BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 198—202(1972)

The Syntheses and Reactions of Sulfenyl-substituted Sulfonium Ylides

Yosio HAYASI and Hitosi NOZAKI

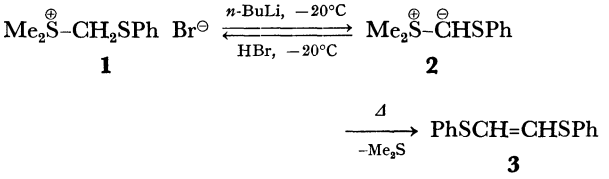
Department of Industrial Chemistry, Kyoto University, Yoshida, Kyoto

(Received April 24, 1971)

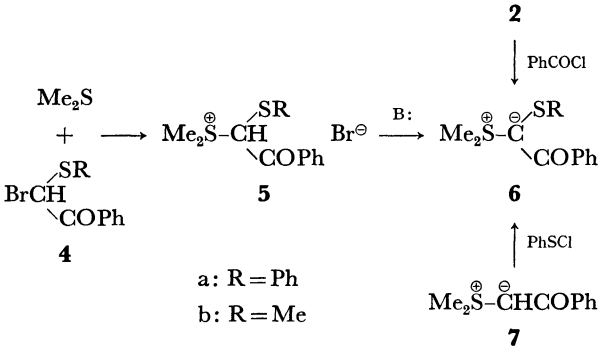
Unstable dimethylsulfonium (phenylthio)methylide (**2**) is prepared in a THF solution from the corresponding sulfonium salt by treating it with *n*-butyllithium. Sulfenyl-substituted stable phenacylides **6a** and **6b** are obtained in three ways. The ylide **6a** decomposes at 120°C in benzene to give (E)-**9**, the dimer of benzoyl(phenylthio)carbene. In contrast, the heating of **6a** in ethanol affords ethanolysis products (**11**, **12**) and ethyl benzoate. The alkylation of **6a** and **6b** with trimethyl- and triethyloxonium fluoroborate gives the vinylsulfonium salt **13**. The ylide **2** reacts with (Z)- and (E)-1,2-dibenzoylethylene and with diethyl fumarate to give cyclopropanes, **15** and **16** respectively.

Sulfonium ylides are often stabilized by the introduction of an electron-withdrawing group or groups on the ylide carbon, such groups as COR, COOR, and SO_2R.[1] Herewith we report on the syntheses and reactions of sulfenyl-substituted sulfonium ylides,[2] as no precedent of this class has yet appeared. The sulfenyl group should effectively delocalize the negative charge by using a 3*d* orbital of the sulfur atom.[3] Incidentally, the cleavage of the ylide bond gave rise to sulfenylcarbenes, whose behavior was also investigated.[5]

Dimethylsulfonium (phenylthio)methylide (**2**) was obtained as a solution in tetrahydrofuran (THF) upon the treatment of the sulfonium salt **1** with *n*-butyllithium. The solution was stable at lower temperatures, as after 1 hr of standing at −20°C **2** was reconverted quantitatively into the sulfonium salt **1** by the addition of hydrogen bromide. The concentration of the ylide solution under reduced pressure below room temperature afforded (Z)-1,2-bis(phenylthio)ethylene (**3a**, 27% yield) and its (E) isomer (**3b**, 43% yield).



When dimethyl sulfide was allowed to react with phenacyl bromides **4a** and **4b**, two sulfonium salts, **5a** and **5b** respectively, were obtained as highly hygroscopic crystals. The treatment of **5a** and **5b** with sodium hydride in THF gave two crystalline ylides, **6a** and **6b** respectively.



The ylide **6a** was also obtained by two alternative methods: the treatment of dimethylsulfonium phe-

1) H. Nozaki, M. Takaku, Y. Hayasi, and K. Kondo, *Tetrahedron*, **24**, 6563 (1968) and the references cited therein.

2) Communicated in part: Y. Hayasi, M. Takaku, and H. Nozaki, *Tetrahedron Lett.*, **1969**, 3179.

3) For the sulfenyl-substituted phosphonium ylides, see Ref. 4.

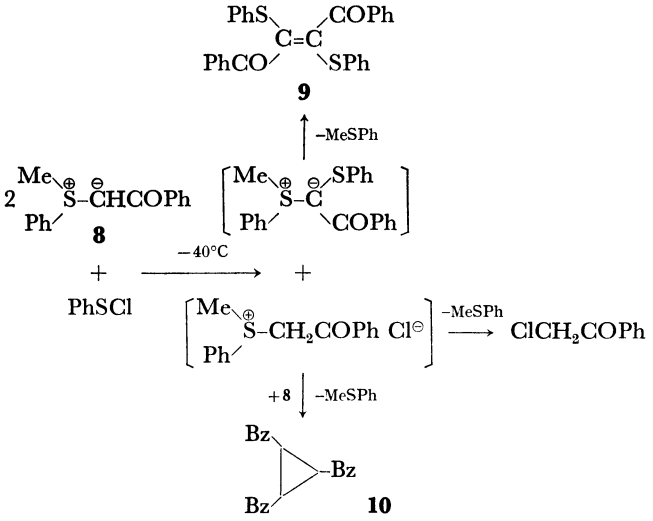
4) a) G. Wittig and M. Schlosser, *Chem. Ber.*, **94**, 1373 (1961); b) T. Mukaiyama, S. Fukuyama, and T. Kumamoto, *Tetrahedron Lett.*, **1968**, 3787.

5) For the sulfenylcarbenes, see Ref. 6. No acylsulfenylcarbene has previously been reported, as far as the authors are aware.

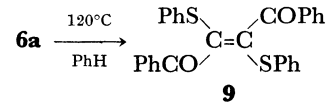
6) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y. (1964), p. 109.

nacylide (**7**)[7] with benzenesulfenyl chloride, and that of **2** with benzoyl chloride. The "ylide carbonyl" IR band of **6a** and **6b** appeared in the same region as that of **7**, whereas the UV absorption experienced a blue shift of *ca.* 20 nm upon the introduction of the sulfenyl group into **7** (see Experimental section). Apparently the sulfenyl group delocalizes the ylide negative charge by utilization of the 3*d* orbital of the sulfur atom.[8]

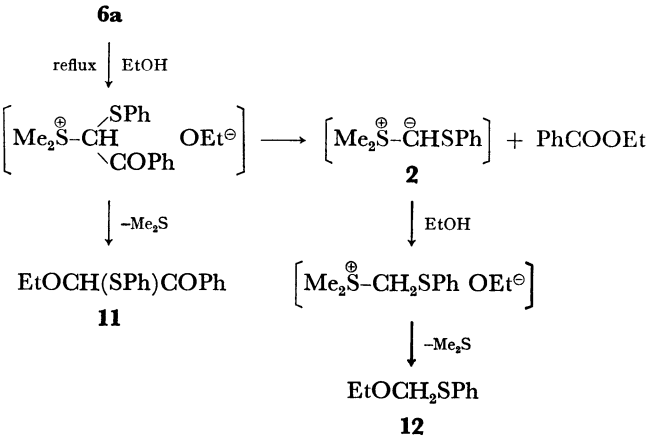
In contrast to the reaction of the ylide **7**, that of two mole equivalents of methylphenylsulfonium phenacylide (**8**)[9] with benzenesulfenyl chloride gave a complex mixture, which consisted of (E)-1,2-dibenzoyl-1,2-bis(phenylthio)ethylene (**9**, 13%), thioanisole (122%), α-chloroacetophenone (50%), and (E)-1,2,3-tribenzoylcyclopropane (**10**, 20%), plus a remainder of unknown substances.



The ylides **6a** and **6b** have been found to serve as precursors of benzoyl(phenylthio)carbene.[10] The ylide **6a** was stable in boiling benzene, but decomposition took place at 120°C to yield (E)-1,2-dibenzoyl-1,2-bis(phenylthio)ethylene (**9**). The analytical and spectral data supported the constitution given, while the (E)-configuration was deduced on the basis of its IR spectrum, which showed a conjugated carbonyl absorption band at 1665 cm^{-1}.[11]

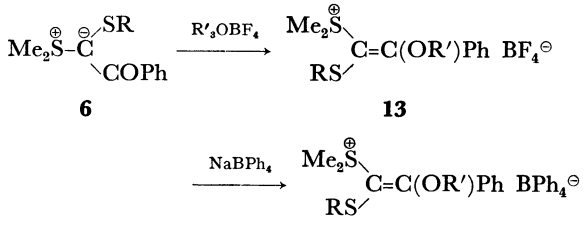


The prolonged heating of **6a** in boiling ethanol afforded α-ethoxy-α-(phenylthio)acetophenone (**11**, 23%), ethyl benzoate (19%), and phenylthiomethyl ethyl ether (**12**, 12%). The olefin **9** and the compound originating from the Wolff rearrangement of benzoyl(phenylthio)carbene could not be detected. A possible scheme of the reaction is shown below:

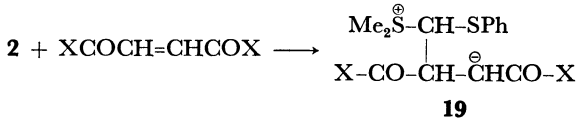


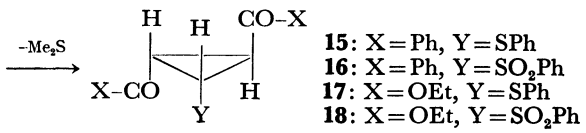
The photolytic decomposition of **6a** was carried out in some solvents, but no single product was isolated.

The treatment of the ylides **6a** and **6b** with trimethyl- and triethyloxonium tetrafluoroborate resulted in O-alkylation, giving vinylsulfonium salts, **13** (Table 1), instead of an S-alkylated product. The oily sulfonium tetrafluoroborates (**13a**: R=Ph, R′=Me and **13c**: R=R′=Me) were converted to crystalline tetraphenylborates (**14a** and **14c**) by treatment with sodium tetraphenylborate. The structure of these vinylsulfonium salts was confirmed by the results of analyses and by the spectral data. Especially, the NMR spectrum of **14c** showed three peaks of methyl protons at δ 2.07 (-SMe), 2.83 (>S-Me), and 3.50 (O-Me) ppm; they supported the structure of **14** and, therefore, that of **13**:



a: R=Ph, R′=Me
b: R=Ph, R′=Et
c: R=R′=Me





7) a) B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 138 (1967); b) A. W. Johnson and R. T. Amel, *Tetrahedron Lett.*, **1966**, 819; c) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).

8) The same explanation has been given in the case of sulfonium sulfonyl-substituted phenacylides. See Ref. 1.

9) H. Nozaki, M. Takaku, and K. Kondo, *Tetrahedron*, **22**, 2145 (1966).

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

11) W. Lüttke and H. Hermann studied the IR and UV spectra of 3,4-bis(methylthio)-3-hexene-2,5-dione, 3,4-bis(phenylthio)-3-hexene-2,5-dione, and related compounds in order to make a definite configurational assignment of these sulfenylsubstituted olefins on the basis of the spectral data. See Ref. 12). In a private communication they advised the authors of having deduced the (E)-configuration of **9** from the IR spectral data. The authors are grateful for their courtesy.

12) a) W. Lüttke, H. Hermann, and M. Klessinger, *Angew. Chem., Int. Ed. Engl.*, **5**, 598 (1966); b) H. Hermann and W. Lüttke, *Chem. Ber.*, **101**, 1708 (1968); c) H. Hermann and W. Lüttke, *ibid.*, **101**, 1715 (1968).

Table 1. Mps and spectral data of novel vinylsulfonium salts **13** and **14**

Compd.	R	R′	mp °C	IR(KBr) cm^{-1}	NMR δ ppm (relative intensity, multiplicity)
14a	Ph	Me	143—145	1542, 1304, 1125	2.63 (s, 6H), 3.65 (s, 3H), 6.7—7.6 (m, 30H)[a]
13b	Ph	Et	89— 94	1554, 1313, 1110, 1050	1.36 (t, 3H), 2.89 (s, 6H), 4.03 (q, 2H), 7.1—7.7 (m, 10H)[a]
14b	Ph	Et	165—167	1565, 1290, 1130, 1110	1.35 (t, 3H), 2.89 (s, 6H), 4.03 (q, 2H), 7.1—7.7 (m, 30H)[b]
14c	Me	Me	174—175	1568, 1300, 1125	2.07 (s, 3H), 2.83 (s, 6H), 3.50 (s, 3H), 6.7—7.6 (m, 25H)[c]

a) In acetone-d_6 solution with TMS as a reference.
b) In $CDCl_3$ solution with TMS as a reference.
c) In DMSO-d_6 solution with sodium 3-(trimethylsilyl)propanesulfonate as a reference.

In view of the well known reaction[13] of dimethylsulfonium methylide with electron-deficient olefins or carbonyl compounds, we have examined the possible reactions of **2** with such substrates. However, benzophenone failed to react with **2** at −20°C, whereas both benzaldehyde and *p*-nitrobenzaldehyde actually reacted with **2** to afford a very complex mixture which could not be characterized.

When (E)-1,2-dibenzoylethylene was allowed to react with **2** in THF, *r*-1,*t*-2-dibenzoyl-*t*-3-(phenylthio)-cyclopropane (**15**) was obtained in a 27% yield as the sole product. The assignment of the indicated configuration is based on the NMR spectral data of the corresponding sulfone, **16** (see Experimental section).

The reaction of **2** with (Z)-1,2-dibenzoylethylene gave the same stereoisomer, **15**, in a 53% yield. Analogously, the treatment of **2** with diethyl fumarate afforded diethyl *t*-3-(phenylthio)-*r*-1,*t*-2-cyclopropanedicarboxylate (**17**) in a 51% yield; its oxidation led to the sulfone **18**. The given configuration was also based on the NMR spectral data, in which the ethyl protons were obviously nonequivalent. The preference for the (E) configuration of **15** and **17** may be ascribed to the intermediacy of the betaines, **19**.

Expectedly, the ylide **6a** did not react with (E)-1,2-dibenzoylethylene and diethyl maleate under reflux in THF.

Experimental

All the melting and boiling points are uncorrected. The microanalyses were performed at the Elemental Analyses Center of Kyoto University. The NMR spectra were taken with JEOL C-60H and Varian ME-100 spectrometers, and the chemical shifts are reported in δ values relative to the TMS internal standard unless otherwise stated. The abbreviations s, t, q, and m refer to singlet, triplet, quartet, and multiplet respectively. The UV absorption spectra were taken in 95% EtOH on a Shimadzu MPS-50L spectrometer.

Preparation of Dimethyl(phenylthiomethyl)sulfonium Bromide (1). A solution of bromomethyl phenyl sulfide[14] (7.0 g, 34.4 mmol) and dimethyl sulfide (2.6 g, 42.0 mmol) in dry acetone (50 m*l*) was stirred at 0°C for 24 hr. The resulting precipitates were collected by filtration, washed with dry acetone, and dried in a vacuum desiccator to afford very hygroscopic crystalline solids **1** (8.0 g, 88%); mp 69—70°C (dec.). NMR (DMSO-d_6): 3.12 (s, 6H), 5.41 (s, 2H), 7.2—7.9 (m, 5H). Found: C, 40.7; H, 5.0%. Calcd for $C_9H_{13}BrS_2$: C, 40.8; H, 4.9%.

Preparation of Dimethylsulfonium (Phenylthio)methylide (2). To a suspension of **1** (2.65 g, 10.0 mmol) in THF (150 m*l*), a solution of *n*-butyllithium (10 mmol) in *n*-hexane (14.7 m*l*) was added in one portion at −20°C under nitrogen, after which the mixture was stirred for five min. Thus we obtained a pale yellow solution of dimethylsulfonium (phenylthio)-methylide (**2**). After standing for 1 hr at −20°C, the solution was treated with HBr gas. The resulting precipitates melted at 69—70°C (mixed mp 69°C) and showed an IR spectrum identical with that of an authentic sample of **1**.

The Decomposition of Dimethylsulfonium (Phenylthio)methylide (2). The solution of **2** in THF (50 m*l*), prepared by the treatment of **1** (2.65 g, 10.0 mmol) with a solution of *n*-butyllithium (10.0 mmol) in hexane (14.7 m*l*) at −20°C, was allowed to warm up to room temperature. The reaction mixture was then concentrated under reduced pressure at 0—5°C to afford a crude oil, which was submitted to chromatography on an alumina column with *n*-hexane. The initial eluate was (E)-1,2-*bis*(phenylthio)ethylene (**3b**, 0.52 g, 43%); mp 61—62°C (from EtOH) (lit.[15] mp 62°C). IR (KBr): 924 cm^{-1}; NMR (CCl_4): 6.44 (s, 2H), 7.0—7.4 (m, 10H). The second one was (Z)-1,2-bis(phenylthio)ethylene (**3a**; 0.33 g, 27%): mp 30.5—31°C (lit,[15] mp 31.5°C). NMR (CCl_4): 6.41 (s, 2H), 7.0—7.4 (m, 10H).

α-Bromo-α-(phenylthio)acetophenone (4a)[16] was prepared by the treatment of α-(phenylthio)acetophenone with bromine in the presence of a catalytic amount of aluminum chloride in dry ether at 0°C.

Preparation of Dimethyl[α-(phenylthio)phenacyl]sulfonium Bromide (5a). A solution of **4a** (20 g, 66 mmol) and an excess of dimethyl sulfide in dry acetone was stirred at 0°C for 5 hr. The resulting precipitates were filtered, washed with dry acetone, and dried over P_2O_5 in a vacuum desiccator to afford hygroscopic crystals **5a** (19 g, 78%), mp 76—78°C (dec.). IR (Nujol): 1675, 1290 cm^{-1}; NMR ($CDCl_3$): 2.07 (s, 6H), 6.42 (s, 1H), 7.2—8.1 (m, 10H). Found: C, 52.3; H, 4.7%. Calcd for $C_{16}H_{17}BrOS_2$: C, 52.0; H, 4.6%.

Preparation of Dimethyl[α-(methylthio)phenacyl]sufonium Bromide (5b). To a solution of α-(methylthio)acetophenone (8.3 g, 50 mmol) in dry benzene (200 m*l*) under nitrogen, we added sodium hydride (2.4 g, a 50% dispersion in mineral oil, 50 mmol) in one portion at 0°C. After the evolution of hydrogen gas had ceased, bromine (8.0 g, 50 mmol) was

13) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).
14) H. Böhme, H. Fischer, and R. Frank, *Ann. Chem.*, **563**, 54 (1949).
15) a) W. E. Truce and R. J. McManimie, *J. Amer. Chem. Soc.*, **76**, 5745 (1954); b) W. E. Parham and J. Heberling, *ibid.*, **77**, 1175 (1955).
16) W. Groebel, *Chem. Ber.*, **92**, 2887 (1959).

added dropwise to the reaction mixture at the same temperature. The mixture was stirred for an additional 5 min and then filtered in order to remove the NaBr. After an excess of dimethyl sulfide had been added to this filtrate, the mixture was stirred at 0°C for 5 hr. The resulting precipitates were filtered, washed with dry acetone, and dried over P_2O_5 under reduced pressure to afford hygroscopic salt **5b** (11.0 g, 72%), mp 92—93°C (dec.); this product was subjected to the following reaction without further purification. IR (Nujol): 1673, 1278 cm^{-1}; NMR ($CDCl_3$): 2.14 (s, 3H), 2.33 (s, 6H), 6.44 (s, 1H), 7.2—8.1 (m, 5H). Found: C, 42.6; H, 4.7%. Calcd for $C_{11}H_{15}BrOS_2$: C, 43.0; H, 4.9%.

Preparation of Dimethylsulfonium α-(Phenylthio)phenacylide (6a). (a) To a solution of **5a** (17.0 g, 46 mmol) in THF (250 m*l*) cooled with an ice-water bath, we added NaH (2.2 g, 50% dispersion in mineral oil, 46 mmol) in one portion. The reaction mixture was stirred until the evolution of hydrogen had subsided. Filtration followed by concentration gave a crystalline solid substance, which was recrystallized from benzene to afford **6a** (11.0 g, 85%), mp 135—136°C. IR (KBr): 1530, 1335 cm^{-1}; λ_{max}^{EtOH} 247 (log ε 4.07), 282 (3.84) nm; NMR ($CDCl_3$): 2.64 (s, 6H), 7.1—7.9 (m, 10H). Found: C, 67.0; H, 5.5%. Calcd for $C_{16}H_{16}OS_2$: C, 66.6; H, 5.6%.

(b) To a solution of **7** (18.0 g, 100 mmol) in THF (300 m*l*), we added, drop by drop, a solution of benzenesulfenyl chloride (7.2 g, 50 mmol) in THF (50 m*l*) under nitrogen at −20°C. After being stirred for an additional 4 hr at the same temperature, the reaction mixture was allowed to warm to room temperature, diluted with water, and extracted with $CHCl_3$. The extract was dried ($MgSO_4$) and concentrated *in vacuo*. The residual solid was recrystallized from benzene to afford **6a** (12.5 g, 87%), mp and mixed mp 135—136°C. Its identity was further confirmed by a study of its IR spectrum.

(c) To a solution of **2** in THF (150 m*l*), prepared by the treatment of **1** (2.65 g, 10.0 mmol) with *n*-BuLi, we added, drop by drop, a solution of benzoyl chloride (0.70 g, 5.0 mmol) in THF (5 m*l*) under nitrogen at −20°C. After being stirred for an additional hour, the reaction mixture was allowed to warm up to room temperature under stirring. Work-up then afforded **6a** (1.00 g, 72%); mp and mixed mp 135—136°C.

Preparation of Dimethylsulfonium α-(Methylthio)phenacylide (6b). A mixture of **5b** (10.0 g, 32.6 mmol) and NaH (1.56 g, 50% dispersion in mineral oil, 32.6 mmol) in THF (250 m*l*) was stirred at 0°C under nitrogen for 5 hr. The reaction mixture was then filtered, and the filtrate was concentrated under reduced pressure. The recrystallization of the residue from petroleum ether (bp 30—50°C) and THF (1:1) afforded **6b** (6.1 g, 83%); mp 85—86°C. IR (KBr): 1485, 1340 cm^{-1}; λ_{max}^{EtOH} 280 (log ε 3.83); NMR ($CDCl_3$): 1.96 (s, 3H), 2.66 (s, 6H), 7.1—7.9 (m, 5H). The compound decomposed slowly on standing at room temperature on exposure to air. Found: C, 58.1; H, 6.4%. Calcd for $C_{11}H_{14}OS_2$: C, 58.4; H, 6.2%.

Reaction of Methylphenylsulfonium Phenacylide (8) with Benzenesulfenyl Chloride. A solution of benzenesulfenyl chloride (2.89 g, 20 mmol) in THF (30 m*l*) was added to a solution of **8** (9.68 g, 40 mmol) in THF (250 m*l*) at −40°C under nitrogen. The mixture was stirred for an additional 8 hr at the same temperature and then filtered. The filtrate was concentrated, and the residual oil was chromatographed on a Florisil column. Elution with hexane gave thioanisole (3.03 g, 122%) and α-chloroacetophenone (1.54 g, 50%). Elution with benzene gave **9** (1.16 g, 13%), mp and mixed mp 173.5—174°C. Final elution with chloroform yielded (E)-1,2,3-tribenzoylcyclopropane (**10**, 1.30 g, 20%), mp and mixed mp 213—214°C.[17]

Thermolysis of 6a in Benzene. A solution of **6a** (2.2 g, 7.8 mmol) in dry benzene (100 m*l*) was heated in a sealed glass tube at 120°C for 3 hr. After the solvent had been removed, the residue was chromatographed (silica gel, benzene) to afford **9** (0.34 g, 10%), mp 173.5—174°C (from benzene). λ_{max}^{EtOH} 212 (log ε 4.63), 256 (4.52) nm; IR (KBr): 1665, 1240 cm^{-1}; NMR ($CDCl_3$): 7.0—8.0 (m). The parent peak in the mass spectrum was observed at *m/e* 452. Found: C, 74.6; H, 4.4%. Calcd for $C_{28}H_{20}O_2S_2$: C, 74.3; H, 4.5%.

Thermolysis of 6a in Ethanol. A solution of **6a** (1.1 g, 3.9 mmol) in 100% EtOH (100 m*l*) was heated to reflux for 22 hr. After the evaporation of the solvent, ether was added to the residual oil (0.83 g). The resulting precipitates were collected and found to be **6a** (0.14 g). The filtrate was concentrated, and the residual oil was subjected to chromatography on a silica gel column. Elution with hexane gave phenylthiomethyl ethyl ether (**12**, 0.08 g, 12%), which was found to be identical with an independently synthesized specimen upon a comparison of their IR and NMR spectra and retention times on glc. Elution with hexane and benzene (2:1) gave ethyl benzoate (0.11 g, 19%). A final elution with benzene gave α-ethoxy-α-(phenylthio)acetophenone (**11**) as an oil (0.24 g, 23%). IR (neat): 1693, 1274, 1098 cm^{-1}; NMR ($CDCl_3$): 1.32 (t, 3H, $J_{AX}=J_{BX}=$ 7.2 Hz), 3.70 (1H, $J_{AB}=9.0$ Hz, $J_{AX}=7.2$ Hz), 4.07 (1H, $J_{AB}=9.0$ Hz, $J_{BX}=7.2$ Hz), 5.40 (s, 1H), 7.1—8.1 (m, 10H). Found: C, 70.7; H, 5.8%. Calcd for $C_{16}H_{16}O_2S$: C, 70.6; H, 5.9%.

Preparation of Phenylthiomethyl Ethyl Ether (12). An authentic sample was prepared as follows. To an EtOH (150 m*l*) solution of sodium thiophenoxide prepared from thiophenol (29.0 g, 26.4 mmol) and an equivalent amount of sodium (6.1 g, 26.4 mmol), we added, drop by drop, chloromethyl ethyl ether (25.0 g, 26.4 mmol) at 0°C. The reaction mixture was then extracted with ether. The removal of the solvent *in vacuo*, followed by distillation at 114—125°C/15 mmHg, afforded a mixture of **12** and chloromethyl ethyl ether (45:55). Purification by preparative glc (10% SE 30 on Chromosorb W) yielded **12**. IR (neat): 1077 cm^{-1}; NMR (CCl_4): 1.20 (t, 3H), 3.62 (q, 2H), 4.92 (s, 2H), 7.0—7.6 (m, 5H). Found: C, 64.5; H, 7.2%. Calcd for $C_9H_{12}OS$: C, 64.3; H, 7.2%.

Photolysis of 6a. A solution of **6a** (3.0 g, 10.5 mmol) in 100% EtOH (350 m*l*) was irradiated by means of a 200-W high-pressure mercury arc (Pyrex filter) for 30 hr. Crystalline precipitates were then collected and found to be sulfur (0.42 g). The evaporation of the solvent afforded an intractable oil.

Reaction of 6a with Trimethyloxonium Tetrafluoroborate. A mixture of **6a** (1.7 g, 5.9 mmol) and trimethyloxonium tetrafluoroborate (1.3 g, 8.8 mmol) in dry CH_2Cl_2 (20 m*l*) was stirred at room temperature under nitrogen for 24 hr. After the evaporation of the solvent, the residual oil was washed with ether to afford **13a** as an insoluble oil (1.47 g). The crude oil was taken up in deionized water (20 m*l*) and treated with sodium tetraphenylborate (1.6 g, 4.7 mmol) to precipitate **14a** (0.97 g, 33%); mp 143—145°C (dec.) (from acetone-water). Found: C, 78.8; H, 5.9%. Calcd for $C_{41}H_{39}BOS_2$: C, 79.1; H, 6.0%.

Reaction of 6a with Triethyloxonium Tetrafluoroborate. A mixture of **6a** (1.0 g, 3.5 mmol) and triethyloxonium tetrafluoroborate (1.0 g, 5.3 mmol) in CH_2Cl_2 (20 m*l*) was stirred at room tempeature for 24 hr. The evaporation residue was then dissolved in ethanol; the subsequent cautious addition of ether to the solution at 0°C resulted in the precipita-

17) G. Maier, *ibid.*, **95**, 611 (1962).

tion of pure crystals of **13b** (0.79 g, 56%); mp 89—94°C (dec.). Found: C, 53.5; H, 5.2%. Calcd for $C_{18}H_{21}BF_4OS_2$: C, 53.5; H, 5.2%.

The treatment of **13b** (0.28 g, 0.7 mmol) with sodium tetraphenylborate (0.24 g, 0.7 mmol) in deionized water (10 m*l*) afforded **14b** (0.41 g, 92%); mp 165—167°C (from acetone-water). Found: C, 79.3; H, 6.7%. Calcd for $C_{42}H_{41}BOS_2$: C, 79.2; H, 6.5%.

*Reaction of **6b** with Trimethyloxonium Tetrafluoroborate.* A mixture of **6b** (2.26 g, 10.0 mmol) and trimethyloxonium tetrafluoroborate (1.48 g, 10.0 mmol) in CH_2Cl_2 (20 m*l*) was stirred at 0°C for 20 hr. Work-up then afforded **13c** as an oil (2.15 g). The treatment of the crude oil with sodium tetraphenylborate (2.36 g, 6.9 mmol) in a mixture of CH_2Cl_2 (40 m*l*) and water (30 m*l*) afforded a crystalline solid, **14c** (1.72 g, 31%); mp 174—175°C (from acetone-water). Found: C, 77.2; H, 6.6%. Calcd for $C_{36}H_{37}BOS_2$: C, 77.1; H, 6.7%.

*Reaction of **2** with (E)-1,2-Dibenzoylethylene.* To a solution of **2** in THF (150 m*l*), prepared by the treatment of **1** (2.65 g, 10.0 mmol) with *n*-butyllithium at −20°C, we added, drop by drop, solution of (E)-1,2-dibenzoylethylene (2.30 g, 9.7 mmol) in THF (50 m*l*). After being stirred for an additional hour at the same temperaure, the reaction mixture was allowed to warm up to room temperature; it was then diluted with water and extracted with chloroform. The chloroform solution was dried ($MgSO_4$) and concentrated, and the residual oil was chromatographed on a silica gel column. Elution with a mixture of benzene and hexane (3:1) afforded *r*-1, *t*-2-dibenzoyl-*t*-3-(phenylthio)-cyclopropane (**15**, 0.96 g, 27%); mp 113.5—114°C (from PhH-hexane). IR (KBr): 1660, 1336, 1208, 1010 cm^{-1}; NMR (CCl_4): 3.40—3.76 (m, 3H), 6.9—8.0 (m, 15H). Found: C, 76.8; H, 5.2%. Calcd for $C_{23}H_{18}O_2S$: C, 77.1; H, 5.1%.

*Reaction of **2** with (Z)-1,2-Dibenzoylethylene.* To a solution of **2** in THF (150 m*l*), prepared by the treatment of **1** (1.92 g, 7.3 mmol) and *n*-BuLi (7.3 mmol) at −50°C under nitrogen, we added, drop by drop, a solution of (Z)-1,2-dibenzoylethylene (1.52 g, 6.4 mmol) in THF (40 m*l*). After being stirred for an additional hour at the same temperature, the reaction mixture was allowed to warm up to room temperature. Work-up then afforded **15** (1.21 g, 53%) (mp and mixed mp 113.5—114°C), which was identical with the above sample.

*Oxidation of **15**.* A solution of **15** (0.09 g, 0.3 mmol) and 30% H_2O_2 (*ca.* 5 m*l*) in AcOH (10 m*l*) was stirred at room temperature for 4 days. The reaction mixture was then diluted with water, neutralized with aqueous $NaHCO_3$ and extracted with $CHCl_3$. After drying ($MgSO_4$), the solution was concentrated to afford *r*-1,*t*-2-dibenzoyl-*t*-3-phenylsulfonylcyclopropane (**16**, 0.10 g, 100%); mp 188—189°C (from benzene). IR (KBr): 1676, 1318, 1270, 1220, 1151 cm^{-1}; NMR ($CDCl_3$): 3.47 (q, 1H, J_{AC}=6.0 Hz, J_{AB}=10.2 Hz), 3.81 (q, 1H, J_{BC}=6.0 Hz, J_{AB}=10.2 Hz), 4.42 (t, 1H, J_{AC}=J_{BC}=6.0 Hz), 7.1—8.2 (m, 15H). Found: C, 70.9; H, 4.8%. Calcd for $C_{23}H_{18}O_4S$: C, 70.8; H, 4.7%.

*Reaction of **2** with Diethyl Fumarate.* To a solution of **2** in THF (150 m*l*), prepared from **1** (2.65 g, 10.0 mmol) and *n*-BuLi (10.0 mmol) at −20°C under nitrogen, we added, drop by drop, a solution of diethyl fumarate (1.55 g, 9.0 mmol) in THF (15 m*l*). After the reaction mixture had then been stirred for 1 hr at the same temperature, it was allowed to warm up to room temperature. Work-up then afforded diethyl *t*-3-(phenylthio)-*r*-1,*t*-2-cyclopropanedicarboxylate (**17**, 1.34 g, 51%); bp 125—126°C/0.05 mmHg. An analytically-pure sample was obtained by preparative GLC (30% High Vacuum Silicone Grease on Celite 535, 220°C). IR (neat): 1729, 1328, 1255, 1172, 1025 cm^{-1}; NMR (CCl_4): 1.15 (t, 3H), 1.31 (t, 3H), 2.30—3.10 (m, 3H), 3.98 (q, 2H), 4.08 (q, 2H), 6.8—7.3 (m, 5H). Found: C, 61.5; H, 6.3%. Calcd for: $C_{15}H_{18}O_4S$: C, 61.2; H, 6.2%.

*Oxidation of **17**.* A solution of **17** (0.31 g, 1.1 mmol) and 30% H_2O_2 (*ca.* 15 m*l*) was heated at 70°C for 12 hr with stirring. Subsequent work-up and chromatography (silica gel column, benzene) afforded diethyl *t*-3-phenylsulfonyl-*r*-1,*t*-2-cyclopropanedicarboxylate (**18**, 0.32 g, 90%) as an oil. This oil solidified on standing at room temperature for several months, mp 60—61.5°C. IR (neat): 1730, 1370, 1320, 1265, 1180, 1150, 1019, 1030 cm^{-1}; NMR (CCl_4): 1.30 (t, 3H), 1.33 (t, 3H), 2.43—3.10 (m, 3H), 4.16 (q, 2H), 4.23 (q, 2H), 7.2—8.0 (m, 5H). Found: C, 54.9; H, 5.6%. Calcd for $C_{15}H_{18}O_6S$: C, 55.2; H, 5.6%.

*Attempted Reaction of **6a** with (E)-1,2-Dibenzoylethylene and Diethyl Fumarate.* A solution of **6a** (1.2 g, 4.3 mmol) and (E)-1,2-dibenzoylethylene (1.0 g, 4.3 mmol) in THF (100 m*l*) was heated under reflux for 6 hr. A work-up then resulted in a complete recovery of the starting materials. The similar treatment of **6a** (1.44 g, 5.0 mmol) and diethyl maleate (0.86 g, 5.0 mmol) also resulted in a complete recovery of the starting materials.

The authors are grateful to Professor K. Sisido for his generous help and to Toray Science Foundation for its financial support. They are also thankful to the Ministry of Education, Japanese Government, for a Scientific Research Grant-in-aid.