395. *Some Reactions of* p-*Tolyl Toluene*-p-*thiolsulphonate.*

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p-Tolyl toluene-*p*-thiolsulphonate has been shown to react with hydroxylamine in solutions of varying acidity to give toluene-*p*-sulphonamide and di-*p*-tolyl disulphide. The reaction of phenylhydrazine with the thiolsulphonic ester under similar experimental conditions yielded di-*p*-tolyl disulphide, toluene-*p*-sulphonylphenylhydrazide, and the phenylhydrazine salt of toluene-*p*-sulphinic acid.

Recently the author has drawn attention to the formation of *p*-tolyl toluene-*p*-thiolsulphonate by the interaction of carboxylic acid chlorides and salts of toluene-*p*-sulphinic acid (*J. Amer. Chem. Soc.*, 1949, **71**, 3240). Other workers (Kohler and Macdonald, *Amer. Chem. J.*, 1899, **22**, 219) by using similar experimental conditions had previously described the isolation of products which were thought to be α-keto-sulphones and which were stated to react with typical carbonyl-group reagents. It was therefore of interest to investigate the behaviour of *p*-tolyl toluene-*p*-thiolsulphonate towards reagents such as hydroxylamine and phenylhydrazine. Preliminary results (Hookway, *loc. cit.*) had shown that in buffered acetic acid solution both phenylhydrazine and hydroxylamine reacted with the thiolsulphonate to give, amongst other products, di-*p*-tolyl disulphide : the work reported in this paper is an extension of these experiments.

It is well known that thiolsulphonic esters are unstable in alkaline solution (see, *e.g.*, Zincke, *Annalen*, 1912, **391**, 55; 1914, **406**, 103), breaking down to give the salt of a sulphinic acid and a disulphide. It is possible that the formation of a sulphenic acid is an essential intermediate step in this decomposition (Child and Smiles, *J.*, 1924, 180) :

$$RSO_2SR \longrightarrow RSO_2^- + RS^+ \quad (1)$$
$$RS^+ + OH^- \longrightarrow RS{\cdot}OH \quad (2)$$
$$2RS{\cdot}OH \longrightarrow RSO_2H + RSH \quad (3)$$
$$RS{\cdot}OH + RSH \longrightarrow RS{\cdot}SR + H_2O \quad (4)$$

The formation of thiolsulphonic esters by heating sulphinic acids with aqueous mineral acids may also be explained on the assumption that sulphenic acids are intermediate products (discussed by Kharasch *et al.*, *Chem. Reviews*, 1946, **39**, 269) :

$$2RSO_2H \longrightarrow RS{\cdot}OH + RSO_3H \quad (5)$$
$$RSO_2H + RS{\cdot}OH \longrightarrow RSO_2{\cdot}SR + H_2O \quad (6)$$

When *p*-tolyl toluene-*p*-thiolsulphonate was heated in aqueous alcoholic solution with hydroxylamine hydrochloride and sodium acetate at an apparent pH of 5·5, the reaction products isolated were toluene-*p*-sulphonamide and di-*p*-tolyl disulphide. If the reaction shown in equation (6) above is reversible in acid solution, a probable mechanism for the formation of toluene-*p*-sulphonamide is :

$$C_7H_7{\cdot}SO_2{\cdot}S{\cdot}C_7H_7 + H_2O \rightleftharpoons C_7H_7{\cdot}S{\cdot}OH + C_7H_7{\cdot}SO_2H \quad (7)$$
$$C_7H_7{\cdot}SO_2H + NH_2{\cdot}OH \longrightarrow C_7H_7{\cdot}SO_2{\cdot}NH_2 + H_2O \quad (8)$$

The formation of di-*p*-tolyl disulphide can then be accounted for by reactions of the type summarised in equations (3) and (4). The disulphide could not have been produced by atmospheric oxidation of toluene-*p*-thiol formed by decomposition of toluene-*p*-sulphenic acid, since in an experiment conducted in an atmosphere of nitrogen di-*p*-tolyl disulphide was again obtained, but no toluene-*p*-thiol. It is very likely that the formation of toluene-*p*-sulphonamide involves the intermediate formation of toluene-*p*-sulphinic acid or of the toluene-*p*-sulphinyl anion in acid solution, for when xanthhydrol was added to a typical reaction mixture of thiolsulphonate and hydroxylamine hydrochloride in aqueous solution *p*-tolyl xanthyl sulphone was obtained. Xanthhydrol is known to give a carbonium cation very readily in acid solution and *p*-tolyl xanthyl sulphone was obtained independently by reaction between toluene-*p*-sulphinic acid and xanthhydrol in acetic acid solution (Thain, Thesis, London, 1949). Further, heating toluene-*p*-sulphinic acid in aqueous alcohol–acetic acid with hydroxylamine gave toluene-*p*-sulphonamide, but no di-*p*-tolyl disulphide could be isolated. Evaporation of an aqueous solution of toluene-*p*-sulphinic acid and excess of hydroxylamine is known to yield toluene-*p*-sulphonamide (Halssig, *J. pr. Chem.*, 1897, (2), **56**, 213).

It was found that lowering the pH of the thiolsulphonate reaction mixture resulted in a progressive decrease in the reaction velocity. This observation is in harmony with the view now advanced, since decreasing pH may be expected to favour an equilibrium more and more to the left of equation (7).

When attention was directed to the reaction between *p*-tolyl toluene-*p*-thiolsulphonate and phenylhydrazine in aqueous alcohol–acetic acid, it was found that the products were di-*p*-tolyl disulphide, toluene-*p*-sulphonylphenylhydrazide, and phenylhydrazine toluene-*p*-sulphinate. Heating toluene-*p*-sulphinic acid with phenylhydrazine under the same reaction conditions gave principally the phenylhydrazine salt of the acid together with a very small amount of toluene-*p*-sulphonylphenylhydrazide. It is probable that the first step in the reaction between the thiolsulphonate and phenylhydrazine involves cleavage of the ester into toluene-*p*-sulphinyl anion and toluene-*p*-thio-cation. The toluene-*p*-sulphinyl fragment then forms the phenylhydrazine salt of toluene-*p*-sulphinic acid; the toluene-*p*-thio-ion forms toluene-*p*-sulphenic acid, this in turn disproportionating to give toluene-*p*-thiol and toluene-*p*-sulphinic acid [equation (3), $R = C_7H_7$]. In addition to these reactions, however, the toluene-*p*-thio-cation can abstract a hydrogen atom with its bonding electrons from phenylhydrazine to give toluene-*p*-thiol and a phenylhydrazine cation. Toluene-*p*-sulphinyl anions may then react with the positively-charged phenylhydrazine residue to give toluene-*p*-sulphonylphenylhydrazide, whilst the toluene-*p*-thiol reacts with toluene-*p*-sulphenic acid produced by the alternative reaction path to give di-*p*-tolyl disulphide. The very small yield of toluene-*p*-sulphonylphenylhydrazide obtained when toluene-*p*-sulphinic acid was heated with phenylhydrazine may be attributable to the fact that, unlike the reaction of this acid with hydroxylamine, the formation of the substituted phenylhydrazide requires the presence of toluene-*p*-thio-ions as well as toluene-*p*-sulphinic acid. Toluene-*p*-sulphinic acid slowly forms the corresponding thiolsulphonate in acetic acid solution; the yield of toluene-*p*-sulphonylphenylhydrazide obtained in the experiment described above corresponded approximately to that expected from the thiolsulphonate which would have been produced if the sulphinic acid had been heated alone with acetic acid.

EXPERIMENTAL.

p-*Tolyl Toluene*-p-*thiolsulphonate.*—This was prepared from toluene-*p*-sulphinic acid by Hilditch's method (*J.*, 1910, 1096), and had m. p. 78°.

Reactions of p-*Tolyl Toluene*-p-*thiolsulphonate with Hydroxylamine.*—All pH measurements were carried out on a "Cambridge" meter using a glass–silver/silver chloride electrode system. The pH values quoted are only intended to give a qualitative estimate of the " acidity " of the reaction mixtures.

(*a*) pH 5·5. Hydroxylamine hydrochloride (0·3 g., 0·0043 mol.) and sodium acetate (0·3 g., 0·0037 mol.) were dissolved in water (2 ml.) and added to a solution of *p*-tolyl toluene-*p*-thiolsulphonate (0·3 g., 0·0011 mol.) in ethyl alcohol (10 ml.; 96%). After 1¾ hours at 70° the reaction mixture was cooled to room temperature. Needle-like crystals of di-*p*-tolyl disulphide (0·05 g.), m. p. 46—47° (crystallised from 96% alcohol), were deposited. Further working up of the reaction mixture gave toluene-*p*-sulphonamide (0·13 g.), m. p. 138·5—139° (white plates from water) (Found : C, 49·5; H, 5·5; N, 8·2. Calc. for $C_7H_9O_2NS$: C, 49·2; H, 5·3; N, 8·2%). The m. p. was not depressed on admixture with authentic sample of toluene-*p*-sulphonamide.

(*b*) pH 3. The thiolsulphonate (0·3 g.) was dissolved in a solution of hydroxylamine hydrochloride (0·4 g.) in aqueous alcohol (5 ml. of 96% alcohol + 2 ml. of water). After being heated at 70° for 2¾ hours the reaction mixture yielded toluene-*p*-sulphonamide (0·06 g.)

(*c*) pH 1·5. The same quantities of reagents were used as in experiment (*b*), but concentrated hydrochloric acid (0·03 ml.) was added to bring the pH to 1·5. After being heated for 4 hours at 70°, thiolsulphonate (0·2 g.) was recovered and toluene-*p*-sulphonamide (0·03 g.) obtained.

(*d*) pH 7. Sodium hydroxide (1·4 ml.; 6N.) was added to a solution of hydroxylamine hydrochloride (0·4 g.) in aqueous alcohol (5 ml. of 96% alcohol + 2 ml. of water). Thiolsulphonate (0·3 g.) was then added and the mixture kept at 70° for 1¼ hours. Di-*p*-tolyl disulphide (0·06 g.), m. p. 47—48°, and toluene-*p*-sulphonamide (0·16 g.), m. p. 138°, were obtained.

(*e*) *The reaction in nitrogen atmosphere.* Hydroxylamine hydrochloride (1·2 g.), sodium acetate (1·2 g.), and *p*-tolyl toluene-*p*-thiolsulphonate (1·0 g.) were dissolved in aqueous alcohol (20 ml. of 96% alcohol + 10 ml. of water). A slow stream of pure nitrogen was bubbled through the reaction vessel. The reaction mixture was kept at 70° for 6 hours and then stored overnight under nitrogen. Di-*p*-tolyl disulphide (0·25 g.) and toluene-*p*-sulphonamide (0·6 g.) were obtained.

The Reaction of p-*Tolyl Toluene*-p-*thiolsulphonate with Xanthhydrol.*—Hydroxylamine hydrochloride (0·6 g.) was dissolved in water (3 ml.) and added to a solution of the thiolsulphonate (0·5 g.) in alcohol (12 ml.; 96%). Xanthhydrol (0·3 g.) was then added and the solution kept at 70° for 5 hours. After 6 days at room temperature the crystals which had deposited (0·2 g.) were filtered off and crystallised from 96% alcohol. M. p. and mixed m. p. (with authentic specimen of *p*-tolyl xanthyl sulphone) 206—207°.

The Reaction between Toluene-p-*sulphinic Acid and Hydroxylamine.*—Toluene-*p*-sulphinic acid (0·7 g.) was dissolved in a solution of sodium acetate (1·2 g.) and hydroxylamine hydrochloride (1·2 g.) in water (7 ml.). After the solution had gently refluxed for 10 hours and then cooled to room temperature, crystals of toluene-*p*-sulphonamide (0·45 g.) were deposited.

The Reaction between Phenylhydrazine and p-*Tolyl Toluene*-p-*thiolsulphonate.*—Phenylhydrazine hydrochloride (1·5 g.) and sodium acetate (1·5 g.) were dissolved in water (10 ml.), and added to a solution of the thiolsulphonate (1·0 g.) in alcohol (25 ml.; 96%). The reaction mixture was kept at 70° for 2 hours and then stored at room temperature for 3 days. The crystals of di-*p*-tolyl disulphide (0·27 g.) which had separated were filtered off; they had m. p. 46—47°. The aqueous-alcoholic mother-liquors were evaporated to dryness on the steam-bath, and the residue was extracted with hot water (25 ml.). The insoluble residue was filtered off from the hot solution and gave, after crystallisation from ethyl alcohol, toluene-*p*-sulphonylphenylhydrazide (0·15 g.), m. p. and mixed m. p. (with authentic specimen) 155° (rapid heating; decomp. at m. p.) (Found: C, 59·6; H, 5·4. Calc. for $C_{13}H_{14}O_2N_2S$: C, 59·5; H, 5·35%).

On cooling, the hot aqueous extract deposited crystals (0·45 g.), m. p. 155° (decomp.), which were shown to be phenylhydrazine toluene-*p*-sulphinate. This salt (0·45 g.) was dissolved in excess of cold sodium hydroxide solution (10 ml.; 1N.) and extracted twice with ether (2 × 10 ml.). The alkaline solution was acidified with dilute hydrochloric acid and toluene-*p*-sulphinic acid (0·2 g.), m. p. 83—84° (from ether–benzene), was precipitated. The ethereal extract yielded phenylhydrazine (acetyl derivative, m. p. 127°).

Note : Toluene-*p*-sulphonylphenylhydrazide was insoluble in cold dilute aqueous alkali.

*Toluene-*p*-sulphonylphenylhydrazide.*—Prepared by Troeger and Uhlmann's method (*J. pr. Chem.* 1895, (2), **51**, 442), this compound had m. p. 155° (decomp.).

*The Reaction between Toluene-*p*-sulphinic Acid and Phenylhydrazine.*—Toluene-*p*-sulphinic acid (0·7 g.) was added to a solution of phenylhydrazine hydrochloride (1·5 g.) and sodium acetate (1·5 g.) in aqueous alcohol (20 ml. of 96% alcohol + 5 ml. of water), and the mixture kept at 70° for 2 hours. On cooling, a bulky white precipitate (0·85 g.) was obtained, and evaporation of the mother-liquors to half the bulk yielded a further crop (0·25 g.) of crystals. The combined yields were extracted with hot water (45 ml.), the aqueous extract yielding phenylhydrazine toluene-*p*-sulphinate (1·08 g.), m. p. 155° (decomp.). The water-insoluble fraction gave toluene-*p*-sulphonylphenylhydrazide (0·01 g.), m. p. 155°) (from 96% alcohol).

*The Action of Glacial Acetic Acid on Toluene-*p*-sulphinic Acid.*—(*a*) Toluene-*p*-sulphinic acid (1·0 g.) was dissolved in glacial acetic acid (10 ml.), and the solution gently refluxed for 2 hours. The mixture was poured into a large volume of saturated aqueous salt solution. The material which separated was *p*-tolyl toluene-*p*-thiolsulphonate (0·1 g.), m. p. 76° (from 96% alcohol) not depressed on mixture with an authentic specimen.

(*b*) The reaction time was increased to 10 hours. The yield of thiolsulphonate, m. p. 75—76°, was 0·45 g.

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