SECTION C
Organic Chemistry

A Convenient Synthesis of Arylbenzenes

By **D. H. Hey, Katherine S. Y. Liang, M. J. Perkins,** and **G. H. Williams,*** Department of Chemistry, King's College, Strand, London W.C.2

An improved procedure for the preparation of arylbenzenes from aroyl peroxides and benzene is described.

In a previous Communication it was reported that the products of the thermal decomposition of benzoyl peroxide in benzene can be modified by the presence in the reaction mixture of a small amount of an aromatic nitro-compound.[1] The effect of the additive is to increase the yields of both biphenyl and benzoic acid from below 50% to approximately 90% according to the equation:

$$(PhCO_2)_2 + PhH \longrightarrow PhCO_2H + Ph_2 + CO_2$$

The mechanism of this "nitro-group effect" is the subject of continuing research in these laboratories. The present Paper describes a convenient procedure for carrying out the reaction, and comments on the scope of its preparative usefulness.

The method is of value for the preparation of a wide range of arylbenzenes where the aryl group contains only halogen or hydrocarbon substituents, the required starting material being the appropriate diaroyl peroxide. Nitrobenzoyl peroxides give good yields of biaryl by means of a "built-in" nitro-group effect, no additive being necessary.[2]

Decomposition of the peroxide in a large excess of dry reagent-grade benzene at 80° under reflux during *ca.* 30 hr., and in the presence of *ca.* 0·1 mole *m*-dinitrobenzene, followed by chromatography on alumina, readily produces a product of adequate purity for most purposes (usually >98% by g.l.c., and with a negligible residue on distillation). Typical experimental details are given below, together with a list of arylbenzenes which have been obtained satisfactorily by this procedure. In addition to the enhanced yield, the method gives a product uncontaminated by partially hydrogenated biphenyls.[3]

The method is not generally applicable to reactions with substituted benzenes,[1] although in these cases transition-metal salts (*e.g.*, copper benzoate) may find some application.[4] In many instances, substituted benzenes react with aroyl peroxides to give reasonable yields of biaryl without additive (*e.g.*, PhBr,[5] $PhNO_2$ [6]).

EXPERIMENTAL

4-*Chlorobiphenyl*.—Bis-*p*-chlorobenzoyl peroxide [7] (12 g.) was added to a boiling solution of *m*-dinitrobenzene (2 g.) in benzene (400 ml.), and the solution was boiled under reflux for 26 hr. The cooled reaction mixture deposited *p*-chlorobenzoic acid (5·5 g., m. p. 240°), which was removed. The remaining solution was concentrated to 25 ml. by distillation, cooled, and a second crop of acid (0·1 g.) was removed. The solution was then chromatographed on basic alumina. Thorough elution with light petroleum (b. p. 40—60°), followed by removal of the solvent from the eluate, gave 4-chlorobiphenyl as a pale yellow crystalline solid, m. p. 72—75° (lit. m. p. 77°) (6·53 g., 90%). No colour reaction was given with acetone and sodium hydroxide, confirming that no *m*-dinitrobenzene had been eluted. A trace (*ca.* 1%) of biphenyl was revealed by g.l.c. One crystallisation from aqueous methanol gave colourless plates, m. p. 76—77°.

In the absence of nitro-compound a 47% yield of 4-chlorobiphenyl has been reported for an otherwise comparable system.[8]

Other arylbenzenes prepared by simple modification of the above procedure include ArPh where Ar = Ph (biaryl yield increased from 40 to 85%); $3,4\text{-}Cl_2\cdot C_6H_3$ (biaryl yield increased from 50 to 80%); as well as $o\text{-}Cl\cdot C_6H_4$; $m\text{-}Cl\cdot C_6H_4$; $m\text{-}Br\cdot C_6H_4$; $o\text{-}Me\cdot C_6H_4$; $m\text{-}Me\cdot C_6H_4$; $p\text{-}Me\cdot C_6H_4$; $p\text{-}Me_2\cdot CH\cdot C_6H_4$. The only differences from the above procedure concern the isolation of aroic acid. More soluble acids, for example, may be extracted with aqueous bicarbonate. Alternatively, if the acid is not to be recovered, it may be removed from the biaryl in the chromatography step. However, for large-scale preparations, or precious reagents, it may be advantageous to convert the acid back into peroxide.

We are indebted to the Distillers Company and to King's College, London, for generous financial support (to K. S. Y. L.).

[7/024 *Received, January 9th*, 1967]

---

* Present address: Department of Chemistry, Birkbeck College, Malet Street, London W.C.1.

[1] D. H. Hey, M. J. Perkins, and G. H. Williams, *Chem. and Ind.*, 1963, 83.

[2] M. Mingin and K. H. Pausacker, *Austral. J. Chem.*, 1965, **18**, 821.

[3] D. F. DeTar and R. A. J. Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4742; D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, 1964, 3412.

[4] D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *Tetrahedron Letters*, in the press.

[5] G. B. Gill and G. H. Williams, *J. Chem. Soc.*, 1965, 7127.

[6] G. B. Gill and G. H. Williams, *J. Chem. Soc.* (*B*), 1966, 880.

[7] W. Cooper, *J. Chem. Soc.*, 1951, 3106.

[8] K. H. Pausacker, *Austral. J. Chem.*, 1957, **10**, 49.