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# TETRACHLOROCYCLOPROPENE AND HEXACHLOROCYCLOPROPANE FROM PENTACHLOROCYCLOPROPANE[1a]

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We have found that addition of $:CCl_2$ to chlorinated olefins provides highly chlorinated cyclopropanes having interesting physical and chemical properties. For example, decarboxylation of $CCl_3CO_2^-Na^+$ in dry 1,2-dimethoxyethane[2] at 80° in the presence of excess $CHCl{=}CCl_2$ will provide pentachlorocyclopropane [I] in 25% yield in isomerically pure form. I is a colorless liquid with a faint minty odor, b.p. 55.5-56.0° [ 7 mm. ] , $n_D^{27.5^\circ}$ 1.5170. Calculated for $C_3Cl_5H$: C, 16.81; Cl, 82.72; H, 0.47%. Found: C, 16.94; Cl, 82.63; H, 0.54%. The NMR spectrum of I shows a singlet at 6.16 tau [ 5% in $CCl_4$ ]. The infrared spectrum of I [ liquid film ] shown in Fig. 2a has no band in the C=C region, but shows a band at 3040 $cm.^{-1}$ [ cyclopropane C-H ], a strong complex band between 950-885 $cm.^{-1}$ [ highly chlorinated cyclopropane ], and a strong band at 768 $cm.^{-1}$ [ $>CCl_2$ ].

When I is shaken with excess 18 M aqueous KOH at 80-85° a moderately exothermic reaction occurs which provides tetrachlorocyclopropene [ II ] in 85% yield. II is a colorless lachrymatory liquid with the odor of rotten tomatoes, b.p. 129.5-130.0° [745 mm. under $N_2$], $n_D^{27.0^\circ}$ 1.5047. Calculated

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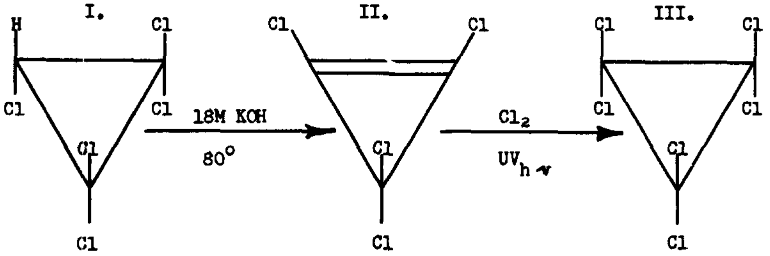
[2] W. M. Wagner, Proc. Chem. Soc., 229 [1959].

for $C_3Cl_4$: C, 20.26; Cl, 79.74; H, 0.00 %, m.w. 177.8 Found: C, 20.26; Cl, 79.70; H, 0.00 %, m.w. 179 ± 3 [ vapor density 200° ]. The very simple infrared spectrum of II [ liquid film ] shown in Fig. 2b displays four strong bands at 617 $cm.^{-1}$ [ C-Cl ], 753 $cm.^{-1}$ [ $>CCl_2$ ], 1055 and 1148 $cm.^{-1}$ [ C-Cl ]. The very weak C=C band at 1810 $cm.^{-1}$ is strong and polarized in the Raman spectrum. This fact, along with the observed matching of all Raman and infrared bands in the NaCl region, indicates a $C_{2v}$ symmetry for the molecule. The unusual position of the C=C band for II is also observed for 1,2-bis-[trifluoromethyl]-3,3-difluorocyclopropene where the C=C band occurs at 1820 $cm.^{-1}$ .[3]

Confirmatory chemical evidence for the cyclopropene structure of II is provided by the fact that chlorination of II in ultraviolet light converts it rapidly and quantitatively to hexachlorocyclopropane [ III ]. III may be synthesized directly in 5 % yield [4] by stirring a 10% [v/v] solution of $CHCl_3$ in $CCl_2=CCl_2$ over excess KOH pellets containing 15% $H_2O$ at 100-105°.

FIG. 1

Summary of Reactions



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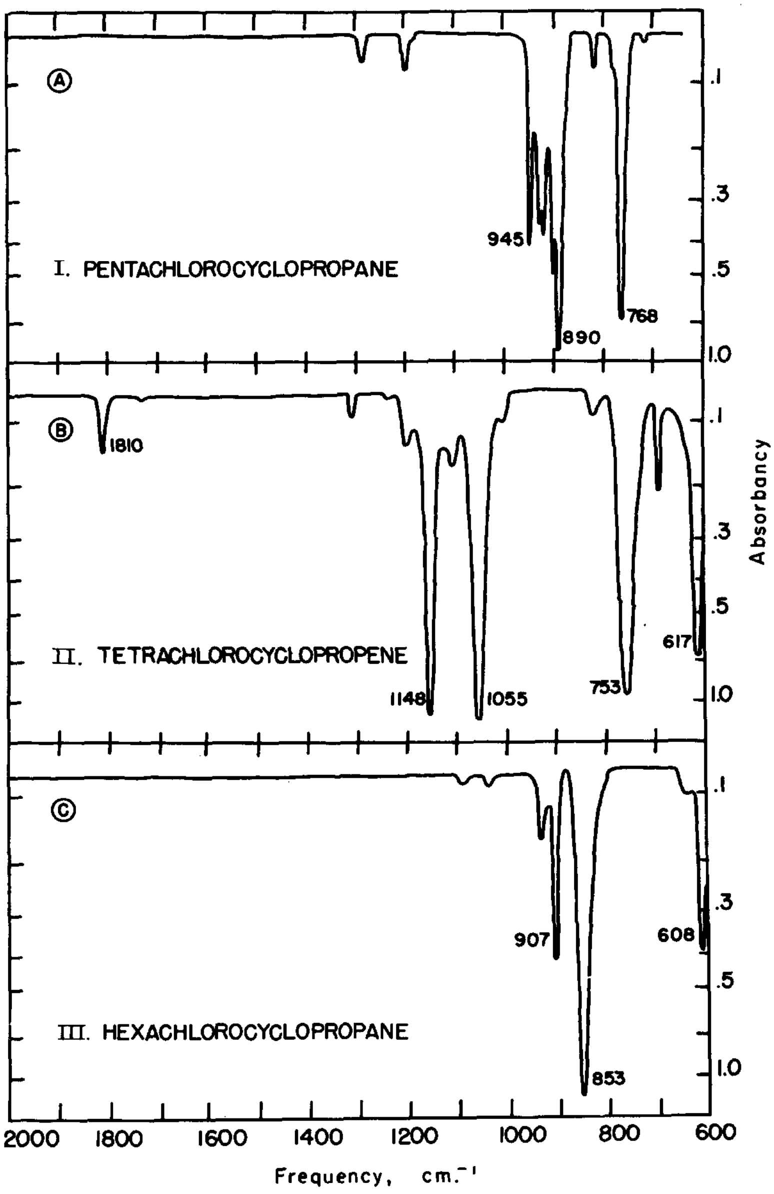
[3] W. Mahler, J. Am. Chem. Soc., **84**, 4600 [1963].

[4] III has also been synthesized recently by W.R. Moore, S.E. Krikorian and J.E. LaPrade using $CCl_3CO_2^-Na^+$ in 0.3% yield, and by D. Seyferth, R.J. Minasz, A.J.H. Treiber, J.M. Burlitch and S.R. Dowd in 75% yield using $C_6H_5$-Hg-$CCl_2Br$. See J. Org. Chem. , **28**, 1163 [1963].

**FIG. 2 Infrared Spectra**



III is a white, readily sublimable solid [ 100°, 1 mm. ] with a pine needle odor, m.p. 103.5-104.5° [ from $CH_3OH$ ], b.p. 198-199° [ 740 mm. ] in air with no decomposition. Calculated for $C_3Cl_6$: C, 14.50; Cl, 85.50%, m.w. 248.8 . Found: C, 14.73; Cl, 85.20% , m.w. 253 ± 1 [ isopiestic in $CH_2Cl_2$ ]. The very simple infrared spectrum of III [ composite of Nujol and $CCl_4$ solutions ] is shown in Fig. 2c. The absence of any C=C band and the strong band at 907 $cm.^{-1}$ indicate the hexachlorocyclopropane structure. A complete Raman and infrared study of III has confirmed the expected $D_{3h}$ symmetry.

The tetrachlorocyclopropene ring system is quite reactive and undergoes a number of interesting ring-opening reactions. Thus, hydrolysis of II in $H_2O$ at 25° converts it in 90+ % yield to CHCl=CCl-CO-O-OC-ClC=CHCl. Reaction of II with alcoholic $NH_4OH$ at 50° provides CHCl=CCl-CN in 30% yield. The reactions of II [ or III in the presence of Zn ] with various alcohols at 50-80° provide almost identical mixtures of $CHCl{=}CCl{-}CO_2R$, $CCl_2{=}CH{-}CO_2R$ and $RO_2C{-}CH_2{-}CO_2R$ esters [ R is Me, Et, n-Bu, i-Pr ]. This indicates that the dechlorination of III gives II as the initial product. In the alcoholyses of II, the rates, reaction products and product ratios are not greatly affected by the addition of gross amounts of $H_2SO_4$, $ZnCl_2$, KOH or pyridine. This suggests that in the primary solvolysis step, addition of a neutral solvent molecule to the double bond of II occurs, forming a cyclopropane intermediate. This intermediate is unstable and undergoes ring-opening reactions which lead to the observed products.

The details of the mechanisms of the above chemical reactions, and others which proceed without opening of the cyclopropene ring,are being investigated and will be the subject of further communication.