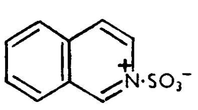
259. *The Ring Fission of* iso*Quinoline–Sulphur Trioxide.*

By K. T. Potts.

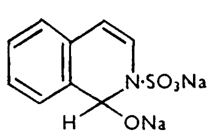
The disodium salt of 1 : 2-dihydro-1-hydroxy*iso*quinoline-2-sulphonic acid (II) is proposed as the constitution of the product obtained by the action of cold aqueous sodium hydroxide on *iso*quinoline–sulphur trioxide.[1]

Baumgarten and Olshausen [1] first investigated the action of cold, aqueous sodium hydroxide on *iso*quinoline–sulphur trioxide (I) and concluded that ring fission occurred, giving a salt (III). The colourless acid, obtained from the salt on treatment with dilute acids, was designated as (IV). This is analogous to the intermediates assumed to be formed in the hydrolysis of pyridine–sulphur trioxide.[2]

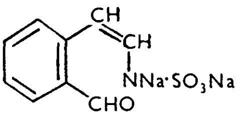
On re-investigation of this reaction it became apparent from spectral studies that the structure of the product obtained was more correctly represented as (II), the disodium salt of 1 : 2-dihydro-1-hydroxy*iso*quinoline-2-sulphonic acid.



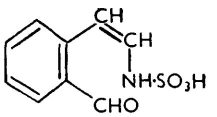
(I)



(II)



(III)



(IV)

The empirical formula was confirmed as $C_9H_7O_4NSNa_2,2H_2O$ and its properties agreed with those previously reported. The infrared spectrum (in Nujol) showed absorption bands at 2·90 (s) * (an associated OH from the water of crystallisation present), 6·14 (m) (aromatic nucleus), and 8·10 and 8·45 μ (s) (sodium sulphonate group). The most significant feature was the absence of carbonyl absorption which should be present for a compound (III). [In the spectrum (Nujol) of the monosodium salt of glutacondialdehyde [3] a characteristic carbonyl absorption band occurs at 6·25 μ (vs), the absorption at slightly longer wavelength (usual absorption, *ca.* 5·9 μ) being due to the extensive conjugation and high symmetry of the molecule.]

The acid liberated by treatment of this salt with dilute acid should likewise have infrared carbonyl absorption if it were correctly represented by (IV). Its spectrum was found to be identical with that of the original *iso*quinoline–sulphur trioxide (I); it had the general broad absorption of salts, a band at 6·25 μ (m) which experience in this laboratory has indicated is generally associated with the carbon–nitrogen double bond present in *iso*quinolinium salts (6·2—6·3 μ), and bands at 9·45 and 9·55 μ (s) (sulphonic anhydride). [In a recent paper, Witkop [4] regards salt formation in pyridines as causing an absorption at 6·07—6·13 μ.] The analytical results and properties of this compound agree with this interpretation and the m. p. was not depressed on admixture with freshly prepared *iso*quinoline–sulphur trioxide.

The ultraviolet spectra of *iso*quinoline–sulphur trioxide (I) (max. at 2650, 2750, and 3320 Å) and the sodium salt (II) (max. at 2750 and 3350 Å) are analogous to those of cotarnine hydrochloride [5, 6] (max. at 2500 and 3278 Å, ammonium form) and aqueous solutions of the hydrochloride in the presence of an excess of 2N-sodium hydroxide (ill-defined max. at 2875 Å, carbinol form) and berberine.[6]

A solution of the salt (II) in 50% ethanol had pH 11·8 and on titration with 0·1N-hydrochloric acid the neutralisation curve indicated the presence of a strong base. An

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* Usual convention.

[1] Baumgarten and Olshausen, *Ber.*, 1931, **64**, 925.

[2] Baumgarten, *Ber.*, 1926, **59**, 1166.

[3] *Idem, Ber.*, 1924, **57**, 1622.

[4] Witkop, *Experientia*, 1954, 420.

[5] Dobbie, Lauder, and Tinkler, *J.*, 1903, **83**, 598.

[6] Skinner, *J.*, 1950, 823.

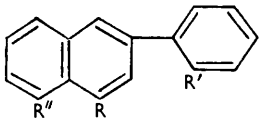
inflexion occurred at pH 4·3 and is due to a process involving addition of a proton to the sulphonate ion and then immediate elimination of water from the resulting sulphonic acid. However, the presence of a strong base in solution can be explained by both formulæ; for a structure (IV) it would be expected that the imino-hydrogen atom would be weakly acidic and the sodium salt (III) would give an equivalent of hydroxyl ions in solution. A similar argument may be used for a structure (II).

Attempts to show that the salt (II) undergoes the normal reactions of *pseudo*-bases, *e.g.*, ether formation and the reaction with nitromethane, were unsuccessful owing to the instability of the molecule.

This type of carbinolamine formation is well established in the *iso*quinoline series, *e.g.*, the carbinolamines derived from 2-methyl*iso*quinolinium salts [7] and various *iso*quinoline alkaloids.

As shown recently,[8] the further action of hot, aqueous sodium hydroxide on the compound (I) affords 4 : 2′-diformyl-2-phenylnaphthalene (V) and not the dialdehyde (VI) as stated by Baumgarten and Olshausen. Hence the naphthalenedicarboxylic acid prepared by the above authors has structure (VII) and accordingly the structure of their 1 : 2-benzofluorenonecarboxylic acid must be amended to (VIII). Their cyclisation of the acid (VII) to 2 : 3-benzofluorenone (IX) by distillation with lime is interesting in that it is an exception to the usual mode of ring closure in the naphthalene series where cyclisation almost always occurs on to the 1-position in preference to the 3-position. It is possible that this ring closure might occur by a method similar to that of the diphenic acid cyclisation,[9] but a more attractive explanation is as follows.

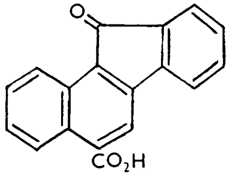
Under the influence of heat there is a tendency for carbon dioxide to be eliminated from the calcium salt of (VII). This leaves a negative charge at position 4, and, after prototropic rearrangement of the hydrogen atom from the 3- to the 4-position of the naphthalene nucleus, a negative charge on the 3-position. The final step probably involves a nucleophilic attack of the 3-position on the carbon atom of the other carboxylate ion. This scheme is represented in (X). No close formal analogy to such a 1 : 2-prototropic rearrangement can be recalled but it would not be surprising in view of the reaction conditions employed.



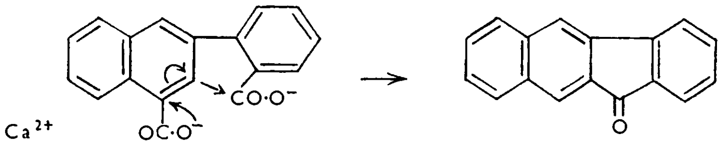
(V): R=R′=CHO, R″=H

(VI): R′=R″=CHO, R=H

(VII): R=R′=CO$_2$H, R″=H



(VIII)



(X) (IX)

Several improvements in the original methods employed by Baumgarten are described in the Experimental section.

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[7] Robinson and Robinson, *J.*, 1914, **105**, 1456.

[8] Potts and Robinson, *J.*, 1955, 2466.

[9] Fittig and Ostermayer, *Annalen*, 1873, **166**, 372.

EXPERIMENTAL

Light absorptions refer to MeOH solutions.

Treatment of iso*Quinoline–Sulphur Trioxide with Alkali.*—*iso*Quinoline–sulphur trioxide[8] (2·1 g.) was triturated with ice-cold sodium hydroxide solution (2·4 g. in 7 c.c. of water) with cooling in an ice-salt bath. An immediate yellow colour was produced and the material soon set to a paste. Washing with cold alcohol removed the yellow impurity and the white, crystalline *disodium salt* of 1 : 2-dihydro-1-hydroxy*iso*quinoline-2-sulphonic acid (3·6 g.) was collected and dried (Found: C, 35·4; H, 4·4; Na, 15·0, 15·2. $C_9H_7O_4NSNa_2,2H_2O$ requires C, 35·2; H, 3·6; Na, 15·0%). Light absorption: $\lambda_{max.}$ 2350, 2750, 3350 Å (log ε 4·40, 3·58, 3·38), $\lambda_{min.}$ 2500, 3000 Å (log ε 3·22, 3·14).

Treatment of the Disodium Salt with Acid.—A solution of the disodium salt (3·6 g.) in water (50 c.c.) was made just acid to litmus with dilute hydrochloric acid; an immediate white precipitate was formed. When washed with ice-water, and dried, this had m. p. 253—256°, not depressed on admixture with freshly prepared *iso*quinoline–sulphur trioxide (Found: C, 51·8, 51·3; H, 3·7, 3·3; N, 7·3, 6·8. Calc. for $C_9H_7O_3NS$: C, 51·6; H, 3·4; N, 6·8%). Light absorption: $\lambda_{max.}$ 2300, 2650, 2750, 3320 Å (log ε 4·38, 3·44, 3·44, 3·72), $\lambda_{min.}$ 2500, 2700, 2950 Å (log ε 3·23, 3·43, 3·05).

2-*Phenylnaphthalene*-2′ : 4-*dicarboxylic Acid.*—2-Phenylnaphthalene-2′ : 4-dialdehyde[8] (2·0 g.) and potassium permanganate (2·0 g.) in acetone (50 c.c.) were refluxed for 90 min. After 12 hr. at room temperature the manganese dioxide was filtered off and suspended in water (30 c.c.), and sulphur dioxide passed into the mixture. The manganese dioxide was replaced by pale cream-coloured needles (2·0 g., 89%), m. p. 258—268° after shrinking at *ca.* 240°. 3-o-*Carboxyphenyl*-1-*naphthoic acid,* crystallized from 50% methanol, had m. p. 261—262° after shrinking (Baumgarten and Olshausen reported m. p. 267—268° (Found: C, 74·2; H, 4·3. $C_{18}H_{12}O_4$ requires C, 74·0; H, 4·1%). Light absorption: $\lambda_{max.}$ 2400, 2950 Å (log ε 4·38, 3·77), $\lambda_{min.}$ 2800 Å (log ε 3·73). The acid gave a yellow colour, changing to a dirty brown on warming, with concentrated sulphuric acid; it was only slightly soluble in concentrated nitric acid, and, on warming, gave a yellow solution with evolution of brown fumes.

2-*Phenylnaphthalene.*—The above dicarboxylic acid (200 mg.), copper bronze (200 mg.), and quinoline (5 c.c.) were heated under reflux for 30 min. After cooling, the mixture was diluted with ether and extracted with dilute hydrochloric acid (3 × 10 c.c.). The ether solution was washed with water and dried (Na_2SO_4). The small amount of oil left on evaporation soon crystallized. It separated from aqueous methanol (charcoal) as white plates, m. p. 100—101° (Breuer and Zincke[10] record m. p. 101·5°).

1 : 2-*Benzofluorenone.*—1 : 2-Benzofluorenone-3-carboxylic acid (200 mg.) was heated with copper bronze (300 mg.) in quinoline (5 c.c.) for 30 min. Working up as in the preceding experiment, but with alkali washing, gave 1 : 2-benzofluorenone, orange-red needles (from methanol; charcoal), m. p. 132° (Bamberger and Burgdorf[11] report m. p. 132·5°) (Found: C, 88·8; H, 4·8. Calc. for $C_{17}H_{10}O$: C, 88·6; H, 4·4%). Light absorption: $\lambda_{max.}$ 2700, 3725 Å (log ε 4·77, 3·54), $\lambda_{min.}$ 3300 Å (log ε 3·13).

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[10] Breuer and Zincke, *Ber.*, 1878, **11**, 1404.
[11] Bamberger and Burgdorf, *Ber.*, 1890, **23**, 2439.