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Stacey A. Stoffregen
Iowa State University

Melanie Heying
Iowa State University

William S. Jenks
Iowa State University, wsjenks@iastate.edu

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Abstract

Photolysis of *S,C*-sulfonium ylides derived from thioanisol, thiophene, benzothiophene, or dibenzothiophene provides products deriving from dicarbomethoxycarbene. In methanol, no rearrangement of the carbene to the ketene derivative is observed. Formation of dibenzothiophene and benzothiophene is quantitative. For the thiophene-based ylide, insertion of the carbene into the α -CH bond of thiophene is observed. Evidence is presented that supports formation of both singlet and triplet carbene.

Disciplines

Chemistry | Organic Chemistry | Other Chemistry | Polymer Chemistry

Comments

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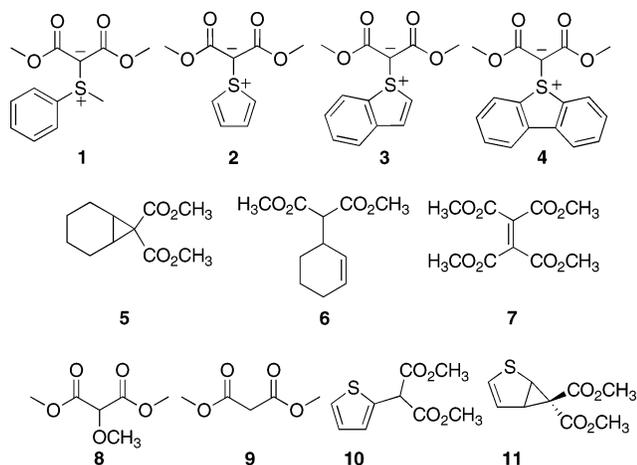
Stacey A. Stoffregen, Melanie Heying, and William S. Jenks*

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

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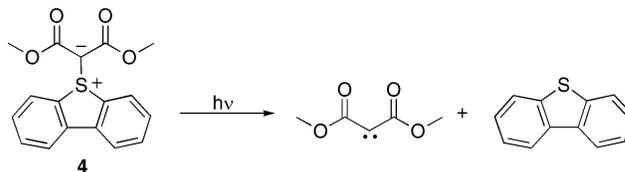
Carbenes remain important and intriguing reactive intermediates in organic chemistry despite years of study for many reasons, among them the access they provide to unusual product compounds, their differing chemistry depending on spin state, and their mechanistic complexity. Photochemical precursors to carbenes, such as diazo compounds and diazirines, are often favored, because they can yield carbenes by photolysis at low temperatures and can be used for laser flash photolysis experiments. However, because these nitrogenous precursors have been shown to undergo reactions in their excited states that mimic chemistry expected from the carbene itself, there is demand for alternative practical precursors. In this Communication, we report the use of *S,C*-sulfonium ylides **1–4** as photochemical carbene precursors, as illustrated in Scheme 1 for compound **4**.

The choice of compounds **1–4** as potential precursors to dicarbomethoxycarbene for this study was driven by two considerations. First *S,C*-ylides of malonates are known to be stable and easy to prepare, at least in part because of the electron withdrawing groups that delocalize the formal negative charge. Second, by generating dicarbomethoxycarbene^{1–3} for the proof-of-concept work of showing carbene generation, we believed we could distinguish between reactions of the carbene and a potential excited state Wolff-like rearrangement that might yield a ketene derivative. Such 1,2-shifts have been demonstrated repeatedly for nitrogenous carbene precursors that are subject to 1,2 hydrogen shifts or carbon shifts to relieve ring strain.^{4–10}

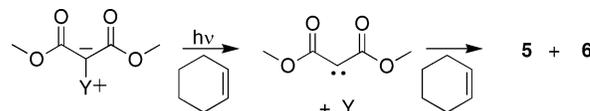


We^{11–13} and others^{14–18} have shown in previous work that photolysis of dibenzothiophene-*S*-oxide and its derivatives leads to chemistry that appears to derive from *S*–*O* cleavage and formation of atomic oxygen. Although direct evidence for this mechanism in the form of spectroscopic detection of O(³P) is lacking, we have recently shown through time-resolved IR experiments that benzoyl nitrene is formed on photolysis of *N*-benzoyl dibenzothiophene sulfilimine.¹⁹ These results, and our knowledge that the photochemistry of methyl phenyl sulfoxide is substantially

Scheme 1



Scheme 2 Trapping by Cyclohexene^a



^a Y = thioanisole, thiophene, benzothiophene, or dibenzothiophene

more complex than that of dibenzothiophene-*S*-oxide, led us to predict that compounds **2** and **4** might be particularly attractive precursors. The photochemistry of benzothiophene-*S*-oxide is not dominated by deoxygenation,²⁰ but we believed that the bond dissociation enthalpy (BDE) for its *S*–*O* bond would be significantly higher than the corresponding *S*–*C* BDE for **3**,²¹ and that **3** might thus also be a reasonable carbene precursor.

Compound **1** was photolyzed at 254 nm in acetonitrile with 10% cyclohexene (by volume), anticipating chemistry shown in Scheme 2. Thioanisole, cyclopropane adduct **5**, and C–H insertion product **6** were observed as part of a complex reaction mixture. The quantum yield of disappearance of **1** was 0.09, while that of the appearance of thioanisole was only 0.01. Compound **7**^{22–24} was not observed during this or any other photolysis.

In contrast to **1**, photolysis of ylides **2–4** in the same solvent mixture with irradiation centered at 300 nm led to quantitative formation of the corresponding sulfide, and in higher quantum yield (Table 1). The expected adducts were formed in reasonable, but not quantitative, yield. The ratio of **5/6** was approximately constant for the three precursors.

Platz and co-workers concluded that the formation of dimethyl 2-cyclohexylmalonate on photolysis of dimethyl diazomalonnate in cyclohexane was at least in part due to a reaction between the excited-state of the diazo compound and cyclohexane, bypassing the free carbene entirely.³ Jones argued that the cyclopropanes obtained by photolysis of methyl diazomalonnate derived both from the conventional carbene addition and from cycloaddition of the excited-state of the diazo compound to the alkene, followed by its decomposition to give alkenes of mixed stereochemistry.²

We thus consider here whether an excited-state of compounds **2–4** might be involved in the cyclohexene insertion product **6**. Although spectroscopic study would be ideal, we can make a reasonable argument on the basis of product yields alone. It is reasonable to expect variation in the overall quantum yields and even the absolute product yields, due either to variation in the excited-state dynamics of the precursors or the competitive reactivity between the nascent sulfide and the cyclohexene trap with the carbene. An increase in the reactivity of thiophene, benzothiophene,

Table 1. Photolysis in Acetonitrile with Cyclohexene

| ylide | Φ_{-ylide} | $\Phi_{+sulfide}$ | yields (%) ^a | | | |
|-------|-----------------|-------------------|-------------------------|-----|----|-----------|
| | | | 5 | 6 | 10 | 5/6 |
| 2 | 0.25 ± 0.02 | 0.25 ± 0.01 | 18.4 | 3.5 | 15 | 5.0 ± 0.8 |
| 3 | 0.20 ± 0.01 | 0.20 ± 0.02 | 40.6 | 8.0 | | 5.2 ± 0.8 |
| 4 | 0.18 ± 0.01 | 0.17 ± 0.01 | 44.1 | 9.2 | | 4.8 ± 0.1 |

^a Relative to sulfide formation, or sulfide + **10** for **2** as precursor. $\Phi_{+sulfide}$ also includes **10** for precursor **2**.

Table 2. Photolysis of **2–4** in Methanol

| ylide | Φ_{-ylide} | $\Phi_{+sulfide}$ | product yields (%) ^a | | |
|-----------------------|-----------------|-------------------|---------------------------------|----|----|
| | | | 8 | 9 | 10 |
| 2 | 0.21 ± 0.03 | 0.20 ± 0.03 | 52 | 5 | 22 |
| 3 | 0.12 ± 0.01 | 0.12 ± 0.01 | 70 | 5 | |
| 4 | 0.17 ± 0.01 | 0.16 ± 0.02 | 54 | 39 | |
| 2-Sens ^{b,c} | | | | | |
| 3-Sens ^c | | | 7 | 65 | |
| 4-Sens ^c | | | 9 | 57 | |

^a Relative to sulfide formation or sulfide + **10**. $\Phi_{+sulfide}$ also includes **10** for precursor **2**. ^b Overlapping absorption spectra made experiment impractical. ^c Sensitized with benzophenone.

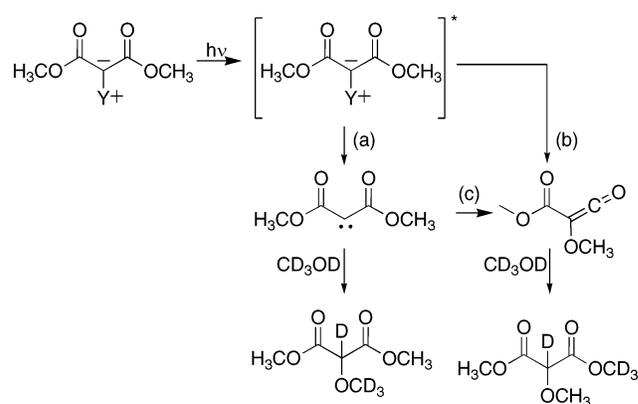
or dibenzothiophene toward dicarbomethoxycarbene would lead to an apparently lower overall quantum yield, if the product so-formed was the original ylide. If another product was formed, then the overall quantum yield might not change, but the total yield of **5** and **6** would. Indeed, with **2** as a precursor, a fraction of the thiophene is trapped as **10**. (We did not observe **11**.)

However, if both **2*** and the carbene contributed to the yields of **5** and **6** (on direct irradiation of **2**), then a pathological coincidence of rate constants would have to occur for the observed ratio of **5/6** to remain the same when **3** or **4** were used. Thus, the ratios of products **5/6** shown in Table 2 are most easily interpreted in terms of a single common intermediate, that is, dicarbomethoxycarbene.

Direct irradiation of ylides **2**, **3**, or **4** in methanol provided the carbene–methanol adduct **8** and small amounts of the double hydrogen abstraction **9** (Table 2). The C–H insertion product **10** was formed in the case of **2** as a precursor.

Product study using CD₃OD as solvent distinguishes whether the adduct **8** arises through formation of the ketene (Scheme 3), either via carbene formation (path a, then c) or by direct rearrangement of the excited-state of the precursor (path b). The overall yields for **8**, **9**, and **10** were essentially identical as when CH₃OH was used. Using CD₃OD, only the ester methyl of **8** was observed by ¹H NMR, even at complete conversion, ruling out intervention of the ketene in the reaction pathway.

On benzophenone-sensitized photolysis of **3** or **4**, the major product was **9**. The most economical conclusion is that triplet-to-singlet intersystem crossing by the carbene is comparatively slow, and is kinetically competitive with the formation of methyl malonate.^{3,25} The very fast rate constant for trapping of singlet dicarbomethoxycarbene ($1.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$)³ implies all of the singlet carbene should be trapped as **8**. Thus, we further infer that the differing balances between **8** and **9** in Table 2 for the different precursors reflect the differing singlet/triplet carbene ratios initially formed by photodissociation of the three ylides. Photolysis of the

Scheme 3

structurally related *N*-benzoyl dibenzothiophene sulfilimine has been shown to yield both singlet and triplet benzoyl nitrene.¹⁹

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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