Arenesulphinic Acids. Nitroso Protecting Reagents Applicable to Some Nitrosoarenes

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Summary Arsenesulphinic acids were used, in acidic media, as protecting reagents for the *C*-nitroso-group against reduction and condensation, leading to a non-reducible hydroxylamine; deprotection is effected by basic hydrolysis.

Protection and deprotection of groups or radicals plays an important role in organic synthesis. Despite interest in protective groups, methods for protection of only a limited number of bonds are known, and protecting reagents for the nitroso-group are not available.[1] We report the use of arenesulphinic acids for the protection of the *C*-nitroso-group, which is susceptible to reduction and condensation.[1] The method is based on the formation of a stable non-reducible *N*-substituted hydroxylamine, as shown by polarographic studies, and has been applied to nitroso-arenes. It is not applicable to the *N*-nitroso-group.

Table

Ar^{1}N(OH)SO$_2$Ar^2		M.p./°C	
Ar^1	Ar^2	(all decomp.)	Yield (%)[a]
Pyridinyl-4-*N*-oxide	Ph	210	99[b]
	p-MeC$_6$H$_4$	216	98[b]
6-Chloropyridin-3-yl	*p*-MeC$_6$H$_4$	194	40[b]
p-NCC$_6$H$_4$	*p*-MeC$_6$H$_4$	164	20[b], 93[c]
p-PhCOC$_6$H$_4$	*p*-MeC$_6$H$_4$	210	37[b], 97[c]
p-O$_2$NC$_6$H$_4$	*p*-MeC$_6$H$_4$	159	95[c]

[a] Based on coulometric measurements. [b] From reduction of corresponding nitroarenes. [c] From oxidation of the corresponding arylhydroxylamines. All compounds show consistent elemental analyses and i.r. spectra.

The protecting reaction [equation (1)] occurs in aqueous acidic media at low pH (0—3). and is quantitative at ordinary temperatures, even with stoicheiometric quantities.[2] The rate of the reaction depends upon the pH and the arene substituent. Unsatisfactory results were obtained for *p*-OH, *p*-NH$_2$, or *p*-NMe$_2$ nitrosobenzenes. The deprotection is effected by hydrolysis[3] [equation (2)] at ambient temperature (pH > 8†), and leads quantitatively to the nitrosoarenes.‡

$$\text{Ar}^1\text{NO} + \text{Ar}^2\text{SO}_2\text{H} \longrightarrow \text{Ar}^1\text{N(OH)SO}_2\text{Ar}^2 \qquad (1)$$

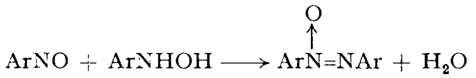
$$\text{Ar-N(OH)SO}_2\text{Ar}^2 + \text{OH}^- \longrightarrow \text{Ar}^1\text{N{=}O} + \text{Ar}^2\text{SO}_2{}^- + \text{H}_2\text{O} \qquad (2)$$

The utility of this method is demonstrated by the synthesis of nitroso-arenes, which cannot be prepared by a one-step reduction because they are more easily reduced than the starting nitro-compounds.[4] We have shown recently that the first step in the electrochemical reduction of the nitro-compounds gives dihydroxy-amines which by loss of water lead to nitrosocompounds[5,6] [equation (3)].

$$\text{ArNO}_2 + 2\text{e} + 2\text{H}^+ \longrightarrow \text{ArN(OH)}_2 \longrightarrow \text{ArNO} + \text{H}_2\text{O} \qquad (3)$$

If the intermediate nitroso-compounds are trapped by arenesulphinic acids during electrolysis as the non-reducible hydroxylamines, the nitroso-compounds can be prepared by a one-step reduction of the nitro-compounds (Table). The presence of the sulphinic acids also avoids the formation of azoxy-derivatives.[5]

It is well known that anodic oxidation of arylhydroxylamines does not normally lead to nitroso-compounds because of the fast formation of azoxy-compounds [equation (4)], but in the presence of arenesulphinic acids the nitroso-compounds can be obtained quantitatively after deprotection (Table).



$$\text{ArNO} + \text{ArNHOH} \longrightarrow \text{Ar}\overset{\overset{\displaystyle\text{O}}{\uparrow}}{\text{N}}{=}\text{NAr} + \text{H}_2\text{O} \qquad (4)$$

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† At pH 4—7 the protecting reaction (1) is an equilibrium depending upon the pH and the substituent.

‡ A typical experiment involved electrolysis on mercury at controlled potential; reduction in N-H$_2$SO$_4$–EtOH (1:1 v/v) at 0 °C, − 0·4 V *vs.* S.C.E.; oxidation in Britton–Robinson buffers, pH 3, + EtOH, 20 °C, + 0·4 V *vs.* S.C.E.

[1] J. H. Boyer, in H. Feuer, 'The Chemistry of the Nitro- and Nitroso-groups,' Wiley, New York, 1969, p. 215; W. Seidenfaden, 'Methoden der Organischen Chemie,' Georg Thieme Verlag, Stuttgart, 1971, vol. 10, p. 1017.

[2] Good yields are also reported if the nitrosobenzene and arenesulphinic acids are mixed in non-aqueous media: E. Bamberger and A. Rising, *Ber.*, 1901, **34**, 228; T. A. Wajer, H. W. Geluk, J. B. Engberts, and Th. J. De Boer, *Rec. Trav. chim.*, 1970, **89**, 696.

[3] O. Piloty, *Ber.*, 1896, **29**, 1564.

[4] H. Lund, in M. M. Baizer, 'Organic Electrochemistry,' Marcel Dekker, New York, 1973, p. 315.

[5] A. Darchen and C. Moinet, *J. Electroanalyt. Chem.*, 1976, **68**, 173.

[6] A. Darchen and C. Moinet, *J.C.S. Chem. Comm.*, 1976, 487.