

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

## The Halogenation of Certain Esters in the Biphenyl Series. II. The Chlorination of 4-Phenylphenyl Benzoate and 4-Phenylphenyl Benzenesulfonate<sup>1</sup>

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Prior to the chlorination of 4-phenylphenyl acetate, recently reported,<sup>2</sup> work was begun on the chlorination of 4-phenylphenyl benzoate and 4-phenylphenyl benzenesulfonate in an endeavor to find a more direct route to 4-(4-chlorophenyl)-phenol than had been used previously.<sup>3</sup> In view of the unanticipated mode of entry of chlorine into the biphenyl nucleus in the case of 4-phenylphenyl acetate and the ease of hydrolysis of the resultant chlorinated ester to 4-(4-chlorophenyl)-phenol, it seemed of value to continue the present problem. The present paper shows that chlorination of 4-phenylphenyl benzoate and 4-phenylphenyl benzenesulfonate results in substitution in the same position of the biphenyl nucleus as does 4-phenylphenyl acetate.

Chlorination of 4-phenylphenyl benzoate in the presence of iodine catalyst, using carbon tetrachloride as the solvent, gave rise to 4-(4-chlorophenyl)-phenyl benzoate. That chlorine had entered the 4'-position of the biphenyl nucleus was proved by hydrolysis of the chlorinated ester to the known 4-(4-chlorophenyl)-phenol and benzoic acid. Benzoylation of 4-(4-chlorophenyl)-phenol, prepared by a different method, yielded the same chlorinated ester.

When 4-phenylphenyl benzenesulfonate was chlorinated, using similar conditions, 4-(4-chlorophenyl)-phenyl benzenesulfonate resulted. The position of entry of chlorine was proved by hydrolysis.

Although 2-chloro-4-phenylphenyl benzoate and 2-chloro-4-phenylphenyl benzenesulfonate were sought for in the above chlorination processes, neither was found.

During the progress of this investigation it was found desirable to prepare the benzenesulfonates of the known chlorophenylphenols. Accordingly, 4-(4-chlorophenyl)-phenyl benzenesulfonate, 2-chloro-4-phenylphenyl benzenesulfonate, 2,6-dichloro-4-phenylphenyl benzenesulfonate and 2,6-dichloro-4-(4-chlorophenyl)-phenyl benzenesulfonate were synthesized by the interaction of

benzenesulfonyl chloride with the corresponding phenols.

A comparison of the yields of 4-(4-chlorophenyl)-phenol by chlorination of the various esters of 4-phenylphenol shows that the route through the acetate gives the best yield. The extreme ease of hydrolysis of the acetate is indeed worthy of mention.

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### Experimental

**4-(4-Chlorophenyl)-phenyl Benzoate.**—A trace of iodine was added to 13.7 g. of 4-phenylphenyl benzoate suspended in 125 cc. of carbon tetrachloride. A solution of 3.9 g. (10% excess) of chlorine in 75 cc. of carbon tetrachloride was introduced dropwise over a period of two hours. When the reaction mixture had been allowed to stand overnight, the white solid was filtered, washed with cold ethanol, and twice digested with ethanol. The purified 4-(4-chlorophenyl)-phenyl benzoate, which melted at 182° weighed 8.5 g. (55% yield). An additional 0.5 g. was obtained upon distillation of the filtrate from the reaction mixture.

This same ester was prepared by benzoylation of 4-(4-chlorophenyl)-phenol. A mixed melting point caused no depression.

*Anal.* Calcd. for C<sub>19</sub>H<sub>15</sub>O<sub>2</sub>Cl: Cl, 11.49. Found: Cl, 11.52.

**Hydrolysis of 4-(4-Chlorophenyl)-phenyl Benzoate.**—A mixture of 5 g. of 4-(4-chlorophenyl)-phenyl benzoate and 10 g. of potassium hydroxide in 100 cc. of 50% ethanol was refluxed for three hours, cooled and poured into 100 cc. of water. After the ethanol had been removed by distillation, the alkaline solution was extracted with ether and the ether extract dried with anhydrous sodium sulfate. Evaporation of the ether and digestion of the remaining solid with ethanol yielded 0.4 g. of unhydrolyzed 4-(4-chlorophenyl)-phenyl benzoate.

Saturation of the aqueous solution with carbon dioxide resulted in the formation of a white precipitate which was extracted with ether and dried over anhydrous sodium sulfate. When the solvent was evaporated, 3.0 g. of solid resulted. Purification of this product by crystallization from chloroform and petroleum ether (b. p. 35–55°) gave rise to a white solid which melted at 145.5–146°, and did not

(1) From a portion of a thesis submitted by Mrs. Savoy to the Graduate Faculty of the University of Texas in partial fulfillment of the requirements for the degree of Master of Arts, August, 1942.

(2) Savoy and Abernethy, *THIS JOURNAL*, **64**, 2219 (1942).

(3) Angelletti and Gatti, *Gazz. chim. ital.*, **58**, 633 (1928).

depress the melting point of 4-(4-chlorophenyl)-phenol, prepared by the hydrolysis of 4-(4-chlorophenyl)-phenyl acetate. The yield was 2.2 g. (87%).

The aqueous solution previously saturated with carbon dioxide was acidified with hydrochloric acid and again extracted with ether. After drying with anhydrous sodium sulfate and removing the ether, 1.4 g. of benzoic acid was obtained.

Benzoylation of 4-(4-chlorophenyl)-phenol gave rise to 4-(4-chlorophenyl)-phenyl benzoate, which did not depress the melting point of the ester prepared by the chlorination of 4-phenylphenyl benzoate.

**4-(4-Chlorophenyl)-phenyl Benzenesulfonate.**—A solution of 5 g. (10% excess) of chlorine in 100 cc. of carbon tetrachloride was introduced, drop by drop, into a solution of 20 g. of 4-phenylphenyl benzenesulfonate,<sup>4</sup> a trace of iodine, and 100 cc. of carbon tetrachloride. After the reaction mixture had been allowed to stand overnight, the solvent was removed by distillation under reduced pressure. The viscous, amber colored liquid which resulted was dried with anhydrous sodium sulfate and distilled at 8 mm. pressure. The portion which distilled between 220 and 300°, when purified with methanol, yielded 15.1 g. of crystals. After five recrystallizations from methanol, the product, m. p. 74–75°, weighed 4.7 g. (21% yield).

*Anal.* Calcd. for C<sub>13</sub>H<sub>13</sub>O<sub>3</sub>ClS: S, 9.303. Found: S, 9.309.

Reaction of benzenesulfonyl chloride with 4-(4-chlorophenyl)-phenol in pyridine yielded this same ester.

**Hydrolysis of 4-(4-Chlorophenyl)-phenyl Benzenesulfonate.**—A mixture of 3 g. of 4-(4-chlorophenyl)-phenyl benzenesulfonate and 10 g. of potassium hydroxide in 100 cc. of 50% ethanol was refluxed for ten hours, cooled and poured into 100 cc. of water. After the ethanol had been removed by distillation, the alkaline solution was extracted with ether. The ether extract was dried with anhydrous sodium sulfate and the solvent was removed by distillation under reduced pressure. No residue was left after all the ether had been removed. The aqueous solution was acidified

with hydrochloric acid and extracted with ether. After drying with anhydrous sodium sulfate and removal of the ether, 1.6 g. of light yellow solid was obtained. Three recrystallizations from chloroform and petroleum ether reduced the yield to 0.7 g. (39% yield) of a pure white solid, m. p. 145–146°. A mixed melting point with known 4-(4-chlorophenyl)-phenol caused no depression.

**Benzenesulfonylation of Certain of the Chlorinated Phenylphenols.**—A mixture of 2 g. of the phenol, 20 cc. of 10% aqueous sodium hydroxide, and 2 cc. of benzenesulfonyl chloride was refluxed for ten minutes, poured into 100 cc. of water and allowed to stand for one hour. Filtration of the product and recrystallization from ethanol yielded the ester. The results are recorded in Table I.

TABLE I  
BENZENESULFONATES FROM CERTAIN CHLORINATED  
PHENYLPHENOLS

Benzenesulfonate	M. p., °C.	Sulfur, %	
		Calcd.	Found
4-(4-Chlorophenyl)-phenyl	74–75	9.303	9.309
2-Chloro-4-phenylphenyl	59–60	9.303	9.287
2,6-Dichloro-4-phenylphenyl	128–129	8.457	8.372
2,6-Dichloro-4-(4-chlorophenyl)-phenyl	125–126	7.753	7.738

### Summary

It has been shown that chlorination of 4-phenylphenyl benzoate and 4-phenylphenyl benzenesulfonate introduces chlorine in the 4'-position of the biphenyl nucleus. Hydrolysis of the resultant chlorinated esters gave rise to 4-(4-chlorophenyl)-phenol.

The benzenesulfonates of 2-chloro-4-phenylphenol, 2,6-dichloro-4-phenylphenol and 2,6-dichloro-4-(4-chlorophenyl)-phenol were prepared for the first time.

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(4) Hazlet, *THIS JOURNAL*, **59**, 1087 (1937).

## NOTES

### The Acylation of Acetonitrile with Ethyl *n*-Butyrate and the Alcoholysis of the Resulting Ketonitrile to Ethyl *n*-Butyrylacetate

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McElvain and co-workers<sup>1</sup> have shown that, in the presence of sodium ethoxide, acetonitrile (and also certain other nitriles) may be acylated satisfactorily with ethyl benzoate or ethyl iso-

butyrate to form  $\beta$ -ketonitriles, which may be alcoholized to form  $\beta$ -keto esters. Apparently, the acylation of acetonitrile with esters capable of undergoing self-condensation in the presence of sodium ethoxide, for example, ethyl *n*-butyrate, was not attempted. The acylation of the relatively reactive nitrile, phenylacetone, with ethyl acetate, however, may be effected satisfactorily.<sup>2</sup>

(1) (a) Dorsch and McElvain, *THIS JOURNAL*, **54**, 2960 (1932); (b) Cox, Kroeker and McElvain, *ibid.*, **56**, 1172 (1934).

(2) "Organic Syntheses," 1925, Vol. XVIII, p. 36.