution of 8 in CH_3CN . The cell was shaken once, then placed in a Cary 219 spectrophotometer. With the monochrometer set at 360 nm the absorbance decay of 2 versus time was recorded on a chart display.

Rate constants for the dimerization of 2 were determined using a least squares method.¹⁵ The resultant rate constants for 2 are the average of at least five kinetic runs.

Procedure for measuring rate constants for the dimerization of 9,10-dimethylene-9,10-dihydrophenanthrene (3)

Kinetic experiments involving 3 were monitored with use of a Bruker WM 300 NMR spectrophotometer equipped with a variable temperature probe.

A typical kinetic run was carried out as follows. The quaternary ammonium salt 10 (10 mg, 0.022 mmol) was combined with CD_3CN (0.35 mL) in a 5 mm NMR tube. To this suspension was added a solution of TBAF (28 mg, 0.11 mmol) in CD_3CN (0.35

mL). The mixture (now a solution) was placed into the NMR probe and spectra were recorded as a function of time.

The singlets occurring at 5.61 and 5.52 ppm, corresponding to the exo-methylene protons of 3, were integrated versus an added mesitylene standard. The concentrations are a result of an average of three integrations. The rate constant, k_3 , for the dimerization of 3 was then calculated from the rate of disappearance of monomer 3 as described previously.^{1,16} The resultant rate constants are the result of at least three kinetic runs.

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APPENDIX

Least-squares Fit to a Straight Line

Rate constants for the dimerization of 1,2-napthoquinodimethane (2) and 9,10-phenanthroquinodimethane (3) were determined using a least-squares method as previously described.^{15,16} The data of the kinetic studies were treated with use of a Hewlett-Packard HP-15C calculator.

Figure 1. ^1H NMR (90 MHz) spectrum (CDCl_3) of [4+2] dimers obtained from dimerization of 1,2-naphthoquinodimethane (2)

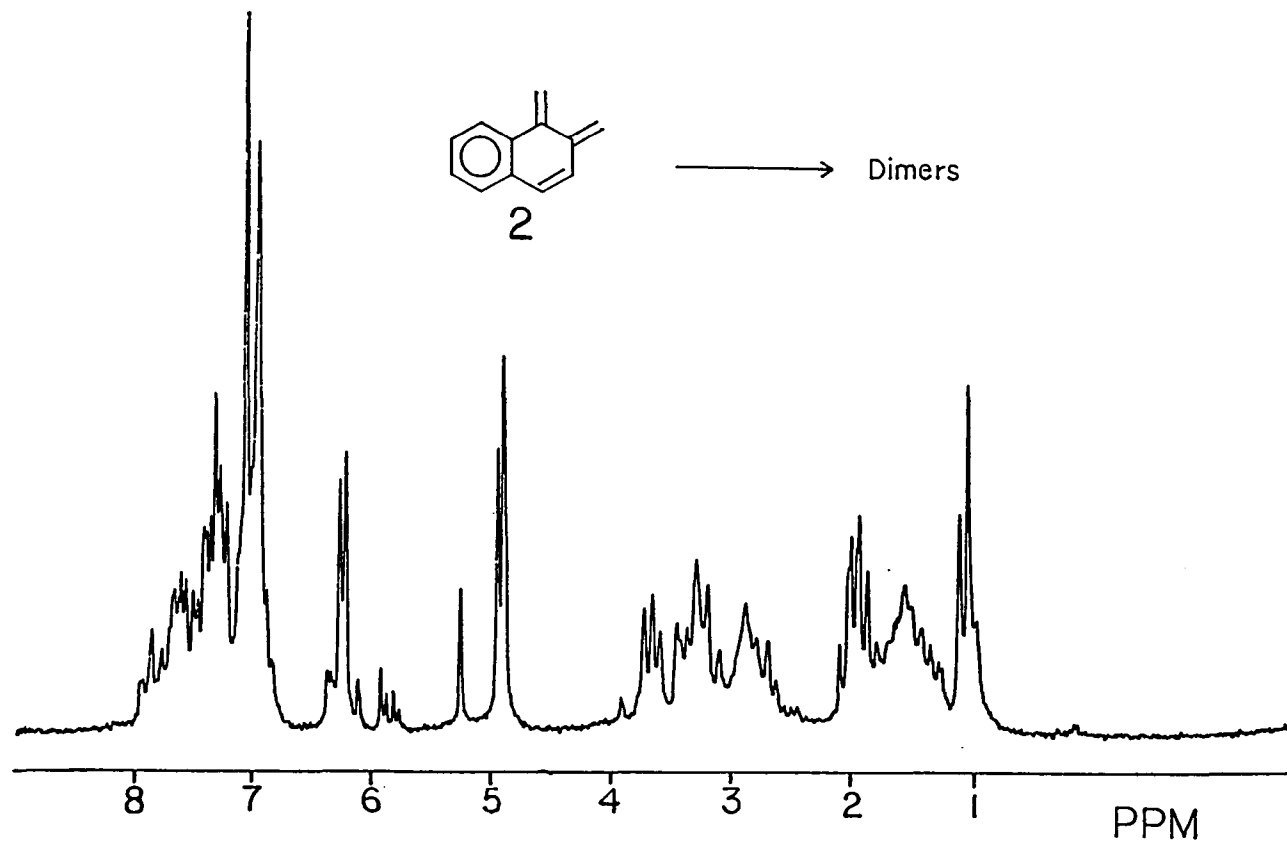
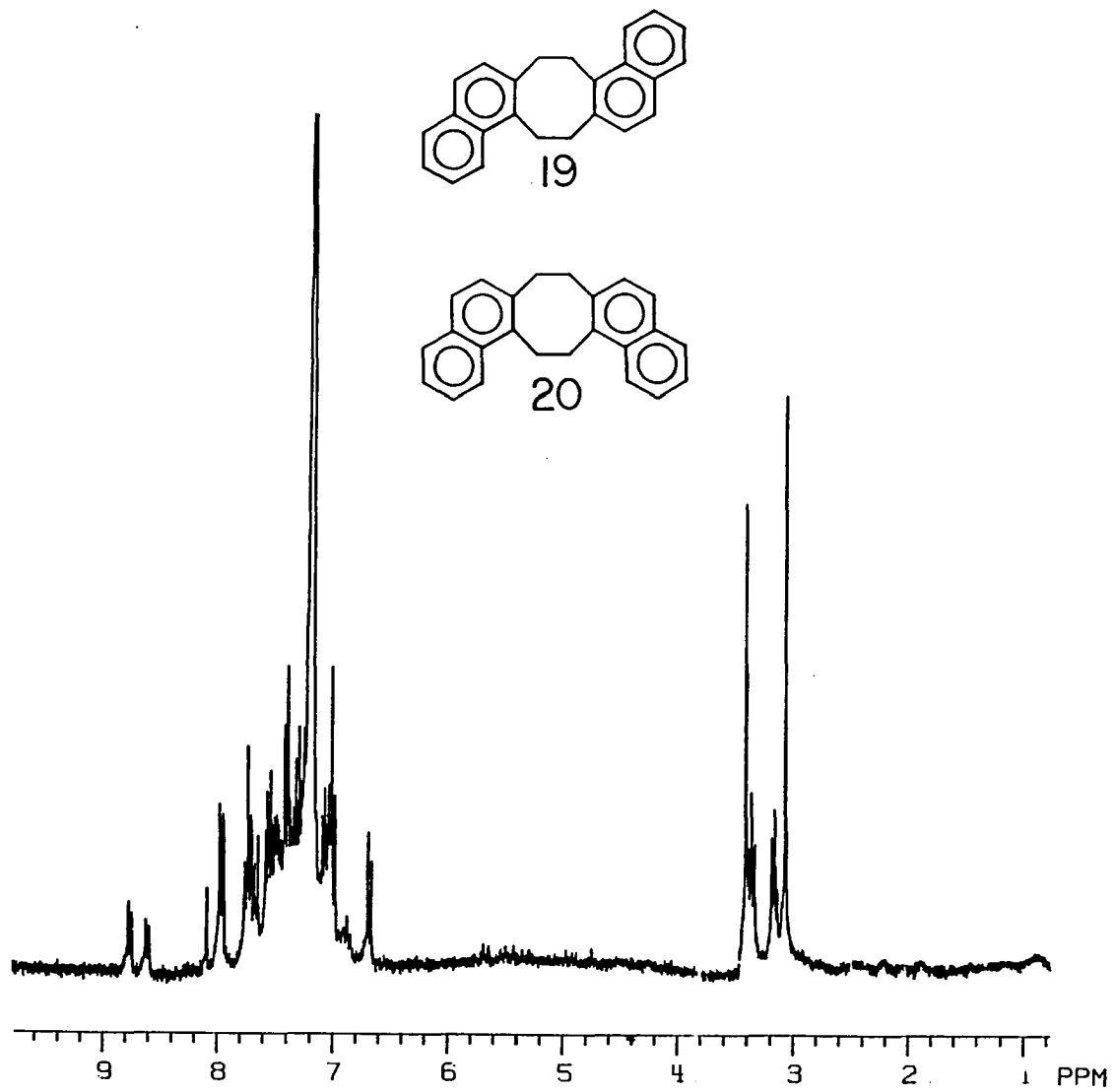


Figure 2. ^1H NMR (300 MHz) spectrum (C_6D_6) of a 1:1 mixture of 1,2,7,8- and 1,2,9,10-dibenzo-5,6,11,12-tetrahydrodibenzo[a,3]cyclooctene (19 and 20)



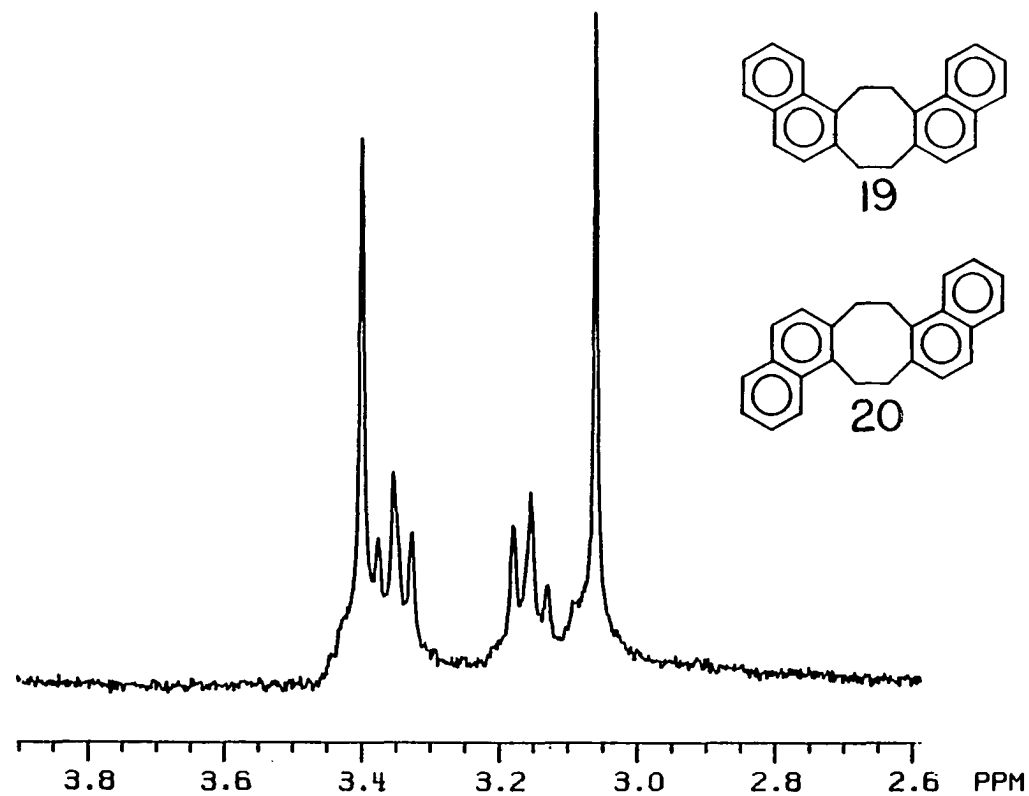
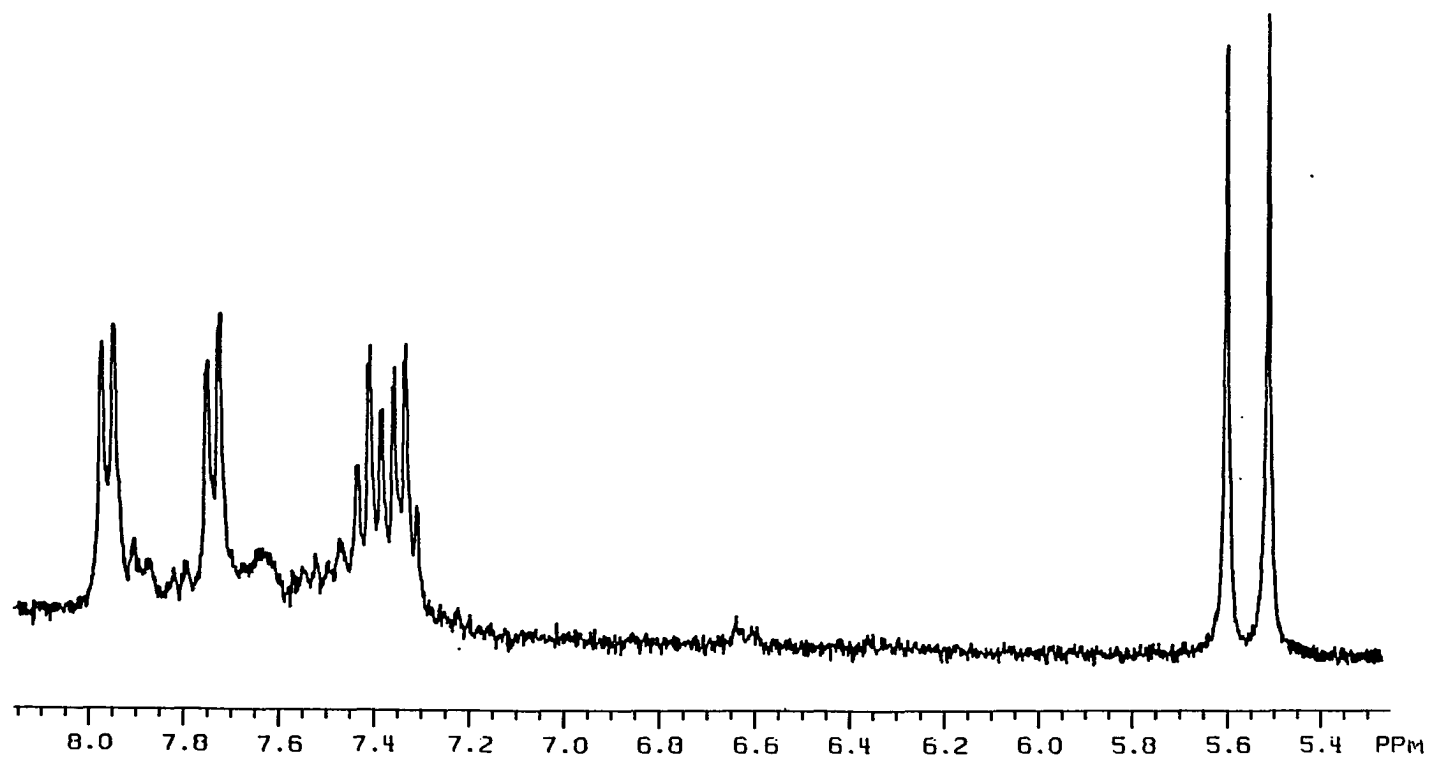
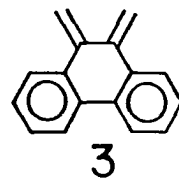


Figure 3. Closeup of the aliphatic region of the ^1H NMR (300 MHz) spectrum (C_6D_6) of a 1:1 mixture of 1,2,7,8- and 1,2,9,10-dibenzo-5,6,11,12-tetrahydrodibenzo-[a,e]cyclooctene (19 and 20)

Figure 4. ^1H NMR (300 MHz) spectrum of 9,10-phenanthroquinodimethane
(3) at 25.0°C



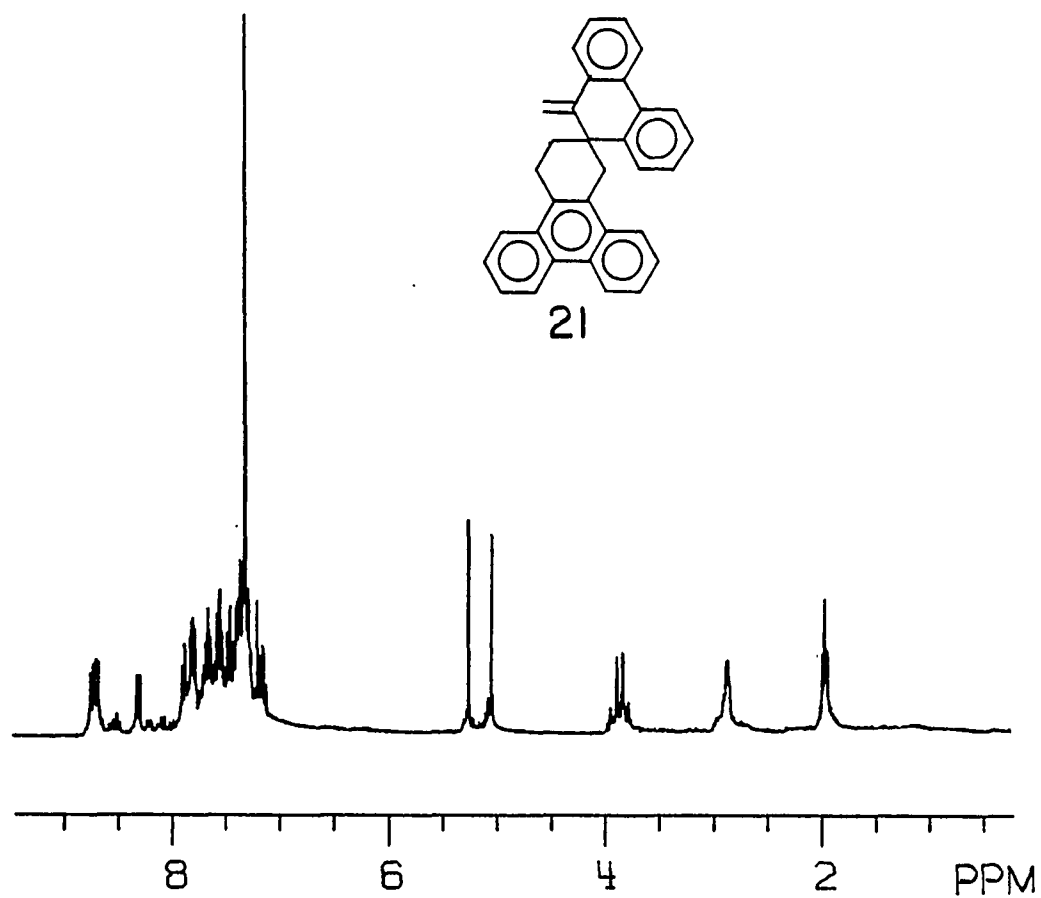
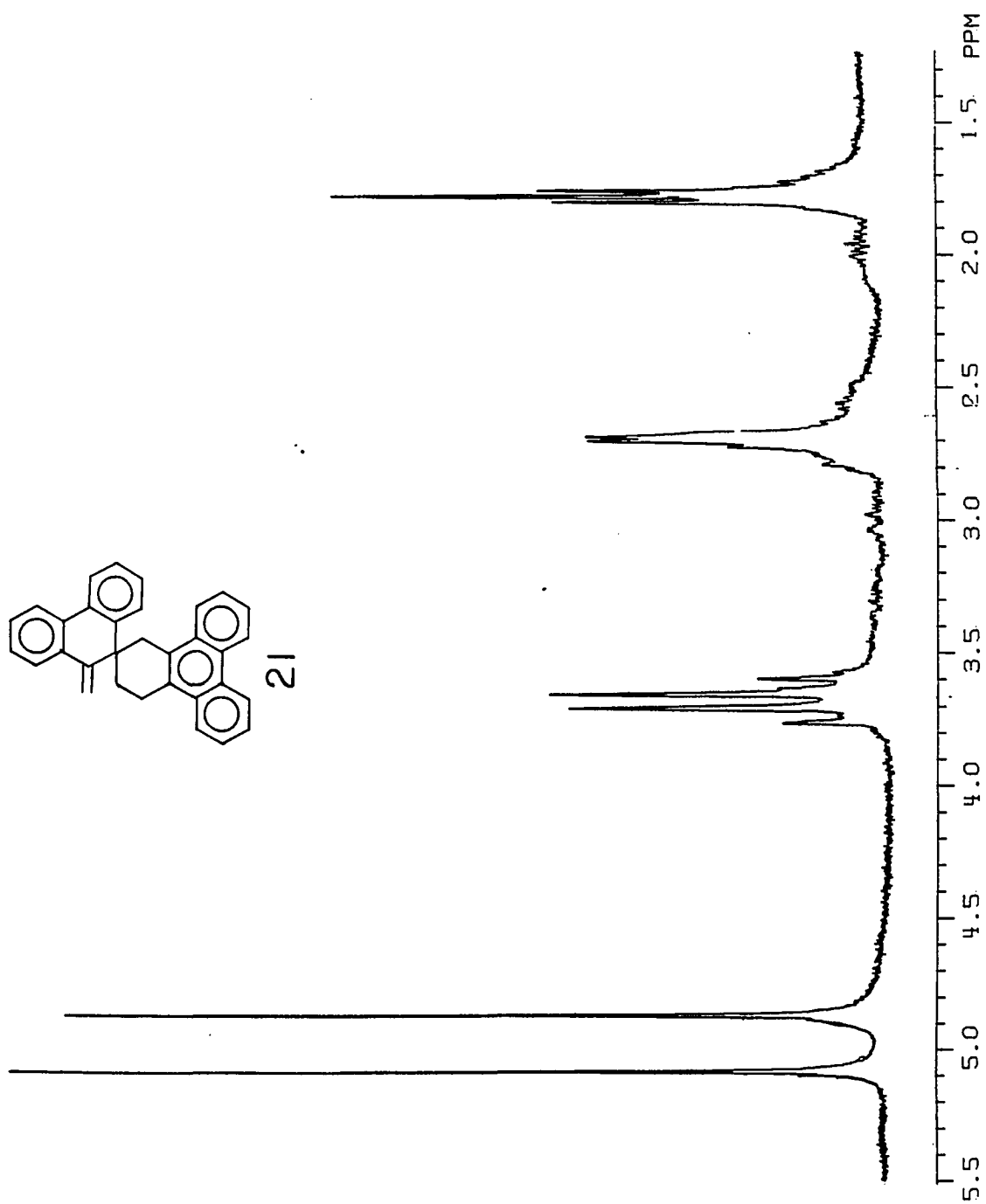


Figure 5. ^1H NMR (300 MHz) spectrum (C_6D_6) of 2-methylene-3,4,5,6-dibenzo-3',4'-(9,10-phenanthro)spirocyclohexane (21)

Figure 6. Closeup of the olefinic and aliphatic regions of the ^1H NMR (300 MHz) spectrum (C_6D_6) of 2-methylene-3,4,5,6-dibenzo-3',4'-(9,10-phenanthro)-spirocyclohexane (21)



Data of Kinetic Study

Table A-1. Rate of disappearance of 1,2-napthoquinodimethane (2) measured at 24.7°C in CH₃CN

Time, min	$[2] \times 10^4,$ mol L ⁻¹	$[2]^{-1} \times 10^{-3},$ L mol ⁻¹
0.33	1.74	5.74
0.66	1.43	6.98
1.00	1.23	8.14
1.33	1.08	9.30
1.66	0.956	10.5
2.00	0.853	11.7
2.33	0.771	13.0
2.66	0.683	14.2
3.00	0.648	15.4
$k_2 = 60.2 \pm 2.0 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-2. Rate of disappearance of 1,2-napthoquinodimethane
(2) measured at 34.5°C in CH₃CN

Time, min	$[2] \times 10^4,$ mol L ⁻¹	$[2]^{-1} \times 10^{-3},$ L mol ⁻¹
0.33	1.59	6.30
0.66	1.28	7.79
1.00	1.08	9.30
1.33	0.922	10.8
1.66	0.802	12.5
2.00	0.706	14.1
2.33	0.635	15.7
2.66	0.577	17.3
$k_2 = 78.9 \pm 3.9 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-3. Rate of disappearance of 1,2-napthoquinodimethane
(2) measured at 44.0°C in CH₃CN

Time, min	$[2] \times 10^4,$ mol L ⁻¹	$[2]^{-1} \times 10^{-3},$ L mol ⁻¹
0.33	1.58	6.31
0.66	1.24	8.09
1.00	1.00	10.0
1.33	0.843	11.9
1.66	0.727	13.8
2.00	0.635	15.7
2.33	0.563	17.7
2.66	0.512	19.5
$k_2 = 94.8 \pm 3.6 \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-4. Rate of disappearance of 9,10-phenanthroquinodimethane ($\tilde{3}$) measured at 22.0°C in CD₃CN

Time, min	$[\tilde{3}] \times 10^2,$ mol L ⁻¹	$[\tilde{3}]^{-1} \times 10^{-2},$ L mol ⁻¹
25	1.80	0.555
40	1.39	0.719
55	1.16	0.862
70	0.958	1.04
85	0.921	1.08
100	0.826	1.21
115	0.742	1.34
140	0.614	1.63
$k_3 = 1.40 \pm 0.07 \times 10^{-2} \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-5. Rate of disappearance of 9,10-phenanthroquinodimethane ($\tilde{3}$) measured at 52.0°C in CD₃CN

Time, min	$[\tilde{3}] \times 10^2,$ mol L ⁻¹	$[\tilde{3}]^{-1} \times 10^{-2},$ L mol ⁻¹
19	0.890	1.12
29	0.620	1.62
39	0.490	2.03
49	0.410	2.46
59	0.350	2.88
69	0.290	3.45
$k_3 = 7.61 \pm 0.37 \times 10^{-2} \text{ L mol}^{-1} \text{ sec}^{-1}$		

Table A-6. Rate of disappearance of 9,10-phenanthroquinodimethane ($\tilde{3}$) measured at 72.0°C in CD_3CN

Time, min	$[\tilde{3}] \times 10^2,$ mol L^{-1}	$[\tilde{3}]^{-1} \times 10^{-2},$ L mol^{-1}
5	0.800	1.26
10	0.600	1.67
15	0.401	2.53
20	0.330	2.99
25	0.261	3.90
30	0.212	4.65
35	0.180	5.65
$k_3 = 2.50 \pm 0.12 \times 10^{-1} \text{ L mol}^{-1} \text{ sec}^{-1}$		

GENERAL SUMMARY

Reactive o-quinodimethanes have been successfully observed in solution by fluoride ion induced eliminations from suitable precursors. Kinetic and product studies on these species have provided insights into the mechanism of their dimerization.

In part I, o-xylylene (1) was observed directly by UV-visible spectroscopy. The dimerization of 1 was observed to follow second-order kinetics. Kinetic studies on ring-substituted derivatives of 1 have shown that when undergoing dimerization the o-quinodimethanes prefer a non-endo approach.

In part II α -methyl-substituted o-quinodimethanes were studied. The dimerization rate of 5-ethylidene-6-methylene-1,3-cyclohexadiene (9) was very similar to that of o-xylylene (1). The dimerization rate of 5,6-bis(ethylidene)-1,3-cyclohexadiene (10) was much slower than that for 1 or 9. The dimerization of 9 and 10 led primarily to one stereoisomer in each case. These observations are taken as evidence that the dimerization of benzenoid o-quinodimethanes occurs in a stepwise manner.

Part III described the first reported direct observation of 1,2-napthoquinodimethane (2). The first ^1H NMR of an o-QDM, 9,10-phenanthroquinodimethane (3), not substituted in the exo-methylene positions was obtained. Both 2 and 3 led to [4+2] dimers following second-order processes. The similarity

in activation parameters for the dimerization of 3 and
2,3-dimethylene-2,3-dihydrofuran (23) suggests that the
dimerization of 3 proceeds in a stepwise manner.

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