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ALL-CIS-1,6-DICHLOROCYCLODECA-1,3,6,8-TETRAENE AND ALL-CIS-1-CHLOROCYCLODECA-1,3,8-TRIEN-6-YNE, DERIVATIVES OF DIHYDRO-[10]ANNULENE[1,2]

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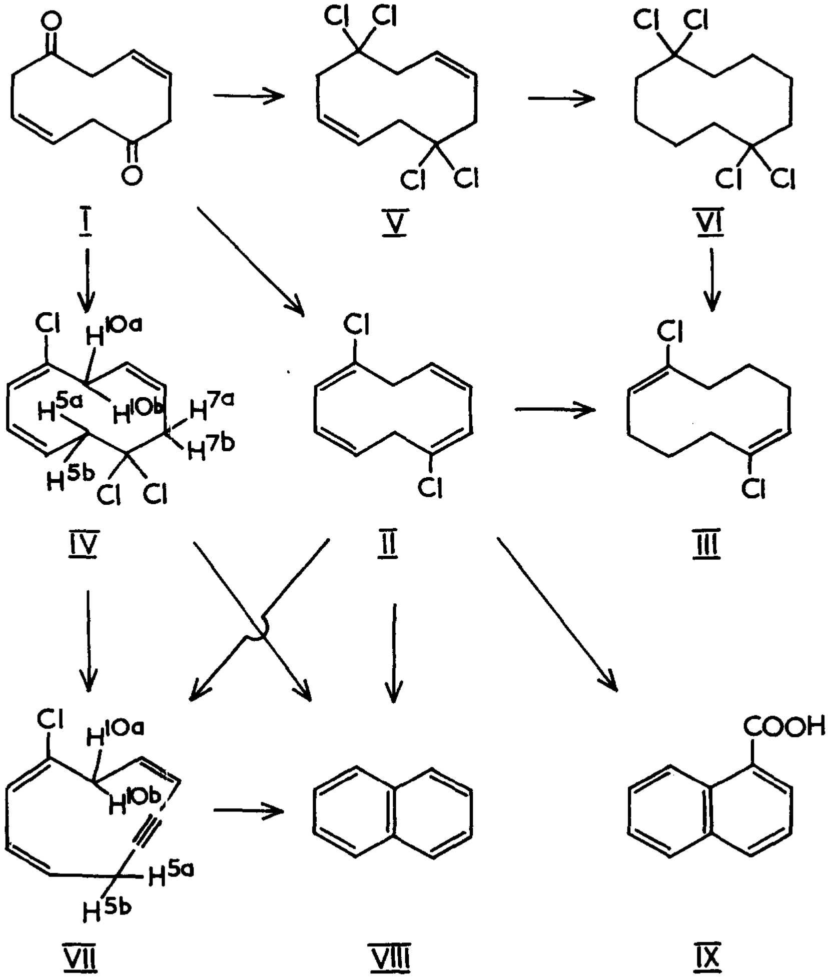
A number of conjugated monocyclic polyenes (annulenes) and polyen-ynes (dehydro-annulenes) have been prepared in recent years.[3] Except for very large rings, the only series in which unbridged conjugated members have not yet been isolated is the ten-membered one.[4] We now describe the first synthesis of unbridged dihydro-[10]annulene derivatives,[5] namely all-_cis_-1, 6-dichlorocyclodeca-1, 3, 6, 8-tetraene (1, 6-dichloro-2, 7-dihydro-[10]annulene) (II) and all-_cis_-1-chlorocyclodeca-1, 3, 8-trien-6-yne (1-chloro-2, 7-dihydro-5-dehydro-[10]annulene) (VII). These substances are of interest _per se_, and are also potential intermediates for the synthesis of [10]annulene and dehydro-[10]annulenes.

The starting material was _cis-cis_-cyclodeca-3,8-diene-1, 6-dione (I)[6], readily prepared from the corresponding tetramethyl ketal[6] in almost quantitative yield by treatment with boron trifluoride etherate and _p_-toluenesulfonic acid in aqueous acetone at room temperature (over-all yield from naphthalene, _ca._ 50%). Chlorination of I with phosphorus pentachloride in chloroform at _ca._ 0° yielded the following four substances, separated by chromatography on a column of alumina and silica gel.

(_a_) All-_cis_-1, 6-dichlorocyclodeca-1, 3, 6, 8-tetraene (II) (18% yield); colourless crystals, m.p. 88-89° dec. (green melt); λ_{max}^{EtOH} 219mμ (ϵ 13, 200); $\nu_{max}^{CCl_4}$ 1640s cm.$^{-1}$



(vinyl chloride); n.m.r. spectrum (100 Mc./sec., CCl_4), 6H multiplet at τ4.1 (olefinic protons), 2H double doublet at τ6.08(J_{gem} = 14 c./sec., J_{vic} = 11 c./sec.) and 2H double doublet at τ7.33 (J_{gem} = 14 c./sec., J_{vic} = *ca.* 4 c./sec.) (allylic protons); mass spectrum, mol. ion *m/e* 200 ($C_{10}H_{10}{}^{35}Cl_2$)[7]. The substance was unstable both in solution and in the solid state, the crystals becoming coated with a polymer on standing. The structure is based on the spectral data and the results of catalytic hydrogenation. The stereochemistry about the double bonds has been determined by a 3-dimensional X-ray crystallographic analysis, as reported in the following Communication.

Hydrogenation of II in acetic acid over platinum gave 50% of cyclodecane (identified with an authentic sample by g.l.p.c.) and 17% of cis-cis-1,6-dichlorocyclodeca-1,6-diene (III), m.p. 103-104°; $\nu_{max}^{CS_2}$ 1650s cm.$^{-1}$; n.m.r. spectrum (100 Mc./sec., CCl_4), 2H quartet at τ 4.43 (olefinic protons) and 12H multiplet at τ 7.0 - 8.7 (aliphatic protons); mass spectrum, mol. ion m/e 204 $(C_{10}H_{14}{}^{35}Cl_2)$[7]. The dichloro-diene III was the major product (62%) when the hydrogenation of II was carried out in ethanol over 10% palladium-charcoal. The 1,6-relationship of the chloro-substituted double bonds in III (and hence in II) was established by successive ozonolysis, oxidation and esterification, which yielded dimethyl glutarate (ca. 50%) as sole product isolated.

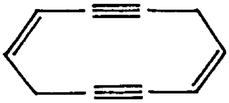
(b) All-cis-1,6,6-trichlorocyclodeca-1,3,8-triene (IV) (35% yield); colourless liquid, b.p. 82-84° (10^{-4}mm.); λ_{sh}^{EtOH} ca. 225 mμ (ε 38,500) and ca. 270 (9900); ν_{max}^{film} 1640s cm.$^{-1}$; n.m.r. spectrum (100 Mc./sec., CCl_4), 5H multiplet at τ4.1 (olefinic protons), 1 H double doublet at τ 6.19 (J_{gem} = 14 c./sec., J_{vic} = 11 c./sec.) (H^{10a}), 2H double doublet at τ6.67 (J_{gem} = 15 c./sec., J_{vic} = 9 c./sec.) (H^{5a}, H^{7a}) and 3H multiplet at τ7.0 - 7.55 (H^{5b}, H^{7b}, H^{10b}); mass spectrum, mol. ion m/e 236 $(C_{10}H_{11}{}^{35}Cl_3)$[7]. Hydrogenation of IV in acetic acid over platinum, followed by reductive dehalogenation with sodium in liquid ammonia, gave cyclodecane in 53% yield. Although the stereochemistry about the chloro-substituted double bond in IV was not determined, it is presumably cis by analogy to II. Attempted dehydrochlorination of IV with phosphorus pentachloride and with various bases did not lead to II.

(c) cis-cis-1,1,6,6-Tetrachlorocyclodeca-3, 8-diene (V) (10% yield); colourless crystals, m.p. 137-138°; no vinyl chloride band at *ca.* 1650 cm^{-1} in the infrared; n.m.r. spectrum (60 Mc./sec., CCl_4), 4H multiplet at τ 4.15 (olefinic protons) and 8H multiplet at τ 7.09 (allylic protons); mass spectrum, mol. ion *m/e* 272 ($C_{10}H_{12}{}^{35}Cl_4$).[7] Hydrogenation of V in ethyl acetate over 10% palladium-charcoal yielded 81% of 1,1,6,6-tetrachlorocyclodecane (VI), m.p. 166-167°, which on dehydrochlorination with potassium *t*-butoxide in boiling *t*-butanol gave 20% of the above-described dichloro-diene III.

(d) A trichloro-azulene (1.5% yield); dark green crystals (blue solution), m.p. 126-127°; λ_{max}^{EtOH} 224mμ (ε 9200), 251 (28,300), 292 (32,600), 296 (31,100), 309sh (11,000), 346 (3300), 356 (4600) and 372 (3400); $\lambda_{max}^{cyclohexane}$ 637mμ (ε 355), 675 (315), 700(285), 744 (165) and 777 (130); n.m.r. spectrum (60 Mc./sec., CCl_4), complex band between τ 1.6 - 3.3; mass spectrum, mol. ion *m/e* 230 ($C_{10}H_5{}^{35}Cl_3$)[7]. The spectral data clearly indicate an azulene structure,[8] but the positions of the chlorine atoms have not been determined. Other substituted azulenes have already been obtained from the dione I under various conditions.[9]

Dehydrochlorination of the dichloro-tetraene II with lithium di-isopropylamide in ether at -75° led to 27% of all *cis*-1-chlorocyclodeca-1,3,8-trien-6-yne (VII) and 48% of naphthalene (VIII). The same two substances were obtained (in 25% and 30% yield, respectively) by similar treatment of the trichloro-triene IV, a reaction which presumably proceeds via II. The chloro-trien-yne VII was a colourless liquid; λ_{max}^{EtOH} 208 mμ (ε 7500) and 275 (6000); ν_{max} 2230m cm.$^{-1}$ (acetylene) and 1650s (vinyl chloride), no allene band at *ca.* 1950 cm.$^{-1}$; n.m.r. spectrum (100 Mc./sec., CCl_4), 5H multiplet at τ 3.8 - 4.8 (olefinic protons), 1H double doublet at τ 5.85 (J_{gem} = 14 c./sec., J_{vic} = 9.5 c./sec.) (H^{10a}), 2H doublet at τ 6.97 (J = 2 c./sec.) (H, ^{5a} H^{5b}), and 1 H double doublet at τ 7.44 (J_{gem} = 14 c./sec., J_{vic} = *ca.* 7 c./sec.) (H^{10b}); mass spectrum, mol. ion *m/e* 164($C_{10}H_9{}^{35}Cl$)[7]. Compound VII was unstable, being completely destroyed after standing for 16 hours in the neat state or in petroleum ether solution.

The bis-dehydrochlorination of the dichloro-tetraene II to naphthalene presumably proceeds via the acetylene VII, since separate treatment of VII with lithium di-isopropylamide in ether at -75° led to naphthalene in over 70% yield. It is possible that the diene-diyne X is an intermediate in the dehydrochlorination of VII to naphthalene, but it has not yet been possible to isolate any intermediate.



$\overline{\underline{X}}$

Treatment of the dichloro-tetraene II with butyl-lithium in tetrahydrofuran at -75° resulted in the instantaneous appearance of a deep red colour, the nature of which is under investigation. Carboxylation of the red solution gave naphthalene-1-carboxylic acid (IX) in 78% yield.

The isolation of the dichloro-tetraene II, described above, is in contrast to the results obtained by Grob and Schiess[10] in the Cope and Hofmann degradation of derivatives of 1, 6-bis-dimethylaminocyclodeca-3, 8-diene (I, - NMe_2 instead of = O). The resulting cyclodeca-1, 3, 6, 8-tetraene underwent further reaction to butycyclohexane derivatives, presumably via a hexahydronaphthalene diradical.[10] It is possible that the failure to isolate the intermediate cyclodeca-1, 3, 6, 8-tetraene in that case is due to the fact that it is not the all-cis tetraene.

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