CHEMISTRY LETTERS, pp. 1055-1060, 1975. Published by the Chemical Society of Japan

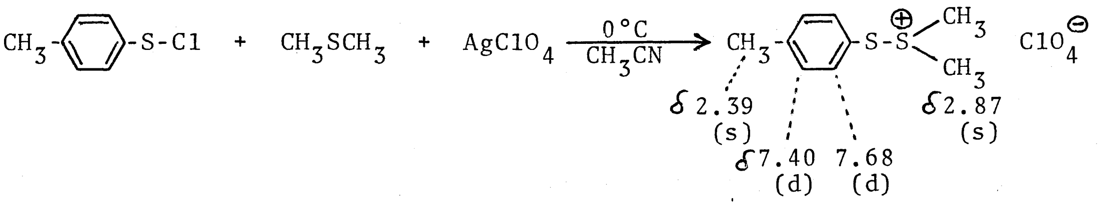
SYNTHESIS OF ARYLTHIODIMETHYLSULFONIUM SALTS AND THEIR REACTIONS WITH NUCLEOPHILES

Hiroshi MINATO,* Takashi MIURA, and Michio KOBAYASHI
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
Fukazawa, Setagaya, Tokyo 158

Arylthiodimethylsulfonium perchlorates (**1**) are prepared from arenesulfenyl chloride, methyl sulfide and silver perchlorate. The reactions of **1** with benzyl methyl sulfide, sodium methoxide, anisole, and 2,6-di-*t*-butylphenol are investigated, and all these nucleophiles attack **1** at its sulfide sulfur atom. The reactivity of **1** is compared with those of anilinosulfonium ion and phenoxysulfonium ion.

Dimethylmethylthiosulfonium salts have been found to be very interesting compounds.[1-3] Their aryl analogs, i. e., dimethylarylthiosulfonium salts, $Me_2\overset{\oplus}{S}$-S-Ar $Y^{\ominus}$, and diarylarylthiosulfonium salts, $Ar_2\overset{\oplus}{S}$-S-Ar $Y^{\ominus}$, have not been described in the literature. We have attempted to synthesize them, and succeeded in preparing the former. The latter could not be prepared, probably because aryl sulfides are much poorer nucleophiles than methyl sulfide.

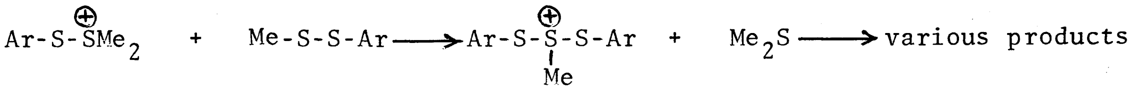
p-Toluenesulfenyl chloride (1 equiv.) was added drop by drop into an acetonitrile solution of methyl sulfide and silver perchlorate (1 equiv. each) at 0°C, and the mixture was stirred for 10 min. After the silver chloride precipitates were removed, dry ether was added to the filtrate. A yellow oil precipitated, which was separated and dried in vacuum. Crystals of dimethyl-*p*-tolylthiosulfonium perchlorate (**1a**) were obtained.



1a

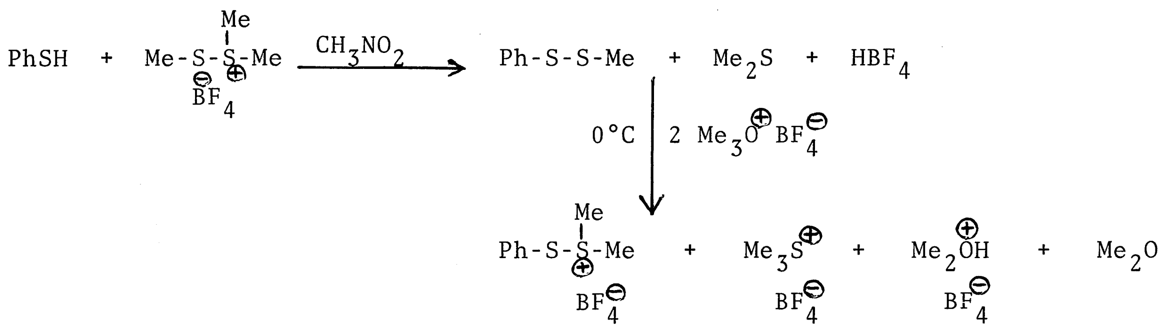
In a similar manner, dimethylphenylthiosulfonium perchlorate (**1b**) was prepared from benzenesulfenyl chloride ($(CH_3)_2\overset{\oplus}{S}$-, δ 3.05 (s), 6H; C_6H_5-S-, 7.5-7.9(m), 5H).

In general, the methylation of aryl methyl disulfide is not a good method for preparing **1**, partly because the **1** formed and the disulfide remaining tend to react further and partly because aryl methyl disulfide tends to disproportionate.



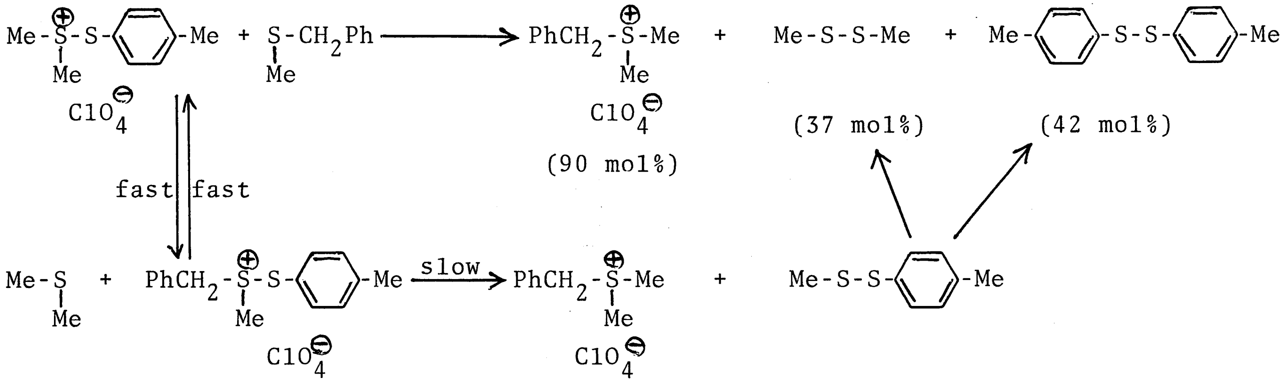
$$\text{Ar-S-}\overset{\oplus}{\text{S}}\text{Me}_2 + \text{Me-S-S-Ar} \longrightarrow \text{Ar-S-}\underset{\text{Me}}{\overset{\oplus}{\text{S}}}\text{-S-Ar} + \text{Me}_2\text{S} \longrightarrow \text{various products}$$

However, it was possible to prepare **1** by methylation of a disulfide by the following procedure. A nitromethane solution of trimethyloxonium tetrafluoroborate (2 equiv.) was added drop by drop to a mixture of dimethylmethylthiosulfonium tetrafluoroborate (1 equiv.) and thiophenol (1 equiv.) at 0°C, and the mixture was stirred for 30 min. Upon addition of dry ether, a mixture of arylthiodimethylsulfonium and trimethylsulfonium tetrafluoroborates precipitated.



Then the reactions of **1** with some nucleophiles were examined.

When **1a** (1.9 mmol) and benzyl methyl sulfide (1.9 mmol) was mixed in nitromethane at room temperature, their NMR spectrum after 15 min showed that benzyldimethylsulfonium salt is present in 35% yield, and reaction was complete in 8 days.



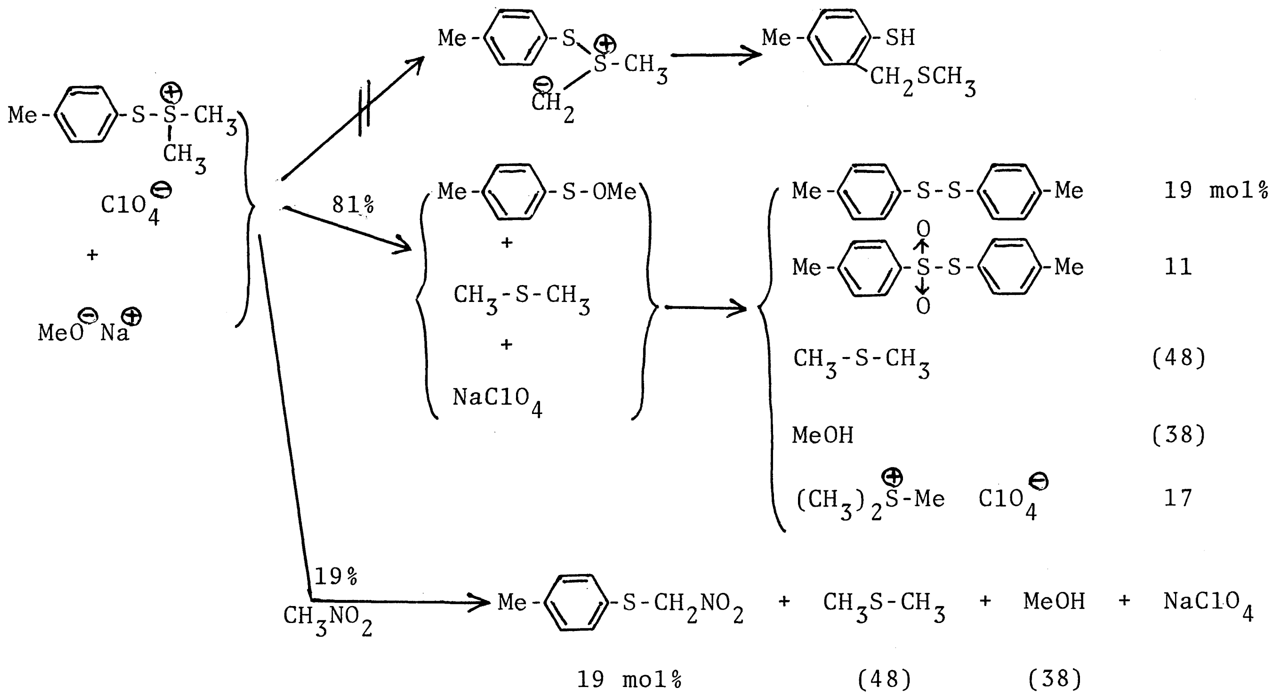
The mixture was subjected to vacuum distillation, and methyl disulfide was collected (0.70 mmol). Extraction from the residue with ether gave p-tolyl disulfide (0.80 mmol). The remaining crystals were benzyldimethylsulfonium perchlorate ($Me_2\overset{\oplus}{S}$-, 2.72(s), 6H; -CH_2-, 4.53(s), 2H) (1.7 mmol). These results suggest that the reaction is represented by the scheme shown above.

Since the reactions between dimethylmethylthiosulfonium salts and sulfides are very rapid,[2] both the forward reaction between **1a** and benzyl methyl sulfide and the backward reaction between methyl sulfide and the benzylmethyl-p-tolylthiosulfonium salt formed must be rapid.

Benzylmethyl-p-tolylthiosulfonium perchlorate must be an intermediate in this reaction, and methyl sulfide may attack it at three sites. Its fast nucleophilic attack takes place at the sulfide sulfur atom. Much slower nucleophilic attack could take place on either the benzyl or methyl carbon atoms, eliminating methyl p-tolyl disulfide or benzyl p-tolyl disulfide. However, the products analysis shows that methyl sulfide attacks exclusively the benzyl carbon atoms and no methyl carbon atoms. In the ordinary S_N2 reactions on carbon atoms (for instance, when halides are the leaving groups), the relative reactivities of benzyl and methyl compounds are not much different from unity.[4,5] Some unique features of the reactions between sulfonium ions and nucleophiles have been pointed out and the formation of tetracovalent sulfur intermediates from sulfonium ions and sulfides has been suggested as a plausible explanation.[2]

The reaction between **1** and a strong base is of interest, since an ylide may be formed, which may rearrange to produce a C-C bond intramolecularly between the ylide carbanion and the aromatic ring. Such intramolecular reactions are reported for anilinosulfonium[6] and phenoxysulfonium[7] ions.

When a nitromethane solution of **1a** (2.9 mmol) and sodium methoxide (2.9 mmol) was allowed to stand at room temperature, its NMR spectrum showed that reaction was complete in 2 days. The evaporation of the mixture in vacuum yielded methyl sulfide (1.4 mmol) and methanol (1.1 mmol). The addition of dry ether to the residue precipitated the crystals of trimethylsulfonium perchlorate (0.50 mmol; δ 2.90 (s)). The filtrate was concentrated, and the residue was subjected to column chromatography; p-tolyl disulfide (0.54 mmol; CH_3, δ 2.29(s)), α-p-tolylnitromethane (0.55 mmol; CH_3, δ 2.36(s), CH_2, 5.29(s)), and p-tolyl p-toluenethiolsulfonate (0.31 mmol; $-O_2S-C_6H_4-CH_3$, δ 2.40(s), $-S-C_6H_4-CH_3$, δ 2.36(s)). These results suggest that the reactions are represented by the following scheme.



The 19% of methoxide anion simply removes the proton of the solvent, and the nitrocarbanion formed attacks the sulfide sulfur atom. The 81% of methoxide anion directly attacks the thiosulfonium ion. The products found can be rationalized by the following equations.

$$4\ \mathrm{Ar\text{-}S\text{-}}\overset{\oplus}{\mathrm{S}}\mathrm{(CH_3)_2ClO_4^{\ominus}} + 4\ \mathrm{NaOMe} = 4\ \mathrm{Ar\text{-}S\text{-}OMe} + 4\ \mathrm{CH_3SCH_3} + 4\ \mathrm{NaClO_4}$$

$$= 2\ \mathrm{ArS(=O)SAr} + 2\ \mathrm{(CH_3)_2}\overset{\oplus}{\mathrm{S}}\mathrm{\text{-}Me\ ClO_4^{\ominus}} + 2\ \mathrm{CH_3SCH_3} + 2\ \mathrm{MeONa} + 2\ \mathrm{NaClO_4}$$

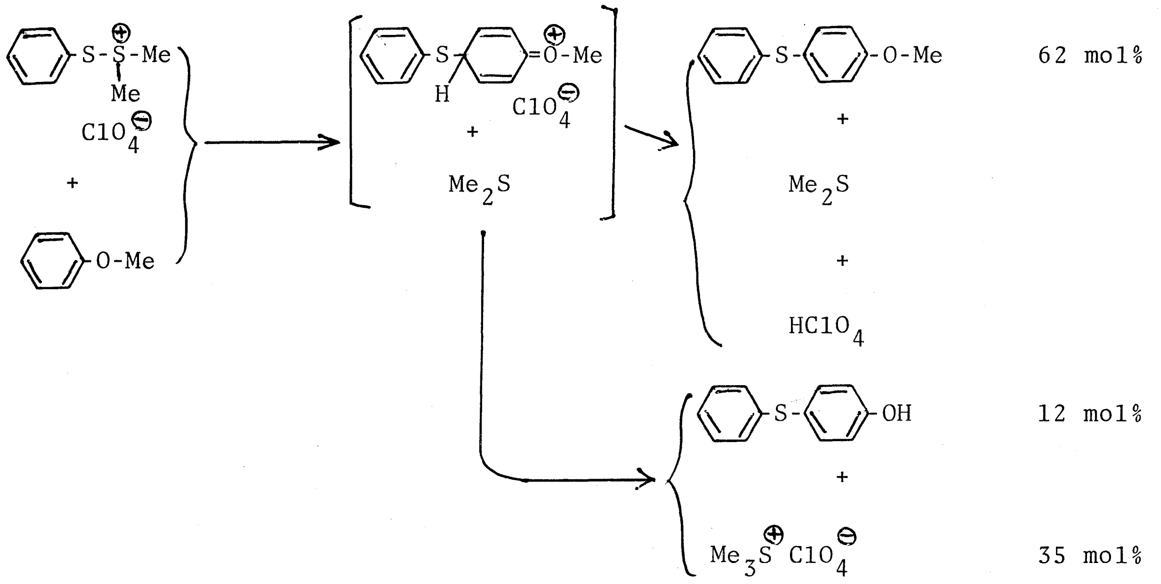
$$= \mathrm{ArSSAr} + \mathrm{ArSO_2SAr} + 2\ \mathrm{(CH_3)_2}\overset{\oplus}{\mathrm{S}}\mathrm{\text{-}Me\ ClO_4^{\ominus}} + 2\ \mathrm{CH_3SCH_3} + 2\ \mathrm{MeONa} + 2\ \mathrm{NaClO_4}$$

Found:	19	11	17	48	38 mol%
Calcd:	20	20	40	59	59 mol%

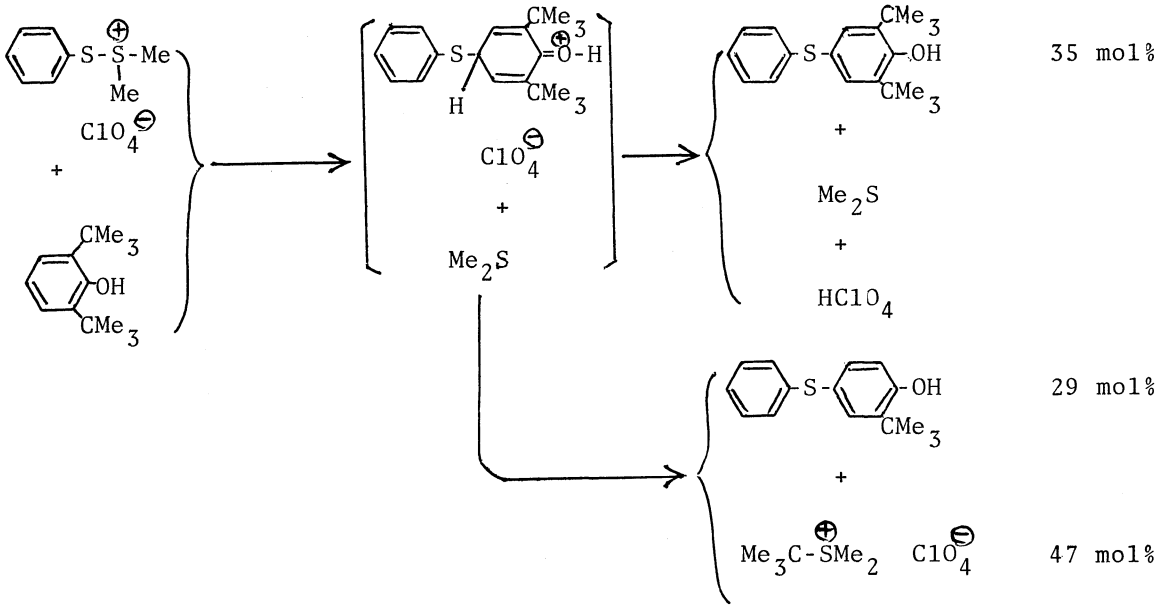
The mol% values shown above as calculated are based on the equations above and the factor of 0.81 (19% of the reaction is the deprotonation of nitromethane). It is of interest that methoxide anion deprotonates nitromethane but not the thiosulfonium ion. This behavior is in contrast with those of anilinosulfonium[6] and phenoxysulfonium[7] ion.

1 was found to react with anisole and phenols even at room temperature, whereas its alkyl analog, dimethylmethylthiosulfonium salts, reacted with them only when they were heated to 60°C.[3]

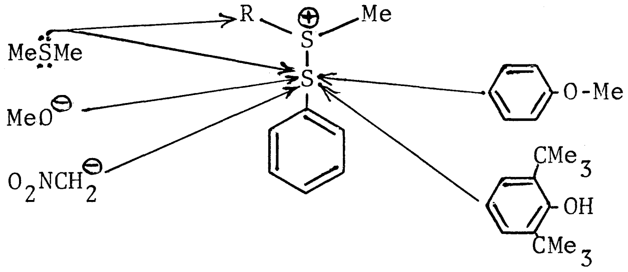
When a mixture of **1b** (2.6 mmol) and anisole (2.7 mmol) was allowed to react in nitromethane at room temperature, its NMR spectrum showed that reaction was complete in 25 hr. The addition of ether precipitated trimethylsulfonium perchlorate (0.90 mmol; CH_3, δ 2.90 (s)). The ethereal filtrate was concentrated, and the residue was chromatographed on a Florisil column. The products obtained were 4-methoxyphenyl phenyl sulfide (1.6 mmol; CH_3O-, δ 3.76 (s); C_6H_5-, δ 7.08 (s); CH_3O-C_6H_4-, δ 7.33 (d) and 6.79 (d), J = 8.4 Hz) and 4-hydroxyphenyl phenyl sulfide (0.30 mmol; OH, δ 4.93 (s), C_6H_5- , 7.16 (s); HOC_6H_4-, 7.34(d) 6.79 (d), J = 8.4 Hz). The low boiling methyl sulfide was removed together with the solvents, and its amount was not determined. The results are summarized as follows.



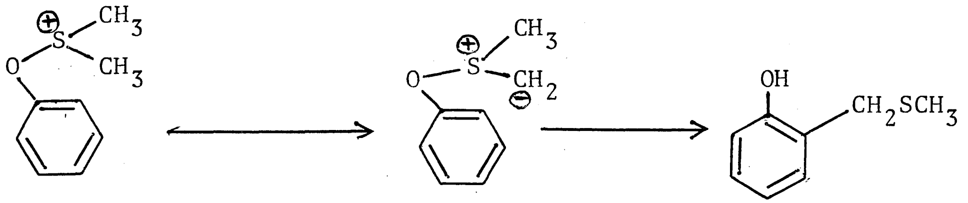
When a mixture of 1b (1.7 mmol) and 2,6-di-t-butylphenol (1.7 mmol) in nitromethane was allowed to react at room temperature, reaction was complete in 8 hr. When dry ether was added to the mixture, crystals of t-butyldimethylsulfonium perchlorate precipitated (0.80 mmol; $(CH_3)_3C$-, δ 1.55 (s), 9H; $(CH_3)_2\overset{\oplus}{S}$-, δ 2.77 (s), 6H). The ethereal filtrate was concentrated, and the residue was chromatographed; 3,5-di-t-butyl-4-hydroxyphenyl phenyl sulfide (0.60 mmol; $(CH_3)_3C$-, δ 1.42 (s), 9H; OH, 5.17 (s); C_6H_5-, 7.11 (s), 5H; $-C_6H_2-$, 7.21(s), 2H), and 3-t-butyl-4-hydroxyphenyl phenyl sulfide (0.50 mmol; $(CH_3)_3C$-, δ 1.38 (s), 9H; OH, 4.74 (s), 1H; C_6H_5-, 7.11 (s), 5H; $-C_6H_3-$, 6.5-7.4 (m), 3H). These results are summarized as follows.



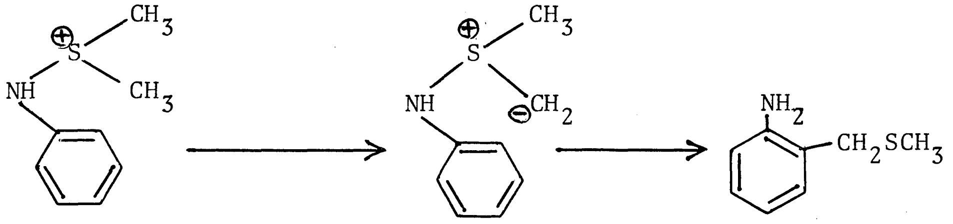
Thus, when 1 is mixed with such nucleophiles as benzyl methyl sulfide, methoxide anion, nitrocarbanion, anisole and 2,6-di-t-butylphenol, the attack of these nucleophiles takes place almost exclusively at the sulfide sulfur atom of 1.



Marino, Pfitzner and Olofson studied the reaction among phenol, dicyclohexylcarbodiimide and dimethyl sulfoxide in a weakly acidic medium, and showed that dimethylphenoxysulfonium ion is the intermediate.[7] It is of interest that the phenoxysulfonium ion is deprotonated even in a weakly acidic medium and the migration of $-CH_2SCH_3$ group to the ring is the main reaction.



Gassman and Drewes treated anilinosulfonium ions with sodium methoxide, and they found that deprotonation and the migration to the ring are the main reaction.[6]



The behavior of thiosulfonium ions toward nucleophiles is quite different from those of anilinosulfonium and phenoxysulfonium ions. Undoubtedly the S_N2 type reactions on the sulfur atom of thiosulfonium ions proceed with great ease. The methyl sulfide in **1** can easily be eliminated by rapid attack of nucleophiles, and **1** can function as a reagent of introducing Ar-S- groups under very mild conditions.

REFERENCES

1) J. K. Kim and M. C. Caserio, J. Amer. Chem. Soc., 96, 1930 (1974).
2) H. Minato, T. Miura, F. Takagi, and M. Kobayashi, Chem. Lett., 1975, 211.
3) H. Minato, T. Miura, and M. Kobayashi, Chem. Lett., 1975, 701.
4) A. Streitwieser, Chem. Rev., 56, 571 (1956).
5) P. B. D. de la Mare and E. D. Hughes, J. Chem. Soc., 1956, 845.
6) P. G. Gassman and H. R. Drewes, Chem. Commun., 1973, 488.
7) J. P. Marino, K. E. Pfitzner, and R. A. Olofson, Tetrahedron, 1971, 4181.

(Received August 14, 1975)