[CONTRIBUTION FROM THE LABORATORIES OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA AND THE UNIVERSITY OF ILLINOIS]

The Bromination of 4-Phenylphenylbenzenesulfonate

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Although much work has been done to determine the orienting effect of phenolic hydroxyl groups, only a few studies have been made of the modification of the directive influence of such functional groups by esterification. In the present work a study has been made of the bromination of 4-phenylphenol and one of its esters. It has been found that bromination of 4-phenylphenol (I) yields 2-bromo-4-phenylphenol (II), but when the hydroxyl group is modified to benzenesulfonyloxy the bromination product is 4-(4-bromophenyl)-phenylbenzenesulfonate (V). The reactions and proof of structure of the compounds are summarized in Chart I.

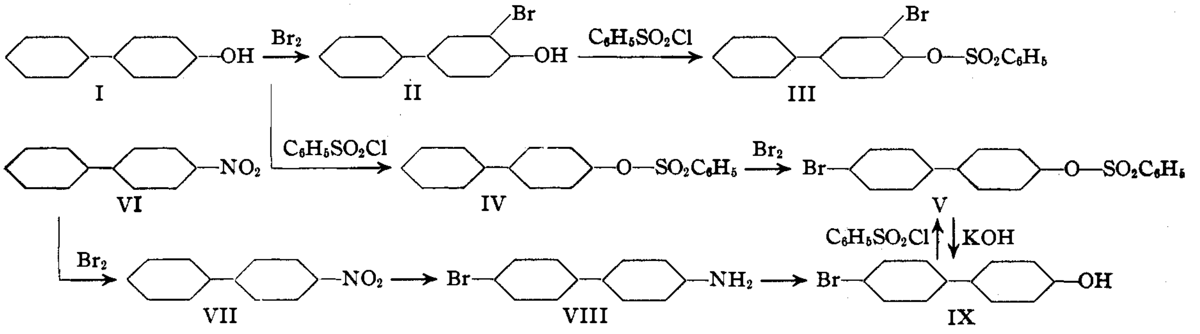

CHART I

There are some other cases on record in which esterification of phenolic groups modified their directive influence. Raiford and Stoesser[2] found that, although bromination of vanillin gives a high yield of the 5-bromo derivative, acetylvanillin, under the same circumstances, gives only the 6-bromo substitution product. Benzoylvanillin was found by Raiford and Milbery[3] to behave in the same manner. It is claimed that halogen takes the position (6) because of the directive influence of the methoxy radical, and that this influence comes into play after the directive power of hydroxyl has been largely suppressed by acylation.

Also it is known that, although halogenation and nitration of 4-phenylphenol[4] follow the normal course, the first substituent entering the position ortho to hydroxyl, when the hydroxyl group is modified to the methoxy group, nitration yields 80% of 2-nitro-4-phenylanisole, and 15% of 4-(4-nitrophenyl)-anisole is obtained as well.[5] When the 4-toluenesulfonyloxy group is present in the molecule rather than the hydroxyl or methoxy, the nitration product is reported[5] as "mainly, if not exclusively" 4-(4-nitrophenyl)-phenyl-4-toluenesulfonate. Apparently the bromination of similar substances has not been studied.

Upon nitration, 4-phenylacetanilide gives 2-nitro-4-phenylacetanilide,[6] and 4′-phenyl-4-toluenesulfonanilide gives 2′-nitro-4′-phenyl-4-toluenesulfonanilide.[5] The bromination of the first of these compounds has been shown to give 50% of 2-bromo-4-phenylacetanilide and 30% of 4-(4-bromophenyl)-acetanilide,[7] and in the case of the sulfonanilide bromination gives a mixture of compounds.[8] Hence, it was desirable to know whether bromination of esters such as IV would parallel nitration. From the results here reported, it is evident that the bromination of IV proceeds as does the nitration of the similar compound.

By the method of mixed melting points, V was shown to be different from III and identical with the benzenesulfonic acid ester of IX. By the same procedure, the phenolic hydrolysis product from V was shown to be IX and not II.

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[2] Raiford and Stoesser, THIS JOURNAL, **49**, 1078 (1927).

[3] Raiford and Milbery, *ibid.*, **56**, 2727 (1934).

[4] Raiford and Colbert, *ibid.*, **47**, 1457 (1925); Colbert and others, *ibid.*, **56**, 202, 2128 (1934).

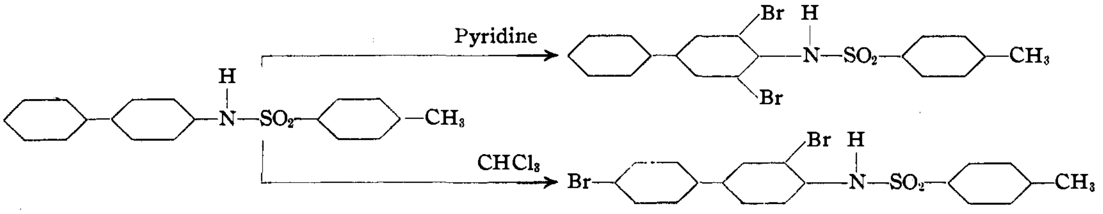
[5] Bell and Kenyon, *J. Chem. Soc.*, **129**, 3046 (1926).

[6] Banus and Tomas, *Anales soc. españ. fís. quím.*, **19**, 293 (1921); Fichter and Schulzberger, *Ber.*, **37**, 878 (1904).

[7] Kenyon and Robinson, *J. Chem. Soc.*, **129**, 3050 (1926).

[8] Bell, *ibid.*, **134**, 2338 (1931).

Since glacial acetic acid was the solvent used in the bromination of IV, whereas chloroform had been used previously in the preparation of II,[7] it was necessary to determine whether the solvent might have caused the difference. Such a difference due to solvent has been observed in the case of the bromination of a sulfonanilide[8]



However, bromination of I in glacial acetic acid under the same conditions which were used for the bromination of the ester (IV) gave the same product (II), in 82.5% yield, as had been obtained using chloroform as solvent. Therefore, the difference in directive influence must be due to the presence of benzenesulfonoxy in place of hydroxyl and cannot be attributed to a solvent effect.

Experimental Part

4 - (4 - Bromophenyl) - phenylbenzenesulfonate (V).—4-Phenylphenylbenzenesulfonate[9] (IV) (20 g.) was suspended in 200 cc. of glacial acetic acid and heated on a boiling water-bath, with vigorous stirring. Bromine (4.5 cc.) was then introduced slowly, and a trace of powdered iron was added. After all of the bromine had been added, the reaction was allowed to proceed for three hours; then the mixture was cooled and poured into five volumes of cold water. After filtering, the reaction product represented a 97% yield. It was recrystallized from alcohol, and a colorless product, m. p. 79–81°, was obtained.

Anal. Calcd. for $C_{18}H_{13}O_3BrS$: Br, 20.57. Found: Br, 20.95.

To prove the structure of the above, it was prepared in the following manner. 4-(4-Bromophenyl)-nitrobenzene (VII) was prepared according to the method of Le Fèvre and Turner.[10] The nitro compound (VII) was reduced to 4-(4-bromophenyl)-aniline (VIII),[10] and this was converted to 4-(4-bromophenyl)-phenol (IX), as directed by Bell and Robinson.[11] The product thus obtained melted between 163 and 165°. When 4-(4-bromophenyl)-phenol (IX), in pyridine solution, was treated with benzenesulfonyl chloride, 4-(4-bromophenyl)-phenylbenzenesulfonate (V), m. p. 78–80°, was obtained. This material was mixed with the brominated ester, and a melting point of 78–80° was observed.

Hydrolysis of 4-(4-Bromophenyl)-phenylbenzenesulfonate.—One gram of the ester (V) was suspended in 100 cc. of a 10% potassium hydroxide solution (alcohol: water: : 1:1), and allowed to reflux for twenty-four hours. The reaction mixture was diluted with an equal volume of water and extracted with ether. The aqueous solution was acidified and the phenolic component extracted with ether. The ethereal solution was dried with anhydrous sodium sulfate to which some Norite had been added. After filtering and removing the solvent by evaporation, an 86% yield of crude 4-(4-bromophenyl)-phenol (IX) was obtained. This was crystallized from alcohol, and the purified material (55% yield) melted at 165–166°. The product prepared in this manner was purified much more easily than that prepared by the method of Bell and Robinson.[11] The mixed melting point of the substances prepared by the two methods was 163–165°.

2-Bromo-4-phenylphenylbenzenesulfonate (III).—Five grams of II was dissolved in pyridine and treated with 1.1 mols. of benzenesulfonyl chloride. The oily product, obtained by extraction with ether in the usual manner,[9] represented an 81% yield. After standing several months, it solidified and was crystallized from slightly diluted methanol. The colorless product (51% yield) melted at 102–103°.

Anal. Calcd. for $C_{18}H_{13}O_3BrS$: S, 8.24. Found: S, 8.18.

2,6 - Dibromo - 4 - phenylphenylbenzenesulfonate.—2,6-Dibromo - 4 - phenylphenol was prepared by a known method.[11] From 5 g. of this hydroxyl compound, the pure benzenesulfonic acid ester was obtained in 84% yield by the usual method;[9] alcohol was used as solvent for recrystallizations. The colorless product melted between 145 and 147.5°.

Anal. Calcd. for $C_{18}H_{12}O_3Br_2S$: Br, 34.19. Found: Br, 34.44.

Summary

1. Although bromination of 4-phenylphenol in glacial acetic acid solution yields 2-bromo-4-phenylphenol, under the same circumstances bromination of 4-phenylphenylbenzenesulfonate yields 4-(4-bromophenyl)-phenylbenzenesulfonate.
2. Some related compounds have been reported.
3. Further work is in progress.

RECEIVED MARCH 29, 1937

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[9] Hazlet, THIS JOURNAL, **59**, 287 (1937).

[10] Le Fèvre and Turner, *J. Chem. Soc.*, **129**, 2045 (1926).

[11] Bell and Robinson, *ibid.*, **130**, 1127 (1927).