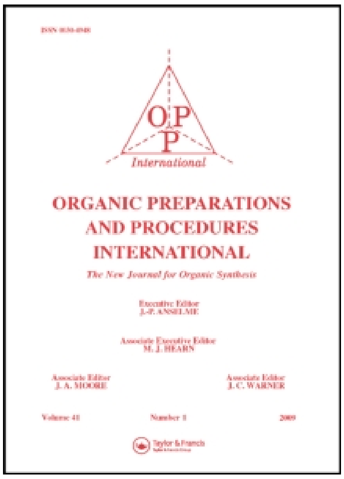

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A CONVENIENT PREPARATION OF DIPHENYLISOBENZOFURAN AND DIPHENYLISOBENZOTHIOPHENE

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A CONVENIENT PREPARATION OF DIPHENYLISOBENZOFURAN AND DIPHENYLISOBENZOTHIOPHENE[1]

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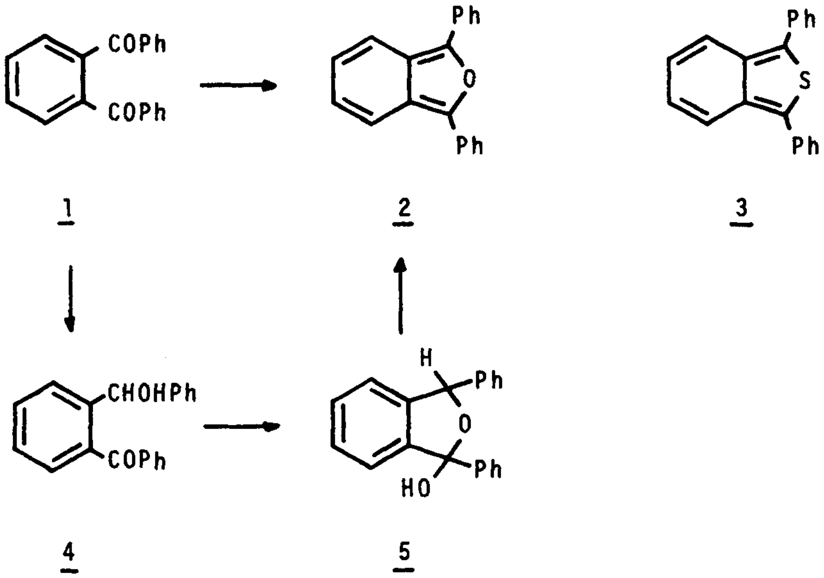

Diphenylisobenzofuran (2), a highly reactive trapping agent for olefinic and acetylenic dipolarophiles,[2] has been prepared[3] from *o*-dibenzoylbenzene (1) by repetitive potassium borohydride reduction followed by treatment of the reduced product with acid. Oxidation of 2 → 1 is a troublesome feature associated with the use of 2 and can only be avoided by rigorous exclusion of air, especially if prolonged reaction times are involved.[4]

We have found the following procedure to be both economical and useful for obtaining 2 free from 1, an impurity often present in many preparations. Reduction of 1 in methanol with an excess of sodium borohydride, followed by removal of the solvent and treatment of the residue with hot acetic anhydride provides 2 in yields of the order of 70%. Isolation of the presumed intermediate alcohol 4 is not necessary nor advisable, since attempted purification of this product leads either to oxidation to 1 or dehydration to 2; it is possible that 5 is the intermediate involved.[3]

Diphenylisobenzothiophene (3) though less reactive than 2, does form adducts with maleic anhydride and benzyne[5] and has been prepared[6] by the action of P_2S_5 and 2. The conversion of 2 into 3 does not go to completion, the separation of 2 and 3 being possible by the preferential reaction of 2 with N-phenylmaleimide.[7] An alternative preparation of 3 from *o*-dibenzoylbenzene (1) by successive treatment with PCl_5 and potassium ethyl xanthate has also been reported.[8] We have found that the direct action of P_2S_5/pyridine[9] on 1 results in excellent yields of diphenylisobenzothiophene (3).

EXPERIMENTAL[10]

Diphenylisobenzofuran (1).- *o*-Dibenzoylbenzene (2.9 g, 0.01 mole) in refluxing methanol (130 ml) was treated with sodium borohydride (0.4 g, 0.012 mole) added portionwise over 10 min. After 15 min. of further reflux, the solvent was evaporated and acetic anhydride (75 ml) was added to the residue. The reaction mixture was heated to reflux (15 min.) and then cooled. The orange-yellow needles of 1 which separated were collected, washed well with cold water and dried to give 1.9 g (70%) of 1, mp. 129-130°, lit.[3] mp 130-131°.

Diphenylisobenzothiophene (3).- *o*-Dibenzoylbenzene (2.9 g, 0.01 mole), P_2S_5 (3.3 g, 0.015 mole), and dry pyridine (100 ml) were heated together under reflux for 3 hr, the reaction mixture cooled, and then poured into 1 L of water. Acetic acid (10 ml) was added to coagulate the precipitate which was collected, washed well with water and dried. It crystallized[11] from cyclohexane as bright yellow needles, 2.1 g (74%), mp. 120-121°, lit.[3] mp. 119-120°.

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(1) Support of this work by U.S. Public Health Service Research Grant HE-09991, National Heart and Lung Institute, is gratefully acknowledged.

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(4) Diphenylisobenzofuran is available commercially. However, this present procedure provides an economic recycling process for the laboratory.

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(6) Ref. 5, p. 357.

(7) C. Dufraisse and D. Daniel, Bull. soc. chim. Fr., 4, 2063 (1937).

(8) A. Schonberg and E. Frese, Chem. Ber., 101, 701 (1968).

(9) Many reports on the use of this reagent have appeared. See e.g., E. Klingsberg and D. Pappa, J. Amer. Chem. Soc., 73, 4988 (1951); E. A. Falco, E. Pappas and G. H. Hitchings, ibid., 78, 1938 (1956); J. J. Fox, I. Wempen, A. Hampton and I. L. Doerr, ibid., 80, 1669 (1958).

(10) All evaporations were done under vacuum using a rotatory evaporator. Mps. were taken in capillaries.

(11) The purity of the pyridine, as well as that of the starting material, has an appreciable effect on the quality of the crude product. In unfavorable cases, chromatography on silica gel (60 g) using benzene as eluent was found to be satisfactory for purification of product.

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