

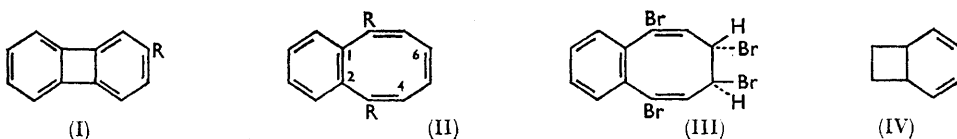
### 319. Biphenylenes. Part XII.<sup>1</sup> Further Studies on the Bromination of Biphenylene.

By J. W. BARTON, D. E. HENN, K. A. McLAUGHLAN, and J. F. W. McOMIE.

The non-catalysed reaction of bromine with biphenylene yields a tetrabromide and two hexabromides. The tetrabromide is 3,5,6,8-tetrabromo-5,6-dihydrobenzocyclo-octatetraene (III). Debromination of each bromo-compound gives 3,8-dibromobenzocyclo-octatetraene (II; R = Br) which can be further debrominated to give biphenylene. The proton magnetic resonance spectra of the products are discussed.

BROMINATION of biphenylene (I; R = H) with bromine in the presence of pyridine,<sup>2</sup> or with iodine monobromide (see Experimental section), gives 2-bromobiphenylene (I; R = Br) in good yield. With an excess of bromine in the absence of a catalyst, only a small amount of 2-bromobiphenylene is formed, the main reaction in this case being one of addition, and greatly accelerated by ultraviolet light. From this reaction three crystalline addition products, (A) (m. p. 129—140°), (B) [m. p. 153—154.5° (decomp.)], and (C) [m. p. 183—185° (decomp.)], have been isolated. Compound (A) is a tetrabromide, C<sub>12</sub>H<sub>8</sub>Br<sub>4</sub>, whilst (B) and (C), are hexabromides, C<sub>12</sub>H<sub>8</sub>Br<sub>6</sub>, having closely similar ultraviolet and infrared spectra.

Debromination of compounds (A), (B), and (C), by heating with an excess of sodium iodide in *NN*-dimethylformamide, gave high yields of dibromide, C<sub>12</sub>H<sub>8</sub>Br<sub>2</sub>, m. p. 93—94°. Prolonged reaction under these conditions gave some biphenylene. Debromination of either the dibromide or tetrabromide (A), by refluxing with zinc dust in acetic acid solution, also gave biphenylene.



The 60 Mc./sec. proton magnetic resonance (p.m.r.) spectra of these compounds are shown in the Table. All the chemical shifts were obtained in acetone solution. For tetrabromide (A) and hexabromide (B) first-order interpretation of these spectra gave the coupling constants, which were similarly obtained for hexabromide (C) from the spectrum of its benzene solution. The symmetric spectrum of the dibromide in acetone solution was

<sup>1</sup> Part XI, Baker, McLean, and McOmie, *J.*, 1964, 1067.

<sup>2</sup> Baker, Barton, and McOmie, *J.*, 1958, 2658.

Proton magnetic resonance spectra of some bromination products of biphenylene.

Compound	Phenyl	Chemical shifts				Coupling constants (c./sec.)					
		$\tau_4$	$\tau_5$	$\tau_6$	$\tau_7$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	$J_{4,7}$	$J_{4,6}$	$J_{5,7}$
Tetrabromide (A).....	2.40	3.27	5.68	5.05	3.8	9.1	11.5	7.8	—	—	—
Hexabromide (B).....	2.32	4.21	4.85	5.52	4.55	5.8	4.5	11.0	—	—	—
Hexabromide (C).....	2.43	4.58	4.63	6.22	4.33	1.4	5.6	11.6	—	—	—
Dibromide.....	2.72	3.49	4.28	4.28	3.49	4.0	11.0	4.0	1.6	-1.5	-1.5

Subscripts 4, 5, 6, and 7 refer to the hydrogens on carbon atoms 4, 5, 6, and 7, respectively.

fully analysed. In all four cases the spectra showed that the four extra-benzene hydrogen atoms are attached to separate, adjacent carbon atoms. However, the p.m.r. spectra are not sufficient to determine the structure of the molecules unambiguously, and recourse has been made to X-ray crystallography. A determination of the positions of all the atoms, except hydrogen, in the molecule of the tetrabromide (A) has been carried out using three-dimensional intensity information; it is 3,5,6,8-tetrabromo-5,6-dihydrobenzocyclooctatetraene (III).<sup>3</sup> Rupture of the bond common to the four- and one of the six-membered rings has occurred to give an eight-membered ring which exists in a skew-tub form. The p.m.r. peaks observed at  $\tau$  3.27 and 3.8 correspond to the olefinic hydrogens H-4 and H-7, respectively, and those at 5.05 and 5.68 to H-6 and H-5, respectively. H-5 experiences a considerable high-field shift with respect to H-6 as a result of the puckering of the larger ring, which causes H-5 to project above the benzene ring, so that it experiences a local magnetic field due to a ring current effect. The relative magnitudes of the coupling constants reflect the deformation of the ring.

Since it was not possible to explain the p.m.r. spectrum of the dibromide in terms of a biphenylene-type structure, it was thought that, in this molecule, there might also have been a ring expansion. In view of the symmetry of the spectrum, and since the four hydrogens of interest are attached to adjacent carbon atoms, it was thought that it might have structure (II; R = Br). A preliminary two-dimensional X-ray study<sup>3</sup> of this compound is in agreement with this conclusion. The p.m.r. peaks observed at  $\tau$  3.49 can be assigned to H-4 and H-7 by consideration of the magnitudes of the coupling constants, and by analogy with similar hydrogens observed in tetrabromide (A). H-5 and H-6 are not  $\beta$ -substituents to bromine atoms, and so are observed at higher field. The larger ring in this molecule exists in a symmetric-tub form whose geometry is such that appreciable long-range coupling constants might be expected. In fact such couplings are observed between H-4 and H-6, H-5 and H-7, and H-4 and H-7.  $J_{4,6}$  and  $J_{5,7}$  are of opposite sign to the other coupling constants, in accordance with expectation. It may be noted that the largest coupling constant in this molecule, 11.0 c./sec., arises between *cis*-olefinic hydrogens and not, as in (A), between *trans*-ethanic ones.

Three-dimensional X-ray intensity information for the dibromide and for the hexabromide (C) is being collected, but it has not yet been possible to obtain crystals of the hexabromide (B) suitable for an X-ray diffraction study. In consequence it is not yet possible to propose structures for compounds (B) and (C), although some conclusions can be reached from the p.m.r. data. Thus, the Table shows that the absorption due to the benzene-ring protons in both of these compounds occurs in the same region as it does in the spectrum of the tetrabromide (A), and significantly to low field of its position in the dibromide. This may suggest that compounds (A), (B), and (C) have similar structures and similar substituents on positions 3, 5, 6, and 8. It seems reasonable to suppose that these three compounds are closely related and the assignments given in the Table are made with this assumption.

It is known that some derivatives of the bicyclo[4,2,0]octa-2,4-diene system (IV) rearrange readily to give cyclo-octa[1,3,5]trienes<sup>4</sup> and it is possible that the initial reaction

<sup>3</sup> Henn and Colton, unpublished results.

<sup>4</sup> Vogel, *Angew. Chem.* (Internat. edn.), 1963, 2, 1.

of bromine with biphenylene (I; R = H) gives an intermediate of this type, which rearranges and finally gives 3,5,6,8-tetrabromo-5,6-dihydrobenzocyclo-octatetraene (III) on further addition of bromine.

The 1,4-elimination of bromine from the dibromide (II; R = Br) to give biphenylene is novel, particularly as it can be effected by iodide ion. Cyclo-octatetraene undergoes a base-catalysed rearrangement at 120°, to give benzocyclobutene,<sup>5</sup> but this is hardly analogous to the present case. The parent compound (II; R = H) has been reported,<sup>6</sup> but nothing is known of its tendency to valency isomerisation.

#### EXPERIMENTAL

The 60 Mc./sec. p.m.r. spectra were obtained on a Varian V4300B high-resolution instrument, and were calibrated using the normal side-band technique with tetramethylsilane as an internal reference.

The X-ray intensities were obtained from integrated equi-inclination Weissenberg photographs, using a Nonius Weissenberg camera with a Ni-filtered Cu  $k_{\alpha}$ -radiation. Computations were carried out using the DEUCE computer.

*Reaction of Biphenylene with Iodine Monobromide.*—Iodine monobromide, from iodine (0.87 g.) and bromine (0.545 g.) in dry carbon tetrachloride (40 ml.), was added dropwise to a solution of biphenylene (0.5 g.) in carbon tetrachloride (20 ml.) at 50°, a slow stream of dry air being drawn through the reaction mixture to remove hydrogen bromide as it was formed. After 1.5 hr., the volume of the solution having fallen to *ca.* 20 ml., more solvent was added, and the solution was washed with sodium hydrogen sulphide solution. After removal of the solvent the residual oil was treated with 2,4,7-trinitrofluorenone in acetic acid-ethanol, giving the complex of 2-bromobiphenylene (0.98 g., 54.5%), m. p. 135–137°.

*Action of Bromine on Biphenylene.*—Biphenylene (2 g.) in dry carbon tetrachloride (70 ml.) was treated with bromine (1.45 ml.). After 30 min. in bright sunlight (Pyrex flask) the solution had become pale yellow. It was washed free from acid, dried, and vacuum evaporated. The residue was chromatographed on a silica column, elution being with hexane, and the following compounds were obtained, in the order given: (i) 2-bromobiphenylene (0.2 g.); (ii) 3,5,6,8-tetrabromo-5,6-dihydrobenzocyclo-octatetraene [tetrabromide (A)], colourless prisms from benzene-methanol (0.65 g.), m. p. 139–140° (Found: C, 30.5; H, 1.8.  $C_{12}H_8Br_4$  requires C, 30.5; H, 1.7%),  $\lambda_{max.}$  (in ethanol) 238  $m\mu$  ( $\log \epsilon$  4.19); (iii) hexabromide (C), colourless leaflets from benzene-methanol (0.7 g.), m. p. 183–185° (decomp.) (Found: C, 22.6; H, 1.2.  $C_{12}H_8Br_6$  requires C, 22.8; H, 1.3%),  $\lambda_{max.}$  (in ethanol) 280  $m\mu$ ,  $\lambda_{min.}$  263  $m\mu$  ( $\log \epsilon$  3.26 and 2.99); (iv) hexabromide (B), colourless needles from benzene-methanol (1.0 g.), m. p. 153–154.5° (decomp.) (Found: C, 22.6; H, 1.0%),  $\lambda_{max.}$  (in ethanol) 284  $m\mu$ ,  $\lambda_{min.}$  263  $m\mu$  ( $\log \epsilon$  3.43 and 3.15).

Yields of the isomers varied; the above were obtained in a typical experiment.

*3,8-Dibromobenzocyclo-octatetraene.*—A solution of 3,5,6,8-tetrabromo-5,6-dihydrobenzocyclo-octatetraene (0.6 g.) and sodium iodide (2 g.) in *NN*-dimethylformamide (20 ml.) was heated on a water-bath for 4 hr., and poured into water. The precipitate was crystallised from aqueous methanol, giving 3,8-dibromobenzocyclo-octatetraene (0.35 g., 88.5%) as colourless prisms, m. p. 93–94° (Found: C, 46.2; H, 2.7.  $C_{12}H_8Br_2$  requires C, 46.2; H, 2.7%),  $\lambda_{max.}$  (in ethanol) 214  $m\mu$  ( $\log \epsilon$  3.85).

Under similar conditions, hexabromides (B) and (C) gave 3,8-dibromobenzocyclo-octatetraene in yields of 84.5 and 81%, respectively.

*Debromination of 3,8-Dibromobenzocyclo-octatetraene.*—(a) A solution of 3,8-dibromobenzocyclo-octatetraene (0.3 g.) and sodium iodide (1 g.) in *NN*-dimethylformamide (10 ml.) was heated at 100° (bath) for 50 hr., diluted, and steam distilled. The oily crystals in the distillate were collected and treated with 2,4,7-trinitrofluorenone in benzene-methanol, giving biphenylene 2,4,7-trinitrofluorenone complex (0.11 g., 24%) as deep red needles. After recrystallisation, the m. p. and mixed m. p. were 156–157°. Starting material (0.09 g.) was recovered from the residue which was non-volatile in steam.

(b) 3,8-Dibromobenzocyclo-octatetraene (0.2 g.), zinc dust (0.5 g.), and acetic acid (20 ml.)

<sup>5</sup> Eglinton, Raphael, and Willis, *Proc. Chem. Soc.*, 1962, 334.

<sup>6</sup> Wittig, Eggers, and Duffner, *Annalen*, 1958, 619, 10.

[1964]

*Chatt, Johnson, and Shaw.*

1625

were refluxed for 6 hr., and poured into water. The oily crystals were treated with 2,4,7-trinitrofluorenone, as in (a), giving the biphenylene complex (0.13 g., 43%), m. p. 152—153°.

Under similar conditions, 3,5,6,8-tetrabromo-5,6-dihydrobenzocyclo-octatetraene gave a 78% yield of biphenylene, isolated as the 2,4,7-dinitrofluorenone complex.

The physical studies reported are a part of the research programme of the National Physical Laboratory, and are published by permission of the Director.

(J. W. B. and J. F. W. McO.) THE UNIVERSITY, BRISTOL 8.

(D. E. H. and K. A. McL.) THE NATIONAL PHYSICAL LABORATORY, TEDDINGTON.

[Received, September 25th, 1963.]

---