Treatment of *N*-Alkyl-*N'*-tosylhydrazines with Oxidizing Agents: a New Route to Alkanesulphinic Esters

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Summary Olefins and toluene-*p*-sulphinic esters were isolated in good yields by oxidation of some *N*-alkyl-*N'*-tosylhydrazines with SeO_2, CrO_3, and HgO.

During a study of tosylhydrazine derivatives, the treatment of *N*-alkyl-*N'*-tosylhydrazines with oxidizing agents was undertaken, to determine the possibility of obtaining tosylazoalkanes or products derived from the decomposition of these compounds.

These studies are related to our previous work on tosylazoalkenes and related compounds.[1] Readily available tosylhydrazine derivatives, such as *N*-hexadecyl-*N'*-tosylhydrazine,[2] *N*-tetradecyl-*N'*-tosylhydrazine,[2] *N*-cycloheptyl-*N'*-tosylhydrazine,[3] and *N*-cyclohexyl-*N'*-tosylhydrazine[3] were used as starting materials.

SeO_2, CrO_3, and HgO were chosen as oxidizing agents, as they are usually employed in the oxidation of NH–NH groups to N=N. Using MnO_2, PbO_2, and TiO_2 slow reactions (*ca.* 7 days) and lower yields were observed. Anhydrous ether, benzene, tetrahydrofuran (THF), acetone, and 1,2-dimethoxyethane were used as solvents: rapid evolution of nitrogen was observed: 1 mol of N_2 was obtained in a few minutes when SeO_2 and CrO_3 were used. In the case of HgO, the reaction was slower and was complete after 24 h at room temperature.

In a typical experiment, 0·2056 g (0·5 mmol) of 1-hexadecyl-2-tosylhydrazine in 10 ml anhydrous THF was stirred with 0·554 g (0·5 mmol) of SeO_2 at room temperature, under an atmosphere of nitrogen, for about 2 h. After centrifugation the mixture was filtered using a "C. Srheicher & Schull" filter paper which is specific for retaining traces of metallic selenium. The filtrates were evaporated and chromatographed on a silica column (0·05—0·2 mm). Elution with n-hexane until the eluant was completely free of olefin, followed by a 95/5 (v/v) mixture of n-hexane and ethyl acetate, gave the sulphinic ester.

$$p\text{-Me}\cdot C_6H_4\cdot SO_2\cdot NH\cdot NH\cdot CH_2\cdot CH_2R \xrightarrow{\text{ox}} [p\text{-Me}\cdot C_6H_4\cdot SO_2\cdot N:N\cdot CH_2\cdot CH_2R]$$

$$\downarrow$$

$$N_2(100\%) + \underset{\substack{\downarrow \text{ox} \\ p\text{-Me}\cdot C_6H_4\cdot SO_3H}}{p\text{-Me}\cdot C_6H_4\cdot SO_2H} + p\text{-Me}\cdot C_6H_4\cdot S(O)\cdot O\cdot CH_2\cdot CH_2R + RCH:CH_2$$

Scheme

The first step of the reaction (see Scheme) may be the oxidation of the hydrazine to an azo-system. Olefins and sulphinic esters were obtained as products in yields which were similar for the three oxidants: tetradecyl and hexadecyl esters, 60—80%; cyclohexyl and cycloheptyl esters, 40—70%; olefins 14—18%.

The structures of the olefins were confirmed by comparison with commercial products using g.l.c., g.l.c.–m.s., i.r., and ^{1}H n.m.r. The structures of the sulphinic esters were determined by physical methods.[4,5]

The i.r. and ^{1}H n.m.r. spectra of these sulphinic esters were identical with those obtained from authentic samples prepared according to Field and Locke's method.[4c] The methyl ester of the toluene-*p*-sulphonic acid, formed by treatment of the reaction mixture with diazomethane, was identified by g.l.c.

Under the experimental conditions and with the reactants used it was not possible to isolate the tosylazo-compounds expected as intermediate products. In the conversion of alkyltosylhydrazines into sulphinic esters and olefins, the reaction is not influenced by variations in the solvent polarity. Conductivity measurements seem to exclude the presence of a detectable quantity of ions in solution. When the reaction was conducted in benzene, substantial amounts of biphenyl were detected: these data support the hypothesis of a radical pathway for the reaction. E.s.r. measurement, however, did not indicate the presence of radicals in solution. Measurements of e.s.r. with flow systems are in progress (*cf.* ref. 6).

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