219. *Macrocyclic Acetylenic Compounds. Part III.*[1] *A Stepwise Synthesis of* 1,2:7,8-*Dibenzocyclododeca*-1,7-*diene*-3,5,9,11-*tetrayne.*

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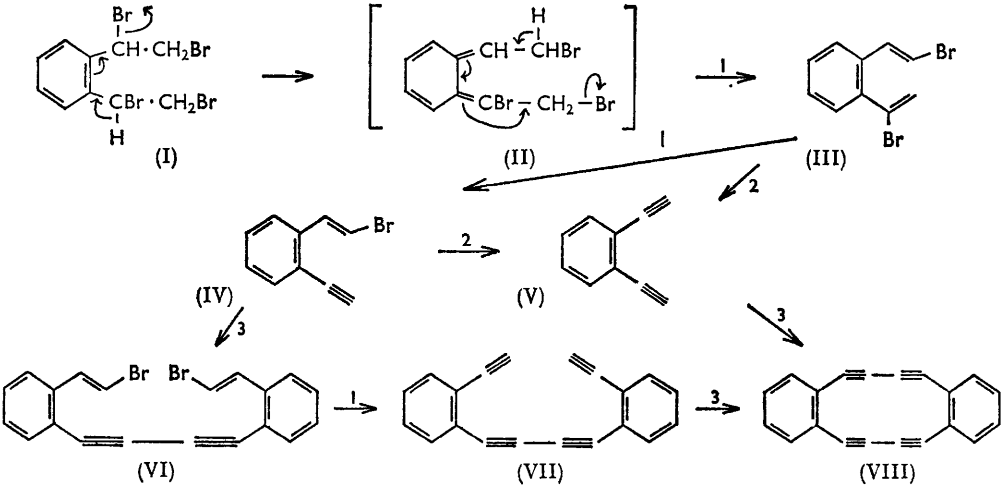
A new stepwise route to the above hydrocarbon (VIII) is described. The unusual sequence of dehydrobromination of *o*-di-(1,2-dibromoethyl)-benzene (I) is discussed.

In a previous paper[1] it was shown that the product obtained from the high-dilution oxidative coupling of *o*-diethynylbenzene (V) was the highly strained cyclic dimer (VIII). One mode of formation of this unexpected product could involve the intramolecular coupling of initially formed 1,4-di-*o*-ethynylphenylbutadiyne (VII). To test the feasibility of this process this latter hydrocarbon was synthesised in the following manner.

It was previously reported[1] that treatment of the tetrabromide (I) with two moles of potassium t-butoxide gave the dibromo-diene (III). Modified conditions for this dehydrobromination have now been found to provide a considerably purer product. The nature of the impurities in the earlier preparations and their detection and isolation have been investigated in considerable detail and are described in the Experimental section. The spectral properties of the pure (g.l.c.) dibromo-diene (III) were uniquely in agreement with the structure assigned: thus, in the i.r. spectrum (in CCl_4) it absorbed[2] at 950m, 935s (*trans*-CH=CHBr), and 903s (CBr=CH_2), and the n.m.r. spectrum showed an AB quartet as two doublets centred on 2·65 and 3·35 τ (J = 14 c./sec.; *trans*-CH=CHBr)[3] and another pair of doublets centred on 4·05 and 4·25 τ ($J \sim 1$ c./sec.; CBr=CH_2). One possible mechanism[4] for this unexpected unsymmetrical dehydrobromination is indicated, *via* an intermediate of type (II). The further double dehydrobromination of (III) to *o*-diethynylbenzene (V) has already been described[1] but the asymmetrical nature of (III) suggested that these two eliminations might proceed at very different rates; only in the 1-bromovinyl grouping is there a *trans*-alignment of hydrogen and bromine atoms. In



Reagents: 1, Bu^tOK in Bu^tOH. 2, Bu^tOK in benzene. 3, $Cu(OAc)_2$ in C_5H_5N-MeOH.

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[1] Part II, Behr, Eglinton, Galbraith, and Raphael, *J.*, 1960, 3614.

[2] Bellamy, "Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 46.

[3] Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 85.

[4] Cf. Cava and Muth, *J. Org. Chem.*, 1962, **27**, 1561; Jensen, *Tetrahedron Letters*, 1959, No. 20, 7; 1962, No. 1, 15.

the event, treatment of the dibromo-diene (III) with one mol. of potassium t-butoxide in t-butyl alcohol effected the expected *trans*-elimination with the formation of 1-*trans*-2′-bromovinyl-2-ethynylbenzene (IV) in high yield. The i.r. spectrum of the pure (g.l.c.) monobromide (IV) showed diagnostic absorptions near 3300 (≡CH), 950, and 938 cm.$^{-1}$ (*trans*-CH=CHBr) while the n.m.r. spectrum had the appropriate singlet at 6·75 τ (≡CH) and the AB quarter centred on 2·45 and 3·18 τ (J = 14 c./sec.; *trans*-CH=CHBr). A further, more vigorous, dehydrobromination treatment converted (IV) into the diyne (V).

A normal cupric acetate coupling of (IV) gave the expected dimer, 1,4-di-*o*-(*trans*-2′-bromovinyl)phenylbutadiyne (VI). Dehydrobromination of (VI) with excess of potassium t-butoxide then smoothly gave the desired diethynyl-diyne (VII). Coupling of this compound under high-dilution conditions surprisingly gave the highly strained cyclic tetrayne (VIII) in good yield, with no detectable amount of the less strained cyclic octayne which might plausibly have been expected.[5] In considering the mechanism of the oxidative coupling of *o*-diethynylbenzene (V) to (VIII) it is therefore permissible to postulate that (V) first dimerises linearly to (VII). Under the high-dilution conditions the statistical probability of further intermolecular coupling of this linear dimer (VII) is small, and, on this count, intramolecular " head-to-tail " ring closure would be preferred. However, the genesis of this and other[6] highly strained cyclic polyacetylenes by Glaser coupling is hard to envisage without involving the existence of some form of intermediate copper complex that would constrain the acetylenic linkages within coupling distance of each other.

EXPERIMENTAL

The following conditions for the physicochemical measurements apply unless otherwise stated. M. p.s were measured on a Kofler hot stage and are uncorrected; nuclear magnetic resonance spectra were obtained with an A.E.I. RS2 spectrometer (60 Mc./sec.); u.v. spectra were generally measured in cyclohexane, by means of a Unicam S.P. 500 spectrophotometer; i.r. survey measurements were recorded on a Perkin-Elmer model 13 or 137, and precise measurements on a Unicam S.P. 100 prism-grating spectrometer (only significant peaks in the infrared region are reported). G.l.c. analyses were run on a Pye " Argon " chromatograph with a 46 in. × ¼ in. column of " Embacel " with 10% Apiezon " L " as stationary phase, at 150°, and a flow rate of 40 ml./min. The proportions of eluates are only approximate as they are based on measurement of peak areas, not weight standardisation. Wider columns (½ in.) and faster (300 ml./min.) flow-rates were used in the preparative separations. The alumina for chromatography was acid-washed, neutralised, and standardised according to Brockmann's method; grade I was used. Light petroleum was of b. p. 40—60°. Thin-layer chromatography (t.l.c.) was carried out with Kieselgel G silica with mixtures of benzene and light petroleum as eluant.

o-*Di*-(1,2-*dibromoethyl*)*benzene* (I).—This was prepared as already described[1]. The n.m.r. spectrum (in CCl_4) showed the expected A_2B pattern with a triplet centred at τ 4·5 and a doublet at τ 5·9 (J_{AB} 7·5 c./sec.), the four aromatic protons forming a broader band centred at τ 2·6.

1-1′-*Bromovinyl*-2-trans-2′-*bromovinylbenzene* (III).—A modification of the previous procedure[1] was found to be advantageous. To a solution of (I) (23·5 g.; 0·052 mole) in dioxan (50 ml.) at 0° was added dropwise a solution of potassium (6·5 g.; 0·17 mole) in t-butyl alcohol (350 ml.) and dioxan (30 ml.) during 1 hr. The mixture was then stirred at room temperature for 18 hr. and worked up as before. The crude product was eluted from an alumina column with benzene–light petroleum (85 : 15). Evaporation gave (III) of 93% purity as estimated by g.l.c. (retention time 25·8 min.); of the three minor impurities present one (1·3%) was shown to be the more exhaustively dehydrobrominated compound (IV) (retention time 9·4 min.); $\nu_{max.}$ (in CCl_4) 950m, 935s (*trans*-CH=CHBr), and 903s ($CBr=CH_2$). The n.m.r. spectrum (in CCl_4) showed an AB quartet as two doublets centred on 2·65 and 3·65 τ (J = 14 c./sec.; *trans*-CH=CHBr) and another pair of doublets centred on 4·05 and 4·25 τ ($J \sim 1$ c./sec.; $CBr=CH_2$).

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[5] *E.g.*, Sondheimer and Amiel, *J. Amer. Chem. Soc.*, 1957, **79**, 5817.

[6] Morimoto, Akiyama, Misumi, and Nakagawa, *Bull. Chem. Soc., Japan*, **35**, 857.

The previous conditions for this preparation [1] frequently gave a product contaminated with the tribromide, 1-(1-bromovinyl)-2-(1,2-dibromoethyl)benzene. This impurity was detected by microanalytical figures and the appearance of a second spot on thin-layer chromatography (t.l.c.) of lower R_F than the desired product (III); no unchanged tetrabromide (I) was detectable by t.l.c. That the major impurity was in fact this tribromide was shown by the appearance of the characteristic A_2B pattern of the $CHBr{\cdot}CH_2Br$ grouping in the n.m.r. spectrum. In addition, the n.m.r. and i.r. spectra of this product showed a preponderant intensity of the bands attributable to $CBr{=}CH_2$ indicating the presence of this grouping in the main impurity. In some runs, two other very minor impurities were detectable by g.l.c. with retention times of 13·6 and 54 min. Collection of these two g.l.c. fractions and i.r. spectral examination strongly suggested that they were, respectively, *o*-di-bis(1-bromovinyl)benzene and *o*-di-(*trans*-2-bromovinyl)benzene.

1-trans-2′-*Bromovinyl*-2-*ethynylbenzene* (IV).—To a solution of the dibromo-diene [1] (III) (6·17 g.) in dioxan (10 ml.) was added a solution of potassium t-butoxide (2·24 g.) in t-butyl alcohol (60 ml.), and the mixture refluxed on the water-bath for 15 min. The reaction mixture was worked up by acidification with dilute hydrochloric acid and ether extraction; washing with water, drying, and evaporation gave a red oil (4·04 g.). G.l.c. showed this product to contain over 90% of the desired (IV), the impurities consisting of *o*-diethynylbenzene (V) and unchanged dibromo-diene (III). Distillation at 65—66°/0·05 mm. gave 1-*trans*-2′-*bromovinyl*-2-*ethynylbenzene* (IV) as a yellow oil, n_D^{25} 1·6225 (Found: C, 58·3, 57·75; H, 3·6, 3·7; Br, 38·35, 38·5. $C_{10}H_7Br$ requires C, 58·0; H, 3·4; Br, 38·5%); $\nu_{\max.}$ (film) 3300s ($\equiv$CH), 3050, 2100, 1605, 950, and 938 cm.$^{-1}$; $\lambda_{\max.}$ (in EtOH) 237, 245, 268sh, 274, and 283sh (log ε 4·27, 4·17, 4·06, 4·03, and 3·92); $\lambda_{\min.}$ 243 and 252 (log ε 4·16 and 3·89).

o-*Diethynylbenzene* (V).—Potassium (1·44 g.) was dissolved in t-butyl alcohol and the excess of t-butyl alcohol removed under vacuum. The residual potassium t-butoxide was then stirred with refluxing benzene (100 ml.). The monobromide (IV; 4 g.) in benzene (20 ml.) was added dropwise to the opalescent solution, and the mixture heated under reflux for 3 hr. Acidification (6N-hydrochloric acid) and ether extraction furnished the neutral fraction as a brown oil (3·17 g.) which was then distilled (bath temp. 90°/0·1 mm.) into a chilled carbon tetrachloride-solid carbon dioxide receiver. The *o*-diethynylbenzene was obtained as a very pale yellow oil (1·96 g., 80%), with spectral properties indistinguishable from those already recorded [1] for the pure compound.

1,4-*Di*-o-(trans-2′-*bromovinylphenyl*)*butadiyne* (VI).—The monobromide (IV; 4·04 g.) was dissolved in methanol (25 ml.), and a solution of cupric acetate (7·0 g.) in pyridine–methanol (1 : 1; 160 ml.) was slowly added. After addition of one third of this solution, the mixture was warmed gently, whereupon the colour changed from deep blue to green. The rest of the cupric acetate solution was then added and the mixture heated under reflux for 5 min., allowed to cool to room temperature, and worked up by acidification with hydrochloric acid, and extraction with ether. The ethereal solution was shaken with a solution of silver nitrate in aqueous ethanol to remove traces of uncoupled ethynyl material. Water was added, the organic material extracted with ether, and the ethereal layer washed several times with water, dried, and evaporated to give a yellow oil (3·85 g.). Filtration through alumina (150 g.) in benzene–light petroleum yielded 1,4-*di*-*o*-(trans-2′-*bromovinylphenyl*)*butadiyne* (2·0 g.; 50%) which crystallised from methanol in needles, m. p. 107—108° (Found: C, 58·55; H, 3·1; Br, 38·55. $C_{20}H_{12}Br_2$ requires C, 58·3; H, 2·9; Br, 38·8%); $\nu_{\max.}$ (in CCl_4) 3060 (=CH), 2220 (C$\equiv$C), 1605, 949, and 936 (*trans*-CH=CHBr) cm.$^{-1}$; $\lambda_{\max.}$ (in ethanol) 249, 262sh, 273sh, 308, 328, and 351 (log ε 4·70, 4·65, 4·57, 4·36, 4·41, and 4·31); $\lambda_{\min.}$ 298, 318, and 342 (log ε 4·25, 4·29, and 4·20). In the n.m.r. spectrum (in CCl_4) there was an AB quartet as a pair of doublets at 2·53 and 3·12 τ, J = 14 c./sec. (*trans*-CH=CHBr) and a multiplet centred on 2·73 τ (aromatic protons).

1,4-*Di*-o-*ethynylphenylbutadiyne* (VII).—To a solution of the dibromovinyl-diyne (VI) (1·35 g.) in dioxan (10 ml.), a solution of potassium t-butoxide in t-butyl alcohol (0·356N; 25 ml.) was added and the mixture then heated under reflux for 1½ hr. The mixture was worked up in the usual way. Evaporation of the solvent left brown crystals (768 mg.), which after purification by charcoal treatment in light petroleum (b. p. 60—80°) crystallised from this solvent to give 1,4-*di*-o-*ethynylphenylbutadiyne* (610 mg.; 75%) as needles, m. p. 124—124·5° (Found: C, 95·6; H, 4·35. $C_{20}H_{10}$ requires C, 95·95; H, 4·05%); $\nu_{\max.}$ (in CCl_4) *ca.* 3300, 3050, 2220, and 2110 cm.$^{-1}$; $\lambda_{\max.}$ (in cyclohexane) 347, 324, 304, 284, 276, 269, 256, 242, and 231 mμ (log ε 4·37, 4·42, 4·29, 4·26, 4·28, 4·40, 4·70, and 4·75; $\lambda_{\min.}$ 336, 312, 294, 266, 253, and 239 mμ (log ε

4·08, 4·16, 4·10, 4·25, 4·38, and 4·69). Attempts were also made to dehydrobrominate the starting material with sodamide in liquid ammonia but no identifiable product was isolated.

Coupling of 1,4-*Di*-o-*ethynylphenylbutadiyne* (VII).—A solution of the diethynyl-diyne (VII) (351 mg.) in pyridine–methanol (1 : 1; 20 ml.) was added dropwise during 2 hr. to a solution of cupric acetate (837 mg.) in pyridine–methanol–ether (7 : 7 : 4; 90 ml.), through a high-dilution system with ether as the circulating phase. After a further ½ hour's refluxing the mixture was worked up in the usual way. The ethereal layer was washed with aqueous ethanolic silver nitrate, dried, and evaporated; the residue was dissolved in benzene and filtered through alumina. Quantitative estimation of the amount of cyclic tetrayne (VIII) in this solution was obtained by measuring the intensity of absorption of a diluted portion at 304 mμ. This procedure showed the presence of 115 mg. (46%) of (VIII). Evaporation of the solvent and crystallisation from benzene gave the cyclic tetrayne (VIII), which had m. p. behaviour and light-absorption properties identical with the product obtained directly from *o*-diethynylbenzene.[1]

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