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PERCHLOROFULVALENE

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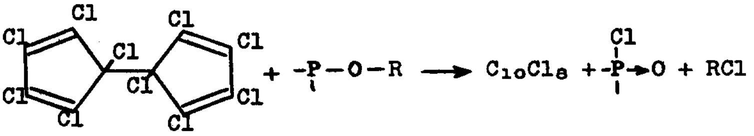
DECACHLOROBI-2,4-cyclopentadien-1-yl, I, reacts with esters of trivalent phosphorus, II, according to the stoichiometry:



I II III (1)

For example, the addition of ethyl phosphite to I yielded III, dark blue crystals [λ_{max} (isooctane) 386 mμ, log ε 4.55 and 590 mμ, log ε 2.71; I.R. maxima 6.55, 7.95, 8.09, 8.61, 13.00, 14.21 and 14.50μ, no C-H modes; decomposes at 200° (without melting);[1] Found: C, 29.1; H, 0.5; Cl, 69.2; mol. wt., 402 (boiling point elevation, benzene); $C_{10}Cl_8$ requires: C, 29.8; Cl, 70.2%; mol. wt., 403.8] in 55% conversion (66% yield, based on I), $(EtO)_2P(O)Cl$ (b.p. 40°/0.4 mm), 77% conversion, and ethyl chloride (identified by its infrared spectrum, gas phase).

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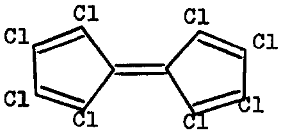
[1] An investigation of the decomposition product, for which a dimeric structure is indicated, is being carried out.

III (0.02 mole) absorbed rapidly about 13.5 equivalent moles of hydrogen [in ethanol and in the presence of platinum oxide at 50 lb/in^2 (3.4 atm) and at 25°, complete in 15 min] to yield bicyclopentyl, IV, (b.p. 60°/7 mm, n_D^{20} 1.4632; reported: b.p. 190°, n_D^{20} 1.4640; identity confirmed also by its infrared spectrum)[2,3] in 77% yield.

These data support the octachlorobicyclopentadienylidene, (perchlorofulvalene), IIIa structure for III and indicate that the phosphorous ester acts as a simple and smooth dechlorinating agent for I.[4]



IIIa

The structure IIIa, however, had already been assigned by Riemschneider to a crystalline compound, V, m.p. 62°, obtained by the reduction of hexachlorocyclopentadiene with zinc and hydrochloric acid.[5]

Subsequently McBee, Roberts and Idol have shown that V was actually 1,2,3,4-tetrachlorocyclopentadiene, m.p. 62°, and reported that perchlorofulvalene was a yellow crystalline compound, VI, m.p. 345-347°, obtained by the thermal dechlorination of I.[6] Their assignment was supported by

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[2] S.W.Ferris, Handbook of Hydrocarbons. Academic Press, New York (1955).

[3] American Petroleum Institute Research Project 45; Spectrum No. 1088.

[4] The dechlorinating action of phosphites on hexachloroethane was reported by G.Kamai [Izv.Akad.Nauk SSSR, Otdel.Khim.Nauk 923 (1952); Bull.Acad.Sci.U.R.S.S., Classe Sci.Chim. 819 (1952)].

[5] R.Riemschneider, Chem. & Ind. 64, 698, footnote 9 (1950); R.Riemschneider, Z.Naturf. 6B, 463 (1951).

[6] E.T.McBee, J.D.Idol, Jr. and C.W.Roberts, J.Amer.Chem.Soc. 77, 4375 (1955); E.T.McBee, C.W.Roberts and J.D.Idol, Jr., Ibid. 77, 4942 (1955).

elemental analyses, mol. wt., spectral data and by hydrogenation of VI over copper chromite to IV.

In view of the conflicting results the reinvestigation of the data cited in support of the structure of VI seemed necessary.

A synthetic sample of VI,[6] m.p. 345-347°, had analyses and ultraviolet absorption spectra (Found: C, 29.24; Cl, 70.15%; Calc. for $C_{10}Cl_8$: C, 29.75; Cl, 70.25%; λ_{max} (cyclohexane) 268 mμ, log ε 4.426; 278 mμ, log 4.510) in agreement with those reported, but differed in the data of the mol. wt. determinations [Found: 564 (benzene, boiling point elevation), 548 (Rast, camphor)] from the reported figure [429 (benzene, vapor pressure depression);[6] Calc. for $C_{10}Cl_8$: 404].

VI absorbed [in a standard Parr apparatus, in ethanol and in the presence of platinum oxide, at 50 lb/in^2 (3.4 atm) and at 25°] approximately 16 equivalent moles of hydrogen in 20 hr and yielded a white crystalline product, VII [m.p. 96-97°; Found: C, 90.27; H, 9.03; Cl, 0.0%; mol. wt., 202 (Rast)]. The mol. wt. thus indicates that hydrocarbon VII has a C_{15} skeleton. Subsequently VII was found to be identical with trindan, $C_{15}H_{18}$, by m.p., mixed m.p. and infrared and ultraviolet spectra.[7] Trindan resisted hydrogenation in the presence of platinum oxide, (even in highly acidic medium) a behavior known for and expected from fully alkylated benzenes.[8]

These data indicate that VI, m.p. 345-347°, is actually $C_{15}Cl_{12}$, (mol. wt., 606) and, most likely, a tetracyclic chlorocarbon with three five membered rings and with six double bonds, such as a dodecachlorodihydrotrindene IX.[9] VI on mild hydrogenation yields trindan, $C_{15}H_{18}$, in 83% yield.

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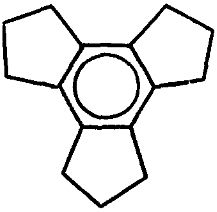
[7] O.Wallach, Ber.Dtsch.Chem.Ges. 30, 1094-1096 (1897).

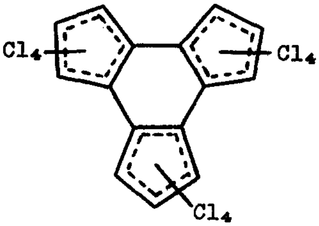
[8] See, e.g. C.M.Buess and D.Lawson, Chem.Rev. 60, 322 (1960) on various attempts to hydrogenate dodecahydrotriphenylene.

[9] Present data do not allow the definition of the position of double bonds in IX and the selection of a single structure from the numerous possibilities. Mechanistic considerations, however, suggest IXa (dodecachloro-3b,6b-dihydro-3aH-trindene) as a likely structure for VI.[10]

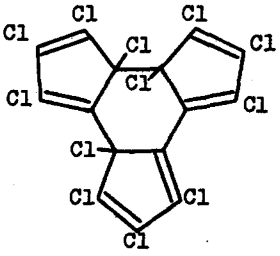
The formation of IV from VI under drastic (copper chromite) hydrogenation conditions[6] is probably due to the hydrogenolysis of the chlorocarbon.



Trindan



IX



IXa

The formation of VI takes place probably by a free radical mechanism which involves the pyrolysis of I into pentachlorocyclopentadienyl radicals; these on addition to I yield the C_{15}-unit, from which the final structure (such as IXa) is derived by elimination of two chlorine atoms, cyclization and a final elimination of a third chlorine atom. The overall stoichiometry is indicated by (2):

$$3\ C_{10}Cl_{10}(I) \longrightarrow 2\ C_{15}Cl_{12}(VI) + 3\ Cl_2 \qquad (2)$$

Acknowledgement is expressed to Dr. B.Katlafsky for the spectra, to Mr. John O'Sullivan for the elemental analyses and to Dr. A.J.Speziale for helpful suggestions and his interest in the program.

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[10] The crystal and molecular structure of VI is being investigated by Dr. P.J.Wheatley at Monsanto-Zurich Research Laboratories.