View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1966. Downloaded by Universiteit Utrecht on 27/10/2014 00:49:15.

A New Method for the Synthesis of Biphenylenes

By R. F. C. BROWN, D. V. GARDNER, J. F. W. McOMIE, and R. K. SOLLY

[(*R.F.C.B. and R.K.S.*) *Chemistry Department, School of General Studies, Australian National University, Canberra, A.C.T.*; (*D.V.G. and J. F. W. McO.*) *Chemistry Department, The University, Bristol*]

As an extension of our previous work on the pyrolysis of organic compounds[1-3] we have studied the pyrolysis of phthalic anhydride, substituted phthalic anhydrides, and a variety of other

View Article Online

Published on 01 January 1966. Downloaded by Universiteit Utrecht on 27/10/2014 00:49:15.

carbonyl-containing compounds.[4] The pyrolyses were carried out by passing the vapour of the compound through a silica tube at 450—1100° under 0·1—2·0 mm. pressure. In some cases the silica tube was packed with short lengths of silica tubing while in others a packing of $\frac{1}{4}$-inch porcelain Lessing rings was used.

The main results obtained are as follows. Phthalic anhydride, 4-chloro-, 4,5-dichloro-, 3,6-dichloro-, 3,4,5,6-tetrachloro-, and 4,5-dimethylphthalic anhydride gave biphenylene (17%)* and its 2,6-dichloro-(15%), 2,3,6,7-tetrachloro-(6·5%), 1,4,5,8-tetrachloro-(4%), octachloro-(26%), and 2,3,6,7-tetramethyl-(3%) derivatives respectively. Biphenylene was also obtained (in the yields indicated) by similar pyrolysis of *o*-bromobenzoic acid (trace), diphenic acid (5%), and *o*-sulphobenzoic anhydride (5·5%). No biphenylene or substituted biphenylene was obtained by the pyrolysis of 4-benzyl- and 4-methoxy-phthalic anhydride, *o*-chlorobenzoic acid, phthalimide, *N*-methylphthalimide, coumaran-2,3-dione, or disalicylide. The scope and limitations of this high-temperature synthesis of biphenylenes are being investigated.

It is probable that benzyne and substituted benzynes are intermediates in the above described formation of biphenylene and its derivatives. The parallelism between the mass-spectral and pyrolytic fragmentation patterns of aromatic carbonyl compounds, which has guided this work as it has that of Fields and Meyerson on the pyrolysis of benzene solutions of phthalic anhydride[5] and *o*-sulphobenzoic anhydride[6] will be described elsewhere.[7]

(*Received, May 27th*, 1966; *Com.* 360.)

---

* In calculating the yields no allowance has been made for recovered starting material.

[1] R. F. C. Brown and R. K. Solly, *Chem. and Ind.*, 1965, 181, 1462.
[2] J. F. W. McOmie and B. K. Bullimore, *Chem. Comm.*, 1965, 63.
[3] R. F. C. Brown, W. D. Crow, and R. K. Solly, *Chem. and Ind.*, 1966, 343.
[4] This is the subject of Australian Patent Application No. 61869/23rd July 1965.
[5] E. K. Fields and S. Meyerson, *Chem. Comm.*, 1965, 474.
[6] S. Meyerson and E. K. Fields, *Chem. Comm.*, 1966, 275.
[7] R. F. C. Brown and R. K. Solly, *Austral. J. Chem.*, 1966, **19**, in the press.