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REARRANGEMENT OF 1,2,3,3-TETRACHLOROCYCLOPROPANE-CIS-1,2-DIACETALDEHYDE TO 2,3,4-TRICHLOROBENZALDEHYDE

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The close juxtaposition of two cis acetaldehyde groups on a cyclopropane ring and the driving force for aromatization have resulted in a novel rearrangement. This type of reaction may lead to new methods of synthesis of halogenated aromatic compounds.

Ozonization of 1,6,7,7-tetrachloro-cis-bicyclo[4.1.0]hept-3-ene (I), m.p. 51-52° (lit.[1] m.p. 50-51°) in a mixture of acetic acid and acetic anhydride at 0° followed by oxidation with refluxing 30% hydrogen peroxide[2] has given 1,2,3,3-tetrachlorocyclopropane-cis-1,2-diacetic acid (II) in 30% yield (found: C, 28.27; H, 1.87; Cl, 47.90). The reaction was accompanied by tar formation, so the oxidation was repeated at 65° instead of the usual 100° to increase the yield of the desired acid. When a potassium iodide test was positive after 15 hrs., saturated aqueous sodium bisulfite solution was added to decompose the peroxides. A very strong exothermic reaction and extensive tar formation occurred. Alkaline extraction gave a 9% yield of the desired acid, m.p. 199-201°. Removal of solvent from the neutral fraction under reduced pressure caused sublimation of crystals of 2,3,4-trichlorobenzaldehyde (III).

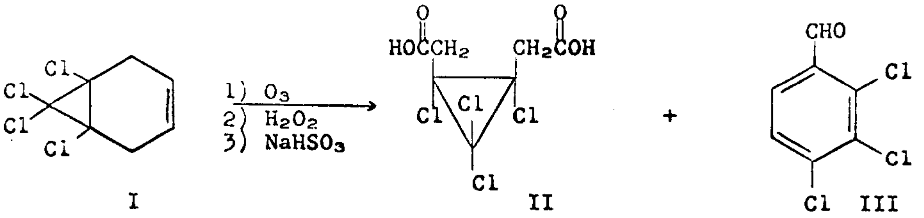

Figure 1

Chromatography of a benzene solution of the entire neutral fraction through silica gel gave a 14% yield of compound III, m.p. 84-85° (lit.[3] m.p. 86°), $\nu^{CCl_4}_{max.}$ 1700 cm^{-1}. This series of reactions is summarized in Figure 1.

Because rearrangement to compound III occurred only under mild oxidizing conditions, it was suspected that 1,2,3,3-tetrachlorocyclopropane-cis-1,2-diacetaldehyde (IV) may have been an intermediate produced by action of bisulfite on ozonides or peroxides which escaped oxidation. This dialdehyde could have then undergone acid-catalyzed aldol condensation (in the presence of newly formed sodium bisulfate) followed by loss of hydrogen chloride and aromatization as shown in Figure 2.

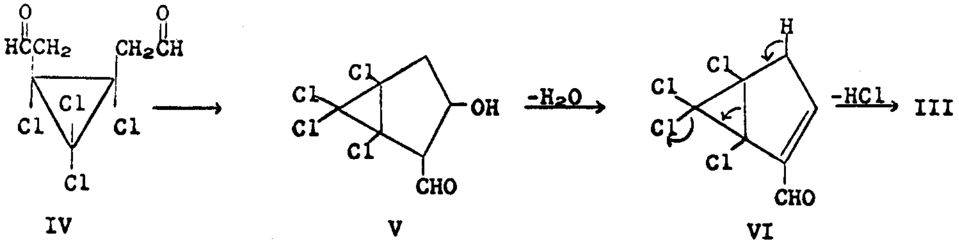

Figure 2

The hypothesis was tested as shown in Figure 3 by osmium tetroxide synthesis of cis-glycol VII[4], m.p. 139-140° (found: C, 31.51; H, 3.04, Cl, 53.57), cleavage to the desired dialdehyde IV ($\nu^{CCl_4}_{max.}$ 1730 cm.$^{-1}$, bis-2,4-dinitrophenylhydrazone m.p. 186-188°, found: C, 37.70; H, 3.00; Cl, 22.41; N, 17.46) with periodic acid, and reaction of the dialdehyde with a saturated solution of sodium bisulfate in glacial acetic acid at 100°. The cyclization was complete in 0.5 hr. yielding 2,3,4-trichlorobenzaldehyde in 82% overall yield from glycol VII. Success of this series of reactions shows 1,2,3,3-tetrachlorocyclopropane-cis-1,2-diacetaldehyde to be a reasonable intermediate in the original ozonization sequence. The bicyclohexanol V and its dehydration product VI

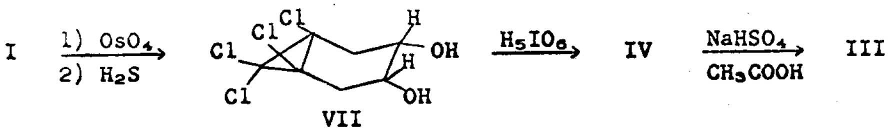

Figure 3

(see Figure 2) are probably short-lived intermediates in the cyclization.

References

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2. S. Winstein and J. Sonnenberg, J. Am. Chem. Soc. 83, 3235 (1961)
3. H. C. Brimelow, R. L. Jones, and T. P. Metcalfe, J. Chem. Soc., 1208 (1951)
4. The *cis*-glycol VII is considered to be the *endo* isomer since attack by osmium tetroxide seems less hindered from that side.