Tetrahedron Letters No. 20, pp. 7-11, 1959. Pergamon Press Ltd. Printed in Great Britain.

FORMATION OF 1,4-DIBROMO-2,3-BENZOBIPHENYLENE, 2,3-BENZOBIPHENYLENE, AND 1,2,5,6-TETRABROMO-3,4:7,8-DIBENZOTRICYCLO [4,2,0,0^{2,5}] OCTADIENE

Frederick R. Jensen and William E. Coleman

Dept. of Chemistry, University of California, Berkeley 4, California

(Received 29 October 1959)

IN recent years there has been considerable interest in derivatives of benzocyclobutene and benzocyclobutadiene.[1,2] Extensive synthetic efforts have been put forth in the preparation of dibenzocyclobutadiene (biphenylene) and its more highly condensed analogs.[3,4,5] This report is concerned with the production of derivatives of benzocyclobutene and

---

[1] M. P. Cava and D. R. Napier, J. Amer. Chem. Soc. **80**, 2255 (1958) and preceding papers.

[2] M. Avram, D. Dinu and C. D. Nenitzescu, Chem. and Ind. 257 (1959).

[3] W. C. Lothrop, J. Amer. Chem. Soc. **64**, 1698 (1942), and preceding paper.

[4] M. P. Cava and J. F. Stucker, ibid. **77**, 6022 (1955).

[5] R. F. Curtis and G. Viswanath, J. Chem. Soc. 1670 (1959), and preceding paper.

biphenylene by reaction of α,α,α',α'-tetrabromo-o-xylene (I) with potassium t-butoxide. It was anticipated that 1,1,2-tribromobenzocyclobutene (II) might be a major product of this reaction.

It is well known that tetrabromo-o-xylene (I) yields an intractable polymer when treated with strong aqueous base. o-Phthalaldehyde can be isolated by aqueous hydrolysis in very weakly basic solutions. There have been no studies made, however, on the reaction of tetrabromo-o-xylene with base under anhydrous conditions.

Treatment of I with one mole equivalent of potassium t-butoxide produced none of the expected tribromobenzocyclobutene (II), and approximately half of the starting material was recovered. All of the starting material was converted when seven mole equivalents of base was used and two dimeric products were isolated. The dimers had empirical formulae of $C_{16}H_8Br_2$ and $C_{16}H_8Br_4$ and proved to be 1,4-dibromo-2,3-benzobiphenylene (III) and 1,2,5,6-tetrabromo-3,4:7,8-dibenzotricyclo $[4,2,0,0^{2,5}]$ octadiene (IV).[6]

Compound III, yellow needles with m.p. 222-223°, was isolated in 69.2% yield, while the compound IV, white plates decomposing at 214°, accounted for 20.6% of the theoretical yield. The two products were separated by fractional crystallization.

---

[6] All compounds gave satisfactory analyses for the formulae shown.

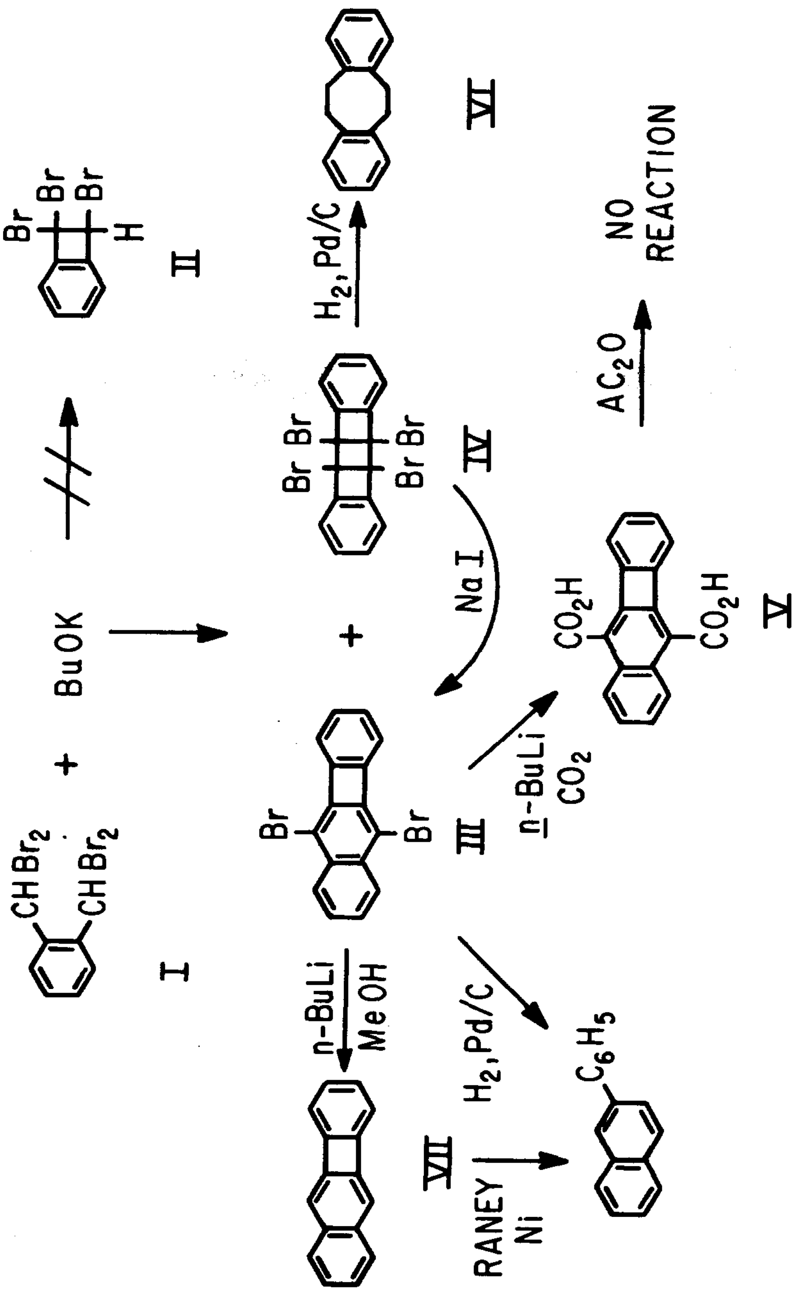

FIG. 1. Reaction of tetrabromo-o-xylene with strong base and subsequent conversions.

Reduction of III with hydrogen, in the presence of palladium on charcoal and triethylamine, produced β-phenylnaphthalene in 84% yield. Three moles of hydrogen were consumed. This result indicates that III is a dibromo derivative of either 1,2- or 2,3-benzobiphenylene.

The bromine atoms were converted to carboxyl groups in order to determine whether they occupy adjacent positions. By refluxing with excess _n_-butyl lithium, III was converted to the dilithium derivative. Treatment of the dilithium compound with carbon dioxide, followed by acidification, gave a diacid (V) in a 57.4% yield. The diacid was recovered unchanged after refluxing for 1.5 hr. in acetic anhydride. These results coupled with the information from the reduction reaction indicate that III is 1,4-dibromo-2,3-benzobiphenylene.

Dimer IV was shown to be 1,2,5,6-tetrabromo-3,4:7,8-dibenzotricyclo[4,2,0,$0^{2,5}$]octadiene by the following reactions. Reduction of IV by hydrogen, in the presence of palladium on charcoal and triethylamine, produced 1,2:5,6-dibenzocyclooctadiene (VI) in 92.3% yield. When IV was refluxed in ethanolic sodium iodide solution for two weeks, 35.8% of dimer III and 61.9% of starting material were obtained.

The ultraviolet and infrared spectral data are in accord with the structural assignments of the two dimers. The reactions are summarized in Fig. 1.

When the dilithium derivative of III was decomposed with methanol, the previously unreported 2,3-benzobiphenylene (VII), m.p. 242.6-243.2°, was obtained in 79% yield. Compound VII was readily reduced with Raney nickel to form β-phenylnaphthalene (95.2%). Cava and Stucker[4] reported that the reduction of 1,2-benzobiphenylene gives 21% of α- and 50% of β-phenylnaphthalene. Treatment of tetrabromo-o-xylene with potassium t-butoxide followed by reaction of III with n-butyl lithium and methanol constitutes a convenient synthesis of 2,3-benzobiphenylene.

Although compound II was not isolated, it is probably an intermediate in the formation of dimer IV. Reaction of II with base would be expected to give 1,2-dibromobenzocyclobutadiene, which would upon dimerization give IV. Dimer III might arise by at least two different types of reactions. One isomer of IV might lose bromine to give III. The Diels-Alder reaction of the compound formed by 1,4-elimination of hydrogen bromide from tetrabromo-o-xylene with 1,2-dibromobenzocyclobutadiene, followed by elimination of hydrogen bromide and loss of molecular bromine would also give dimer III. A full account of the above results will be reported shortly.