

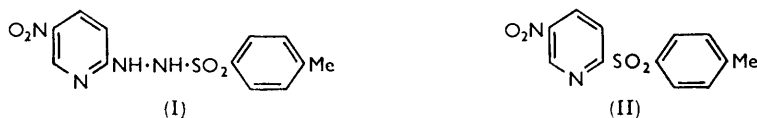
978. Some Unusual Reactions of Toluene-*p*-sulphonhydrazide.

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Toluene-*p*-sulphonhydrazide reacts with 2-chloro-5-nitropyridine in hot ethanol to give, not the expected hydrazino-compound (I), but the sulphone (II); the mechanism of the reaction is discussed. Products of decomposition of toluene-*p*-sulphonhydrazide in boiling ethanol are identified.

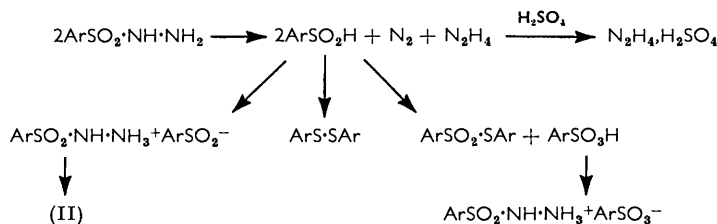
Toluene-*p*-sulphonhydrazidium toluene-*p*-sulphonate (VI) is shown to be the product obtained by Hälssig by heating toluene-*p*-sulphinic acid with hydrazine hydrochloride.

A CONVENIENT method for the removal of a reactive halogen atom from heterocyclic compounds containing other easily reduced groups is reaction with toluene-*p*-sulphonhydrazide followed by alkaline decomposition of the product.¹⁻³ When this method was applied to the preparation of 3-nitropyridine from 2-chloro-5-nitropyridine an anomalous reaction occurred. 2-Chloro-5-nitropyridine and toluene-*p*-sulphonhydrazide in chloroform or ethanol kept at room temperature for up to two weeks gave none of the expected 5-nitro-2-toluene-*p*-sulphonhydrazidopyridine (I), and only traces were formed on heating the ethanolic solution. The pyridine-containing product was 5-nitro-2-toluene-*p*-sulphonylpyridine (II). The pyridylhydrazide (I) was prepared from 2-hydrazino-5-nitropyridine and toluene-*p*-sulphonyl chloride; it did not yield the sulphone (II) in boiling ethanol even when toluene-*p*-sulphonhydrazide and hydrochloric acid were added



to simulate the conditions under which the sulphone was obtained. Under these conditions *p*-tolyl toluene-*p*-thiolsulphonate was isolated, and this was also formed, together with di-*p*-tolyl disulphide, from toluene-*p*-sulphonhydrazide and ethanolic hydrochloric acid, when the pyridylhydrazide (I) was omitted. When toluene-*p*-sulphonhydrazide was heated alone in ethanol the toluene-*p*-thiolsulphonate was not formed but the disulphide was obtained, together with toluene-*p*-sulphinic acid, toluene-*p*-sulphonhydrazidium toluene-*p*-sulphonate and toluene-*p*-sulphonate. The toluene-*p*-thiolsulphonate was also not detected when the hydrochloric acid was replaced by small amounts of water or sulphuric acid. In the presence of the latter the other products mentioned above were formed together with hydrazine sulphate. Benzenesulphonhydrazide has been reported⁴ to yield 1,2-dibenzenesulphonylhydrazine when heated in ethanol, but none of the corresponding ditoluenesulphonyl compound was found in our reactions.

The annexed scheme summarises the likely routes to the compounds isolated when toluene-*p*-sulphonhydrazide ($\text{ArSO}_2\cdot\text{NH}\cdot\text{NH}_2$) decomposes in ethanol:



¹ Dewar, *J.*, 1944, 619.

² Albert and Royer, *J.*, 1949, 1148.

³ Alford and Schofield, *J.*, 1953, 609.

⁴ Curtius and Lorenzen, *J. prakt. Chem.*, 1898, 58, 166.

refluxed for a further 3 hr., though the presence of a very small amount was indicated by the red colour produced by addition of aqueous sodium hydroxide. (It was also found that only a trace of the hydrazide was formed on storage of the reaction mixture, in ethanol or chloroform, for up to 2 weeks.) The volume of the solution was reduced to one half and the sulphone (II) was separated; after recrystallisation from ethanol this had m. p. and mixed m. p. 160—161° (Found: C, 52.4; H, 3.7; N, 10.3. Calc. for $C_{12}H_{10}N_2O_4S$: C, 51.8; H, 3.6; N, 10.1%).

(c) The same reaction mixture as for (b) was heated under reflux for 50 hr. and the ethanol removed. Trituration of the residue yielded a solid which was extracted with 2*N*-sodium hydroxide (40 ml.). The solid (1.75 g.) crystallised from ethanol to give the sulphone, m. p. and mixed m. p. 159.5—160°.

(d) 2-Chloro-5-nitropyridine (0.3 g.) and sodium toluene-*p*-sulphinat dihydrate¹² (0.4 g.) in ethanol (25 ml.) were heated under reflux for 1.5 hr.; sodium chloride separated. More sulphinate (0.4 g.) was added and heating continued for a further 1 hr. The volume was reduced to 10 ml. and water (15 ml.) was added with stirring, whereupon the sulphone (0.3 g.), m. p. and mixed m. p. 158—160°, separated.

Stability of 5-Nitro-2-toluene-p-sulphonhydrazidopyridine (I) in Boiling Ethanol.—(a) The hydrazide (I) (1.5 g.) in ethanol (50 ml.) was heated under reflux for 60 hr. On cooling, starting material (0.52 g.), m. p. 213—214°, was collected and more (0.1 g.) was obtained on removal of the solvent.

(b) The hydrazide (I) (1.0 g.) was suspended in ethanol (40 ml.) containing 5.5*N*-aqueous hydrochloric acid (0.3 ml.) and heated under reflux for 18 hr. After cooling, starting material (0.82 g.), m. p. 214—215°, was recovered.

(c) The hydrazide (I) (0.70 g.) and toluene-*p*-sulphonhydrazide (0.98 g.) in ethanol (30 ml.) containing 5.5*N*-aqueous hydrochloric acid (2.2 ml.) were heated under reflux for 23 hr. From the cooled solution unchanged hydrazide (I) (0.36 g.) was obtained. Removal of the ethanol and extraction of the residue with 2*N*-sodium hydroxide left a solid (0.3 g.) which, after two recrystallisations from ethanol, gave *p*-tolyl toluene-*p*-thiolsulphonate (III), m. p. and mixed m. p. with authentic material¹³ 76—78°.

Thermal Decomposition of Toluene-p-sulphonhydrazide in Ethanol.—(a) *Alkali-insoluble products.* Toluene-*p*-sulphonhydrazide (3.85 g.) in ethanol (120 ml.) containing concentrated hydrochloric acid (0.28 g.) was heated under reflux for 72 hr. The ethanol was removed and the residue (3.5 g.) was extracted with 2*N*-sodium hydroxide (15 ml.) to leave an insoluble solid (0.63 g.), m. p. 30—75°, separated by light petroleum (b. p. 40—60°) into the soluble di-*p*-tolyl disulphide (0.34 g.), m. p. and mixed m. p. with authentic material¹⁴ 39—42°, and the insoluble *p*-tolyl toluene-*p*-thiolsulphonate (0.24 g.), m. p. and mixed m. p. 68—72°. In similar reactions, but with the hydrochloric acid omitted or replaced by sulphuric acid or by water, the ester was not detected but the disulphide was isolated in yields of up to 40%. In the presence of sulphuric acid, hydrazine sulphate, m. p. and mixed m. p. 251°, separated from the ethanolic solution.

(b) *Alkali-soluble products.* The sodium hydroxide extracts from the decompositions described in (a) were acidified with 4*N*-hydrochloric acid, and a typical isolation procedure was as follows. The precipitate (0.62 g.) crystallised from water to give toluene-*p*-sulphinic acid, m. p. and mixed m. p. with an authentic specimen¹³ (87.5—88.5° (Found: C, 53.5; H, 5.2; S, 20.7. Calc. for $C_7H_5O_2S$: C, 53.8; H, 5.2; S, 20.5%). This compound gave an orange precipitate with ferric chloride solution and a deep purple-blue colour in concentrated sulphuric acid with anisole (Smiles's test). On storage, the acid mother liquor deposited crystals which recrystallised from ethanol to give *toluene-p-sulphonhydrazidium toluene-p-sulphonate* (0.1 g.), m. p. and mixed m. p. with a sample prepared as described later, 178.5—180° (decomp.) (Found: C, 46.8; H, 5.0; S, 17.3. $C_{14}H_{18}N_2O_5S_2$ requires C, 46.9; H, 5.1; S, 17.8%). In another experiment on storage of this acid mother liquor a crystalline solid (0.13 g.) separated which melted with resolidification at 95—100° and finally melted at 169—173°. Since heating this solid at 100—150° converted it into toluene-*p*-sulphonhydrazidium toluene-*p*-sulphonate, m. p. and mixed m. p. 172—175°, it was considered to be *toluene-p-sulphonhydrazidium toluene-p-sulphinat* (Found: C, 48.8; H, 5.0. $C_{14}H_{18}N_2O_4S_2$ requires C, 49.1; H, 5.3%). Its initial m. p., 95°, was undepressed on admixture with a sample prepared as described below.

¹² Whitmore and Hamilton, *Org. Synth.*, Coll. Vol. I, 492.

¹³ Smiles, *J.*, 1924, **125**, 180.

¹⁴ Field and Grunwald, *J. Org. Chem.*, 1951, **16**, 952.

Toluene-p-sulphonhydrazidium Toluene-p-sulphonate.—Toluene-*p*-sulphonhydrazide (1.7 g.) suspended in water (20 ml.) was just dissolved by addition of concentrated hydrochloric acid, and toluene-*p*-sulphonic acid hydrate (2 g.) in water (5 ml.) was added. The precipitate was crystallised from ethanol to give the salt, m. p. 179—180° (decomp.).

*Toluene-p-sulphonhydrazidium Toluene-p-sulphinat*e.—Toluene-*p*-sulphinic acid (0.04 g.) in 2*N*-sodium hydroxide (0.5 ml.) and toluene-*p*-sulphonhydrazide (0.05 g.) in 2*N*-hydrochloric acid (1 ml.) were mixed, and the white crystalline mass was collected and washed with water. It melted with resolidification at 90—95°, finally melting at 169—175°.

Reaction between Toluene-p-sulphinic Acid and Hydrazine Hydrochloride.—Cf. Hälssig.⁹ Toluene-*p*-sulphinic acid (0.73 g.) was added to hydrazine hydrochloride (0.32 g.) in water (6.5 ml.) containing 5.5*N*-hydrochloric acid (0.16 ml.), and the mixture was gently heated and then boiled for 1 hr. The precipitated oil solidified to give *p*-tolyl toluene-*p*-thiolsulphonate (0.25 g.), m. p. and mixed m. p. 76—78°, when the solution cooled. The crystals (0.03 g.), formed throughout the mother-liquor, were collected, washed with ether, and shown by mixed m. p. and identity of the infrared spectra (Nujol mull) to be toluene-*p*-sulphonhydrazidium toluene-*p*-sulphonate. A higher yield (0.17 g.) was obtained if the mother-liquor was stored overnight.

Benzoylation of the salt or of toluene-*p*-sulphonhydrazide by the Schotten-Baumann method yielded the *dibenzoyl* derivative of the latter, with variable melting-point, between 206° and 235°, depending on the rate of heating (Found: C, 64.2; H, 5.0; N, 6.9. $C_{21}H_{18}N_2O_4S$ requires C, 64.0; H, 4.6; N, 7.1%). Hälssig reports⁹ m. p. 209.5°.

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