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DIMERS OF PERCHLORO-(3,4-DIMETHYLENECYCLOBUTENE) II.

PERCHLORO-(3,4,7,8-TETRAMETHYLENECYCLOOCTADIENE)

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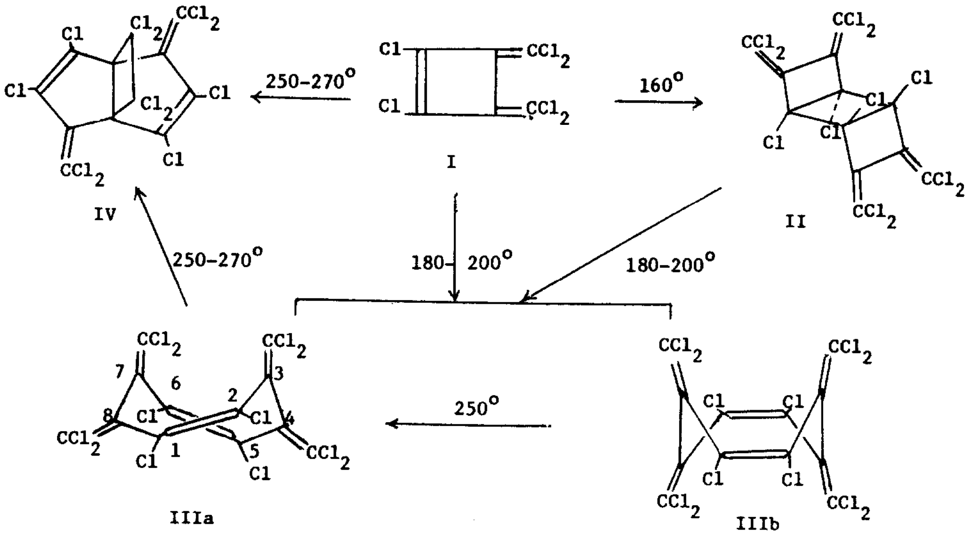
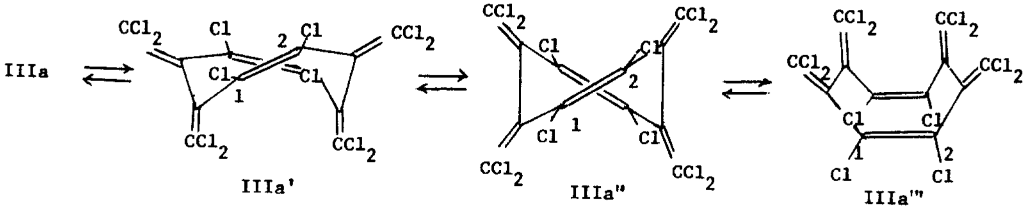
For the first and the fourth dimers of perchloro-(3,4-dimethylenecyclobutene) (I), the structures of perchloro-(3,4,7,8-tetramethylenetricyclo[4.2.0.0^{2,5}]octane) (II)[1,2,3] and perchloro-(4,8-dimethylenetricyclo[3.3.2.0^{1,5}]deca-2,6-diene) (IV)[4] have respectively been reported. Difficulties in the structure elucidation of the rest isomers, the second (mp 215°C) (IIIa)[1] and the third (mp 262°C)[1], were much lessened by the achievement of X-ray analysis for IV and our further investigation on their spectral and chemical properties coupled with the molecular stereochemistry has revealed that both IIIa and IIIb are perchloro-(3,4,7,8-tetramethylenecyclooctadiene) which differs from each other only in their ring configuration. The tentatively postulated structure[1] for IIIa should be corrected accordingly.

On heating in nitrobenzene at 180-200°C both I and II were converted into the mixture of IIIa and IIIb (yield, 31 and 43 %, respectively), from which the latter was isolated as an insoluble part in the careful recrystallization of the former with a large amount of ether. The average content of IIIb in the mixture product was ca. 3 %. Capillary thermolysis at 270°C for 30 min. changed the pure IIIa partly to IV, whereas the similar treatment with IIIb at 250°C afforded no IV but IIIa with some carbonized material. This suggests the possibility that a step-to-step conversion involving IIIb $\longrightarrow$ IIIa $\longrightarrow$ IV might also occur in the thermolysis of I and II.

A close similarity in structure between IIIa and IIIb is quite obvious at a glance of their infrared finger prints over 1500-700 cm^{-1}. Although the other spectral data (Table 1) are more than a simple interpretation, some of the double bonds in IIIa are evidently in higher conjugation than those in IIIb.


IV
250-270°
I
160°
II
180-200°
180-200°
250-270°
250°
IIIa
IIIb
CCl2
Cl
1
2
3
4
5
6
7
8


IIIa
IIIa'
IIIa"
IIIa'"
CCl2
Cl
1
2

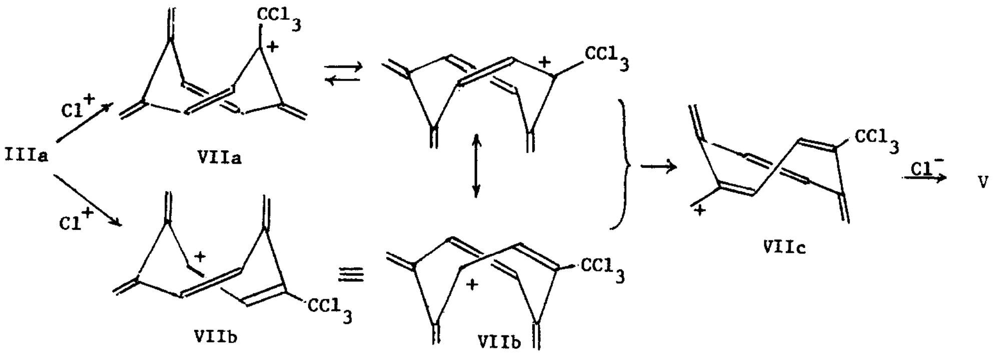

IIIa
Cl+
Cl+
VIIa
VIIb
VIIb
VIIc
CCl3
+
Cl-
V

TABLE I $\nu_{c=c}^{Nujol}$ and $\lambda_{max}^{n\text{-}hexane}$ (ε) of III (* shoulder band)

IIIa	1590w, 1570s, 1555s,		239(27,900), 275(11,000), 300(17,700)*
	1535m		312(21,600), 342(12,000)*
IIIb	1607m, 1582s, 1542m	(cm^{-1})	242(21,900), 260(19,800), 273(15,900)
			284(16,100), 309(8,600) (mμ)

This difference is remarkable enough to conform IIIa and IIIb respectively to a labile and a rigid form of perchloro-(3,4,7,8-tetramethylenecyclooctadiene), the only possible intermediacy between II and IV. In the labile form the double bonds in the ring can take up positions coplanar with the adjacent dichloromethylene groups on either side. If, as in one conformer IIIa, the ring double bonds (at $C_{1,2}$ and $C_{5,6}$) are respectively conjugated with those at $C_{8,8'}$ and $C_{4,4'}$, the rest dichloromethylene groups ($C_{3,3'}$ and $C_{7,7'}$) necessarily come so close to each other as their planes are almost parallel. Most probably, this conformer as well as IIIa' (identical with IIIa) would also be preponderant over other possible conformers (e.g. IIIa'', IIIa''' etc.) in the thermal cycloaddition of IIIa at $C_{3,7}$ and $C_{3',7'}$ to IV.

The following are the experiments carried out to confirm the configuration assignment for III. Chlorination with liquid chlorine in a sealed tube converted IIIa almost quantitatively into a tetradecachloro-derivative (mp 275°C) (V), ($\nu_{c=c}^{Nujol}$ 1605w, 1582w, 15625, cm^{-1}; $\lambda_{max}^{n\text{-}hexane}$ 222(15,900), 265(11,200), 305(12,100), mμ(ε)), the trichloromethyl groups of which were hydrolyzed with conc. sulfuric acid to the carboxyl groups. The dicarboxylic acid (mp 290°C) (VI) thus obtained furnished no anhydride on being refluxed with acetic anhydride. In contrast to IIIa, IIIb strongly resisted the chlorination. IIIa was recovered in more than 50 % yield when V was subjected to the dechlorination with Raney nickel. The occurrence of a very interesting 1,6- and not 1,2- or 1,4- chlorine addition to IIIa was proved by the X-ray crystallographic determination of V$^{5)}$. This ostensibly unusual mode of addition is well explained as a uniquely favorable stereochemical process by assuming, for example, a labile intermediate cation (VIIa) which is formed by the addition of Cl^+ to the $C_{3,3'}$ double bond and can eventually be stabilized as a rigid ion (VIIc) through the less labile conformeric ion (VIIb) identical with that formed by the Cl^+ addition to the $C_{4',4}-C_{5,6}$ system of IIIa itself. Thus, no 1,2- or 1,4- adduct could be formed.

IIIa was oxidized by fuming nitric acid at 100°C to give a dianhydride (mp 325°C) (VIII) of perchloro-(cyclooctatetraene)-1,2,5,6-tetracarboxylic acid in 40 % yield along with an uncharacterized oily acidic fraction. The reactivity retardation of IIIb toward the same reagent again resulted in the complete recovery of the substrate. Dianhydride VIII, obtained in brightly yellow crystals ($\nu_{c=c}^{KBr}$ 1850s, 1790s, $\nu_{c=c}$ 1665m, 1600m. 1575m, cm^{-1}; λ_{max}^{ether} 222(23,600), 262(10,800), 280(9,000),$m\mu(\varepsilon)$), is hardly soluble in ether, chloroform, carbon tetrachloride and benzene and very sensitive to moisture. Slightly moistened acetone rapidly hydrolyzed VIII, with some decomposition, to the corresponding tetracarboxylic acid (mp 270°C) (IX). Even the exposure of the solid VIII to air without solvent for several days changed it to IX contaminated with other decomposed material. The smooth conversion of IX to the tetramethyl ester (mp 123°C) (X) was effected by treatment with diazomethane in ether. Catalytic hydrogenation of X over palladium charcoal led to a chlorine-free compound (mp 140°C, no $\nu_{c=c}$ absorption) to which is assigned the structure of tetramethyl cycloocta-1,5-diene-1,2,5,6-tetracarboxylate.

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