Tetrahedron, 1967, Vol. 23, pp. 1211 to 1224. Pergamon Press Ltd. Printed in Northern Ireland

PENTACYCLODECANE CHEMISTRY—II

SOME REACTIONS OF DODECACHLOROPENTACYCLO[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]DECANE AND RELATED COMPOUNDS[1]

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Abstract—The perchlorocarbon, dodecachloropentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane, was converted to the corresponding hydrocarbon and *endo*-dicyclopentadiene by reaction with lithium and t-butyl alcohol. Under varying conditions of this reaction several partially hydrogenolyzed caged compounds were isolated. The unsymmetrical hydrocarbon, pentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]decane, was prepared by two routes and was shown to be different from the symmetrical hydrocarbon above. The mechanism of ring opening in the hydrogenolysis reaction has been examined and is believed to involve an incipient carbanion on a methylene bridge. Several derivatives of the perchloroketone, decachloropentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decan-5-one, were prepared, including the mono- and dihydro-chlorocarbons, the alcohol and hydrazones.

INTRODUCTION

SINCE the discovery of the caged dimer (I) of hexachlorocyclopentadiene by Prins[3] in 1945, a considerable amount of work has been carried out on the structural elucidation, synthesis and chemistry of the pentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane (II) system[4] and the isomeric pentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]decane (III) system.[4o,s,w,5,6]

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[1] [a] Part I, *J. Org. Chem.* **27**, 2704 (1962); [b] Taken in part from the Ph.D. Thesis of W. L. Dilling, Purdue University, 1962; for a preliminary communication of part of the work reported here see part I.

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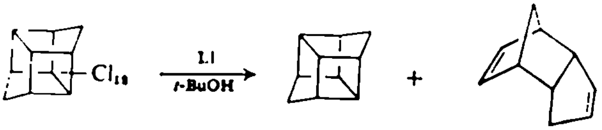
[3] H. J. Prins, *Rec. Trav. Chim.* **65**, 455 (1946).

[4] [a] J. S. Newcomer and E. T. McBee, *J. Amer. Chem. Soc.* **71**, 946, 952 (1949); [b] E. E. Gilbert and S. L. Giolito, U.S. Patents 2,616,825 and 2,616,928 (1952); *Chem. Abstr.* **47**, 2424 (1953); **54**, 7765 (1960); [c] E. E. Gilbert, U.S. Patent 2,671,043 (1954); *Chem. Abstr.* **48**, 10290 (1954); **54**, 7965 (1960); [d] E. E. Gilbert, U.S. Patent 2,702,305 (1955); *Chem. Abstr.* **50**, 2665 (1956); [e] E. T. McBee, J. D. Idol, Jr. and C. W. Roberts, *J. Amer. Chem. Soc.* **77**, 4375 (1955); [f] J. D. Idol, Jr., Ph.D. Thesis, Purdue University (1955); [g] E. T. McBee, C. W. Roberts, J. D. Idol, Jr. and R.H. Earle, Jr., *J. Amer. Chem. Soc.* **78**, 1511 (1956); [h] R. H. Earle, Jr., Ph.D. Thesis, Purdue University (1957); [i] D. H. Zijp and H. Gerding *Rec. Trav. Chim.* **77**, 682 (1958); [j] R. D. Crain, Ph.D. Thesis, Purdue University (1958); [k] H. E. Ungnade and E. T. McBee, *Chem. Revs.* **58**, 249 (1958); [l] C. W. Roberts *Chem. & Ind.* 111 (1958); [m] P. E. Hoch, *A Review of the Chemistry of C-56.* Hooker Chemical Corporation (1958); [n] P. Eaton, E. Carlson, P. Lombardo and P. Yates, *J. Org. Chem.* **25**, 1225 (1960); [o] P. E. Eaton, Ph.D. Thesis, Harvard University (1960); [p] E. E. Gilbert and P. Lombardo, U.S. Patent 3.037,906 (1962); *Chem. Abstr.* **57**, 5068 (1962); [q] P. E. Hoch and J. S. Newcomer, U.S. Patent 3,055,948 (1962); *Chem. Abstr.* **59**, 7393 (1963); [r] H. E. Wales, Brit, Patent. 908,620 (1962); *Chem. Abstr.* **58**, 6718 (1963); [s] W. L. Dilling, Ph.D. Thesis, Purdue University (1962); [t] P. E. Hoch and J. S. Newcomer, U.S. Patent 3,096,239 (1963); *Chem.*

At present the structures of the compounds of these series appear to be reasonably well established,[4e,i,n,w] but at the time this work was undertaken there was still some question concerning the structures.[4n,o] Few reactions of the perchloro caged compound I have been reported,[4h,o] and these offered little insight into its structure. The present paper presents some reactions of I, in particular the hydrogenolysis of the carbon-chlorine bonds, and some reactions of the related ketone, IV, which serve to relate their carbon skeletons and that of the isomeric structure, III.

RESULTS AND DISCUSSION

Treatment of the perchlorocarbon I with lithium and t-butyl alcohol in tetrahydrofuran[7] at 0–15° gave a saturated hydrocarbon (30%) to which structure II was assigned based on evidence presented below. In addition *endo*-dicyclopentadiene, V, (56%) was also found. The hydrocarbon II was found to be saturated as judged from its nonreactivity with bromine in carbon tetrachloride or ozone at −78° in methylene chloride, and from spectral data. The IR spectrum (Fig. 1) of II indicated the absence of unsaturation, and in addition showed the presence of methylene groups, 6·93 μ, and hydrogen atoms on tertiary carbon atoms, 7·66 and 7·89 μ.[8] The UV spectrum



I II V

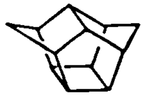
Abstr. **59**, 6936 (1963); [u] E. E. Gilbert and P. Lombardo. Belg. Patent 624,290 (1963); *Chem. Abstr.* **60**, 15752 (1964); [v] Allied Chemical Corp., French Patent 1,340,382 (1963); *French Patent Abstracts* Vol. 3, No. 46; p. 5-1, Derwent Publications, London (1963) [w] G. W. Griffin and A. K. Price, *J. Org. Chem.* **29**, 3192 (1964); [x] Allied Chemical Corp., Neth. Patent 6,400,694 (1964); *Chem. Abstr.* **62**, 3955 (1965); [y] Allied Chemical Corp., Neth. Patent 6,400,728 (1964); *Chem. Abstr.* **62**, 11705 (1965); [z] Allied Chemical Corp., Neth. Patent 6,402,964 (1964); *Chem. Abstr.* **62**, 7658 (1965); [a'] T. B. Wieliczko, M. S. Thesis, Purdue University (1964).

[5] [a] P. Yates and P. Eaton, *Tetrahedron Letters* No. 11, 5 (1960); [b] R. C. Cookson, J. Hudec, and R. O. Williams, *Ibid.* No. 22, 29 (1960); [c] P. Yates and P. Eaton, *Tetrahedron* **12**, 13 (1961); [d] G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belg.* **71**, 781 (1962); [e] G. O. Schenck and R. Steinmetz, *Chem. Ber.* **96**, 520 (1963); [f] P. E. Eaton and T. W. Cole, Jr., *J. Amer. Chem. Soc.* **86**, 962, 3157 (1964); [g] R. C. Cookson, R. R. Hill and J. Hudec, *J. Chem. Soc.* 3043 (1964); [h] R. C. Cookson, E. Crundwell, R. R. Hill and J. Hudec, *Ibid.* 3062 (1964); [i] K. V. Scherer, Jr., R. S. Lunt, III, and G. A. Ungefug, *Tetrahedron Letters* 1199 (1965); [j] E. Vogel and E.-G. Wyes, *Chem. Ber.* **98**, 3680 (1965).

[6] Alternate names, used in *Chemical Abstracts* for II and III are octahydro-1,3,4-metheno-2H-cyclobuta[cd]pentalene and octahydro-1,2,4-metheno-3H-cyclobuta[cd]pentalene respectively.

[7] [a] P. Bruck, D. Thompson and S. Winstein, *Chem. & Ind.* 405, (1960); [b] S. Winstein and R. L. Hansen, *J. Amer. Chem. Soc.* **82**, 6206 (1960); [c] P. Bruck, *Tetrahedron Letters* 449 (1962); [d] E. T. McBee, W. L. Dilling, and H. P. Braendlin, *J. Org. Chem.* **28**, 2255 (1963); [e] C. F. Wilcox, Jr., and J. G. Zajacek, *Ibid.* **29**, 2209 (1964).

[8] L. de Vries and S. Winstein, *J. Amer. Chem. Soc.* **82**, 5363 (1960), attributed an IR max at 6·88 μ to the methylene groups and max at 7·67, 7·74, and 7·83 μ to the tertiary carbon-hydrogen bending vibrations of the caged compound *i*.



i

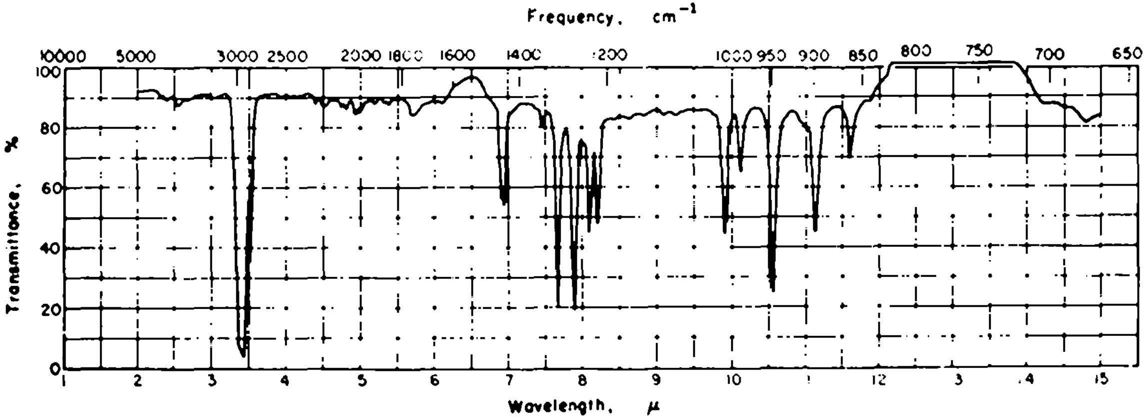


FIG. 1. Infrared spectrum of Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane—II

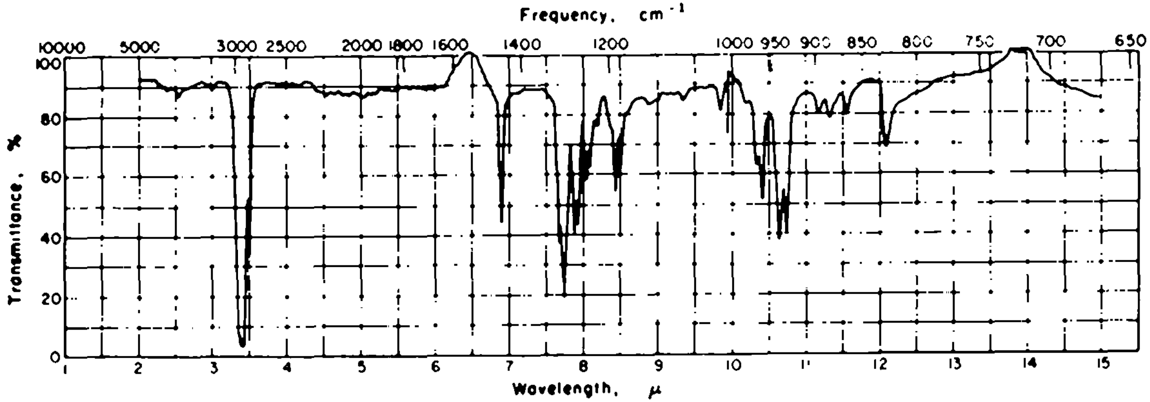


FIG. 2. Infrared spectrum of Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane—III

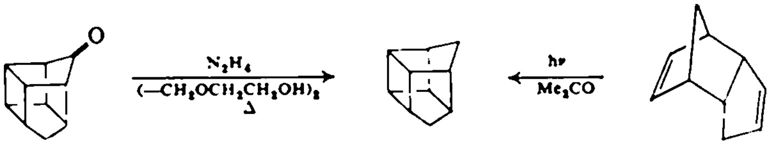
showed no significant absorption above 200 mμ; a very weak absorption was noted at ca. 213 mμ ($\epsilon = 80$) possibly due to an impurity. Since the NMR spectrum showed the absence of vinyl hydrogen atoms, any unsaturation would have to arise from a tetrasubstituted double bond. However, in contrast to II, four different tetrasubstituted symmetrical ethylenic systems, 2,3-dimethyl-2-butene, 1,2-dimethylcyclopentene, 1,2-dimethylcyclohexene and $\Delta^{9,10}$-octalin, were shown to have "apparent" absorption maxima[9] in the UV between 213 and 217 mμ, with extinction coefficients between 1300–1600. The NMR spectrum of II (Fig. 3, Table 1) revealed three distinct peaks of equal area in agreement with the proposed structure. The hydrocarbon II was stable on heating at 300° for 5 hr in a sealed tube.

TABLE 1. NMR DATA OF PENTACYCLO[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]DECANES[a]

Compound number	Formula	δ[b]	Relative area	Width of peak at half-height[c]
II	$C_{10}H_{12}$	−2·82	4·0	7·9
		−2·50	4·0	7·4
		1·36	4·1	3·0
VII	$C_{10}H_8Cl_4$	−3·21	4·0	1·9
		−2·36	4·1	2·0
IX	$C_{10}H_6Cl_6$	−3·16	2·0	1·3
		−2·58	4·0	1·6
VIII	$C_{10}H_2Cl_{10}$	2·56		--
XII	$C_{10}HCl_{11}$	−4·28		3·0
XI	$C_{10}HCl_{11}$	−3·74	—	2·6

[a] All determinations were carried out with ca. 10% sol of the compounds in CCl_4 except with IX where a ca. 10% benzene sol was used. [b] Chemical shift from TMS used as an internal standard. [c] In c/s.

The closely related unsymmetrical hydrocarbon III was prepared by two routes: Wolff-Kishner reduction of the ketone VI[5b] and acetone sensitized irradiation[5d,e] of the diene V. Like II, III was also saturated as shown by its nonreactivity with bromine



VI III V

and the IR (Fig. 2), UV ($\epsilon_{200m\mu}$ — 0), and NMR spectra (Fig. 4). The latter showed two unsymmetrical doublets ($\delta = -1{\cdot}21$ and $-1{\cdot}64$, $J = 10{\cdot}7$ c/s) with relative areas of 1·9 to 1·9 indicative of a methylene group containing nonequivalent hydrogen atoms. The peaks at −2·52 and −2·72 of relative areas 5·8 and 2·4, respectively, were attributed to the eight remaining hydrogen atoms on the tertiary carbon atoms. The NMR spectrum of II showed only a singlet ($\delta = -1{\cdot}36$) in the region attributed to the hydrogen atoms attached to the secondary carbon atoms, whereas a triplet would

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[9] O. H. Wheeler and J. L. Mateos, *J. Org. Chem.* 21, 1110 (1956) report, and cite Refs. to, the appearance of "false energy" max at 200–215 mμ when UV absorption is measured with standard photoelectric spectrometers.

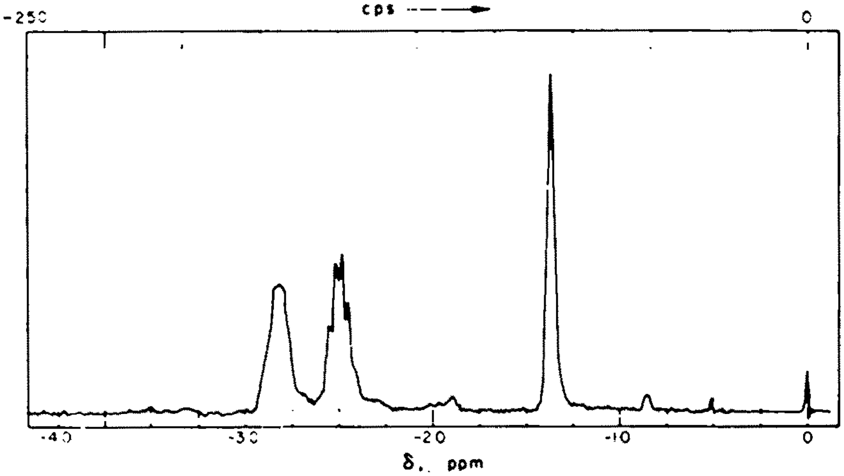

Fig. 3. N.M.R. Spectrum of Pentacyclo[5.3.0.0.^{2,6}.0^{3,9}.0^{4,8}]decane II.

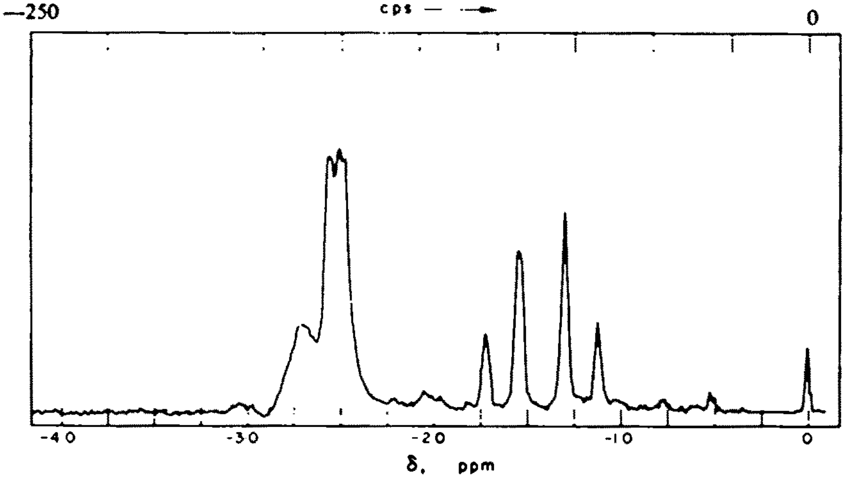

Fig. 4. N.M.R. Spectrum of Pentacyclo[5.3.0.0.^{2,5}.0^{3,9}.0^{4,8}]decane III.

be expected since these methylene groups are each flanked by two equivalent hydrogen atoms. The absence of observable coupling with these hydrogen atoms may be attributed to the dihedral angle.[10] The IR spectra of II and III were consistent with the assigned structures in that the higher degree of symmetry of II produced fewer absorption bands in the 7·5–12 μ region.

The mass spectra of II and III (Table 2) determined at 50 volts ionization potential were nearly identical. The intense fragment ion at *m/e* 66 may be due to the cyclopentadiene ion ($C_5H_6^+$) resulting from cleavage of the molecular ion in half. This cleavage of molecules with carbon skeletons of II and III in half is a common occurrence.[11]

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[10] [a] M. Karplus, *J. Chem. Phys.* **30**, 11 (1959); [b] H. Conroy, *Advan. Org. Chem.* **2**, 308 (1960).

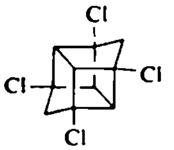
[11] W. L. Dilling and M. L. Dilling, *Tetrahedron* in press.

TABLE 2, MASS SPECTRA OF PENTACYCLO[5.3.0.0.^{2,5}.0^{3,9}.0^{4,8}]DECANE II AND PENTACYCLO[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]DECANE III

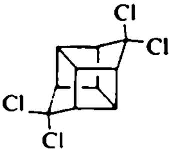
m/e	*I*,* II	*I*,* III	*m/e*	*I*, II	*I*, III
25	0·2	0·1	77	2·7	4·1
26	0·7	1·0	78	2·3	7·6
27	2·8	4·8	79	1·1	2·9
			80	0·3	0·6
29	0·4	1·6			
			89	0·4	0·6
38	0·4	0·5			
39	7·0	9·2	91	3·2	6·8
40	3·3	4·5	92	0·5	1·3
41	2·1	3·0			
42	—	0·3	101	0·3	0·2
43	—	0·1	102	0·4	0·6
44	—	0·1	103	0·7	1·3
			104	0·6	1·7
50	0·7	0·7	105	0·5	1·1
51	2·4	3·3			
52	1·4	2·1	115	1·7	2·7
53	1·5	2·3	116	1·3	2·1
54	0·7	4·5	117	1·6	5·6
55	-	0·5			
			127	0·4	0·4
62	0·3	0·3	128	0·8	0·8
63	1·2	1·8	129	0·8	1·0
64	1·0	1·8	130	0·4	0·5
65	4·4	6·5	131	0·7	1·7
66	100·0	100·0	132	4·0	5·1
67	14·0	13·6	133	0·7	1·1
68	1·4	2·2			

* Relative intensity based on *m/e* 66 as 100·0.

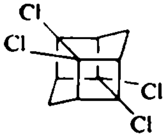
Reaction of I with lithium and t-butyl alcohol at −78° for varying lengths of time afforded several partially hydrogenolyzed derivatives. Reaction for 18 hr gave an octahydro derivative VII whose IR spectrum indicated the absence of unsaturation. The NMR spectrum (Table 1) of this compound showed the presence of only two types of hydrogen atoms of equal number, allowing three possible structures, VIIa, b or c.



VIIa

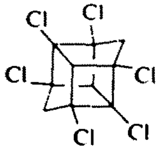


VIIb

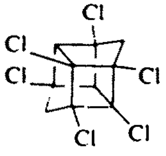


VIIc

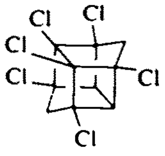
The lack of splitting of either peak and the narrow width at half-height lent support to structure VIIa, since both VIIb and VIIc have adjacent nonequivalent hydrogen atoms and some splitting or broadening, as in II, should be observed under normal circumstances. However structure VIIc cannot be ruled out with as much certainty as can VIIb on this basis. Moreover, the peak at −2·36 may be ascribed to the methylene hydrogen atoms since the chemical shift was in fair agreement with that observed for the dihydro compound VIII (Table 1) which will be discussed below. In addition to VII, a considerable amount of an unsaturated liquid mixture was obtained which contained only traces of V, as shown by analytical gas chromatography (GC), and probably consisted of partially chlorinated *endo*-dicyclopentadienes since only II and V are obtained on complete hydrogenolysis. Repetition of the low temperature reaction with lithium and t-butyl alcohol for one hour again gave a mixture of products. A hexahydro derivative IX was isolated as well as an impure trihydro derivative X. The IR spectra of both compounds indicated the absence of unsaturation. The NMR spectrum of IX (Table 1) showed the presence of only two kinds of hydrogen atoms, as narrow singlets, in a ratio of 2:1. The chemical shift of the larger peak corresponded to that observed for the methylene hydrogen atoms in VIII. Structures IXa, b, and c were the most consistent with the data. The mass spectrum showed an intense fragment ion for $C_5H_3Cl_3^+$ and none for $C_5H_2Cl_4^+$ or $C_5H_4Cl_2^+$ indicating that the correct structure is probably either IXa or b.[11] Each isomer, moreover, could easily be the precursor to the octahydro compound VIIa. No conclusion could be drawn for the impure trihydro derivative X. The NMR spectrum was in agreement with that expected for a molecule containing three hydrogen atoms (Experimental). As in the reaction carried out for eighteen hours, a liquid mixture containing unsaturated material was isolated.



IXa

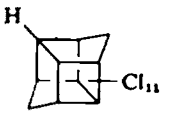


IXb

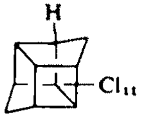


IXc

A modification of the hydrogenolysis reaction consisted of the use of water, in conjunction with Dry Ice, as the hydrogen source. Five compounds were isolated, all saturated as judged by their IR and NMR spectra. A monohydro derivative XI (Table 1) was different, on the basis of NMR and IR spectral comparisons, from the monohydro derivative XII described below. Therefore, XI had either structure XIa or b.



XIa



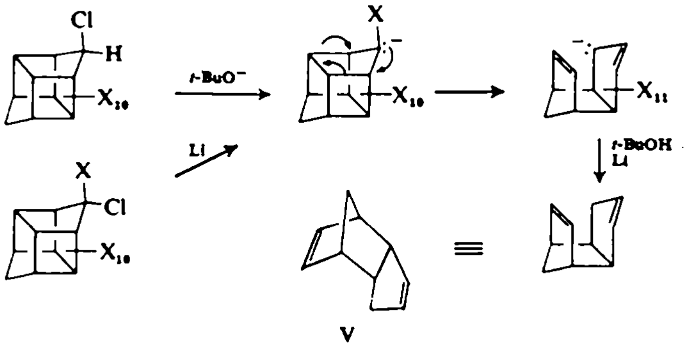
XIb

Also isolated was an impure dihydro derivative XIII. Its NMR spectrum was poorly resolved but indicated the presence of two doublets of equal area, i.e., two adjacent nonequivalent hydrogen atoms, but no structural assignment was attempted. In addition to these two compounds containing ten carbon atoms, three saturated products were isolated whose elemental analyses and mol. wts indicated the following formulas: $C_{18}H_8Cl_{10}$ XIV, $C_{15}H_{10}Cl_{10}$ XV, and $C_{18}H_{13}Cl_9$ XVI. The NMR spectra were complicated and showed considerable splitting. Apparently these products arose from carbon-carbon bond fission and recombination of fragments, possibly by Wurtz type coupling reactions in the presence of lithium.

The origin of V in the reaction of I with lithium and t-butyl alcohol was of considerable interest. The mechanism of the chlorine replacement reaction is thought to involve the formation of a lithium alkyl which is rapidly alcoholyzed by the t-butyl alcohol to form a t-butoxide ion for each chlorine atom replaced by a hydrogen atom.[11]

$$\text{R—Cl} + 2\,\text{Li} + \text{t-BuOH} \rightarrow \text{R—H} + \text{LiCl} + \text{LiOt—Bu}$$

Neither II nor V was affected by lithium t-butoxide under the reaction conditions. Hence, V was not derived from II or *vice versa*. Lithium alone did not react significantly with I in tetrahydrofuran, 86% of the latter being recovered after stirring for 6 days. The tetrachloride VII did not react with lithium t-butoxide under the reaction conditions, and gave only the saturated hydrocarbon II on treatment with lithium and t-butyl alcohol. The monohydro compound XII did react with lithium t-butoxide. The product, which we were unable to obtain in pure form showed IR absorptions in the 6·0–6·3 μ region characteristic of olefins. The dihydro compound VIII, on treatment with lithium and t-butyl alcohol, gave II and V in 71% and 27% yields, respectively, compared with yields of 30% and 56%, respectively, from I. An explanation for the formation of V consistent with these facts is either the base-catalyzed isomerization of a species such as XII, which contains a chloromethylene group, or the ring opening of a lithium alkyl at the methylene group.



V

X = H and/or Cl

The hydrogen atom of a chloromethylene group is more acidic than a hydrogen atom of a methylene group due to the electron withdrawing effect of the chlorine atom. Thus the failure of II and VII to react with lithium t-butoxide can be explained by the absence of chloromethylene groups. The appreciably larger amount of II obtained from VIII than from I is consistent with the intermediate formation of only one chloromethylene group or two lithium alkyls at the methylene bridge of VIII, whereas I can form two chloromethylene groups or four lithium alkyls at the methylene bridges as precursors to V. The tetrachloride with no chlorine atoms on the methylene bridges would not give V according to the proposed mechanisms.

An attempt was made to detect the presence of a lithium alkyl in the reaction of I with lithium by carbonation with Dry Ice. A small amount of a base-soluble material was isolated whose IR spectrum indicated the presence of a carboxyl group, (nujol) 3·0(s), 5·83(s)μ. The material was insoluble in common organic solvents and water. Purification was not achieved.

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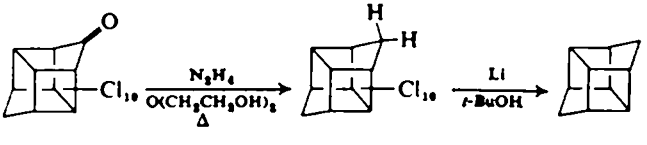
[11] S. Winstein, private communication.

The ketone IV is known to give I on treatment with phosphorus pentachloride at elevated temperatures.[4b] However, since rearrangement may occur in this type of reaction,[4c] the structural correlation of IV and I by this method was rendered uncertain.[13] These compounds have now been related by Huang-Minlon[14] modified Wolff-Kishner reduction of IV to the dihydro derivative VIII and its conversion to

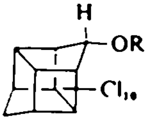


IV VIII II

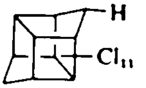
the hydrocarbon II as noted above. The single NMR peak observed for VIII (Table 1) also indicated a symmetrical structure. These results are in agreement with those of Griffin and Price.[4e]

While studying the Wolff-Kishner reduction of IV, a control experiment was run in the absence of hydrazine hydrate. Reaction of IV with potassium hydroxide in diethylene glycol at 200° unexpectedly gave the alcohol XVII. The IR spectrum showed a characteristic hydroxyl band at 2·82 μ and the NMR spectrum exhibited two singlets of equal area.[15] The acetate XVIII of XVII was prepared, and although refluxing thionyl chloride had no effect on XVII, phosphorus pentachloride gave the undecachloro derivative XII.[16]

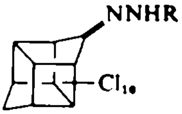
The hydrazone XIX and phenylhydrazone XX of IV were prepared in good yield. Treatment of XIX with potassium hydroxide in diethylene glycol at 200° afforded a low yield of alcohol XVII. None of the normal reduction product VIII was found. It has been observed previously that Wolff-Kishner reduction sometimes gives alcohols rather than methylene compounds.[17,18]



XVII $R = H$
XVIII $R = CH_3CO$



XII



XIX $R = H$
XX $R = C_6H_5$

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[13] We have confirmed the conversion of octachloropentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]decane-4,10-dione to I on heating with PCl_5 at 150–165°.

[14] Huang-Minlon, *J. Amer. Chem. Soc.* 68, 2487 (1946).

[15] The alcohol XVII has recently been synthesized by the LAH reduction of the ketone IV.

[16] The same prpduct, XII was recently obtained in an analogous manner.[4e]

[17] D. Todd, *Org. Reactions* IV, 380 (1948).

[18] The probable reason for obtaining the methylene compound from IV directly was that an excess of hydrazine hydrate was employed, whereas this was not the case in the reaction of the performed hydrazone. The hydrazone XIX and the phenylhydrazone XX were both sensitive to protic solvents. Recrystallization of XIX from EtOH gave a product from which nearly all the N had been eliminated. The phenylhydrazone XX reacted with water, but the product was not identified.

EXPERIMENTAL[19]

Dodecachloropentacyclo[5.3.0.0^{2,6}0^{3,9}.0^{4,8}]decane I

Crude I obtained from the Hooker Chemical Corporation was purified by recrystallization from benzene, m.p. 475–477° (sealed capillary) (lit.[4a] m.p. 485°); X-ray powder diffraction data: 7·03 Å(100), 6·07(8·5), 3·66(5·7), 3·51(28), 3·36(5·7), 3·24(6·7), 3·03(5·7), 2·96(47), 2·86(27), 2·78(17), 2·71(14), 2·65(25), 2·59(5·7), 2·37(6·4), 2·33(7·4), 2·25(9·2), 2·22(5·3), 2·08(2·8), 2·02(2·1), 1·97(1·8), 1·90(2·8), 1·79(3·5), 1·68(4·3), 1·65(3·2), 1·61(4·2). The X-ray pattern is consistent with a simple cubic system having a unit cell length of 12·1 Å.[21]

Decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]*decan-5-one hydrate* XXI

Reaction of hexachlorocyclopentadiene with liquid SO_3 by the method of Gilbert and Giolito[4a] gave XXI, m.p. 346–348°; (CCl_4) 2·80 μ (no absorption in 5–6 μ region); X-ray powder diffraction data: 6·86 Å(100), 6·28(35), 3·74(34), 3·43(24), 3·16(24), 2·98(20), 2·88(17), 2·82(33), 2·71(43), 2·66(24), 2·56(21), 2·49(16), 2·26(16).

Decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]*decan-5-one* IV

Azeotropic distillation of a soln of XXI in benzene (25 g/100 ml) under a Dean-Stark water trap for several days, followed by cooling, gave large white crystals of IV whose IR spectrum indicated the presence of a slight amount of hydrate (2·80 μ). This material was suitable where "anhydrous" IV was required. The last traces of hydrate (IR analysis) could be removed by refluxing II as prepared above with AcCl (10 g/100 ml) for several days, m.p. 348–349° (lit.[4a] m.p. 349°), (CCl_4) 5·54 μ; X-ray powder diffraction data: 8·76 Å(25), 7·09(100), 6·03(10), 3·53(34), 3·29(22), 3·30(33), 3·05(23), 2·99(32), 2·96(34), 2·91(24), 2·84(16), 2·77(14), 2·68(59), 2·53(25), 2·37(23), 2·36(32), 1·77(15), 1·64(12) 1·63(12), 1·62(25).

Reaction of I *with lithium and* t-*butyl alcohol*

(1) *Reaction at* 0–15°. *Preparation of pentacyclo*[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]*decane* II. Small pieces of Li wire (16·7 g, 2·4 g atoms) were added in one portion to a soln of I (27·3 g, 0·05 mole) and t-butyl alcohol (89·0 g, 1·2 mole) in 500 ml dry THF (dried over CaH_2). The reaction mixture was stirred

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[19] M.ps were taken in capillary tubes and were uncorrected. B.ps were uncorrected. Elemental microanalyses were determined by Dr. C. S. Yeh, Mrs. K. Keblys and Mrs. B. Groten, Purdue University. IR and UV spectra were obtained by Mrs. W. L. Dilling, Purdue University, using Perkin-Elmer Model 21 or 221 (NaCl optics) and Bausch and Lomb-Spectronic 505 spectrophotometers. Mr. W. E. Baitinger, Purdue University, obtained the NMR spectra with either a Varian V-4311 spectrometer operating at a radio frequency of 56·4 or 60 Mc/s or a Varian A-60 spectrometer operating at 60 Mc/s. The spectra from the V-4311 instrument were calibrated using the side-band technique.[20] The chemical shifts are reported as δ in ppm from TMS used as an internal reference. The areas under the peaks obtained from the V-4311 instrument were measured with a planimeter and are reported as the average of two or three measurements of different spectra. The mass spectra were obtained by Dr. J. W. Amy and Mr. L. J. Brand, Purdue University, using a Bendix "Time of Flight" mass spectrometer and by Mrs. W. L. Dilling, Dow Chemical Co., using a 90 sector magnetically scanning mass spectrometer. The powder X-ray diffraction patterns were determined by Dr. J. L. White and Mrs. A. F. Burns, Purdue University Agronomy Department, using a general Electric XRD-5 X-Ray Diffractometer employing the unresolved copper K_α radiation ($\lambda = 1·5418$ Å). The values reported are the interplanar spacings (d) in Å The values in parenthesis are relative intensities (peak hts) with the strongest peak of each pattern arbitrarily assigned a value of 100. Analyses by g.c. were determined with either a Perkin-Elmer Model 154 Vapor Fractometer or an Aerograph Dual Column Programmer Gas Chromatograph using helium as the carrier gas. Preparative scale g.c. was achieved using a Fisher Preparative Partitioner Model 11-133.

[20] J. A. Pople, W. G. Schneider and H. Bernstein, *High Resolution Nuclear Magnetic Resonance*, p. 74. McGraw-Hill, New York (1959).

[21] N. F. M. Henry, H. Lispon and W. A. Wooster, *The Interpretation of X-ray Diffraction Photographs* (2nd Edition), p. 179. Macmillan, London (1960).

under N for 12 hr at 0–15° and poured into 3 l. crushed ice to destroy the unreacted Li. After extraction several times with ether, washing well with water, and drying over anhydrous $CaSO_4$, the ether was distilled. Distillation of the residue gave 5·7 g (86%) of colourless distillate, b.p. 90–108° (45 mm), n_D^{30} 1·5088–1·5129. GC analysis of the distillate on a polyethylene glycol column showed the presence of V and II in a relative area ratio of ca. 65:35. Separation of II by preparative GC on a silicone oil or polyethylene glycol column was followed by further purification by sublimation at 25° (1 atm); m.p. 125–127°; X-ray powder diffraction data: 5·37 Å(100), 4·65(21), 2·69(0·8). This X-ray diffraction pattern is consistent with either a simple of face-centered cubic system having a unit cell length of 9·3 Å. (Found: C, 90·40; H, 9·51; mol. wt., 129 (cryoscopy, benzene); 132 (mass spectrometry). Calc. for $C_{10}H_{12}$: C, 90·85: H, 9·15%; mol. wt., 132.)

A portion of the distillate (1·32 g) was treated with 1·19 g phenyl azide[32] for 20 hr at room temp. Cooling the reaction mixture to --78°. gave 0·90 g crude V-phenyl azide adduct XXII. Decolorization of a 95% EtOH sol of the crude product with charcoal and recrystallization from 95% EtOH gave 0·41 g (28%) of XXII as white crystals, m.p. 125–127°, mixed m.p. 124·5–127° (lit.[33] m.p. 128–129°). The IR spectrum was identical with that of an authentic sample of XXII.

(2) *Reaction at −78° for 18 hr. Preparation of* 1,4,6,9-*tetrachloropentacyclo*[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]-*decane* VII. The preceding experiment was repeated using the same quantities of reactants and solvent as under (1), while the flask was cooled at −78°. After stirring for 18 hr the reaction mixture was worked up as before. Distillation of the residue gave 4·8 g of dark liquid, b.p. 130–154° (35 mm), n_D^{30} 1·5166–1·5389; (neat) 3·29(s), 6·17(s), 6·32(m), 6·39(m) μ. GC analysis on a polyethylene glycol column revealed the presence of very little V and no II, but of several components with longer retention times than V. A portion of the distillate 0·2 g, crystallized on standing as did the distillation residue, 2·8 g. These crystals were combined in heptane, decolorized with charcoal, and crystallized to give 1·2 g (9%) of white crystalline VII, m.p. 246–247°; (CCl_4) 3·35(m), 3·40(m), 3·51(w), 4·28(w), 6·95(m), 7·78(s), 8·08(s), 8·16(s), 8·66(m), 9·33(w), 9·91(s), 10·34(w), 10·58(s) μ; mass spectrum: *m/e* 233 (M^+–Cl).[34] (Found: C, 44·64; H, 2·74; Cl, 52·66; mol. wt., 276 (cryoscopy, benzene). Calc. for $C_{10}H_8Cl_4$: C, 44·48; H, 2·99; Cl, 52·52%; mol. wt., 270.)

(3) *Reaction at −78° for 1 hr; preparation of* 1,2,4,6,(7 or 8),9-*hexachloropentacyclo*[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]*decane* IX. The preceding experiment was repeated using I (27·3 g, 0·05 mole), t-butyl alcohol (44·5 g, 0·60 mole). and Li (8·4 g, 1·20 g atom) in 500 ml dry THF. After stirring at −78° for 1 hr, the reaction mixture was worked up as before. The dark residue, 19·5 g, was recrystallized from heptane, after decolorizing the soln with charcoal. The first crop of crystals was recrystallized from benzene—heptane, giving two types of crystals. Small prisms, 2·0 g, were separated mechanically from unreacted I, recrystallized from acetone, and vacuum sublimed at 160° (0·2 mm) to give 1·1 g (7%) of white crystalline IX, m.p. 321–323° (sealed capillary); (Nujol and Fluorolube) 3·34(w), 3·37(w), 7·83(s), 7·91(s), 8·12(s), 8·24(m), 8·59(m), 8·71(w), 9·90(s), 10·05(m), 10·52(m), 10·68(s), 12·23(s), 13·43(s), 14·82(m) μ; mass spectrum: *m/e* 301 (M^+–Cl). (Found: C, 35·28; H, 1·76; Cl, 62·66; mol. wt., 344 (cryoscopy, benzene). Calc. for $C_{10}H_6Cl_6$: C, 35·44; H, 1·78; Cl, 62·77%; mol. wt., 339.)

Concentration of the heptane mother liquor gave a solid which, on recrystallization from acetone gave I and a material which was vacuum sublimed and recrystallized from heptane to give 0·2 g (1%) of white crystals of X, m.p. 188–300°; NMR spectrum (CCl_4): a singlet at −3·30 (1·9)[35] and a singlet at −4·09 (1·0). (Found: C, 28·42; H, 0·79; Cl, 71·58%.)

Complete evaporation of the heptane mother liquor left an oil, 5·0 g, (neat) 6·15 (s), 6·29(m) μ. The total recovery was I was 37%.

Reaction of I *with lithium, water and dry ice*

Method A; *reaction with a deficiency of lithium and water.* A solution of I (27·3 g, 0·5 mole) in 500 ml THF was flushed with N and cooled to −78°. Approximately 500 g powdered Dry Ice and Li (1·4 g, 0·20 g atom) were added to the THF sol. The mixture was stirred at −78° for 24 hr, allowed to come to room temp over a period of 52 hr, and refluxed for 7 hr. The cooled reaction mixture was poured into 2 l. crushed ice and extracted with ether. The ether, after washing with

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[32] R. O. Lindsay and C. F. H. Allen, *Org. Synthesis Coll. Vol.* III, 710 (1955).

[33] P. D. Bartlett and J. S. Goldstein, *J. Amer. Chem. Soc.* **69**, 2553 (1947).

[34] The reported *m/e* values for the chlorinated compds are based only on the Cl^{35} isotope.

[35] Relative areas are given in parentheses.

water and drying, was evaporated to give 23·6 g of dark solid. Recrystallization from benzene–MeOH, sublimation at 170° (0·2 mm), recrystallization from benzene–EtOH and from acetone gave a mixture of large white prisms and fine white needles. These two forms of crystals were separated mechanically, and each was recrystallized from acetone and sublimed at 170° (0·2 mm). The large white prisms gave 0·8 g of crystals of XIV, m.p. 177–177·5°; NMR spectrum (CCl_4): broad multiplet centered at −2·10 (6·0), at least 4 peaks at −3·80 (5·0) and a broad multiplet at −4·43 (1·0). (Found: C, 30·52, 30·74; H, 1·20; 1·29; Cl, 68·12, 68·25; mol. wt., 536 (vapor pressure osomometry, benzene), 554 (cryoscopy, benzene). Calc. for $C_{13}H_6Cl_{10}$: C, 30·21; H, 1·17; Cl, 68·62%; mol. wt., 517.)

Fine needles, 0·4 g, of XV had m.p. 194–196°; NMR spectrum ($CDCl_3$): a singlet at −1·26 (3), at least 4 peaks centered at −2·05 (3), at least seven peaks at −3·77 (3), and at least six peaks at −4·31 (1). (Found: C, 32·90; H, 1·78; Cl, 64·33; mol. wt., 506 (vapor pressure osmometry, benzene). Calc. for $C_{15}H_{10}Cl_{10}$: C, 33·07; H, 1·85; Cl, 65·08%; mol. wt. 545.)

Evaporation of the combined benzene–EtOH mother liquors gave material which was recrystallized from MeOH to give 0·3 g (1%) of white crystals of XIII dec above 250° without melting; NMR spectrum (CCl_4): two poorly resolved doublets at −2·04 (1) and −3·67 (1). (Found: C, 25·82; H, 0·77; Cl, 73·68; mol. wt., 532 (cryoscopy, benzene). Calc. for $C_{10}H_2Cl_{10}$: C, 25·19; H, 0·42; Cl, 74·39%; mol. wt., 477.)

Method B; *reaction with an excess of lithium and water; preparation of* 1,2,3,4,5,5,6,7,(8 or 9),10,10-*undecachloropentacyclo*[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]*decane* XI. The preceding reaction was repeated using the same amount of I and an excess of Li (16·7 g, 2·40 g atoms). A soln of water (21·6 g, 1·20 mole) in 100 ml THF was added through an addition funnel over a period of 3½ hr. The mixture was stirred at −78° for 42 hr, allowed to come to room temp, and stirred for an additional 22 hr, whereupon it was worked up as before. The residue, 14·4 g, obtained on evaporation of the ether, was extracted with boiling hexane. After concentration, the extract was chromatographed on alumina. Elution with hexane afforded 2·1 g crystals which, after vacuum sublimation at 150° (0·3 mm) and recrystallization from aqueous EtOH gave 0·9 g (3%) of white crystalline XI, dec above 300° without melting; (CCl_4) 3·29(w), 8·11(s), 8·67(s), 8·83(s), 9·00(m) 9·39(s), 9·70(w), 9·99(s), 10·31(w), 11·28(w), 11·96(s), 14·73(w), 15·27(m) μ. (Found: C. 23·52; H, 0·30; Cl, 76·18; mol. wt., 509 (cryoscopy, benzene); 506 (mass spectrometry). Calc. for $C_{10}HCl_{11}$: C, 23·50; H, 0·20; Cl, 76·30%; mol. wt., 511.)

Continued elution with hexane gave 1·6 g of XIV. Benzene eluted 1·5 g of light yellow solid. Recrystallization from heptane gave 0·7 g of white crystals of XVI m.p. 255–256°; NMR spectrum ($CDCl_3$); a singlet at −1·27 (0·3), at least 6 peaks centered at −2·13 (4·4), at least 4 peaks at −3·75 (3·0), and a triplet at −4·26 (1·0); mass spectrum: *m/e* 509 (M^+–Cl), isotope ratio indicated 8 Cl atoms. A much less intense set of peaks was observed in the mass spectrum at *m/e* 540 (M^+ for $C_{18}H_9Cl_9$), with Cl isotope ratio indicating 9 Cl atoms, possibly due to an impurity (Found C, 39·68; H, 2·46; Cl, 58·62; mol. wt., 526, 530 (cryoscopy, benzene). Calc. for $C_{18}H_{13}Cl_9$: C, 39·42; H, 2·39; Cl, 58·19%; mol. wt., 548.)

Preparation of pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]*decane* III

(1) *By reduction of the ketone* VI. A soln of VI[14] (2·00 g, 0·0137 mole) and hydrazine hydrate (99%; 1·65 g, 0·033 mole) in 80 ml triethylene glycol was allowed to stand at room temp for 24 hr. The flask was equipped with a distillation head and a thermometer extending below the liquid level. 85% KOH (10·5 g, 0·16 mole) was added, and the soln was heated at 200° for 3 hr. When the temp reached ca. 150° a large volume of gas evolved, and a solid condensed in the distillation head. This solid was dissolved in 200 ml of pentane, washed with water, and dried. After filtration and distillation of the solvent, the residue was sublimed at 90° (atm press) to give 1·33 g (74%) of white crystalline III, m.p. 142–143° (lit.[16] m.p. 134–136°); $\epsilon_{200\,m\mu} = 0$ (EtOH); X-ray powder diffraction data: 5·72 Å(67), 5·44(63), 5·07(100), 4·67(6·7), 3·95(3·4), 3·90(3·9). (Found: C, 90·96; H, 9·16; mol. wt., 132 (mass spectrometry). Calc. for $C_{10}H_{12}$: C, 90·85; H, 9·15%; mol. wt., 132.)

(2) *By irradiation of the diene* V. As described by Schenck and Steinmetz[16] a soln of V (7·0 g) in 130 ml acetone under N was irradiated through quartz with a 450 watt Hanovia medium press Hg arc lamp at ca. 30° for 24 hr. After distillation of the acetone the residue was sublimed to give III (ca. 20%), m.p. 138–141°. The IR and NMR spectra were identical with that of III prepared above. The sublimation residue was vacuum distilled to give 2·1 g of liquid, b.p. 77° (25 mm) −71° (2 mm). A polymeric residue, 8·3 g, remained. The major components of the distillate were identical as pinacol and acetonylacetone by preparative GC and comparison of the retention times and the mass, IR,

and NMR spectra with those of authentic samples. Also a 1:1 adduct of acetone and $C_{10}H_{12}$ was detected by mass spectrometry. The spectrum indicated a partial structure to be $C_{10}H_{11}CMe_2OH$, *m/e* 190 (M^+), 175 (M^+–CH_3), 172 (M^+–H_2O). At least 15 other components were detected but not identified.

Preparation of 1,2,3,4,5,5,6,7,8,9-*decachloropentacyclo*[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]*decane* VIII.

A soln of IV (24·5 g, 0·05 mole), hydrazine hydrate (6·0 g, 0·125 mole), and KOH (9·5 g, 0·17 mole) in 500 ml diethylene glycol was heated at 200° for 4 hr. After cooling, the reaction mixture was filtered. An extract of the residue with 200 ml acetone was added to the filtrate. Dilution of the filtrate with 2 l. water precipitated 13·2 g of crude VIII. Reprecipitation from acetone with water, sublimation at 150° (0·15 mm), followed by recrystallization from hexane and from 95% EtOH, gave 2·7 g (11%) of white crystalline VIII, m.p. 374–375° dec; (CCl_4) 3·34(vw), 3·38(vw), 3·49(vw), 6·97(m), 7·89(s), 8·30(m) 8·72(s), 8·89(s), 9·02(w), 9·62(w), 9·78(s), 10·17(w), 10·45(m), 10·74(w), 10·90(w), 11·45(s) μ; X-ray powder diffraction data: 7·97 Å(71), 7·44(27), 6·92(86), 6·42(5·7), 6·24(36), 5·91(29), 3·45(32), 3·21(100), 3·00(55), 3·86(53), 2·80(47), 2·72(31), 2·68(34), 2·44(24), 2·41(24), 2·22(17); mass spectrum: *m/e* 437 (M^+–Cl). (Found: C, 25·07; 25·01; H, 0·41; 0·50; Cl, 74·50; 74·75 mol. wt., 466 (cryoscopy, benzene). Calc. for $C_{10}H_2Cl_{10}$: C, 25·19; H, 0·42; Cl, 74·39%; mol. wt., 477.)

Preparation of 1,2,3,4,5,5,6,7,8,9-*decachloropentacyclo*[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]-10-*decanol* XVII

A soln of IV (4·9 g, 0·01 mole) and KOH (1·9 g, 0·034 mole) in 100 ml diethylene glycol was heated at 200° for 3 hr. After cooling and filtration, the residue was extracted well with acetone, which was added to the filtrate. Dilution of the filtrate with 500 ml water precipitated crude XVII. Reprecipitation from acetone-water, vacuum sublimation at 150° (0·14 mm) and recrystallization from heptane gave 1·5 g (31%) white crystalline XVII, m.p. 372–373° dec (lit.[4e] dec 360°); (CCl_4) 2·82(m), 3·47(w), 7·23(w), 7·75(m), 8·28(m), 8·39(m), 8·79(s), 8·88(s), 9·01(s), 9·12(m), 9·39(s), 9·51(s), 9·67(m), 10·46(m), 10·73(m), 11·50(m), 11·72(s), 14·12(m), 15·34(s) μ: NMR spectrum (CCl_4): two singlets of equal area at −2·40 and −4·25; mass spectrum: *m/e* 453 (M^+–Cl). (Found: C, 24·18; H, 0·47; Cl, 72·37; mol. wt., 530 (cryoscopy, benzene). Calc for $C_{10}H_2Cl_{10}O$: C, 24·38; H, 0·41; Cl, 71·97; mol. wt., 493.)

Preparation of 1,2,3,4,6,7,8,9,10,10-*decachloropentacyclo*[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]*dec-5-yl acetate* XVIII

A soln of XVIII (0·20 g, 0·00041 mole) in 25 ml AcCl was refluxed for 4 days. Distillation of the excess AcCl gave 0·20 g crude XVIII. Decolorization with charcoal and recrystallization from heptane gave 0·10 g (46%) white crystalline XVIII, m.p. 168–168·5°; (CCl_4) 3·41(w), 5·66(s) μ. (Found: C, 27·27; H, 0·90; Cl, 66·48; mol. wt., 530 (mass spectroscopy). Calc. for $C_{12}H_4Cl_{10}O_2$: C, 26·95; H, 0·75; Cl, 66·32%; mol. wt., 535.)

Preparation of 1,2,3,4,5,5,6,7,8,9,10-*undecachloropentacyclo*[5,3,0,$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]*decane* XII

A soln of XVII (0·20 g, 0·00041 mole) and PCl_5 (0·17 g, 0·00082 mole) in 10 ml CCl_4 was refluxed for 10 days. The soln was poured into 200 ml water and shaken vigorously. The aqueous layer was extracted with CCl_4 and the combined organic extracts were washed with 10% $NaHCO_3$ and water, and dried. Distillation of the solvent and sublimation of the residue at 150° (0·2 mm) gave 0·18 g (87%) of white crystals of XII. Resublimation gave a pure sample, m.p. 387° dec (lit.[4e] m.p. 380°); (CCl_4) 3·39(w), 7·99(s), 8·04(s), 8·34(m), 8·75(s), 8·84(s), 9·02(m), 9·49(s), 9·69(m), 10·40(m), 10·85(m), 11·32(m), 11·53(m) μ; mass spectrum; *m/e* 471 (M^+–Cl). (Found: C, 23·64; H, 0·11; Cl, 76·02. Calc. for $C_{10}HCl_{11}$: C, 23·50; H, 0·20; Cl, 76·30%.)

Reaction of XII *with lithium* t-*butoxide*

A soln of XII (0·08 g, 0·00016 mole) and Li t-butoxide, prepared from Li (0·02 g, 0·003 g atom) and t-butyl alcohol (0·22 g, 0·003 mole), in 2 ml dry THF was stirred at room temp for 24 hr. The reaction mixture was poured into 100 ml water and extracted with ether. The ether was washed well with water. After drying and evaporation of the solvent, a light brown crystalline residue, 0·06 g remained. Vacuum sublimation at 150° (0·1 mm) gave 0·04 g yellow solid, m.p. 100–300° with dec above 200°; (CCl_4) 6·02, 6·25, 6·32 μ.

Preparation of decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]*decan-5-one hydrazone* XIX

A mixture of IV (9·8 g, 0·02 mole) 100% hydrazine hydrate (1·0 g, 0·02 mole) and 500 ml benzene was refluxed under a Dean-Starke trap for 30 hr. Benzene was distilled until a volume of 50 ml remained. On cooling, 9·6 g XIX separated. Recrystallization from benzene–heptane gave 7·8 g (77%) of white platelets, dec above 220° without melting; (Nujol) 2·86(w), 3·00(m), 6·24(m), 6·31(m) μ. (Found: C, 23·60; H, 0·65; Cl, 70·01; N, 5·40; mol. wt., 542 (cryoscopy, benzene). Calc. for $C_{10}H_2Cl_{10}N_2$: C, 23·80; H, 0·40; Cl, 70·26; N, 5·55%; mol. wt., 505.)

Two recrystallizations of 2·0 g of XIX from aqueous EtOH gave 1·8 g of a white powder, m.p. 278–280°; (CCl_4) 2·81, 3·00 μ, no peaks in 5·0–6·5 μ region. (Found: C, 24·50; H, 0·43; Cl, 71·85; N, 0·79%.)

Preparation of decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]*decan-5-one phenylhydrazone* XX

A soln of IV (9·8 g, 0·02 mole) and phenylhydrazine (2·2 g, 0·02 mole) in 400 ml benzene was heated at reflux under a Dean-Starke trap for 10 days. Distillation of the solvent afforded 11·6 g crude XX. Decolorization of the hexane soln with charcoal and three recrystallizations from hexane gave 7·1 g (61%) of XX as white needles, m.p. 165–166°; (CCl_4) 2·86(m), 3·04(w), 3·31(w), 6·23(s) μ. (Found: C, 32·77; H, 1·25: Cl, 60·95; N, 4·91; mol. wt., 568 (cryoscopy, benzene). Calc. for $C_{16}H_6Cl_{10}N_2$: C, 33·09; H, 1·03; Cl, 61·05; N, 4·82%; mol. wt., 581.)

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