# Di- and Trimethylenebis(ethylphenacyl)sulfonium Ylides

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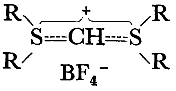
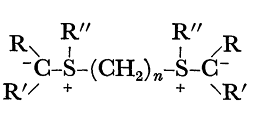
Bissulfonium phenacylides were obtained by the reactions of dimethylene and trimethylene bisethylphenacylsulfonium salts with sodium hydride. The chemical properties of these bis-ylides are similar to those of monosulfonium phenacylides. Biscarbamoylsulfonium phenacylides were obtained as stable crystals by the reactions of the above bis-ylides with phenyl isocyanate.

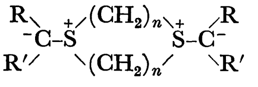
Recently, considerable information has accumlated concerning sulfur-stabilized ylides.[1-5] However, bissulfonium ylides have received little attention, except for the bissulfonium ylide of structure I.[6] In this paper, an attempt at the syntheses and reactions of bis-ylides of the II and III structures will be described.


$\mathrm{R(R')S{=\!=}\overset{+}{C}H{=\!=}S(R)(R')\ \ BF_4^-}$

I
R: Methyl
　Ethyl


$\mathrm{^{-}C(R)(R')\text{-}\overset{+}{S}(R'')\text{-}(CH_2)_n\text{-}\overset{+}{S}(R'')\text{-}C^{-}(R)(R')}$

II
R : H
R′ : Benzyl
R″: Ethyl


$\mathrm{^{-}C(R)(R')\text{-}\overset{+}{S}\langle(CH_2)_n\rangle_2\overset{+}{S}\text{-}C^{-}(R)(R')}$

III
R: H
R′: Benzyl

By the use of open-chain sulfides (methylene, dimethylene, and trimethylene bisethylsulfide) and cyclic sulfides (1,3-dithiolane, 1,3-dithiane, 1,4-dithiane, and 1,3,5-trithiane) as the starting materials, an attempt has been made to synthesize phenacyl bissulfonium salts. Dimethylene and trimethylene sulfides among these sulfides gave bissulfonium salts by reactions with phenacylbromide. The subsequent treatment of these bissulfonium salts with sodium hydride gave bissulfonium phenacylide (Structure II). Several reactions of the above-mentioned bis-ylides were carried out (*cf.* Chart 1).

## Results and Discussion

*Bissulfonium Salts.* Dimethylenebissulfonium

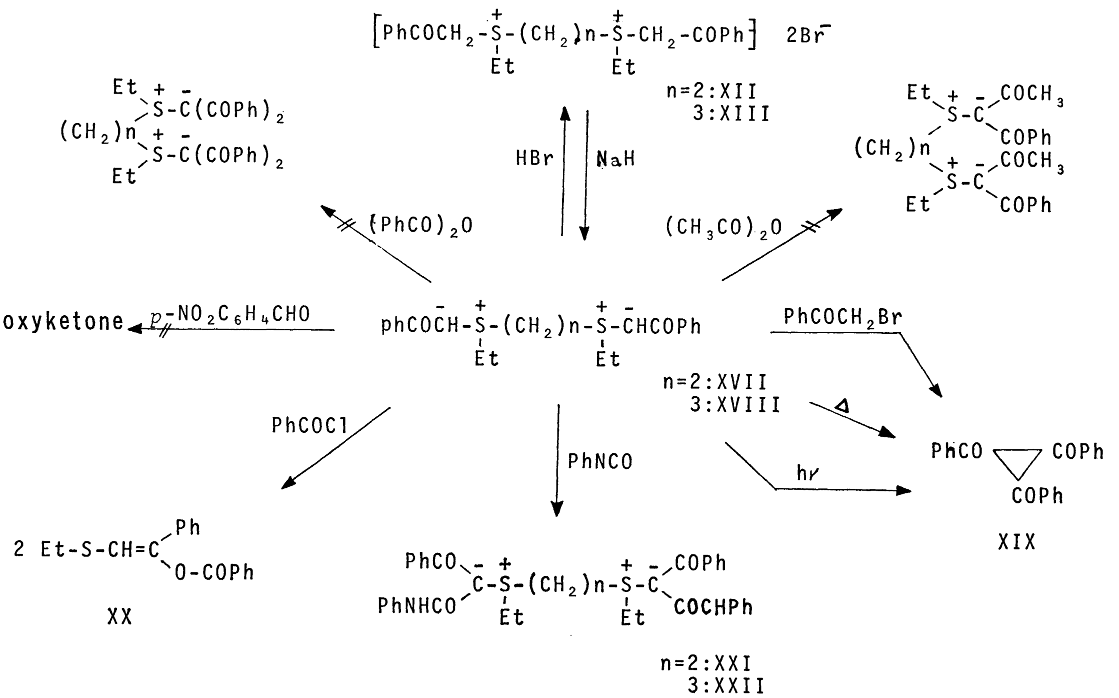


Chart 1. Reactions of Bissulfonium ylides

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[1] H. Nozaki, M. Takaku, D. Tsunemoto, Y. Yamamoto, and K. Kondo, *Nippon Kagaku Zasshi*, **81**, 1 (1967).

[2] Y. Kishida, *Yuki Gosei Kagaku Kyokai Shi*, **26**, 1037 (1968).

[3] Preparation a) H. Nozaki, D. Tsunemoto, Z. Morita, K. Nakamura, K. Watanabe, M. Takaku, and K. Kondo, *Tetrahedron*, **23**, 4279 (1967). b) A. F. Kook and S. G. Moffatt, *J. Amer. Chem. Soc.*, **90**, 740 (1968). c) W. Ando, T. Yagihara, S. Tozune, S. Nakado, and T. Migita, *Tetrahedron, Lett.*, **1969**, 1979.

[4] Reaction. a) K. W. Ratts and A. Yao, *J. Org. Chem.*, **33**, 66 (1968). b) M. T. Hatch, *ibid.*, **34**, 2133 (1969). c) Y. Hayashi, and R. Oda, *Tetrahedron Lett.*, **1968**, 853. d) U. Schöllkopf, *ibid.*, **1969**, 2619. e) G. Schmidt, *ibid.*, **1969**, 2623. f) T. Mukaiyama, M. Higo, H. Takei, This Bulletin, **43**, 2566 (1970).

[5] was prepared by the reaction of the corresponding diethylphenacylsulfonium bromide in THF with sodium hydride: mp 77—78°C; IR (KBr): $\nu_{C=O}$ 1505 cm.$^{-1}$)

[6] C. P. Lillya and P. Millar, *J. Amer. Chem. Soc.*, **88**, 1560 (1966).

Table 1. Mono- and bissulfonium salts, and bis-ylides

| Compound | Mp (°C) | Formula | Analysis (%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Found | | | | | Calcd | | | | |
| | | | C | H | N | S | Br | C | H | N | S | Br |
| XI | oil | $C_{12}H_{19}OS_2Br$ | 46.1 | 5.5 | | 19.1 | 23.5 | 46.58 | 5.67 | | 19.08 | 33.82 |
| XII | 128—130 | $C_{21}H_{28}O_2S_2Br$ | 48.3 | 5.1 | | 16.2 | 29.2 | 48.00 | 5.09 | | 16.36 | 29.09 |
| XIII | 136—138 | $C_{22}H_{30}O_2S_2Br$ | 48.6 | 5.2 | | 11.2 | 28.1 | 48.94 | 5.32 | | 11.53 | 28.37 |
| XIV | 99—100 | $C_{11}H_{13}OS_2Br$ | 43.0 | 4.2 | | 20.5 | 26.0 | 43.28 | 4.26 | | 20.98 | 26.33 |
| XV | 110—111 | $C_{12}H_{15}OS_2Br$ | 45.1 | 4.6 | | 20.3 | 25.1 | 45.14 | 4.70 | | 20.06 | 25.08 |
| XVI | 130—131 | $C_{12}H_{15}O_2S_2Br$ | 45.2 | 4.7 | | 19.9 | 25.0 | 45.14 | 4.70 | | 20.06 | 25.08 |
| XVII | oil | $C_{21}H_{27}O_2S_2$ | 67.8 | 6.8 | | 16.5 | | 67.69 | 6.67 | | 16.42 | |
| XVIII | — | $C_{22}H_{29}O_2S_2$ | 68.5 | 6.9 | | 12.7 | | 68.32 | 6.93 | | 12.62 | |
| XXI | 184—185 | $C_{36}H_{36}N_2O_4S_2$ | 67.0 | 5.6 | 4.3 | 9.8 | | 66.87 | 5.57 | 4.33 | 9.90 | |
| XXII | 194—195 | $C_{37}H_{38}N_2O_4S_2$ | 67.2 | 6.0 | 4.2 | 9.6 | | 67.27 | 6.06 | 4.24 | 9.69 | |

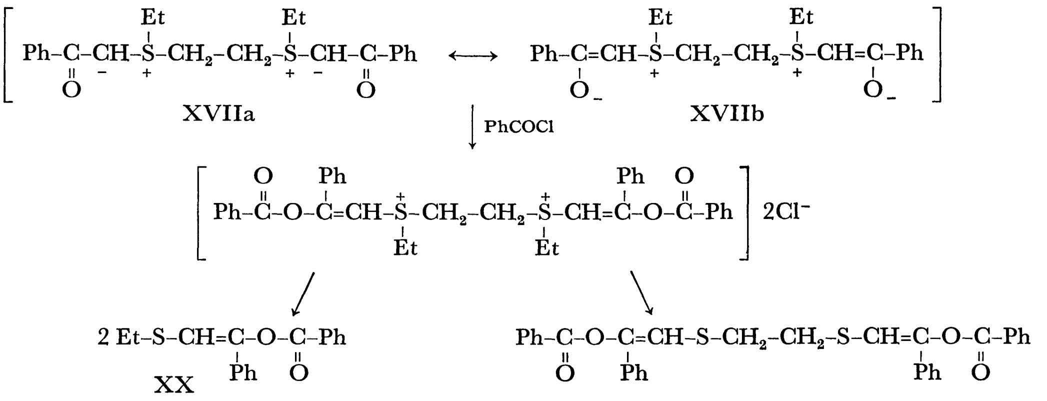
bromide (XII) was obtained as a white solid in a 40% yield by the reaction of dimethylene bisethylsulfide and phenacylbromide. The structure was confirmed by a study of its IR spectrum ($\nu_{C=O}$ 1662 cm$^{-1}$) and elemental analysis. A similar procedure for trimethylenebisethylsulfide gave trimethylene bisethylphenacylsulfonium bromide (XIII) as a white solid in a 55% yield. However, similar procedures for methylenebisethylsulfide and cyclic sulfides gave only monosulfonium salts in 30—90% yields, except for 1,3,5-trithiane.

The UV absorption curves of the bissulfonium salts (XII and XIII) do not obery Beer's law in cyclohexane solutions. Similar deviations from Beer's law by bissulfonium salts have been reported by Lillya[6] and Nicholson.[7]

*Bissulfonium Phenacylides.* The reaction of the bis-salt (XII) with sodium hydride in THF at 0—−5°C gave a light yellow dimethylene bisethylsulfonium phenacylide (XVII). The structure of XVIII was confirmed by the results of elemental analysis and the spectroscopic data. This structure was further chemically confirmed by the formation of XII through the action of hydrogen bromide in an aqueous ethanol, and by the formation of XXI (as crystals in over a 50% yield) through the action of phenyl isocyanate in THF by an analogous treatment of XIII with sodium hydride, trimethylenebisethylsulfonium phenacylide (XVII) was obtained in a 72% yield (Table 1).

These bis-ylides (XVII and XVIII) were solids (although they could not be crystallized) and were fairly stable below 0°C. They decomposed on standing in the atmosphere or in a solution (ethanol and THF at room temperature), and the absorption due to ylide carbonyl in the 1520—1500 cm$^{-1}$ range disappeared completely after two weeks. Furthermore, the addition of a few drops of water to XVII and XVIII accelerated their decomposition. They were also subject to thermal decomposition. The heating of the bis-ylide (XVII) in THF gave *trans*-1,2,3-tribenzoylpropane (XIX) in a 47% yield (based on the XVII used). The same products was obtained from XVII in 85% and 22% yields by treatment with phenacylbromide and by irradiation (UV) in THF at room temperature respectively.

It has been reported that the course of the acylation of the mono-ylides varied with the nature of the acylating agent and with the structure of the mono-ylides; dimethyl-oxy-sulfonium phenacylide[8] underwent a *C*-acylation with benzoylchloride, while methylphenylsulfonium phenacylide[9] and dimethylsulfonium phenacylide[10] underwent an *O*-acylation with benzoylchloride, but a *C*-acylation with benzoic anhydride.



Scheme 1

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[7] D. C. Nicholson, E. Rothstein, R. W. Saville, and R. Whitly, *J. Chem. Soc.*, **1953**, 4019.

[8] H. König and H. Metzger, *Chem. Ber.*, **98**, 3733 (1965).

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

[10] A. W. Johnson and R. T. Amel, *J. Org. Chem.*, **34**, 1240 (1969).

The acylation of XVII and XVIII with benzoylchloride resulted in an *O*-acylation, affording the enol benzoate (XX) of ethylmercaptoacetophenon in 78 and 71% yields respectively (Scheme 1)

The IR spectrum and the results of the elemental analysis of XX were consistent with those of an authentic sample prepared by the reaction of diethylsulfonium phenacylide (XXIII)[5] with benzoylchloride. The results suggest that the contribution of the enol form in the bis-ylides (XVII and XVIII) was stronger than that in dimethyl-oxy-sulfonium phenacylide.

The reaction of XVII and XVIII with benzoic anhydride did not give a product corresponding to *C*- or *O*-acylation; from the reaction products, benzoic acid in a 60% yield (based on the benzoic anhydride used), together with traces of the cyclopropane (XIX) and of a product with a melting point over 300°C, were obtained on a column chromatographic separation (alumina).

The treatment of the bis-ylides (XVII and XVIII) with phenyl isocyanate in THF at 0—−5°C afforded other bis-ylides (XXI and XXII)[11] as colorless crystals in 53 and 87% yields respectively.

Johnson and Amel[10] reported that dimethylsulfonium phenacylide (XXIII) reacted with *p*-nitrobenzaldehyde to give a epoxide in a 10% yield, while Nozaki *et al.*[8] reported that the reactions of methylphenylsulfonium phenacylide with benzaldehyde or *p*-nitrobenzaldehyde did not afford epoxyketones. We have not been able to obtain mono- or bis-epoxyketone by the reactions of bis-ylides (XVII and XVIII) with *p*-nitrobenzaldehyde.

Nozaki[9] and Johnson[10] reported that the irradiation of monosulfonium phenacylide gave the cyclopropane (XIX). Ratt[12] and Johnson[10] reported the trapping of the carbene intermediate from monosulfonium phenacylide and *p*-nitrophenacylide by the use of triphenylphosphine and dimethylbenzylamine. We carried out the irradiation of the bis-ylides (XVII and XVIII) in THF with a high-pressure mercury lamp (300 W) and thus obtained the cyclopropane (XIX in a 20% yield), along with unidentified oily substances. We failed, however, to trap the benzoylcarbene with the above trapping reagents.

## Experimental

*General.* All the melting points are uncorrected. The IR spectra were recorded on a JASCO grating infrared spectrophotometer IR-G. The UV spectra were measured on a Hitachi 124 spectrophotometer. The photochemical reactions were effected by the use of a Eikosha high-pressure mercury apparatus.

*α,ω-alkanedithiols* were prepared by the reactions of α,ω-dibromoalkanes with thiourea and by the subsequent hydrolysis of the salts: 1,2-ethanedithiol,[13] bp 61—63°C/45 mmHg; 1,3-propanedithiol, bp 72°C/25 mmHg.

*Open-chain Sulfides and Cyclic Sulfides* were prepared according to the directions in the literature and were purifided by distillation or recrystallization: methylenebisethylsulfide (IV),[14] bp 95—97°C/39—40 mmHg; dimethylenebisethylsulfide (V),[15] bp 209—213°C/760 mmHg; trimethylenebisethylsulfide (VI),[16] bp 86.0—87.5°C/8—9 mmHg; 1,3-dithiolane (VII),[17] bp 56—68°C/8—10 mmHg; 1,3-dithiane (VIII),[18] mp 52—53°C; 1,4-dithiane (IX),[19] mp 111.0—111.5°C; 1,3,5-trithiane (X),[20] mp 212—213°C.

The data of elemental analyses for mono- and bissulfonium bromides and phenacylides given below are summarized in Table 1.

*Methylene Bisethylmonophenacylsulfonium Bromide (XI).*[21] A solution of phenacylbromide (8.0 g, 0.04 mol) and IV (2.7 g, 0.02 mol) in methanol (150 m*l*) was refluxed for 6 hr. After the subsequent removal of the methanol, we added ether (200 m*l*) to the residue; further extraction of the insoluble parts with several portions of ether afforded 2.7 g (24.5%) of a clear, brownish residue (XI): IR (neat): $\nu_{C=O}$ 1670 cm$^{-1}$.

*Dimethylenebisethylphenacylsulfonium Bromide (XII) and Trimethylenebisethylphenacylsulfonium Bromide (XIII).* A mixture of phenacylbromide (8.0 g, 0.04 mol) and V (3.0 g, 0.02 mol) was warmed for 15 min at 50—60°C and then allowed to stand for two days at room temperature. To the reaction mixture (a light yellow solid), we then added several portions of acetone. The insoluble parts were recrystallized from hot acetone-ether to give IX (4.6 g, 41.8%) as colorless, microfine crystals: mp 128—130°C; IR (KBr): $\nu_{C=O}$ 1662 cm$^{-1}$. Similarly, a reaction mixture (a dark brown solid) of phenacylbromide (8.0 g, 0.04 mol) and VI (3.2 g, 0.02 mol) gave XIII (5.8 g, 57.2%) as colorless, microfine crystals on recrystallization from hot acetone - water: mp 136—138°C; IR (KBr): $\nu_{C=O}$ 1662 cm$^{-1}$.

*1,3-Dithiolane-1-phenacylsulfonium Bromide (XIV) and* 1,3-*Dithianephenacylsulfonium Bromide (XV).* A mixture of phenacylbromide (8.0 g, 0.04 mol) and VII (2.2 g, 0.02 mol) was warmed for 5 min at 50—60°C and then allowed to stand for two days below 15°C. To the reaction mixture (a dark red solid) we then added several portions of acetone. The insoluble part (a white solid) was recrystallized from methanol - acetone (3:1) to give XIV (4.2 g, 67.1%) as colorless, microfine crystals: mp 99—100°C; IR (KBr): $\nu_{C=O}$ 1662 cm$^{-1}$. Similarly, a reaction mixture of phenacylbromide (8.0 g, 0.04 mol) and VIII (2.4 g, 0.02 mol) gave XV (4.4 g, 69.2%) as colorless crystals after recrystallization from hot acetone - water: mp 110—111°C; IR (KBr): $\nu_{C=O}$ 1662 cm$^{-1}$.

*1,4-Dithiane-1-phenacylsulfonium Bromide (XVI).* 1,4-dithiane (2.4 g, 0.02 mol) was dissolved in phenacylbromide (8.0 g, 0.04 mol) at 80—90°C, and then the mixture was kept for 5 min at 90—100°C. To the reaction mixture (a light yellow solid) we then added several portions of hot methanol to give XVI (6.4 g, 93.7%) as colorless, microfine crystals; mp 130—131°C; IR (KBr): $\nu_{C=O}$ 1668 cm$^{-1}$.

*Reaction of 1,3,5-Trithiane (X) with Phenacylbromide.* A

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[11] The structures of XXI and XXII were comfirmed by their IR spectra and elemental analyses. The crystalline bis-ylides (XXI and XXII) were readily soluble in THF, chloroform, methanol, and water, and were fairly stable on standing in atmosphere at room temperature and on refluxing in THF.

[12] K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).

[13] A. J. Speziale, "Organic Syntheses," Coll. Vol. IV, p. 401.

[14] S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 427 (1964).

[15] A. Fraling, *Rec. Trav. Chim.*, **81**, 1009 (1966).

[16] A. W. Wedkind, *Ber.*, **58**, 2513 (1925).

[17] A. Schönberg and N. Preafko, *Chem. Ber.*, **100**, 778 (1967).

[18] D. T. Gibson, *J. Chem. Soc.*, **1930**, 12.

[19] R. C. Fuson, R. D. Lipscomb, B. C. Mckusick, and L. J. Reed, *J. Org. Chem.*, **11**, 513 (1946).

[20] R. W. Bost and E. W. Constable, "Organic Syntheses," Coll. Vol. II, p. 610.

[21] In order to obtain methylenebisethylsulfonium salts, a mixture of IV and phenacylbromide in methylenechloride was treated with silvertetraflurorborate. The glistering colorless crystals (mp 153—154°C) was obtained, but this compound was unstable.

solution of X (1.4 g, 0.01 mol) and phenacylbromide (5.2 g, 0.03 mol) in benzene (200 m*l*) was refluxed for 10 days. After the removal of the benzene, methanol was added to the residue. By washing the insoluble part with several portions of methanol - acetone, trithiane (1.3 g) was then recovered.

*Dimethylenebisethylsulfonium Phenacylide (XVII).* To a suspension of XII (2.2 g, 0.04 mol) in 30 m*l* of anhydrous THF at 0——5°C, sodium hydride (0.008 mol) was added: the mixture was then vigorously stirred for 5 hr below 5°C. After the removal of the sodium bromide from the reaction mixture, the evaporation of the THF and treatment with petroleum-ether gave a pale yellow residue which solidified below 5°C, but which could not be crystallized. The chromatography of this residue on alumina gave XVII (62%) and a trace of *trans*-1,2,3-tribenzoylpropane (XIX); IR (neat): $\nu_{C=O}$ 1515 cm$^{-1}$; UV: $\lambda_{max}^{EtOH}$ 229 m$\mu$ ($\varepsilon$ $2.12\times10^4$), 308 m$\mu$ ($\varepsilon$ $2.12\times10^4$). The IR spectrum of XIX was identical with that of an authentic sample prepared by the treatment of phenylmethylsulfonium phenacylide with phenacylbromide.

*Trimethylenebisethylsulfonium Phenacylide (XVIII):* Yield, 72%; IR (neat): $\nu_{C=O}$ 1510 cm$^{-1}$; UV: $\lambda_{max}^{EtOH}$ 229 m$\mu$ ($\varepsilon$ $2.61\times10^4$), 308 m$\mu$ ($\varepsilon$ $2.50\times10^4$).

*Acylation of the bis-ylides (XVIII). Enolbenzoate of Mercapto-acetophenone (XX):* A solution of XVII (1.1 g, 0.0025 mol) and benzoylchloride (0.7 g, 0.005 mol) in anhydrous THF was stirred for 3 hr at room temperature. The white precipitates were then washed with THF - *n*-hexane (1:4) and dried over $P_2O_5$ to give XX (0.9 g, 64%): mp 107—108°C; IR (KBr): $\nu_{C=O}$ 1738 cm$^{-1}$; $\nu_{C-O-C}$ 1190 cm$^{-1}$, Found; C, 71.4; H, 5.6; S, 11.5%, (Calcd for $C_{17}H_{16}O_2S$: C, 71.83; H, 5.63; S, 11.27%). The melting point the results of elemental analysis, and the IR spectrum were identical with those of an authentic sample prepared by the reaction of diethylsulfonium phenacylide with benzoylchloride.

A similar treatment of XVIII (1.1 g, 0.0025 mol) with benzoylchloride (0.7 g, 0.0025 mol) gave XX (0.99 g, 71%).

*Reaction of the bis-ylides (XVII and XVIII) with* p-*Nitrobenzaldehyde.* A solution of XVII (1.1 g, 0.0025 mol) and *p*-nitrobenzaldehyde (0.75 g, 0.005 mol) in 30 m*l* of anhydrous THF was refluxed for 20 hr. After the subsequent evaporation of the THF, the chromatography of the residue on alumina gave *p*-nitrobenzylalcohol (0.8 g, 23%), together with a trace of the cyclopropane (XIX) and an intractable oil (1.0 g).

A similar treatment of XVIII (1.1 g, 0.0025 mol) with *p*-nitrobenzaldehyde gave *p*-nitrobenzylalcohol, the cyclopropane (XIX), and an intractable brown oil in a ratio analogous to that above.

*Reaction of the bis-ylide (XVII and XVIII) with Phenyl Isocyanate. Dimethylenebisethylsulfonium Benzoyl (*N-*phenylcarbamoyl) Methylide (XXI):* Phenyl isocyanate (0.6 g, 0.005 mol) and XVII (1.1 g, 0.0025 mol) were stirred in anhydrous THF (30 m*l*) for 5 hr at 0——5°C. After the subsequent evaporation of the THF, the recrystallization of the residue from AcOEt or chloroform - AcOEt gave XXI (0.85 g, 53%): mp 184—185°C; IR (KBr): $\nu_{C=O}$ 1640 and 1513 cm$^{-1}$; UV: $\lambda_{max}^{EtOH}$ 243 m$\mu$ ($\varepsilon$ $4.44\times10^4$), 284 m$\mu$ ($\varepsilon$ $4.32\times10^4$).

*Trimethylenebisethylsulfonium Benzoyl (*N-*phenylcarbamoyl) Methylide (XXII):* A similar treatment of XVIII (1.1 g, 0.0025 mol) with phenyl isocyanate (0.6 g, 0.005 mol) gave XXII (1.0 g, 61%): mp 194—195°C; IR (KBr): $\nu_{C=O}$ 1635 cm$^{-1}$; UV: $\lambda_{max}^{EtOH}$ 243 m$\mu$ ($\varepsilon$ $4.28\times10^4$), 284 m$\mu$ ($\varepsilon$ $4.11\times10^4$). trans-1,2,3-*Tribenzoylpropane (XIX). XVIII and Phenacylbromide:* An equimolar mixture of XVIII (1.1 g, 0.0025 mol) and phenacylbromide (0.5 g, 0.0025 mol) in THF was stirred at room temperature for 5 hr. The subsequent concentration of the solution and recrystallization of the residue from benzene gave the cyclopropane XIX (0.32 g, 48% based on the XVIII); mp 214—215°C.

*Thermolysis of XVIII:* A solution of XVIII (1.05 g, 0.0025 mol) in THF (20 m*l*) was heated under reflux for 24 hr. The subsequent evaporation of the solvent and the recrystallization of the residue from benzene gave a 47% yield (0.105 g, based on the XVII) of the XIX cyclopropane.

A similar treatment of XVIII (1.1 g, 0.0025 mol) gave a 40% yield (0.088 g, based on the XVIII) of the XIX cyclopropane.

*Photolysis of XVIII:* A solution of XVIII (1.1 g, 0.0025 mol) in THF (10 m*l*) was irradiated for 15 hr in a Pyrex tube. The subsequent concentration of the solution and recrystallization of the residue gave an 8% yield of XIX.