Perchloro-(3,4-dimethylenecyclobutene)

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The dechlorination of perchloropropene in an anhydrous ether solution with several kinds of aluminum (chips, granules or powder) principally produces perchloro-(3,4-dimethylenecyclobutene) (I)[1-3] in quite good yields. In the sufficiently high dechlorination degree range, I is the only reaction product isolated in many runs. This result is remarkably different from that of Roedig's report,[4] in which perchlorofulvene (II), two perchlorohexatrienes (α- : IIIa and β- : IIIb, respectively) and perchloro-4-methylenecyclopentene (IV) were given as the ordinary products duplicating the carbon atom number of this substrate, and in only two particular runs was there the poorly reproducible formation of I on the dechlorination of perchloropropane with granulated aluminum. Depending mainly on the reaction conditions, I in the product mixture is sometimes accompanied by perchloro-(3,4-dimethylenecyclobutane) (V),[1-5] m. p. 93°C, the dechlorination intermediate first obtained directly from perchloropropene. The identification of V has been established by comparing it with the specimen synthesized from 1,1,2,3,3-pentachloropropene.[6] It has also been found that V is easily dechlorinated with aluminum - aluminum chloride to give I.[1,3]

The aluminum metal used for the dechlorination is a comparatively pure one (ca. 99% for chips), with which alone the reaction does not start readily, as Roedig noted; a small amount of anhydrous aluminum chloride must first be added to the system. Even with this initiation, the autocatalytic acceleration of reaction is so mild that the whole system is necessarily heated to a violent refluxing. It has been found, however, that the pre-amalgamation of aluminum makes the reaction proceed far more smoothly, without the addition of the catalyst, and causes a remarkable increase in the yield of I up to 44% (chips, $D^*=54\%$), 51% (granules, $D=51\%$) and 62% (powder, $D=66\%$). In general, the incomplete corrosion-treament requires a prolonged reaction time, followed by the partial formation of V. The careful examination of Roedig's dechlorination of perchloropropene with the granulated aluminum - aluminum chloride available in the authors' laboratory has unexpectedly resulted in the random production of either I or II. Perchlorohexa-1,5-diene (VI), a primary coupling product of perchloropropene in Prins' method,[7] was not dechlorinated at all to yield I by amalgamated aluminum, but it was dechlorinated quantitatively to yield IIIa.

I (m. p. 147—148°C, colorless prisms with a slightly irritative odor, crystallized in the triclinic system from ether) is stable in the solid state, whereas it gradually decomposes with the evolution of hydrogen chloride, when allowed to stand in such solvents as ether, benzene and carbon tetrachloride; some of these solvents are, however, applicable in its recrystallization. The ultraviolet light irradiation (principally 2537Å) also destroyed I in

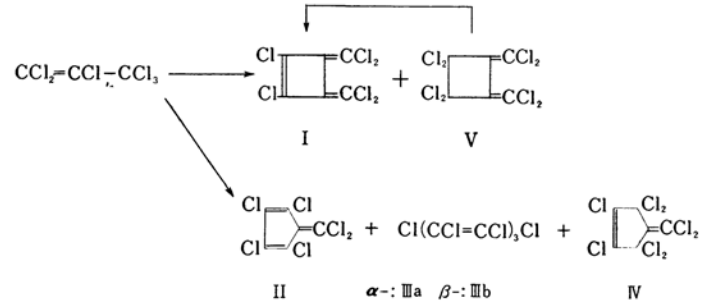

Chart I

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[1] The establishment of the structure was reported by the authors at 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961. Abstracts p. 320.

[2] A. Roedig and F. Bischoff, *Naturwissenschaften*, **49**, 448 (1962); J. Brandmüller, E. Ziegler and A. Roedig, ibid., 49, 1466 (1962).

[3] A. Roedig, F. Bischoff, B. Heinrich and G. Märkl, *Ann.*, **670**, 8 (1963).

[4] A. Roedig, *Ann.*, **569**, 161 (1950).

[5] A. Roedig and P. Bernemann, ibid., **600**, 1 (1956).

[6] H. J. Prins, *Rec. trav. chim.*, **68**, 898 (1949).

* Dechlorination degree defined by Roedig in Ref. 4.

[7] H. J. Prins, ibid., **68**, 419 (1949).

hexane at a markedly rapid rate. The detailed work on both the autodegradation in solution and the photochemistry will be reported later.

Contrary to the disordered results observed in the molecular weight determination of I by the Rast method,[8] the cryoscopic measurement with a fresh benzene solution afforded consistent values, which, however, confusedly became higher even after being stored for only 1/2 hr. The observed dipole moment is 0.43 D. This value is not, however, fully reliable as a result of the instability of the material in carbon tetrachloride.

By long heating with concentrated sulfuric acid at 100°C, I was partially converted, with the evolution of hydrogen chloride, to a carboxylic acid, m. p. 146—147°C, one which has not been yet characterized. A mild alkali-fusion test showed no indication that I has suffered from the degradation. I also resisted the bromine addition in chloroform, as commonly observed in perchloro-polyolefins, but it consumed permanganate in acetone almost instantly.

With a small excess of liquid chlorine in a sealed tube, I was converted in low yield to a chlorocarbon, C_5Cl_6 (VII), m. p. 77—78°C, to which the structure of perchloro-(3-methylenecyclobutene) has been assigned. When chlorinated with a large excess of the reagent for a short period, three crystalline products and an oily fraction were obtained: C_6Cl_{10}, perchloro-(1,2-dimethylcyclobutene), (VIII), m. p. 146—148°C, C_5Cl_8, perchloro-(1-methylenecyclobutane) (IX), m. p. 73—74°C; $C_{12}Cl_{18}$, possibly a dimeric chlorinated product (X), m. p. 163°C (decomp.), and an oil, b. p. 110—130°C (bath temp.)/0.008 mmHg. The purity of the oil remains equivocal.

An attempt to reduce I with zinc and alcohol to some hydrocarbon equivalent has been unsuccessful; the product was merely an amorphous solid mass, which had hardly been purified to serve as an analyltical sample.

The oxidation of I with potassium permanganate in acetone, chromic oxide in acetic acid, or fuming nitric acid always gave the same dicarboxylic acid (XII), $C_6Cl_4H_2O_4$, m. p. 215°C (decomp.), always in very low yields. The rate of oxidation is seemingly decreased in this order of reagents. No definite neutral products have been isolated in the first two cases, whereas, in the slowest nitric acid oxidation, a neutral nitrogeneous material (XIII), $C_6Cl_6N_2O_4$, m. p. 114—115°C (decomp.), was obtained. XII is doubtlessly perchloro-(dimethylenesuccinic) acid; it was converted, by refluxing it with acetic anhydride, to the corresponding anhydride (XIV), m. p. 119—120°C. which was then smoothly hydrolyzed to the original acid by heating it with an aqueous bicarbonate solution. Chart II summarizes the reaction schemes related to I.

Discussion

Obviously, the most interesting feature of the preceding results is the course of reaction, which is distinctly different from that described by Roedig, whose extensive work pioneering this kind of dechlorination has mainly been concentrated on studies of the production of five-membered ring compounds and of acyclic olefinics. The purity of Roedig's aluminum chips has been reported to be 85—87% (with copper, silicon and zinc as the major impurities, in quantities of 4—5, 3—5 and 2—4% respectively), while the authors' chips in the routine use contain far less impurities (Cu, 0.04; Fe, 0.51; Si, 0.25%). Although Roedig noted the unsuitability of pure aluminum for the reaction, it has been

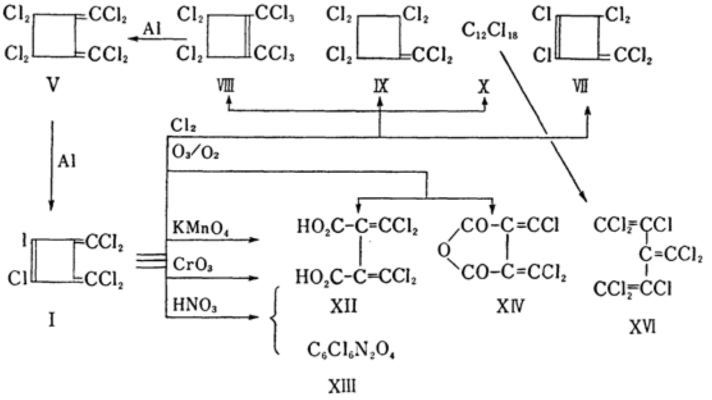

Chart II

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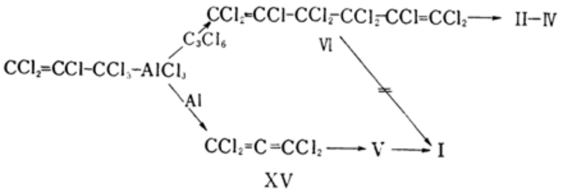
[8] The observed values are disorderly low as seen in the experimental. Although Roedig reported the value of 279[3] as observed by Rast, it seems highly probable that, with camphor, the thermal decomposition of I above 170°C will affect the determination result.

proved that even a high grade aluminum (99.99%) reacts, after amalgamation, with perchloropropene to give I (in a 55% yield) under essentially the same conditions. It is, therefore, possible to point out that the leading cause of the different results in the dechlorination reactions can be attributed to the quality of the metal, in which some foreign element might function specifically at an early stage of the reaction. The fact that I has not been produced in the dechlorination of VI by the amalgamation procedure strongly excludes the possibility that VI might be an intermediate in the process of the formation of I from perchloropropene. Thus, it is most likely that perchloroallene (XV) is an unstable precursor of V, the formation and the chemical behavior of which have recently been shown in the elaborate synthetic work³⁾ related to the dehydrochlorination of 1,1,2,3,3-pentachloropropene.



It is also reasonable to assume that the formation of a four-membered ring could be possible only under some specifically accommodated participation of the allene components.⁹⁾ This mechanistic speculation would not, however, contradict the observation that I and II have seemed to be incompatible in the product of the Roedig's dechlorinations closely-reexamined with aluminum granules, since, particularly in this case, the metal reagent possibly has a lower and less homogeneous purity than the chips and also a wide-ranging size distribution, both of which more or less affect the reaction process.

The *D*-values determined and the yield of I are illustrated in Table I. So far as the aluminum chips are concerned, the whole reaction appears basically to proceed in a way similar to that of Roedig's reaction in terms of *D*-values (approximately 50—60%). In the runs with granules the *D*-values are much higher than those (less than 5%) reported, and no particular difference has been observed between the "amalgamated" and the "with aluminum chloride." Remarkable indeed is the difference between the two runs with aluminum powder, where the amalgamation causes a tremendous increase in *D* as well as in the yield of I.

Some interesting problems in the course of the structure investigations of I and other related compounds will be briefly discussed below.

The structure of VII is derived from the observation of the very close relationship of the ultraviolet spectral feature of this compouud and that of I, with only a small hypsochromic shift of λ_{max} in the former, and from the fact that its infrared spectrum exhibits the $\nu_{C=C}$ doublet (1680 and 1580 cm^{-1})** instead of the

TABLE I. THE DECHLORINATION OF PERCHLOROPROPENE WITH ALUMINUM METAL

Sort of Al	Amalgamated or with AlCl₃	Reactants C₃Cl₆ mol.	Reactants Al mol.	Reaction periods hr.	*D* %	Yield of I %
Al-chips[a]	A[b]	0.32	0.74	5	54	44
	A	0.32	0.74	5	59	41
	A	0.32	0.74	5	47	39
	A	0.32	0.74	5	58	37
	A	0.32	0.74	5	15	21[c]
	A	0.32	0.74	10	61	38
	A	0.32	0.74	35	67	25
Al-granules	A	0.08	0.19	6	51	51
	B	0.08	0.19	6	50	46
	B	0.15	0.37	35	—	8.6[d]
Al-powder	A	0.08	0.19	8	66	62
	A	0.08	0.19	5	63	56
	A	0.08	0.19	6	58	45[e]
	B	0.08	0.19	12.5	22	0

a) Chips are small, cross-shaped pieces of the metal stamped out from thin plates.
b) A and B indicate "amalgamated" and "with AlCl₃" respectively.
c) The low yield is due to insufficient amalgamation and/or inefficient stirring.
d) The yield of II. The *D* value was not determined in this run.
e) The figure does not include the additional crop composed of I and V.

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9) J. D. Roberts and C. M. Sharts, "Organic Reactions," Vol. 12, 24 (1962).

** All IR spectra have been measured with Nujol mull unless noted.

triplet (1695, 1625 and 1550cm^{-1} (KBr)) in I. The first $\nu_{C=C}$ band of I is noteworthy because of its extremely high frequency, which is probably next to the 1810 cm^{-1} value in perchlorocyclopropene,[10] the highest ever observed in the chlorocarbon series. Conceivably, this band is connected with the presence of the endocyclic double bond involved in a four-membered ring. This interpretation further explains the respective presence and lack of band in the corresponding high frequency region in VII and IX. Special caution must be taken before assigning the 1625 cm^{-1} band for VIII, since in position it coincides with the band in IX and rather seems to be for an exocyclic structure. The first reason to favor VIII, however, is its very weak intensity in contrast to the strong one for the double bond of the exocyclic type, as in IX. A $>C=C<$ bond with no chlorine-substituent is suggested here. Secondly, if it has an exocyclic double bond, a considerably intense band can be expected to arise in the 930—900 cm^{-1} range with reference to the $-\underset{|}{C}=CCl_2$ group in the molecule.[11] Only three weak peaks (955 vw, 905 vw and 895 w (cm^{-1})) are practically found in this vicinity, however. In additional consideration of the chemical evidence for the skeletal structure of VIII, established through its dechlorinative conversion to V, the double bond in question can most easily be located at the C_{1-2} position.

The assumption of an exocyclic double bond in IX could also be justified by interpreting the strong 910 cm^{-1} band as characteristically arising from the $-\underset{|}{C}=CCl_2$ group. Although the complete elucidation of the structure of X is a future problem, it may be worth noting here that this chlorocarbon is decomposed above its melting point, or even at a lower temperature under a vacuum, to ε-C_6Cl_8 (XVI), m. p. 45°C, which was recently proposed to be perchloro-3-methylene-1, 4-pentadiene by Roedig[2] on the basis of its Raman spectroscopic analysis.

The structure of perchloro-(dimethylenesuccinic) acid was earlier suggested for a carboxylic acid, with an m. p. of 219°C (decomp.), obtained by the alkaline hydrolysis of α, α'-bis-trichloromethylsuccinic acid (XVII),[12] a minor by-product in the reaction of diethyl maleate with benzoyl peroxide in carbon tetrachloride. The re-investigated runs of this reaction have not, however, reproduced XVII and so made the final identification of XII impossible. Nevertheless, the interpretation of the infrared spectrum of XIV leaves little doubt about the structure of XII, since the possible alternatives may all be excluded on the basis of either extremely high carbonyl frequencies (1835 and 1765 cm^{-1}) and the magnitude of $\Delta\nu_{C=C}$[13] (70 cm^{-1}), or two closely-located bands (930 and 920 cm^{-1}) assigned to the two exocyclic dichloromethylene groups. Roedig reported the production of only chloropicrin and oxalic acid dihydrate in the nitric acid oxidation of I, but the small amount of XII and XIII may have been overlooked. The application of ozone to I also affords XII and XIV. It is, however, obscure whether or not the real attack of ozone has occurred in this degradation, because I is very readily decomposed to XII, even with oxygen in some moistened organic solvents, as will be reported in the succeeding paper.

The formation of XIII in the oxidation is interesting enough to mention, since it would be the first case that I is converted to a nitrogeneous compound without losing any chlorine atom in the molecule. The infrared absorption band at 1580 vs and 1315 s (cm^{-1}) reveals at least one nitro-group attached to the carbon with two chlorine atoms.[14] The very high intensity of the former band is partially due to the $\nu_{C=C}$ absorption. The investigation is present under way to clarify the structure of XIII.

The ultraviolet absorption spectra data do not seem capable of giving sufficient information about the structural problem of the products mentioned above unless some more compounds of various and appropriate types of four-membered cyclic chlorocarbons are available. However, it is interesting to emphasize that the estimated wavelength values for VII and VIII are in good accordance with those observed, if, on the basis of the available data, the bathochromic displacement factors caused by chlorine substitution ($+8.5\,m\mu$ for a vinylic substituent,[15] $+7.5\,m\mu$ for an allylic one,[16] and $+10\,m\mu$ for a trichloromethyl group attached to the unsaturated carbon,[16]) are taken into account. An extraordinarily large bathochromic shift ($+64\,m\mu$) of the λ_{max} in the K band from 1, 2-dimethylenecyclobutane[17] to V can also be rationally explained by the con-

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[10] S. W. Tobey and R. West, *Tetrahedron Letters*, **1963**, 1179.

[11] Unpublished. From the accumulated IR data of perchlorocarbons it may be noted that the compounds holding $-\underset{|}{C}=CCl_2$ group in the molecule generally give a strong absorption band in the range of 930—900 cm^{-1}, while those with $-\underset{Cl}{\underset{|}{C}}=CCl_2$ group absorb in some higher frequency range, 965—940 cm^{-1}.

[12] C. S. Marvel, E. J. Prill and D. F. DeTar, *J. Am. Chem. Soc.*, **69**, 52 (1947).

[13] R. G. Cook, *Chem. & Ind.*, **1955**, 142.

[14] J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955).

[15] A. Roedig and E. Klappert, *Ann.*, **605**, 126 (1957).

[16] Unpublished.

[17] A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, **77**, 1806 (1955).

sideration that such a larger increment is due to the allylic chloro-substitution on the four-membered ring carbon rather than to that (less than +5mμ) in the case of five-membered cyclic compounds.[18]

Roedig et al.[3] suggested the lack of an extended conjugation in I on the basis of the close relationship between the K bands in the ultraviolet spectra of I and those of the corresponding hydrocarbon,[19] which also exists as a cross-conjugated form. The particularly high reactivity of the C_{1-2} double bond in I suffices to reflect this indication. It is, therefore, eagerly desirable to make, in the near future, an extensive stereochemical study of whether or not the whole molecule, or, more interestingly, the cyclobutene ring itself, of I is twisted under the influence of its vicinal dichloromethylene groups. If the van der Waals radius of 1.80 Å for the chlorine atom operates in I, it is not possible to keep all four chlorine atoms in the groups coplanar; in addition, its spacial requirement appears to be too large to afford the distortion of only two severely interacting C–Cl bonds (one bending up and one down, from the sp^2 plane of each methylene carbon).

Experimental

Starting Materials.—Hexachloropropene was prepared from 1,1,1,2,2,3,3-heptachloropropane[20] by dehydrochlorination according to the literature[21]; b. p. 103—104°C/28 mmHg.

Aluminum Amalgam.[22]—A necessary amount of aluminum was corroded thrice with 4 ml./g. (Al) of a 10% aqueous solution of sodium hydroxide and then amalgamated thrice with 5 ml./g. (Al) of a 0.5% aqueous mercuric chloride solution. After having been carefully washed with water, ethanol, ether and anhydrous ether, the compound metal was immediately covered with anhydrous ether in the volume necessary for the reaction.

The Dechlorination of Perchloropropene. The Production of Perchloro-(3, 4-dimethylenecyclobutene) (I) (An example).—In a three-necked, round-bottomed, 500 ml.-flask, fitted with a mechanical stirrer and a reflux condenser, the top of which was connected to a calcium chloride tube, an aluminum amalgam (5.0 g. Al) was prepared as has been mentioned above; then 20.2 g. (0.081 mol.) of perchloropropene was vigorously stirred into the contents. The volume of the solvent was 75 ml., including that for rinsing. The exothermic reaction soon occurred, and the solution came to have a tinge of yellow. After an 8-hr. refluxing, the reaction mixtre was allowed to cool; it was then separated into the dark brown muddy material and an ether solution by filtration. The former was decomposed with 10% nitric acid, and the latter with water. The residual dark brown amorphous solid was repeatedly extracted with ether.

The combined ethereal solution was washed with water, shaken with the saturated aqueous sodium bicarbonate solution, and dried over calcium chloride. On the removal of the solvent, the residual oil began to crystallize and afforded the crude product of I (7.2 g.; 62% of the theoretical yield). Vacuum sublimation (110—120°C/5 mmHg) and recrystallization from ether produced the analytical sample as colorless prisms; m. p. 147—148°C.

Found: C, 25.57; H, 0.49; Cl, 74.93. Calcd. for C_6Cl_6: C, 25.30; H, 0.00; Cl, 74.70%. Mol. Wt. Found: 238, 230 (Rast method with camphor); 289, 278 (cryoscopic method with benzene). Calcd. for C_6Cl_6: 285.

The aqueous solutions were combined, and 5 ml. taken from the whole was titrated with a N/10-silver nitrate solution, using uranine as an indicator to determine the degree of dechlorination.

After having been recovered from the bicarbonate solution by acidification and ether extraction, the acidic fraction gave a small amount of a white crystalline solid, which was recrystallized twice from ligroin; m. p. 74 — 75°C (perchloroacrylic acid[4]; m. p. 76—77°C).

The Formation of Perchloro-(1, 2-dimethylenecyclobutane) (V).—In some runs similar to the above, the sublimate of the crude product showed a lower melting point with a wide range (e. g., 118—134°C). The crops collected from the mother liquor in the course of recrystallizations from ether furnished, after several recrystallizations from benzene, hexagonal plates of V with an m. p. of 92—93°C. Although I is a little more volatile than V, an attempted separation of I from V by means of fractional vacuum sublimation was not successful.

Found: C, 20.52; H, 0.69; Cl, 80.38. Calcd. for C_6Cl_8: C, 20.26; H, 0.00; Cl, 79.74%.

The Synthesis of V from 1, 1, 2, 3, 3-Pentachloropropene.—According to Prins' method,[23] 1,1,1,2,3,3-hexachloropropane (65 g.), b. p. 95—97°C/14 mmHg, n_D^{24} 1.5213, was obtained from chloroform (300 g.), trichloroethylene (131 g.) and aluminum chloride (30 g.). Subsequent dehydrochlorination[24] in carbon tetrachloride (65 ml.) with aluminum chloride (0.78 g.) at 30—40°C for 1/2 hr., followed by refluxing for 4 hr., gave 1, 1, 2, 3, 3-pentachloropropene (44 g., 80%), b. p. 75—76.5°C/19 mmHg. Further dehydrochlorination with the base-paste (potassium hydroxide, 36.9 g.; calcium oxide, 26.3 g., and water, 7.4 g.) suspended in benzene (70 ml. in all) in accordance with the manner previously described[6] resulted in the production of V (17 g., 36.5%). Recrystallization from trichloroethylene-ethanol afforded white prisms, with an m. p. of 91—92°C, which were identical in all respects (mixture m. p. test, ultraviolet and infrared absorption spectra) with those obtained from perchloropropene.

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[18] J. D. Idol, Jr., C. W. Roberts and E. T. McBee, *J. Org. Chem.*, **20**, 1743 (1955).

[19] A. T. Blomquist and P. M. Maitlis, *Proc. Chem. Soc.*, **1961**, 332.

[20] M. W. Farlow, "Organic Syntheses," Coll. Vol. II, 312 (1948).

[21] P. Fritsch, *Ann.*, **297**, 314 (1897).

[22] J. Houben, "Die Methoden der organischen Chemie," Vol. II, Verlag Georg Thieme, Leipzig (1925), p. 256.

[23] H. J. Prins, *J. Prakt. Chem.*, **89**, 414 (1914).

[24] H. J. Prins, *Rec. trav. chim.*, **65**, 455 (1946).

The Chlorination of I.—*a) With a Small Excess of Chlorine.*—In a thick-walled sealed glass tube, 3.0 g. of I and 2.0 g. (a 2.8 mol. equivalent) of liquid chlorine were allowed to stand for 3 weeks. After the evaporation of the unreacted chlorine, the residue (4.05 g.) was separated into two parts: 0.09 g. of crystals, m. p. 63—76°C, and the filtrate, from which the second crop (1.05 g.) of the solid material crystallized out. The former was repeatedly recrystallized from ethanol until it became a pure sample, with an m. p. of 78—79°C. UV: λ_{max}^{EtOH} 236 (32000), 278 (7000), λ_{sh} 228 (26000), 244 (22000), λ_{min} 256 (5500) mμ (ε).

Found: Cl, 78.34. Calcd. for C_5Cl_6: Cl, 77.99%.

The second crystals, after having been washed with ethanol, melted at 43—60°C. Either vacuum sublimations or recrystallizations from methanol and ethanol gave unpurified samples which showed a fairly intense absorption peak at 310 mμ. The filtered viscous oil was 0.98 g.

b) With a Large Excess of Chlorine. — The same amount of I was treated with about three times as much liquid chlorine as in the experiment above. The total content was ca. 6 ml. The reaction mixture became clear in 72 hr., after which period the sealed tube was opened. By passing nitrogen gas through, a viscous crystal sludge was obtained. After filtration, 1.2 g. of a solid, white material was recrystallized from benzene-ethanol as VIII, m. p. 146—148°C. 0.35 g.

Found: C, 17.17; H, 0.39; Cl, 83.18. Calcd. for C_6Cl_{10}: C, 16.89; H, 0.00; Cl, 83.11%. UV: λ_{max}^{EtOH} 223 mμ(ε 8200).

Methanol was added carefully to a slightly greenish yellow viscous filtrate (3.2 g.) dissolved in benzene. The deposited mass was filtered and recrystallized from ether to afford a colorless pure sample of X, m. p. 163°C (decomp.). 0.20 g.

Found: C, 18.78; H, 0.33; Cl, 81.48. Calcd. for $(C_4Cl_6)_x$: C, 18.42; H, 0.00; Cl, 81.58%. UV: λ_{max}^{EtOH} 224 mμ (ε 12000); IR: $\nu_{C=C}$ 1600 s cm^{-1}.

After the removal of the solvent, the oily fraction was distilled; b. p. 110—130°C (bath temp.)/0.008 mmHg; a colorless clear distillate.

Found: C, 17.76; H, 0.64; Cl, 81.66%.

This sample turned turbid very gradually. When it was stored over two years about one-fifth of the oil crystallized. The separated solid (0.30 g.) melted at 73—74°C after recrystallization from ether-methanol.

Found: C, 17.47; H, 0.61; Cl, 83.07. Calcd. for C_5Cl_8: C, 17.47; H, 0.00; Cl, 82.55%. UV: λ_{max}^{EtOH} 223 mμ (ε 6500).

The residual oil weighed 1.50 g.

The Oxidation of I.—*a) With Potassium Permanganate.*—Into a solution of 50 g. of I in 350 ml. of acetone, 10.1 g. of potassium permanganate dissolved in 510 ml. of the same solvent was stirred at room temperature. The decolorization of the reagent occurred very quickly. Manganese dioxide was removed by filtration and boiled thrice with 100 ml. of water. The filtrate was, after the evaporation of acetone, dissolved in ether in order to be shaken with a saturated aqueous sodium bicarbonate solution. One gram of crude I was recovered from the dried ether solution. The acidified bicarbonate solution and the concentrates of the combined hot water extracts gave, through separate ether extractions, 45 mg. and 11 mg. of perchloro-(dimethylenesuccinic acid), XII, which were combined and recrystallized from ether to a pure sample; m. p. 214°C (decomp.).

Found: C, 26.41; H, 0.92; Cl, 51.08. Calcd. for $C_6Cl_4H_2O_4$: C, 25.75; H, 0.72; Cl, 50.67%.

b) With Chromic Trioxide.—To the 100 ml.-solution of acid containing 1.40 g. of chromic trioxide and a trace of water, 1.00 g. of I was added and the mixture was allowed to stand for 48 hr. After the reduction of the excess oxidizing reagent with methanol, the solvent was removed under diminished pressure. A small amount of water was added, and the product was isolated in the usual manner. The acidic fraction gave only a trace of crystals, m. p. 214°C (decomp.) which were pressed on the clay plate, washed with chloroform, and identified with the XII obtained by the nitric acid oxidation of I through infrared sepectra comparison.

c) With Fuming Nitric Acid. — Five grams of I was oxidized with 1.0 ml. of fuming nitric acid (sp. gr. 1.52) by warming it on a steam bath until all the excess oxidizing reagent was evaporated off. The ether solution of the remaining oil gave, after being shaken with a bicarbonate solution and upon the evaporation of the solvent, a viscous oil (0.69 g.), from which the pale yellow crystals were precipitated on cooling. The crystals were collected by filtration; 2.27 g. of XIII; m. p. 103—108°C. Recrystallization from methanol elevated its m. p. to 114—115°C (decomp.).

Found: C, 19.47; H, 0.56; N, 7.48; Cl, 56.31. Calcd. for $C_6Cl_6N_2O_4$: C, 19.12; H, 0.00; N, 7.43; Cl, 56.41%. UV: λ_{max}^{EtOH} 318 (14500); λ_{sh} 328 (13500); λ_{min} 265 (2700) mμ (ε). IR: $\nu_{C=C}$ 1610 m, 1580 vs cm^{-1}.

0.13 g. of crystals of m. p. 215°C (decomp.) were obtained from the acidified bicarbonate solution.

Found: C, 26.14, H, 1.44; Cl, 51.13%. UV: λ_{max}^{EtOH} 230 mμ (ε 13900); IR: $\nu_{C=O}$ 1790 s; $\nu_{C=C}$ 1580 s, 1560 s cm^{-1}.

The oily acidic fraction weighed 1.12 g.

Anhydride (XIV) Formation from perchloro-(dimethylenesuccinic) Acid. —Thirty milligrams of XII was refluxed at 140—145°C with 0.5 ml. of acetic anhydride for 1/2 hr. in a small tubing vessel equipped with a cold finger. After the reaction had been completed, the cold finger was taken off and the unreacted acetic anhydride and acetic acid were thoroughly removed by heating the mixture on a steam bath under reduced pressure. Vacuum sublimation was applied to the residue. At ca. 100°C (bath temp.)/5 mmHg, 25 mg. of white crystals were obtained. Repeated sublimations gave a pure sample with an m. p. of 119—120°C.

Found: C, 27.83; H, 0.37; Cl, 54.01. Calcd. for $C_6Cl_4O_3$: C, 27.52; H, 0.00; Cl, 54.15%. UV: $\lambda_{max}^{cyclohexane}$ 227 (13300), 300—303 (12400); λ_{min} 250 (3700) mμ (ε); IR: $\nu_{C=O}$ 1835 m, 1765 s; $\nu_{C=C}$ 1580 s, 1543 s cm^{-1}.

XIV was heated with a saturated aqueous sodium bicarbonate solution until the all crystals had dissolved completely. The regenerated material was extracted with ether from the acidified solution, followed by the usual procedure. The acid thus obtained melted at 212°C (decomp.) and gave an infrared chart identical with that of XII.

The Ozonolysis of I.—A stream of ozone was passed for 5 hr. under cooling (0°C) through a 40 ml.-chloroform solution in which 2.0 g. of I was dissolved. The removal of the solvent under reduced pressure gave a greenish yellow oil which began to evolve hydrogen chloride when it was left in the air. When heated with a small amount of water for 10 min., the ozonide was thoroughly decomposed.

By the usual procedure, 108 mg. of the crystalline product, XIV, with an m. p. of 119—120°C, was obtained from the neutral oil. The acidic fraction (662 mg.) also partly crystallized to the carboxylic acid, m. p. 215°C (decomp.), identical with that of XII.

The Dechlorination of V to I.—In a three-necked, 50 ml.-flask, 360 mg. of I was dissolved in 15 ml. of anhydrous ether. Fifteen milligrams of aluminum powder and 2—3 mg. of anhydrous aluminum chloride were then added to the solution, and the solution was refluxed for 3 hr. under vigorous stirring. The same treatment as the usual dechlorination furnished 276 mg. (95%) of white crystals, m. p. 146—148°C, which were in all respects identical with I.

The Partial Dechlorination of Perchloro-(1,2-dimethylcyclobutene) (VIII) to V.—A mixture of 170 mg. of VIII, 250 mg. of aluminum powder, and 30 mg. of anhydrous aluminum chloride in 15 ml. of anhydrous ether was heated under refluxing for 5 hr. After ordinary handling, the neutral oil was kept in a refrigerator for 5 days. The crstallized solid was filtered and purified by vacuum sublimation. White crystals; m. p. 120—127°C; 40 mg. From ultraviolet and infrared spectra it was inferred that the mixing ratio of V to VIII was ca. 0.8.

The Dechlorination of Perchlorohexa-1,5-diene (VI) with Amalgamated Aluminum.—A mixture of 1.50 g. of VI, synthesized by the action of cuprous chloride on perchloropropene in methanol-water,(7) 0.150 g. of amalgamated aluminum chips (99.99% pure) and 30 ml. of anhydrous ether was stirred for 1.5 hr. at room temperature and then heated under refluxing for the same period. The neutral product was distilled at 110—120°C (bath temp.)/0.09 mmHg. The infrared spectrum of this distillate was identical with the IIIa synthesized by the dechlorination of VI with alcoholic potassium hydroxide in acetone.(25)

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(25) A. Roedig, G. Voss and E. Kuchinke, *Ann.*, **580**, 24 (1955).