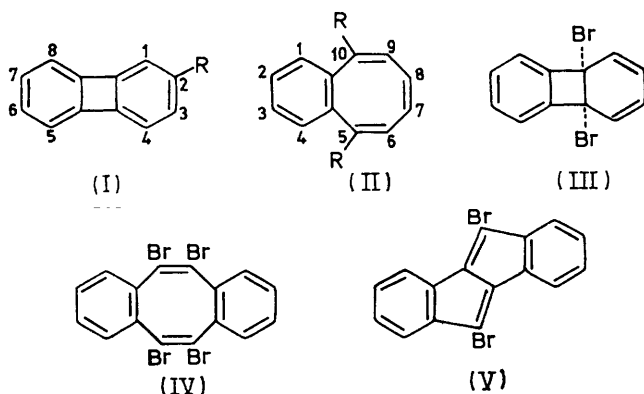


Benzocyclo-octenes. Part III.¹ † Reactions of 5,10-Dibromobenzocyclo-octene

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The thermal decomposition of 5,10-dibromobenzocyclo-octene gives biphenylene and 2-bromobiphenylene. Reactions of this dihalide with silver salts also give 2-substituted biphenylenes, whereas reaction with sodium methoxide gives 1-methoxybiphenylene as the main product. The mechanisms of these reactions are discussed. The dihalide undergoes normal halogen-metal exchange to give 5,10-dilithiobenzocyclo-octene, thus providing routes to the parent hydrocarbon and other 5,10-disubstituted benzocyclo-octenes.

In earlier papers it was reported that 5,10-dibromobenzocyclo-octene (II; R = Br) was formed by the photo-induced addition of bromine to biphenylene (I; R = H)² and that this dihalide could be converted back



into biphenylene by heating it with either zinc dust in acetic acid or sodium iodide in *NN*-dimethylformamide.³ The latter unexpected finding prompted us to examine the reactions of the dibromide (II; R = Br) with other nucleophiles. It did not react with piperidine, sodium cyanide, or sodium azide in protic or dipolar aprotic solvents, but it became apparent that it decomposed on prolonged heating in solvents, giving rise to mixtures of biphenylene and 2-bromobiphenylene (I; R = Br). The addition of phenol to the reaction mixture to act as a bromine scavenger lowered the amount of 2-bromobiphenylene formed relative to biphenylene; thus the latter is formed by direct thermal elimination of bromine from (II; R = Br) and it then undergoes substitutive bromination to some extent. The absence of 2-bromobiphenylene as a product when sodium iodide is present must be due to the effectiveness of iodide ion as a bromine scavenger. Transannular thermal elimination of bromine in a cyclo-octatetraene derivative has been observed previously with the sterically crowded 5,6,11,12-tetrabromodibenzo[*a,e*]cyclo-octene (IV), which gives 5,10-dibromoindeno[2,1-*a*]indene (V) rather than 5,10-dibromobenzocyclo-octene.⁴ This reaction is thought

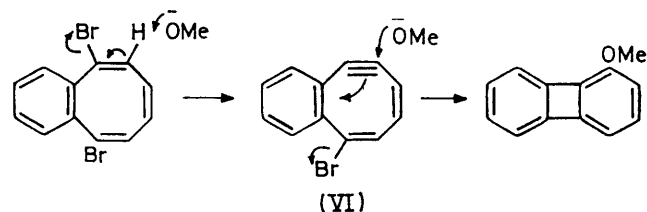
† This series was previously entitled 'Benzocyclo-octatetraenes.' Changes in nomenclature have been made in order to conform with the system used by the Ring Index and *Chem. Abs.* and recommended by the I.U.P.A.C.

¹ Part II, J. W. Barton and K. E. Whitaker, *J. Chem. Soc. (C)*, 1968, 1663.

² J. W. Barton and K. E. Whitaker, *J. Chem. Soc. (C)*, 1968, 28.

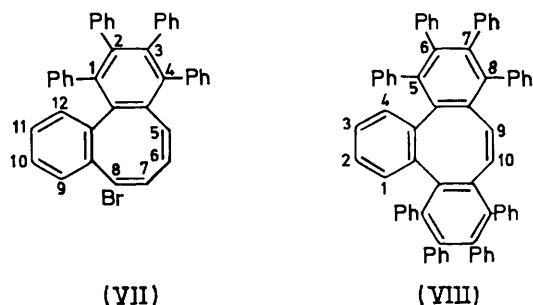
to proceed by a free-radical process and the conversion of compound (II; R = Br) into biphenylene probably takes place in the same way, with or without the involvement of the valence tautomer (III). Attempts to trap (III) by reaction with dienophiles have been unsuccessful (*cf.* benzocyclo-octene⁵); only the thermal decomposition products of (II; R = Br) could be isolated.

When the dibromide (II; R = Br) was treated with sodium methoxide or potassium hydroxide in refluxing methanol the only isolable product was 1-methoxybiphenylene (20–25%). The position of the entering nucleophile suggested that an elimination-addition



SCHEME 1

process was involved, as in Scheme 1. The intermediacy of 'ynes' akin to 10-bromo-5,6-didehydrobenzocyclo-octene (VI) is now well established,^{5,6} and when this reaction was conducted in the presence of



2,3,4,5-tetraphenylcyclopentadienone it gave 8-bromo-1,2,3,4-tetraphenyldibenzo[*a,c*]cyclo-octene (VII), the initial adduct of (VI) having aromatised with extrusion of carbon monoxide. The use of potassium *t*-butoxide as base in the reaction gave a very low yield of 5,6,7,8,11,12,13,14-octaphenyltribenzo[*a,c,e*]cyclo-octene

³ J. W. Barton, D. E. Henn, K. A. McLaughlan, and J. F. W. McOmie, *J. Chem. Soc.*, 1964, 1622.

⁴ M. P. Cava, R. Pohlke, and M. J. Mitchell, *J. Org. Chem.*, 1963, 28, 1861.

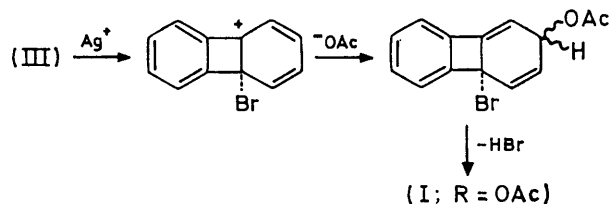
⁵ J. A. Elix and M. V. Sargent, *J. Amer. Chem. Soc.*, 1969, 91, 4734.

⁶ A. Krebs and D. Byrd, *Annalen*, 1967, 707, 66.

(VIII), the product of two successive 'yne' additions. The ^1H n.m.r. spectra of these two products are in good agreement with the structures (VII) and (VIII) assigned to them. In the former, the cyclo-octene ring protons H-6 and H-5 give rise to a quartet and a doublet, at τ 4.38 and 3.68, respectively. As expected, the signal for H-7, adjacent to the bromine atom, is masked by the aromatic multiplet. In the symmetrical structure (VIII) H-9 and H-10 give a singlet at τ 3.87. A sharp peak (4H) at τ ca. 2.8 in the aromatic region of each spectrum is probably due to the benzenoid protons.

The dibromide (II; R = Br) underwent normal halogen-metal exchange with *n*-butyl-lithium to give the dilithio-derivative (II; R = Li), which on carboxylation gave the dicarboxylic acid (II; R = CO₂H) in high yield. Despite the proximity of its carboxy-groups this acid showed no tendency to form a cyclic anhydride. Treatment of the dilithio-derivative with methanol gave benzocyclo-octene (II; R = H) in high yield, thus providing an alternative synthesis of this rather inaccessible hydrocarbon (*cf.* ref. 5) from biphenylene (20–25% overall), which is now available by a one-step process from anthranilic acid.⁷ The 5,10-dideuterio-derivative (II; R = D) was obtained in the same way; its ^1H n.m.r. spectra support the assignments previously made for the spectrum of (II; R = H)⁸ and for that of the benzohomotropylium ion.⁹

Some reactions of the dibromide (II; R = Br) with silver salts were also investigated. Acetolysis with silver acetate in acetic acid proceeded rapidly to give 2-acetoxibiphenylene (I; R = OAc), together with small amounts of biphenylene. Here again, as in the reaction with methoxide ion, the attacking nucleophile has entered a previously unsubstituted position, in this case β to one of the original bromine atoms. The mechanism of this process is not clear but a direct ionisation of or an allylic attack on (II; R = Br) is unlikely, and reaction through the valence tautomer (III) by ionisation, allylic attack of acetate ion, and subsequent 1,4-elimination of hydrogen bromide (Scheme 2) seems more probable. Participation of the valence



SCHEME 2

tautomer (III) in this particular process would be in keeping with observations of the effect of silver salts on equilibria in similar valence tautomeric systems.¹⁰ Replacement reactions with other silver salts gave poor results. The reaction of the dibromide (II; R = Br) with silver nitrite in dimethyl sulphoxide gave 2-nitro-

biphenylene (3%) (I; R = NO₂) together with biphenylene (8%); that with silver cyanide gave low yields of biphenylene containing only traces of material corresponding (g.l.c.) to 2-cyanobiphenylene (I; R = CN). No 1-substituted biphenylenes were detected in these reactions. In hydrocarbon solvents the reaction of the dibromide (II; R = Br) with silver nitrite proceeded slowly to give yellow gums which showed strong nitro-group absorptions in their i.r. spectra.

All the monosubstituted biphenylenes used here as reference compounds were known with the exception of 1-cyanobiphenylene, which was prepared by the reaction of 1-iodobiphenylene with copper(I) cyanide in *NN*-dimethylformamide.

EXPERIMENTAL

I.r. spectra were determined for Nujol mulls and u.v. spectra for solutions in cyclohexane. ^1H N.m.r. spectra were taken for solutions in carbon tetrachloride with tetramethylsilane as internal reference, unless otherwise stated. G.l.c. analyses were carried out at 200° on columns of 10% Apiezon L on Chromosorb W with nitrogen as carrier gas and flame ionisation detection.

Thermal Decomposition of 5,10-Dibromobenzocyclo-octene.

(a) A solution of the dihalide ² (1 g) in acetic acid (40 ml) was refluxed for 19 h, then poured into water (350 ml). The resulting oil was collected by benzene extraction and shown (g.l.c.) to consist of a mixture of 2-bromobiphenylene¹¹ and biphenylene in the ratio 2.6:1 by comparison with standard mixtures. Evaporation of the solvent and chromatography of the residue on silica with *n*-hexane as eluant gave 2-bromobiphenylene (0.29 g, 39%), m.p. 64–65° (from methanol), then biphenylene (0.135 g, 27%), m.p. 110–111° (from methanol).

(b) The decomposition was conducted as in (a) with the addition of phenol (1.5 g). After additional washing with dilute alkali to remove phenolic material the crude product was found to contain 2-bromobiphenylene and biphenylene in the ratio 1.33:1.

(c) The decomposition was conducted as in (a), with the addition of sodium iodide (3 g). After washing with sodium hydrogen sulphite solution to remove iodine the product was chromatographed as in (a) giving biphenylene (0.26 g, 53%), m.p. 110–111°.

Reaction of 5,10-Dibromobenzocyclo-octene with Sodium Methoxide.—A solution of the dibromo-compound (0.5 g) and sodium methoxide (0.5 g) in methanol (10 ml) was refluxed for 3 h, then evaporated to dryness *in vacuo*, and the residue was shaken with benzene and water. The dried benzene extracts were evaporated giving a yellow oil which on treatment with successive portions of 2,4,7-trinitrofluorenone in benzene-methanol gave the complex of 1-methoxybiphenylene¹¹ (0.185 g, 23%) as deep maroon needles, m.p. 156–157° (from benzene-methanol). Chromatographic cleavage of the complex over alumina in benzene solution gave 1-methoxybiphenylene, identical with an authentic sample.¹¹ Solutions of sodium methoxide in *NN*-dimethylformamide, with or without added copper salts, gave similar results, as did a solution of potassium hydroxide in methanol. In no case was any 2-methoxy-

⁷ W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, 1968, **90**, 814.

¹⁰ W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, 1967, **89**, 4788.

¹¹ W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 1958, 2658.

⁷ F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, 1968, **48**, 12.

⁸ H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.* (1 g)¹ 1968, **90**, 6096.

biphenylene¹¹ detected, as shown by g.l.c. of the crude products.

Reactions of 5,10-Dibromobenzocyclo-octene with Alkoxides in the Presence of 2,3,4,5-Tetraphenylcyclopentadienone.—

(a) Sodium methoxide (0.5 g) was added in portions to a stirred solution of the dibromo-compound (0.75 g) and 2,3,4,5-tetraphenylcyclopentadienone (3 g) in *NN*-dimethylformamide (20 ml) at room temperature. Next day the mixture was diluted with water (150 ml) and extracted with benzene-ether. After concentration of the extracts and removal of the bulk of the unchanged tetraphenylcyclopentadienone by filtration the residue was chromatographed on silica. Elution with benzene-hexane (30:70) gave first unchanged 5,10-dibromobenzocyclo-octene (0.612 g), followed by 8-bromo-1,2,3,4-tetraphenyldibenzo[a,c]cyclo-octene (VII) which was obtained as small prisms (0.18 g, 68% based on reacted dibromide), m.p. 236–237.5° (from hexane) (Found: C, 82.2; H, 4.6; Br, 13.6%; M^+ , 586.128, 588.128. $C_{40}H_{27}Br$ requires C, 81.8; H, 4.6; Br, 13.6%; M , 586.129, 588.127), λ_{max} 213 and 245 nm ($\log \epsilon$ 4.63 and 4.62), τ 2.65–3.52 (25H, 4 \times Ph, H-9, H-10, H-11, H-12, and H-7), 3.68 (1H, d, H-5), and 4.38 (1H, q, H-6), $J_{6,7}$ 12, $J_{5,6}$ 4 Hz.

(b) A slurry of potassium *t*-butoxide (3 g) in dry ether (80 ml) was added to a stirred, refluxing solution of the dibromo-compound (0.5 g) and tetraphenylcyclopentadienone (3.4 g) in ether (80 ml) under dry nitrogen. After 1 h the mixture was cooled and shaken with water. The ethereal layer was dried, concentrated and, after removal of the tetraphenylcyclopentadienone which separated, applied to a silica column. Elution with benzene-hexane (30:70) gave a yellow oil which gave no complex with 2,4,7-trinitrofluorenone and which was shown by t.l.c. to consist of a complex mixture. Further elution with benzene-hexane (50:50) gave 5,6,7,8,11,12,13,14-octaphenyltribenzo[a,c,e]-cyclo-octene as microcrystals (0.085 g, 5%), m.p. 308–312° (from benzene-methanol) (Found: C, 94.55; H, 5.55. $C_{88}H_{46}$ requires C, 94.6; H, 5.4%), M^+ 862, λ_{max} 212.5 and 251 nm ($\log \epsilon$ 4.85 and 4.80), τ 2.40–3.64 (44H) and 3.87 (2H, s, H-9 and H-10).

Benzocyclo-octene-5,10-dicarboxylic Acid.—A 1.5M-solution of *n*-butyl-lithium in hexane (10 ml) was added dropwise under dry nitrogen to a stirred solution of 5,10-dibromobenzocyclo-octene (1.0 g) in hexane (10 ml) at room temperature. After 1 h the solution was poured on to a slurry of solid carbon dioxide in dry ether and the mixture was allowed to come to room temperature. The ether-hexane solution was shaken with dilute hydrochloric acid, then extracted with 2*N*-sodium hydroxide. Acidification of the extracts precipitated the *dicarboxylic acid* (0.6 g, 77%); crystallisation from aqueous methanol gave small, pale yellow prisms, m.p. 293° (decomp.) (Found: C, 69.4; H, 4.05. $C_{14}H_{10}O_4$ requires C, 69.4; H, 4.1%), ν_{max} 1680 cm^{-1} (C=O); m/e 242 (M^+ , 75%), 152, and 153.

The *diamide*, prepared *via* the acid chloride, was obtained as off-white micro-crystals, m.p. 232° (Found: C, 69.9; H, 4.9; N, 11.9. $C_{14}H_{12}N_2O_2$ requires C, 70.0; H, 5.0; N, 11.7%), ν_{max} 1675 cm^{-1} (C=O).

Benzocyclo-octene and 5,10-Dideuteriobenzocyclo-octene.—The dibromo-compound (1.0 g) was treated with *n*-butyl-lithium as in the previous experiment. After 1 h the solution was treated with methanol (10 ml), stirred for a

¹² L. Friedman and D. F. Lindow, *J. Amer. Chem. Soc.*, 1967, **90**, 2329.

¹³ J. W. Blatchly, D. V. Gardner, and J. F. W. McOmie, *J. Chem. Soc. (C)*, 1967, 272.

further 10 min, then diluted with hexane and shaken with dilute hydrochloric acid. Evaporation of the dried hexane solution gave a crystalline residue which was purified by chromatography over silica in benzene-hexane (1:2), giving benzocyclo-octene (0.42 g, 84.5%), m.p. 45–48°, identical (i.r. and n.m.r. spectra; g.l.c. retention time) with a sample prepared by the addition of benzyne to benzene.¹²

The use of methan[²H]ol in the reaction gave 5,10-dideuteriobenzocyclo-octene, τ 2.89–3.32 (4H, A_2B_2), 4.17 (2H, s, H-6, H-9), and 4.30 (2H, s, H-7, H-8); τ (D_2SO_4) 1.12–2.63 (8H); τ (FSO_3H) 1.12–2.68 (8H), 5.15 (*ca.* 0.5H, d, H-5a), and 8.95 (*ca.* 0.5H, d, H-5b). When the latter spectrum was scanned rapidly at –30° immediately after dissolution of the compound in fluorosulphonic acid the absorption at τ 8.95 (outside proton) was almost zero and that at τ 5.15 (inside proton) approximately 1H (broad s).

Reactions of 5,10-Dibromobenzocyclo-octene with Silver Salts.—(a) The dibromo-compound (1.0 g) and silver acetate (1.0 g) in acetic acid (20 ml) were refluxed with stirring for 45 min. The solution was filtered and evaporated *in vacuo* and the resulting brown oil chromatographed on a silica column with benzene-hexane (1:1) as eluant. After the elution of biphenylene (0.017 g), the main fraction gave 2-acetylbiphenylene (0.35 g, 51.5%) as needles, m.p. 93–94° (from aqueous methanol), identical with an authentic sample.¹³

(b) The dibromo-compound (1.0 g) and silver nitrite (0.8 g) in dimethyl sulphoxide (20 ml) were stirred and heated on a water-bath for 2 h. The resulting orange-brown solution was filtered, diluted with water, and extracted with benzene-hexane (1:1). Vacuum evaporation of the dried extracts gave a viscous oil which was shown by g.l.c. to contain biphenylene and 2-nitrobiphenylene.¹¹ Chromatography over silica with benzene-hexane (1:1) as eluant gave first biphenylene (0.04 g, 8%), m.p. 110–111°, followed by 2-nitrobiphenylene (0.02 g, 3%), yellow needles, m.p. 107–108° (from methanol), identical with an authentic sample.¹¹

(c) When a reaction was carried out as in (b), using silver cyanide in place of the nitrite, only traces of an oily product were obtained on extraction of the diluted reaction mixture. This was shown by g.l.c. to contain biphenylene and some material corresponding in retention time to 2-cyanobiphenylene.¹⁴ It was not further investigated.

1-Cyanobiphenylene (with J. B. Chadwick).—A suspension of copper(I) cyanide (0.1 g) and 1-iodobiphenylene² (0.3 g) in *NN*-dimethylformamide (3 ml) was stirred and refluxed for 4 h. It was added to a solution of hydrated iron(III) chloride (0.3 g) in water (2.5 ml) and hydrochloric acid (0.1 ml), heated on a water-bath for 20 min, then diluted with water and extracted with benzene. The extracts were washed with 6*N*-hydrochloric acid, 2*N*-sodium hydroxide, and water, then dried and evaporated, giving a yellow oil which was chromatographed on silica in benzene solution. After a small fore-run containing biphenylene and 1-iodobiphenylene the main fraction gave 1-cyanobiphenylene (0.11 g, 58%) as yellow needles, m.p. 59–59.5° (from hexane) (Found: C, 88.3; H, 4.1; N, 7.8. $C_{18}H_{17}N$ requires C, 88.1; H, 4.0; N, 7.9%), ν_{max} 2240 cm^{-1} (C≡N).

We thank the S.R.C. for a studentship (to K. E. W.).

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¹⁴ W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 1958, 2666.