

centration of hydrochloric acid increased from 0.47 to 1.9 mole per cent., the hydrolysis "constants" decreased as follows: methyl formate 0.155 to 0.122; ethyl formate 0.246 to 0.195; *n*-propyl formate 0.239 to 0.193.

The free energies of formation of the esters at 298°K., as calculated from our data, are: -69,000 cal. for methyl, -69,000 cal. for ethyl, and -70,300 cal. for *n*-propyl formate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

## The Bromination of 4-Phenylphenyl Benzoate

BY STEWART E. HAZLET, GLEN ALLIGER<sup>1</sup> AND RALPH TIEDE<sup>1</sup>

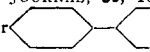
In a previous report<sup>2</sup> it has been shown that although the bromination of 4-phenylphenol results in substitution at a position ortho to the hydroxyl group, modification of hydroxyl to benzenesulfonyloxy hinders substitution in the ring to which the group is attached and yields 4-(4-bromophenyl)-phenyl benzenesulfonate. In the present work a study has been made of the bromination of 4-phenylphenyl benzoate to determine whether the benzoyloxy group would hinder substitution in the ring to which it is attached as had been noted in the case of benzenesulfonyloxy. The results of the present study indicate that the substitution does proceed in a manner analogous to that in the case of the sulfonyl compound. The reactions and proof of structure are summarized in Chart I.

The structure of III was established by its hydrolysis to V and VI and also by its synthesis from a sample of V obtained by the hydrolysis of IV.<sup>2</sup> Further, the preparation of VIII from VII showed that III was definitely different from the benzoate of VII.

In general, yields of purified products were not so satisfactory as in the study of the sulfonyl compounds. The bromination of II did not take place readily and the hydrolysis of III was less satisfactory than that of the analogous compound (IV) previously reported. Therefore, the preparation of V from IV is a method superior to its preparation from III here reported.

Slightly differing accounts of the preparation and properties of IX have appeared in the literature.<sup>3</sup> This compound and VII have been

(1) Seniors in the Department of Chemistry.

(2) Hazlet, *THIS JOURNAL*, **59**, 1087 (1937). Compound VII, Chart I should be Br--NO<sub>2</sub>, as described in the paper.

(3) (a) Raiford and Colbert, *ibid.*, **47**, 1454 (1925); (b) Bell and Robinson, *J. Chem. Soc.*, 1127 (1927). (c) The dibromo compound, m. p., 96°, obtained by Raiford and Colbert [*THIS JOURNAL*, **47**,

prepared, carefully purified and analyzed; the results are recorded in the Experimental Part. Likewise, reported melting points of II differ considerably.<sup>3a,4</sup> Uniformly, in this work, a product melting at 149-150° was obtained.

### Experimental Part<sup>5</sup>

**4-Phenylphenyl Benzoate (II).**<sup>3a,4</sup>—This compound was prepared by the treatment of 4-phenylphenol (I), dissolved in pyridine, with 1.1 moles of benzoyl chloride in the usual manner.<sup>6</sup> The crude product was obtained in almost quantitative yield, but considerable loss was involved in its purification. For recrystallizations toluene, ethanol, glacial acetic acid, and methanol have been used.<sup>7</sup> The purified product melted between 149 and 150°.

**4-(4-Bromophenyl)-phenyl Benzoate (III).**—4-Phenylphenyl benzoate (II) (10 g.) was suspended in 150 cc. of glacial acetic acid and heated on a boiling water-bath with vigorous stirring. A trace of iron powder was added and bromine (2.8 cc., approximately 1.5 molecular proportions) was then introduced drop by drop. The heating and stirring were continued for three hours after the last of the bromine had been added; then the mixture was cooled and poured into 300 cc. of cold water. The product, which solidified, was collected by filtration and represented an

1457 (1925) by bromination of 4-phenylphenol was regarded as the 2,6-dibromo derivative, though analysis for halogen indicated that the product was not quite pure. Nitration of it by the Zincke method gave a nitro compound that melted at 171° and for which halogen analysis indicated that all bromine had been retained.

In a similar way Bell and Robinson [*J. Chem. Soc.*, 1132 (1927)] prepared from the same starting material what they recorded as 2,6-dibromo-4-phenylphenol. Their product showed a melting range of 91-94°, it was not analyzed, and oxidation of it gave some 4-bromobenzoic acid, all of which leaves considerable doubt as to the purity of their product. The formation of 4-bromobenzoic acid indicates the presence of 4-(4-bromophenyl)-phenol or 2-bromo-4-(4-bromophenyl)-phenol. The presence of the latter in Raiford and Colbert's product could have accounted for the nitro-dibromo compound they isolated.

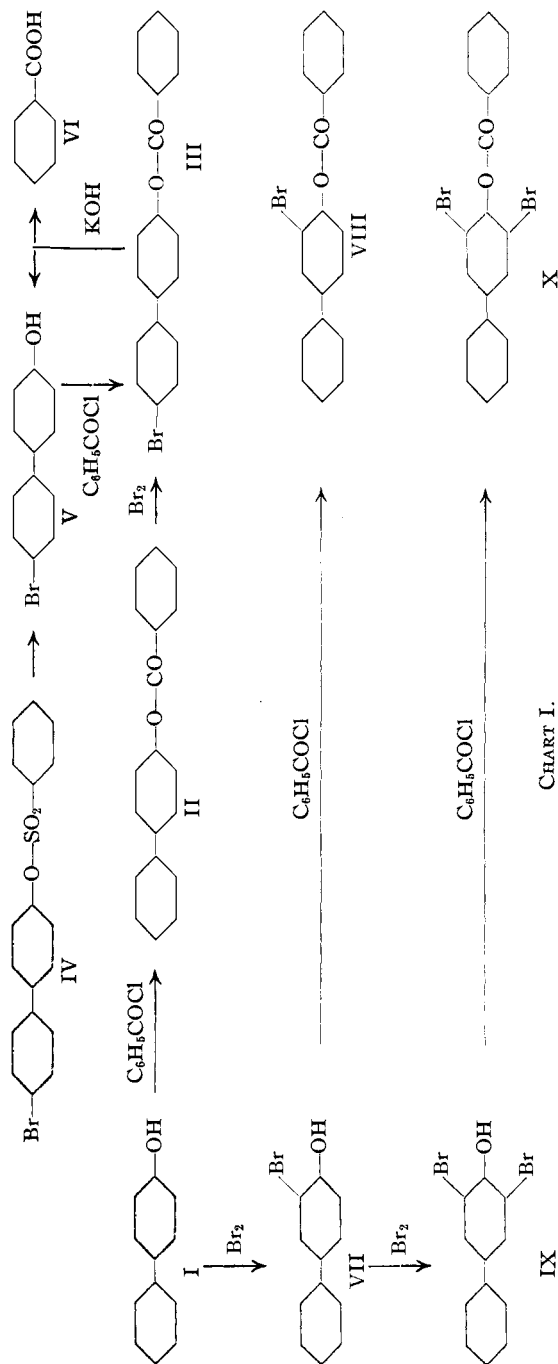
Because of these possibilities, and in the light of the results obtained by Raiford and Miller [*THIS JOURNAL*, **55**, 2125 (1933)] in an extended study of the Zincke nitration, the dibromo compound in question will be investigated further.—L. Chas. Raiford, The State University of Iowa, Iowa City.

(4) Kaiser, *Ann.*, **257**, 101 (1890).

(5) Semi-micro methods were used for all analyses.

(6) Hazlet, *THIS JOURNAL*, **59**, 287 (1937).

(7) One of us (S. E. H.) prefers the use of methanol. Although large volumes of this solvent are required, the character of the crystalline product from this solvent seems superior.



82% yield. A sample of maximum melting point was most readily obtained by recrystallizing the crude material from a mixture of methanol and ethanol; the product thus obtained was flaky and colorless and melted between 192 and 193°. Glacial acetic acid, methanol, and a mixture of methanol and acetone also have been used as solvents. With any solvent, considerable loss was involved. This was due in part to the fact that bromination was incomplete, for from one preparation (using methanol as solvent for recrystallization) 25% of starting material (II) was

recovered from the mother liquor; this was identified by a mixed melting point determination. The material as recovered melted over a range of 143–148° and this was not lowered when an equal amount of pure II was added. No other compound was isolated.

*Anal.* Calcd. for  $C_{10}H_{10}O_2Br$ : Br, 22.6. Found: Br, 22.5.

To prove the structure of III it was prepared in the following manner. 4-(4-Bromophenyl)-phenol (V) was prepared by the hydrolysis of 4-(4-bromophenyl)-phenyl benzenesulfonate (IV).<sup>2</sup> This phenol was benzooylated in pyridine solution and the product obtained melted between 193 and 194° after it had been recrystallized from a methanol-ethanol mixture. This product was mixed with the brominated ester (III) and a melting point of 192–193.5° was observed.

The structure of the brominated ester (III) was established further by hydrolysis. In a solution containing 50 cc. of water, 50 cc. of ethanol, and 9 g. of potassium hydroxide, 3 g. of III was refluxed for twenty-four hours. The ethanol was then removed by distillation, the residual solution was diluted with 100 cc. of water and then extracted with ether; a small amount of non-hydrolyzed material was recovered. Next the alkaline solution was saturated with carbon dioxide and the phenolic precipitate was extracted with ether. This ethereal solution was dried with anhydrous sodium sulfate in the presence of Norite, filtered and evaporated. The residue (1.5 g.) was recrystallized from slightly diluted methanol and melted at 164–165°. When mixed with a sample of a compound known to be V (this compound had been prepared in a different manner and its structure had been established; it had a melting point of 165–166°<sup>2</sup>) its identity was established, for the mixture melted between 164 and 165°. Benzoic acid (VI) was recovered from the aqueous solution by acidifying it and extracting with ether. The material recovered from the ether solution was recrystallized from water. It melted between 121 and 122° and when mixed with a carefully purified sample of benzoic acid there was no depression of the melting point.

**2-Bromo-4-phenylphenol (VII).**<sup>3</sup>—Ten grams of 4-phenylphenol (I) was suspended in 100 cc. of glacial acetic acid and treated with 1.1 molecular proportions of bromine under the conditions described above for the bromination of II. Crude product was obtained in nearly quantitative yield and recrystallized from a gasoline fraction of b. p. 75–98°. A colorless product was obtained which melted between 93.5 and 94.5°.

*Anal.* Calcd. for  $C_{12}H_9OBr$ : Br, 32.1. Found: Br, 31.6.

**2,6-Dibromo-4-phenylphenol (IX).**<sup>3</sup>—This compound was prepared in exactly the same manner as VII except that 2.1 molecular proportions of bromine was used. The crude product was obtained in nearly quantitative yield and was recrystallized from ligroin, b. p. 50–70°, giving a colorless crystalline product melting from 93.5 to 94°. The compound has also been recrystallized from dilute ethanol with satisfactory results.

*Anal.* Calcd. for  $C_{12}H_8OBr_2$ : Br, 48.7. Found: Br, 48.8.

**2-Bromo-4-phenylphenyl Benzoate (VIII).**—Five grams of VII was dissolved in pyridine and treated with 1.1

molecular proportions of benzoyl chloride in the usual manner.<sup>8</sup> After recrystallizing from ethanol, a colorless product, m. p. 93–94°, was obtained in 70% yield.

*Anal.* Calcd. for C<sub>19</sub>H<sub>13</sub>O<sub>2</sub>Br: Br, 22.6. Found: Br, 22.5.

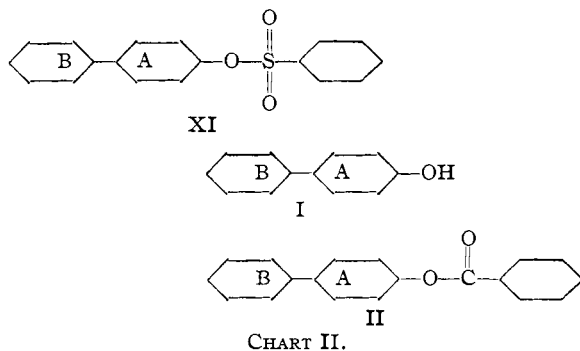
**2,6-Dibromo-4-phenylphenyl Benzoate (X).**—This compound was prepared from 5 g. of IX in exactly the same manner as in the preparation of VIII from VII. From a mixture of ethanol and acetone a colorless product, m. p. 169–170.5°, was obtained in 68% yield. Butyl cellosolve also has been found suitable for recrystallizing this compound.

*Anal.* Calcd. for C<sub>19</sub>H<sub>12</sub>O<sub>2</sub>Br<sub>2</sub>: Br, 37.0. Found: Br, 37.0.

### Discussion of Results

An attempt has been made to correlate the results obtained in this work and some of the "substitution rules." The older suggestions<sup>8</sup> of Hübner, Nölting, Crum-Brown and Gibson, Flürscheim, and Vorländer are inadequate.

Predictions based on the arguments of Hammick and Illingworth<sup>9</sup> are not in keeping with the experimental results. Although both S and O are in the same group in the periodic system, since S is lower than O in their group, ortho substitution in ring A of compound XI, Chart II, might be expected just the same as in compound I, Chart II, where H is of lower periodic classification than O. A somewhat similar argument might be made for compound II, Chart II, where C is of lower periodic classification than O.



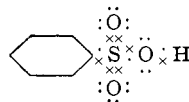
Latimer and Porter<sup>10</sup> proposed the "residual charge" method for predicting the directive in-

(8) Hübner, *Ber.*, **8**, 873 (1875); Nölting, *ibid.*, **9**, 1797 (1876); Crum-Brown and Gibson, *J. Chem. Soc.*, **61**, 367 (1892); Flürscheim, *J. prakt. Chem.*, **66**, 321 (1902); Vorländer and Meyer, *Ann.*, **320**, 122 (1902).

(9) Hammick and Illingworth, *J. Chem. Soc.*, 2358 (1930).

(10) Latimer and Porter, *THIS JOURNAL*, **52**, 206 (1930).

fluences of substituent groups. Thus, for the SO<sub>3</sub>H group



the calculations are

$$6 - (2 \times 6/10) - 3(2 \times 6/12) = +1.8$$

They concluded that if the calculated value is: (a) about zero or less, the group is ortho and para directing; (b) between +0.1 and +0.6, mixtures may be expected; (c) above +0.6, meta substitution should result. Making the necessary calculations for the compounds in question, I, XI, and II, Chart II, we have: (a) according to Latimer and Porter,<sup>10</sup> OH corresponds to a value of -0.2; (b) for compound XI, Chart II, -OSO<sub>2</sub>- corresponds to  $6 - 4 - (2 \times 6/10) - (2 \times 6/12) = -0.2$ ; (c) for compound II, Chart II, -OCO- corresponds to  $6 - 4 - 2(2 \times 6/10) = -0.4$ . In the light of these calculations the substituent group in compound XI should have the same directive influence as the OH group in compound I, and the benzoyloxy group in compound II should be an even more effective ortho directing group. (Since the para position is occupied by the phenyl group in each instance, substitution in that position is impossible.) The experimental results are not in keeping with the arguments based upon these calculations.

It may be that the acyl groups in compounds XI and II exert a greater steric effect than is present in compound I and that steric hindrance may be the cause of substitutions in the B rings of compounds XI and II, Chart II.

### Summary

1. The bromination of 4-phenylphenyl benzoate in glacial acetic acid solution proceeds as does the bromination of 4-phenylphenyl benzene-sulfonate and not as the bromination of 4-phenylphenol.

2. The results of these substitutions in esters are not what would be predicted on the basis of the usual substitution rules. It may be that steric hindrance is involved.

3. Some related compounds have been prepared and their properties reported.

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