ume concentration and to the sixth power of the distance of closest approach, are added to the Debye–Hückel expression for the logarithm of the activity coefficient.

3. It is shown that only at high concentrations do the activity coefficients become sufficiently sensitive functions of the distance of closest approach to make the determination of this parameter really precise.

4. The determination of this parameter by the method of least squares is described.

5. The theory is applied to the alkali chlorides, bromides and iodides with remarkable success. A set of mean ionic diameters is obtained, and various remarks as to the extent of hydration, penetration of ions at contact, etc., are derived from a comparison of these diameters with the sums of the standard crystalline radii.

6. Activity coefficients in 0.001 and 0.01 molar solutions are calculated with the weighted mean ionic diameters obtained at high concentrations. In eight cases out of fifteen comparison with experimental values is possible and shows more than satisfactory agreement.

STANFORD UNIVERSITY, CALIF.

RECEIVED AUGUST 11, 1939

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

The Bromination of 4-Phenylphenyl Acetate

BY STEWART E. HAZLET AND HARRY A. KORNBERG

In previous reports it was shown that although the bromination of 4-phenylphenol results in substitution at a position ortho to the hydroxyl group, when the benzenesulfonate[1] or the benzoate[2] of the phenol is brominated, the substitution occurs at the position in the molecule most remote from the ester linkage (*viz.*, *p'*). The study of the introduction of bromine into the esters of 4-phenylphenol has been extended now to 4-phenylphenyl acetate, which is analogous to the benzenesulfonate and the benzoate previously considered.

It was suggested in an earlier report[2] that perhaps steric hindrance is responsible for the change in directive influence when hydroxyl is modified to benzenesulfonyloxy or benzoyloxy. In the work here reported (see Chart I for the outline) the hydroxyl of 4-phenylphenol (I) was replaced by the acetyloxy group. On the basis of the calculations of Latimer and Porter[3] the acetyloxy group of compound II should possess the same residual charge as the benzoyloxy group in one of the compounds previously studied. The acetyloxy group is, however, much smaller than the benzoyloxy group and should be expected to exert less steric effect. Therefore it was considered possible that the bromination of 4-phenylphenyl acetate (II) might result in substitution in a position ortho with respect to the acetyloxy group. This was realized; it was found that the first bromine atom to enter 4-phenylphenyl acetate (II) gave rise to 2-bromo-4-phenylphenyl acetate (IV). Furthermore, under conditions only slightly different from those used in the preparation of compound IV and in the earlier studies,[1,2] a second atom of bromine entered the ester molecule (II) in the same relative position as in the case of the phenol (I), *viz.*, the second ortho position; thus 2,6-dibromo-4-phenylphenyl acetate (VI) was formed.

A bromine substitution product of compound II, 4-(4-bromophenyl)-phenyl acetate (IX), isomeric with compound IV obtained by direct bromination of the acetate (II) was prepared by the acetylation of a phenol (VIII) of known structure. The two isomers had distinctly different physical properties.

The experimental steps and the proofs of structure of the compounds are outlined in Chart I, and the details of procedures are given in the Experimental Part.

Experimental Part

4-Phenylphenyl Acetate (II).[4]—This compound was prepared in almost quantitative yield by gently refluxing for three hours one mole of 4-phenylphenol (I) and 0.25 mole of anhydrous sodium acetate in an excess of acetic anhydride. The reaction mixture was allowed to cool, poured into ten volumes of water, and permitted to stand overnight. The ester was collected by filtration and recrystallized from methanol. The colorless, irregular crystals melted between 87 and 88°.

2-Bromo-4-phenylphenyl Acetate (IV).—Fifteen grams of 4-phenylphenyl acetate (II) was dissolved in 30 ml. of

(1) Hazlet, THIS JOURNAL, **59**, 1087 (1937).
(2) Hazlet, Alliger and Tiede, *ibid.*, **61**, 1447 (1939).
(3) Latimer and Porter, *ibid.*, **52**, 206 (1930).
(4) Kaiser, *Ann.*, **257**, 95 (1890).

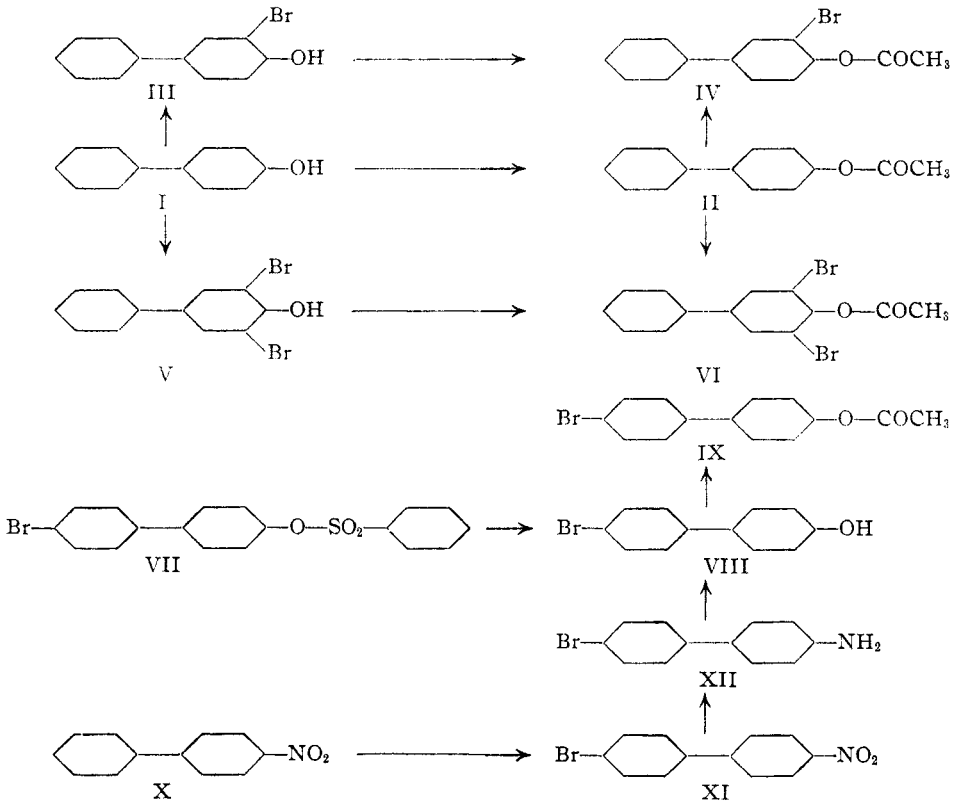


CHART I

glacial acetic acid. The mixture was stirred vigorously and was heated to 100 ± 2° in an oil-bath. A trace of iron powder was added, and then 6 ml. of bromine (approximately 1.5 moles) was added dropwise over a period of thirty minutes. The heating and stirring were continued for ten hours. Upon pouring the cooled mixture into 400 ml. of water, a dark brown viscous mass separated. After adding an excess of sodium carbonate solution, the mixture was extracted with ether. The viscous liquid (23.1 g.), which was obtained from the ether solution, was dissolved in boiling methanol. Upon cooling, a brown solid separated. Ligroin[5] was used for recrystallizations. The product (11.7 g., 57% yield) was obtained as elongated hexagonal plates; m. p. 74–75°.

This compound (IV) was also prepared from 5 g. of 2-bromo-4-phenylphenol (III)[2] in 20 ml. of acetic anhydride; 0.25 mole of anhydrous sodium acetate was added. The mixture was heated for five hours on a steam-bath, cooled, and poured into 300 ml. of cold water. The crude product (4.7 g.) represented a 90% yield. After treatment with Norite and two recrystallizations from methanol, the product was obtained as colorless hexagonal plates; m. p. 74–75°.

Anal. Calcd. for $C_{14}H_{11}O_2Br$: Br, 27.5. Found: Br, 27.6.

When equal amounts of the two samples prepared by the different methods were mixed, there was no depression of the melting point.

(5) The boiling range of the ligroin used in all of the experimental work was from 90 to 120°.

2,6-Dibromo-4-phenylphenyl Acetate (VI).—Fifteen grams of 4-phenylphenyl acetate (II) was treated as in the bromination described above except that 8 ml. of bromine (approximately 2 moles) was used, the temperature of the oil-bath was 110 ± 2°, and the time of the reaction was eight hours. The product was recovered as indicated in the case of the monobromo compound (IV). The yield of the crude material was only 40% (14.8 g.), and after several treatments with Norite and recrystallizations from ligroin, the colorless irregular crystals obtained (4.2 g.) represented only a 16% yield; m. p. 81–83°.

Anal. Calcd. for $C_{14}H_{10}O_2Br_2$: Br, 43.3. Found: Br, 43.4.

A second method was also used for the preparation of this compound (VI). To 0.8 g. of 2,6-dibromo-4-phenylphenol (V)[2] in 20 ml. of acetic anhydride, 0.5 g. of sodium acetate was added. The mixture was gently refluxed for two hours, cooled, poured into 200 ml. of water, and allowed to stand overnight. After filtration, treatment with Norite, and recrystallization from ligroin, the product was obtained in almost quantitative yield as irregular crystals which melted between 81.5 and 83°.

Anal. Calcd. for $C_{14}H_{10}O_2Br_2$: Br, 43.3. Found: Br, 43.7.

A mixture of equal amounts of this compound prepared by the two different methods melted from 81 to 83°.

4-(4-Bromophenyl)-phenyl Acetate (IX).—4-Phenylnitrobenzene (X) was converted to 4-(4-bromophenyl)-nitrobenzene (XI),[6] the nitro compound was reduced to 4-

(6) Le Fèvre and Turner, *J. Chem. Soc.*, 2041 (1926).

(4-bromophenyl)-aniline (XII),[7] and the amine converted to 4-(4-bromophenyl)-phenol (VIII).[7] The crude product so obtained was refluxed with an excess of acetic anhydride and 0.25 mole of anhydrous sodium acetate for two hours, and the product (IX) was recovered in the usual manner. A mixture of ligroin and benzene was used for recrystallizations. The product was obtained as colorless irregular plates; m. p. 128–129°. On the basis of the amount of compound X used, the yield was low.

Anal. Calcd. for $C_{14}H_{11}O_2Br$: Br, 27.5. Found: Br, 27.2.

A sample of 4-(4-bromophenyl)-phenol (VIII) obtained by the hydrolysis of 4-(4-bromophenyl)-phenyl benzenesulfonate (VII)[1] was also used for the preparation of this compound (IX). The yield of the crude acetate (IX) corresponded to 92% on the basis of the benzenesulfonate used. The m. p. 128–129° was the same as for the product described above, the crystals were similar, and a mixture of samples of the two preparations melted between 128 and 129°.

(7) Bell and Robinson, *J. Chem. Soc.*, 1127 (1927).

Summary

1. Although the bromination of 4-phenylphenyl benzenesulfonate or 4-phenylphenyl benzoate yields the 4-(4-bromophenyl)-phenyl ester, the introduction of bromine into 4-phenylphenyl acetate results in substitution in the ortho position (or positions) with respect to the acetyloxy group. The behavior of the acetate, therefore, is analogous to that of 4-phenylphenol.

2. These results are in keeping with a previous suggestion that steric effects may determine the positions taken by substituents entering an ester molecule.

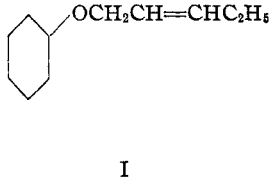
PULLMAN, WASHINGTON RECEIVED AUGUST 21, 1939

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

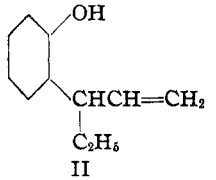
The Rearrangement of Phenyl Allyl Ethers. III. The Synthesis of α-(ortho-Methoxyphenyl)-propionic Acid

BY WALTER M. LAUER AND LOUIS I. HANSEN[1]

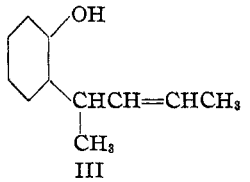
The rearrangement of γ-ethylallyl phenyl ether (I) yields both o-(α-ethylallyl)-phenol (II), and o-(α,γ-dimethylallyl)-phenol (III).[2]



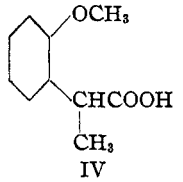
I



II



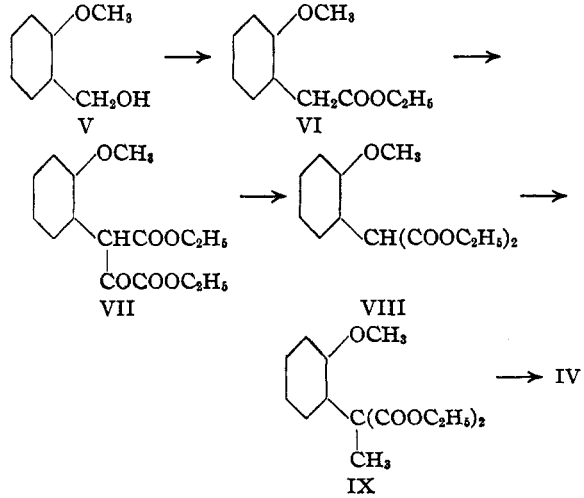
III



IV

The structure of the abnormal rearrangement product (III) is based upon several lines of evidence which need not be considered here. However, one method of approach which was used involves the conversion of this abnormal rearrangement product into α-(o-methoxyphenyl)-propionic acid (IV). This acid has not been described previously. Therefore, it was the purpose of the present study to synthesize this acid and to compare it with the product obtained by the degradation of the abnormal rearrangement product (III).

A number of promising syntheses were studied and the desired acid was prepared in two independent ways. The synthetic product proved to be identical with that obtained from the abnormal rearrangement product. An outline of the most satisfactory synthesis follows



The corresponding compounds in the para series were also prepared.

(1) Abstract of Ph.D. thesis, submitted to the University of Minnesota, March, 1938. Paper III, THIS JOURNAL, **58**, 1392 (1936).

(2) Lauer and Filbert, THIS JOURNAL, **58**, 1388 (1936); Hurd and Puterbaugh, *J. Org. Chem.*, **2**, 381 (1938).