

Product sensitization in the photochemical generation of carbenes from sulfonium ylides

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ABSTRACT

Photolysis of thiophene ylides provides a route to certain carbenes with adjustable photophysical parameters, in that the absorption spectrum of the precursor and the initial spin population of the carbene can be varied. However, the accumulated thiophene from extensive photolysis can act as a triplet sensitizer leading to triplet carbene. It is demonstrated that dibenzothiophene has this property and 2,5-dichlorothiophene does not.

1. Introduction

S,C-Sulfonium ylides based on the thiophene moiety can be useful photochemical precursors of carbenes, as previously demonstrated for dicarbomethoxycarbene [1–3]. The reaction finds good analogy to formation of nitrenes from sulfilimines [4–8] and atomic O(³P) from sulfoxides [9–18]. As illustrated in Scheme 1, photolysis of ylides analogous to the dibenzothiophene ylide **DBTY** regenerates the aromatic sulfide (in this case dibenzothiophene, **DBT**), along with the transient carbene **C** (quantum yield ~0.16 for **DBTY**). Previous work demonstrated the important finding that the initial spin multiplicity distribution of the carbene depended on the exact nature of the thiophene derivative [1,3], thus allowing manipulation of that parameter. This phenomenon was attributed to the variation of photophysics contained within the thiophene chromophores, as contrasted to the fixed photophysics available from diazo compounds, where the chromophore of the photochemical leaving group cannot be varied. It is this latter feature of the thiophene ylides as a class (whether generating carbenes, nitrenes or O(³P)) that can be exploited make them attractive photochemical precursors for various reactive intermediates.

Proof of this concept can be developed through trapping reactions that occur rapidly compared to intersystem crossing of the carbene. Singlet dicarbomethoxy carbene (¹C) in neat methanol is trapped as methoxymalonate **MeOM**, whereas the triplet carbene (³C) is indirectly observed as the reduced malonic ester **M**. Adventitious or intentionally added oxygen diverts ³C to the oxomalonate **OM** (Scheme 2). Similarly, addition of ¹C to alkenes to form cyclopropanes is stereospecific. A mixture of *cis* and *trans* cyclopropanes that favors the more stable isomer is obtained from either the *cis* or *trans* oct-4-ene and ³C (Scheme 3).

In our initial work [1], we stated that control photolyses showed constant product ratios (e.g., **M**: **MeOM**) with conversion, but as shown here, that is not true in every case. This paper tests the hypothesis that variation of such product ratios is due to triplet sensitization by the resulting sulfide product (e.g., **DBT**) in appropriate cases.

2. Materials and methods

The ylides **DBTY** and **DCTY** were prepared as described previously [1–3]. The *cis*-cyclopropane **cCP** was isolated as a pure compound and the *trans* cyclopropane **tCP** was prepared as a mixture [19]. Commercially available oct-4-enes were distilled under Ar from CaH₂ to remove small quantities of oxidized impurities. Solvents were the highest grade commercially available. Methanol was used as received. Acetonitrile was ≤30 ppm water commercially and handled to minimize air exposure.

Photolyses were carried out much as previously described. Briefly, solutions containing the ylide were prepared in initial concentrations of 5–8 mM in the solvent of interest. Dodecane at 0.50 mM was used as an internal standard for GC analysis; a standard DB-5 (5% phenyl) microbore column was used for separation. Unless otherwise noted, solutions in methanol had no other initial components; photolyses using *cis*-oct-4-ene as trap were done with 10% alkene in acetonitrile (v/v) instead of methanol. Solutions were deoxygenated or saturated with oxygen by bubbling for ca. 20 min with Ar or O₂, respectively. Sample volume was 3.0 mL in a standard 1 cm fluorescence cell equipped with a small stir bar and sealed with a septum for sparging and sampling through a needle. The light source was a 75 Xe lamp filtered through a monochromator set to ± 12 nm dispersion. Samples were mounted directly in front of the monochromator exit slit and magnetically stirred

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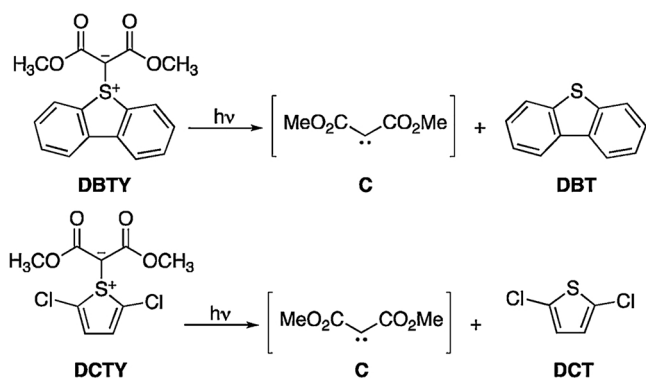
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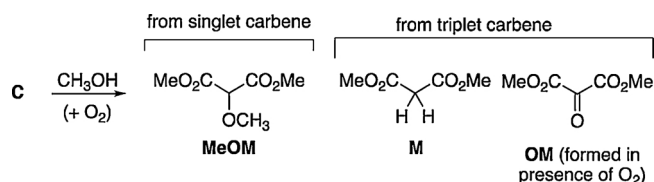
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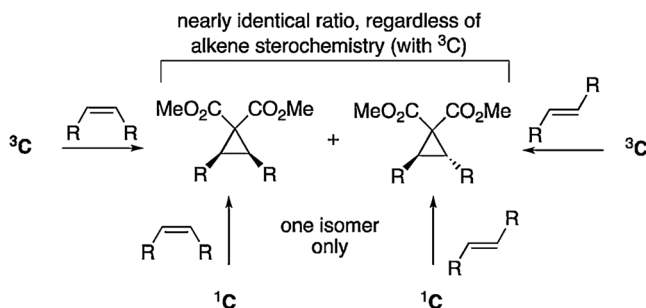
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Scheme 1. Photochemical formation of dicarbomethoxy carbene, C.



Scheme 2. Reaction of dicarbomethoxy carbene with methanol.

Scheme 3. Reaction of dicarbomethoxy carbene with *cis* or *trans* alkenes.

to ensure even irradiation. GC retention times and relevant response factors were determined with authentic samples. Samples for GC injection (e.g., for watching the time course of a reaction) were obtained by piercing the septum with a GC needle and withdrawal of a couple of microliters.

Extrapolations of product ratios to zero conversion were done by polynomial fits to appropriate fractions of the data sets. No physically meaningful inferences were made from fit data, but it was assumed that the curves would extrapolate smoothly. Thus, greater uncertainty should be attributed to product ratios at zero conversion than to those at full conversion, which were determined directly. For the photolyses in *cis*-oct-4-ene/acetonitrile mixtures, estimation of the total percentage of products derived from singlet or triplet carbene requires knowledge of the cyclopropane mixture hypothetically generated by a sample of pure ¹³C. Based on our previous work and a closely related reaction studied by Platz and coworkers [20], a 9:1 ratio of *trans* to *cis* was used for this study, and residual *cis* cyclopropane from observed ratios was attributed to singlet chemistry, as was observed oxazole.

3. Results and discussion

In the course of expanding work on this set of carbene precursors, a set of data was obtained for the direct photolysis of dibenzothioyl ylide (DBTY) at 270 nm in methanol showed that the product ratio obtained between methoxymalonate MeOM (the singlet-attributed product) and malonate M (the triplet-attributed product) was not constant with conversion (Fig. 1), in contrast to our prior

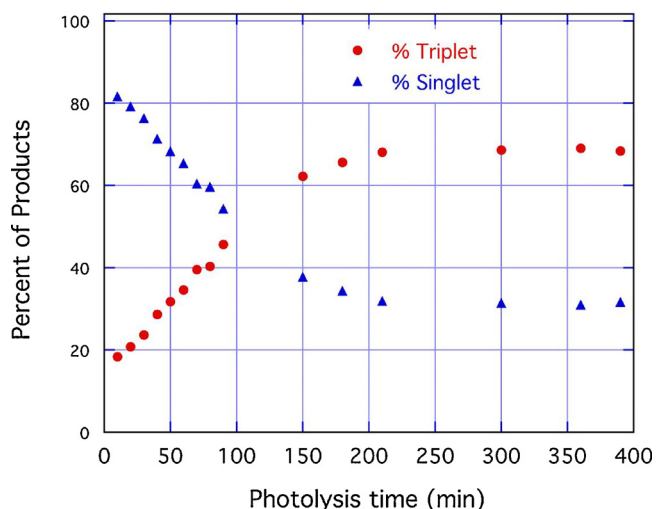


Fig. 1. Product mixture for direct photolysis of DBTY at 270 nm as a function of photolysis time. The singlet product is MeOM and the triplet products are M and OM. Total yield at complete conversion is 72% for the three compounds, determined by comparison to formed DBT.

generalization. In fact, extrapolation to zero conversion suggested that the initial product distribution was roughly 15% triplet-derived and 85% singlet-derived (hereafter noted as T:S = 15:85). It should be noted that detection limits made determining the product ratios at very low conversion untenable, so these initial product ratios are extrapolated and should be treated as qualitative data. (See supporting information for figures illustrating the same phenomenon in the remaining examples.)

Over the course of bringing the reaction to full conversion in just over 200 min, that ratio reversed smoothly to 68:32 (Table 1, entry 1). We use T:S₀ to denote the extrapolated product ratio at zero conversion and T:S_f to denote the observed final product ratio. As described below, similar time-course measurements were made for a series of related photolysis conditions. For example, photolysis with 300 nm excitation provided very similar results. See Table 1, entry 3.

It was found that over the course of many septum piercings in some experiments, admission of adventitious oxygen meant that oxomalonate OM was formed in addition to M. Control experiments sampling only at the final time point showed that (M + OM) was approximately constant when only adventitious O₂ was present. Thus both are counted as part of the triplet product mixture.

In retrospect, it was hypothesized from data in Fig. 1 that the great difference between T:S₀ and T:S_f was due to competitive absorption of light by accumulating DBT, which could be acting as a triplet sensitizer. According to literature data [21,22], the triplet yield of DBT at room temperature is nearly quantitative ($\Phi_T = 0.97$). Thus, as DBT begins to compete with DBTY for light absorption, a new triplet-only channel is

Table 1
Photolysis of DBTY in methanol.

Entry	[DBT] ₀ , mM ^a	λ_{ex} , nm	Gas ^b	T:S ₀	T:S _f	% Yield ^c
1	0	270	Ar	15:85	68:32	72
2	7 (15%) ^c	270	Ar		75:25	78
3	0	300	Ar	14:86 ^d	71:29	61
4	0	300	O ₂	0:100	47:53	55
5	8 (79%) ^c	325	Ar	75:25	84:16	84

^a Estimate of the initial percentage of excitation light absorbed by DBT given in parentheses.

^b Solutions saturated with Ar to remove O₂, except entry 3, which was saturated with O₂.

^c Summed yield of M, MeOM, and OM. All yields are quoted at completion, summing all stated products, relative to DBT.

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