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NITRIC ACID ACTION ON METHYLPHENYLSULPHOXIDE AND DIPHENYLSULPHOXIDE

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A series of experiences , intended to provide further informations on the behaviour of some sulphurated aromatic compounds by action of nitric acid (1,2) , has been recently started by us.

We wish to report here some preliminary results obtained when methylphenylsulphoxide and diphenylsulphoxide are treated with the same electrophilic reagent under different experimental conditions.

The latter have been choosen conveniently varying initial reagent concentrations and reaction time , in order to avoid -as far as possible- either consecutive reactions to the primary ones , or those depending from the sulphoxide-solvent interaction (3,4). Previous researches on diphenylsulphoxide , accomplished by several Authors (5,6), do show , for instance , dinitroderivatives formation when nitric acid in great excess has been used.

The most significant experiences are listed in table I (for methyl phenylsulphoxide) and in table II (for diphenylsulphoxide).

TABLE I

Reaction products of methylphenylsulphoxide by action of nitric acid in concentrated sulphuric acid at 20°

$[PhSOCH_3]$ = 0.4 M/l. ; $[HNO_3]$ = 0.6 M/l; reaction time = 1 h

H_2SO_4 (wt%)	78 a)	80 a)	83	85	87	89	91
$H_3CSO_2C_6H_5$	+	+	+	+	+	+	–
$H_3CSOC_6H_4NO_2$ (*o*,*m*,*p*)	–	–	+	+	+	+	+

a) $[PhSOCH_3]$ = 0.45 M/l. , $[HNO_3]$ = 0.45 M/l. , T° = 30 ;
reaction time = 2 h.

TABLE II

Reaction products of diphenylsulphoxide by action of nitric acid in concentrated sulphuric acid at 20°

$[PhSOC_6H_5]$ = 0.4 M/l. , $[HNO_3]$ = 0.25 M/l. ; reaction time = 1 h

H_2SO_4 (wt%)	75	80	82	85	87	89a)	91a)
$H_5C_6SO_2C_6H_5$	+	+	+	+	+	–	–
$H_5C_6SOC_6H_4NO_2$ (*o*,*m*,*p*)	–	+	+	+	+	+	+

a) reaction time = 1/2 h.

The experiences have been performed by mixing equal volumes of the two solutions (containing , respectively, sulphoxide and nitric acid) regularly thermostated [anhydrous nitric acid (1) has been always used].

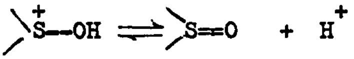
The mixtures , kept under constant stirring for the whole reaction time , poured into water at the end , have been carefully neutralized, then extracted with chloroform. Such solutions , divided in two portions, have been , partly analyzed without any further treatment , and partly after reduction with excess of hydroiodic acid in acetic acid. Previous experiments established that reduction was selective for the sulphoxide (7) , leaving unchanged both sulphonyl and nitro groups. The products obtained have been identified by gas and thin-layer chromatography.

Working with 90% sulphuric acid -particularly in the case of methylphenylsulphoxide- presence of by-products has been ascertained ,although in very small amounts (3,4).

The results,listed in Tables indicate that , for the sulphoxides taken into consideration , reaction products are dependent from experimental conditions. Working with sulphuric acid below the range of 80% , indeed, only the change of sulphoxides into sulphones took place (in this case , nevertheless, sulphone amounts did reach very low conversion values). For sulphuric acid near 90% concentration , only substitution reaction has been observed . In all other cases both oxidation and substitution reactions did occur; more precisely , in such concentration limits , substitution has a tendency to progressively increase together with medium acidity. Furthermore , in the latter cases, quantities of meta-substituted compounds , compared with ortho- , para-isomers follow analogous behaviour.

On the other hand , oxidation does play a different role , wheter as a function of reaction meditum or of molecular structure. In the case of methylphenylsulphoxide , in fact , has been observed that the amount of sulphone derivative , initially negligible , does increase in the range of 82% sulphuric acid , decreasing , then , progressively at higher concentrations. For diphenylsulphoxide, instead , the amount of sulphone , in all cases considered , has been always restricted to very small values.

We have actually in progress a series of quantitative measurements in order to determine percentages of the products formed in every experiment, whether in connection with oxidation/substitution ratio, or percentage variation of nitro derivatives. Such quantitative treatment of the problem seems to be particularly useful in order to give informations on the weight of each of the two limit forms



varying reaction medium (8,9) , at the equilibrium concentration.

Beside experiences cited above , some reactions have been performed, with similar technique , using different solvents.

In acetic anhydride , with both sulphoxides examined , the only reaction product isolated has been identified as sulphone derivative ; for diphenylsulphoxide such result is in agreement with data given by other Authors (5,6).

From reactions performed in acetic acid and in nitroethane , at 30°C and equimolar ratio of the two reagents (corresponding to 0.45 mol /l) unaltered sulphoxides have been recovered. Analogous result has been obtained in nitroethane with a sulphoxide/nitric acid ratio equal to 1:3.

These experiments allow us to establish the reasons for nitrosulphoxides formation when methylphenylsulphide and diphenylsulphide were treated with nitric acid (1,2).

On the bases of such results already reached, bearing in mind that *para*-nitrodiphenylsulfide - with nitric acid in identical experimental conditions - gives para -nitrodiphenylsulphoxide as primary reaction product (10), we think reasonable and acceptable the assumption that nitrosulphoxides are formed by oxidation of the parent nitrosulphides.

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