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RAPID REACTION BETWEEN SULFONIUM ION AND SULFIDE. PREPARATIVE REDUCTION OF SULFOXIDE TO SULFIDE

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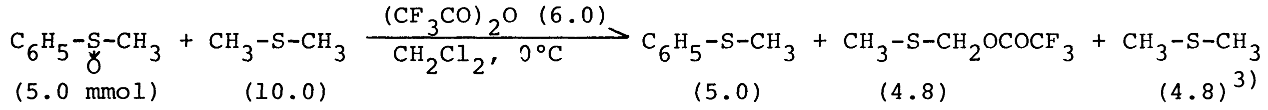
A very rapid oxygen exchange reaction between a sulfoxide and dimethyl sulfide took place with trifluoroacetic anhydride. A plausible mechanism involves the nucleophilic attack of a sulfide on a sulfonium sulfur atom. From these findings a convenient method for the reduction of a sulfoxide to a sulfide is described.

An oxygen exchange between a sulfoxide and a sulfide via a sulfonium ion was first reported by Bordwell.[1)] Recently, Minato observed by the NMR technique the reaction between dimethyl sulfide and di-t-butyl methyl sulfonium ion, forming t-butyl dimethyl sulfonium ion and t-butyl methyl sulfide.[2)]

We wish to report our findings on a very rapid oxygen exchange reaction between a sulfoxide and a sulfide using trifluoroacetic anhydride (TFAA), and its application to the facile reduction of various sulfoxides.

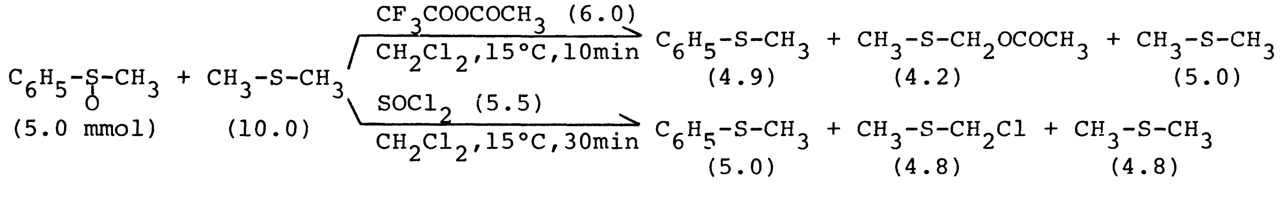
When TFAA was added to a solution of phenyl methyl sulfoxide and dimethyl sulfide in dichloromethane, phenyl methyl sulfide and methyl trifluoroacetoxymethyl sulfide were obtained within a few seconds.



$$\underset{(5.0\ \text{mmol})}{C_6H_5\text{-}\underset{O}{\underset{\|}{S}}\text{-}CH_3} + \underset{(10.0)}{CH_3\text{-}S\text{-}CH_3} \xrightarrow[CH_2Cl_2,\ 0^\circ C]{(CF_3CO)_2O\ (6.0)} \underset{(5.0)}{C_6H_5\text{-}S\text{-}CH_3} + \underset{(4.8)}{CH_3\text{-}S\text{-}CH_2OCOCF_3} + \underset{(4.8)^{3)}}{CH_3\text{-}S\text{-}CH_3}$$

Even when immediately after the addition of TFAA at -78°C was added an aq. NH_4Cl solution, phenyl methyl sulfide was obtained quantitatively.

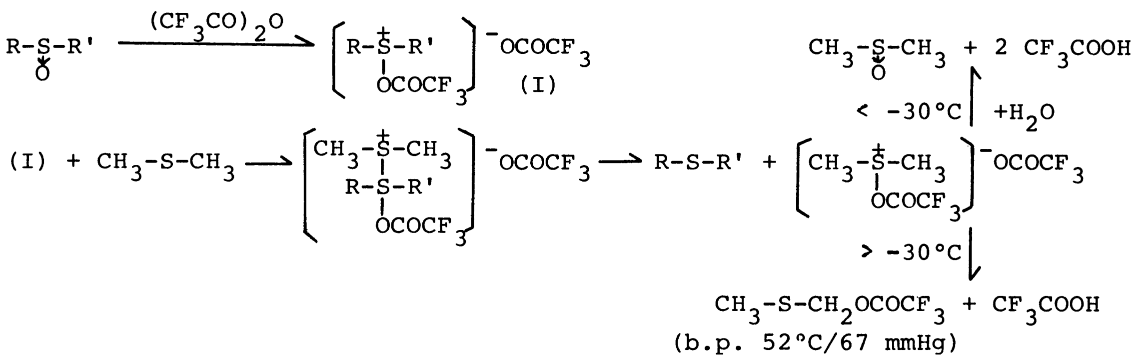
The similar reaction took place when acetyl trifluoroacetate or thionyl chloride was used in the place of TFAA.



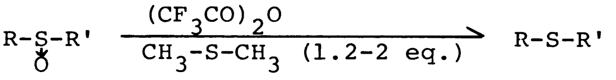
$$\underset{(5.0\ \text{mmol})}{C_6H_5\text{-}\underset{O}{\underset{\|}{S}}\text{-}CH_3} + \underset{(10.0)}{CH_3\text{-}S\text{-}CH_3} \xrightarrow[CH_2Cl_2,15^\circ C,10min]{CF_3COOCOCH_3\ (6.0)} \underset{(4.9)}{C_6H_5\text{-}S\text{-}CH_3} + \underset{(4.2)}{CH_3\text{-}S\text{-}CH_2OCOCH_3} + \underset{(5.0)}{CH_3\text{-}S\text{-}CH_3}$$

$$\xrightarrow[CH_2Cl_2,15^\circ C,30min]{SOCl_2\ (5.5)} \underset{(5.0)}{C_6H_5\text{-}S\text{-}CH_3} + \underset{(4.8)}{CH_3\text{-}S\text{-}CH_2Cl} + \underset{(4.8)}{CH_3\text{-}S\text{-}CH_3}$$

A sulfoxide easily reacts with TFAA to form a sulfonium ion (I) at a low temperature, and various nucleophilic reactions occur on a sulfur atom of I.[4,5)] Therefore, a plausible reaction mechanism is the following, which involves the nucleophilic attack of a sulfide on a sulfonium sulfur atom.[6)]



From these results, we found the following convenient method for the reduction of a sulfoxide to a sulfide.



$$\underset{O}{R-\overset{}{S}-R'} \xrightarrow[CH_3-S-CH_3\ (1.2\text{-}2\ eq.)]{(CF_3CO)_2O} R-S-R'$$

$R = C_6H_5$, $R' = CH_3$, $(CH_2)_5CH_3$, $CH=CH_2$, $(CH_2)_2OCH_2CH=CH_2$, $(CH_2)_2OCH_2C_6H_5$, $(CH_2)_2SC_6H_5$, $(CH_2)_2C(NO_2)(CH_3)_2$, $(CH_2)_2C(CN)(SO_2C_6H_4CH_3)(C_3H_7)$, $(CH_2)_2CH(CO_2CH_3)_2$, C_6H_5, C_6H_4-*o*-NO_2.(7)

$R = CH_3$, $R' = (CH_2)_3CH_3$, $(CH_2)_7CH_3$.

The yields (isolated) were almost quantitative ($>$ 95%) in all cases. Various solvents (dichloromethane, benzene, acetonitrile or diethyl ether) were available, and a wide range of a reaction temperature (-78°C ~ room temperature) was possible. The reaction finished within a few seconds at 0°C. The reduction also proceeded under a basic condition using 2,6-lutidine.

General Procedure. To a solution of phenyl methyl sulfoxide (10 mmol) and dimethyl sulfide (15 mmol) in dichloromethane (20 ml) at 0°C, was added a solution of TFAA (12 mmol) in dichloromethane (10 ml). After stirring for a few seconds, the reaction mixture was washed with a dil.aq. $NaHCO_3$ solution and water, and dried over anhydrous $MgSO_4$. Removal of a solvent under reduced pressure (ca. 20 mmHg) gave phenyl methyl sulfide in 97 % yield. TLC, GC, NMR and IR showed the pure sulfide was obtained.(8)

1) F.G.Bordwell and B.M.Pitt, J.Am.Chem.Soc., 77, 572 (1955).
2) H.Minato, T,Miura, F.Takagi,and M.Kobayashi, Chem.Lett., 1975, 211.
3) The yields were determined by GC and NMR analysis.
4) A.K.Sharma and D.Swern, Tetrahedron Lett., 1974, 1503.
5) Y.Hiraki, M.Kamiya, R.Tanikaga, N.Ono,and A.Kaji, Bull.Chem.Soc.Jpn., 50, 447 (1977).
6) The effects of a sulfide and a leaving group of a sulfonium ion will be described elsewhere.
7) It took 5 hours at a room temperature to reduce this compound, presumably because it was difficult to form I.
8) A sulfoxide can also be reduced to a sulfide in a TFAA - iodide system: J.Drabowicz and S.Oae, personal communication.

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