Equivalent results were obtained when a proportionate weight of polyphosphoric acid (20% P2O5) was used as the solventcatalyst instead of p-toluenesulfonic acid.

Reaction of 4-Methyl-1-naphthol with 1.-A mixture of 500 mg (2.73 mmol) of 1, 432 mg (2.73 mmol) 4-methyl-1-naphthol (K & K Laboratories), and 5.0 g p-toluenesulfonic acid mono-hydrate²⁰ was heated in a 115° oil bath for 2 hr. In contrast to the reaction of 1 alone in p-toluenesulfonic acid no CO_2 evolution was evident. The mixture was poured into water and the precipitated solid collected on a filter, washed acid free and dried in vacuo to constant weight to give 915 mg of a pinkish-colored solid which smelled of 4-methyl-1-naphthol. The crude product was triturated with two 25-ml portions of 50% ethanol to extract unreacted 4-methyl-1-naphthol, and the residue dried in vacuo to give 685 mg of a product whose ir spectrum showed it to consist almost entirely of 2 along with a small amount of 4-methyl-1naphthol. Infrared analysis (see below) of this mixture indicated, as a least favorable figure, 89% lactone (2) corresponding to 610 mg (1.79 mmol) of pure 2. This is 66% of theory for the reaction of 1 mol of 1 with 1 mol of the naphthol, or 131%of theory for the self-condensation of 1 alone.

Ir Analysis of the Mixture of 2 and 4-Methyl-1-naphthol.-The 1761- and 1690-cm⁻¹ C=O bands of the lactone were calibrated using pure samples of 2 in CHCl₃ solution, the absorbance in the 1850-2000-cm⁻¹ range serving as base line. 4-Methyl-1naphthol has only very weak absorption over the whole 1670-2000-cm⁻¹ region. Straight-line Beers law plots were obtained for both bands. The mixture referred to in the preceding section was found to have 94% 2 using the 1761-cm⁻¹ band and 89% 2 when analyzed by the 1690-cm⁻¹ band.

Registry No.---1, 21615-50-9; 2, 21615-51-0.

The Preparation of 3-Arylphthalides by the **Clemmensen Reduction of 2-Aroylbenzoic Acids**

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In the course of our research² we carried out a Clemmensen reduction of 2-benzoylbenzoic acid (1a), expecting to obtain a high yield of 2-benzylbenzoic acid (2a) as reported in the literature.^{3,4} We isolated, instead, a compound (80% yield) which was insoluble in base and was identified as 3-phenylphthalide (3a). Only a small amount of 2-benzylbenzoic acid was recovered. Clemmensen reduction of several 2-(p-substituted benzoyl)benzoic acids gave good yields of the corresponding 3-(*p*-substituted phenyl) phthalides.



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(3) H. L. Bradlow and C. A. VanderWerf, J. Amer. Chem. Soc., 69, 1254 (1947)

(4) E. L. Martin, ibid., 58, 1438 (1936).

It is possible that variations in particle size and impurities in the zinc are responsible for these conflicting results.⁵ We believe, however, that there was an error in the structure assignment of the Clemmensen reduction product of 1a, probably due to the almost coincident melting points of 2a and 3a. Thus, the melting point of 2-benzylbenzoic acid (2a) is reported as 111-113°6 and 114°7,8 and the melting point of 3-phenylphthalide (3a) as 115°,^{7,9} 115.5°,¹⁰ and 117°.¹¹ Hauser and coworkers¹² found that 3-phenylphthalide is the major product of the Clemmensen reduction of 1a.

Horning and Reisner⁶ have reported that catalytic hydrogenation of 2-benzoylbenzoic acid gives high yields of 2-benzylbenzoic acid.¹³ We have successfully repeated this work and believe that catalytic hydrogenation is a superior method for effecting this conversion.

Experimental Section

Melting points are uncorrected. Microanalyses were by Alfred Bernhardt, Germany, and Micro-analysis, Inc., Wilmington, Del.

Reduction procedure A of Bradlow and VanderWerf³ was followed exactly. The reaction mixture was extracted with benzene and the aqueous layer discarded. The benzene solution was extracted with 5% sodium carbonate solution. The 3-arylphthalide was isolated upon removal of the benzene and was recrystallized from methanol. Acidification of the carbonate solution precipitated a small amount of the benzylbenzoic acid which was recrystallized from methylene chloride.

Reduction of 2-Benzoylbenzoic Acid (1a).-2-Benzoylbenzoic acid, 11.5 g (0.051 mol) yielded 8.4 g (79%) of 3-phenylphthalide (**3a**): mp 114-115° (lit.¹¹ mp 117°); ir (CHCl₃) 1755 cm⁻¹ (lactone C=O); nmr (CDCl₃) δ 6.38 (s, 1) and 7.28-7.93 ppm (m, 9).

The sodium carbonate extract yielded 2.3 g (21%) of 2-benzyl-benzoic acid (2a): mp 112-115° (lit.⁶ mp 111-113°); ir (Nujol) 1690 cm⁻¹ (acid C=0); nmr (CDCl₃) δ 4.46 (s, 2) and 7.33-8.00 ppm (m, 9), carboxyl proton not observed.

Reduction of 2-(p-Chlorobenzoyl)benzoic Acid (1b).-2-(p-Chlorobenzoyl)benzoic acid, 12 g (0.045 mol), yielded 8.8 g (80%) of 3-(*p*-chlorophenyl)phthalide (**3b**): mp 121-122°; ir (Nujol) 1750 cm⁻¹; nmr (CDCl₃) δ 6.24 (s, 1) and 6.97-7.86 ppm (m, 8).

Anal. Caled for C14H9ClO2: C, 68.73; H, 3.71. Found: C, 68.50; H, 3.68.

Reduction of 2-p-Anisoylbenzoic Acid (1c).-2-p-Anisoylbenzoic acid, 6 g (0.023 mol), yielded 3.4 g (62%) of 3-*p*-anisylphthalide (3c): mp 113-114.5°; ir (Nujol) 1756 cm⁻¹; nmr (CDCl₃) δ 3.73 (s, 3), 6.24 (s, 1), and 6.66–7.87 ppm (m, 8).

Anal. Calcd for C₁₅H₁₂O₃: C, 74.99; H, 5.04. Found: C, 75.18; H, 5.05.

Reduction of 2-p-Toluylbenzoic Acid (1d).-2-p-Toluylbenzoic acid, 6 g (0.025 mol), yielded 1.5 g (27%) of 3-p-tolyphthalide (3d): mp 127-128°; ir (Nujol) 1755 cm⁻¹; nmr (CDCl₃) δ

2.28 (s, 3), 6.23 (s, 1), 6.99 (s, 4), and 7.06–7.85 ppm (m, 4). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.13; H, 5.30.

A large amount of starting material was isolated indicating that the low yield of 3d was due to low conversion.

Registry No.-3a, 5398-11-8; 3b, 4889-69-4; 3c, 21615-74-7; 3d, 21615-75-8.

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benzoic acid comes from ref 3. The cited melting point thus may be that of 3-phenylphthalide.