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Sulphur–Nitrogen Compounds. Part IV[a]. Reactions of Bis(tolylsulphonyl)hydroxylamine with Bases

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The oxidation of N,N-bis(arylsulphonyl)hydroxylamines, $HON(SO_2R)_2$ ($R = p\text{-}XC_6H_4$; X = H, F, Cl, CH_3, CH_3O) yields nitrate(V) and N,N,O-tris(arylsulphonyl)hydroxylamines $RSO_2ON(SO_2R)_2$ [1]: the postulated course of this oxidation reaction is *via* the bis(arylsulphonyl)aminyl oxide radicals ${}^{\bullet}ON(SO_2R)_2$ which dissociate according to eqn. 1, subsequent cross-combination of the radicals ${}^{\bullet}ON(SO_2R)_2$ and $RSO_2^{\bullet}$ yielding the observed products.

$$ {}^{\bullet}ON(SO_2R)_2 \longrightarrow ONSO_2R + RSO_2^{\bullet} \qquad (1) $$

A number of reactions designed to yield nitrosyl arenesulphinates $ONSO_2R$ gave a wide range of products [2], but never $ONSO_2R$. Oxidation of the N-aryl-N-(arylsulphonyl)hydroxylamines, $HON(SO_2R)R'$ ($R,R' = p\text{-}ClC_6H_4$, $p\text{-}CH_3C_6H_4$, $p\text{-}CH_3OC_6H_4$) similarly yields analogous N,N,O-trisubstituted hydroxylamines $RSO_2ON(SO_2R)R'$ [3] *via* radicals ${}^{\bullet}ON(SO_2R)R'$ which dissociate to ONR' and $RSO_2^{\bullet}$ (eqn. 2).

$$ {}^{\bullet}ON(SO_2R)R' \longrightarrow ONR' + RSO_2^{\bullet} \qquad (2) $$

The radicals ${}^{\bullet}ON(SO_2R)_2$ and ${}^{\bullet}ON(SO_2R)R'$, but not $RSO_2^{\bullet}$, have been identified in these reactions, by use of e.s.r. spectroscopy [3].

The action of bases on $HON(SO_2R)R'$ yields ONR' and arenesulphinate [4] (eqn. 3), in a process analogous to reaction (2) but at an oxidation level lower by one electron per mol.

$$ HON(SO_2R)R' \xrightarrow{-H^+} {}^{-}ON(SO_2R)R' \longrightarrow ONR' + RSO_2^- \qquad (3) $$

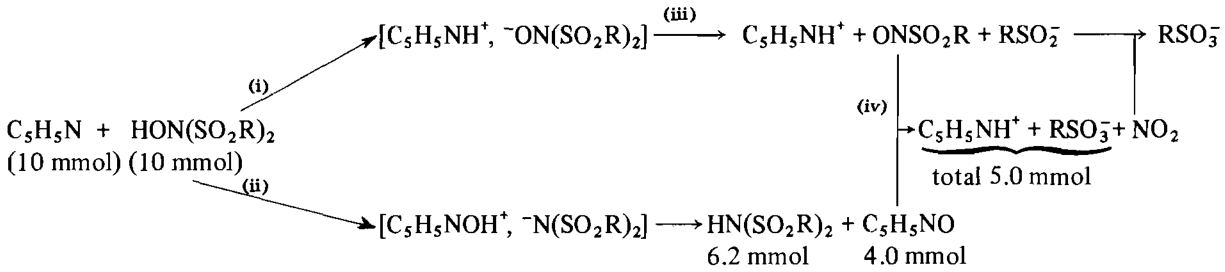
Consequently we have investigated the reactions of $HON(SO_2R)_2$ ($R = p\text{-}CH_3C_6H_4$ hereafter) with base in the hope of preparing $ONSO_2R$ in a reaction (eqn. 4) analogous to reaction (1) but at a lower oxidation level, again by one electron per mol.

$$ HON(SO_2R)_2 \xrightarrow{-H^+} {}^{-}ON(SO_2R)_2 \longrightarrow ONSO_2R + RSO_2^- \qquad (4) $$

With aqueous bases, $HON(SO_2R)_2$ yields RSO_2^- and nitrate(III), (eqn. 5): this reaction is the reverse of that employed [1] to prepare $HON(SO_2R)_2$ under acid conditions.

$$ HON(SO_2R)_2 + 3OH^- \longrightarrow 2RSO_2^- + NO_2^- + 2H_2O \qquad (5) $$

With anhydrous solid KOH in toluene, extensive decomposition occurs: however with pyridine in benzene a complex reaction, proceeding *via* two independent pathways, occurs involving transfer of both H^+ and OH^+ from the hydroxylamine to the base. Thus on mixing equimolar solutions of $HON(SO_2R)_2$ and pyridine in benzene, at room temperature, a white precipitate of pyridinium arenesulphonate $C_5H_5NH^+{\cdot}SO_3R^-$ (25% yield), rather than the expected arenesulphinate $C_5H_5NH^+SO_2R^-$ (*cf.* eqn. 4) is formed,



(i) H^+ transfer
(ii) OH^+ transfer: ratio of OH^+ transfer to H^+ transfer ≃ 5:1
(iii) Reaction (4)
(iv) H_2O/air

SCHEME. Reaction of $HON(SO_2R)$ with Pyridine.

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leaving in solution the bis(arylsulphonyl)amine, $HN(SO_2R)_2$ (62%) and pyridine-N-oxide (40%).

Control experiments showed that C_5H_5NO does not oxidise SO_2R^- to SO_3R^-, although both NO and NO_2 can do so. However, the observed stoichiometry can be adequately rationalised (see Scheme) if it is supposed firstly, that H^+ transfer from the hydroxylamine to the pyridine is followed by reaction 4; and secondly, that C_5H_5NO is capable of oxidising the intermediate $ONSO_2R$ (eqn. 6).

$$C_5H_5NO + ONSO_2R + 1/2H_2O \xrightarrow{\text{Air}} C_5H_5NH^+ + SO_3R^- + NO_2 \quad (6)$$

No products other than $C_5H_5NH^+SO_3R^-$, $HN(SO_2R)_2$ and C_5H_5NO were detected, and the recovered yields of these products account for 87% of the initial SO_2R groups, and 90% of the initial C_5H_5N.

In an attempt to detect the transient presence of $ONSO_2R$ in the reactions of $HON(SO_2R)_2$ both with base and with oxidants, reactions of $HON(SO_2R)_2$ with pyridine and with PbO_2 [1] were conducted also in the presence of cyclopentadiene monomer, since transient ONX species have been detected by trapping as Diels–Alder adducts with 1,3-dienes [5]. With PbO_2, oxidation occurred as usual to yield $RSO_2ON(SO_2R)_2$ [1], and the C_5H_6 was recovered unchanged. However, the reaction of $HON(SO_2R)_2$ with pyridine takes a different course when cyclopentadiene is present. $HN(SO_2R)_2$ was formed as in the reaction described above, but neither $C_5H_5NH^+$-SO_xR^- (x = 2, 3) nor an adduct of $ONSO_2R$ with C_5H_6 was detected: instead, the only product containing C_5H_5 groups was $C_5H_5OSO_2R$ [m/e found: 236.0511 u; ${}^{12}C_{12}{}^{1}H_{12}{}^{16}O_3{}^{32}S_1$ requires 236.0507 u]. This interesting derivative is a rare example of an oxygen-substituted cyclopentadienide.

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