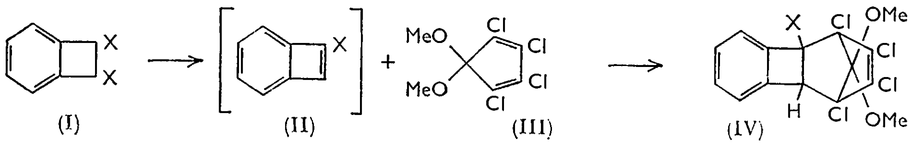
463. *Benzocyclobutenes. Part III.*[1] *Conversion of Some Benzocyclobutenes into Derivatives of Benzocyclo-octatetraene and of Biphenylene*

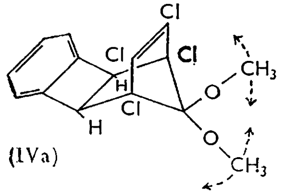
By A. J. BOULTON and J. F. W. McOMIE

The trapping of benzocyclobutadiene and 3-bromobenzocyclobutadiene with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene gave 1 : 1 adducts, which were converted into 4,5,6,7-tetrachlorobenzocyclo-octatetraene and 1,2,3,4-tetrachlorobiphenylene, respectively. Some further transformations of the benzocyclobutadiene adduct are described.

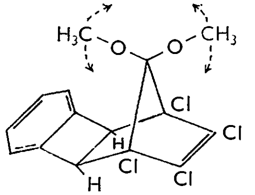
THIS Paper describes work directed towards a synthesis of the biphenylene nucleus, but although this end was ultimately realised, it proved impracticable as a preparative method. Several examples are known of Diels–Alder additions of benzocyclobutadienes to cyclic dienes,[2,3] and the conversion of one of the adducts so formed into a biphenylene is also known.[2b,3b] 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene functions as a diene in the Diels–Alder reaction,[4] and since the dimethyl ketal bridge of the products can be removed without difficulty,[4] a route to the ring system of biphenylene appeared open.

Generation of benzocyclobutadiene (II; X = H) [from its di-iodide (I; X = I), using zinc dust in ethanol] in the presence of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (III) gave a 1 : 1 adduct (IV; X = H) in 60% yield. The proton nuclear magnetic resonance (n.m.r.) spectrum of this compound was fully consistent with the assigned structure, and furthermore indicated that the *endo*- (IVa) was preferable to the *exo*-configuration (IVb), because drawings indicate that in the latter isomer one of the methyl groups of the ketal bridge rotates to a large extent within the shielding influence of the benzene ring. The adduct in fact shows only a small chemical shift (0·09 p.p.m.) between the two methyl groups, which is more in accord with structure (IVa). Cyclopentadiene itself with benzocyclobutadiene gives the hydrocarbon analogue of compound (IV),[2a] probably in the *endo*-configuration, in contrast to the product of reaction of norbornadiene with benzyne, which is the *exo*-compound.[5]





(IVa)



(IVb)

Concentrated sulphuric acid converted the ketal (IV; X = H) into the bridged ketone (V), and n.m.r. evidence (persistence of absorption due to angular benzylic protons) showed that the four-membered ring remained intact. When the ketone was heated, however,

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[1] Part II, W. Baker, J. F. W. McOmie, and D. R. Preston, *J.*, 1961, 2971.

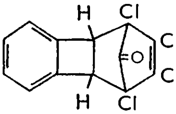
[2] (*a*) (Cyclopentadiene) C. D. Nenitzescu, M. Avram, and D. Dinu, *Chem. Ber.*, 1957, **90**, 2541; (*b*) (2,5-Diphenyl-3,4-benzofuran, spiro[2,4]hepta-4,6-diene, and 5,5-dimethylfulvene) M. Avram, G. D. Mateescu, D. Dinu, I. G. Dinulescu, and C. D. Nenitzescu, *Studii si Cercetari Chim.* (*Acad. R.P.R.*), 1961, **9**, 435.

[3] (*a*) (Cyclopentadiene and furan). M P. Cava and M. J. Mitchell, *J. Amer. Chem. Soc.*, 1959, **81**, 5409; (*b*) (2,5-Diphenyl-3,4-benzofuran) M. P. Cava and R. Pohlke, *J. Org. Chem.*, 1962, **27**, 1564.

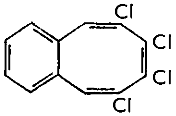
[4] E. T. McBee, W. R. Diveley, and J. E. Burch, *J. Amer. Chem. Soc.*, 1955, **77**, 385; E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav, and H. P. Braendlin, *ibid.*, 1962, **84**, 3557.

[5] H. E. Simmons, *J. Amer. Chem. Soc.*, 1961, **83**, 1657.

carbon monoxide loss was accompanied by opening of this ring, and the product was the chlorinated benzocyclo-octatetraene (VI), with olefinic proton absorption in the n.m.r. spectrum, rather than the angular benzylic proton absorption expected of the tricyclic structure (VII). The same product (VI) was also obtained directly from the ketal by boiling it with hydrogen bromide in acetic acid. Attempts were therefore made to circumvent the ring-opening by bromination of the ketal or the ketone at an angular benzylic position, in the hope that dehydrobromination and loss of carbon monoxide from the ketone would provide the fully unsaturated tricyclic ring system of biphenylene. Brominations with *N*-bromosuccinimide, however, failed to yield the desired products. An alternative route to the brominated compound (IV; X = Br) seemed to be provided by Diels–Alder addition of 3-bromobenzocyclobutadiene (II; X = Br) to the cyclopentadiene (III). Cava and Pohlke [3b] reported a 60% yield of adduct from the monobromobenzocyclobutadiene and 2,5-diphenyl-3,4-benzofuran; however, we find that, in the presence of the diene (III), 1,2-dibromobenzocyclobutene (I; X = Br) and potassium t-butoxide gave only a 1% yield of the bromo-adduct (IV; X = Br), the major product being the bromobenzobiphenylene (VIII).[6] When this bromo-adduct was boiled with hydrogen bromide in acetic acid it gave the tetrachlorobiphenylene (IX), which possessed an ultraviolet absorption spectrum characteristic of biphenylenes.



(V)



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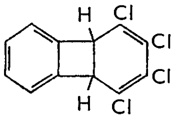
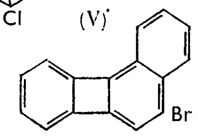
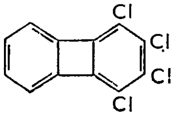


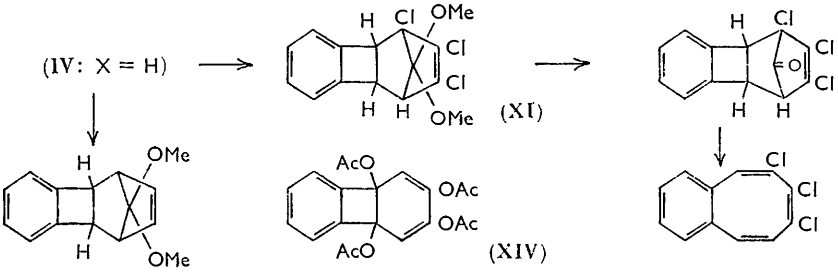
(VII)

(VIII)





(IX)



(XI) (XII) (X) (XIV) (XIII)

Dechlorination of the ketal adduct (IV; X = H) was next investigated. Lithium and t-butyl alcohol in tetrahydrofuran provided a single product, which proved to be the chlorine-free compound (X), along with about 30% of starting material. From this result, it was supposed that removal of one chlorine atom facilitated removal of the rest. It was, however, found that sodium amalgam and ethanol would remove one chlorine atom only (from a bridgehead carbon atom) to give the trichloro-ketal (XI), which was unaffected by further prolonged action of the same reducing agent.

The trichloro-ketal was smoothly converted into the ketone (XII) by concentrated sulphuric acid, and this gave 4,5,6-trichlorobenzocyclo-octatetraene (XIII) on decarbonylation at 140°. The n.m.r. spectrum of compound (XIII) showed, besides a broad peak due to the protons on the benzene ring, a singlet (1 proton), and an AB quartet (2 protons) with a coupling constant of 9·5 c./sec., in the region τ 3—4, thus confirming the presence of the bridgehead proton in the trichloro-ketal (XI) and -ketone (XII).

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[6] M. P. Cava and J. F. Stucker, *J. Amer. Chem. Soc.*, 1957, **79**, 1706.

Attempts were made to convert the chlorine-free ketal (X) into benzocyclo-octatetraene, but treatment with acids led only to blackening and extensive decomposition.

This work has established the predominance of bicyclic [*e.g.*, (VI)] over tricyclic [*e.g.*, (VII)] structures for two new benzocyclo-octatetraenes. The n.m.r. spectrum of benzocyclo-octatetraene[7] itself shows that this compound also exists in the bicyclic form and the same situation probably obtains with biphenylene dibromide.[8] In the case of a fifth example, previously formulated[9] as 2,3,4a,8b-tetra-acetoxy-4a,8b-dihydrobiphenylene (XIV), a firm conclusion is difficult to reach, on account of the lack of bridgehead vinyl protons.

EXPERIMENTAL

Infrared spectra were recorded for Nujol mulls, and ultraviolet spectra for solutions in 95% ethanol, unless otherwise specified. Some proton n.m.r. spectra were taken at 60 Mc./sec., others at 40 Mc./sec., with tetramethylsilane as internal standard. The light petroleum fraction used throughout had b. p. 60—80°.

1,2,3,4-*Tetrachloro*-1,4,4a,8b-*tetrahydro*-9,9-*dimethoxy*-1,4-*methanobiphenylene* (IV; X = H).—1,2-Di-iodobenzocyclobutene[10] (14·5 g.) and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene[4] (11·0 g.) in ethanol (150 ml.) was added under nitrogen, during 20 min. to a stirred suspension of activated[10] zinc dust (35 g.) in ethanol (70 ml.) containing more of the cyclopentadiene (5·0 g., 45% excess). A slight rise in temperature was observed; the mixture was stirred for a further 15 min., refluxed for 2 hr., cooled, diluted with benzene (300 ml.), filtered through a Celite pad, and the filtrate extracted with water (3 × 100 ml.). After drying ($MgSO_4$), the benzene layer was evaporated and the residue dissolved in light petroleum (50 ml.). Crystals of the *adduct* were deposited on cooling, and were collected after 24 hr. The mother-liquors were evaporated, and the residue was heated (bath *ca.* 140°) under reduced pressure (10 mm.) to drive off the excess of cyclopentadiene. The remaining solid, dissolved in benzene–light petroleum (1 : 1), was run through a short column of alumina, providing, after evaporation of solvents and recrystallisation as before, a further crop of the adduct. The combined solids (8·9 g., 60%) were recrystallised from light petroleum giving large prisms, m. p. 132—133° (Found: C, 49·0; H, 3·3. $C_{15}H_{12}Cl_4O_2$ requires C, 49·2; H, 3·3%), $\lambda_{max.}$ 271·5, 265, 259·5 mμ (ε 1750, 1650, 960) with an inflection at 254 mμ and absorption increasing below 250 mμ to a peak below 210 mμ (ε 12,700 at 210 mμ).

The n.m.r. spectrum (CCl_4) showed a symmetrical multiplet centred at 2·88 τ (4 aromatic protons), and single sharp peaks at 5·95 (2 angular protons), 6·36 and 6·45 τ (each 3 methoxyl protons).

The preparation was repeated without using nitrogen to exclude air; the small diminution in yield observed was probably not significant.

1,2,3,4-*Tetrahydro*-1,4,4a,8b-*tetrahydro*-1,4-*methanobiphenylen*-9-*one* (V).—The above ketal (IV; R = H) (3·0 g.) was finely powdered and mixed with concentrated sulphuric acid (30 ml.). After being kept for 3·5 hr. at room temperature the mixture was heated to 60° for 10 min., while being ground with a glass rod. It was then cooled and poured into ice-water (200 ml.). Filtration, followed by crystallisation of the washed and dried solid from light petroleum, provided the *ketone* (1·89 g., 72%) as long needles, m. p. 139° (decomp.) after sublimation (95°/3 × 10^{-6} mm.) (Found: C, 48·9; H, 2·3. $C_{13}H_6Cl_4O$ requires C, 48·8; H, 1·9%), $\nu_{max.}$ 1810m cm.$^{-1}$ (C=O) (broad peak with a subsidiary maximum at 1785 cm.$^{-1}$), $\lambda_{max.}$ 270·5, 264·5, 259 mμ (ε 1760, 1740, 1100) with an inflection at 253·5 mμ and ε 14,200 at 210 mμ (solvent cut-off). The spectrum was almost identical in cyclohexane. No carbonyl absorption in the ultraviolet region was detected; presumably it was masked by the benzenoid absorption.

The n.m.r. spectrum ($CHCl_3$) showed a single resonance (5·92 τ) due to the angular protons: absorption due to the aromatic protons was almost completely masked by the solvent peak.

4,5,6,7-*Tetrachlorobenzocyclo-octatetraene* (VI).—(*a*) *From the bridged ketone* (V). The ketone (V) (0·5 g.) was heated at 160° without solvent. Evolution of carbon monoxide (identified by its infrared spectrum) ceased after *ca.* 15 min., when 33 ml./25° (90%) had been produced.

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[7] G. Wittig, H. Eggers, and P. Duffner, *Annalen*, 1958, **619**, 10.

[8] J. W. Barton, D. E. Henn, K. A. McLauchlan, and J. F. W. McOmie, *J.*, 1964, 1622.

[9] J. M. Blatchly, J. F. W. McOmie, and S. D. Thatte, *J.*, 1962, 5090.

[10] M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, 1957, **79**, 1701.

The residue was crystallised from light petroleum (charcoal), giving the cyclo-octatetraene (VI) (0·34 g., 75%) as prisms, m. p. 122—123°.

(*b*) *Directly from the ketal* (IV; X = H). The ketal adduct (3·0 g.) was boiled for 4·5 hr. with a 30% solution of hydrogen bromide in acetic acid (60 ml.). On cooling, much of the *product* crystallised out as blades. Dilution with water precipitated the remainder, which was filtered off, washed, dried, and crystallised from light petroleum as prisms, m. p. 122—123° (2·2 g., 92%), identical with the product obtained as in (*a*) above (Found: C, 49·35; H, 2·0. $C_{12}H_6Cl_4$ requires C, 49·35; H, 2·1%), $\lambda_{max.}$ 221 mμ (ε 28,900), with inflections at *ca.* 238 and 247 mμ. The n.m.r. spectrum (CCl_4) showed a symmetrical multiplet centred at 2·76 τ (4 aromatic protons) and a single sharp absorption at 3·10 τ (2 olefinic protons).

N-*Bromosuccinimide Reactions.*—The ketal adduct (IV; R = H) (1·0 g.) was almost quantitatively recovered after being refluxed in carbon tetrachloride with *N*-bromosuccinimide (0·5 g.) and benzoyl peroxide (0·2 g.) for 5 hr. Likewise, the bridged ketone (V) (0·11 g.) was unchanged after a similar treatment with an equivalent quantity of *N*-bromosuccinimide.

8b-*Bromo*-1,2,3,4-*tetrachloro*-1,4,4a,8b-*tetrahydro*-9,9-*dimethoxy*-1,4-*methanobiphenylene* (IV; X = Br).—Potassium (2·0 g.) was dissolved in t-butyl alcohol (100 ml.), and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (3·0 g.) added. To the stirred solution, heated to *ca.* 50° in nitrogen, a solution of 1,2-dibromobenzocyclobutene [11] (6·8 g.) and the tetrachlorodimethoxycyclopentadiene (6·3 g.) in t-butyl alcohol (30 ml.) was added over 15 min. A bright yellow solution resulted, which was refluxed for 20 min. after the addition was complete. It was allowed to cool for a few minutes then treated with glacial acetic acid (20 ml.), followed by water (100 ml.), cooled to room temperature, and filtered. The yellow-orange precipitate was crystallised from ethanol, yielding 3-bromo-1,2-benzobiphenylene (VIII), m. p. 122—125° (lit.,[6] 126—127°) as orange needles (2·28 g., 62%). The mother-liquors from this crystallisation, on standing for 6—7 days, deposited colourless crystals (0·11 g., 1·0%) of the *adduct* (IV; X = Br), m. p. 133° (from light petroleum) (Found: C, 40·1; H, 2·5. $C_{15}H_{11}BrCl_4O_2$ requires C, 40·5; H, 2·5%).

1,2,3,4-*Tetrachlorobiphenylene* (IX).—The adduct (IV; X = Br) (35 mg.) was refluxed for 4 hr. with a solution of 30% hydrogen bromide in acetic acid (2 ml.). On cooling, pale yellowish-green needles (12 mg., 53%) of the *tetrachlorobiphenylene* (m. p. 176°) separated, and were crystallised from ethanol (Found: C, 49·0; H, 1·4. $C_{12}H_4Cl_4$ requires C, 49·7; H, 1·4%). There was insufficient material for an accurate combustion analysis.

The u.v. spectrum (qualitative) showed peaks at 373, 357, 353sh, and 339 mμ and at 265 and 258sh mμ, with an intensity ratio of the most intense peaks of the two band systems 1 : 12. This pattern closely follows that of biphenylene itself.[12]

1,2,3-*Trichloro*-1,4,4a,8b-*tetrahydro*-9,9-*dimethoxy*-1,4-*methanobiphenylene* (XI).—The tetrachloro-ketal (IV; X = H) (2·0 g.) in ethanol (15 ml.) and tetrahydrofuran (40 ml.) was shaken with sodium amalgam (1%, 150 g.) for 15 hr. Ether (100 ml.) was added, and the organic layer shaken with water (3 × 50 ml.). Drying ($MgSO_4$) and removal of solvents left a white residue of the *trichloro-ketal*, which crystallised from light petroleum as prisms (1·61 g., 89%), m. p. 108° (Found: C, 54·4; H, 3·6. $C_{15}H_{13}Cl_3O_2$ requires C, 54·3; H, 3·9%), $\lambda_{max.}$ 273, 267, 261 (ε 2200, 2100, 1250) with an inflection at 256 mμ and ε 13,500 at 210 mμ. The n.m.r. spectrum (in CCl_4) showed absorptions at 6·56 and 6·56 τ (2 methoxyl groups), and an unsymmetrical multiplet *ca.* 2·7—3·2 τ (4 aromatic protons). The remainder of the spectrum was not fully analysed; it consisted of multiplets *ca.* 5·9—6·2 τ (both angular benzylic protons) and 6·6—6·95 τ (1 bridgehead proton, partly concealed by one of the methoxyl absorptions).

The trichloro-ketal (XI) was recovered (70—85%) after being shaken in 2 : 1 tetrahydrofuran–ethanol with 1·5% sodium amalgam, and in ethanol with 2% sodium amalgam, for 16—18 hr.

1,4,4a,8b-*Tetrahydro*-9,9-*methoxy*-1,4-*methanobiphenylene* (X).—Lithium (0·6 g.) was added in small portions to a refluxing solution of the tetrachloro-ketal (IV; X = H) (4·0 g.) in t-butyl alcohol (10 ml.) and dry tetrahydrofuran (40 ml.) under nitrogen. After 2 hr. the solution was cooled, filtered through glass wool, poured into water (200 ml.), and the mixture extracted with benzene (50 ml.) then with chloroform (50 ml.). The combined extracts were washed with water, dried ($MgSO_4$), and the solvents removed by distillation. The residue, which partly solidified, was shaken with light petroleum (30 ml.) and filtered. The filtrate was distilled, the *dechlorinated ketal* (X) being collected at *ca.* 110°/0·02 mm., leaving a residue of tetrachloro-ketal

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[11] M. P. Cava, A. A. Deana, and K. Muth, *J. Amer. Chem. Soc.*, 1959, **81**, 6458.

[12] W. Baker, M. P. V. Boarland, and J. F. W. McOmie, *J.*, 1954, 1476.

(1·30 g., with the residue from the petroleum extract). The ketal (X) formed prisms with a camphoraceous odour (1·18 g., 73%, based on unrecovered tetrachloro-ketal) of m. p. 76—78° (from light petroleum) (Found: C, 79·25; H, 7·1. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·1%), $\lambda_{max.}$ 273·5, 267·5, 262 mμ (ε 2100, 2150, 1380) with an inflection at 257 mμ and ε 10,000 at 210 mμ. The n.m.r. spectrum (CCl_4) showed a symmetrical multiplet centred at 3·14 τ (4 aromatic protons), 2 sharp singlets at 6·85 and 6·95 τ (each 3 methoxyl protons), a triplet (*J* = 2·5 c./sec.) at 4·48 τ (2 vinyl protons, each with approximately equal coupling constants with both the 2 bridgehead protons), a doublet (*J* = *ca.* 5 c./sec., with further weak coupling (*J* = *ca.* 1 c./sec.) at 6·35 τ (2 angular benzylic protons), and further absorption, largely obscured by the methoxyl peaks, for which analysis was impossible, at *ca.* 7·1 τ (2 bridgehead protons).

Both sulphuric and hydrobromic acids produced a blackening of the dechlorinated ketal (X); no " parsley-like odour," said to be characteristic of benzocyclo-octatetraene,[7] was detected.

1,2,3-*Trichloro*-1,4,4a,8b-*tetrahydro*-1,4-*methanobiphenylen*-9-*one* (XII).—The trichloro-ketal (XI) (0·5 g.) was triturated with concentrated sulphuric acid (5 ml.) for 2 hr., then poured on to ice and set aside for *ca.* 30 min. The *ketone* (XII) (0·25 g., 58%) separated, and was collected), washed, dried, and crystallised from light petroleum as plates, m. p. 124° (decomp.) (Found: C, 54·9; H, 2·5. $C_{13}H_7Cl_3O$ requires C, 54·7; H, 2·5%), $\nu_{max.}$ 1805s cm.$^{-1}$ (C=O). The n.m.r. spectrum (CCl_4) showed an irregular multiplet at 2·4—3·2 τ (4 aromatic protons), a doublet at 6·45 τ (1 bridgehead proton), a doublet at 6·16 τ (1 angular benzylic proton), and a triplet at 5·90 τ (the other angular proton), with both vicinal coupling constants (*ca.* 4·5 c./sec.) approximately equal.

4,5,6-*Trichlorobenzocyclo-octatetraene* (XIII).—The trichloro-ketone (XII) (0·10 g.) was heated at 140° for 15 min., at the end of which time evolution of carbon monoxide had ceased. The *residue* was crystallised from light petroleum and sublimed (75°/0·1 mm.), giving prisms (0·085 g., 95%) (Found: C, 56·1; H, 2·9. $C_{12}H_7Cl_3$ required C, 56·0; H, 2·75%), $\lambda_{max.}$ 217 mμ (ε 44,300), with a shoulder at 235 mμ (32,600). The n.m.r. spectrum consisted of a broad peak at 2·90 τ (4 aromatic protons), a singlet at 3·28 τ (lone vinyl proton), and an AB quartet from protons with chemical shifts of 3·38 and 3·82 τ (*J* = 9·5 c./sec.) (2 adjacent vinyl protons). The low-field doublet of the AB system was very slightly broadened and less intense than the high, probably indicating a small degree of coupling with an aromatic proton.

The authors are grateful to Professor G. Wittig and Dr. G. Steinhoff for a copy of the n.m.r. spectrum of benzocyclo-octatetraene. They are also indebted to Dr. K. A. McLauchlan and Dr. R. E. Reavill for the n.m.r. spectra, to Dr. K. A. Mackenzie for helpful discussions, and to the D.S.I.R. for a grant.

THE UNIVERSITY, BRISTOL. [*Received, October* 26*th*, 1964.]