122. *The Condensation of* p-*Toluenesulphinic Acid and its Esters with Acetone.*

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p-Toluenesulphinic acid and its esters condense with acetone to produce p-*tolyl-*β-(β-*methylpentan*-δ-*onyl*)*sulphone* (I) and evidence supporting this formulation of the condensation product is given. Further evidence is adduced that the condensation proceeds, not by an exchange of carbonium kations, but probably by a rearrangement of diacetonyl *p*-toluenesulphinate which results from alcoholysis of the sulphinic esters by the diacetonyl alcohol present in the equilibrium mixture.

During an investigation of the molecular rearrangement of phenylmethylcarbinyl *p*-toluenesulphinate (Arcus, Balfe, and Kenyon, this vol., p. 485) the condensation of this ester, and also of β-octyl *p*-toluenesulphinate, with acetone was observed; it was known from a previous unpublished investigation in this laboratory that ethyl *p*-toluenesulphinate and *p*-toluenesulphinic acid condense with acetone. These observations have been correlated and are now presented.

From a solution of *p*-toluenesulphinic acid in acetone there separates, after heating, a compound, m. p. 94°, which has been identified as p-*tolyl*-β-(β-*methylpentan*-δ-*onyl*)*sulphone* (I) on the following evidence. It contains no free hydroxyl group, since it does not undergo acetylation, but contains a carbonyl group, since it furnishes a *semicarbazone*, from which the original ketone is regenerated by hydrolysis. It is a sulphone and not a sulphinic ester, since it is not oxidised by perhydrol, a reagent which converts sulphinates into sulphonates. It may be oxidised with acid permanganate solution, but the only product isolable is *p*-sulphobenzoic acid.

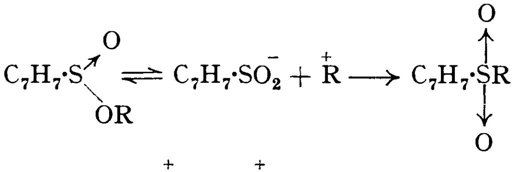
Decomposition with aqueous alkali yields *p*-toluenesulphinic acid and mesityl oxide, the latter indicating the nature of the aliphatic portion of the molecule.

Finally this compound may be synthesised by the slow condensation of *p*-toluenesulphinyl chloride with diacetone alcohol:

$$CMe_2(OH)\cdot CH_2\cdot CO\cdot CH_3 + C_7H_7\cdot SOCl \longrightarrow CMe_2(SO_2\cdot C_7H_7)\cdot CH_2\cdot CO\cdot CH_3 \qquad \text{(I.)}$$

The sulphinic esters do not condense with acetone nearly so readily as the free acid, since di-*p*-tolyl disulphoxide is the only isolable product after ethyl *p*-toluenesulphinate has been heated in acetone solution. On prolonged keeping at room temperature of solutions in acetone of ethyl, β-octyl, and phenylmethylcarbinyl *p*-toluenesulphinates, however, condensation to *p*-tolyl-β-(β-methylpentan-δ-onyl)sulphone occurs. The alcohols displaced in the last two cases have been isolated.

In view of the last result, and also of the non-formation either of olefinic compounds or of ethyl-, β-octyl-, and α-phenylethyl-sulphones, dissociation of the sulphinic esters to give carbonium kations is improbable, *e.g.*,



$$C_7H_7\cdot S\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OR} \rightleftharpoons C_7H_7\cdot\overset{-}{SO_2} + \overset{+}{R} \longrightarrow C_7H_7\cdot\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}R$$

also $$\overset{+}{R} \longrightarrow \overset{+}{H} + \text{olefin}$$

In the presence of a constant equilibrium proportion of diacetone alcohol, alcoholysis of the sulphinic esters will occur, without rupture of the O–R bond; such alcoholyses have been observed for (—) phenylmethylcarbinyl *p*-toluenesulphinate (Kenyon and Phillips, J., 1930, 1676) and for ethyl *p*-toluenesulphinate by *l*-β-octyl alcohol (Phillips, J., 1925, **127**, 2552). The *p*-toluenesulphinic ester of diacetone alcohol first produced can then undergo rearrangement into *p*-tolyl-β-(β-methylpentan-δ-onyl)sulphone, as it appears to do during the synthesis of this substance from diacetone alcohol and *p*-toluenesulphinyl chloride.

EXPERIMENTAL.

The Interaction of Ethyl p-*Toluenesulphinate and Acetone.*—(a) *At the ordinary temperature.* A solution of ethyl *p*-toluenesulphinate (17 g.) in acetone (75 c.c.) was kept in a closed vessel for 5 years. On evaporation of the solution, crystalline leaflets (23·3 g.), m. p. 72—75°, separated, which after recrystallisation from ether had m. p. 94° (Found: C, 61·6; H, 7·3; S, 13·3. $C_{13}H_{18}O_3S$ requires C, 61·4; H, 7·1; S, 12·6%).

(b) *At higher temperatures.* A solution of ethyl *p*-toluenesulphinate (3 g.) in acetone (15 c.c.) was heated under reflux for an hour and then kept at the ordinary temperature for several days. The crystals (0·8 g.) which separated consisted entirely of di-*p*-tolyl disulphoxide, m. p. 76°.

The Interaction of dl-*Phenylmethylcarbinyl* p-*Toluenesulphinate and Acetone.*—A solution of *dl*-phenylmethylcarbinyl *p*-toluenesulphinate (7·5 g.) in acetone (25 g.) was kept at the ordinary temperature for 7 months. On evaporation, crystals separated, which had m. p. 87—90° (2·6 g.) after washing with light petroleum, m. p. 94° after recrystallisation from benzene (Found: S, 12·2%), and furnished the semicarbazone, m. p. 173° (decomp.), by the method described below. The light-petroleum wash-liquor yielded phenylmethylcarbinol (1 g.), b. p. 70°/20 mm., $n_D^{20^\circ}$ 1·5243.

The Interaction of dl-β-*Octyl* p-*Toluenesulphinate and Acetone.*—A solution of *dl*-β-octyl *p*-toluenesulphinate (5 g.) in acetone (30 c.c.) was kept for 6 months. The crystalline residue obtained on evaporation was washed with ethyl alcohol and recrystallised, yielding colourless plates (2·0 g.), m. p. 94° alone and when mixed with the product of the condensation of *dl*-phenylmethylcarbinyl *p*-toluenesulphinate with acetone. The substance furnished the semicarbazone, m. p. 172° (decomp.). From the alcoholic wash-liquor, *dl*-β-octyl alcohol (1 g.), b. p. 81°/20 mm., $n_D^{20^\circ}$ 1·4285, was obtained.

The Interaction of p-*Toluenesulphinic Acid and Acetone.*—A solution of *p*-toluenesulphinic acid (7 g.) in dry acetone (30 c.c.) was gently heated for 1 hour and then allowed to evaporate at the ordinary temperature; crystals separated which, after washing with sodium carbonate solution and recrystallisation from ether, had m. p. 94° (4·8 g.).

p-*Tolyl*-β-(β-*methylpentan*-δ-*onyl*)*sulphone.*—The compound, m. p. 94°, which separated during the above reactions is assigned the structure of p-*tolyl*-β-(β-*methylpentan*-δ-*onyl*)*sulphone* and undergoes the following reactions.

It is slightly soluble in boiling water, from which, on cooling, it crystallises in leaflets. It separates unchanged from a warm solution in acetic anhydride, and is unaffected by perhydrol in acetone solution. It is oxidised by potassium permanganate in warm acetic acid solution, but the only product which could be isolated was *p*-sulphobenzoic acid, m. p. 257—259° (decomp.).

The compound (3 g.) was added to sodium carbonate (1 g.) in aqueous solution and the distillate obtained on passing a current of steam was warmed with semicarbazide hydrochloride (2 g.) and sodium carbonate (1 g.); on cooling, crystals (0·75 g.), m. p. 156°, of mesityl oxide semicarbazone separated. From the residual liquor of the steam distillation, on acidification, *p*-toluenesulphinic acid (1·7 g.), m. p. 86°, was obtained.

The compound (5 g.), when heated in aqueous alcoholic solution with semicarbazide hydrochloride (5 g.) and sodium acetate (4·2 g.), furnished leaflets (5·0 g.), which on recrystallisation from hot alcohol yielded the *semicarbazone* of *p*-tolyl-β-(β-methylpentan-δ-onyl)sulphone, m. p. 173° (decomp.) (Found: C, 53·4; H, 6·8; S, 9·9. $C_{14}H_{21}O_3N_3S$ requires C, 54·0; H, 6·8; S, 10·3%).

This semicarbazone is unaffected by hot aqueous alcoholic solutions of either oxalic acid or sodium hydroxide, but is rapidly hydrolysed on dissolution in cold concentrated hydrochloric acid, from which crystals, m. p. 94° alone or mixed with the original compound, separate after a few seconds.

Preparation of p-*Tolyl*-β-(β-*methylpentan*-δ-*onyl*)*sulphone from Diacetone Alcohol and* p-*Toluenesulphinyl Chloride.*—*p*-Toluenesulphinyl chloride (9·0 g.) was added in portions to an ice-cold mixture of diacetone alcohol (5·8 g.) and pyridine (4·5 g.), and the whole kept at the ordinary temperature for 5 weeks. The solid product was then triturated with dilute hydrochloric acid and recrystallised from ether, forming leaflets (5·0 g.), m. p. 94° alone or when mixed with the compound obtained by the interaction of acetone and ethyl *p*-toluenesulphinate.

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