Formation and Pyrolysis of Bis(chloroalkyl)tellurium Dichloride

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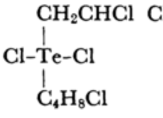
The present work was undertaken in connection with the tellurium-catalyzed allylic chlorination of olefins.1) Little is known as to the reaction of tellurium tetrachloride(I) with olefins.2,3)

The treatment of I with excess cyclohexene at 5°C afforded bis(2-chlorocyclohexyl)tellurium dichloride(II) in a 80% yield (based on I) as colorless needles (from acetic acid); mp 134—135.5°C (decomp). Found: C, 33.4; H, 4.9; Cl, 33.1%. Calcd for $C_{12}H_{20}TeCl_4$: C, 33.2; H, 4.6; Cl, 32.8%. Previously De Moura Campos and Petragnani3) had reported the formation of 2-chlorocyclohexyltellurium trichloride(III), mp 113°C(decomp). III was obtained when I was allowed to react with an equivalent amount of cyclohexene in carbon tetrachloride. Thus, whether a 1/1 or a 1/2 adduct is formed depends on the reaction conditions.

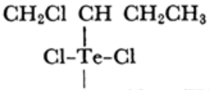
The pyrolysis of II (at 150°C, under 1 mmHg pressure) gave, besides hydrogen chloride and inorganic telluride, cyclohexene (41%), chlorocyclohexane(33%), benzene (11% based on II), and a small amount of 3-chlorocyclohexene. The formation of chlorocyclohexane shows that tellurium-catalyzed hydrogen transfer occurs between the alkyl groups of II.

Butene-1 was bubbled into an acetonitrile solution of I at room temperature. After evaporating acetonitrile *in vacuo*, the mixture of the isomer of bis(chloro-*n*-butyl)tellurium dichloride(IV) was obtained in a quantitative yield as a faint yellow viscous oil. Found: Te, 33.2%; mol wt (cryoscopic in benzene), 385. Calcd for $C_8H_{16}TeCl_4$: Te, 33.4%; mol wt, 382.



$$\begin{array}{l} CH_2CHCl\ CH_2CH_3 \\ |\\ Cl\text{-}Te\text{-}Cl \\ | \\ C_4H_8Cl \end{array}$$

(IVa)

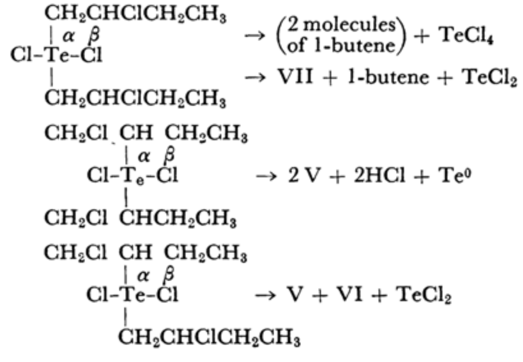


$$\begin{array}{l} CH_2Cl\ CH\ CH_2CH_3 \\ \quad\quad\ |\\ \quad Cl\text{-}Te\text{-}Cl \\ \quad\quad\ | \\ \quad\quad C_4H_8Cl \end{array}$$

(IVb)

The IR spectrum did not show the presence of a double bond. The NMR spectrum of IV in deuteriochloroform showed bands at 6.3 ppm from benzene as the internal standard (a pair of triplets; for methyl, relative area 3), 5.5 ppm (a multiplet; for methylene; relative area 2), and 2.5—3.7 ppm (multiplets; for chloromethyl and methine protons; relative area 3). If methyl protons of IVa absorbed at a higher field than those of IVa, the ratio of formation, IVa/IVb, was estimated to be about 0.6.

IV was pyrolyzed at 150°C, under 1 mmHg pressure, and the products except inorganic compounds were analyzed by gas chromatography. The liquid contained 1-chloro-2-butene (V, 52%), 2-chlorobutane (VI, 21%), 3-chloro-1-butene (14%), and 1,2-dichlorobutane (VII, 13%). The gaseous products were 1-butene (88%), *cis*- and *trans*-2-butenes (3%), butadiene (4%), and an unidentified compound (5%). The absence of vinylic chloride suggests that the preliminary formation of the carbonium cation at α-carbon is not probable as a mechanism of the pyrolysis. By postulating that chlorine is more preferentially attacked than hydrogen when both chlorine and hydrogen are bonded to the same carbon atom, most of the products can be explained by β-Cl elimination, β-Cl transfer, β-H elimination, or β-H transfer, as is shown in the following equations, respectively.



$$\begin{array}{ll} CH_2CHClCH_2CH_3 & \\ \ |\ \alpha\ \beta & \rightarrow \begin{pmatrix}\text{2 molecules}\\ \text{of 1-butene}\end{pmatrix} + TeCl_4 \\ Cl\text{-}Te\text{-}Cl & \\ \ | & \rightarrow \text{VII} + \text{1-butene} + TeCl_2 \\ CH_2CHClCH_2CH_3 & \end{array}$$

$$\begin{array}{ll} CH_2Cl\ CH\ CH_2CH_3 & \\ \quad |\ \alpha\ \beta & \\ Cl\text{-}Te\text{-}Cl & \rightarrow 2\,\text{V} + 2HCl + Te^0 \\ \quad | & \\ CH_2Cl\ CHCH_2CH_3 & \end{array}$$

$$\begin{array}{ll} CH_2Cl\ CH\ CH_2CH_3 & \\ \quad |\ \alpha\ \beta & \\ Cl\text{-}Te\text{-}Cl & \rightarrow \text{V} + \text{VI} + TeCl_2 \\ \quad | & \\ CH_2CHClCH_2CH_3 & \end{array}$$

However, the formation of 3-chloro-1-butene and 2-butene, which were produced in minor amounts, cannot be accounted for by the above schemes, and a sort of allyl or π-allyl intermediate should be considered for their formation in the course of pyrolysis. The results with other olefins will be reported elsewhere.

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1) Höchst A. G., German Pat. 1224301.

2) C. H. Fischer and A. Eisner, *J. Org. Chem.*, **6**, 169 (1941).

3) M. De Moura Campos and N. Petragnani, *Tetrahedron Letters*, No. 6, 11 (1959); *Tetrahedron*, **18**, 521 (1962).