The Reaction of Disulfides with Dinitrogen Tetroxide

Norio KUNIEDA and Shigeru OAE

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka

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Dinitrogen tetroxide displays a unique feature in various oxidation processes. It can restrict a reaction to a single oxidation stage, when further oxidation still appears to be possible. Several workers have, therefore, used this reagent for the oxidation of alkyl,[1] aryl,[2] and alicyclic[3] sulfides to the corresponding sulfoxides.

In this note, we would like to report the oxidation of several disulfides with this reagent; this oxidation was carried out in a manner similar to the oxidation of sulfides.[2] We expected that the oxidation of disulfides with this reagent would proceed to yield, successively, thiolsulfinates (RSO·SR), thiolsulfonates (RSO_2SR), and disulfones (RSO_2SO_2R), since such a step-by-step oxidation is known to take place in the oxidation reaction of disulfides with hydrogen peroxide[4] or peroxy acids.[5] However, when alkyl or aryl disulfides were allowed to react with an excess of dinitrogen tetroxide in carbon tetrachloride, only the corresponding sulfonic anhydrides were obtained in good yields; neither thiolsulfinates nor thiolsulfonates were obtained. The yields and melting or boiling points of the products are listed in Table 1.

These products were allowed to react with aniline to afford the corresponding sulfonanilides quantitatively. In an attempt to isolate a possible intermediate of this reaction, diethyl disulfide (7.0 g, 0.057 mol) was treated with an equimolar amount of dinitrogen tetroxide (5.2 g, 0.057 mol), but only ethanesulfonic anhydride (4.7 g) was thus obtained, together with the recovered disulfide (2.8 g); no other intermediary products could be detected.

We have also found that *p*-toluenesulfonic anhydride was obtained in a 94% yield when *p*-toluenethiolsulfinate was treated with an excess of this reagent in a manner similar to that used for the disulfides, but *p*-tolyl *p*-toluenethiolsulfonate and *p*-tolyl disulfone did not react with this reagent, even without a solvent.

In view of these results, it is not probable that the oxidation of disulfides with this reagent proceeds through a step-by-step oxidation involving the successive formation of thiolsulfonate, sulfinylsulfone, and disulfone, such as is the case with peroxy acids; rather, it appears to proceed in a fashion similar to that which Barnard has postulated for the ozonolysis of disulfides.[6] However, further investigation is necessary before we can obtain any clear understanding of the dinitrogen tetroxide oxidation.

Experimental

Materials. *Disulfides* were prepared by the oxidation of the corresponding mercaptans with iodine by the method described by McAllan.[10]

TABLE 1. YIELDS OF SULFONIC ANHYDRIDES (RSO_2OSO_2R)

R	Yield, %	Mp or bp (°C) (lit)	Elemental analysis Found, % C	Elemental analysis Found, % H	Elemental analysis Calcd, % C	Elemental analysis Calcd, % H
CH_3	85	69.5—70.5 (69.5—70)[7]				
C_2H_5	78	110—110.5/3 mmHg (94/0.5 mmHg)[7]	23.91	5.05	23.76	4.98
n-C_3H_7	74	131.5—132/4 mmHg (85/10^{-3} mmHg)[6]				
C_6H_5	81	88—90.5 (88—91)[8]				
p-CH_3-C_6H_4	92	129.5—131 (129.5—131.5)[8]	51.17	4.47	51.50	4.32
p-Cl-C_6H_4	90	149—151 (150)[9]				

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p-Tolyl p-Toluenethiolsulfinate was prepared by the reaction of *p*-tolyl mercaptan with *p*-toluenesulfinyl chloride. Mp 94—94.5°C, yield 92%.

p-Tolyl p-Toluenethiolsulfonate was prepared by the oxidation of di-*p*-tolyl disulfide with hydrogen peroxide. Mp 77—78°C, yield 86%.

p-Tolyl Disulfone was prepared by the reaction of sodium *p*-toluenesulfinate with *p*-toluenesulfonyl chloride. Mp 206—206.5°C, yield 83%.

Dinitrogen Tetroxide was prepared by the pyrolysis of dinitrogen pentoxide.[11]

Reaction of Disulfides with Dinitrogen Tetroxide. The carbon tetrachloride solution of dinitrogen tetraoxide was cooled under 0°C, then a solution of disulfides, in which the mole ratio of the disulfide to the dinitrogen tetroxide was 1 : 3—5, was added slowly. The mixture was kept standing for 2 hr under 0°C, and then warmed at 30—50°C for 2 hr. Finally the mixture was distilled under reduced pressure to remove the excess reagent and solvent. The residual crude products were distilled or recrystallized. Methane-, benzene-, *p*-toluene-, and *p*-chlorobenzenesulfonic anhydrides were recrystallized from ether-benzene.

Sulfonanilides. The sulfonic anhydrides were dissolved or suspended in dry ether into which two molar equivalent of aniline had been added, then the anilinium sulfonate thus formed was filtered off. In this manner the sulfonanilides were obtained from the filtrate in good yields. ($C_6H_5NHSO_2R$); (R, mp(°C) (Lit)); (CH_3, 99(96)[12]), (C_2H_5, 59—60(55)[12]), (C_6H_5, 108.5 (112)[13]), (*p*-CH_3-C_6H_4, 101—102(101—102.5)[14]), (*p*-Cl-C_6H_4, 104.5 (105.5)[15]).

The Reaction of *p*-Tolyl *p*-Toluenethiolsulfinate with Dinitrogen Tetroxide. *p*-Tolyl *p*-toluenethiolsulfinate was reacted with 4.6 times the molar quantity of dinitrogen tetroxide in the same treatment as that used for disulfides. The anhydride was thus obtained in a 94% yield; mp 130—130.5°C.

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