Nucleophilic Displacement of the Nitro-group from Nitroalkanes

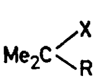
By Michael Benn* and Adri C. M. Meesters

(*Department of Chemistry, The University, Calgary, Alberta, Canada* T2N 1N4)

Summary Reaction of toluene-*p*-thiolate anion, with primary or secondary, but not tertiary, nitroalkanes yields among other products the corresponding alkyl *p*-tolyl sulphides, apparently by a conventional S_N2 displacement of the nitro-group.

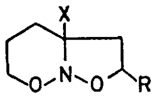
Only recently has it been shown[1–3] that a nitro-group attached to an sp^3-hybridised carbon atom can act as a leaving group[4] in nucleophilic substitution reactions. An example of the many discovered by Kornblum[1] is the conversion (**1a**) → (**1b**). Both this and the conversion (**2a**) → (**2b**)[3] involve activated tertiary nitro-functions: the first requires appropriate phenyl substitution [(**1c**) $\rightarrow\!<\!\longrightarrow$ (**1d**)], and proceeds by a radical–radical anion mechanism,[1] while the second is thought to involve an S_N1 reaction,[3] the nitrogen atom stabilising the intermediate cation.

We now report that the nitro-group can also be displaced from simple, unactivated, primary and secondary nitroalkanes (**3**) by the powerfully nucleophilic toluene-*p*-thiolate anion to yield the corresponding sulphides [Scheme, path (a)], and that this reaction is mechanistically different from the previous cases.



(1)

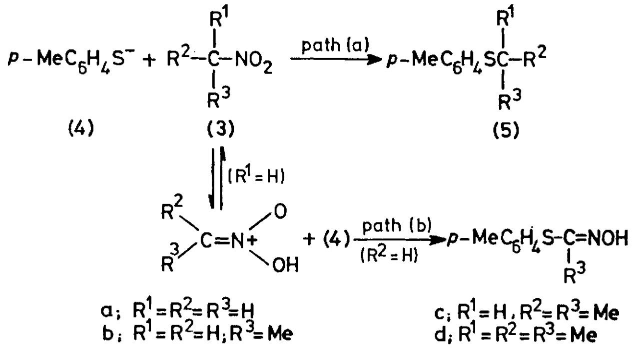
a; R = *p*-$NO_2C_6H_4$, X = NO_2
b; R = *p*-$NO_2C_6H_4$, X = Ph
c; R = Ph, X = NO_2
d; R = Ph, X = SPh



(2)

R = Et, CH_2Cl, or CO_2Me
a; X = NO_2
b; X = OMe

When nitromethane (**3a**) and potassium toluene-*p*-thiolate (**4**) were stirred together in dimethylformamide (DMF) at 85 °C, they gave nitrite ion and (**5a**) in 80% yield. Under similar conditions other primary nitroalkanes gave



SCHEME

much lower yields of sulphides [*e.g.* (**3b**) → (**5b**) (3%)], the major reaction being the formation of thiohydroximates[5] [Scheme, path (b)]. With 2-nitropropane (**3c**) only traces of (**5c**) (0·5%) were formed, and no (**5d**) could be detected in the reaction of (**4**) with 2-nitro-2-methylpropane (the nitroalkene and *p*-thiocresol were recovered in reasonable yield).

The rate of formation of (**5a**) in DMF at 45 °C was unaffected by added (up to 5 mol %) *p*-dinitrobenzene or 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxyl or by light. Hence a radical or radical anion-chain mechanism seems to be excluded.

The competing reactions (Scheme) complicate rate measurements, but the rate of formation of (**5a**) was approximately first order in nitromethane and (**4**), and this, together with the observed sensitivity to steric effects, and the fact that sulphide-formation proceded best in dipolar aprotic solvents (hexamethylphosphoramide > DMF >> EtOH) leads us to propose that the nitro group is displaced by (**4**) in a conventional S_N2 process, an unprecedented, and intriguing, finding.

This work was supported by an operating grant (to M.H.B.) by the National Research Council of Canada, and a scholarship (to A.C.M.M.) from the Killam Foundation. We also thank Professor T. S. Sorensen for helpful comments.

(*Received*, 16*th May* 1977; *Com.* 473.)

[1] N. Kornblum, *Angew. Chem. Internat. Edn.*, 1975, **14**, 734, and references therein.

[2] G. A. Russel and W. C. Danen, *J. Amer. Chem. Soc.*, 1966, **88**, 5363.

[3] I. E. Chelnor, I. M. Petrova, and V. A. Tartakovskii, *Izvest. Akad. Nauk. S.S.S.R., Ser. Khim.*, 1973, 2644.

[4] Interestingly, in a very recent discussion of some nucleophilic substitutions in aromatic systems (G. Bartoli and P. E. Todesco, *Accounts Chem. Res.*, 1977, **10**, 125) the nitro group has been described as a very good nucleofuge (leaving group), much superior to fluorine.

[5] J. W. Copenhaver, U.S. P. 2,786,865; *Chem. Abs.*, 1957, **51**, 13,920; A. J. Mulder and R. van Helden, *U.S. P.* 3,821,266; *Chem. Abs.*, 1974, **81**, 120,027 g.