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Reaction of Perchloro-(3, 4-dimethylenecyclobutene) with Molecular Oxygen*

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The reaction of perchloro-(3, 4-dimethylenecyclobutene) (I) with molecular oxygen in the solutions of carbon tetrachloride, benzene and ether was investigated. The identified products were phosgene, perchloro-(dimethylenesuccinic) acid (IIa), its dichloride, its anhydride, perchloro-(2, 3-dimethylenecyclobutanone) (IV) and 2, 2, 3′, 3′, 4-pentachloro-3-methyleneglutaric acid (VIII) in carbon tetrachloride. In benzene the products were the same as in carbon tetrachloride except VIII. Phosgene, oxalic acid, IIa and perchloro-(3-cyclobutene)-1, 2-dicarboxylic acid were obtained in ether. A radical chain mechanism is suggested for the degradations in the former two solvents on the basis of the similar reaction of I with oxygen in tetrachloroethylene yielding phosgene, IV, VIII and trichloroacetyl chloride. A possibility that I could be a chlorine radical source for the chain initiation by forming an unstable adduct with oxygen in the solution is also discussed.

In connection with our interest in the chemistry of unsaturated chlorocarbons with a small ring, the reaction of perchloro-(3, 4-dimethylenecyclobutene) (I) was studied for the purpose of both products identification and elucidation of the reaction mechanism. As suggested in a previous paper,[1] I is slowly decomposed when dissolved in some organic solvents, whereas it is stable in the solid state, and the double bond at C_{1-2} seems most reactive in the oxidations mentioned therein.

Results

It has been further revealed that the decomposition of I in solution is definitely due to the attack of the dissolved oxygen since the deaerated solvents do not significantly affect I even under warmed conditions. There is of course a certain limitation in the variety of solvents for an effective autoxidation. In carbon disulfide, chloroform, carbon tetrachloride and benzene, the uptake of oxygen by I proceeded very smoothly (*ca.* 1 mol of O_2 in 2 hr, respectively attaining a saturated value), and the value in carbon tetrachloride was approximately three times as high as those in *n*-hexane and cyclohexane (Fig. 1, the typical examples). No essential O_2-uptake was observed in ether, methanol and ethanol. It was found, however, that a very gradual decomposition of I does occur during several week exposure of its ether solution to air. The alcohols rather seem to behave as a retarder for the oxygen absorption. Characterization work for the degradation products was done in detail when carbon tetrachloride, benzene and ether were used. The similar decomposition in

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*1 Perchloro-compounds. III.

[1] A. Fujino, Y. Nagata and T. Sakan, This Bulletin, **38**, 295 (1965).

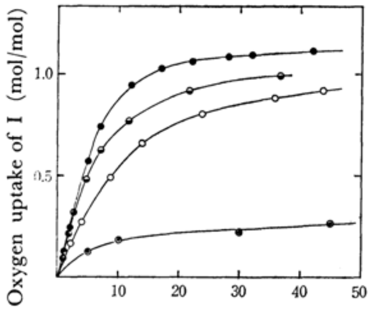

Fig. 1

tetrachloroethylene was also carried out in expectation of a substantial evidence for mechanistic consideration.

The complexity of the reaction in the former two solvents was easily perceived by the gas chromatographic examination that for both indicates seven product peaks with the solutions shaken with oxygen for one hour. On the other hand, only one product peak with a small area was found from the reaction in ether after being refluxed for 56 hr. So far, eight of the degradation products have been identified or characterized—involving one with a minor ambiguity, and two of which had been unknown compounds.

Phosgene, the only commonly detected gaseous product,[*2] was led to diphenylurea[2] for identification. There appeared to be a close similarity in the mode of autoxidation of I between in carbon tetrachloride and in benzene, since three of the crystalline products, *i. e.*, perchloro-(dimethylenesuccinic) acid[1] (IIa), its anhydride[1] (III) and perchloro-(2, 3-dimethylenecyclobutanone) (mp 67—68°C) (IV) were common in these cases. IV was found in a mixture (oil, bp 130°C (bath)/4 mmHg) with the dichloride (IIb) of IIa. It was unsuccessful to isolate IIb in a pure form although this component was usually more abundant. A treatment of the mixture with aniline resulted in the formation of *N*-phenylimide (mp 174°C) (V) of IIa, while, with an aqueous alkali, the mixture was converted to III in a good yield. IV was also obtained from perchloro(dimethylenecyclobutane-1, 2-dione)[3] (VI) by heating it with phosphorus pentachloride at 100°C. The identity of IV was further confirmed by chlorinating it with the same reagent at 120°C to perchloro-(1, 2-dimethylenecyclobutane) (VII), and in a sealed tube at 140—160°C to perchloro(3-methylene-1, 4-pentadiene).[4]

When the carbon tetrachloride solution of I was allowed to stand at room temperature for about two weeks, a small amount of crystals (mp 196°C, decomp.) gradually deposited on the wall of glass vessel. It was an acid, $C_6Cl_5H_3O_4$, which is formed only with the use of the solvents of chlorocarbon type, and for which the structure of 2, 2, 3′, 3′, 4-pentachloro-3-methyleneglutaric acid (VIII) may be postulated. Besides this, was observed a considerable difference in the relative yields of IV that are higher in benzene than in carbon tetrachloride. The investigation of the oily acid fractions in these degradations is now under way.

In the degradation in ether, neither III nor IV was found as a neutral product. The major neutral fraction (bp 100—120°C (bath)/4 mmHg) remained oily, and the presence of ethoxycarbonyl group in it was inferred from its infrared spectrum. An attempt for the characterization of this ester by alkaline hydrolysis to the corresponding acid has been unsuccessful. The acidic products were, except for an oily fraction (bp 150—160°C (bath)/0.3 mmHg), oxalic acid dihydrate, IIa and perchloro-(3-cyclobutene)-1, 2-dicarboxylic acid (mp 206°C) (IX), which was identical with that obtained in the oxidation of VII with fuming nitric acid according to Roedig *et al.*[5] The elucidation study of the oily acid fractions is also now in progress.

It was further found that the oxygen uptake of I is very efficiently stopped by the addition of a small amount of phenol or hydroquinone known as inhibitors for autoxidation. In either case the rate of O_2-uptake after the inhibition was essentially the same as that without such a reagent. It was necessary to add a much larger amount of ethanol to cause a complete inhibiton, although its retarding effect was noticeable. There was no difference in the rates of the normal oxygen uptake between in dark and at light place.

The most effective consumption of oxygen was achieved with the tetrachloroethylene solution. Although O_2-uptake was not observed at all with this solvent alone, it initiated smoothly when I was added to the system, and as seen in Fig. 1, ended with the highest saturation value. Six peaks were observed in the gas chromatogram of the products, among which trichloroacetyl chloride was identified by converting it to trichloroacetic acid, and finally to trichloroacetanilide. The major product peak corresponds to the acid chloride IIb, as in the cases with carbon tetrachloride and with benzene, and the succeeding one to the ketone IV. In some runs with this solvent the dicarboxylic acid VIII was directly isolated as crystals from the concentrate of the

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[*2] In whatever solvent hydrogen chloride was also detected in the product unless the moisture was completely excluded.

[2] W. Hentschel, *J. prakt. Chem.*, **27**, 499 (1883).

[3] A. Fujino, K. Kusuda and T. Sakan, This Bulletin, **39**, 160 (1966).

[4] J. Brandmüller, E. Ziegler and A. Roedig, *Naturwissenschaften*, **49**, 466 (1962).

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

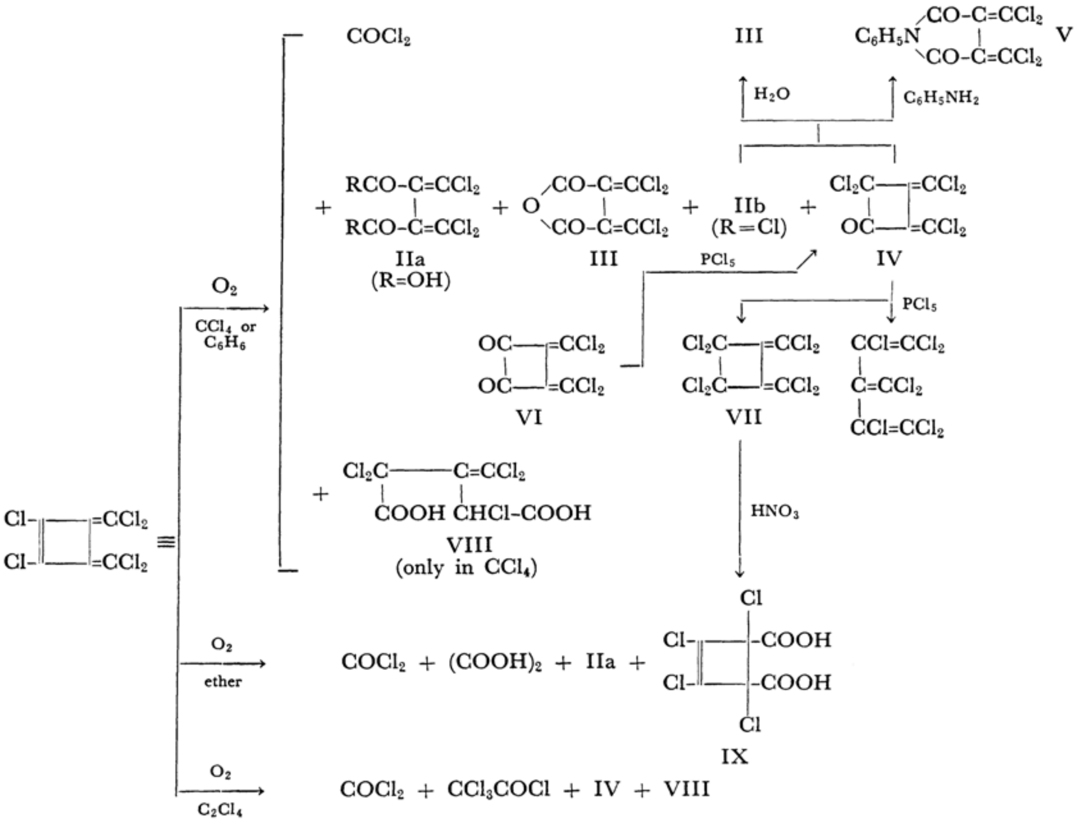

Chart 1

product mixture. The results described above may be summarized in Chart 1. Interestingly, an uptake of oxygen by I in the solid state was also observed in a sealed system even though it was very slow, and restricted to an extremely small volume from the quantitative point of view.

Discussion

It has already been suggested in a previous paper[1] that the production of IIa and III in the ozonolysis of I in chloroform would not simply be attributed to the real attack of ozone on I. A remarkable retardation in the reactivity of a perchlorinated double bond or bonds toward ozone was described earlier in many cases, whereas some examples of a facile photochemical reaction between that type of double bond and molecular oxygen has been known as a halogen-sensitized photochemical oxidation. Thus, perchlorobutadiene[6] and hexatrienes[7] are almost perfectly inert against ozonization, while tetrachloroethylene reacts with oxygen in carbon tetrachloride in the presence of chlorine radical to form trichloroacetyl chloride plus a small amount of phosgene.[8] The formation of the various compounds in the autoxidation of I in benzene and carbon tetrachloride is particularly interesting in the sense that the reaction proceeds without UV-light and any sensitizer. The degradation to IIa appears to be parallel to that observed with the ordinary oxidizing agents,[1] and IIb may be a precursor of IIa and III in the autoxidation. Besides those chemical conversions mentioned above, the first structural evidence for IV was in the spectral data. In the ultraviolet absorption, the λ_{max}'s at 263 and 344 mμ (log ε 3.62 and 4.10) in cyclohexane were observed. The position of the latter band which shifted to 350 mμ in a fresh ethanol solution is close to that of the band transiently appeared at 335 mμ when dione VI is freshly dissolved in ethanol. A VI-ethanol-adduct has been postulated[3] for the structure of this intermediate. The difference of 15 mμ seems reasonable when the substituent effect (*e. g.*, red shift of 15 mμ from 1, 2, 3, 4-tetrachloro-5, 5-dimethoxycyclopentadiene to perchlorocyclopentadiene[9]) is taken into account. The infrared

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[6] O. Fruhwirth, *Ber.*, **74B**, 1700 (1941).

[7] A. Roedig, G. Voss and E. Kuchinke, *Ann.*, **580**, 24 (1953).

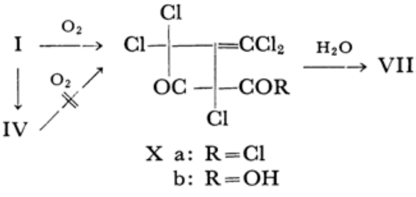
[8] R. A. Dickinson and J. A. Leermakers, *J. Am. Chem. Soc.*, **54**, 3852 (1932).

[9] E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav and H. P. Braendlin, *ibid.*, **84**, 3557 (1962).

spectrum of IV also supports the structure of a four-membered cyclic ketone (1805 cm^{-1} s) with some exocyclic perchlorinated methylene groups (1616 s, 1570 s and 920 s cm^{-1}). The presence of a carbonyl group was further informed from the test with 2, 4-dinitrophenylhydrazine. IV gradually reacted with ethanol to form an uncharacterized ester. This behavior is also similar to that reported in the ethanolysis of VI.³⁾

The compound IIb gives rise to bands at 1773, and 1568, 1535 and 955 cm^{-1} in the infrared spectrum, respectively indicative of carbonyl and dichloromethylene groups.*³ The weak absorption in 1265—1240 cm^{-1} region (ν_{C-O}) further suggests that the isolated fraction contains little perchloro-(1, 2-dimethylenebutyro)-lactone even if there exists an equilibrium between IIb and the lactone. The conversion of IIb to either the *N*-phenylimide derivative or the corresponding acid IIa is also consistent with this structure. There remains, however, a minor ambiguity about the structure thus assigned since the compound IIb has never been isolated in a pure form from the partner product IV. The production of perchloro-(3-methylene-1, 4-pentadiene) in a higher temperature chlorination of IV with phosphorus pentachloride is interpreted as arising from the secondary thermal degradation of VII¹⁰⁾ preferentially formed under the applied conditions.

The degradation of I to VIII is worthy of a special mention. So far as examined, VIII has not only been obtained uniquely in the solvents of chlorocarbon type, but also through the process of a simultaneous attack of two molecular oxygens on the double bonds at C_{1-2} and $C_{3-3'}$ of I. It is hardly assumed that, in this degradation, ketone IV could be the first intermediate further decomposing to VIII through Xa and Xb, since no absorption of oxygen by IV has been observed under the similar conditions.

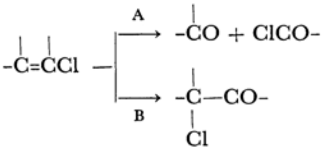


X a: R=Cl
b: R=OH

The evidences supporting the formulation VIII included: 1) neutralization equivalent: 155; 2) ultraviolet (λ_{sh}^{EtOH} 230 mμ, log ε 3.82) and infrared (ν_{OH} 3500—2400, $\nu_{C=O}$ 1745, 1725, $\nu_{C=C}$ 1580 cm^{-1}) spectra; 3) NMR spectrum (singlet at 3.20 τ); 4) The λ_{sh} changed to a λ_{max} with the same wavelength value when measured in alkaline medium and the original absorption was not reproduced on acidification. This suggests the presence of a functional group irreversibly changeable with a base and accords with the observation that VIII does not react with the fuchsin-sulfurous acid, whereas does it with the Tollen's reagent. Thus, VIII has a character of potential aldehyde, as has been discussed in the case of the solvolytic product of diketone VI.³⁾

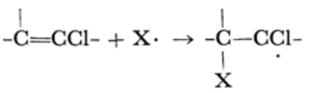
Roedig *et al.*⁵⁾ reported that one of the separable acidic products in the oxidation of VII with fuming nitric acid was a dicarboxylic acid with a melting point of 174°C, which was thermally transformed to an isomer (mp 196°C) above its melting point. The structure of IX was given to the latter. Although the former acid has not yet been found in the degradation in ether, our finding of the identical compound directly from I under milder reaction conditions will provide an additional support for the structure. It also reveals that, in this case, the oxidation has occurred at both $C_{3-3'}$ and $C_{4-4'}$ double bonds, leaving the one at C_{1-2} unchanged.

Although the partner of phosgene in the oxidation has not been characterized, it may be summarized from the observations described above that there is no essential difference in the reactivity with molecular oxygen between two differtyped double bonds in I, except some solvent-dependency of the products, oxalic acid, IV, VIII and IX. From the scheme illustrated in Chart 1, it may further be possible to discuss some mechanistic features of the degradation. The whole products are derived by either one of the courses, A and B, generally shown as:

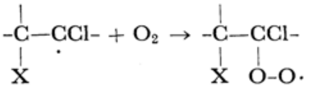


The degradation of type B where the double bond is not cleaved apparently involves the migration of a chlorine atom to the adjacent carbon atom.

Since the O_2-uptake is effectively inhibited by the addition of a small amount of suitable materials, the whole degradation, at least in carbon tetrachloride and in benzene, must further involve radical chain processes. A mechanistic scheme similar to that suggested by Walling¹¹⁾ for the halogen-sensitized photoxidation of tetrachloroethylene would also be possible in our case:



$$-\overset{|}{C}=CCl- + X\cdot \rightarrow -\underset{X}{\overset{|}{C}}-\underset{\cdot}{C}Cl- \qquad (1)$$

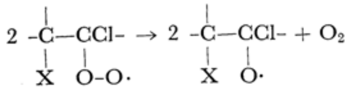


$$-\underset{X}{\overset{|}{C}}-\underset{\cdot}{C}Cl- + O_2 \rightarrow -\underset{X}{\overset{|}{C}}-\underset{O\text{-}O\cdot}{\overset{}{C}}Cl- \qquad (2)$$

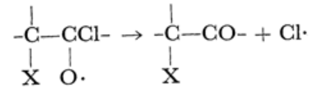
[*3] Another $\nu_{C=O}$ band (weak), possibly due to the contaminating IV, was observed at 1800 cm^{-1}.

10) H. J. Prins, *Rec. trav. chim.*, **72**, 253 (1953).

11) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York (1957), p. 448.

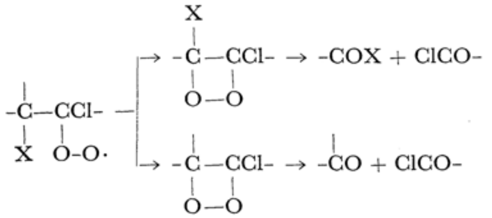


$$2\ -\underset{\mathrm{X}}{\overset{|}{\mathrm{C}}}-\underset{\mathrm{O{-}O\cdot}}{\mathrm{C}}\mathrm{Cl}- \rightarrow 2\ -\underset{\mathrm{X}}{\overset{|}{\mathrm{C}}}-\underset{\mathrm{O\cdot}}{\mathrm{C}}\mathrm{Cl}- + \mathrm{O_2} \qquad (3)$$



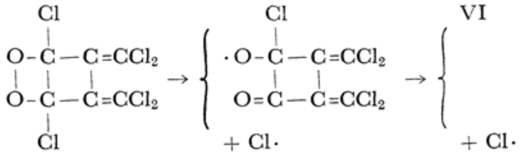
$$-\underset{\mathrm{X}}{\overset{|}{\mathrm{C}}}-\underset{\mathrm{O\cdot}}{\mathrm{C}}\mathrm{Cl}- \rightarrow -\underset{\mathrm{X}}{\overset{|}{\mathrm{C}}}-\mathrm{CO}- + \mathrm{Cl\cdot} \qquad (4)$$

where X· is a radical caused from I in some way and could be a chlorine atom itself. In one of the termination processes, the radical formed in (2) might be vanished through the cyclic intermediates such as



which explains the formation of phosgene, IIa, IIb, and III, all resulting in double bond cleavage (type A). The isolation of trichloroacetic acid as a major by-product in the degradation of I in tetrachloroethylene provides a supporting evidence for this mechanism (1)—(4), for the acid obviously causes through the initial attack of chlorine atom on the solvent.

It should further be noted that there have been two significant observations that are different from those for an ordinary radical reaction. Firstly, the chain initiator must be produced from I by the process other than photochemical sensitization. On the basis of ESR inspection*4 it is assumed that, in carbon tetrachloride, I neither exists as a biradical nor be cleaved to any species releasing the radical that corresponds to X·. It has generally been established, on the other hand, in autoxidations with various kinds of substrates that a primary direct reaction of oxygen with substrate molecule hardly occurs even though oxygen is biradically reactive in nature. Therefore, the source of X· should be pursued necessarily in the I-O_2-solvent system. It appears not to be improper to speculate that oxygen directly reacts with I to form an unstable adduct such as [I·O_2]. If it does, oxygen can be expected to react also with I in the solid state, even if slowly. Our manometric observation with O_2-solid I (freshly prepared) system difinitely proved that the absorption of more than 10^{-4} (mol O_2/mol I), in fact, takes place very slowly with a slight yellow coloration of the surface of the fine substrate powder. The structure of this adduct might be closely related to the intermediate shown in (5′). One of its disruption courses in solution may be envisioned as below to give two chlorine atoms and VI which is probably stable under the condition employed.



Hence it is highly probable that the initiation radical X· in the chain reaction might be a chlorine atom originating from I.

The second point to be discussed is the solvent-dependency of the production of oxalic acid, IV, VIII and IX. Both the lack of IV and the unique production of oxalic acid and IX in the degradation in ether should be interpreted in view of a mechanism other than that mentioned above. The oxygen uptake in ether is very slow and requires a long period of exposure to air. Accordingly, in this case the dissolved oxygen might first react with the solvent molecule to give the ether peroxide which would then enter into a reaction with I through a process either radical or ionic. The clear difference between carbon tetrachloride and benzene in the production of VIII can easily be accounted for by the radical chain mechanism; only in the former solvent which plays a role as an extra source of the chain carrier Cl·, the contribution of a term $[\mathrm{Cl\cdot}]^2$ in the reaction rate of simultaneous attack of two chlorine atoms on I would be more important. The reason for the production of VIII in tetrachloroethylene is possibly the same. In our conclusion it may be pointed out that I is a special and very interesting compound in the chemical reactivity with molecular oxygen; in some solution the O_2-adduct is a potential Cl-radical generator significant for the chain oxidation process.

Experimental†

Oxygen Absorption of Perchloro-(3, 4-dimethylenecyclobutene) (I). The rate of the oxygen absorption was measured with an equipment ordinarily used for catalytic hydrogenation (50 m*l* flask for substrate and 0.01 m*l* minimum reading for the gas consumed). In average, 370 mg (1.5 mmol) of I was dissolved in 10 m*l* of a solvent and the solution was shaken under the atmosphere of oxygen at 16—17°C. No special care was paid to the room light since any difference in the absorption rates between light and dark had not been observed.

Inhibition of Oxygen Absorption. I (450 mg) was dissolved in carbon tetrachloride (25 m*l*) and, after the addition of hydroquinone (25.5 mg), the solution was shaken with oxygen. The inhibition of the oxygen absorption of at least 1.2 hr was observed. A smaller amount 97.5 mg) of hydroquinone also affected a larger amount of I (3.00 g) in the same solvent (20 m*l*) for more

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*4 The spectra were measured with a X-band ESR spectrometer (magnetic field modulation) at Osaka University by Mr. K. Nishikida.

† All the melting points were measured under microscope and not corrected.

than 5 min. Phenol (2 mg) inhibited the absorption by I (370 mg) in carbon tetrachloride (10 m*l*) for more than 1.5 hr (all at 17°C).

Absorption of Oxygen by Solid I. The lower ends of two glass tubes, A (1.8 cm OD × 10 cm) and B (0.8 cm OD × 3 cm) were connected with a capillary U-type tubing (2.5 mm OD, 15 cm in one side length). A constricted part between A and the capillary was packed with some glass wool. A sample (3.18 g) of I, freshly recrystallized from ethanol immediately after one vacuum sublimation and quickly fine-powdered was put in A. The upper end of A was burnt off as an opened capillary. The oxygen from a cylinder was gently passed through the tubing from the upper end of B untill all the atmosphere was thoroughly exchanged by the gas. A small amount of water was put into the bottom of the U-tubing from the top of B so that its meniscuses were approximately at the middle of the U-tubing height. The upper ends of A and B were then both sealed off carefully so as to make the difference between meniscuses least even after thermal equilibration. The whole tubing was vertically immersed in thermostat water. The observed manometric change due to the consumption of oxygen was 7.2 cm in 14 hr and 0.6 cm for the additional 48 hr.

Characterization of the Products. The oxidation was carried out either by the same procedure as the above but with a larger scale or by bubbling the oxygen gas in the solution. Some of the products were obtained in a higher yield than those in the bubbling degradation when the solution was exposed to air for a long period. The separation of the individual product was performed by the ordinary procedure unless otherwise described.

Phosgene. The gas evolved during the experiment with I (5.90 g in benzene) absorbing 456 m*l* of oxygen at saturation was swept by a nitrogen stream into an ether solution (30 m*l*) of aniline (2.81 g), cooled with ice water. The solid product obtained was recrystallized from ethanol to give a sample (172 mg) with a melting point of 246—247°C, identical with an authentic sample of diphenylurea.

Perchloro-(dimethylenesuccinic) Acid (IIa). Mp 215°C (decomp.). Yield in average: 0.10, 0.13 and less than 0.04 (g/g of I), respectively in benzene, carbon tetrachloride and ether solution.

Mixture of Perchloro-(dimethylenesuccinyl) Dichloride (IIb) and Perchloro-(2,3-dimethylenecyclobutanone) (IV). The ratios of the yield of IIb to that of IV were determined by comparison of the peak areas on the gas chromatogram on the assumption that their molecular sensitivities to the FID[††] were approximately the same. Values obtained were 4.1 (benzene) and 11.4 (carbon tetrachloride). The yield of IV practically isolated was, in average, 0.15 g/g of I in benzene. Melting point of pure IV: 67°C.

Found: C, 24.52; H, 0.61; Cl, 71.40%. Calcd for C_6Cl_6O: C, 23.96; H, 0.00; Cl, 70.72%.

Perchloro-(dimethyleneduccinyl) *N*-Phenylimide (V). The carbon tetrachloride solution (15 m*l*) of I (1.18 g) was shaken with oxygen. In one hour, 110 m*l* of the gas was absorbed. After the removal of the solvent under reduced pressure, a benzene solution of aniline (1.5 g) was portionwise added to the residue and the mixture was heated on a water bath for 5 min. Being washed with water, the neutral fraction in benzene was chromatographed on silica gel. From the brown oil eluted, 114 mg of crystals was obtained. Several recrystallizations from benzene-ligroin afforded a sample with a melting point of 172—174°C.

Found: C, 42.69; H, 1.52; N, 4.30%. Calcd for $C_{12}Cl_4H_4O_2N$: C, 42.85; H, 1.19; N, 4.17%. IR: $\nu_{C=O}^{Nujol}$ 1765 m, 1720 s; $\nu_{C=C}$ 1600 m, 1575 m (cm^{-1}).

Perchloro-(dimethylenesuccinic) Anhydride (III). Mp 120°C. Yield: 0.1 g/g of I (carbon tetrachloride, three week exposure); 108 mg from a mixture (333 mg) of IIb and IV (benzene, by alkaline hydrolysis).

2, 2, 3′, 3′, 4-Pentachloro-3-methyleneglutaric Acid (VIII). The carbon tetrachloride solution (300 m*l*) of I (60 g) was allowed to stand under the exposure to air at room temperature for 18 days, during which period the solution was shaken occasionally. The crystals floating in the solution were collected by filtration and recrystallized from chloroform to give a sample of VIII with a melting point of 196°C (decomp.). Yield: 227 mg. The filtrate was served for the isolation of IIa, III and IV.

Found: C, 23.01; H, 1.04; Cl, 55.50%. Calcd for $C_6Cl_5H_3O_4$: C, 22.74; H, 0.95; Cl, 56.11%. $pK'_{a1} <$ 3, pK'_{a2} 3.95. IR: $\nu_{C=O}^{Nujol}$ 1740 s, 1720 s; $\nu_{C=C}$ 1575 m (cm^{-1}).

Degradation in Ether; Oxalic Acid Dihydrate, IIa and Perchloro-(3-cyclobutene)-1, 2-dicarboxylic Acid (IX). The solution of I (6 g) in ether (200 m*l*) was allowed to stand under the exposure to air at room temperature for 40 days, during which period the solvent had to be frequently supplied to keep I dissolved. In the later period, a mild evolution of hydrogen chloride was observed. At the end when the solvent was evaporated, was obtained the product which was composed of two layers, aqueous and organic. The crystals in the oily organic fraction were filtered and proved to be the recovered I (mp 144—148°C). The filtrate was dissolved in chloroform and separated into a neutral and an acid fraction. Distillation of the former fraction furnished an oil (bp 100—120°C (bath)/4 mmHg, 397 mg, IR: $\nu_{C=O}$ 1740 cm^{-1} s), from which a small amount (5 mg) of needles crystallized out during a long storage. Mp 98—99°C. The identity with oxalic acid dihydrate was established by IR comparison with an authentic specimen. The acid fraction (3.1 g) remaining oily was distilled at 50°C (bath)/0.15 mmHg to remove any volatile materials (0.3 g). The tarry residue crystallized during storage and, being filtered and washed with chloroform, afforded 150 mg of IIa, mp 212°C (decomp.), identical with that previously reported.1) Distillation of the filtrate gave an oily acid (bp 135—145°C (bath)/0.15 mmHg).

In some runs, crystals (IX) with a melting point of 192—193°C (by capillary method without microscope) were isolated from the above residue when volatile acid fraction was distilled off at 150—160°C (bath)/0.3 mmHg. Recrystallization from ether-chloroform raised its melting point to 206°C (decomp.) (196°C without microscope).

Found: C, 25.69; H, 1.21; Cl, 50.51%. Calcd for $C_6Cl_4H_2O_4$: C, 25.75; H, 0.52; Cl, 50.67%. IR: $\nu_{C=O}^{Nujol}$ 1700 s; $\nu_{C=C}$ 1680 m (cm^{-1}).

[††] Hitachi Perkin-Elmer Gas Chromatography Model F6-D. Carrier gas: Nitrogen; Column: 3 mm OD × lm, packed with SE-30 silicon oil on chromosorb-W. The same shall apply hereinafter.

Oxidation of Perchloro-(1, 2-dimethylenecyclobutane) (VII) to IX. VII (10 g) was heated with fuming nitric acid (sp. gr. 1.50, 50 m*l*) at 135°C for 10 min.⁵⁾ The first three crystalline acid fractions obtained by elution with boiling carbon tetrachloride from the product cake were identical. Mp 176°C; 1.66 g in total. When a portion of this acid was heated over its melting point for a short period, it was quantitatively transformed to the material (mp 206°C, decomp.), which is identical with IX in its IR comparison.

IV from Perchloro-(dimethylenecyclobutane-1, 2-dione) (VI). A mixture of I (160 mg) and phosphorus pentachloride (380 mg) was heated on a water bath for 1/2 hr. The reaction initiated smoothly and the mixture became homogeneous under melting. The neutral fraction was distilled at 130—135°C (bath)/ 3 mmHg. The yellow solid material crystallized out from the distillate during storage was filtered and pressed between the clean filter papers. Yield: 53 mg Mp 66.5°C. It was identified with IV obtained by the degradation of I.

Perchloro-(1, 2-dimethylenecyclobutane) (VII) from IV. IV (94 mg) was heated with phosphorus pentachloride (220 mg) at 120°C for 5 hr. A small portion of the reaction mixture was directly injected to the gas chromatograph, which detected five peaks. The one with the largest retention volume showed the gas chromatographically identical behavior with VII.

Perchloro-3-methylene-pentadiene-1, 4 from IV. IV (215 mg) was heated with phosphorus pentachloride (312 mg) in a sealed tube at 140—160°C for 3 hr. The neutral fraction boiling at 110—120°C (bath)/ 3 mmHg gave an almost identical IR spectrum with that of sample (mp 45°C) obtained by the thermal rearrangement of VII at 200°C according to the literature.¹⁰⁾ Because of a minor contamination the isolation in a crystalline form was unsuccessful.

Degradation of I in Tetrachloroethylene. I (1.23 g) was dissolved in tetrachloroethylene (20.0 m*l*) and the solution was shaken with oxygen as ordinarily. For 70 min, totally 128 m*l* (0°C) of oxygen was absorbed. After the saturation water (25 m*l*) was added and the shaking was continued for additional 40 min. The aqueous layer was separated, combined with the one (10 m*l*) for the subsequent washing of the organic layer, and concentrated under reduced pressure at below 40°C. After the concentrate was dried in a desiccator over anhydrous calcium chloride for a day, 280 mg of white crystals (mp 40°C) was obtained. The whole crystals were, after being dried with phosphorus pentoxide in vacuum, heated under reflux with thionyl chloride (269 mg) in dry benzene (3.0 m*l*) for 2 hr. Aniline (165 mg) was then added to the cooled reaction mixture and the product was extracted with benzene-ether after 10 min. The crystals from the extract were further recrystallized from benzene-ligroin to give plates with a melting point of 79—91°C, which were identified as trichloroacetanilide by IR comparison.

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