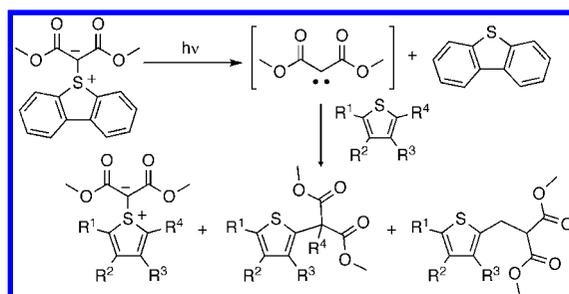# Reaction of Dicarbomethoxycarbene with Thiophene Derivatives

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Received December 30, 2008

Photolysis of derivatives of dimethylmalonate thiophene-*S,C*-ylide provides dicarbomethoxycarbene, which can react with thiophene to form dimethyl (2-thienyl)malonate. By generation of dicarbomethoxycarbene from the dibenzothiophene-based ylide in neat thiophene, it is shown that the thienylmalonate is not a product of rearrangement of the thiophene ylide, in contrast to thermolysis results. Formation of the thienylmalonate is suppressed by substitution of any sort in the 2- and 5-positions on the thiophene and by substitution with an electron-withdrawing substituent.

Introduction

We recently communicated that *S,C* sulfonium ylides could be used as photochemical precursors to carbenes.[1] Photolysis of compounds **1**−**4** in methanol or cyclohexene produces reaction mixtures that contain products deriving from both singlet and triplet dicarbomethoxycarbene, as illustrated in Scheme 1. Of the four precursors, **1**−**3** cleanly produced the corresponding thiophene derivative and apparently carbene-derived products, while **4** produced a considerably more complex mixture. This behavior is consistent with the analogous photochemical deoxygenation of sulfoxides, in which direct irradiation often produces very high chemical yields of sulfide for derivatives of dibenzothiophene (and sometimes thiophene).[2−13] In contrast, α-cleavage reactions tend to predominate for other sulfoxides.[14−19] Additionally, it has been shown that nitrenes can be generated from analogous sulfilimine precursors.[20−24]

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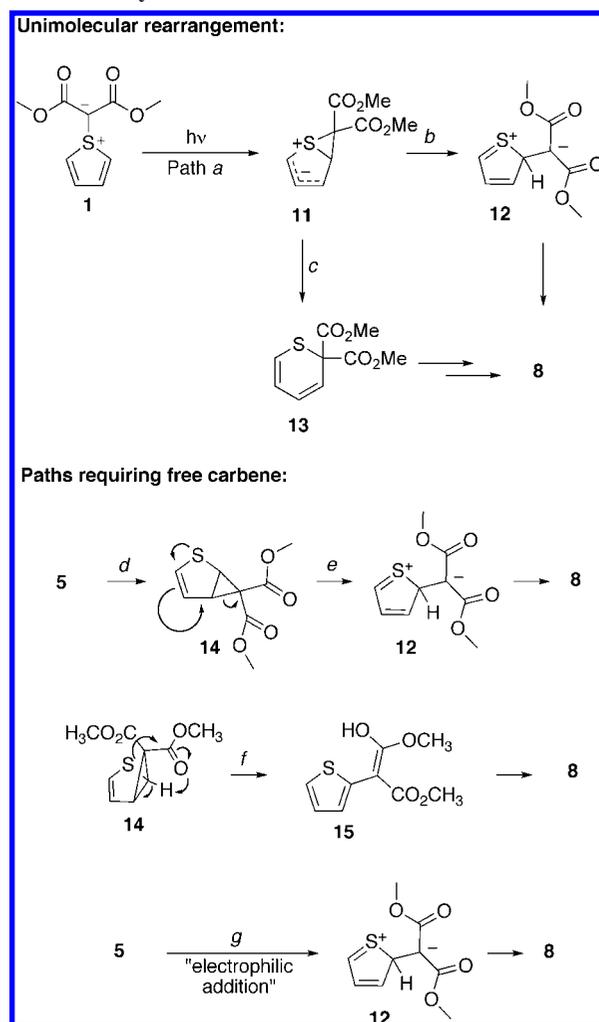
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SCHEME 1. Generation of Dicarbomethoxycarbene from Photolysis of 1−4 and Trapping by Cyclohexene or Methanol[a]
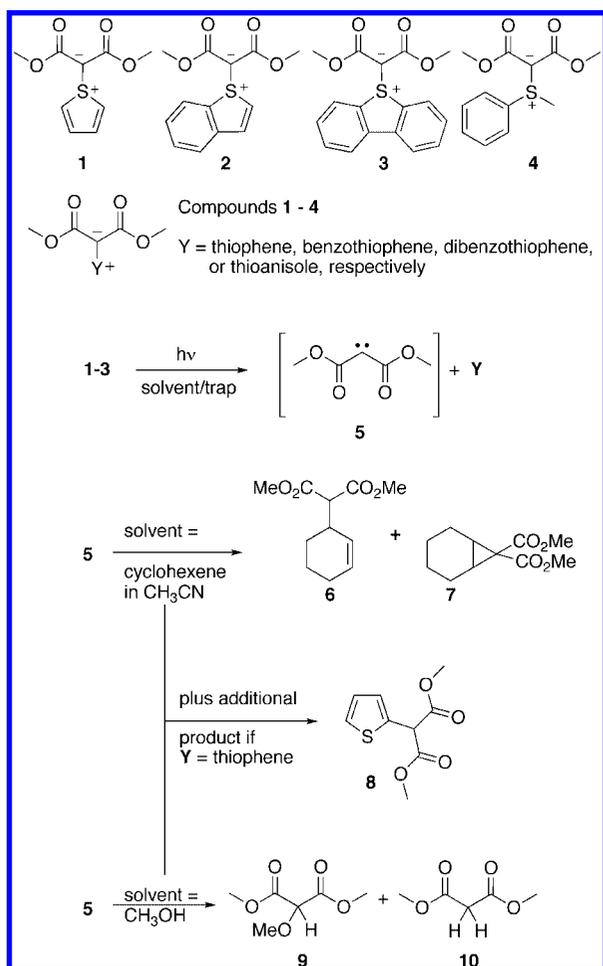
[a] Adduct **8** is observed when **1** is the starting material.

SCHEME 2. Potential Mechanistic Pathways for Formation of 8 on Photolysis of 1

Consistent chemoselectivity in the photochemical reaction of **1−3** with cyclohexene (**6** vs. **7**) was interpreted as representative of a common intermediate, presumably the singlet carbene **5**. However, when **1** was used as a precursor, the additional product **8** was observed. Photolysis of **1−3** in methanol gave differing ratios of **9** to **10**, which was interpreted by proposing that the initial spin populations of the carbenes differed from one precursor to another, and that spin equilibration was not faster than trapping under these conditions.[25] Again, when **1** was the precursor, the adduct **8** was observed. No analogous adducts were observed on photolysis of **2** or **3** in either solvent.

The mechanism for formation of **8** is of interest, in part because closely related chemistry has led to varying products discovered over the years.[26−28] Thermolysis of **1** at reflux was reported to result in formation of **8** without intervention of the carbene (**5**), as demonstrated by the lack of trapping by olefins or crossover from one thiophene to another.[27,28] Thermolysis of closely related derivatives (e.g., using the *t*-Bu, rather than methyl, ester) led to the isolation of thiopyran derivatives analogous to **13**, presumably through intermediate **11**.[28] (These compounds are illustrated in Scheme 2.) On the other hand, treatment of ethyl diazoacetate with either Cu or Rh-based catalysts, which leads to singlet metal carbenoids as intermediates, yielded a bicyclic product analogous to **14**.[29,30] Careful reaction of dimethyl diazomalonate and thiophene with Rh$_2$(OAc)$_4$ catalyst gave only **1**, and the same reaction of methyl diazoacetoacetate gave the appropriate analogues of **1**, **8**, *and* **14**.[30] Photolysis of dimethyl diazomalonate in thiophene was reported to give a low yield of **1**; an unreported yield of **3** was obtained from dimethyl diazomalonate photolyzed in the presence of dibenzothiophene.[31,32]

In this paper, we report a series of experiments designed to explore the chemistry of dicarbomethoxycarbene with thiophene derivatives and to attempt to elucidate the mechanism of the formation of **8** from among the several possibilities suggested by these previous works. We show that the reaction does require a diffusible intermediate, which we take to be dicarbomethoxy-

(25) This hypothesis will be addressed again in a separate publication.

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carbene, and that the intermediate is both electrophilic and sensitive to steric interference.

Scheme 2 illustrates several potential pathways, largely drawn from the literature. A unimolecular process, as suggested by the reported thermal chemistry, might proceed via path a to give the zwitterion **11**. Final formation of **8** might be through spontaneous or photochemical ring opening (path b) or by ring expansion to **13** (path c) followed by known chemistry to form **8**.[26−28]

Our initial presumption for this photochemical reaction, however, was that reaction of carbene **5** with thiophene would produce the bicycle **14** (path d). This was based on the chemistry of ethyl diazoacetate, Rh$_2$(OAc)$_4$, and thiophene,[29,30] and on the known photolysis of dimethyl diazomalonate in benzene, which provided a 1:1.6 mixture of **16** and the equilibrating mixture of **17** and **18**.[33]
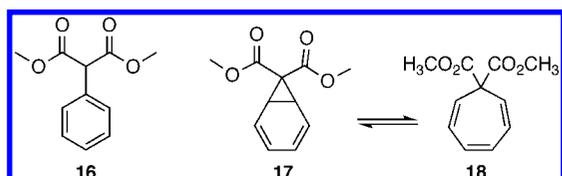
Once **14** is formed, the rearrangement to **8** must be addressed. Heterolytic opening of **14** to give **12** might be spontaneous, although this does not explain the isolability of the methyl diazoacetoacetate derivative.[28] Alternatively, a low barrier rearrangement via path f might provide the enol of the final product.

Finally, we posited that the specific regiochemistry of addition might be attributable to a carbene addition mechanism that resembles electrophilic addition. In this mechanism, **12** might be generated directly, without intervention of **14**, as illustrated as path g in Scheme 2.

Results and Discussion

Of the mechanisms shown in Scheme 2, the most straightforward distinction to be made was to separate the unimolecular and bimolecular pathways. This was accomplished by using the ylide **3** as a precursor. Direct photolysis of **3** using broad irradiation centered at 350 nm in neat thiophene resulted in a near quantitative yield of **8**. However, it became apparent that the lamps being used would also photolyze **1**, and thus a sequential mechanism of **3** → **1** → **8** could not be ruled out. A second set of experiments, using a Xe lamp filtered through a monochromator centered at 365 nm (±12 nm linear dispersion), was carried out. At these wavelengths, **1** does not absorb significantly. Upon photolysis of **3** in thiophene, nearly equal yields of **1** and **8** were obtained. Control experiments showed that almost no secondary photolysis of **1** was possible on the time scale of the formation of **8**. Thus (1) formation of **8** does not require formation of **1** as an intermediate step, (2) dicarbomethoxycarbene is almost certainly involved in formation of **8**, and (3) the first "committed step" of the carbene toward **8**, whatever that may be, occurs at almost an identical rate as the capture of the carbene as the ylide in thiophene.

Several experiments were performed to look for the presumed initial adduct **14**, even though it had not been observed in the formation of **8** by other means. Photolysis of **1** by using 350 nm bulbs in degassed deuterated methanol at −30 °C was followed by NMR, but there was no sign of any photolytic product other than **8**, **9**, and **10**.

As a positive control, photolyses of **2** and **3** were carried out in benzene and toluene. These experiments show again that
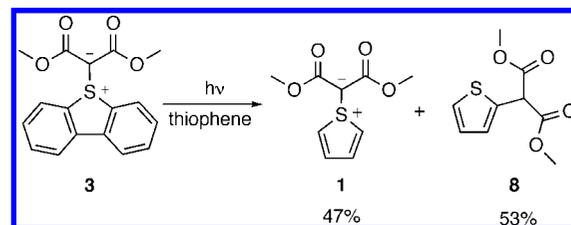
diffusible dicarbomethoxycarbene is shown and that our conditions do not necessarily degrade all arene adducts of the carbene. By NMR analysis of the reaction mixture, good yields of **17** and **18**[34−36] were observed to the exclusion of **16**. Conversely, only the benzyl insertion product **19** was observed in toluene, to the exclusion of **20** (and/or its tautomer).[37] Data are shown in Table 1.
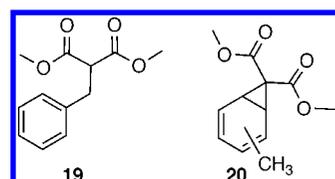

TABLE 1. Photolysis of Ylides 2 and 3 in Benzene and Toluene

		product yields[a]	
ylide	solvent	Cylopropanation products **17/18** or **20**	Net insertion products **16** or **19**
2	benzene	73	
3	benzene	79	
2	toluene		85
3	toluene		76

[a] Relative to consumed starting material. Products identified by comparison to literature spectra.

Further attempts were made to observe **14** or an analogue by using 2-substituted or 2,5-disubstituted thiophenes. It was reasoned that the absence of a labile hydrogen in the 2(or 5)-position of the thiophene ring after cyclopropanation to give **21** would leave the bicyclic adduct unable to rearrange to the formal C−X insertion product **23** through **22** (Scheme 3). It further seemed that this tactic would block a direct rearrangement, as shown for the parent system as path f in Scheme 2.

**SCHEME 3. Blocking of Rearrangement to the C−H Insertion Product by Substitution on Thiophene**
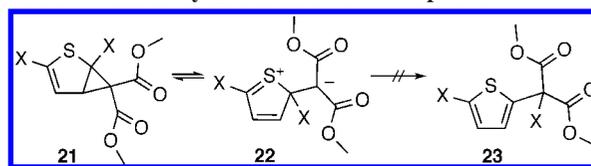
Two approaches to this experiment were taken. First the analogues to **1** with 2,5-dimethyl (**1a**), 2,5-dichloro (**1b**), and 2-bromo (**1g**) substitutions on the thiophene (Scheme 4) were prepared. Photolysis of any of these derivatives in CD$_3$OD did not result in observation of any bicyclic compound (analogue

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SCHEME 4. Photolysis of Ylide 3 in Neat, Substituted thiophenes[a]
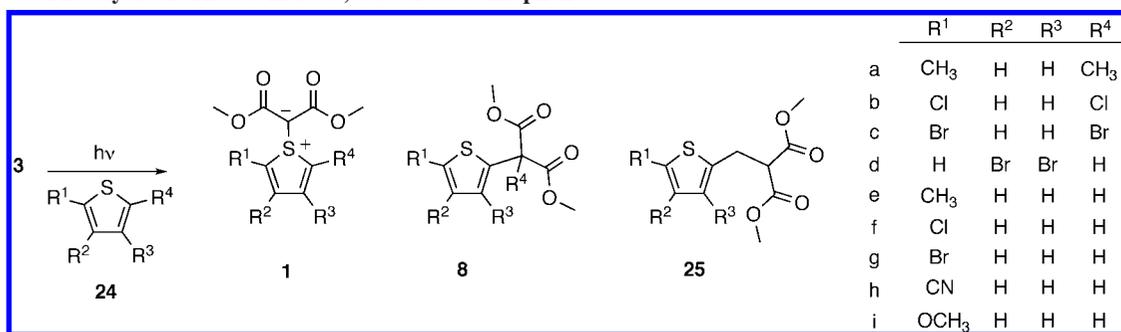
[a] The letter is used as an index to denote the substitution pattern.

of **14**) or any analogue of **8**. Instead, only the corresponding thiophenes, dimethyl methoxymalonate (**9**), and dimethyl malonate (**10**) were observed. A similar result was also obtained for the 3,4-dibromo analogue **1d**.[38]

A more widely applicable approach to observing analogues of **8** or **21** was envisioned, in which **3** would be photolyzed in neat substituted thiophene. Several thiophenes (**24a–i**) were selected, as shown in Scheme 4 and Table 2. However, in no case was the bicyclic analogue **21** observed on direct photolysis of **3** in any of the neat thiophenes.

The observed products are shown in Table 2, and discernible patterns emerge. All three 2,5-disubstituted thiophenes resulted in total suppression of the apparent insertion analogue of **8**. Indeed, even dibromo substitution at the 3- and 4-positions (3,4-dibromothiophene, **24d**) suppressed formation of **8d**. Instead, photolysis (using 365 nm irradiation) resulted only in formation of the ylide analogues **1a–d**, with the exception of a benzyl insertion product **25a**.

Thermolysis of **3** in thiophene at 80 °C yielded **8** quantitatively, whereas its thermolysis in 2,5-dichlorothiophene did not yield any isolable products. Photolysis of **3** in 2,5-dichlorothiophene provided **1b** as the only isolable product (Table 2). The thermolysis of **1b** in 2,5-dichlorothiophene was previously reported to provide a mixture of unidentifiable compounds.[27] All these results are reconciled if it is posited that the thermolysis conditions make formation of **1** or **1b** effectively reversible. In the former case, eventually the carbene reacts with thiophene irreversibly to form **8**, and in the latter, the reaction with 2,5-dichlorothiophene (or other compounds present in the mixture) gives the unidentified products.

Several monosubstituted thiophenes were also used as solvents for the photolysis of **3** in the current work. It was reasoned that purely steric effects could allow for C–H insertion on the "other" side of the thiophene, e.g., by cyclopropanation across the C4–C5 (or C5–S) bond. In the cases where the π-donation of the substituent is weak (Br, CN), only the ylide analogue of **1** was observed and identified. On the other hand, when the substituent was a better π-donor (CH₃, Cl, OCH₃), the analogue of C–H insertion product **8** (with the substituent on the other side of the thiophene ring) was formed.

It seems self-evident that there is a greater variability for the relative rates of formation of **8** than for **1**: without substitution or with π-donation, formation of **8** competes effectively with formation of **1**. But if formation of **8** is slowed by electron-

TABLE 2. Photolysis of Ylide 3 in Substituted Thiophenes 24i[a]

		product yields (%)		
thiophene	conversion	1[a]	8[a]	25[a]
24a	95	13	-	76
24b	95	81	-	na
24c	12[b]	65	-	na
24d	68	82	-	na
24e	93	-	78	-
24f	93	39	47	na
24g	89	63	-	na
24h	95	68	-	na
24i	93	-	84	na

[a] The subscript *i* is used to indicate the appropriate modified structure, e.g., **1a**, **8a**, and **25a** for 2,5-dimethylthiophene (**24a**) as the solvent. [b] Debromination of **1c** was noted along with decomposition of **3**.

withdrawing substituents (or inhibited by substitution at both the 2- and 5-positions), the ylide is formed instead. These substituent effects would appear to be a strong contraindication of the pathways for formation of **8** that begin by addition to give **11** and its analogues. Surely, 2,5-electron-donating substituents would be destabilizing to **11**, and its formation would be suppressed, relative to simple ylide formation.

Competitive kinetics were used to explore the substituent effect further. Photolyses of **3** were done in solvent mixtures containing thiophene and one of 2-methylthiophene, 2-chlorothiophene, or 2-methoxythiophene. Product ratios were converted into selectivities, and multiple solvent ratios were used to ensure linearity. It was assumed that the product formation was under kinetic control, so that the product selectivities could be converted to relative rate constants. The results of these experiments are given in Table 3. Plotting the log of the relative

(37) Small additional NMR peaks were observed, but they were not assignable to compounds **13** or **14** in benzene or toluene, respectively.
(38) Unsuccessful attempts were made to prepare the corresponding ylide from 2,5-dibromothiophene.

TABLE 3. Substituent Effects on the Relative Rate of Formation of Analogues of 8

substituent	$\sigma^{+\,a}$	$k_R/k_H{}^b$	$\log (k_R/k_H)$
Cl	0.11	0.6	−0.222
H	0	1	0.000
Me	−0.31	11	1.041
OMe	−0.78	30	1.477

^{a} The para values of σ^+ were used because of the carbon-to-carbon relationship. We are unaware of analogous thiophene-specific values. ^{b} Relative rates were determined from average selectivities from multiple ratios of unsubstituted to substituted thiophene.

rates vs σ^+ (taken from benzene analogues;[39] data are not available for thiophene analogues) results in a slope of -2.0 ± 0.4 ($r^2 = 0.92$). The σ^+ values for 2-bromothiophene ($\sigma^+ = 0.15$) and 2-cyanothiophene ($\sigma^+ = 0.66$) are consistent with the pattern established in Table 3.[40]

These results clearly show that dicarbomethoxycarbene is an electrophilic partner in the eventual formation of **8**, but are not definitive in other details. The sign of ρ, of course, shows that partial positive charge is developed on the thiophene in the rate-determining step. Magnitudes of ρ for electrophilic aromatic substitution of toluene range from about -2.5 to about -12 with the most active electrophiles generally having the largest magnitudes.[41] However, the interpretation of the values is complex, even for closely related reactions of this class. (See for example refs 39 and 42.) The observed ρ value for dicarbomethoxycarbene adding to thiophene of about -2.0 is consistent with the carbene being a neutral electrophile in reacting with the thiophene π-system. However, the experimentally obtained ρ of -2.0 does not distinguish between cyclopropanation to give **14** and direct formation of **12**.

Regardless of the magnitude of ρ, though, classic electrophilic aromatic substitution, in which the dicarbomethoxycarbene is protonated before reaction with thiophene, can be ruled out because no proton source is available in most of the reaction conditions reported here. However, one could speculate that the reaction of dicarbomethoxycarbene **5** with thiophene to form **12** might be a single step that begins with a transition state similar to that of a classic cyclopropanation, but finds a low energy path that diverts to **12** without formation of **14**. If this were the case, it might be argued that small steric differences in monosubstituted thiophenes could direct the carbene away from the substituted side of the thiophene, until it found either the unsubstituted side or the sulfur atom.

Another alternative that was considered was that **14** does form, but undergoes a rapid intramolecular rearrangement to an enol with ring-opening, i.e., path f in Scheme 2. Given that no evidence for **14** was found, even at -30 °C, it was assumed that the barrier to the rearrangement from **14** to **15** would have to be low. The potential reaction would be pseudopericyclic and thus not "forbidden" (see, for example refs 43−46). Thus, a computational investigation was undertaken. Compound **14**

was optimized at HF, MP2, and B3LYP levels of theory with various basis sets, and a search was undertaken for the appropriate transition state. In spite of considerable effort, no low-energy transition state that connected **14** and the enol could be found. However, examination of computational and physical models suggests that the orbital alignment for such a rearrangement would be poor. Thus, while not finding a low-energy transition state by computational means is by no means strong evidence that one does not exist, we no longer consider formation of **14** and its rapid decomposition by means of path f to be a likely explanation for the experimental results.

Interestingly, previous workers report that photolysis of dimethyl diazomalonate in the presence of vinyl sulfides and thiophene resulted in only modest yields of sulfonium ylides, not in any cyclopropanation.[32,47] Though it is clear that the photolysis of **3** in the presence of thiophene is cleaner than these reported photolyses of dimethyl diazomalonate, we cannot resolve the apparent conflict with our report, i.e., that no cyclopropanation or other C−C bond formation was observed in the earlier work.

Conclusions

Reaction between thiophene and dicarbomethoxycarbene produces both the ylide **1** and the net C−H insertion product **8**, in almost equal part. Electronic donating substituents on the 2-position of the thiophene ring increase the relative yield of **8** at the unsubstituted 5-position. In contrast to certain thermal reactions, formation of **8** is not a direct rearrangement of the ylide **1**. Furthermore, the substituent effects strongly imply that an intermediate such as **11** is not involved in the formation of **8**, either.

Beyond this, definitive conclusions are more difficult. Despite observations of close analogues, **14** has, to the best of our knowledge, never been detected in any experiment that generates free dicarbomethoxycarbene (**5**) or a free carbenoid, or in which **1** is heated. Analogues deriving from the reaction of **5** and benzene or between thiophene and slight structural variants of **5** have all been detected, though. This suggests that **14** may be formed, but decomposes easily. We cannot disprove a low-energy pathway that converts **14** to the monocyclic enol **15**, but did not find any positive computational evidence. Alternatively, it is possible that **14** is never actually formed, but rather that the addition of the carbene to the π bond of the thiophene is diverted to a more "downstream" intermediate, e.g., **12**, through a very asynchronous transition state.

Experimental Section

Materials. Unless otherwise noted, all solvents were the highest purity commercially available, and reagents were used as received. All NMR spectra were obtained with CDCl$_3$ as solvent. The formally carbanionic carbon typically does not show in the ^{13}C spectra.

Thiophene Ylides. In a small round-bottomed flask, 1 equiv (approximately 5 mmol) of the thiophene derivative was mixed with 3 equiv of the dimethyl diazomalonate and 2 mg of rhodium acetate dimer. In occasions when the thiophene derivative was a solid, a minimal amount of 1,2-dichloroethane was added. The mixture was allowed to stir until the color changed from dark green or a

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precipitate formed. Analysis by IR showed no diazo stretch. The crude product was washed with hexane, decanted, washed again with 50/50 ethyl acetate/hexane solution, and decanted again. The remaining light green solid was then recrystallized from ethanol to yield a white solid. Compounds **1−4** were previously reported by us.[1]

Dimethylmalonate-2,5-dimethylthiophene-*S,C*-ylide (1a):[48] Yield 85%. ^{1}H NMR δ 6.95 (s, 2H), 3.76 (s, 6H), 2.16 (s, 6H).

Dimethylmalonate-2,5-dichlorothiophene-*S,C*-ylide (1b):[32,49] Yield 72%. ^{1}H NMR δ 7.02 (s, 2H), 3.78 (s, 3H), 3.62 (s, 3H).

Dimethylmalonate-2,5-bromothiophene-*S,C*-ylide (1c):[32] Yield 5.3%. ^{1}H NMR δ 7.13 (s, 2H), 3.77 (s, 3H), 3.65 (s, 3H).

Dimethylmalonate-3,4-dibromothiophene-*S,C*-ylide (1d): Yield 23%. ^{1}H NMR δ 6.99 (s, 2H), 3.70 (s, 6H). [13]C δ 165.4, 129.0, 127.3, 51.9. HRMS calcd 371.8468, obsd 371.8449.

Dimethylmalonate-2-methylthiophene-*S,C*-ylide (1e):[28,32] Yield 87%. ^{1}H NMR δ 7.12 (d, J = 3.6 Hz, 1H), 6.84 (d, J = 5.4 Hz, 1H), 6.79 (dd J = 5.4, 3.6 Hz 1H), 3.75 (s, 6H), 2.50 (s, 3H).

Dimethylmalonate-2-chlorothiophene-*S,C*-ylide (1f):[48,50] Yield 77%. ^{1}H NMR δ 7.18 (d, J = 3.2 Hz, 1H), 7.05 (d, J = 4.8 Hz, 1H), 6.91 (dd J = 4.8, 3.2 Hz, 1H), 3.73 (s, 6H).

Dimethylmalonate-2-bromothiophene-*S,C*-ylide (1g):[28,32] Yield 89%. ^{1}H NMR δ 7.33 (d, J = 6.0 Hz, 1H), 7.23 (d, J = 3.2 Hz, 1H), 7.17 (dd J = 6.0, 3.2 Hz, 1H), 3.76 (s, 6H).

Dimethylmalonate-2-thiophenecarbonitrile-*S,C*-ylide (1h): Yield 88%. ^{1}H NMR δ 7.21 (d, J = 4.0 Hz, 1H), 7.02 (d, J = 6.0 Hz, 1H), 6.95 (dd, J = 6.0, 4.0 Hz, 1H), 3.72 (s, 6H). ^{13}C NMR δ 171.4, 136.9, 133.3, 127.2, 116.1, 114.7, 60.6. Note: This reaction was considerably less reliable than the others reported here.

Dimethylmalonate-2-methoxythiophene-*S,C*-ylide (1i): Yield 69%. ^{1}H NMR δ 6.78 (dd, J = 4.2, 3.0 Hz, 1H), 6.63 (d, J = 4.2 Hz, 1H), 6.29 (d, J = 3.0 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR δ 171.4, 164.7, 123.6, 117.1, 60.6, 59.1. HRMS calcd 244.041, obsd 244.044.

Photolyses. All solutions were deoxygenated by bubbling with Ar for a minimum of 15 min. Irradiations were done with either broadly emitting low pressure fluorescent tubes centered at either 300 or 350 nm or a Xe arc lamp filtered through a monochromator with ±12 nm linear dispersion. Initial concentrations were 1−4 mM. The products **8e**,[28,29] **8f**, **8j**,[51] and **25** were identified by their ^{1}H NMR spectra. Representative proton spectra of product mixtures containing **8f** and **25** are given in the Supporting Information. **8f:** ^{1}H NMR δ 7.23 (d, J = 4.8 Hz, 1H), 7.01 (d, J = 4.8 Hz, 1H), 4.90 (s, 1H), 3.86 (s, 6H). **25a:** ^{1}H NMR δ 6.64 (d, J = 4.5 Hz, 1H), 6.51 (d, J = 4.5 Hz, 1H), 4.58 (t, J = 6.4 Hz, 1H), 3.73 (s, 6H), 2.36 (d, J = 6.4 Hz, 2H), 2.31 (s, 3H).

Photolysis at Low Temperature. A methanol bath, chilled to −30 °C by means of careful addition of dry ice, was used in conjunction with a Rayonet minireactor and 300 nm bulbs. The sample, held in an NMR tube, was taken directly from the bath and examined in a precooled NMR probe at the same temperature.

Competition Experiments. A weighed mixture of thiophenes or a neat thiophene was mixed with 4−6 mg of **3**, degassed, and photolyzed at 365 nm in the Rayonet until completion. Afterward, the low-boiling thiophenes were gently evaporated, and the remaining substances analyzed by ^{1}H NMR. In the cases where the thiophenes were too high boiling, the mixture was analyzed by GCMS.

Thermolyses. Initial concentrations of ylide were 2−4 mM and the solvent was purged with Ar. The sealed samples were placed in an oven held at 80 °C and periodically analyzed over a time scale of 12 −36 h.

Supporting Information Available: Spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO802823S

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