357. *A Rearrangement of Aryl Salicylates.*

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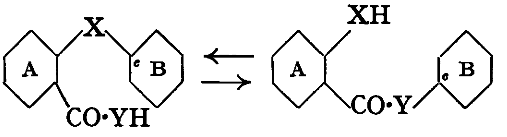
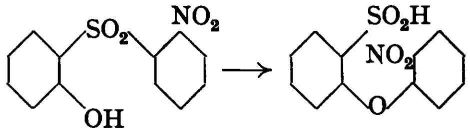
According to the results obtained in previous studies of intramolecular displacements the conversion of aryl salicylates (a) into *o*-carboxydiphenyl ethers may be expected. It is now shown that, given suitable intramolecular conditions, this process may be realised under relatively mild external conditions. For example, in presence of aqueous sodium hydroxide at 100° (1·25 mols., N) 4-nitrophenyl salicylate gave a high yield of *4'-nitro-2-carboxydiphenyl ether*. The extension of this type of rearrangement to derivatives of phenyl esters of phenol-*o*-sulphonic acids (b) also is demonstrated. In esters of types (a) and (b) the tendency of carboxyl and sulphonyl to acquire the alkali metal of the phenoxides is shown by the isolation of covalent *sodium* derivatives from both types and it is suggested that this tendency assists the rearrangements in question.

THE behaviour of carbamyl sulphones and sulphides (Evans and Smiles, J., 1936, 329) showed the possibility of interconverting systems such as (I) and (II); moreover, the inactivity of 2'-nitrodiphenylsulphone-2-carboxylic acid compared with the easy conversion (J., 1934, 184) of 2'-nitro-2-hydroxydiphenylsulphone (III) into the sulphinic acid (IV) indicates the relative displacement values of phenolic and carboxylic hydroxyl in these rearrangements. According to these views and the results of previous experiments dealing with the general intramolecular conditions favouring this type of process (J., 1934, 422; 1935, 181) it may be expected that aryl salicylates (II, X = Y = O) in which the carbon atom *c* is sufficiently positive should be converted in alkaline media into the *o*-carboxydiphenyl ethers (I, X = Y = O). Some confirmation of this is found in the work of Graebe (*Ber.*, 1888, **21**, 502) and of Arbenz (*Annalen*, 1890, **257**, 78), who showed that under intense conditions (280° approx.) the potassium derivative of phenyl salicylate yields the salt of *o*-carboxydiphenyl ether, the high temperature required and the poor yields being apparently due to the feebly positive character of the phenyl group. By increasing the positive character of *c* it has now been shown that this process is, within the limits of suitable substitution in A and B, of general application. When the nucleus B contains a *p*-nitro-group, the rearrangement may be effected at 100° with high yield of the diphenyl ether; 4-nitrophenyl salicylate, for example, yielded *4'-nitro-2-carboxydiphenyl ether*. The process is illustrated by four other examples; in most of these the carboxylic acid has been identified by decarboxylation and comparison of the resulting ether with synthetic material. A quantitative study of the influence of substitution in the salicylic nucleus (II, A) has not been possible owing to concurrent hydrolysis which was observed in all the cases studied. It should, however, be noticed that 4-nitrophenyl 5-nitrosalicylate did not undergo rearrangement; this result accords with those previously obtained in the study of the rearrangement of 2′-nitro-2-hydroxydiphenylsulphones and is evidently due to increased stability of the phenolic ion under the influence of *p*-nitro-substitution.

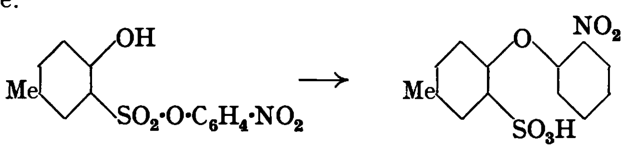


(I.) (II.)

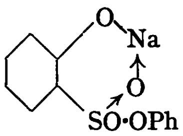


(III.) (IV.)

The obvious extension of this type of intramolecular displacement to the corresponding sulphonates has been realised. In illustration the conversion of *2-nitrophenyl 4-hydroxytoluene-3-sulphonate* (V) into 2-nitrophenyl 3-sulpho-*p*-tolyl ether (VI) may be noticed; the product was identified by conversion into the anilide, which was available from another source.



(V.) (VI.)



(VII.)

In conclusion attention is directed to the isolation of the *sodium* salts of phenyl salicylate and phenyl 4-hydroxytoluene-3-sulphonate in the covalent state (compare VII). The behaviour of the latter is similar to that of the *o*-hydroxy-sulphones (this vol., p. 899) and it is suggested that this tendency of carboxyl and sulphonyl in the esters to acquire the alkali metal assists the initial stage of the rearrangements now described.

EXPERIMENTAL.

The 4-nitrophenyl esters were prepared either (a) by the method described in D.R.-P. 43,713, which consists in fusing (140°) 4-nitrophenol (1 mol.) with the acid concerned (1 mol.) in presence of phosphorus pentachloride (0·25 mol.) until liberation of hydrogen chloride ceases, or (b) more generally and with higher yield by boiling a solution of the reactants in xylene which contained phosphorus pentachloride (0·35 mol.) in suspension. After the solvent had been removed by steam, the residue was triturated with aqueous sodium carbonate and purified from a suitable solvent. The yield was usually about 50% of the theoretical.

(1) *4-Nitrophenyl 4-hydroxy-*m*-toluate*, from 4-nitrophenol and *p*-cresotic acid, formed plates m. p. 136°, from alcohol (Found : C, 61·4; H, 4·0; N, 5·2. $C_{14}H_{11}O_5N$ requires C, 61·5; H, 4·0; N, 4·5%).

(2) *4-Nitrophenyl 2-hydroxy-*m*-toluate*, from 4-nitrophenol and *o*-cresotic acid, formed plates, m. p. 153°, from alcohol (Found : C, 62·0; H, 3·9; N, 5·0. $C_{14}H_{11}O_5N$ requires C, 61·5; H, 4·0; N, 5·1%).

(3) *4-Nitrophenyl 5-chloro-2-hydroxybenzoate*, from 5-chlorosalicylic acid by method (b), formed needles, m. p. 164°, from acetic acid (Found : C, 53·1; H, 3·0. $C_{13}H_8O_5NCl$ requires C, 53·1; H, 2·7%).

(4) *4-Nitrophenyl 2-hydroxy-3-naphthoate* formed yellow prisms, m. p. 164°, from benzene (Found : C, 66·2; H, 3·8; N, 4·3. $C_{17}H_{11}O_5N$ requires C, 66·0; H, 3·6; N, 4·5%).

(5) *4-Nitrophenyl 5-nitro-2-hydroxybenzoate* formed needles, m. p. 200°, from acetone (Found : N, 9·4. $C_{13}H_8O_7N_2$ requires N, 9·2%).

(6) 2 : 4 : *6-Trichlorophenyl salicylate*, by method (a), formed needles, m. p. 125°, from alcohol (Found : C, 48·8; H, 2·5. $C_{13}H_7O_3Cl_3$ requires C, 49·1; H, 2·2%).

The rearrangement of 4-nitrophenyl salicylate and the esters 1, 2, 3 and 4 was effected by boiling N-sodium hydroxide (1·25 mols.) (1·25 hrs.). In most cases a sparingly soluble sodium salt of the phenolic ester was at first formed, but this dissolved as the reaction proceeded. The product was liberated from the cooled solution by dilute sulphuric acid and purified by resolution in aqueous sodium carbonate before recrystallisation from a suitable solvent. Decarboxylation of the acid was attained by heating the dry silver salt (190°), the required ether being generally removed from the product by a current of steam.

Synthesis of the 4-nitrodiphenyl ethers was effected by usual methods.

4′-Nitro-2-carboxydiphenyl ether, prisms, m. p. 161°, from benzene (Found: C, 60·3; H, 3·6; N, 5·3. $C_{13}H_9O_5N$ requires C, 60·2; H, 3·5; N, 5·4%), was obtained from 4-nitrophenyl salicylate (m. p. 150°). The yield (70%) was improved by heating the aqueous suspension of the yellow sodium salt of the ester and diminished by the use of more concentrated alkali, hydrolysis being then more extensive. Decarboxylation of the acid gave 4-nitrodiphenyl ether, which was identical with a synthetic specimen.

*4-Nitrophenyl 3-carboxy-*p*-tolyl ether* formed long needles, m. p. 173°, from alcohol (Found: C, 61·6; H, 4·0; N, 5·1. $C_{14}H_{11}O_5N$ requires C, 61·5; H, 4·0; N, 5·1%). It was obtained (60%) from the ester (1) and when decarboxylated yielded 4-nitrophenyl *p*-tolyl ether, m. p. 64°, which was identical with a sample synthesised from 4-chloronitrobenzene and sodium *p*-tolyloxide.

*4-Nitrophenyl 3-carboxy-*o*-tolyl ether*, from the ester (2), formed plates, m. p. 143°, from acetic acid (Found: C, 61·4; H, 3·7; N, 5·2. $C_{14}H_{11}O_5N$ requires C, 61·5; H, 4·0; N, 5·1%). The *methyl* ester formed prisms, m. p. 99°, from methyl alcohol (Found: C, 62·8; H, 4·3. $C_{15}H_{13}O_5N$ requires C, 62·7; H, 4·5%).

4-Chloro-4′-nitro-2-carboxydiphenyl ether, from the ester (3) in 75% yield, separated from benzene in needles, m. p. 174—175° (Found: C, 53·2; H, 3·0; N, 5·0; Cl, 12·1. $C_{13}H_8O_5NCl$ requires C, 53·1; H, 2·7; N, 4·8; Cl, 12·1%). By decarboxylation it gave 4-chloro-4′-nitrodiphenyl ether, m. p. 77°, which was identical with a product of synthesis (Raiford and Gilbert, *J. Amer. Chem. Soc.*, 1926, **48**, 2660).

4-Nitrophenyl 3-carboxy-β-naphthyl ether, from the ester (4) in 70% yield, had m. p. 208° after purification from hot alcohol (Found: C, 66·0; H, 3·7; N, 4·5. $C_{17}H_{11}O_5N$ requires C, 66·0; H, 3·6; N, 4·5%). Attempts to decarboxylate the substance were not successful.

The esters (5) and (6) were partly hydrolysed under the stated conditions and no evidence of rearrangement was found.

2-Nitrophenyl 4-Hydroxytoluene-3-sulphonate (V).—Potassium *o*-nitrophenoxide (1 mol.) and *O*-carbethoxy-*p*-cresol-3-sulphonyl chloride (1 mol.) (Bennett, Lesslie, and Turner, J., 1937, 445) were heated (100°, ½ hr.). After the cooled and powdered mass had been washed with dilute sodium hydroxide solution and then with water, the carbethoxy-group was removed by hydrolysis with N-alcoholic sodium hydroxide (3 mols., 15°). The solvent was removed from the resulting solution after this had been neutralised. An ethereal solution of the residual oil was dried and evaporated, the crystalline residue being finally purified by diluting the cold solution in acetic acid. The *ester* (V) formed needles, m. p. 88°, which gave a sparingly soluble sodium salt, and a greenish-yellow colour with ferric chloride in alcohol (Found: C, 50·6; H, 3·5; N, 4·5. $C_{13}H_{11}O_6NS$ requires C, 50·5; H, 3·5; N, 4·5%). Rearrangement of this ester was effected by boiling its solution in alcoholic sodium hydroxide (0·25N; 1 mol.; ½ hr.). After the solvent and some *o*-nitrophenol had been removed by steam, the remaining solution was evaporated and the residue, consisting of the sodium sulphonate (VI), was identified by conversion into the chloride and anilide.

*4-*o*-Nitrophenoxytoluene-3-sulphonyl Chloride.*—(a) The dried (120°) sodium sulphonate (1 mol.) resulting from the rearrangement of (V) was heated (130°, 1 hr.) with phosphorus pentachloride (1 mol.). The *product*, isolated as usual, crystallised from acetic acid in pale yellow prisms, m. p. 132° (Found: N, 4·5. $C_{13}H_{10}O_5NClS$ requires N, 4·3%). (b) 2-Nitrophenyl 3-sulphino-*p*-tolyl ether (J., 1931, 3267) was converted into the sulphonyl chloride by the method of Thomas (J., 1900, **77**, 342). When aqueous sodium hypochlorite (38 c.c., 6%) was added to the solution of the sodium sulphinate (6 g.), the sulphonyl chloride separated as a semi-solid mass; this, after purification, had m. p. 132° and was identical with the product obtained by method (a).

*4-*o*-Nitrophenoxytoluene-3-sulphonanilide* was obtained from the chloride resulting from either (a) or (b) by reaction with aniline; it formed prisms, m. p. 157°, from alcohol (Found: N, 7·4. $C_{19}H_{16}O_5N_2S$ requires N, 7·3%).

Phenyl 4-Hydroxytoluene-3-sulphonate.—This was obtained by boiling an acetone solution of phenol (1 mol.) and *O*-carbethoxy-*p*-cresol-3-sulphonyl chloride (1 mol.) which contained potassium carbonate in suspension. The product was decarbethoxylated by alkaline hydrolysis as described in the case of the 2-nitrophenyl ester (V), and the phenolic ester then liberated was isolated by a current of steam. The product had m. p. 57° (Arndt and Martius, *Annalen*, 1932, **499**, 276, give m. p. 55°). The *sodium* derivative (VII) was formed when alcoholic sodium ethoxide (1 mol.) was added to an ethereal solution of the ester (1 mol.). It had m. p. 220—230° and was sparingly soluble in ether and readily soluble in cold chloroform. When the solution in hot benzene was cooled, the substance separated as a transparent jelly. It was dried at 118° before analysis (Found: Na, 8·0. $C_{13}H_{11}O_4SNa$ requires Na, 8·0%) and in this condition retained its m. p.

The *sodium* derivative of phenyl salicylate was prepared in alcoholic solution by a similar method. It was soluble in hot benzene or toluene and sparingly soluble in water; purified from hot chloroform, it formed needles, m. p. 193—195°, which were dried at 120° under diminished pressure before analysis (Found: Na, 9·4. $C_{13}H_9O_3Na$ requires Na, 9·7%).

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[*Received, October 5th*, 1938.]