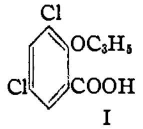
[Contribution from the Department of Chemistry of the University of Rochester]

The Rearrangement of Benzyl Ethers of Some Salicylic Acids

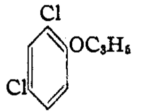
By D. S. Tarbell and V. P. Wystrach

It is known[1] that benzyl phenyl ethers do not undergo a ready thermal rearrangement comparable to that of the allyl phenyl ethers. However, under drastic conditions, benzyl phenyl ether can be rearranged thermally,[2] but the yields are poor, and a mixture of benzylated phenols is formed.

It has been noted[3] that the allyl ether of a substituted salicylic acid, such as I, rearranges more rapidly, with displacement of carbon dioxide, than the ether without the *ortho* carboxyl (II).

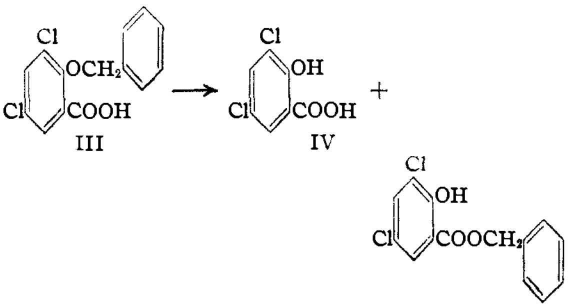


I



II

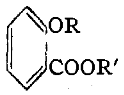
These facts suggested that a benzyl ether of a salicylic acid such as III might undergo a smooth rearrangement with the loss of carbon dioxide. The experiments reported in this paper show that benzyl ethers do not give a reaction of this kind, although they do undergo a thermal rearrangement. In a following paper, it is shown that the 9-phenanthrylmethyl group does resemble the allyl group in its ability to migrate with displacement of carbon dioxide.



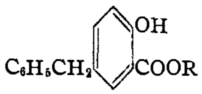
2-Benzyloxy-3,5-dichlorobenzoic acid (III) when heated for forty minutes at 153° yielded 20% of the cleavage product, 3,5-dichlorosalicylic acid (IV) and about 65% of benzyl 3,5-dichlorosalicylate (V), in which the benzyl group has migrated from the ether oxygen to the carboxyl group. A small amount (8–10%) of carbon dioxide was observed, but no product resulting from decarboxylation could be found in the mixture. Compound V as isolated from the reaction mixture was shown to be identical with a product synthesized from 3,5-dichlorosalicylic acid (IV) and benzyl chloride, by the method of Volwiler and Vliet.[4] The transformation of III to V can also be brought about by refluxing the ether-acid in acetic acid for two hours, although the change is less than 20% complete in that time; the ether-acid III was recovered unchanged, however, after heating in a hydrocarbon solvent at 116–117° for two hours.

The amounts of IV and V formed in the rearrangement were determined readily by extraction of the mixture with sodium bicarbonate solution, yielding the acid IV; the bicarbonate-insoluble material was then saponified, and the acid IV, present in the original mixture as the ester V, was isolated by bicarbonate extraction.

The O-benzyl derivative of salicylic acid (VI), on heating at 185–190° for three hours, gave 35% of salicylic acid, 35% of benzyl salicylate (VII) and a small amount of benzyl 5-benzyl-salicylate (VIII); this was identified by saponification to benzyl alcohol and 5-benzylsalicylic acid (IX), which was identical with a synthetic sample.[5]

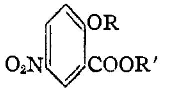


VI, $R = -CH_2C_6H_5, R' = H$
VII, $R = H, R' = -CH_2C_6H_5$



VIII, $R = -CH_2C_6H_5$
IX, $R = H$

Similar results were obtained with 2-benzyloxy-5-nitrobenzoic acid (XI); XI, when heated at 175° for nine minutes, yielded 63% of benzyl 5-nitrosalicylate (XII), 28% of 5-nitrosalicylic acid (X) and a few per cent. of carbon dioxide. When the preparation of XI was attempted by saponification of ethyl 2-benzyloxy-5-nitrobenzoate (XIII) by hot methanolic potassium hydroxide, the product was 2-methoxy-5-nitrobenzoic acid (XIV) instead of XI. The benzyl group originally on the ether oxygen had been exchanged for a methyl group under the influence of the methanolic potash.[6] When the saponification was carried out using more dilute methanolic potash at room temperature, the ether-exchange did not take place and XI was obtained in good yield.



X, $R = R' = H$
XI, $R = -CH_2C_6H_5, R' = H$
XII, $R = H, R' = -CH_2C_6H_5$
XIII, $R = -CH_2C_6H_5, R' = C_2H_5$
XIV, $R = CH_3, R' = H$

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[1] Powell and Adams, This Journal, **42**, 646 (1920); Claisen, Kremers, Roth and Tietze, *Ann.*, **442**, 210 (1925).

[2] Hickinbottom, *Nature*, **143**, 520 (1939); Behagel and Freiensehner, *Ber.*, **67**, 1368 (1934).

[3] Claisen and Eisleb, *Ann.*, **401**, 21 (1913); Tarbell and Wilson, This Journal, **64**, 607 (1942).

[4] Volwiler and Vliet, *ibid.*, **43**, 1673 (1921).

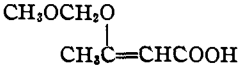
[5] Földi, *Ber.*, **61**, 1609 (1928).

[6] Fox and Bogert, This Journal, **63**, 2996 (1941), report an analogous exchange reaction of some alkoxynitrobenzothiazoles, and give references to previous examples.

To determine the effect of base on the shift of the benzyl group from the ether oxygen to the carboxyl, 2-benzyloxy-3,5-dichlorobenzoic acid (III) was rearranged in dimethylaniline solution. The same products were formed in the same proportions as in the absence of base.

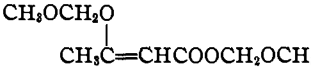
The possibility that the high-temperature reaction was catalyzed by traces of base from the glass vessels in which it was run was eliminated by a run carried out in a quartz tube, which yielded the same results as runs in glass tubes. The reaction is thus a purely thermal one, and is not a base catalyzed ester-interchange reaction. Salicylic acid is a vinylog of carbonic acid and, on this basis, the shift of the type III → V might be regarded as an ester-interchange involving carbonic esters. Ester-interchanges are catalyzed by bases, however, and the facts just cited, as well as the failure to get a shift of the benzyl group during the preparation of compounds III, VI and XI by saponification of the corresponding methyl or ethyl esters, indicates that the rearrangement is not to be regarded as an ester-interchange.

Analogous reactions involving shifts of alkyl groups in hydroxy acids have been noted by several workers. Thus, 2-methoxybenzoic acid yields 50–60% of methyl salicylate when heated at 220–240° for some time, and numerous other examples have been observed by Pollak.[7] The presence of nitro groups favors the shift, for the series anisic acid, nitroanisic and dinitroanisic acids show increasing ease of isomerization on heating.[7] Transformation of XV to XVI on distillation at atmospheric pressure has been reported.[8] This is obviously an intermolecular reaction, as are some of those reported by Pollak.



$CH_3C(OCH_2OCH_3){=}CHCOOH$

XV



$CH_3C(OCH_2OCH_3){=}CHCOOCH_2OCH_3$

XVI

The formation of benzyl 5-benzylsalicylate (VIII) in the present work shows that the benzyl group can migrate intermolecularly, *i. e.*, that 2-benzyloxybenzoic acid can act as a benzylating agent, just as benzyl benzenesulfonate can.[5] The isolation of benzyl 5-benzylsalicylate does not prove, of course, that the shift of the benzyl group (*e. g.* VI → VII) is intermolecular, although it may well be so. An intramolecular shift of the benzyl group involving hydrogen bonding between the carboxyl and the ether oxygen is also a possibility. The fact that III rearranges to V in refluxing acetic acid favors an intramolecular shift, because an intermolecular mechanism would lead to benzyl acetate in considerable amount.

It would be anticipated that, if the electrophilic character of the benzyl group were increased, the ease of rearrangement to the ester would increase also. This might be done by replacing the benzyl group by a *p*-nitrobenzyl, benzhydryl or trityl group. The *t*-butyl group might rearrange also, due to its tendency to become cationoid.

Experimental[9]

Methyl 2-Benzyloxy-3,5-dichlorobenzoate.—A solution of 16.6 g. (0.12 mole) of potassium carbonate in 25 cc. of water was added dropwise to a stirred refluxing mixture of 26.6 g. (0.12 mole) of methyl 3,5-dichlorosalicylate,[10] 19.0 g. (0.15 mole) of pure benzyl chloride and 18.2 g. (0.12 mole) of sodium iodide[11] in 75 cc. of methyl ethyl ketone. The mixture was stirred and refluxed for fourteen hours; then the solvent was removed, and the excess benzyl chloride removed by steam distillation. Upon cooling, a solid cake of the crude ether-ester remained, weighing 35.8 g. (96%), m. p. 40.5–42.5°. A small sample recrystallized twice from dilute ethanol gave colorless needles, m. p. 42.5–43.5°.

Anal. Calcd. for $C_{15}H_{12}O_3Cl_2$: C, 57.89; H, 3.88. Found: C, 58.02; H, 4.01.

2-Benzyloxy-3,5-dichlorobenzoic Acid (III).—Twenty-five g. of the crude ester was refluxed for forty-five minutes with 60 cc. of Claisen alkali,[12] 400 cc. of water was added and the solution made acid to congo red with dilute hydrochloric acid. The precipitate of the crude ether-acid III weighed 23.2 g. (97%); m. p. 145–146.5°. Recrystallization from a mixture of 100 cc. of ethanol and sufficient water to cause slight precipitation at the b. p. gave 21.0 g. (88%) of the desired product, in the form of colorless needles, m. p. 148–148.5°.

Anal. Calcd. for $C_{14}H_{10}O_3Cl_2$: C, 56.59; H, 3.39; neut. equiv., 297.1. Found: C, 56.68; H, 3.21; neut. equiv., 295.3. A second crop of less pure material amounted to 0.95 g., m. p. 146–148°.

The Rearrangement of 2-Benzyloxy-3,5-dichlorobenzoic Acid (III).—The optimum temperature for the rearrangement of this compound was found to be about 155°, a few degrees above its m. p. (148–148.5°). Carbon dioxide is given off to the extent of 8–10% at this temperature, as shown by both gasometric and gravimetric methods; no decarboxylation products could be isolated, however. Decarboxylation of the ether-acid may be concurrent with the main reaction, because carbon dioxide evolution begins at the outset of the pyrolysis and is virtually complete in half an hour. A typical run made in a quartz vessel gave precisely the same results as the usual runs made in Pyrex tubes.

A 5.06-g. sample was heated at 153° for thirty-eight minutes (refluxing cyclohexanone). After cooling, the reaction mixture was dissolved in 80 cc. of ether and extracted with a total of 75 cc. of 5% sodium bicarbonate solution. Acidification with dilute hydrochloric acid gave 0.69 g. of a white solid, which, after recrystallization from dilute ethanol, yielded 0.66 g. of small white needles, m. p. 220–223°. A mixed m. p. with an authentic sample of 3,5-dichlorosalicylic acid, m. p. 224–225°, showed no depression. This represents a 19% cleavage of the ether-acid to the parent hydroxy acid.

The ether solution was evaporated almost to dryness and the residue allowed to solidify. Recrystallization from ethanol yielded 2.39 g. of small white plates, m. p. 108.5–110°. Hydrolysis of this substance with 10% sodium hydroxide gave 3,5-dichlorosalicylic acid, identified by a mixed m. p., and benzyl alcohol, which gave a 3,5-dinitrobenzoate, m. p. 111–112.5°, identified by a mixed m. p. with an authentic sample of benzyl 3,5-dinitrobenzoate

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[7] Pollak and Feldscharek, *Monatsh.*, **29**, 139 (1908); *cf.* also Pollak and Goldstein, *Ann.*, **351**, 161 (1906).

[8] Simonsen and Storey, *J. Chem. Soc.*, **95**, 2106 (1909).

[9] All melting points are corrected; analyses by Robert Bauman and V. P. Wystrach.

[10] Claisen, *Ann.*, **418**, 85 (1919).

[11] Mauthner, *J. prakt. Chem.*, [2] **148**, 95 (1937); Smith, Hoehn and Whitney, THIS JOURNAL, **62**, 1863 (1940).

[12] Prepared by dissolving 350 g. of potassium hydroxide in 250 cc. of water and diluting to one l. with methanol; Claisen, ref. 10, p. 96.

(m. p. 113–113.5°). Apparently, the main reaction product is benzyl 3,5-dichlorosalicylate. A mixed m. p. of the isolated material with a sample of benzyl 3,5-dichlorosalicylate (V; m. p. 110.5–111.5°), the preparation of which is described elsewhere, was 109–110.5°. Recrystallization of a small amount of V from ethanol gave colorless plates of m. p. 109.5–110.5°.

Anal. Calcd. for $C_{14}H_{10}O_3Cl_2$: C, 56.59; H, 3.39. Found: C, 56.54; H, 3.58.

The 2.39 g. of this ester isolated corresponds to a 47% yield of the rearrangement product. Residues from the ether solution and mother liquors gave 1.65 g. of a brown, semi-solid material, some of which was shown to be less pure product. The remainder was not identified.

It was found that extraction with 10% sodium hydroxide after removal of the 3,5-dichlorosalicylic acid resulted in the precipitation of a sodium derivative of benzyl 3,5-dichlorosalicylate which is practically insoluble in both ether and water. The desired ester was recovered by refluxing this "salt" with 1% hydrochloric acid. Other benzyl salicylates encountered in this research were found to exhibit this behavior toward aqueous alkali solutions; methyl salicylate reacts in the same manner.[13]

Analysis of the Reaction Mixture by Saponification.—2-Benzyloxy-3,5-dichlorobenzoic acid (III) (2.02 g.) was heated at 153° (refluxing cyclohexanone) for forty minutes and the cooled reaction product taken up in 50 cc. of ether. Extraction with 50 cc. of 5% sodium bicarbonate followed by acidification of the soda solution gave 0.29 g. of 3,5-dichlorosalicylic acid, m. p. 217–221°, indicating 21% cleavage. Other similar runs showed 17–22% cleavage.

The ether was evaporated and the residue containing benzyl 3,5-dichlorosalicylate saponified by heating for fifteen minutes on the steam-bath with 10 cc. of Claisen alkali. The alkali solution was diluted with water and acidified with dilute hydrochloric acid. The resulting precipitate was taken up in ether, from which the 3,5-dichlorosalicylic acid, resulting from the hydrolysis of the benzyl 3,5-dichlorosalicylate, was extracted with 75 cc. of 5% sodium bicarbonate solution. Acidification yielded 0.98 g. (70%) of the crude acid. Recrystallization from dilute ethanol gave 0.91 g. of 3,5-dichlorosalicylic acid, m. p. 219–224°, representing a 65% rearrangement of 2-benzyloxy-3,5-dichlorobenzoic acid (III) to benzyl 3,5-dichlorosalicylate (V). In duplicate runs 69–72% of rearrangement was found.

This method of analysis was employed in other reactions studied, and is considered valid, since 2-benzyloxy-3,5-dichlorobenzoic acid (III), the only other source of 3,5-dichlorosalicylic acid, was found to be stable to Claisen alkali when refluxed for six and one-half hours.

Rearrangement of 2-Benzyloxy-3,5-dichlorobenzoic Acid in (A) Dimethylaniline Solution.—The ether (2.38 g.) in 10 g. of purified dimethylaniline was heated for ninety minutes at 155° (refluxing cyclohexanone). Treatment of the reaction product with 50 cc. of 15% hydrochloric acid left undissolved 2.16 g. of material, m. p. 80– > 160°. Recrystallization from methanol gave 1.08 g. of benzyl 3,5-dichlorosalicylate, m. p. 109–110°; a second crop of 0.12 g. was obtained, m. p. 108–109°, giving a total of 51% of rearrangement product. The residue from the mother liquor gave 0.4 g. (25%) of 3,5-dichlorosalicylic acid, m. p. 205–212°, when extracted with boiling petroleum ether (b. p. 60–70°), in which this acid is insoluble.

(B) In Acetic Acid.—When refluxed for two hours in glacial acetic acid, a sample of III was converted into V, m. p. 109–110°, in 14% yield; about 45% of III was recovered unchanged, the remainder being lost in recrystallizations.

The ether-acid III was recovered unchanged after two hours of refluxing in a toluene–xylene mixture (b. p. 116–117°).

Benzyl 3,5-Dichlorosalicylate (V).—Following Volwiler and Vliet,[4] 2.3 g. of sodium 3,5-dichlorosalicylate, 2.40 g. of benzyl chloride and five drops of triethylamine, after heating twenty-four hours at 135°, yielded 2.47 g. of recrystallized V, m. p. 110.5–111.5°. The analysis is given in a preceding paragraph.

Rearrangement of 2-Benzyloxybenzoic Acid (VI).[14]—The most satisfactory temperature for the rearrangement was found to be 185–190°. 2-Benzyloxybenzoic acid (18.5 g.) was heated in an oil-bath at 185–190° for three hours and ten minutes. The reaction mixture was taken up in 100 cc. of ether and extracted with 70 cc. of 5% sodium bicarbonate solution; the red oil which was formed on acidification yielded, on repeated extraction with boiling water, 1.9 g. (17%) of salicylic acid, identified by a mixed m. p. In several other runs, about 35% of salicylic acid was obtained.

After removing the solvent from the ether solution, the residue was fractionally distilled under diminished pressure; a small fore-run of phenol was identified through its tribromo derivative. The second fraction consisted of 6.5 g. of benzyl salicylate, b. p. 118–121° (0.3 mm.), $n^{20}D$ 1.5829.[15] It formed a trinitrobenzene complex,[16] m. p. 88–89°, but did not form a crystalline phenyl- or α-naphthylurethan, even with a basic catalyst. Saponification of a sample of the ester yielded salicylic acid and benzyl alcohol, identified through its 3,5-dinitrobenzoate. The 6.5 g. of benzyl salicylate represents 35% rearrangement, and the next fraction of 1.75 g., b. p. 126–177° (0.3 mm.), undoubtedly contained a few per cent. more of benzyl salicylate.

Benzyl 5-Benzylsalicylate (VIII).—A higher fraction (3.56 g.) from the run above, of b. p. 180–195° (0.3 mm.), mainly 190–192°, when hydrolyzed, yielded benzyl alcohol, identified by a mixed m. p. through its *p*-nitrobenzoate, and 5-benzylsalicylic acid (IX), m. p. 139.5–140.5°. The identity of this was proved by a mixed m. p. with an authentic sample of IX, m. p, 140.5–141°.[17] When the preparation of benzyl 5-benzylsalicylate was attempted using 5-benzylsalicylic acid and benzyl chloride by the general method of Volwiler and Vliet,[4] a product was obtained of b. p. 193° (1 mm.); it did not, however, give the correct analysis or molecular refraction.

Ethyl 5-Nitrosalicylate.—Fifty grams of 5-nitrosalicylic acid (Eastman Kodak Co.), 200 cc. of absolute ethanol and 100 g. of concentrated sulfuric acid were refluxed on the steam-bath for four hours. Upon cooling, 47.8 g. of the crude ester crystallized out as purplish needles, m. p. 96–97°. Recrystallization from 100 cc. of ethanol gave 41.5 g. (69%) of almost colorless needles, m. p. 97–97.5°.[18]

Ethyl 2-Benzyloxy-5-nitrobenzoate (XIII).—Twenty-three grams of potassium carbonate in 35 cc. of water was added dropwise to a stirred and refluxing mixture containing 35 g. of ethyl 5-nitrosalicylate, 25 g. of benzyl chloride and 25 g. of sodium iodide in 125 cc. of methyl ethyl ketone. After refluxing for twelve hours, the solvent was distilled off and the excess benzyl chloride removed with a current of steam. Dilution with water precipitated the crude ester. When recrystallized from ethanol a yield of 45.7 g. (92%) of pale yellow needles was obtained, m. p. 74–75°. A small sample recrystallized again from ethanol came out in long thin colorless needles of m. p. 75–75.5°.

Anal. Calcd. for $C_{16}H_{15}O_5N$: C, 63.79; H, 5.02. Found: C, 63.62; H, 5.06.

2-Methoxy-5-nitrobenzoic Acid (XIV).—Crude ethyl 2-benzyloxy-5-nitrobenzoate (XIII) (15.2 g.) was heated on the steam-bath for fifteen minutes with 75 cc. of Claisen

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(13) Similar insoluble alkali derivatives have been reported from salicylic esters [Tozer and Smiles, *J. Chem. Soc.*, 1897 (1938)], from salicylaldehydes [Brady and Bodger, *ibid.*, 952 (1932)] and from *o*-hydroxyketones [Ralston and Bauer, *J. Org. Chem.*, **5**, 165 (1940)].

(14) This compound was prepared by the method of Cohen and Dudley, *J. Chem. Soc.*, **97**, 1745 (1910), and had m. p. 76.5–77.5° in agreement with them.

(15) Eastman Kodak Co. benzyl salicylate has $n^{20}D$ 1.5814; a value of 1.5805 is reported by Ma, Hoo and Sah, *C. A.*, **28**, 133 (1934).

(16) Sudborough and Beard, *J. Chem. Soc.*, **99**, 212 (1911), give a m. p. of 89° for this derivative.

(17) Földi, ref. 5, gives the m. p. as 135–136°, and Paternò and Fileti, *Gazz. Chim. Ital.*, **3**, 128 (1873), give 139–140°.

(18) Hirsch, *Ber.*, **33**, 3240 (1900), reports a melting point of 93°.

alkali. Dilution with 400 cc. of water followed by acidification with dilute hydrochloric acid yielded 8.5 g. of acidic material, m. p. 146–152°. Reprecipitation from sodium bicarbonate solution and three recrystallizations from water gave 3.3 g. of pale yellow prisms of 2-methoxy-5-nitrobenzoic acid (XIV), m. p. 159.5–160.5°[19]; neutral equivalent: calcd. 197.1. Found: 196.9, 197.6.

2-Benzyloxy-5-nitrobenzoic Acid (XI).—Ethyl 2-benzyloxy-5-nitrobenzoate (XIII) (40 g.) in a mixture of 75 cc. of Claisen alkali and 300 cc. of methanol stood at room temperature for one day. The solution was then diluted to 1 liter with water and acidified with dilute hydrochloric acid. The product which precipitated was collected and recrystallized twice from methanol, yielding 30.0 g. (83%) of 2-benzyloxy-5-nitrobenzoic acid (XI), m. p. 166–166.5°. The product crystallizes from methanol as long colorless needles, which, when separated from the mother liquor, disintegrate into smaller dull white crystals.

Anal. Calcd. for $C_{14}H_{11}O_5N$: C, 61.54; H, 4.06; neut. equiv., 273.1. Found: C, 61.41; H, 4.09; neut. equiv., 275.3.

Rearrangement of 2-Benzyloxy-5-nitrobenzoic Acid (XI).—2-Benzyloxy-5-nitrobenzoic acid (2.11 g.) was heated for seven minutes at 175° (refluxing hydrocarbon bath). The reaction mixture was taken up in 25 cc. of ether and extracted with three 10-cc. portions of 5% sodium bicarbonate solution. Acidification of the extract with dilute hydrochloric acid gave 0.40 g. of 5-nitrosalicylic acid (X), m. p. 225–229°, which represents 28% cleavage of XI to the parent acid.

The ether was evaporated and the residue heated on the steam-bath for three hours with 25 cc. of 10% aqueous sodium hydroxide. The solution was diluted with 50 cc. of water and extracted with ether. The ether layer was discarded, the aqueous layer acidified with dilute hydrochloric acid, the precipitated acid was taken up in ether and the ether solution extracted with three 10-cc. portions of 5% sodium bicarbonate solution. Acidification gave 0.88 g. of fine white needles, m. p. 228–231°. A mixed m. p. with 5-nitrosalicylic acid (Eastman Kodak Co.) was 232–234°. This amount of acid represents a 63% rearrangement of 2-benzyloxy-5-nitrobenzoic acid (XI) to benzyl 5-nitrosalicylate (XII).

Isolation of Benzyl 5-Nitrosalicylate (XII).—In a similar experiment, the reaction product was taken up in benzene and after removal of the 5-nitrosalicylic acid (X) by sodium bicarbonate extraction, the benzyl 5-nitrosalicylate (XII) was precipitated from the benzene solution as its sodium derivative by shaking with an excess of 10% sodium hydroxide. The product was a bright yellow powder. Refluxing for two hours with 1% hydrochloric acid gave a brown oil which solidified on cooling. Two recrystallizations from ethanol (Nuchar) gave white needles of m. p. 83.5–85.5°.

Anal. Calcd. for $C_{14}H_{11}O_5N$: C, 61.54; H, 4.06. Found: C, 61.81; H, 4.18.

This substance gave no depression on mixed m. p. with a sample prepared from sodium 5-nitrosalicylate and benzyl chloride by the method already described. It was not possible to get the synthetic material analytically pure.

Summary

1. 2-Benzyloxy-3,5-dichlorobenzoic acid, heated for forty minutes at 153°, yielded 20% of 3,5-dichlorosalicylic acid, 65% of benzyl 3,5-dichlorosalicylate and 10% of carbon dioxide. The same result was obtained in dimethylaniline solution, and in a quartz tube. A slow rearrangement was also observed in refluxing acetic acid solution.

2. 2-Benzyloxybenzoic acid, after three hours at 185–190°, gave 35% of salicylic acid, 35% of benzyl salicylate and smaller amounts of benzyl 5-benzylsalicylate.

3. 2-Benzyloxy-5-nitrobenzoic acid, after nine minutes at 175°, gave 63% of benzyl 5-nitrosalicylate, 28% of 5-nitrosalicylic acid and a few per cent. of carbon dioxide.

4. The rearrangement is not base catalyzed. The benzyl ethers do not resemble the corresponding allyl ethers in behavior on heating.

ROCHESTER, N. Y. RECEIVED JULY 23, 1943

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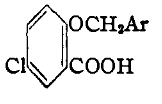
(19) Pohlmann, *Rec. trav. chim.*, **55**, 737 (1936), reports the m. p. to be 161°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

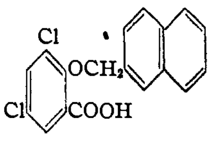
The Effect of Heat on the β-Naphthylmethyl and the 9-Phenanthrylmethyl Ether of 3,5-Dichlorosalicylic Acid

BY D. S. TARBELL AND V. P. WYSTRACH

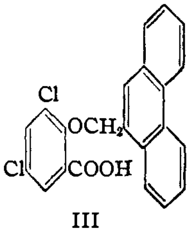
In the preceding article[1] it was shown that the benzyl ether of salicylic acids, such as I (Ar = C_6H_5), changes into the benzyl ester of the acid on heating, instead of rearranging with the loss of carbon dioxide as the analogous allyl ethers do. The present paper reports a study of 2-(β-naphthylmethoxy)-3,5-dichlorobenzoic acid (II) and the corresponding 9-phenanthrylmethyl ether (III).



I



II



III

The considerations leading to a study of these compounds are as follows. The contrast in behavior between an allyl ether (I, Ar = $-CH=CH_2$) and a benzyl ether (I, Ar = C_6H_5) must be due to the lack of an aliphatic double bond in the benzene nucleus. It is well-known, from both experimental and theoretical grounds,[2] that the 1,2-bond in naphthalene behaves more like an aliphatic double bond than like a bond in

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(1) Tarbell and Wystrach, THIS JOURNAL, **65**, 2146 (1943).

(2) Fieser and Lothrop, *ibid.*, **57**, 1459 (1935); Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 142.