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THE REACTION OF SYMMETRIC DISULPHIDES WITH SODIUM 2-NITROPROPAN-2-IDE

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The reaction of disulphides with nucleophiles has been widely studied,[1] but the use of carbanions has received less attention, with the exception of the cyanide ion. The use of 2-nitropropan-2-ide (I), an ambident anion,[2] allows the possibility of reaction via the oxygen or carbon atoms.

Each of the disulphides (IIa-f) (approx. 1g) was reacted with (I) in dry DMF (25 ml) at room temperature under an atmosphere of oxygen. The results are shown in Table I. The disulphides (IIc, d, e) could not be induced to react even at anion:disulphide ratios of 10:1. The di-(o-aminophenyl)-disulphide did yield some α-nitrosulphide but only under more extreme conditions. In the case of (IIa and b) the reaction proceeded readily to give entirely the C-sulphenylated product (IIIa and b respectively).+

TABLE I. RSSR + $(CH_3)_2CNO_2^{\ominus} \rightarrow (CH_3)_2C(NO_2)SR + RS^{\ominus}$

DISULPHIDE II, RSSR	MOLAR RATIO (ANION:DISULPHIDE)	TIME	YIELD % OF α-NITROSULPHIDE
a, R = p-nitrophenyl	10:1, 2:1, 1:1	3, 24, 3 hrs	80, 77, 34 resp.
b, R = p-chlorophenyl	10:1, 5:1, 2:1	2, 1, 24 hrs	86, 95, 70 resp.
	10:1 (& 5 molar % galvinoxyl)	2 hrs	86
c, R = methyl	10:1	24 hrs	0
d, R = p-tolyl	10:1, 1:1	12 hrs	0
e, R = phenyl	10:1	12 hrs	0
f, R = o-aminophenyl	10:1	24 hrs	<10

Large amounts of 2,3-dimethyl-2,3-dinitrobutane (IV) were isolated in the latter reactions, when carried out under a nitrogen atmosphere, or lesser amounts in air, with a corresponding decrease in the α-nitrosulphide. Separate reactions of 2-nitropropan-2-ide with α-nitrosulphides (IIIa and b) in DMF under an atmosphere of nitrogen yielded up to 50% of (IV) in 2 hrs. The use

$$(CH_3)_2C(NO_2)SR + (CH_3)_2CNO_2^{\ominus} \rightarrow (CH_3)_2C(NO_2)C(NO_2)(CH_3)_2 + RS^{\ominus}$$

of an atmosphere of oxygen (Table I) prevents the formation of (IV). We therefore assume that

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+ Satisfactory analyses and spectral data were obtained.

this side reaction proceeds by a $S_{RN}1$[3] mechanism and is inhibited by oxygen as a radical inhibitor of the chain reaction. The yield of α-nitrosulphides was unaffected by 5 molar % of galvinoxyl or oxygen indicating that the mechanism is unlikely to involve radical intermediates.

The reaction is most probably an S_N2 mechanism, second order kinetics (k_2 = 20 mols^{-1} min^{-1} at 25^0) being observed by measuring the appearance of thiolate (424.5 nm) in the reaction of (I) and (IIa).

The results are in accord with the HSAB principle. In the 2-nitropropan-2-ide anion the carbon centre is classed as soft and that of the oxygens hard. Sulphenyl sulphur is regarded as soft, but the nature of the leaving group must also be taken into account, so that in reactions of nitroanions with sulphenyl halides,[4,5] thiocyanates,[5] and disulphides one would predict C-sulphenylation while O-sulphenylation is observed[4] when the leaving group is hard ($BF_4^{\ominus}$ or $SbF_4^{\ominus}$). Trost et al[6] found that C-sulphenylation was observed for the reaction of disulphides with the enolates of ketones and esters.

Nucleophilic displacements[1] from sulphur only take place when the attacking base has a greater affinity for sulphur than the displaced group. This helps to explain the reaction of the disulphides (IIa and b). These react to give stable anions that are poor nucleophiles, while the other disulphides would react to give strong nucleophiles. A similar situation is encountered in the reaction of cyanide ion with disulphides. The reverse reaction (α-nitrosulphide and thiolate anion) in DMF only occurs when R = p-nitrophenyl and p-chlorophenyl. As would be predicted the reaction of (IIIa and b) with sodium p-tolyl thiolate is faster than with p-nitrophenyl or p-chlorophenyl thiolates.

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