

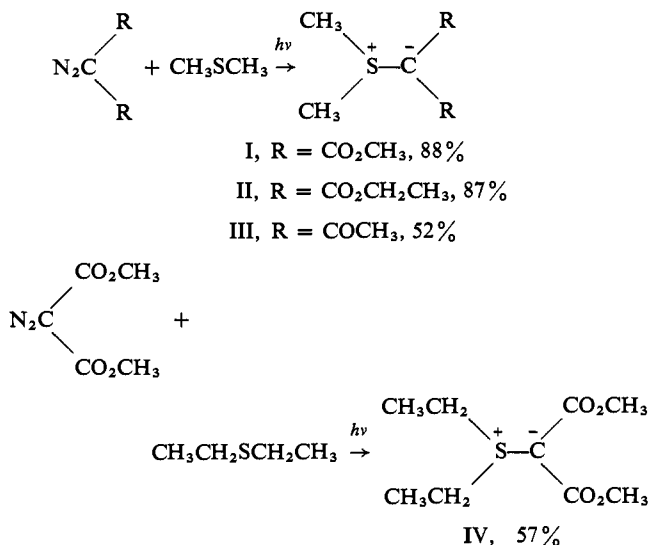
# Communications to the Editor

## Formation of Stable Sulfonium Ylides via Photodecomposition of Diazocarbonyl Compounds in Dimethyl Sulfide

Sir:

The photochemical decomposition of diazobiscarbonyl compounds is known to yield bis(carbonyl)carbenes. While the reactions of such carbenes with carbon-oxygen bonds have been studied,<sup>1,2</sup> there are only few reports on the reaction with carbon-sulfur bonds.<sup>3</sup> We describe the formation of a stable sulfonium ylide by the photoinduced reaction of diazocarbonyl compounds with dimethyl sulfide.

Irradiation of a solution of dimethyl diazomalonate in dimethyl sulfide was carried out in a Pyrex vessel with a high-pressure mercury lamp.<sup>4</sup> Dimethylsulfonium bis(methoxycarbonyl)methylide (I) was obtained as a pure white solid in 88% yield by decanting the unreacted dimethyl sulfide and washing the remaining solid with petroleum ether (bp 30–60°), mp 169–170° (recrystallized from ethanol). *Anal.* Calcd for C<sub>7</sub>H<sub>12</sub>O<sub>4</sub>S: C, 43.74; H, 6.29; S, 16.67; Found: C, 43.68; H, 6.53; S, 16.41. This product showed two singlet nmr signals at 3.71 (–CO<sub>2</sub>CH<sub>3</sub>) and 2.89 ppm (–SCH<sub>3</sub>) in equal intensity, and ir absorption maxima at 1625 and 1675 cm<sup>-1</sup>.



Reactions of other diazo compounds were also studied. Photolysis of diethyl diazomalonate and acetyldiazoacetone in dimethyl sulfide gave dimethylsulfonium bis(ethoxycarbonyl)methylide (II) and dimethylsulfonium bis(acetyl)methylide (III), respectively. The structures of these ylides are derived by comparing their spectra and

(1) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y. 1964, p 107 ff.

(2) M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *Tetrahedron Letters*, 1391 (1967).

(3) J. Diekmann, *J. Org. Chem.*, **30**, 2272 (1965). Bis(phenylsulfonyl)diazomethane was photolyzed in sulfides to yield the ylide.

(4) Rikoshā 400-W high-pressure mercury lamp with maximum output at 3660 Å.

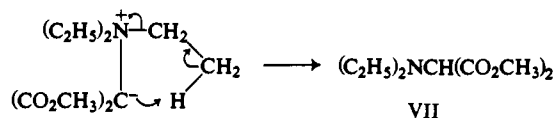
Table I. Yields of Products from Dimethyl Diazomalonate in Cyclohexene and Dimethyl Sulfide

Mole ratio, cyclohexene/sulfide	Products, %	
	Ylide I	Adducts to cyclohexene
1	61	15
2	49	25
5	36	41
∞	0	92

Table II. Yield of Products of Dimethyl Diazomalonate in Equimoles of Reactants

Pair of reactants	Products, %	
	Ylide I	Adducts to the other <sup>a</sup>
CH <sub>3</sub> SCH <sub>3</sub> , cyclohexene	61	15
CH <sub>3</sub> SCH <sub>3</sub> , 2-methyl-2-butene	57	8.3
CH <sub>3</sub> SCH <sub>3</sub> , cyclopentadiene	44	...
CH <sub>3</sub> SCH <sub>3</sub> , CH <sub>3</sub> OH	78	10
CH <sub>3</sub> SCH <sub>3</sub> , CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	73	12
CH <sub>3</sub> SCH <sub>3</sub> , (CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N	20	Trace <sup>b</sup>

<sup>a</sup> It has been reported that carboalkoxycarbene reacts with ether or amine to form the carbon-oxygen or carbon-nitrogen insertion product which may be explained in terms of an ylide mechanism, but no quantitative data are yet available for the reactivities of these substrates. See ref 1, p 107 ff. <sup>b</sup> The main products from the reaction were the sulfonium ylide and dimethyl malonate, accompanied by a trace amount of the product VII which can be presumed to be formed via a nitrogen ylide.



other physical properties with those of ylides prepared recently by Cook and Moffatt.<sup>5</sup>

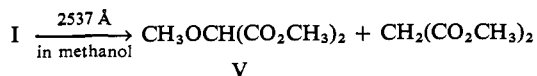
Irradiation of dimethyl diazomalonate in diethyl sulfide gave the product IV, mp 149–150°; nmr signals, 1.26 (–CH<sub>3</sub>, triplet), 2.72 (–CH<sub>2</sub>–, quartet), and 3.76 ppm (–CO<sub>2</sub>CH<sub>3</sub>, singlet) in the intensity ratio 3:2:3, respectively; ir absorption maxima at 1620 and 1655 cm<sup>-1</sup>.

From our preliminary experiments, the benzophenone-sensitized photodecomposition of diazo compounds in dimethyl sulfide did not result in formation of the sulfonium ylide. This indicates that the triplet carbene cannot be an intermediate of the formation of sulfonium ylide. These observations suggest a mechanism of ylide formation in which a singlet bis(carbonyl)carbene attacks an unshared electron pair on a sulfur atom of dimethyl sulfide.<sup>6</sup>

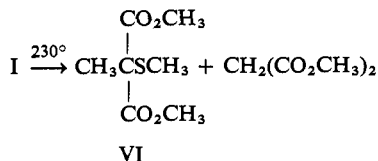
Although ylide I is stable to radiation from the high-pressure mercury lamp, 2537 Å irradiation in methanol gave dimethyl methoxymalonate (V) and dimethyl malonate.

(5) A. F. Cook and J. G. Moffatt, *J. Am. Chem. Soc.*, **90**, 740 (1968).

(6) Excited diazo compound itself may add to a sulfur atom with formation of an unstable intermediate which loses nitrogen to give a sulfonium ylide. This possibility cannot be eliminated, since there is no evidence that the excited diazo compound loses nitrogen before it reacts with sulfide.



When sulfonium ylide I was heated in a sealed tube at 230° for 3 hr, rearranged product<sup>7</sup> VI and dimethyl malonate were obtained. This fact is noteworthy since it



is the first direct evidence of a thermal rearrangement of a sulfonium ylide, although there have been several reports suggesting rearrangements of unstable sulfur ylide intermediates.<sup>8</sup>

The relative reactivity of the sulfur atom in dimethyl sulfide was investigated. Product distributions from the photolysis of dimethyl diazomalonate in mixtures of cyclohexene and dimethyl sulfide are shown in Table I. Control experiments showed that the products are stable under the reaction conditions. The results indicate that bis(carbomethoxy)carbene reacts with dimethyl sulfide four times faster than with cyclohexene. Experiments with other olefins showed similar results (see Table II). Table II also shows the yields of reaction products from the photolysis of dimethyl diazomalonate in equimolar mixtures of dimethyl sulfide and other nucleophiles. In all cases, sulfonium ylide was separated and weighed, and reaction products from the other nucleophiles were determined by gas chromatography using an appropriate internal standard.

These observations suggest that dimethyl sulfide can be used as a more effective and more convenient acceptor of negatively substituted carbenes than olefins when the sulfonium ylides are stable under the reaction conditions, because of the high reactivity of dimethyl sulfide and the ease of isolating ylide products.

Because of the high yield of sulfonium ylides, the reaction will be useful for synthesis of ylides. Concerning scope and limitation, further extensive investigation is in progress.

(7) The rearranged product (VI) was identified by the analysis of nmr spectra (3.75 ppm,  $-\text{CO}_2\text{CH}_3$ ; 2.13 ppm,  $-\text{SCH}_3$ ; 1.61 ppm,  $-\text{SCH}_3$ ; intensity ratio 2:1:1) and an ir absorption maximum at  $1745 \text{ cm}^{-1}$ .

(8) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, p 304.

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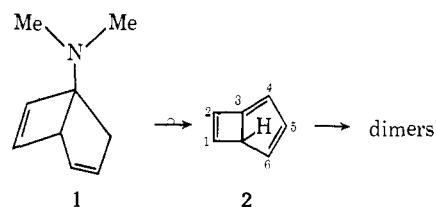
### Bicyclo[3.2.0]hepta-1,3,5-triene

Sir:

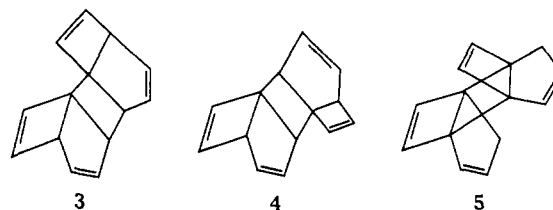
The interesting results on the bicyclo[3.2.0]heptatrienyl system recently communicated to this journal by Breslow's group galvanize us to report our own closely related results which parallel those of Breslow except for the structure of the interesting dimer of bicycloheptatriene (2).<sup>1</sup>

(1) R. Breslow, W. Washburn, and R. C. Bergman, *J. Am. Chem. Soc.*, **91**, 196 (1969).

Amine **1**<sup>2</sup> was converted by excess methyl iodide in ethanol (room temperature, 3 hr) to its methiodide salt and by hydrogen peroxide in methanol to its N-oxide.  $\beta$  eliminations on the former by sodium methoxide in



DMSO (room temperature, 3 hr) and on the latter by pyrolysis at 120° both gave rise to the same *ca.* 50:50 mixture of isomeric hydrocarbon dimers, separated by vpc (silicone oil-chromosorb W, 160°). Both have *m/e* 180 and no  $\lambda_{\text{max}} > 210 \text{ m}\mu$ , but they are differentiated by their nmr spectra: dimer A,  $\tau$  3.7–3.9 (4 H, AB,  $J = 1.3 \text{ Hz}$ , cyclobutenes), 4.2 (4 H, s, cyclopentenes), 6.45 (2 H, m, methines), 7.35 (2 H, m, methines); dimer B,  $\tau$  3.8 (4 H, s, cyclobutenes), 4.2–4.4 (4 H, AB,  $J = 2.9 \text{ Hz}$ , cyclopentenes), 6.4 (2 H, m, methines), 6.7 (2 H, m, methines). The equivalence of the two cyclopentene and cyclobutene rings in both dimers and the presence of but two different types of methine hydrogen in each precludes, barring an inadmissible series of coincidences, the possibility that either of the present dimers is of the type suggested by Breslow's group. The nmr and uv data effectively rule out all reasonable dimeric structures except **3**, **4**, and **5** (all as *syn-anti* pairs).<sup>3</sup> Structure **5** is inconsistent



with the very small ( $< 2 \text{ Hz}$ ) coupling constant observed between the two types of hydrogen bound to saturated carbon. A much larger, geminal, splitting would be expected of **5**. Structures **3** and **4** would both result from olefin cycloaddition across the strained 3,4 double bond of triene **2**. Of these, **3** is preferred on the basis of the two-step mechanism of olefin cycloaddition and the expectation that more strain would be relieved if the two bridgehead (3) positions couple initially. Triene **2** has also been trapped as its diphenylisobenzofuran and cyclopentadiene adducts, which have structures analogous to **3**. Interestingly, triene **2**, though readily trapped by dienes, could not be trapped by reactive dienophiles such as dimethyl acetylenedicarboxylate and dimethyl fumarate. Thus, under our conditions, dienophilic properties are much more in evidence than dienyl properties in **2**.

The results of our own deuterium-exchange experiments also differ from those reported by the Columbia group. No deuterium incorporation was found in the dimers when the methiodide of **1** was treated with potassium *t*-butoxide in  $\text{DMSO-}d_6$ , *t*-butoxide in *t*-butyl alcohol- $\text{O-}d$ , or *t*-butoxide in  $\text{THF-DMSO-}d_6$ —

(2) A. P. ter Borg, E. Razenberg, and H. Kloosterziel, *Chem. Commun.*, **23**, 1210 (1967).

(3) There is also another pair of stereoisomers of **5** having different relative dispositions of the cyclopentene double bonds.