Synthesis of Unsymmetrical Azoxyalkanes and Alkylazoxyarenes from Nitroso-compounds and *NN*-Dichloroamines

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Summary Unsymmetrical azoxyalkanes and alkylazoxyarenes are produced in good yields from nitroso-compounds and *NN*-dichloroamines in the presence of methanolic KOH; unsymmetrical azoxy-compounds containing tertiary-alkyl substituents can be prepared by this method.

SYNTHETIC approaches to unsymmetrical azoxyalkanes and alkylazoxyarenes have recently been reviewed.[1] Only the reaction of arylazoxy tosylates with Grignard reagents,[2] and the alkylation[1] of alkyl diazotates afford a single, predictable product, but both these reactions have limitations. We herein report a novel synthesis of azoxy compounds which has advantages over the prior techniques, and is applicable to unsymmetrical and symmetrical azoxyalkanes, as well as to alkylazoxyarenes [equation (1)].

$$R^1NCl_2 + R^2NO \xrightarrow{KOH} \underset{(\mathbf{1})}{R^1N{=}N(O)R^2} \qquad (1)$$

R^1 = alkyl; R^2 = alkyl or aryl

In a typical procedure, the *NN*-dichloroamine (0·01 mol), prepared by the reaction of the amine with calcium hypochlorite,[3] was added to an equimolar quantity of the nitroso-compound in methanol. 50% aqueous KOH

(0·02 mol) was added dropwise to the mixture maintained at 25—30 °C which was then stirred until the colour faded. After work-up, the azoxy-compounds were purified by preparative g.l.c. Representative compounds which have been synthesized are in the Table.

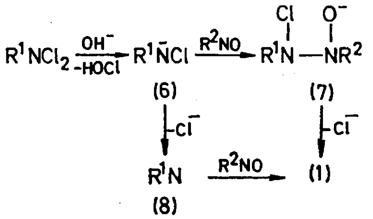
TABLE Azoxy-compounds from R^1NCl_2 and R^2NO

Compound	R^1	R^2	Yield(%)[a]
(2)	Bu^t	Ph	80
(3)	Bu^n	Ph	36[b]
(4)	1-Adamantyl	Bu^t[c]	49
(5)[d]	CMe_2CN	CMe_2CN[e]	48[f]

[a] Minimum yields (small scale runs). [b] 2:1 molar ratio of Bu^nNCl_2–PhNO; ref. 2. [c] Prepared by the method of W. D. Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 6522, from Bu^tNHOH, H. Stetter and E. Smulders, *Chem. Ber.*, 1971, **104**, 917. [d] M.p. 36·5—37·5 °C[4] identical to material prepared by an alternative route (RNHOH + RNO). [e] O. Piloty and B. G. Schwerin, *Chem. Ber.*, 1901, **34**, 1863. [f] At 5 °C.

New compounds gave satisfactory elemental analyses, and the i.r.[5] and n.m.r.[6] spectra of the products were consistent with the designated structures.

We suggest mechanisms involving intermediates (**7**) or (**8**) (Scheme). Nucleophilic attack on the nitroso-group has been reported;[7] there is also evidence[8] for interaction between nitrene and nitroso-groups.



SCHEME

The present route is simple and gives reasonable yields; it also provides azoxyalkanes and alkylazoxyarenes containing tertiary-alkyl substituents, a type not readily obtainable by prior methods.[1]

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