

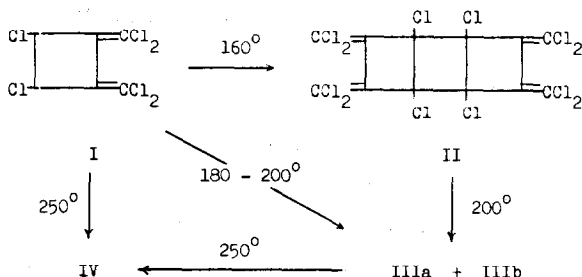
DIMERS OF PERCHLORO-(3,4-DIMETHYLENECYCLOBUTENE) I.
PERCHLORO-(3,4,7,8-TETRAMETHYLENE-TRICYCLO(4.2.0.0^{2,5})OCTANE)

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In the course of our study on the chemistry of unsaturated chlorocarbons with a four-membered ring, it was found that the pyrolysis of perchloro-(3,4-dimethylenecyclobutene) (I) (1, 2) affords, depending on the heating temperature applied, at least four different isomeric compounds, C₁₂Cl₁₂. As shown in the following chart, perchloro-(3,4,7,8-tetramethylene-tricyclo(4.2.0.0^{2,5})octane) (II), m.p. 266°, was obtained from I in 30 % yield in the pyrolysis at ca. 160°. When heated to ca. 200°, directly or in nitrobenzene, II was further transformed in almost the same yield to a mixture (III) of other isomers in which one (IIIa) with a m.p. of 215° dominates over another (IIIb), m.p. 262°. With the exception of its close melting point IIIb is doubtlessly different from II in all respects. Lastly, the application of pyrolysis at ca. 250° to III resulted in the low yield formation of the fourth isomer (IV), m.p. 273°. III and IV were also derived directly from I in the pyrolysis at 180-200° and 250°, respectively. Their yields were, however, much lower than those for step-by-step conversion since the direct transformation was always accompanied by the production of perchlorobenzene (ordinarily major), perchlorofulvene, perchloro-4-methylenecyclopent-1-ene and an uncharacterized glassy material with the composition of (CCl)_x, which is major particularly in higher temperature pyrolysis in solution. The observation of these distinguishing

courses of dimer transformation are in accord with the results of differential thermal analysis of I, II and III, which also markedly indicate the occurrence of some drastic exothermic change in the corresponding temperature ranges.

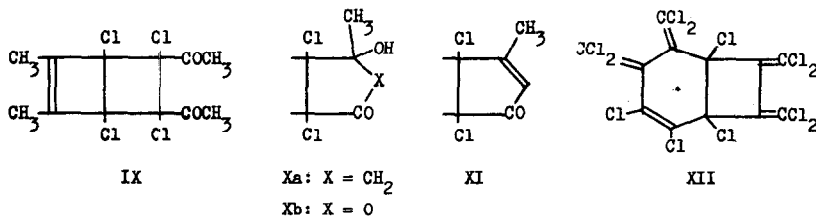


II is almost insoluble in the ordinary organic solvent and is not sublimated under vacuum. Contrary to the thermal instability, it is stable against UV-light irradiation and acid or alkaline hydrolysis. The spectral data ($\lambda_{\text{max}}^{\text{Cyclohexane}}$ 287, 299 and 312 μ ; ϵ , 28,100, 44,800 and 27,000; $\nu_{\text{C=C}}^{\text{Nujol}}$ 1610 and 1580, $-\text{C}=\text{CCl}_2$ group: 910 cm^{-1} (2)) suggest that the carbon skeleton of perchloro-(1,2-dimethylenecyclobutane) (V) (1) must be involved in this dimer. In fact, II, as V, resisted the attack of liq. chlorine and was oxidized in a low yield with permanganate in acetone to perchloro-(dimethylenesuccinic) acid (2). In addition, it was confirmed that II is also formed in considerably good yield (60%) under the condition of ionic reaction mechanism; i.e., from I in dichloromethane with anhydrous aluminum chloride at room temperature. It is, therefore, very possible that the cyclodimerization occurs, in either process from I to II, between each C_{1-2} double bond of two I's, which was reported to be most reactive (2, 3) in the molecule.

II was reduced in ethanol or acetic acid by heating with zinc powder to $\text{C}_{12}\text{Cl}_8\text{H}_4$ (VI), m.p. 223-5° (new ν_{CH} 3060 and 3050 cm^{-1} ; disappearance of 910 cm^{-1} band; $\lambda_{\text{max}}^{\text{EtOH}}$ 278 and 290 μ ; ϵ , 18,100 and 10,900). The observed λ_{max} value is in good accordance with the calculated one based on that for 1,2-dimethylenecyclobutane (4). VI was further reduced to tetramethyl derivative (VIIa), m.p. 180°

mode of their ozone degradation. VIIa was cleaved in methanol-carbon tetrachloride by ozone to diketone (IX), m.p. 113-115° ($\nu_{\text{C}=\text{C}}^{\text{Nujol}}$ 1720, 1710; $\nu_{\text{C}=\text{O}}$ 1680; δ_{CH_3} 1380, 1360 cm^{-1} ; 8.15 τ (5H), 7.65 τ (6H), both singlet). However, the second $>\text{C}=\text{C}<$ bond in IX strongly resisted further ozonolysis even for 56 hr. passing, while VIIc was reported to suffer from either successive or exhaustive double bond cleavage.

In connection with the diketone, ketol (Xa), m.p. 158-159°, α,β -unsaturated ketone (XI), m.p. 192-193°, and lactol (Xb), m.p. 167-169° were isolated and characterized.



Although the elucidation study of the structure for IIIa, IIIb and IV is under way, it is tentatively proposed on the basis of the available data of chlorination, oxidation and selective reduction, and particularly of the very similar IR absorption between IIIa and IIIb, that the plane structure for III is perchloro-(2,3,7,8-tetramethylene-bicyclo[4.2.0]octa-4-ene) (XII).

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