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Mechanism of Transylidation of Stable Sulfonium Ylids with Alkyl Sulfides in the Presence of Catalytic Disulfides[1]

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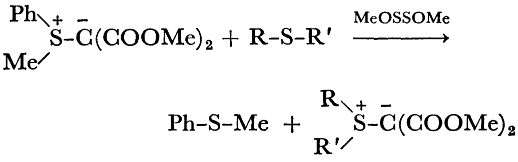
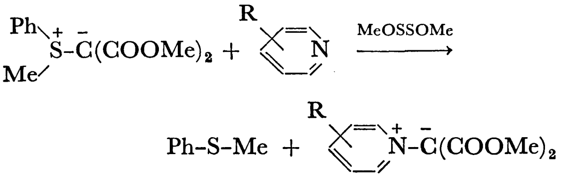
In the presence of bis(trifluoromethyl) disulfide, methylphenylsulfonium bis(methoxycarbonyl)methylid is readily attacked by a nucleophile (an alkyl sulfide or a pyridine) and the corresponding new ylid is produced. In the NMR spectrum of a mixture of an ylid, an alkyl sulfide, and a catalytic disulfide, a remarkable broadening in the signals of the α-hydrogen of the sulfide was observed. A mechanism is suggested, which involves a complex from the two reactants and the catalyst.

In the presence of a dialkoxy disulfide or thiocyanogen an alkyl sulfide or pyridine attacks the ylid carbon atom of a sulfonium ylid and the corresponding new ylid is formed.[2)]

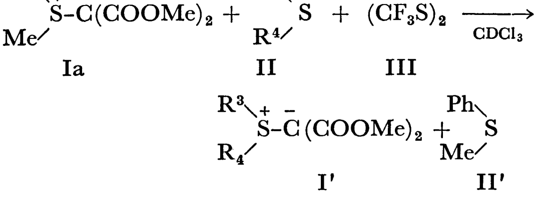




It has been found that bis(trifluoromethyl) disulfide possesses a similar catalytic activity, and with this catalyst some NMR spectroscopic evidence suggesting the formation of a complex has been obtained.

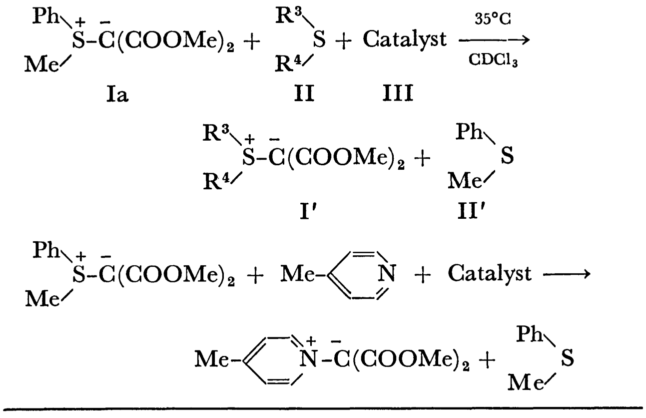
Results and Discussion

Transylidation of methylphenylsulfonium bis(methoxycarbonyl)methylid (Ia) was carried out with several sulfides and 4-methylpyridine in the presence of bis(trifluoromethyl) disulfide (III). In Table 1, the results are compared with those obtained in the presence of dimethoxy disulfide or thiocyanogen. It is clear that when III was used as the catalyst the transylidation proceeds much more slowly than when dimethoxy disulfide or thiocyanogen was used.



a: $R^3=R^4=Me$, b: $R^3=Me$, $R^4=Et$, c: $R^3, R^4=(CH_2)_4$

Table 1. Transylidation of ylid Ia with a sulfide or a pyridine in $CDCl_3$ at 35°C[a)]



Nucleophile	Catalyst	Time (min)	Products (mol%) Recovered Ia	I'	II'
MeSMe	$(CF_3S)_2$	90	—	93	100
MeSEt	$(CF_3S)_2$	267	—	93	94
$(CH_2)_4S$	$(CF_3S)_2$	30	—	91	98
Me-pyridine	$(CF_3S)_2$	594	64	31	31
MeSMe	$(MeOS)_2$	7	—	100	98
Me-pyridine	$(N{\equiv}CS)_2$	3	—	96	96

a) A mixture consists of Ia (0.5 mmol), a nucleophile (1.0—1.5 mmol) and a catalyst (0.07—0.12 mmol).

[1)] Organic Sulfur Compounds. Part XLV.

[2)] H. Matsuyama, H. Minato, and M. Kobayashi, This Bulletin, **46**, 2845 (1973).

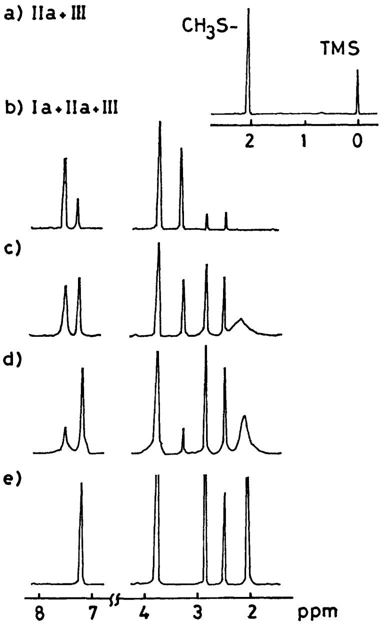


Fig. 1. NMR spectra of mixtures of Ia, IIa, and III in $CDCl_3$ at 35 °C.

a) IIa (1.82 M) and III (0.20 M) in $CDCl_3$
b) 9 min after Ia (0.91 M) was added to IIa and III. The yield of PhSMe was 21%.
e) 40 min after addition. PhSMe, 50%.
d) 60 min after addition. PhSMe, 79%.
e) 90 min after addition. PhSMe, 100%.

$\underline{Ph}Me\overset{+}{S}$- ($\delta$, 7.52 ppm), $\underline{Ph}SMe$ (7.25 ppm), $C(COO\underline{Me})_2$ (3.68 ppm), $Ph\underline{Me}\overset{+}{S}$- (3.30 ppm), $\underline{Me_2}\overset{+}{S}$- (2.88 ppm), $PhS\underline{Me}$ (2.49 ppm), $\underline{Me_2}S$ (2.10 ppm).

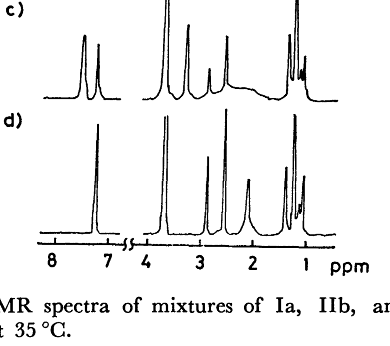


Fig. 2. NMR spectra of mixtures of Ia, IIb, and III in $CDCl_3$ at 35 °C.

a) IIb (2.51 M) and III (0.20 M) in $CDCl_3$.
b) 8 min after Ia (0.89 M) was added to IIb and III. The yield of PhSMe was 6%.
c) 82 min after addition. PhSMe, 27%.
d) 267 min after addition. PhSMe, 94%.

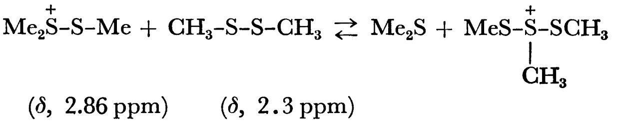
$\underline{Ph}Me\overset{+}{S}$- ($\delta$, 7.53 ppm), $\underline{Ph}MeS$ (7.26 ppm), $C(COO\underline{Me})_2$ (3.69 ppm), $Ph\underline{Me}\overset{+}{S}$- (3.32 ppm), $\underline{Me}Et\overset{+}{S}$- (2.88 ppm), $PhS\underline{Me}$ (2.50 ppm), $\underline{Me}SEt$ (2.10 ppm).

When the NMR spectrum of a mixture of Ia, IIa, and III was determined, surprisingly the sharp singlet of IIa was not observed. The NMR spectrum of a mixture containing two components out of the three (Ia and IIa; IIa and III; or III and Ia) was simply the sum of the spectra of the corresponding components, and the methyl signals of IIa disappeared only when all of the three components were mixed. When the NMR spectrum of a mixture of Ia, IIa, and III was determined after about 50% completion of the transylidation, the methyl signal of the remaining IIa was observed as a broad absorption. Throughout the reaction, the methyl signal ($Ph\underline{Me}\overset{+}{S}$-, δ, 3.31 ppm) of ylid Ia showed no broadening. When ethyl methyl sulfide (IIb) or tetrahydrothiophene (IIc) was used in place of IIa, a similar broadening of the α-hydrogens (underlined in the formulas shown below) was observed. The results are summarized in Figs. 1 and 2.

$\underline{CH_3}\text{-S-}\underline{CH_3}$ $CH_3\text{-S-}\underline{CH_2}\text{-}CH_3$ $(\underline{CH_2}CH_2)_2S$

Reports on broadening of NMR absorptions are mainly those concerning intramolecular rotation or inversion.[3]

Smallcombe and Caserio[4] reported on the rapid exchange of S–CH_3 between methyl disulfide and dimethylthiomethylsulfonium ion.

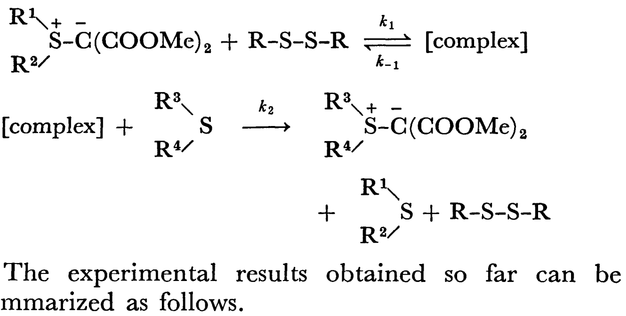


$$Me_2\overset{+}{S}\text{-S-Me} + CH_3\text{-S-S-}CH_3 \rightleftarrows Me_2S + MeS\text{-}\underset{\displaystyle CH_3}{\overset{+}{S}}\text{-SCH}_3$$

(δ, 2.86 ppm) (δ, 2.3 ppm)

The NMR spectrum of the mixture did not show the S–CH_3 signals of two components, but a broad signal. The NMR data show that a rapid equilibrium is maintained as shown above.

We have investigated the transylidation catalyzed by a dialkoxy disulfide, and propose the following scheme which represents what is probably taking place in a mixture of I, II, and III.[2]



$$\genfrac{}{}{0pt}{}{R^1}{R^2}\!\!>\overset{+}{S}\text{-}\overset{-}{C}(COOMe)_2 + R\text{-S-S-}R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{complex}]$$

$$[\text{complex}] + \genfrac{}{}{0pt}{}{R^3}{R^4}\!\!>S \xrightarrow{k_2} \genfrac{}{}{0pt}{}{R^3}{R^4}\!\!>\overset{+}{S}\text{-}\overset{-}{C}(COOMe)_2 + \genfrac{}{}{0pt}{}{R^1}{R^2}\!\!>S + R\text{-S-S-}R$$

The experimental results obtained so far can be summarized as follows.

1) In a mixture of an S-ylid and a catalytic disulfide, no broadening of NMR signals is observed.

2) In a mixture of an S-ylid and a sulfide, no broadening of NMR signals is observed, and almost no transylidation takes place at room temperature.

3) In a mixture of a sulfide and a catalytic disulfide, no broadening of NMR signals is observed.

4) When all of the three components (an S-ylid, a catalytic disulfide and a sulfide (or a pyridine)) are

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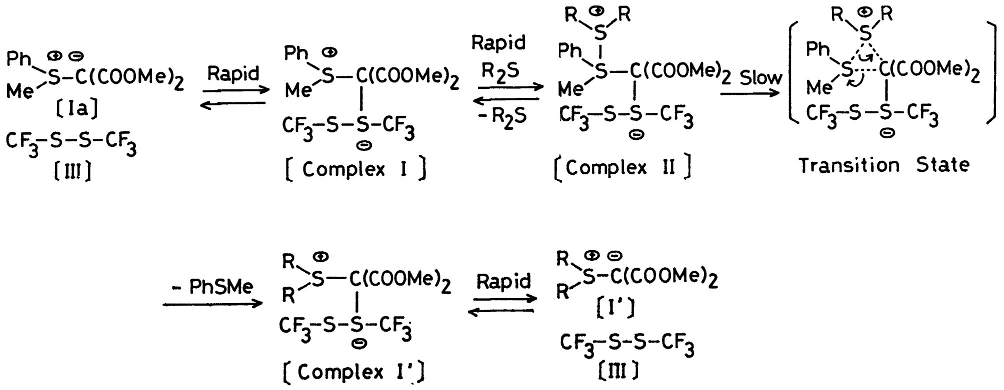
[3] G. Binsch, "Topics in Stereochemistry," John Wiley & Sons, New York (1968), Vol. 3, p. 97.

[4] S. H. Smallcombe and M. C. Caserio, *J. Amer. Chem. Soc.*, **93**, 5826 (1971).



Scheme.

mixed, the NMR signals of the α-hydrogens of the sulfide (or a pyridine) are much broadened.

5) A broadening of NMR signals is observed only when transylidation takes place.

6) When a sulfide (or pyridine) is not added, an olefin is formed.

7) In the case of a phenacylid, an olefin and a cyclopropane derivative are formed even when a sulfide is present.

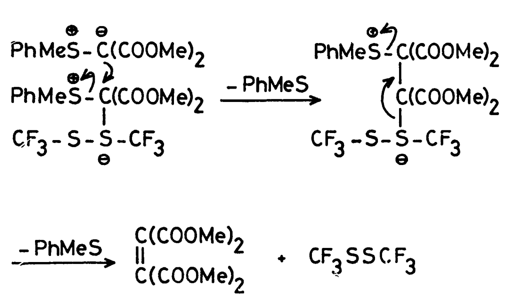
A plausible mechanism consistent with these results is shown in the Scheme.

The first step is the reversible formation of Complex I from Ia and III. Nucleophilic attack of an alkyl sulfide (or pyridine) on the sulfonium sulfur atom of Complex I results in the formation of the termolecular Complex II. The NMR data can be explained by assuming that the formation of Complex II from Complex I and the sulfide (or pyridine) is reversible and rapid, and molecules of the sulfide (or pyridine) rapidly combine with and depart from Complex I one after another. Therefore, the absorption of the α-hydrogens of the sulfide (or pyridine) is broadened between that of the free sulfide (or pyridine) and that of the sulfide (or pyridine) in Complex II. An example of the tetravalent sulfur atom with one unshared electron pair in Complex II is found in the case of sulfuranes.[5]

Formation of Complex I′ from Complex II by removal of methyl phenyl sulfide is probably slow and is the rate-determining step of the whole reaction. Decomposition of Complex I′ gives III and a new ylid I′. The step from Complex II to Complex I′ should be irreversible since a mixture of I′, III, and methyl phenyl sulfide does not give Ia under similar conditions.

The role of a catalytic disulfide is withdrawal of the negative charge on an ylid carbanion so that the nucleophilic attack of a sulfide on the sulfonium sulfur atom is facilitated. Therefore, disulfides possessing strongly electronegative substituents can act as the catalysts for transylidation. The combination of a catalytic disulfide with an S-ylid should be reversible, since the disulfide must be regenerated for repetition of the reaction.

When a sulfide (or pyridine) is not present in the medium, the negatively charged carbon atom of another molecule of the ylid attacks Complex I, and an olefin is produced.



Thus, the mechanism postulated above is consistent with all the experimental findings, and can explain the transylidation[2] and decomposition[6] of ylids in the presence of a catalytic disulfide.

Experimental

Materials. Sulfonium ylid Ia was prepared by the method described in the literature.[7] Methyl sulfide, tetrahydrothiophene, 4-methylpyridine were of reagent grade and used without purification. Bis(trifluoromethyl) disulfide was synthesized by the method of Tullock and Coffman.[8]

Measurements. NMR spectra were determined with a Hitachi NMR spectrometer R-203 (60 MHz). 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.[2]

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5) J. C. Martin and R. J. Anhart, *J. Amer. Chem. Soc.*, **93**, 2341 (1971); R. J. Anhart and J. C. Martin, *ibid.*, **94**, 4997 (1972).

6) H. Mastuyama, H. Minato, and M. Kobayashi, This Bulletin, **46**, 3158 (1973).

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

8) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).