

Anal. Calcd. for  $C_{19}H_{20}O_5N_4$ : C, 59.36; H, 5.24; N, 14.59. Found: C, 59.23; H, 5.29; N, 14.60.

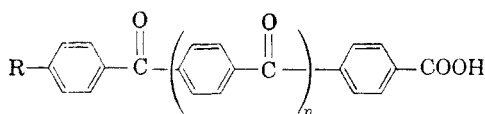
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### *p*-(*p*-Benzoylbenzoyl)benzoic Acid

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Information concerning the synthesis of linear polybenzoylbenzoic acids of type I is sparse. Koelsch and Bryan<sup>2</sup> prepared dibasic acids (Ia, n



Ia, R = COOH

Ib, R = H

= 1, 2, 3) by acylating toluene with acid chlorides such as those derived from terphthalic acid, *p,p'*-benzophenonedicarboxylic acid, etc., and subsequently oxidizing the end methyl groups to carboxylic acid groups. Acylation of benzene with *p,p'*-benzophenonedicarbonyl chloride gave *p*-(*p*-benzoylbenzoyl)benzoic acid as a by-product.<sup>3</sup> Finally, the acid catalyzed condensation of benzyl alcohol yields polymers which oxidized to a mixture of polyketones containing both ortho and para linkages.<sup>4</sup>

A possible route to compounds of type Ib is the Friedel-Crafts arylation of *p*-benzylbenzoic acid by halides such as benzoyl chloride and *p*-benzoylbenzoyl chloride. In this way the preparation of *p*-(*p*-benzoylbenzoyl)benzoic acid and its oxidation product, *p*-(*p*-benzoylbenzoyl)benzoic acid, was readily achieved. However, the few attempts to extend the synthesis were unsuccessful.

#### EXPERIMENTAL

*p*-(*p*-Benzoylbenzoyl)benzoic acid. A solution of 0.05 mole of benzoyl chloride in 30 ml. of carbon disulfide was added with stirring to 0.04 mole of *p*-benzylbenzoic acid<sup>5</sup> and 0.16 mole of aluminum chloride in 30 ml. of carbon disulfide. The mixture was stirred and heated under reflux for 3 hr. after which it was hydrolyzed with ice and hydrochloric

acid. The carbon disulfide was removed by steam distillation and the residue was dissolved in aqueous alkali and filtered. Acidification precipitated the crude acid which was twice recrystallized with decolorization from 150-ml. portions of methanol to give 6.6 g. (52%) of *p*-(*p*-benzoylbenzoyl)benzoic acid, m.p. 181.5–182.5°.

Anal. Calcd. for  $C_{21}H_{16}O_5$ : C, 79.73; H, 5.10; N.E. 316. Found: C, 79.50; H, 5.17; N.E. 316.

*p*-(*p*-Benzoylbenzoyl) benzoic acid. A solution of 3.5 g. of sodium dichromate in 5 cc. of water, 8 cc. of acetic acid, and 1.7 cc. of concentrated sulfuric acid was added dropwise over a 20-min. period to a boiling solution of 3.0 g. of *p*-(*p*-benzoylbenzoyl)benzoic acid in 25 ml. of acetic acid. After 45 min. it was poured into water and the precipitate was collected. This was difficultly soluble in dilute sodium hydroxide and methanol. Crystallization from 30 ml. of dioxane gave 2.0 g. (64%) of *p*-(*p*-benzoylbenzoyl)benzoic acid, m.p. 268.5–269.5° (lit., m.p. 268°).<sup>3</sup>

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### Estrogen Esters<sup>1</sup>

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In the steroid field the same acylating group can promote a desirable physiological response in more than one hormone category.<sup>2,3</sup>

This study extended our observations with the acylation of androgens<sup>4</sup> to the synthetic estrogens diethylstilbestrol (I) and hexestrol (II). More particularly, we were interested in varying the character of the acylating group so that the estrogenic activity inherent in I and II would be increased as well as decreased. This objective is an outgrowth of the provocative concept of Myers<sup>5</sup> and coworkers who have stressed the importance of the steroid sex

(1) Presented at the Meeting-in-Miniature, North Jersey Section, American Chemical Society, January 1958.

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(5) Prepared in very good yield by the Wolff-Kishner reduction of *p*-benzoylbenzoic acid using the general directions of Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).