847. *Studies of Sultones.*

By (Mrs.) E. M. Philbin, E. R. Stuart, R. F. Timoney, and T. S. Wheeler.

Sultones are obtained by treatment of *o*-acetylphenyl methane- or toluene-ω-sulphonate (I; R = H or Ph) with potassium hydroxide and pyridine.

Nowlan, Slavin, and Wheeler [1] were unable to effect a Baker–Venkataraman rearrangement with *vic*-acetylnaphthyl arenesulphonates. It has now been found that treatment of *o*-acetylphenyl toluene-ω-sulphonate (I; R = Ph) with potassium hydroxide in pyridine yields 2-hydroxy-2-*o*-hydroxyphenyl-1-phenylpropane-1-sulphonic sultone (II) and, by prolonged action, 2-*o*-hydroxyphenyl-1-phenylprop-1-ene-1-sulphonic sultone (III; R = Ph). The structure of the former product was confirmed by analysis and by reactions (shown in the diagram) which yielded compounds (III; R = Ph), (IV), (V; R = Ph), and (VI). Further, the infrared spectra of the first three of these compounds confirm the structure (II) and exclude the alternative structure (I*a*). The formation of the sultone (III) is analogous to the production of coumarins by the Kostanecki–Robinson method from *o*-acetylaryl acetates,[2] and to the synthesis of 2-hydroxyquinolines from *o*-acylaminoacetophenones of the type *o*-$C_6H_4(NH{\cdot}CO{\cdot}CH_2R){\cdot}COMe$ by the Camps reaction.[3]

2-*o*-Hydroxyphenyl-1-phenylpropanesulphonic sultone (V; R = Ph), m. p. 107—108°, gave by refluxing with aqueous sodium hydroxide an isomer (VIII), m. p. 158—160°. The infrared spectra of compounds (V; R = Ph) and (VIII) differed slightly. That of the former had bands for the sulphonyloxy-function at 1152 and 1171 cm.$^{-1}$, while compound

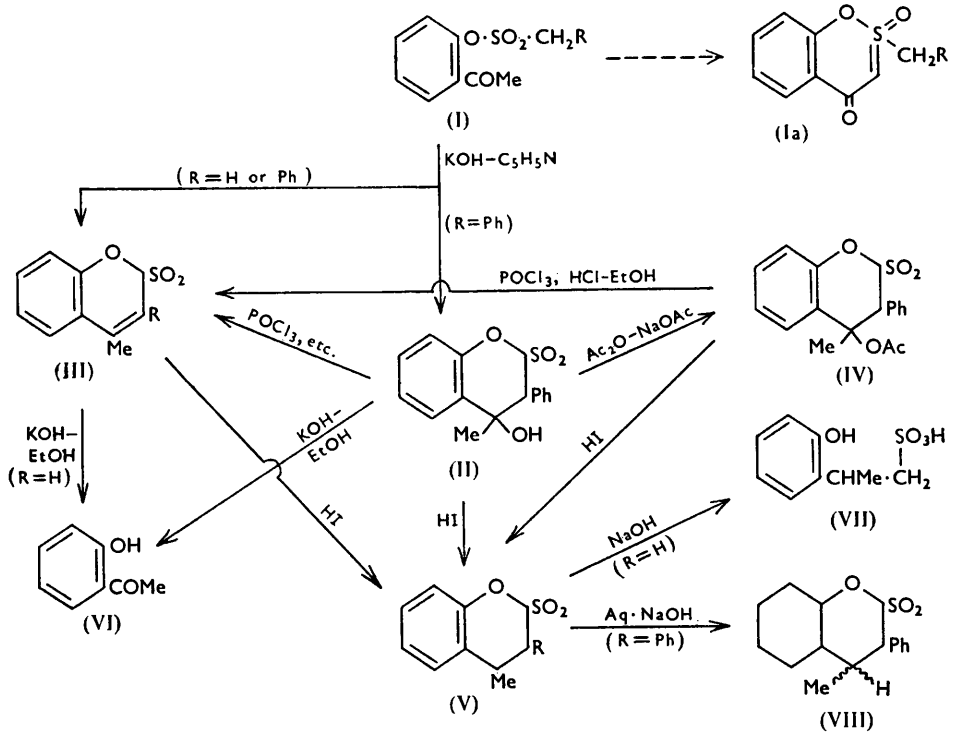
[1] Nowlan, Slavin, and Wheeler, *J.*, 1950, 340.
[2] Heilbron, Hey, and Lythgoe, *J.*, 1936, 295.
[3] Camps, *Ber.*, 1899, **32**, 3228.

(VIII) had a single band for the same function at 1169 cm.$^{-1}$. It is suggested that alkaline enolic epimerisation occurred, and that these compounds are geometrical isomers.

Infrared spectra.

Compound	$-O-SO_2-$ Bands (cm.$^{-1}$)		Compound	$-O-SO_2-$ Bands (cm.$^{-1}$)
	1145—1200 (s)	1330—1420 (s)	IV; R = Ph	1173, 1364
II; R = Ph	1164, 1348, 1384		V; R = Ph	1152, 1171, 1368
III; R = Ph ...	1164, 1372, 1384		VIII	1169, 1363

o-Acetylphenyl methanesulphonate (I; R = H) gave with potassium hydroxide and pyridine 2-*o*-hydroxyphenylprop-1-ene-1-sulphonic sultone (III; R = H), which with ethanolic alkali yielded *o*-hydroxyacetophenone (VI), and reacted as shown in the diagram to yield compound (V; R = H), and the acid (VII) which was characterised as the *S*-benzylthiuronium salt.



o-Acetylphenyl benzenesulphonate and toluene-*p*-sulphonate remained unchanged when treated with potassium hydroxide and pyridine. Attempts to effect the Baker–Venkataraman transformation of a number of *o*-acetylphenyl aroates using acid catalysts proved unsuccessful.

Experimental

Ethanol was employed for crystallisation if no solvent is mentioned.

Derivatives of o-Acetylphenyl Toluene-ω-sulphonate (I; R = Ph).—The product of the interaction of toluene-ω-sulphonyl chloride (5 g.), *o*-hydroxyacetophenone (3·5 g.), and pyridine (25 g.) was *o-acetylphenyl toluene-ω-sulphonate* which crystallised in plates (2·8 g.), m. p. 85—86° (Found: C, 61·9; H, 4·9; S, 10·9. $C_{15}H_{14}O_4S$ requires C, 62·1; H, 4·9; S, 11·0%). A mixture of this compound (5 g.), powdered potassium hydroxide (1 g.), and pyridine (25 g.) was shaken for 48 hr., acidified, and extracted with ether. Removal of the solvent gave *2-hydroxy-2-o-hydroxyphenyl-1-phenylpropane-1-sulphonic sultone* (II) which separated in prisms (2·3 g.), m. p. 202—203° (Found: C, 61·9; H, 5·1; S, 11·0. $C_{15}H_{14}O_4S$, see above). When the

toluenesulphonate was similarly treated with powdered potassium hydroxide and pyridine for 14 days it gave 2-o-*hydroxyphenyl*-1-*phenylprop*-1-*ene*-1-*sulphonic sultone* (III; R = Ph), which crystallised in prisms (4·6 g.), m. p. 173—174° (Found: C, 66·2; H, 4·5; S, 11·5. $C_{15}H_{12}O_3S$ requires C, 66·2; H, 4·4; S, 11·8%).

Reactions of Compound (II).—A mixture of the sultone (II) (5 g.) and phosphorus oxychloride (35 ml.) was refluxed for 2½ hr. The product was compound (III; R = Ph), m. p. and mixed m. p. 173—174°. This compound was also obtained by treatment of the sultone (II) for 14 days with powdered potassium hydroxide and pyridine or with acetic anhydride and perchloric acid (1 drop) for 1½ hr. Acetylation of the sultone (II) by acetic anhydride and sodium acetate gave 2-*acetoxy*-2-o-*hydroxyphenyl*-1-*phenylpropane*-1-*sulphonic sultone* (IV) which crystallised from ligroin in prisms, m. p. 148—150° (Found: C, 61·6; H, 5·0; S, 10·3. $C_{17}H_{16}O_5S$ requires C, 61·4; H, 4·9; S, 9·7%). Treatment of the sultone (II) with hydriodic acid in acetic anhydride at 150—160° for 1½ hr. gave 2-o-*hydroxyphenyl*-1-*phenylpropane*-1-*sulphonic sultone* (V; R = Ph), which crystallised from ligroin in needles, m. p. 107—108° (Found: C, 65·5; H, 4·9; S, 12·2. $C_{15}H_{14}O_3S$ requires C, 65·7; H, 5·1; S, 11·7%). Compound (II) was not changed by treatment with acetic anhydride and pyridine at 100°, or with selenium dioxide in boiling ethanol. It was insoluble in 10% aqueous sodium hydroxide. Hydrolysis with ethanolic alkali gave *o*-hydroxyacetophenone (VI).

Reactions of Compound (III; R = Ph).—When this compound was refluxed with hydriodic acid and acetic anhydride at 150—160° for 1½ hr. it gave the saturated sultone (V; R = Ph), m. p. and mixed m. p. 106—108°. It did not change when treated at the b. p. with potassium permanganate in glacial acetic acid, nor was it hydrolysed by ethanolic alkali.

Reactions of Compound (IV).—This compound when refluxed with hydriodic acid in acetic anhydride at 150—160° for 1½ hr. gave the saturated sultone (V), m. p. and mixed m. p. 106—108°; with phosphorus oxychloride for 2½ hr. at the b. p., or with hydrochloric acid (30%) and ethanol for 1 hr. at the b. p., it gave the unsaturated sultone (III; R = Ph), m. p. and mixed m. p. 173—174°.

Action of Alkali on the Sultone (V; R = Ph).—The sultone (0·5 g.) and 10% aqueous sodium hydroxide (10 ml.) were refluxed together for 3 hr. The *product* (VIII) crystallised in needles (0·3 g.), m. p. 158—160° (Found: C, 65·4; H, 4·8; S, 11·7. $C_{15}H_{14}O_3S$ requires C, 65·7; H, 5·1; S, 11·7%).

Derivatives of o-*Acetylphenyl Methanesulphonate* (I; R = H).—Interaction of methanesulphonyl chloride, *o*-hydroxyacetophenone, and pyridine gave o-*acetylphenyl methanesulphonate* which separated from light petroleum (b. p. 60—80°) in needles, m. p. 42—44° (Found: C, 50·7; H, 4·5; S, 14·5. $C_9H_{10}O_4S$ requires C, 50·5; H, 4·7; S, 14·9%). A mixture of this (2·5 g.), powdered potassium hydroxide (0·5 g.), and pyridine (30 g.) was shaken for 48 hr., acidified, and extracted with ether. Removal of the solvent gave 2-o-*hydroxyphenylprop*-1-*ene*-1-*sulphonic sultone* (III; R = H) which crystallised in plates (1·7 g.), m. p. 86—87° (Found: C, 55·2; H, 3·9; S, 16·4. $C_9H_8O_3S$ requires C, 55·1; H, 4·1; S, 16·3%).

Reactions of the Sultone (III; R = H).—A mixture of the sultone (1 g.), benzaldehyde (1 g.), ethanol (25 ml.), and 50% aqueous sodium hydroxide (2·5 g.) was kept for 48 hr. The solid product was added to ice and hydrochloric acid. The precipitate crystallised in yellow needles, m. p. and mixed m. p. with *o*-hydroxyphenyl styryl ketone, 88—89° (Found: C, 80·8; H, 5·5. Calc. for $C_{15}H_{12}O_2$: C, 80·3; H, 5·4%). The sultone was not hydrolysed when refluxed with aqueous sodium hydroxide (15%, 25%, or 35%) for 30 min. Ethanolic alkali gave the phenol (VI). 2-o-*Hydroxyphenylpropane*-1-*sulphonic sultone* (V; R = H), which was obtained when the sultone (III; R = H) was refluxed with hydriodic acid for 1½ hr., separated from ligroin in needles, m. p. 62—64° (Found: C, 54·6; H, 5·1; S, 16·4. $C_9H_{10}O_3S$ requires C, 54·5; H, 5·1; S, 16·2%).

A mixture of the sultone (V; R = H) (1·3 g.) and 10% aqueous potassium hydroxide (15 ml.) was refluxed for 3 hr. The product was added to aqueous *S*-benzylthiuronium chloride. S-*Benzylthiuronium* 2-o-*hydroxyphenylpropane*-1-*sulphonate* (see VII) crystallised from aqueous ethanol in plates (1·6 g.), m. p. 171—173° (Found: C, 53·2; H, 6·1; N, 7·3; S, 16·8. $C_{17}H_{22}O_4N_2S_2$ requires C, 53·4; H, 5·8; N, 7·3; S, 16·7%).

Attempts to cyclise *o*-acetylphenyl methanesulphonate (I; R = H) to 2-*o*-hydroxyphenylprop-1-ene-1-sulphonic sultone (III; R = H) by using boron trifluoride at 0° or anhydrous glycerol[4] at 270—280° proved unsuccessful.

o-*Acetylphenyl benzenesulphonate* (from *o*-hydroxyacetophenone, benzenesulphonyl chloride,

[4] Dunne, Gowan, Keane, O'Kelly, O'Sullivan, Roche, Ryan, and Wheeler, *J.*, 1950, 1252.

and pyridine) separated from light petroleum (b. p. 60—80°) in plates, m. p. 71—72° (Found : C, 60·9; H, 4·5; S, 11·7. $C_{14}H_{12}O_4S$ requires C, 60·9; H, 4·4; S, 11·6%).

o-*Acetylphenyl toluene*-p-*sulphonate* separated in needles, m. p. 95—96° (Found : C, 62·2; H, 4·9; S, 10·7. $C_{15}H_{14}O_4S$ requires C, 62·1; H, 4·9; S, 11·0%).

COLLEGE OF PHARMACY, DUBLIN.
TRINITY COLLEGE, DUBLIN.
UNIVERSITY COLLEGE, DUBLIN.

[*Received, June 15th,* 1956.]