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Studies on Lignin

XVIII.* Sulphite Cooking of Salicil

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Salicil (II) when subjected to a sulphite cook in neutral or slightly alkaline medium gave phenol, salicoylformic acid and xanthene-9-sulphonic acid (VIII). Similarly 4,5-dihydro-2,3;6,7-dibenzoxepin-dione-(4,5) (IX) and salicilic acid (V), the former in excellent yield, both furnished VIII. Salicil was oxidised to disalicylide (IV) with lead *tetra*-acetate indicating that salicil can react in the cyclised form IIIa.

At one stage in our researches on the sulphonation of lignin it was suggested that "group B" which is sulphonated only at a low pH but not with neutral sulphites might possess a *cyclo*-acetal structure of the type I [1]. However, our further studies especially on the sulphonation of various benzylalcoholic model substances and their ethers soon made this hypothesis superfluous [2] and in a recent publication [3] we have shown that *cyclo-hemi*-acetals of this type (I, R = H) are unstable.

Not entirely unexpectedly salicil (II) shows a greater tendency to react in the *bis-cyclo*-acetal form (IIIa) and for example we have found that it readily forms a dimethyl acetal (IIIb) which will be described in a forthcoming publication. Further it gives disalicylide (IV) in good yield when treated with lead *tetra*-acetate in acetic acid.

Hence it was of interest to investigate whether salicil reacts, when subjected to sulphite cooking, with formation of a sulphonic acid.

However, salicil did not react with a normal "acid sulphite cooking acid" and was recovered unchanged, but at pH 7—10 a series of interesting reactions occurred resulting in the formation of phenol, salicoylformic acid, and a sulphonic acid, (Scheme 1, VI, VII and VIII, respectively) the sparingly soluble sodium salt of which separated from the reaction mixture on cooling.

The free sulphonic acid was very unstable but the sodium salt when oxidised with permanganate furnished xanthone in good yield. This lead to the assumption that the sulphonic acid was xanthene-9-sulphonic acid and this

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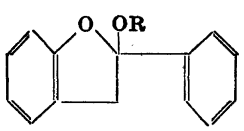
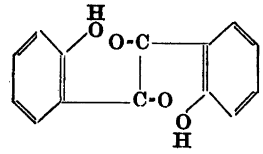
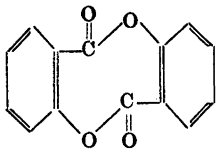


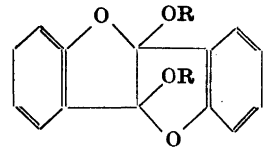
I



II



IV

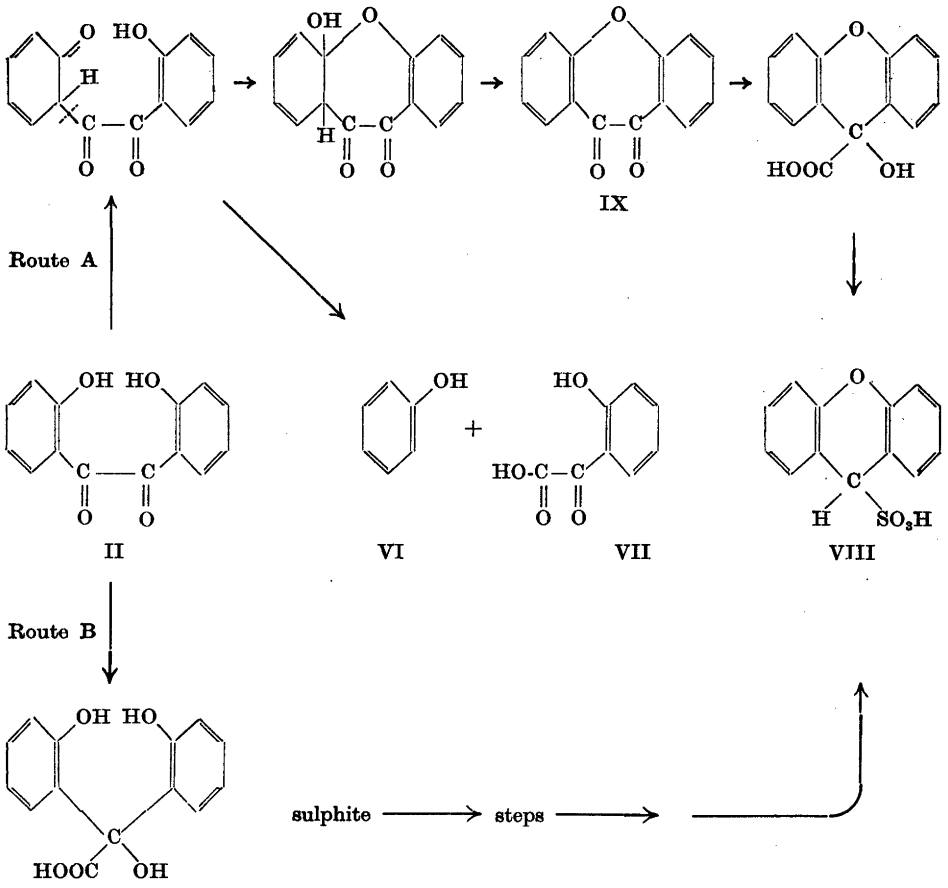


III a R = H
III b R = CH_3

was confirmed by direct sulphonation of xanthydrol and identification of the sodium salts of the sulphonic acids by means of their X-ray powder photographs.

The formation of phenol and salicoylformic acid is easy to understand. It simply represents a hydrolytic fission as indicated in scheme 1 (Route A) and phenol was, moreover, obtained when salicil was heated with a saturated sodium bicarbonate solution in the same way as in the case of the sulphite cook. A similar case has recently been recorded [4].

There are several ways in which the formation of xanthene-9-sulphonic acid can be explained. One is illustrated in scheme 1 (Route B) and involves the intermediate formation of salicilic acid (V) which suffers dehydration, decarboxylation and sulphonation to xanthene-9-sulphonic acid as indicated in the scheme. Salicilic acid was obtained by a rather drastic treatment of salicil with strong alkali although it was impossible to isolate the compound in a completely pure state. It was characterised by conversion into the dimethyl ether and into the diacetate of salicilic acid lactone both of which are readily obtainable in good yield from the crude salicilic acid preparation. This crude preparation, when subjected to a sulphite cook under the conditions employed for salicil furnished xanthene-9-sulphonic acid in moderate yield. In view of this and because it seems improbable that salicil would readily undergo a benzilic acid rearrangement under the conditions employed it appears doubtful that the formation of xanthene-9-sulphonic acid from salicil proceeds *via* salicilic acid. An alternative reaction mechanism was therefore considered involving the intermediate formation of 4,5-dihydro-2,3;6,7-dibenzoxepindione-(4,5) (IX, Scheme 1: route A) which would bear some analogy with tropolones and therefore might readily rearrange to 9-hydroxyxanthene-9-carboxylic acid. A synthesis of this compound was contemplated when recently Mathys, Prelog and Woodward [5] reported its synthesis and also commented upon its facile rearrangement to 9-hydroxyxanthene-9-carboxylic acid with even weak alkali. Through the courtesy of Professor V. Prelog to whom we extend our



Scheme 1.

gratitude, we have been able to investigate the action of sulphite on this compound. It was found to give an excellent yield of xanthene-9-sulphonic acid and it therefore appears probable that the formation of xanthene-9-sulphonic acid from salicil largely follows route A in scheme 1.

EXPERIMENTAL *

Lead tetra-acetate oxidation of salicil. To salicil (0.5 g) in acetic acid (15 ml) was added a solution of lead *tetra*-acetate (1 g) in acetic acid (10 ml). The mixture was heated to 70° and then left for one hour at room temperature. On cooling disalicylide precipitated in rhombic crystals. The crude reaction product (0.4 g, yield 80 %) had a m. p. 165—195° which was raised to 225—230° by repeated crystallisation from chloroform. The compound gave an I. R. spectrum identical with that of authentic disalicylide prepared according to Baker *et al.*[6].

* All melting points uncorrected.

Sulphite cooking of salicil. Here and in the following experiments the "cooking acid" was prepared by bubbling sulphur dioxide into 10 % aqueous sodium hydroxide until the desired pH was reached. The cookings were all carried out in sealed tubes at 135° C.

pH 1.5. Salicil (1.1 g) was heated with "cooking acid" (50 ml) for 20 hours. After cooling the solid (1.07 g) was collected and recrystallised from ethanol to give yellow needles, m. p. 153—154°, undepressed on admixture with salicil.

pH 7.1. Salicil (5 g) was heated with "cooking acid" (70 ml) for 8 hours. After cooling, the sodium salt of the sulphonic acid VIII (1.5 g, yield 25 %) was collected by filtering. The filtrate (pH 6.9) was extracted with ether and the ether solution evaporated to give phenol (1 g, yield 51 %). The aqueous phase was run through a cation exchanger, immediately neutralised with barium carbonate and filtered and evaporated to give the barium salt of salicoylformic acid (3.5 g, yield 72 %).

Identification of phenol (VI). The phenol was transformed into phenoxyacetic acid and into *tri*-bromophenol, both derivatives showing no melting point depression when mixed with authentic specimens.

Identification of salicoylformic acid (VII). The barium salt (1.5 g) was dissolved in water, excess of 2 N sodium hydroxide (5 ml) was added and carbon dioxide bubbled into the solution which was then filtered and weakly acidified with dilute hydrochloric acid. Phenylhydrazine (0.5 ml) was added and the solution heated to boiling. After cooling the reaction product (1 g), m. p. *ca.* 148°, was collected and dissolved in acetic acid (20 ml). Conc. hydrochloric acid (1 drop) was added and the solution heated to boiling. A crude reaction product (about 1 g, yield 67 %) was obtained which was recrystallised from acetic acid to yield yellow prisms, m. p. 184—185°, undepressed on admixture with coumarandion-3-phenylhydrazone prepared according to Fries *et al.*[7].

Identification of the sulphonic acid (VIII). The sodium salt was recrystallised from ethanol to yield white needles. A sample of the salt (0.93 g) was dissolved in water (5 ml) and heated for one hour on a steam bath, finely powdered potassium permanganate (0.59 g) g) being added from time to time. After cooling the reaction mixture was saturated with sulphur dioxide and filtered. A crystalline product (0.4 g, yield 67 %) was obtained which was recrystallised from ethanol to give colourless needles m. p. 172—173°. The reaction product was soluble in conc. sulphuric acid with a yellow colour exhibiting a strong blueish fluorescence. Admixture with xanthone did not depress the melting point.

After drying in a high vacuum a sample of the sodium salt (43.8 mg) was dissolved in water and after cation exchange titrated with 0.0417 N sodium hydroxide (3.68 ml). (Found: Equiv. weight 285. Calc. for $C_{13}H_9O_4S$ Na: Equiv. weight 284). The *cyclohexylammonium salt* of the sulphonic acid was prepared by running an ethanolic solution of the sodium salt through a cation exchanger into an ethereal solution of *cyclo*hexylamine. The crystalline precipitate was collected and recrystallised several times from ethanol yielding white needles without distinct melting point which started to decompose with a red colour at about 230°. (Found: C 62.9; H 6.5; N 4.0; S 8.9. Calc. for $C_{19}H_{23}NO_4S$: C 63.1; H 6.4; N 3.9; S 8.9).

Sulphite cooking of xanthydrol. Xanthydrol (5 g) was heated with "cooking acid" (70 ml, pH 7) for 8 hours. The crystalline reaction product (6.5 g, yield 91 %) was recrystallised from ethanol and the product shown to have an X-ray powder photograph identical with that of the sulphonic acid sodium salt obtained by sulphite cooking of salicil.

Salicilic acid (V). With vigorous mechanical stirring salicil (5 g) in 2 N sodium hydroxide (50 ml) was heated on a steam bath and solid sodium hydroxide (100 g) was added in portions. A yellowish brown semi-solid product was precipitated which crystallised on continued stirring forming an almost colourless suspension. The reaction mixture was poured into finely crushed ice (1 l) and carefully acidified with conc. hydrochloric acid (250 ml) and extracted with ether. The ether solution was washed with water and then extracted with saturated aqueous sodium bicarbonate (2 × 25 ml). The bicarbonate solution was acidified with 2 N hydrochloric acid (40 ml) to yield the reaction product as an oil which crystallised on standing. The crude salicilic acid (5 g) was collected by filtration, washed with cold water and dried. M. p. 100—110°. Repeated attempts to recrystallise the acid from water and from benzene yielded a red-coloured product without distinct melting point.

Salicilic acid dimethyl ether. The crude salicilic acid (2.6 g) was dissolved in 2 N sodium hydroxide (20 ml) and shaken with dimethyl sulphate (3 ml). The reaction mixture was boiled for five minutes, then cooled and acidified with dilute sulphuric acid. The crystalline reaction product (2 g, yield 71 %) was recrystallised several times from ethanol to yield the pure dimethyl ether, m. p. 160.5—161°, undepressed on admixture with *o,o'*-dimethoxybenzilic acid prepared according to Ford-Moore [8].

Salicilic acid lactone diacetate. The crude salicilic acid was dissolved in pyridine and acetic anhydride added. The solution was heated for some minutes and then poured into ice. The crystalline reaction product was collected and recrystallised from ethanol (charcoal) to yield colourless plates, m. p. 167—169.5°. Distillation at 1 mm Hg raised the m. p. to 169—169.5°. (Found: C 66.2; H 4.5. Calc. for $C_{18}H_{14}O_6$: C 66.3; H 4.3).

Sulphite coking of salicilic acid. Crude salicilic acid (0.5 g) was heated with "cooking acid" (10 ml, pH 7) for 8 hours. The reaction mixture was cooled and filtered to yield xanthene-9-sulphonic acid sodium salt (0.1 g, yield 18 %).

Sulphite cooking of 4,5-dihydro-2,3:6,7-dibenzoxepindione-(4,5). The dihydrodibenzoxepindione (90 mg) was heated with "cooking acid" (1 ml, pH 7) for 8 hours. On cooling, the sodium salt of xanthene-9-sulphonic acid (100 mg, yield 87 %) precipitated.

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