Preparation of *o*-Dibenzoylbenzene and *o*-Dibenzylbenzene

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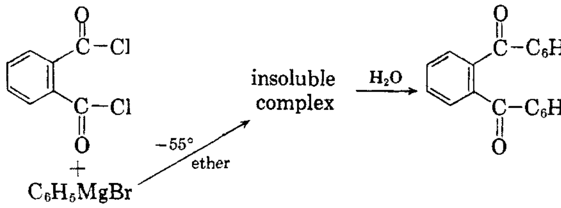
o-Disubstituted benzene derivatives are frequently difficult to prepare, and often cannot be synthesized by conventional methods. No convenient methods have been reported for the preparation of the useful compounds, *o*-dibenzoylbenzene and *o*-dibenzylbenzene. Since it was desired to obtain substantial quantities of these compounds, a number of methods for their preparation were investigated. The most satisfactory methods found are reported here.

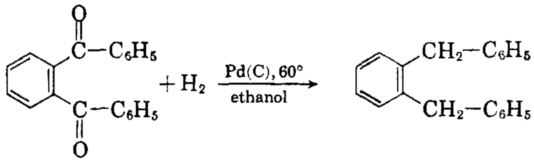
Although the yield is poor (32%) in the method given for the preparation of *o*-dibenzoylbenzene, the procedure involves a simple reaction using cheap, commercially available starting materials. The reaction was carried out by adding phenylmagnesium bromide to a solution of phthaloyl chloride in ether at −55° (Equation 1). The product forms an ether insoluble complex with magnesium bromide. The side products are largely removed by decanting the ether solution from the complex. Addition of water liberates the *o*-dibenzoylbenzene from the complex.



(1)

The preparation of *o*-dibenzoylbenzene from phthaloyl chloride and phenylmagnesium bromide (unreported yield) has been carried out previously,[1] but the preparation could not be repeated satisfactorily. Cason and Reist[2] have shown that succinyl dichloride gives reactions with ethylmagnesium bromide characteristic of the unsymmetrical form at room temperature and the symmetrical form at low temperature. It had been hoped that *o*-dibenzoylbenzene could be prepared by the reaction of diphenylcadmium with phthaloyl chloride,[3] but the principal product of the reaction was diphenylphthalide.

It was found that *o*-dibenzylbenzene can be conveniently prepared by reducing *o*-dibenzoylbenzene with hydrogen in the presence of palladium on charcoal (Equation 2). *o*-Dibenzylbenzene has usually been obtained previously from the complex mixture resulting from the reaction of benzyl chloride and diphenylmethane in the presence of aluminum chloride.[4]



(2)

EXPERIMENTAL

o-Dibenzoylbenzene. A solution containing 1.11 mol. phenylmagnesium bromide and 1000 ml. ether was prepared in the usual manner. This solution (without cooling) was added over a period of 15 min. to a stirred mixture of 107.6 g. (0.53 mol.) phthaloyl chloride (Eastman Organic Chemical Co., practical grade) and 1000 ml. anhydrous ether, which was cooled in a Dry Ice–trichloroethylene bath. The temperature in the reaction vessel was about −55°. During the addition, a solid separated from the solution. (A powerful stirred was found necessary to keep the mixture agitated.) After the addition was complete, the low temperature bath was removed and the mixture was allowed to warm to room temperature while being stirred.

The ether solution was decanted from the solid, 2000 ml. technical ether was added to the complex, and then the solid complex was decomposed by adding 1000 ml. water containing 5 ml. acetic acid. The ether solution was separated, and then washed with 500-ml. portions of water, 5% sodium bicarbonate solution, and water. Ether was added as necessary to keep the product in solution. After drying the solution with magnesium sulfate, the bulk of the ether was removed. *o*-Dibenzoylbenzene separated in almost pure form, in a yield of 45.7 g. (32%), m.p. 146–147°. The crystals contained a very small amount of highly colored material which was difficult to remove. This product was found to be suitable for most purposes. Recrystallization from ethanol was found to be convenient, but the product was yellow with m.p. 147.6–148.5°. Pure *o*-dibenzoylbenzene, m.p. 147.6–148.8° (lit.,[5] m.p. 148°), was obtained by clarifying and recrystallizing the compound in heptane-acetone.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.92; H, 4.89. Found: C, 84.08; H, 5.07.

o-Dibenzylbenzene. A mixture of 23 g. (0.081 mol.) *o*-dibenzoylbenzene (m.p. 146–147°), 4 g. palladium (5%) on charcoal and 200 ml. absolute ethanol was placed in a Parr low-pressure hydrogenation unit. After heating the reaction vessel to 60°, the hydrogenation was started using an initial pressure of 44 p.s.i. In 10 hr., the calculated amount of hydrogen was taken up, and the hydrogenation was stopped. Since the hydrogen uptake continued slowly beyond the calculated amount, the yield was diminished if the reaction was allowed to continue.

The reaction mixture was heated to boiling and then filtered while hot. After allowing the mixture to cool to room temperature, the solution was placed in a refrigerator at 6°. The crystals were collected, and recrystallized from absolute ethanol to give 13.9 g. (0.054 mol.) *o*-dibenzylbenzene (66%) as white needles with m.p. 78.7–79.4° (lit.,[3] m.p. 78°).

Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.07. Found: C, 92.73; H, 6.86.

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