room temperature for seven days. The tube was then opened and the contents poured over ice. The mixture was extracted with ether, the extract was dried (sodium sulfate) and the solvent was removed under reduced pressure. The residue after one crystallization from petroleum ether (b. p. 60–68°) weighed 3.3 g. and melted at 140–141°. After crystallization twice more from the same solvent, the substance melted at 143–145°. It was the butene III, identical with the product obtained above from crotyl alcohol. The diacetate (IV) m. p. 84° was likewise identical with a specimen prepared from crotyl alcohol.

No condensation occurred when gaseous butadiene was bubbled through a warm solution of the hydroquinone in acetic acid in the presence of zinc chloride; nor could any product other than unchanged hydroquinone be isolated if the sealed tube were heated; likewise no condensation occurred when dioxane and oxalic acid were substituted for the acetic acid and zinc chloride, respectively, whether the tube was heated or not.

Condensation of Methylvinylcarbinyl Chloride with Trimethylhydroquinone.[3,9b]—The chloride (3.6 g., freshly distilled) and the hydroquinone (4.0 g.) were added to dry petroleum ether (80 cc., b. p. 90–100°) containing zinc chloride (4.0 g., freshly fused), and the mixture was refluxed on the steam-bath for five hours while a continuous stream of dry nitrogen was bubbled through the liquid. The clear yellow solution was decanted from a red oily solid and the latter was extracted with four 80-cc. portions of hot petroleum ether. The petroleum ether solutions were combined, an equal volume of ether was added and the mixture was washed six times with water (100 cc. each time), twice with potassium hydroxide (2 *N*, 100 cc. each time) and filtered. After drying, the solution was concentrated to a small volume (20 cc.) and cooled. The white solid (1.5 g.) melted at 116–118°, alone or when mixed with the coumaran II. A second crop of 2.0 g., m. p. 116–117°, and a third crop of 0.8 g., m. p. 115–116°, were obtained.

Condensation of Crotyl Chloride with Trimethylhydroquinone.—This condensation was a duplicate of the above, using crotyl chloride (6.0 g., freshly distilled) and the same amounts of the other reagents. The product (3.5 g.) melted at 117–118°, alone or when mixed with the coumaran II.

Condensation of Crotyl Bromide with Trimethylhydroquinone.[3]—The hydroquinone (4.0 g.), crotyl bromide (4.3 g.) and zinc chloride (3.0 g., freshly fused) were mixed with petroleum ether (100 cc., b. p. 60–68°) and the mixture was refluxed until all of the hydroquinone dissolved (about forty minutes). The petroleum ether solution was decanted from the black residue and mixed with an equal volume of ether. The solution was washed twice with water (100 cc. each time), once with sodium carbonate (5%) and twice more with water. After drying, the solution was concentrated to about 50 cc., cooled and the product (4.2 g., m. p. 102–109°) was removed. By repeated crystallization from petroleum ether (b. p. 60–68°), each time allowing only about two-thirds of the solid to separate, there were obtained ultimately 10–15 mg. of the less soluble chroman I, m. p. 138–140°, and 3.0 g. of the more soluble coumaran II, m. p. 116–118°.

Summary

1. Pseudocumohydroquinone, when condensed with crotyl *alcohol* or with butadiene, forms trimethylcrotylhydroquinone.

2. Pseudocumohydroquinone, when condensed with crotyl *chloride* or methylvinylcarbinyl *chloride*, forms 2-ethyl-4,6,7-trimethyl-5-hydroxycoumaran.

3. Pseudocumohydroquinone, when condensed with crotyl *bromide*, forms a mixture which consists largely of the above coumaran, but which contains also some 2,5,7,8-tetramethyl-6-hydroxychroman.

4. The relation of these facts to the mechanism of the condensations is discussed.

MINNEAPOLIS, MINNESOTA RECEIVED APRIL 18, 1941

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

The Bromination of 2-Phenylphenyl Acetate

BY STEWART E. HAZLET AND HARRY A. KORNBERG

The studies on substitutions in esters containing diphenyl groups[1] have been continued, and the acetate of 2-phenylphenol[2] has now been brominated. The bromination of this ester gives rise chiefly to 4-bromo-2-phenylphenyl acetate when the ester is allowed to react with somewhat more than one molecular proportion of the halogen. By the interaction of slightly more than two molecular proportions of the halogen with one of 2-phenylphenyl acetate, 4,6-dibromo-2-phenylphenyl acetate is formed. Similar substitutions occur when 2-phenylphenol is brominated.[3]

4-Bromo-2-phenylphenol is a liquid; therefore, when it was encountered in this work, it was converted to the corresponding aryloxyacetic

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[1] For the last paper in this series see Hazlet and Kornberg, THIS JOURNAL, **61**, 3037 (1939).

[2] Vorozhtsov and Troshchenko, *J. Gen. Chem.* (U. S. S. R.), **8**, 424 (1938) (*Chem. Abst.*, **32**, 7907 (1938)).

[3] (a) Auwers and Wittig, *J. prakt. Chem.*, **108**, 99 (1924); (b) Harris and Christiansen, *J. Am. Pharm. Assoc.*, **22**, 723 (1933).

acid by a method which is similar to a standard procedure.[4] This was done with both the brominated phenol which was obtained by the hydrolysis of 4-bromo-2-phenylphenyl acetate and the phenol which was obtained by the bromination of 2-phenylphenol. The products in the two cases were shown to be identical. The analogous reaction was carried out with 4,6-dibromo-2-phenylphenol, but the yield of the aryloxyacetic acid was so low that it cannot be recommended as a suitable derivative for the identification of the dibromo compound.

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

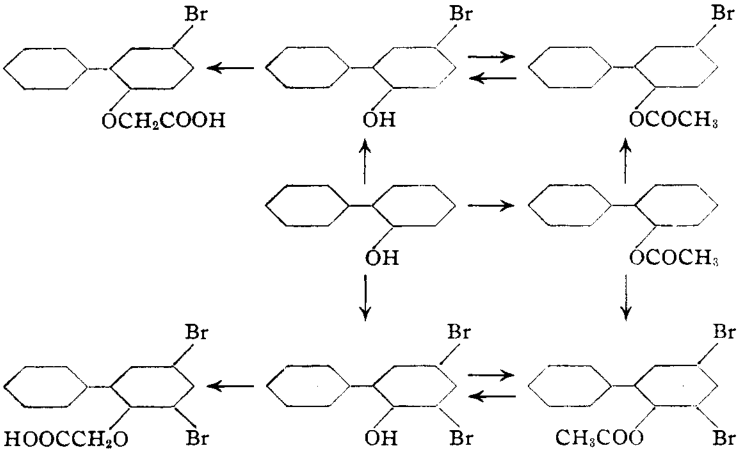

CHART I

Experimental Part

2-Phenylphenyl Acetate.—This compound was prepared in a manner which is strictly analogous to that used for the preparation of 4-phenylphenyl acetate.[1] The crude product represented an 86% yield. It was purified by distillation (130° at 1 mm.) and recrystallization from ethanol. The product was obtained in the form of colorless needles; m. p. 62–63° (Vorozhtsov and Troshchenko[2] reported 64° for the compound crystallized from petroleum ether).

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.24; H, 5.66. Found: C, 79.1; H, 5.64.

4-Bromo-2-phenylphenol.—This compound was prepared by a method which is similar to the one used by Harris and Christiansen; chloroform was used as the solvent during the bromination. The product was a viscous oil; b. p. 169–171° at 5 mm. (Harris and Christiansen[3b] reported 158–160° at 4 mm.).

4,6-Dibromo-2-phenylphenol.—The method of Auwers and Wittig was used for the preparation of this compound; m. p. 56–58° (Auwers and Wittig[3a] reported 56–57°). In the purification steps, solidification was first effected by cooling the material in a mixture of acetone and dry-ice.

4-Bromo-2-phenylphenyl Acetate.—(a) Ten grams of 2-phenylphenyl acetate was dissolved in 20 ml. of glacial acetic acid and treated with approximately 1.5 molecular proportions (11.3 g.) of bromine, as described previously for the preparation of 2-bromo-4-phenylphenyl acetate.[1] The heating and stirring were continued for twelve hours after the last of the bromine had been added. The product was obtained as a viscous oil which solidified after several days; the crude product weighed 13.8 g. The solid was melted and purified by distillation (192–200° at 11 mm.). The distillate was crystallized from ligroin,[5] and colorless needles resulted; the yield was 7 g. (51%); m. p. 65–66°.

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

The residue remaining in the flask after the distillation mentioned above was found to be 4,6-dibromo-2-phenylphenyl acetate, as is described in a subsequent section of this report.

(b) 4-Bromo-2-phenylphenyl acetate was prepared also by acetylation of 4-bromo-2-phenylphenol. Ten grams of the phenol was refluxed for three hours with 20 ml. of acetic anhydride to which had been added 2 g. of anhydrous sodium acetate. The reaction mixture was poured into 400 ml. of water, and excess sodium carbonate was added. The mixture was extracted with ether, and the ester was recovered in the usual manner. The compound was recrystallized from ligroin, and colorless needles (9.1 g. or 78% yield) were obtained; m. p. 65–66°.

Mixtures of the two samples melted without depression at 65–66°, and it was concluded that the two products were identical.

Hydrolysis of 4-Bromo-2-phenylphenyl Acetate.—Two and three-tenths grams of 4-bromo-2-phenylphenyl acetate, which was prepared by the bromination of 2-phenylphenyl acetate, was refluxed for twenty hours in 100 ml. of 20% sodium hydroxide solution (ethanol:water::1:1). From the resulting mixture the ethanol was removed by distillation, and the residual aqueous solution was extracted with ether. The aqueous layer was acidified, and the phenolic component was extracted with ether. After drying the ethereal solution with anhydrous sodium sulfate in the presence of Norite and removing the ether by distillation, 1.5 g. (76% yield) of colorless oil was obtained.

4-Bromo-2-phenylphenoxyacetic Acid.—(a) From the oil obtained as described immediately above, this compound was prepared by a method similar to that reported by Koelsch.[4] The oil, the substituted phenol, was refluxed for four hours with 80 ml. of 1.0 *N* sodium hydroxide solution and 4 g. of chloroacetic acid. From the resulting solution the crude product was obtained in almost quantitative yield, and, after recrystallization from ethanol, colorless needles (1.6 g. or 65% yield) resulted; m. p. 138–139° (Harris and Christiansen[3b] reported 138–139°).

(b) This compound was prepared in the same manner

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(4) Koelsch, THIS JOURNAL, **53**, 304 (1931).

(5) The boiling range of the ligroin which was used in all experimental work was 90–120° unless otherwise indicated.

from 4-bromo-2-phenylphenol, which had been obtained by the bromination of 2-phenylphenol; m. p. 138–139.5°. Ethanol, ethanol–water (1:1), and ligroin were found to serve as suitable solvents for recrystallization.

Anal.[6] Calcd. for $C_{14}H_{11}O_3Br$: Br, 26.06; neut. equiv., 307. Found: Br, 26.1; neut. equiv., 305.

The two samples were shown to be the same compound; mixtures of them melted without depression at 138–139°.

4,6-Dibromo-2-phenylphenyl Acetate.—(a) The residue (3 g.) after the distillation of 4-bromo-2-phenylphenyl acetate solidified on cooling and was crystallized from ligroin. Light yellow needles resulted, m. p. 73–74°.

(b) Ten grams of 2-phenylphenyl acetate was dissolved in 20 ml. of glacial acetic acid and treated in exactly the same manner as in the monobromination of this ester except that more bromine (18.8 g. or approximately 2.5 molecular proportions) was added. The heating and stirring were continued for eleven hours. The product was recovered in the same manner as the monobromo compound, and, after crystallization from ligroin, an 80% yield (14 g.) of fine, colorless needles resulted; m. p. 73–74°.

Anal. Calcd. for $C_{14}H_{10}O_2Br_2$: Br, 43.24. Found: Br, 43.3.

(c) This compound was prepared also by the following procedure. Five grams of 4,6-dibromo-2-phenylphenol was refluxed gently for three hours with 10 ml. of acetic anhydride to which had been added 1 g. of anhydrous sodium acetate. The ester was recovered in the usual way, and a nearly quantitative yield (5.6 g.) of a viscous yellow oil was obtained. This was crystallized from ligroin (boiling range 70 to 90°), and colorless needles resulted; m. p. 73–74°.

The three samples which were obtained by the methods described above were shown to be the same compound; mixtures of them melted without depression at 73–74°.

Hydrolysis of 4,6-Dibromo-2-phenylphenyl Acetate.—Four grams of the dibromo ester, which had been prepared by method (b), was refluxed for sixty hours in a solution containing 22 g. of sodium hydroxide and 50 ml. each of ethanol and water. Two and five-tenths grams (70% yield) of the phenolic component was obtained, and, after recrystallization from ligroin (boiling range 70 to 90°), light yellow needles were obtained; m. p. 59–60°.

That this was 4,6-dibromo-2-phenylphenol was demonstrated by mixing equal amounts of this sample and 4,6-dibromo-2-phenylphenol, which had been prepared by the method of Auwers and Wittig; the mixture melted without depression at 58–60°.

4,6-Dibromo-2-phenylphenoxyacetic Acid.—4,6-Dibromo-2-phenylphenol, which had been prepared by the method of Auwers and Wittig, was treated with chloroacetic acid as in the preparation of 4-bromo-2-phenylphenoxyacetic acid. The procedure was carried out a number of times, but in each case the yield was very low; *e. g.*, 0.4 g. (8.5% yield) of the aryloxyacetic acid was obtained from 4 g. of the phenol. (The major portion of the phenol was recovered.) From ligroin the compound was obtained as long, colorless needles; m. p. 123–124°.

Anal. Calcd. for $C_{14}H_{10}O_3Br_2$: Br, 41.5; neut. equiv. 386. Found: Br, 41.6; neut. equiv., 394.

Summary

The bromination of 2-phenylphenyl acetate, as is the case with the 4-isomer, proceeds in a manner which is strictly analogous to that of the corresponding phenol. The first bromine atom enters the molecule in the position para with respect to the acetyloxy group, and the second bromine goes to the available ortho position.

4,6-Dibromo-2-phenylphenoxyacetic acid has been prepared, but the yield is very poor.

PULLMAN, WASHINGTON RECEIVED APRIL 21, 1941

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(6) In ref. 3b carbon and hydrogen analyses were reported.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Alkyl Substituted Hexaarylethanes. XI.[1] Symmetry and Steric Effects as Factors in Dissociation

BY C. S. MARVEL, JULIUS F. KAPLAN AND CHESTER M. HIMEL

In previous communications from this Laboratory it has been shown[2] that the introduction of two *para*-alkyl groups into a hexaarylethane (I) gives an ethane which is dissociated to the extent of 5 to 10% at 0.1 molar concentration; whereas, if six alkyl groups are introduced in similar positions (III) the effect upon the dissociation is more marked and the free radical exists to the extent of 17 to 27% at 0.08 molar concentration. Where R is cyclohexyl,[1] the disubstituted ethane dissociates to the extent of 9% at 0.1 molar solution and the hexasubstituted to the extent of 50 ± 7% in 0.01 molar solution. Strangely enough the tetrasubstituted ethane (II, R = cyclohexyl) is no more dissociated than is the disubstituted ethane at the same concentration. This surprising result led us to prepare a number of di- and tetraalkyl substituted ethanes with the alkyl groups in the ortho-, meta- and para-positions. Magnetic susceptibility measurements

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(1) For the tenth communication see THIS JOURNAL, **62**, 1550 (1940).

(2) Marvel, Mueller, Himel and Kaplan, *ibid.*, **61**, 2771 (1939).