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Transylidations of Stable Sulfonium Ylids[1)]

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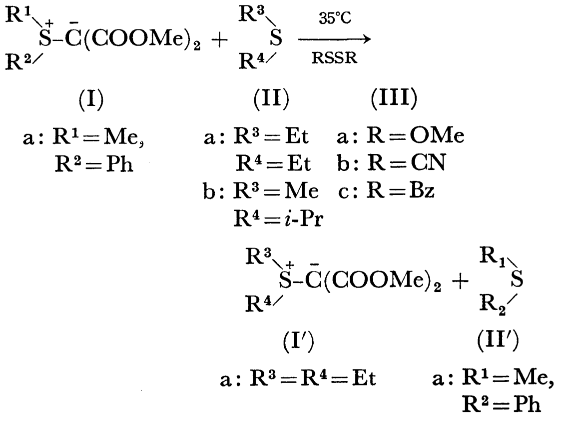
In the presence of a dialkoxy disulfide, sulfonium bis(methoxycarbonyl)methylids underwent transylidation with a dialkyl sulfide or pyridine at 35 °C. Thiocyanogen and benzoyl disulfide showed a similar catalytic effect. The kinetics of this reaction were investigated, and its mechanism was discussed.

A sulfur ylid containing two electron-withdrawing substituents on its negatively charged carbon atom is thermally stable, and the nucleophilicity of its negatively charged carbon atom is much less than that of an ylid containing only one electron-withdrawing substituent. While the mono-substituted ylids are used for various synthetic purposes by using their reactivity with carbonyl compounds and electron-deficient olefins,[2)] the di-substituted ylids show almost no reactivity with these electrophiles. Recently, reactions between dialkyl-sulfonium bis(methoxycarbonyl)methylids and several electrophiles have been reported on, but they require a fairly long time at high temperatures.[3)]

In the presence of a dialkoxy disulfide, dimethyl diazomalonate smoothly reacted with dialkyl sulfides at room temperature and the corresponding ylids were formed in good yields.[4)]

We have found that in the presence of a catalytic amount of dialkoxy disulfide (III), ylid (I) ($R^1R^2S^+C^-(COOMe)_2$) underwent transylidation with a dialkyl sulfide (II) very easily.



$$\begin{matrix}R^1\\ & \overset{+}{S}\text{-}\overset{-}{C}(COOMe)_2\\ R^2\end{matrix} + \begin{matrix}R^3\\ & S\\ R^4\end{matrix} \xrightarrow[\text{RSSR}]{35^\circ\text{C}}$$

(I)　(II)　(III)

a: $R^1 = Me$, $R^2 = Ph$

a: $R^3 = Et$, $R^4 = Et$
b: $R^3 = Me$, $R^4 = i\text{-}Pr$

a: $R = OMe$
b: $R = CN$
c: $R = Bz$

$$\begin{matrix}R^3\\ & \overset{+}{S}\text{-}\overset{-}{C}(COOMe)_2\\ R^4\end{matrix} + \begin{matrix}R_1\\ & S\\ R_2\end{matrix}$$

(I′)　(II′)

a: $R^3 = R^4 = Et$

a: $R^1 = Me$, $R^2 = Ph$

The only one example of transylidation in the literature is the case of methylarylsulfonium phenacylid in which the ylid dimerizes by dipolar attraction and then the dimer redissociates with the sulfide function scrambled.[5)]

The scope and mechanism of the transylidation between ylid I and dialkyl sulfides or pyridines are discussed in this paper.

Results and Discussion

In the absence of III, I is very stable and shows no transylidation when it is mixed with II at 35 °C.

[1)] Organic Sulfur Compounds. Part XLII.

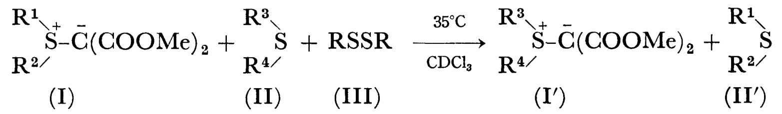
[2)] J. Adams, L. Hoffman, and B. M. Trost, *J. Org. Chem.*, **35**, 1600 (1970); G. B. Payne, *ibid.*, **33**, 3517 (1968), *ibid.*, **32**, 3351 (1967).

[3)] T. Yagihara and S. Oae, *Int. J. Sulfur Chem.*, **A**, **1**, 159 (1971).

[4)] H. Matsuyama, H. Minato, and M. Kobayashi, This Bulletin, **46**, 1512 (1973).

[5)] H. Nozaki, T. Takaku, D. Tsunemoto, Y. Yamamoto, and K. Kondo, *Nippon Kagaku Zasshi*, **88**, 1 (1967).

TABLE 1. TRANSYLIDATION OF STABLE SULFONIUM YLIDS WITH SULFIDES[a)]



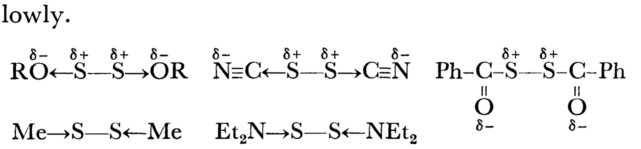
$$\underset{(I)}{\begin{matrix}R^1\\R^2\end{matrix}\overset{+}{S}-\overset{-}{C}(COOMe)_2} + \underset{(II)}{\begin{matrix}R^3\\R^4\end{matrix}S} + \underset{(III)}{RSSR} \xrightarrow[CDCl_3]{35^{\circ}C} \underset{(I')}{\begin{matrix}R^3\\R^4\end{matrix}\overset{+}{S}-\overset{-}{C}(COOMe)_2} + \underset{(II')}{\begin{matrix}R^1\\R^2\end{matrix}S}$$

$R^1R^2\overset{+}{S}$– of I	II	III	Time (min)	Products (mol%)		
				Recovered I	I′	II′
$PhMe\overset{+}{S}$–	Me_2S	$(MeOS)_2$	10	—	93	99
$PhEt\overset{+}{S}$–	Me_2S	$(MeOS)_2$	10	—	100	91
$Me_2\underset{\substack{\downarrow\\ O}}{\overset{+}{S}}$–	Me_2S	$(MeOS)_2$	150	—	91	100
$Me_2\overset{+}{S}$–	PhSMe	$(MeOS)_2$	3140	55	—	26
$Me_2\overset{+}{S}$–	Et_2S	$(MeOS)_2$	313	55	33	45
$Et_2\overset{+}{S}$–	Me_2S	$(MeOS)_2$	250	50	40	50
$EtMe\overset{+}{S}$–	Et_2S	$(MeOS)_2$	270	55	26	45
$Et_2\overset{+}{S}$–	MeSEt	$(MeOS)_2$	255	52	36	47
$PhMe\overset{+}{S}$–	Me_2S	$(BzS)_2$	900	14	78	85
$PhMe\overset{+}{S}$–	Py	$(BzS)_2$	30	—	100	100
$PhMe\overset{+}{S}$–	Me_2S	$(NCS)_2$	177	—	88	95

a) Reaction mixture consists of I (0.5—0.6 mmol), II (0.5—1.0 mmol), and III(0.2—0.4 mmol).

When Ia was heated with excess IIa (15 mol/mol Ia) in nitromethane at 86 °C for 25 hr, the mixture contained the original Ia (58%), Ia′ (34%), and IIa′ (42%). Thus, transylidation takes place upon heating, but very slowly.

However, when a catalytic amount of III is present, transylidation proceeds very easily. The results are summarized in Table 1. It is shown that dialkyl sulfides can attack all the ylids studied whereas methyl phenyl sulfide cannot carry out transylidation. It is also clear that alkyl phenyl ylids react with dialkyl sulfides rapidly but dialkyl ylids react with them rather slowly.



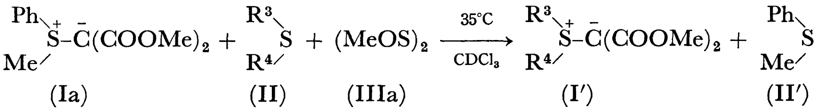
$$\overset{\delta-}{RO}\leftarrow\overset{\delta+}{S}-\overset{\delta+}{S}\rightarrow\overset{\delta-}{OR}\quad \overset{\delta-}{N}\equiv C\leftarrow\overset{\delta+}{S}-\overset{\delta+}{S}\rightarrow C\equiv\overset{\delta-}{N}\quad Ph-\underset{\substack{\|\\ \overset{}{O}\\ \delta-}}{C}-\overset{\delta+}{S}-\overset{\delta+}{S}-\underset{\substack{\|\\ O\\ \delta-}}{C}-Ph$$

$$Me\rightarrow S-S\leftarrow Me\quad Et_2N\rightarrow S-S\leftarrow NEt_2$$

Various disulfides were examined as regards their catalytic activity in this transylidation. Neither dimethyl disulfide nor diethylamino disulfide[6)] was effective, but thiocyanogen and benzoyl disulfide possessed a catalytic activity similar to that of III (Tables 1 and 3). Thus the disulfides containing electron-withdrawing substituents catalyze the transylidation, the electron-deficiency on the –S–S–probably being responsible for the catalytic activity.

Since methylphenylsulfonium bis(methoxycarbonyl)-methylid easily reacts with dialkyl sulfides, the steric effect of alkyl groups of II on transylidation was examined by using this ylid. The results are shown in Table 2. It is evident that the sulfides with more bulky alkyl groups react more slowly; the order of reactivity is $Me_2S>(CH_2)_4S>MeSEt>Et_2S>MeSPr\text{-}i\sim MeSBu\text{-}n\gg t\text{-}BuSBu\text{-}t$.

TABLE 2. STERIC EFFECTS IN THE TRANSYLIDATION OF Ia WITH VARIOUS DIALKYL SULFIDES[a)]



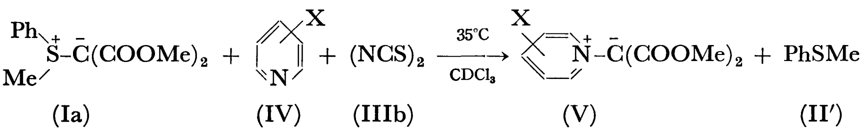
$$\underset{(Ia)}{\begin{matrix}Ph\\Me\end{matrix}\overset{+}{S}-\overset{-}{C}(COOMe)_2} + \underset{(II)}{\begin{matrix}R^3\\R^4\end{matrix}S} + \underset{(IIIa)}{(MeOS)_2} \xrightarrow[CDCl_3]{35^{\circ}C} \underset{(I')}{\begin{matrix}R^3\\R^4\end{matrix}\overset{+}{S}-\overset{-}{C}(COOMe)_2} + \underset{(II')}{\begin{matrix}Ph\\Me\end{matrix}S}$$

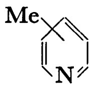
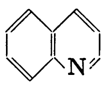
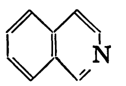
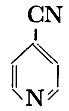
II	Time (min)	Products (mol%)		
		Recovered Ia	I′	II′
MeSMe	7	—	100	98
MeSEt	35	—	94	98
MeSPr-*i*	260	23	77	77
MeSBu-*n*	28	50	50	48
EtSEt	39	25	75	75
$(CH_2)_4S$	17	9	91	91
t-BuSBu-*t*	1500	100	—	—

a) Mixture consists of Ia (0.5 mmol), II(0.6—0.8 mmol), and IIIa (0.2—0.3 mmol).

[6)] Q. E. Thompson, *Quart. Reports on Sulfur Chem.*, **5**, 251 (1970).

TABLE 3. STERIC EFFECTS IN THE TRANSYLIDATION OF Ia WITH PYRIDINE DERIVATIVES[a)]



IV		Time (min)	pK_a	Products (mol%)		
				Recovered (Ia)	(V)	(II')
		2	5.2	—	100	100
	4-	4	6.0	—	96	98
	3-	3	5.7	—	96	96
	2-	714	6.0	72	25	28
		409	4.9	86	14	14
		93	5.4	83	17	17
		1203	1.9	89	7	7

a) Mixture consists of Ia(0.5 mmol), II (0.6—0.8 mmol), and IIIb (0.07—0.12 mmol).

It was found that S-ylids can be converted into N-ylids when pyridine derivatives are used instead of dialkyl sulfides. Table 3 shows the results of such experiments with Ia and thiocyanogen (IIIb). The methyl groups at positions 3 and 4 of pyridine show very little effect on the rate, whereas the methyl group at position 2 reduces it considerably. A similar steric retardation of rate by the 2-methyl group of 2-methylpyridine was described in its S_N 2 reaction with methyl iodide.[7,8)]

The slow reaction with quinoline can be ascribed to the steric effect exerted by the hydrogen atom at position 8. The reaction with isoquinoline is a little faster than that with quinoline, and considerably slower than that of pyridine. This small reactivity of isoquinoline cannot be explained easily. The slow reaction with 4-cyanopyridine can be ascribed to its smaller nucleophilicity due to the presence of the electron-withdrawing CN group.

The reaction between isopropyl methyl sulfide (IIb) and ylid Ia was slow enough to determine its rate. The effects of concentrations of reactants and catalyst IIIa were examined. The results are summarized in Table 4. The second-order rate constants calculated by assuming $-d[Ia]/dt=k[Ia][IIb]$ increased with the initial concentration of IIb; apparently the rate depends on [IIb] to a greater extent than that expressed by means of this equation. The rates increased also with the initial concentration of IIIa.

Similarly the effects of concentrations of reactants in the reaction among Ia, 4-methylpyridine (IVa), and IIIa were examined. The results are shown in Table 5. The second-order rate constants calculated decreased with the initial concentration of IVa; apparently the rate depends on [IVa] much less. When the first-order rate constants were calculated by assuming that $-d[Ia]/dt=k[Ia]$, they were found to be almost independent of the initial concentration of IVa. As regards the initial concentration of IIIa, the rates were found to increase with [IIIa].

TABLE 4. RATES OF TRANSYLIDATION BETWEEN YLID Ia AND METHYL ISOPROPYL SULFIDE IN $CDCl_3$ AT 35 °C

Reactants (mol/l)			Second-order rate constants
$PhMe\overset{+}{S}\overset{-}{C}(COOMe)_2$ (Ia)	i-Pr–S–Me (IIb)	$(MeOS)_2$ (IIIa)	calculated from $-d[Ia]/dt=k[Ia][IIb]$ $10^4\times k$ (M^{-1} sec^{-1})
0.85	0.73	0.27	4.7
0.85	1.37	0.27	7.7
0.85	2.01	0.27	13.9
0.85	1.37	0.55	21.8
0.85	1.37	1.09	34.8

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7) H. C. Brown and A. Cahn, *J. Amer. Chem. Soc.*, **77**, 1715 (1955).

8) R. G. Pearson, H. Sobel, and J. Songstad, *ibid.*, **90**, 319 (1968).

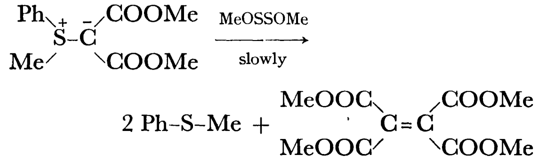
TABLE 5. RATES OF TRANSYLIDATION BETWEEN YLID Ia AND 4-METHYLPYRIDINE (IVa) IN $CDCl_3$ AT 35 °C

Reactants (mol/l)			Second-order rate constants calcd from $-d[Ia]/dt=k[Ia][IVa]$ $10^4\times k$ ($M^{-1}sec^{-1}$)	First-order rate constants calcd from $-d[Ia]/dt=k[Ia]$ $10^4\times k$ (sec^{-1})
(Ia)	(IVa)	(IIIa)		
0.85	0.66	0.27	33.3	5.7
0.85	1.32	0.27	7.5	8.1
0.85	1.98	0.27	4.3	7.4
0.85	1.32	0.55	12.7	12.3
0.85	1.32	1.09	41.6	30.1

TABLE 6. RATES OF DECOMPOSITION OF YLID Ia IN THE PRESENCE OF IIIa

Reactants (mol/l)		First-order rate constant calculated from $-d[Ia]/dt=k[Ia]$ $10^5\times k$ (sec^{-1})
$PhMeS^{+}-C^{-}(COOMe)_2$ (Ia)	$(MeOS)_2$ (IIIa)	
0.85	1.36	0.8
0.85	2.27	2.7

In the absence of dialkyl sulfides, ylid Ia remained unchanged but was found to decompose slowly at 35 °C when about the same amount of IIIa was present. The products were methyl phenyl sulfide and methyl ethylenetetracarboxylate.



IIIa remained unchanged during the course of reaction. Table 6 shows the results of rate measurements. The first-order rate constants calculated by assuming $-d[Ia]/dt=k[Ia]$ increased with [IIIa]. The rate constants were much smaller than those obtained in the reactions among Ia, IIb, and IIIa or Ia, IVa, and IIIa. This means that almost no decomposition of Ia took place during transylidation between Ia and IIb or Ia and IVa.

The results obtained can be summarized as follows.

1) Transylidation does not take place unless an electron-deficient disulfide (MeOSSOMe, NC–SS–CN or Bz–SS–Bz) is present.

2) When I and III are mixed, I slowly decomposes. Thus, some interaction exists between I and III.

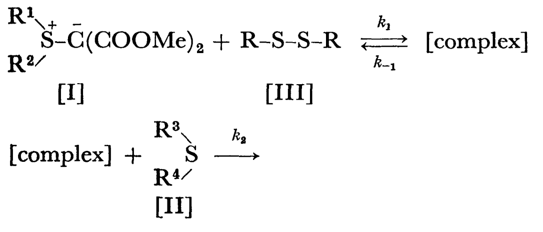
3) Substrates which can attack I possess electron-rich S or N atoms.

4) Transylidation is slower with bulky nucleophiles.

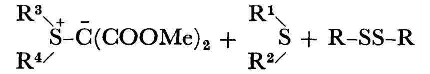
5) The rates of transylidation increase with the concentration of III.

6) During the transylidation, III does not decompose.

A plausible reaction scheme which is consistent with these results is as follows.



(1)



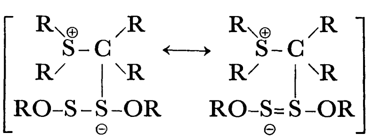
(2)

By assuming that concentration of the complex is very small and applying the steady state assumption, the rate of transylidation can be expressed as

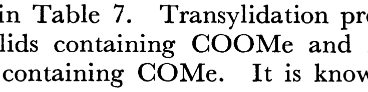
$$-\frac{d[I]}{dt}=\frac{k_1k_2[I][II][III]}{k_{-1}+k_2[II]}$$

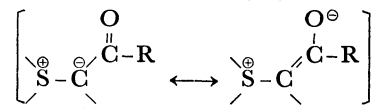
When 4-methylpyridine (IVa) was used in place of II, the rates appeared to be approximately of first-order in both [I] and [III], and not to depend upon [IVa]. This can be explained by assuming that in the case of 4-methylpyridine the second step proceeds very fast in comparison with the backward reaction of the first step, $k_2[IVa]\gg k_{-1}$.

Although attempts for obtaining supporting evidence by spectroscopic methods were not successful, the following structure is most plausible as the complex between I and III.



Effects of the substituents on the negatively charged carbon atom of ylid I were investigated. The results are shown in Table 7. Transylidation proceeds faster with the ylids containing COOMe and more slowly with those containing COMe. It is known that contribution of a betaine structure is greater in acetyl ylids than that in alkoxycarbonyl ylids.9)





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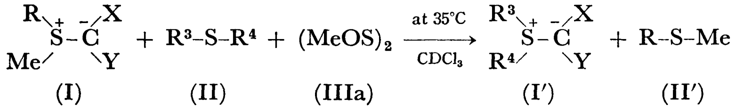
9) A. W. Johnson and R. T. Amel, *J. Org. Chem.*, **34**, 1240 (1969).

TABLE 7. TRANSYLIDATION OF YLIDS CONTAINING VARIOUS SUBSTITUENTS ON YLID CARBANION ATOMS$^{\text{a)}}$



$$\underset{\text{(I)}}{\overset{R\diagdown_{+}\ _{-}\diagup X}{\underset{Me\diagup\qquad\diagdown Y}{S-C}}} + \underset{\text{(II)}}{R^3\text{-}S\text{-}R^4} + \underset{\text{(IIIa)}}{(MeOS)_2} \xrightarrow[\text{CDCl}_3]{\text{at }35^\circ\text{C}} \underset{\text{(I}'\text{)}}{\overset{R^3\diagdown_{+}\ _{-}\diagup X}{\underset{R^4\diagup\qquad\diagdown Y}{S-C}}} + \underset{\text{(II}'\text{)}}{R\text{-}S\text{-}Me}$$

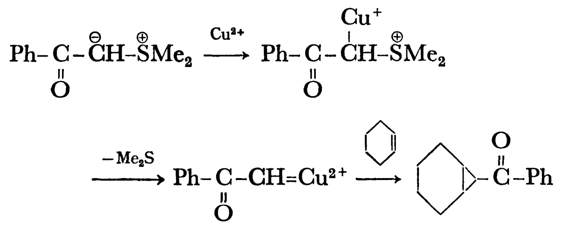
(I)	R	X	Y	(II)	Time (min)	Products (mol%)		
						Recovered (I)	Ylid (I′)	(II′)
(Ia)	Ph	COOMe	COOMe	Me$_2$S	7	—	100	98
(Ib)	Ph	COMe	COOMe	Me$_2$S	460	39	36	61
(Ic)	Ph	COMe	COMe	Me$_2$S	770$^{\text{b)}}$	47	32	40
(Id)	Me	COOMe	COOMe	Et$_2$S	313	55	33	45
(Ie)	Me	CN	CN	Et$_2$S	174$^{\text{c)}}$	—	—	92
(If)	Me	H	COPh	—	57$^{\text{c)}}$	—	—	95

a) Mixture consists of I (0.5 mmol), II(0.6—0.8 mmol), and IIIa (0.2—0.3 mmol), except in the case of Ic.
b) Mixture consists of Ic (0.5 mmol), II (6.5 mmol), and IIIa (0.3 mmol).
c) Catalytic decomposition of ylid proceeded rapidly.

It is reasonable that the greater the nucleophilicity of the ylid carbanion, the easier the formation of complex with III and the faster the transylidation process.

In the presence of III, dimethylsulfonium phenacylid (I$_f$) was found to decompose rapidly, producing dimethyl sulfide in a quantitative yield. This suggests that the ylid carbanion with strong nucleophilicity tends to form a complex with III very rapidly.

In a study on the thermolysis of dimethylsulfonium phenacylid in cyclohexene in the presence of CuSO$_4$ or ZnI$_2$, Trost[10] proposed the formation of a complex between electron-deficient Cu^{2+} or Zn^{2+} and electron-rich ylid carbanion. This complex is similar to the one we proposed as regards the reaction between an electron-deficient disulfide and electron-rich ylid carbanion.



Experimental

Materials. Sulfonium bis(methoxycarbonyl)methylids were prepared by copper-catalyzed decomposition of dimethyl diazomalonate in large excess sulfides.[11]

Dimethyl sulfide, tetrahydrothiophene, di-*t*-butyl sulfide, dimethyl disulfide, pyridine, methylpyridines, 4-cyanopyridine, quinoline, and isoquinoline were of reagent grade and used without further purification. Other sulfides were prepared from the corresponding sodium mercaptides and alkyl halides.[12]

Dimethoxy disulfide was synthesized by the method of Thompson.[13] Thiocyanogen[14] and benzoyl disulfide[15] were prepared by the methods described in the literature. Diethylamino disulfide was synthesized by adding sulfur monochloride (0.1 mol) to a dichloromethane solution of diethylamine (0.4 mol) at 0 °C; bp 115 °C/6 mmHg (lit,[16] bp 137 °C/29 mmHg).

General Procedure. A CDCl$_3$ solution of I, II, and III containing nitromethane (internal standard) was placed in an NMR tube at 35 °C, and the intensity changes of the signals of the original ylid(I), new ylid(I′) and new sulfide (II′) were determined. After the original ylid(I) completely disappeared, *n*-hexane was added to the reaction mixture. The ylid crystals which precipitated were filtered and recrystallized from methanol. The melting points, IR, and NMR spectra of the ylids obtained were identical with those reported in the literature.[17]

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10) B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 138 (1967).

11) W. Ando, T. Yagihara, S. Tozune, S. Nakaido, and T. Migita, *Tetrahedron Lett.*, **1969**, 1979.

12) A. I. Vogel, *J. Chem. Soc.*, **1948**, 1822.

13) Q. E. Thompson, M. M. Crutchfield, M. M. Dietrich, and E. Pierron, *J. Org. Chem.*, **30**, 2692 (1965).

14) L. F. Fieser and M. Fieser, "Reagents for Organic Syntheses," Vol. 1, John Wiley, New York (1967), p. 1152.

15) "Organic Syntheses," Coll. Vol. 3, p. 116.

16) Q. E. Thompson, *Quart. Reports on Sulfur Chem.*, **5**, 258 (1970).

17) W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, **37**, 1721 (1972).