

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

By ORAZIO ATTANASI

[Laboratorio dei composti del Carbonio contenenti eteroatomi e loro applicazioni -C.N.R., Via Tolara di Sotto 89, Ozzano Emilia (Bologna) Italy]

LUCIANO CAGLIOTI\* and FRANCESCO GASPARRINI

(Istituto di Chimica Organica, Via Castro Laurenziano 9, Università di Roma, Italy)

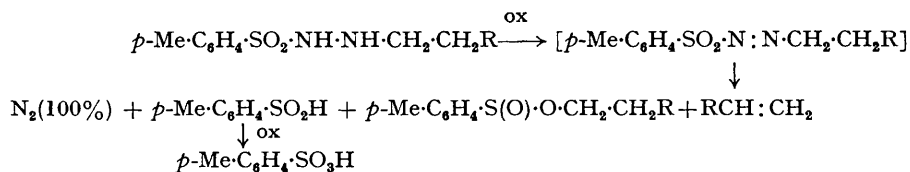
**Summary** Olefins and toluene-*p*-sulphinic esters were isolated in good yields by oxidation of some *N*-alkyl-*N'*-tosylhydrazines with SeO<sub>2</sub>, CrO<sub>3</sub>, and HgO.

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.<sup>1</sup> Readily available tosylhydrazine derivatives, such as *N*-hexadecyl-*N'*-tosylhydrazine,<sup>2</sup> *N*-tetradecyl-*N'*-tosylhydrazine,<sup>2</sup> *N*-cycloheptyl-*N'*-tosylhydrazine,<sup>3</sup> and *N*-cyclohexyl-*N'*-tosylhydrazine<sup>3</sup> were used as starting materials.

rapid evolution of nitrogen was observed: 1 mol of N<sub>2</sub> was obtained in a few minutes when SeO<sub>2</sub> and CrO<sub>3</sub> 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<sub>2</sub> at room temperature, under an atmosphere of nitrogen, for about 2 h. After centrifugation the mixture was filtered using a "C. Srreicher & 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.



SCHEME

SeO<sub>2</sub>, CrO<sub>3</sub>, and HgO were chosen as oxidizing agents, as they are usually employed in the oxidation of NH-NH groups to N=N. Using MnO<sub>2</sub>, PbO<sub>2</sub>, and TiO<sub>2</sub> slow reactions (*ca.* 7 days) and lower yields were observed. Anhydrous ether, benzene, tetrahydrofuran (THF), acetone, and 1,2-dimethoxyethane were used as solvents:

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  $^1\text{H}$  n.m.r. The structures of the sulphinic esters were determined by physical methods.<sup>4,5</sup>

The i.r. and  $^1\text{H}$  n.m.r. spectra of these sulphinic esters were identical with those obtained from authentic samples prepared according to Field and Locke's method.<sup>4c</sup> 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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