Thiabenzenes. IX. The Rearrangement of 1-(*p*-Dimethylaminophenyl)-2,4,6-triphenylthiabenzene to Isomeric Thiopyrans

CHARLES C. PRICE* AND HOOSHANG PIRELAHI[1]

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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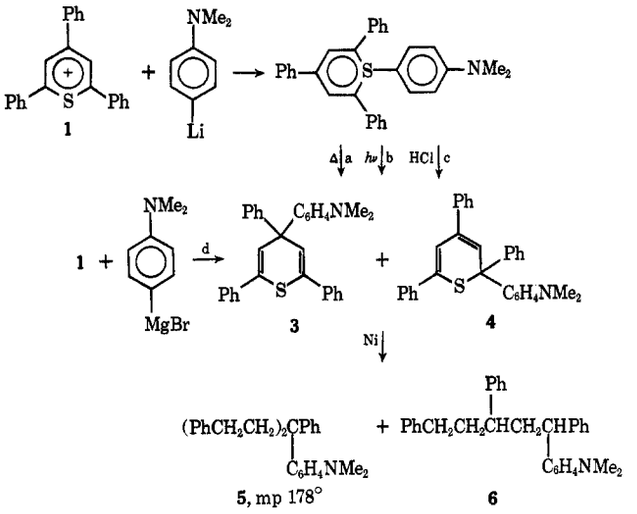
While 1-(*p*-dimethylaminophenyl)-2,4,6-triphenylthiabenzene (**2**) is much more stable than the analog without the *p*-dimethylamino group, it has been shown to produce a mixture of two isomeric thiopyrans, **3** and **4**, by heat, by light, or by acid. The same mixture of thiopyrans is produced directly by the reaction of 2,4,6-triphenylthiopyrylium ion with *p*-dimethylaminophenylmagnesium bromide. The mixed thiopyrans, **3** and **4**, were desulfurized by Raney nickel to a mixture of two amines, **5** and **6**, from which pure **5** was obtained.

An earlier report[2] of the synthesis of *p*-dimethylaminophenylthiabenzene (**2**) disclosed that this compound was crystalline, and, although its intense purple color slowly disappeared, **2** was much more stable than the analog without the *p*-dimethylamino group. It has now been possible to identify the main product from the decomposition of **2** in boiling benzene, on exposure to light at room temperature, or on treatment with ethereal hydrogen chloride as an amorphous mixture of the isomeric thiopyrans **3** and **4** (see Chart I).

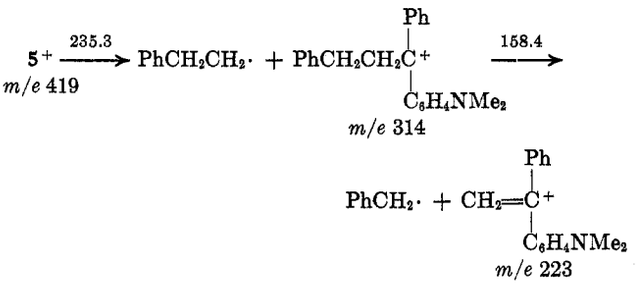
CHART I



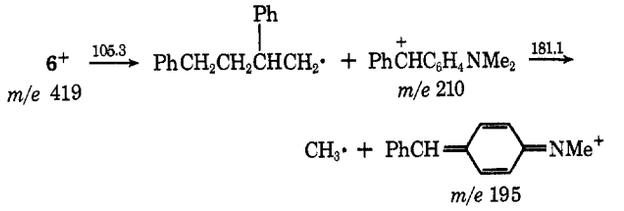
Because of the instability of the 1-phenyl analog of **2** with respect to rearrangement to the isomeric thiopyrans, it was never possible to be certain whether the isolation of the thiopyrans (rather than the thiabenzene) on treatment of **1** with phenyl Grignard reagents indeed may have proceeded through the thiabenzenes.[3] In view of the much greater stability of **2**, we have investigated the reaction of **1** with *p*-dimethylaminophenylmagnesium bromide. This produced as the major product the orange-yellow mixture of thiopyrans, but again with temporary purple color indicating that at least some **2** may have been formed.

A conceivable alternate structure to the thiopyrans **3** and **4** for the rearrangement product, 1,3,5-triphenyl-*x*-(*p*-dimethylaminophenylmercapto)cyclopentadiene, was eliminated as the major component of the rearrangement mixture by the isolation of a good yield (1.8 g) of sulfur-free oily solid from Raney nickel desulfurization of 2 g of **3** + **4**. Only 18 mg of acid-soluble unidentified product was obtained; the cyclopentadiene isomer should have given over 500 mg of dimethylaniline in the acid extract. From the 1.8 g of oily solid, tlc gave 680 mg of a mixture of **5** and **6**. Recrystallization of this mixture gave pure crystalline **5**, mp 176–178°. The nmr, mass, ir, and uv spectra were in accord with the assigned structures. The methyl and methylene peaks in the nmr spectrum for the mixture of **5** and **6** indicated the ratio of the isomers to be about 3:1.

The mass spectra of **5** and of the mixture of **5** and **6** revealed metastable peaks, two of which (*m/e* 235.3 and 105.3, corresponding to $314^2/419$ and $210^2/419$, respectively) particularly support the structure assignments. The former is present in both and presumably arises from the parent molecular ion **5** by loss of a phenethyl group to give the carbenium ion (*m/e* 314), resonance stabilized by the amino group.



The second is present only from the mixture and corresponds to the loss of the alkyl group from the molecular ion **6** which leaves a similarly stabilized



carbenium ion (*m/e* 210). Both these primary metastable peaks are confirmed by the further fragmentations indicated (*m/e* 158.4 and 181.1, respectively).

The mixtures of **3** and **4** obtained by all four processes (a, b, c, and d) were amorphous (by X-ray) orange solids softening near 100°. They were purified by chromatography on alumina, but all efforts to separate them by crystallization or through their hydrochloride or picrate salts were unsuccessful in our hands. The

(1) Abstracted from the doctoral dissertation of Hooshang Pirelahi, 1971; supported in part by the National Science Foundation Grant No. GP-16236 and a grant from the Gulf Oil Company.

(2) C. C. Price, J. Follweiler, H. Pirelahi, and M. Siskin, *J. Org. Chem.*, **36**, 791 (1971).

(3) See, *e.g.*, G. Suld and C. C. Price, *J. Amer. Chem. Soc.*, **84**, 2090 (1962).

TABLE I

CHANGES IN ULTRAVIOLET SPECTRUM FOR 2 (2.4×10^{-5} M) IN CYCLOHEXANE ON EXPOSURE TO DAYLIGHT (UNDER N_2)

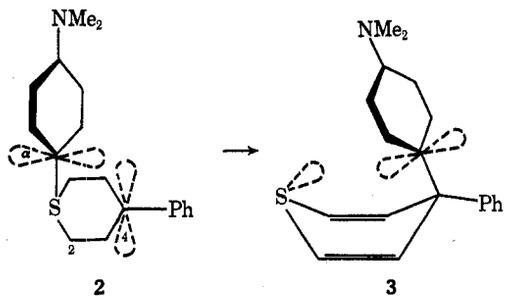
Time	λ_{max}	A[a]	λ_{max}	A	λ_{max}	A	λ_{max}	A	λ_{max}	A
0	534	0.270	357	0.322	311	0.630	271	0.600	231	0.490
10 min	534	0.261	357	0.318	311	0.620	271	0.637	231	0.479
1 hr	534	0.187	357	0.252	311	0.525	271	0.729		
3 hr	534	0.053	355[b]	0.131	310[b]	0.325	271	0.799		
5 hr	534	0.017	355[b]	0.120	310[b]	0.273	271	0.802		
7 hr	534	0.003	355[b]	0.098	310[b]	0.260	272	0.788		
9 hr					310[b]	0.254	272	0.753		
50 hr					310[b]	0.253	272	0.709	250[b]	0.570
7 days			350[b]	0.160			272	0.682	250[b]	0.590
14 days			350[b]	0.160	298[b]	0.350	272	0.673	250[b]	0.620

[a] Absorbance. [b] Point of inflection or shoulder.

infrared spectra in KBr for all four were clean and sharp and virtually identical. There were also no significant differences observed for the nmr or uv spectra.

The yields of the mixed thiopyrans from rearrangement were about 30% after chromatography. Examination of the changes in ultraviolet spectra during a photochemical rearrangement (Table I) reveals complete and rapid loss of the 534-nm band characteristic of **2** and intensification of absorbance at 272 nm. This latter band, corresponding to the λ_{max} at 275 nm for the mixture of **3** and **4**, subsequently decreases in intensity while a new absorbance at 250 nm develops, an absorbance not shown by the isolated mixture of **3** and **4**. The data in Table I thus suggest that, at least for the photochemical rearrangement, the low yield of the thiopyrans is due to formation of by-products, apparently by further reaction of the thiopyrans. This view is supported by the fact that route d gave a 70% yield of the **3** and **4** mixture, since, in this case, isolation was effected without exposure to "rearrangement" conditions.

Some comment on the ultraviolet spectra of the thiopyran mixtures is in order. We[3] have earlier reported that 4-methyl-2,4,6-triphenylthiopyran showed a single λ_{max} at 235 nm (log ϵ 4.45) while the 2-methyl isomer showed λ_{max} at 257 nm (log ϵ 4.32) and 347 (3.75). The mixtures of **3** and **4** showed λ_{max} 275 nm (log ϵ 4.45) and 395 (3.1–3.8). Presumably this red shift is due to "homoconjugation" effects of sulfur with the dimethylamino group. This would be normally expected in **4**, where sulfur–carbon homoconjugation over a single intervening saturated carbon is involved. It is somewhat less expected in **3**. However, the transition geometry for rearrangement of an aryl group from the sulfur in **2** to the 4 carbon in **3** would indicate that such orbital overlap may be possible.



2 **3**

The remarkable similarity between the mass spectra

TABLE II

MAJOR MASS SPECTRAL PEAKS FOR 2, 3, AND 4

m/e	2[a]	3 + 4[b]
445	14	6
368	10	3
325	4	2
304	8	9
294	24	8
215	13	7
209	12	4
191	5	9
167	1	5
165	6	8
153	52	53
152	100	100
137	8	11
136	13	16
121	9	10
120	12	14
109	7	9
105	13	52
91	10	8
77	12	30

[a] 120°, 50 eV. [b] 90°, 70 eV.

of **2** and of **3** + **4** (see Table II), and especially the *m/e* 152 peak, earlier[2] shown to be due to dimethylaminophenylmercapto cation, also suggests easy bonding of the *p*-dimethylaminophenyl group and sulfur in **3** (and **4**). The homoconjugation in **3** would be envisaged as electron donation from the electron-rich p orbital (in **3**) to a vacant 3d orbital on sulfur. The rearrangement would be envisaged as electron donation from the electron-rich p orbital on carbon 4 of the thiazbenzene ring **2** to the p orbital on the α carbon of the *S*-aryl ring. Enhanced electron density at carbon 4 (and carbon 2) would arise from ylide contributions to the thiabenzene ring structure. The rearrangement would then be enhanced by low electron density at the α carbon, offering an explanation for the marked differences in rate of rearrangement of the *S*-aryl group, depending on the para substituent: $Me_2N \ll CH_3 < H \ll Me_2NH^+$. The somewhat greater stability produced by a *p*-methyl group has been reported earlier.[2] The marked decrease in stability produced by a *p*-dimethylammonio group is inferred from the extremely rapid rearrangement induced by HCl.

Experimental Section

Rearrangement of 2. A. Thermal.—A solution of 1.0 g (2.25 mol) of **2** in 120 ml of degassed benzene was refluxed overnight with stirring in an atmosphere of nitrogen. The color of

the solution remained purple for 1.5 hr. Benzene was then removed from the resulting orange-brown solution under reduced pressure and the residue was placed on a 250 × 32 mm column of Merck 71707 alumina in benzene. Developing the column with benzene resulted in a diffuse orange band which began to come off the column at 30% ether–70% benzene. The orange solution was collected through to 100% ether. Removal of solvent and triturating with petroleum ether (bp 30–60°) yielded 600 mg of dark orange solid which, after several recrystallizations from ethanol under nitrogen, furnished 375 mg (37.5% yield) of orange solid melting at 94–102°.

B. By Light.—A solution of 500 mg (1.12 mmol) of **2** in 800 ml of dry ether was left standing at room temperature with exposure to daylight in an atmosphere of nitrogen for 2 weeks. After this period, the purple color, which had been retained for 7 days, turned to orange. (In a parallel experiment in the dark, no visible change in purple color was observed after 5 weeks.) Removal of the solvent under reduced pressure and recrystallization from ethanol under nitrogen gave 192 mg (38.4% yield) of orange solid melting at 95–106°. Further treatments in ethanol or other common organic solvents failed to narrow the melting range.

C. By Acid.—To a purple solution of 2.910 g (6.5 mmol) of **2** in 100 ml of benzene and 200 ml of dry ether was added 116.5 ml of a 0.17 *N* ethereal solution of hydrogen chloride (19.8 mmol, 3 equiv) at 0° under nitrogen. A yellow solid precipitated immediately. (In another experiment, it was observed that this precipitate was soluble in the presence of excess hydrogen chloride gas.) The yellow suspension was stirred for 0.5 hr and then treated with 200 ml of 5% aqueous sodium hydroxide solution under nitrogen. The color of the organic layer changed from yellow to orange. After about 1 hr of stirring, the resulting orange ethereal solution was thoroughly washed with water and dried over anhydrous sodium sulfate overnight. Evaporation of the solvent under reduced pressure gave an orange solid (2.75 g). The solid was subjected to column chromatography on alumina, as had been the product of thermal rearrangement, and recrystallized from ethanol under nitrogen. The resulting orange solid weighed 720 mg (24.7% yield) and melted at 90–95°.

In a similar experiment, adding 0.105 *N* acetic acid in ether gave no change in spectrum, even with 55 equiv of excess acid.

Reaction of 1 with *p*-Dimethylaminophenylmagnesium Bromide (D).—To a yellow suspension of 6.36 g (0.015 mol) of **1** in 120 ml of dry ether, 80 ml (0.0672 mol) of 0.84 *M* *p*-(dimethylamino)phenylmagnesium bromide[4] (4.48 equiv) in THF was added at room temperature, under a nitrogen atmosphere over a 5-min period. An immediate reaction was indicated by formation of the characteristic purple color. The reaction mixture was stirred for 30 min and then placed in an ice–water bath. The reaction was quenched after 15 min with 100 ml of cold saturated ammonium chloride solution. The color changed from purple to wine red. Removal of the ice–water bath and stirring the reaction mixture for an additional 1 hr changed the color to orange-red, and stirring overnight changed the latter color to orange. The orange organic layer was washed, dried, and evaporated. The orange-brown residue was held for 48 hr at 0.01 mm, and 5.250 g of *N*,*N*-dimethylaniline was distilled over into the cold trap. The remaining glassy orange-brown solid was dissolved in 40 ml of ether, filtered from a few milligrams of greenish-yellow solid, cooled in an ice–water bath, and added dropwise to 500 ml of cold (0°) petroleum ether. The orange-yellow precipitate (5.2 g), mp 98–104°, was chromatographed over alumina as before to give 4.720 g (70.7% yield) of orange solid. Recrystallizations from ethanol under nitrogen afforded an orange solid which melted at 108–115°.

Anal. Calcd for $C_{31}H_{27}NS$: C, 83.59; H, 6.07; N, 3.15; S, 7.19. Found: (A) C, 83.43; H, 6.10; N, 3.11; S, 7.13; (B) C, 83.67; H, 6.15; N, 3.08; S, 7.12; (C) C, 83.37; H, 6.25; N, 2.90; S, 7.31; (D) C, 83.44; H, 6.04; N, 3.13; S, 7.05.

The ultraviolet spectra of the mixtures of **3** and **4** were run in 1–1.5 mg/100 ml EtOH showing λ_{max}, nm (log ϵ), as follows: (A), 275 (4.45), 395 (3.40); (B) 275 (4.43), 395 (3.58); (C) 275 (4.45), 395 (3.12); (D) 275 (4.46), 385 (3.79). The varying intensities of the longer wavelength absorbance presumably reflect the amount of isomer **4** in the mixture.

The infrared spectra (KBr) showed the following major bands, cm^{-1} (per cent absorbance): 700 (80), 760 (70), 815 (50), 950 (30), 1030 (40), 1195 (50), 1350 (55), 1440 (65), 1490 (60), 1500 (70), 1595 (80). All bands were sharp and essentially identical for all four samples.

The nmr spectra (CCl_4) showed a slightly broadened singlet at δ 2.75 (6 H) and broad multiplets at δ 6–6.7 (4 H) and 6.77–7.77 (17 H). The multiplet at 6–6.7 (4 H), corresponds to the two vinylic protons on the thiopyran ring and the two aromatic hydrogens ortho to the dimethylamino group.

The mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6D spectrometer. Typical data are summarized in Table II. Detailed data are recorded.[1] The observed ratio of parent peak (P_{445} = 100) to P + 1 = 35.4 to P + 2 = 10.4 is very close to the calculated ratio from isotope abundances (100:35.1:10.4).

TABLE III
MAJOR MASS SPECTRAL PEAKS FOR **5** AND THE MIXTURE OF **5** AND **6**

m/e	**5**[a]	**5** + **6**[b]
419	31	50
314	100	82
223	69	62
210	63	100
194	6	18
165	8	23
121	7	23
105	6	12
91	33	59

[a] Broad peaks from metastable ions at *m/e* 235.3, 221, and 158.4. [b] Metastable ion peaks as for **5** plus *m/e* 181.1, 164, 131.2, and 105.3.

Reductive Desulfurization of the Isomeric Mixture of 3 and 4.—Raney nickel W-2 catalyst[5] (30 g) in ethanol was added to a solution of 2 g (4.5 mmol) of the isomeric mixture (A), in a small amount of benzene and 200 ml of ethanol. The mixture was refluxed with stirring for 6 hr. After cooling and removal of the catalyst by filtration, 100 ml of benzene was added to the filtrate and the solution was washed with water. The benzene layer was then extracted four times with a dilute solution of hydrochloric acid. The acid layer was made alkaline with a concentrated solution of sodium hydroxide and extracted several times with small portions of ether. The ether extract was washed with water and dried over anhydrous potassium carbonate. Evaporation of the ether solution under reduced pressure at room temperature gave only 18 mg of a light brown liquid whose thin layer chromatography on silica gel with trichloroethylene showed a mixture of unidentified components (R_f 0.84, 0.44, 0.15, 0.04, 0.00).

The benzene layer was washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure furnished 1.80 g of a light yellow, oily solid which gave a negative test for sulfur after sodium fusion. The residue was subjected to preparative thin layer chromatography on silica gel with trichloroethylene and methylene chloride (30:70) as the solvent. Five 20 × 20 cm plates, with fluorescent indicator and a layer thickness of 2 mm, were used. Spots with R_f 0.86, 0.46, 0.17, 0.06, and 0.00 were identified under ultaviolet light. The major spot (R_f 0.46) was removed and extracted several times with small portions of methylene chloride. Removal of the solvent gave 680 mg of a yellow-white semisolid.

Anal. Found (semisolid): C, 86.24; H, 7.80; N, 2.83.

Recrystallization from *n*-hexane afforded a white, crystalline solid which melted at 176–178°.

Anal. Calcd for $C_{31}H_{33}N$: C, 88.78; H, 7.88; N, 3.34. Found (mp 178°): C, 88.62; H, 7.93; N, 3.10.

Attempts to separate the other isomer from the mother liquor by crystallization and thin layer chromatography on alumina or silica gel were unsuccessful.

The ultraviolet spectrum of the semisolid mixture (1.5 mg/100 ml EtOH) showed λ_{max} 258 and 300 nm, while the solid with mp 178° showed λ_{max} (log ϵ) 258 (4.27) and 300 (3.57). The infrared spectrum (KBr) of **5** showed the following major bands,

(4) T. C. Owen, *J. Chem. Soc.*, 465 (1961).

(5) R. Mozingo, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 181.

cm^{-1} (per cent absorbance): 700 (90), 755 (65), 810 (50), 1350 (50), 1450 (55), 1490 (60), 1520 (80), 1615 (65).

The nmr spectrum ($CDCl_3$) for the solid with mp 178° (**5**) showed a broadened singlet at δ 2.37 (8 H), a singlet at 2.90 (6 H), a doublet at 6.67 and 6.58 (2 H), and a multiplet at 7–7.4 (17 H). The doublet at δ 6.67 and 6.58 corresponds to the two aromatic hydrogens ortho to the dimethylamino group. The semisolid shows two broad bands at δ 0.90–1.05 (~2 H), and 1.25–1.40 (~2 H), which may be due to solvent impurities, as well as an extra methyl singlet at δ 2.83 and methylene absorbance at δ 2.25. Assuming that these latter are due to **6**, the ratio of **5** to **6** is about 3:1.

The mass spectral data are summarized in Table III. The observed ratio of parent peak (P_{419} = 100) to P + 1 = 34.3 and P + 2 = 5.6 is in good agreement with the ratios calculated from isotope abundances of 100:34.4:5.7.

Registry No.—**2**, 28278-49-1; **3**, 34347-83-6; **4**, 34347-84-7; **5**, 34347-85-8; **6**, 34347-86-9.

The Reactions of Dimethyl Diazomalonate with Divalent Sulfides

WATARU ANDO,* TOMIO YAGIHARA, SHIGERU TOZUNE, ISAMU IMAI, JUNJI SUZUKI, TADAO TOYAMA, SETUKO NAKAIDO, AND TOSHIHIKO MIGITA

Department of Chemistry, Gunma University, Kiryu, Gunma, Japan

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Biscarbomethoxycarbene, generated photochemically from dimethyl diazomalonate, reacts with alkyl and aryl sulfides to form stable sulfonium biscarbomethoxymethylides. The reaction of the carbene with alkyl disulfides forms alkylthiomalonate as the major product instead of the sulfonium ylides. The triplet carbene, generated from benzophenone-photosensitized decomposition of the diazomalonate, also reacts with dimethyl sulfide to produce the sulfonium ylide. This ylide formation is considered to involve the fast intersystem crossing from the triplet to the singlet carbene in the presence of dimethyl sulfide. Copper salt catalyzed thermal decomposition of diazomalonate in alkyl or aryl sulfides produces sulfonium ylides in high yields.

Photochemically induced reactions of diazo compounds with various types of compounds containing heteroatoms have been studied extensively.[1-4] Most of these reactions have been proposed to proceed through ylide formation by reactions of carbenes derived from diazo compounds and this has been supported by the recent synthesis of sulfonium ylides by the reaction of highly electrophilic carbenes with alkyl sulfides.[5-7]

Previously, we reported in preliminary form that the photolysis and copper salt catalyzed thermal decomposition of dimethyl diazomalonate in neat dimethyl sulfide gave dimethylsulfonium biscarbomethoxymethylide, and we showed that the reaction may be useful for synthesis of such stable sulfonium ylides.[6,7]

This paper deals with the details of the reaction and some properties of the ylides thus prepared.

$$N_2CR_2 \xrightarrow{h\nu} :CR_2 \xrightarrow{R'SR'} R_2'\overset{+}{S}-\bar{C}R_2$$

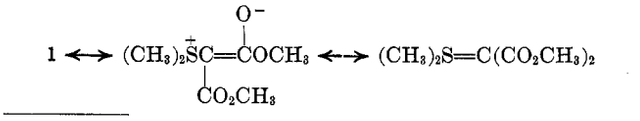
Several studies on the chemical behavior of triplet carbenes have documented that the most marked difference in the chemical nature between singlet and triplet carbenes is found in the stereochemistry of addition to olefins.[8-15]

Jones and coworkers have shown that direct photolysis of diazomalonate generates singlet biscarbomethoxycarbene, which adds to olefins in a stereospecific manner, while photosensitized decomposition generates the corresponding triplet carbene, which reacts with olefins to give nonstereospecific addition products.[16,17]

Now, it is not unreasonable to suppose that carbenes in the two different spin states may react in different ways with molecules containing heteroatoms; *i.e.*, the singlet carbene might react with such a molecule to afford ylide, whereas the triplet might not. From this viewpoint, the photosensitized reactions of diazomalonate in alkyl sulfides were also investigated.

Results and Discussions

Formation of Sulfonium and Sulfoxonium Ylides in the Reactions of Dimethyl Diazomalonate in Sulfides and Sulfoxides.—Photolysis of dimethyl diazomalonate in various alkyl and aryl sulfides was carried out in Pyrex tubes with a high pressure mercury lamp. The crystalline major products of the reactions were stable sulfonium ylides. Thus, the reaction of dimethyl diazomalonate with dimethyl sulfide gave in 88% yield dimethylsulfonium biscarbomethoxymethylide (**1**), ν_{CO} 1625 and 1675 cm^{-1}, δ ($CDCl_3$) 3.71 (s, -COOMe) and 2.89 (s, $-SCH_3$). The proton shift of the SCH_3 and the carbonyl shift are analogous to those observed in other sulfonium ylides[18] and suggest that the ylide **1** is strongly resonance stabilized by partici-



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