

## Highly Condensed Polycyclic Systems. Part III.<sup>1</sup> Pentacyclo-[5,5,1,0<sup>2,6</sup>,0<sup>3,10</sup>,0<sup>4,8</sup>]tridec-11-enes

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Addition of hexachlorocyclopentadiene or 1,2,3,4-tetrachloro-5,5-ethylenedioxycyclopentadiene to cyclo-octa-1,3,6-triene at the 6,7-double bond is followed by an intramolecular diene addition, to give the pentacyclo-[5,5,1,0<sup>2,6</sup>,0<sup>3,10</sup>,0<sup>4,8</sup>]tridec-11-ene system (I). However, attempts to obtain the more highly strained tetracyclo[4,4,0,0<sup>2,9</sup>,0<sup>5,8</sup>]dec-3-ene skeleton (VII) by an analogous intramolecular process failed.

OUR interest in the dienophilic behaviour of cyclic polyenes<sup>1-3</sup> led us to examine that of cyclo-octa-1,3,6-triene, obtained by partial reduction of cyclo-octa-tetraene with zinc in aqueous alcoholic sulphuric acid.<sup>4</sup> Treatment of the triene with hexachlorocyclopentadiene at *ca.* 100° for 24 hr. gave (in low yield) a high-melting 1:1 adduct, the i.r. spectrum of which showed no absorption in the region (near 1600 cm.<sup>-1</sup>) characteristic of ClC=CCl in a norbornene system; there was however a very weak C=C band at 1645 cm.<sup>-1</sup>. The n.m.r. spectrum

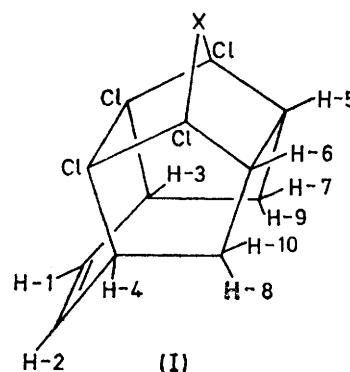
(H-9 and H-10). The product thus contained only two vinylic protons, and could be formulated as the pentacyclic mono-olefin (I; X = CCl<sub>2</sub>). The approximate coupling constants (evaluated with the aid of double

Approximate coupling constants (Hz) for (I; X = CCl<sub>2</sub>)  
(from 100 MHz spectrum; sweep-width 500 Hz)

$$\begin{array}{ll} J_{1,3} = J_{2,4} = 5.5 & J_{5,7} = J_{6,8} = 4 \\ J_{1,4} = J_{2,3} = 3 & J_{5,8} = J_{6,7} = 2.5^a \\ J_{3,7} = J_{4,8} = 12 & J_{5,9} = J_{6,10} = 0^b \\ J_{3,9} = J_{4,10} = 3.5 & J_{7,9} = J_{8,10} = -14^c \end{array}$$

<sup>a</sup> W-Form coupling (*cf.* ref. 5). <sup>b</sup> The dihedral angles between H-5 and H-9, and between H-6 and H-10, are close to 90°. <sup>c</sup> Negative sign assumed.

exhibited complex but symmetrical resonances at  $\tau$  3.7—3.95 (H-1 and H-2), 6.4—6.75 (H-3 and H-4), 7.0—7.15 (H-5 and H-6), 7.25—7.7 (H-7 and H-8), and 8.45—8.75



irradiation) (see Table) are in full accord with this assignment.

An analogous adduct (I; X =  $\overline{\text{C}\cdot\text{O}}\cdot[\text{CH}_2]_2\cdot\text{O}$ ) was

<sup>3</sup> G. I. Fray and D. P. S. Smith, *J. Chem. Soc. (C)*, 1969, 2710; I. A. Akhtar and G. I. Fray, preceding paper.

<sup>4</sup> W. O. Jones, *J. Chem. Soc.*, 1954, 1808.

<sup>5</sup> J. Meinwald, Y. C. Meinwald, and T. N. Baker, *J. Amer. Chem. Soc.*, 1964, **86**, 4074; S. Sternhell, *Quart. Rev.*, 1969, **23**, 236, and references cited therein.

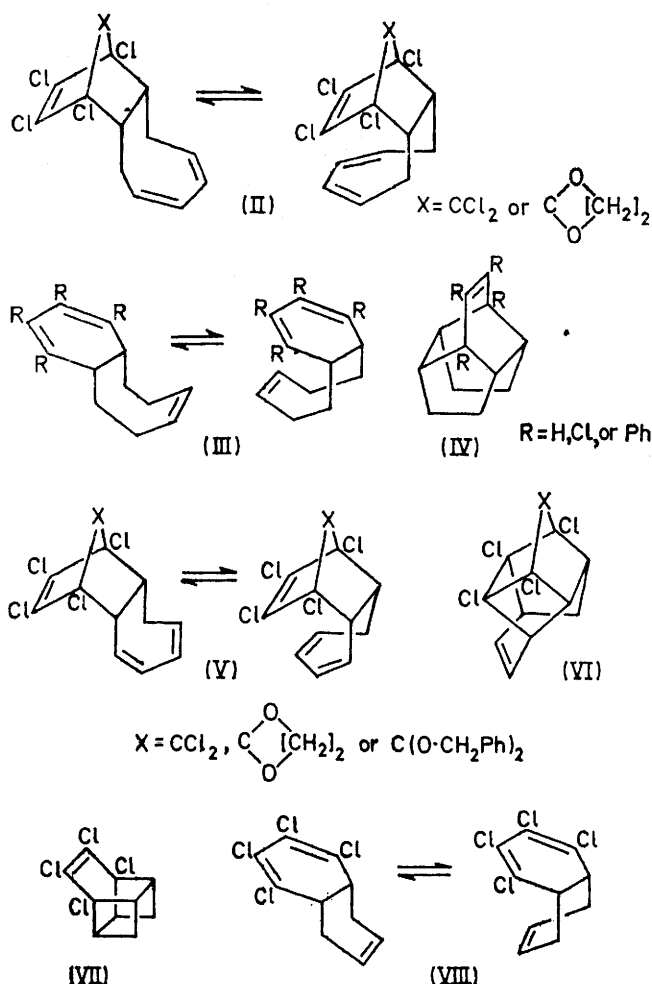
<sup>1</sup> Part II, I. A. Akhtar, D. M. Bratby, and G. I. Fray, *J. Chem. Soc. (C)*, 1969, 2716. This paper is more correctly entitled 'Pentacyclo[5,5,0,0<sup>2,6</sup>,0<sup>3,10</sup>,0<sup>4,8</sup>]dodec-11-enes.'

<sup>2</sup> I. A. Akhtar, G. I. Fray, and J. M. Yarrow, *J. Chem. Soc. (C)*, 1968, 812.

Org.

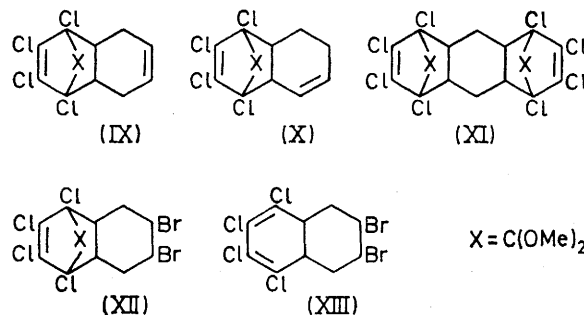
obtained (in better yield) from 1,2,3,4-tetrachloro-5,5-ethylenedioxcyclopentadiene.<sup>6</sup> It is evident that these products arose by initial diene addition to the 6,7-double bond of cyclo-octa-1,3,6-triene, with the formation of the product (II), followed by an intramolecular (4 + 2) $\pi$  cyclo-addition (*cf.* refs. 1 and 2).

Intramolecular Diels-Alder reactions occur not only in the systems (II) [ $\rightarrow$  (I)] and (III) [ $\rightarrow$  (IV)],<sup>2</sup> but also in system (V) [ $\rightarrow$  (VI)]<sup>1</sup> where the formation of a four-membered ring in the product must introduce considerable strain. It was therefore of interest to examine the possibility of preparing the even more highly strained tetracyclo[4,4,0,0<sup>2,9</sup>,0<sup>5,8</sup>]dec-3-ene (VII) in a similar way, *via* the bicyclo[4,4,0]deca-2,4,8-triene (VIII). The latter was synthesised as follows (*cf.* ref. 2).



Treatment of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene<sup>7</sup> with an excess of cyclohexa-1,4-diene afforded the 1 : 1 adduct (IX) \* (*cf.* ref. 8), together with some 2 : 1 adduct (XI). The 1 : 1 adduct (IX) formed a dibromo-derivative (XII), which on hydrolysis of the

acetal group and subsequent decarbonylation yielded the bicyclic diene (XIII). Debromination with zinc in ethanol then gave the required triene (VIII), the structure of which was fully confirmed by its i.r. ( $\nu_{\max}$  1650 and 1594  $\text{cm}^{-1}$ ), u.v. (multiple absorption in the region <sup>9</sup> 260—320 nm.), and n.m.r. [ $\tau$  ( $\text{CCl}_4$ ) 4.4br (2H, s), 6.9—7.2 (2H), and 7.4—8.0 (4H)] spectra.



However, attempts to effect an intramolecular Diels-Alder reaction in the bicyclic triene (VIII) failed. When the triene was heated in refluxing xylene for 2 days, a product of m.p. 191—193° was obtained, which was probably a mixture (although no separation of components could be achieved by t.l.c.), since the n.m.r. spectrum showed the presence of aromatic, vinylic, and other protons in ratios which were not small integers; it is evident that hydrogen-transfer processes occurred under these reaction conditions.

#### EXPERIMENTAL

Unless stated otherwise, light petroleum means the fraction of b.p. 60—80°; u.v. spectra were measured for solutions in ethanol and n.m.r. spectra at 100 MHz for solutions in deuteriochloroform. I.r. spectra were determined for Nujol mulls.

**2,3,4,5,5,6-Hexachloropentacyclo[5,5,1,0<sup>2,6</sup>,0<sup>3,10</sup>,0<sup>4,8</sup>]tridec-11-ene (I; X =  $\text{CCl}_2$ ).**—A mixture of hexachlorocyclopentadiene (2.0 g.), cyclo-octa-1,3,6-triene<sup>4</sup> (4.0 g.), and toluene (10 ml.) was kept on a steam-bath for 24 hr. The solvent was removed under reduced pressure, and the residue chromatographed on silica. Elution with 50% benzene—light petroleum afforded the *pentacyclic olefin* (0.3 g., 10%), which was recrystallised from methanol. The product decomposed above *ca.* 300° without melting [Found: C, 41.2; H, 2.7; Cl, 55.9%; *M* (mass spectrum), 376.  $\text{C}_{13}\text{H}_{10}\text{Cl}_6$  requires C, 41.2; H, 2.7; Cl, 56.1%; *M*, 376 ( $^{35}\text{Cl}$ )];  $\nu_{\max}$  1645  $\text{cm}^{-1}$ . For n.m.r. spectrum see Discussion section.

**2,3,4,6-Tetrachloro-5,5-ethylenedioxcyclopentacyclo[5,5,1,0<sup>2,6</sup>,0<sup>3,10</sup>,0<sup>4,8</sup>]tridec-11-ene (I; X =  $\text{C}(\text{O}[\text{CH}_2]_2\text{O})$ .**—A similar experiment with 1,2,3,4-tetrachloro-5,5-ethylenedioxcyclopentadiene<sup>6</sup> (2.0 g.) (reaction time 3 days) gave, after removal of solvent and recrystallisation from methanol,

<sup>6</sup> K. Mackenzie, *J. Chem. Soc.*, 1964, 5710.

<sup>7</sup> J. S. Newcomer and E. T. McBee, *J. Amer. Chem. Soc.*, 1949, **71**, 946; E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav, and H. P. Braendlin, *ibid.*, 1962, **84**, 3557.

<sup>8</sup> R. J. Stedman, L. S. Miller, and J. R. E. Hoover, *Tetrahedron Letters*, 1966, 2721.

<sup>9</sup> K. Mackenzie, *J. Chem. Soc.*, 1965, 4646, and references quoted therein.

\* In order to be certain that no shift of the double bond in the six-membered ring had occurred, the adduct (IX) was compared with the corresponding product (X) from cyclohexa-1,3-diene (sample kindly supplied by J. R. Telford), and the two adducts were shown to be non-identical (mixed m.p. and i.r. spectra).

the *pentacyclic compound* (1.9 g., 68%), m.p. 221—222° [Found: C, 48.7; H, 3.8; Cl, 38.4; *M* (mass spectrum), 366.  $C_{15}H_{14}Cl_4O_2$  requires C, 48.9; H, 3.8; Cl, 38.55%; *M*, 366 ( $^{35}Cl$ );  $\nu_{max}$ , 1645  $cm^{-1}$ ;  $\tau$  3.7—4.05 (2H), 5.55—6.05 (4H), 6.5—6.9 (2H), 7.1—7.75 (4H), and 8.35—8.75 (2H).

1,8,9,10-Tetrachloro-11,11-dimethoxytricyclo[6,2,1,0<sup>2,7</sup>]-undeca-4,9-diene (IX).—A mixture of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene<sup>7</sup> (6.0 g.), cyclohexa-1,4-diene (8.0 g.), and xylene (50 ml.) was heated under reflux for 24 hr., and then the solvent and excess of cyclohexadiene were removed under reduced pressure. Distillation of the residue yielded the 1:1 *adduct* (4.0 g., 51%), b.p. 125—130°/0.5 mm., m.p. 72—73° (from light petroleum) (Found: C, 45.4; H, 4.3; Cl, 41.0.  $C_{13}H_{14}Cl_4O_2$  requires C, 45.4; H, 4.1; Cl, 41.2%;  $\nu_{max}$ , 1632 and 1605  $cm^{-1}$ ;  $\tau$  (CCl<sub>4</sub>) 4.1—4.4 (2H), 6.51 (3H, s), 6.56 (3H, s), and 7.1—8.45 (6H).

The distillation residue crystallised from chloroform-ethanol to give the 2:1 *adduct* (XI) (2.1 g.), m.p. 254—255° (Found: C, 39.7; H, 3.3; Cl, 46.6.  $C_{20}H_{20}Cl_8O_4$  requires C, 39.8; H, 3.3; Cl, 46.7%;  $\nu_{max}$ , 1603  $cm^{-1}$ ;  $\tau$  6.48 (6H, s), 6.52 (6H, s), 7.3—7.7 (4H), 8.0—8.3 (2H), and 9.3—9.7 (2H).

4,5-Dibromo-1,8,9,10-tetrachloro-11,11-dimethoxytricyclo[6,2,1,0<sup>2,7</sup>]-undec-9-ene (XII).—Bromination of the foregoing 1:1 *adduct* (IX) (3.8 g.) in carbon tetrachloride afforded the *dibromo-derivative* (5.0 g., 90%), m.p. 101—102° (from methanol) (Found: C, 31.2; H, 2.8; Br, 31.4; Cl, 28.4.  $C_{13}H_{14}Br_2Cl_4O_2$  requires C, 31.0; H, 2.8; Br, 31.2; Cl, 28.1%;  $\nu_{max}$ , 1600  $cm^{-1}$ ).

8,9-Dibromo-2,3,4,5-tetrachlorobicyclo[4,4,0]deca-2,4-diene (XIII).—A mixture of the dibromide (XII) (3.0 g.), dichloromethane (15 ml.) and concentrated sulphuric acid (5 ml.) was stirred vigorously at *ca.* 35° for 2.5 hr., and then poured on ice. The product was collected in dichloromethane, and the solution was washed successively with sodium hydrogen carbonate solution and water. Evaporation of the dried (MgSO<sub>4</sub>) solution afforded a product ( $\nu_{max}$ , 1812  $cm^{-1}$ ), which was heated in xylene (25 ml.) under reflux overnight. Removal of the solvent and recrystallisation of the residue from methanol furnished the *diene* (1.5 g., 59%), m.p. 152.5—153.5° (Found: C, 27.9; H, 1.7; Br, 37.9; Cl, 32.9.  $C_{10}H_8Br_2Cl_4$  requires C, 28.1; H, 1.9; Br, 37.8; Cl, 32.8%;  $\nu_{max}$ , 1598  $cm^{-1}$ ;  $\lambda_{max}$ , 275sh, 283, 295, and 305sh nm. ( $\epsilon$  4750, 6090, 6150, and 3540).

2,3,4,5-Tetrachlorobicyclo[4,4,0]deca-2,4,8-triene (VIII).—A mixture of the diene (XIII) (1.5 g.), zinc dust (1.0 g.), and ethanol (50 ml.) was heated under reflux for 4 hr., and then filtered. The filtrate was evaporated, and the residue was washed with water and crystallised from light petroleum (b.p. 40—60°) to give the *triene* (0.8 g., 85%), m.p. 76—77° (Found: C, 45.0; H, 3.1; Cl, 52.7.  $C_{10}H_8Cl_4$  requires C, 44.8; H, 2.85; Cl, 52.55%;  $\nu_{max}$ , 1650 and 1594  $cm^{-1}$ ;  $\lambda_{max}$ , 273sh, 283, 294, and 305sh nm. ( $\epsilon$  5460, 7190, 6500, and 3420);  $\tau$  (CCl<sub>4</sub>) 4.4br (2H, s), 6.9—7.2 (2H), and 7.4—8.0 (4H).

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