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Addition of Tellurium Tetrachloride to Olefins and Pyrolysis of the Adduct

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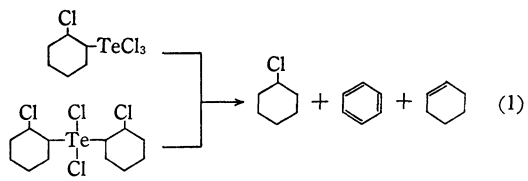
The tellurium tetrachloride-cyclohexene adduct, 2-chlorocyclohexyltellurium trichloride (I) and bis(2-chlorocyclohexyl)tellurium dichloride (II), both gave, on pyrolysis, chlorocyclohexane as the chlorinated compound. An intermolecular hydrogen transfer is required for the formation of chlorocyclohexane from I. Chloro-*n*-propyltellurium trichloride (III) and bis(chloro-*n*-propyl)-tellurium dichloride (IV) were formed by the addition of tellurium tetrachloride to propylene. The pyrolysis of III afforded allyl chloride, 1,2-dichloropropane, and hydrogen chloride, while tellurium was simultaneously reduced. Besides these products, isopropyl chloride was also obtained from IV. Some properties of the adduct and the effect of the temperature on the thermal decomposition were studied.

In an earlier communication[1] the formation of bis(chloroalkyl)tellurium dichloride by the addition of tellurium tetrachloride (TTC) to olefins and the pyrolysis of the adducts affording organic chlorides were briefly reported. The lower-valent tellurium compounds produced in the pyrolysis are reoxidized by oxygen and hydrogen chloride. Thus, the oxychlorination of olefins for the production of allylic chloride is thought to be possible; the process is now being investigated.[2]

The present paper will deal with the behavior of the TTC-propylene adducts, including the hydrogen transfer observed in the pyrolysis of the TTC-cyclohexene adducts. The results will give a clue to the catalysis of the tellurium compound in the chlorination reaction.

Results and Discussion

Pyrolysis of the TTC-cyclohexene Adducts. In the addition of TTC to cyclohexene,[1] 2-chlorocyclohexyltellurium trichloride (I) was obtained when TTC was allowed to react with less than an equivalent amount of cyclohexene, while bis-(2-chlorocyclohexyl)tellurium dichloride (II) was obtained from the reaction with excess cyclohexene. Both I and II gave, on pyrolysis, chlorocyclohexane, benzene, and cyclohexene, as well as hydrogen chloride and inorganic tellurium compound.



(1)

A certain amount of 3-chlorocyclohexene was expected to be found in the pyrolysate. In fact, it was assumed by gas chromatography. However, its amount was very small; if it was present at all, it was estimated at less than 1% of the products. In contrast to the pyrolysis of the TTC-propylene adducts (Table 3), the yield of allylic chloride was very low, probably because the concurrent dehydrogenation to benzene predominated over the allylic chlorination. The product distribution in the pyrolysis of I is shown in Table 1, along with the corresponding data for II.

TABLE 1. PRODUCTS FROM THE PYROLYSIS OF I AND II

Compound	Organic product (g/g)	Product distribution (%)		
		Chlorocyclohexane	Benzene	Cyclohexene
I[a]	0.18	51	28	21
I[b]	0.17	55	28	17
II[a]	0.27	38	13	49

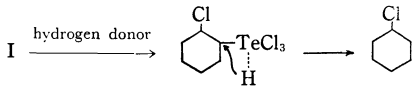
a) Decomposed at 150°C. b) At 200°C.

It seems natural that a tellurium-catalyzed intramolecular hydrogen transfer should be involved in the pyrolysis of II, which has hydrogens available within the molecule, while the intermolecular hydrogen transfer is bound to occur in the pyrolysis of I.

During the thermal decomposition of I and II, an intermediate formation of the tellurium-hydrogen

1) M. Ogawa, This Bulletin, **41**, 3031 (1968).
2) A.G. Höchst, Ger., 1224302 (1967); Japan, 17134 (1966).
3) G. Centini, P. L. Stanghellini, R. Rossetti and O. Gambino, *J. Organometal. Chem.*, **15**, 373 (1968) and the literatures cited therein.

bond, a probable representation of which is shown in Eq. (2), may be implied before the complete cleavage of the tellurium-carbon bond.



and other products (2)

It is known that the atomic valency of the VIb-group element, particularly that of covalent tellurium,[3] increases to 6 and more upon the participation of vacant *d* orbitals; this character of the element is thought to be related to the hydrogen transfer (perhaps the hydride transfer) observed in the experiment.

Addition of TTC to Propylene. The reaction of propylene with TTC in an organic solvent, after the solvent had been evaporated, afforded the adduct as an faint yellow viscous oil. The IR spectrum showed that the adduct had no double bond in it. The NMR spectrum coincided with the structure of addition compound.

When TTC in acetonitrile was allowed to react, in a sealed tube, with an equivalent amount of propylene, one type of product (named III) was exclusively obtained. On the other hand, another product (named IV) was formed together with III in the reaction with excess propylene. (See Figs. 2 and 3 in the "Experimental" section.) The same results were observed when nitromethane instead of acetonitrile was used as the solvent. Accordingly, compared with the case of cyclohexene, III and IV are thought to be 2-chloropropyltellurium trichloride and bis(2-chloropropyl)tellurium dichloride respectively.

CH_3-CHCl-CH_2-$TeCl_3$ (III)

$(CH_3$-CHCl-$CH_2)_2TeCl_2$ (IV)

Neither the NMR spectrum nor the chemical reaction was conclusive as to the orientation of the addition, but Markownikoff addition was tentatively estimated from the product of the pyrolysis. The Markownikoff additions of aryltellurium trichloride[4] and I[5] to 2,2-disubstituted-penten-4-oic acid, and of selenium tetrachloride[6] to the simple olefins, have been reported, while the random orientation has been manifested in the addition of sulfenyl chloride[7] and sulfur dichloride[8,9] to olefins.

It was suggested in the previous paper[1] that the TTC-butene-1 adduct was a mixture of isomers of bis(chloro-*n*-butyl)tellurium dichloride; this suggestion was based on the analytical method which is now found to involve considerable uncertainties in the determination of tellurium. The estimation must, then, be in error and must be corrected in view of the present results. The TTC-butene-1 adduct can now be thought to be a mixture of bis(2-chlorobutyl)tellurium dichloride and a minor amount of 2-chlorobutyltellurium trichloride.

The effects of the solvent on the addition were investigated, though the number of usable solvents was limited because of the reaction with TTC[10] and the solubility requirements. Gaseous propylene was introduced into a solution of TTC in an organic solvent at room temperature for a sufficiently long period.

Table 2. Solvent effect in addition reaction
TTC 2 g; solvent, 20 ml; reaction time, 1 hr

Solvent	Dielectric constant	Time (min)[a]	III (%)[b]	IV (%)[b]
Ethyl acetate[c]	6.03	60	98	2
Acetic acid	6.19	45	83	17
Methylene dichloride[d]	8.9	14	81	19
Acetonitrile	37.5	13	56	44
Nitromethane	39.0	11	32	68

a) The approximate time required for the disappearance of the yellow color of TTC in solution.
b) The ratio of III and IV was calculated approximately from the relative intensity of the NMR signals.
c) The reaction was not completed within an hour.
d) TTC was not fully dissolved in this solvent.

The reaction is generally faster, and IV is more preferentially formed, with increases in the dielectronic constant and in the solvating power of the solvent used. In such a polar solvent, the ionization and the subsequent addition of III to the olefin is accelerated; consequently, the formation of IV, at the expense of III, is favored.

Properties of the TTC-propylene Adduct. The adduct (III or IV) was relatively stable at room temperature, but it began to decompose at approximately 80°C. Sensitive to water, it was hydrolyzed to a white, insoluble mass,[11] losing the chlorine atoms attached to tellurium. With

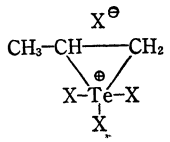
4) M. De Moura Compos and N. Petragnani, *Chem. Ber.*, **93**, 317 (1960).
5) M. De Moura Compos and N. Petragnani, *Tetrahedron*, **18**, 521 (1962).
6) R. F. Riley, J. Flato and D. Bengels, *J. Org. Chem.*, **27**, 2652 (1962); H. Brintzinger. K. Pfannstiel and H. Vogel, *Z. Anorg. Allgem. Chem.*, **256**, 75 (1948).
7) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **88**, 2866 (1966); *J. Org. Chem.*, **33**, 2111 (1968); *ibid.*, **90**, 2075 (1968).
8) J. R. Nooi and G. J. Huijben, *J. Appl. Chem.* (London), **18**, 84 (1968).
9) F. Lautenschlager, *J. Org. Chem.*, **33**, 2620 (1968).
10) H. Rheinbolt, "Methoden der Organischen Chemie," Vol. IX Georg Thieme Verlag (1956) p. 1156.
11) M. P. Balfe, C. A. Chaplin and H. Phillips, *J. Chem. Soc.*, **1938**, 341.

reducing agents such as sodium sulfite and hydrazine hydrochloride, propylene and elemental tellurium were recovered. When the adduct was dissolved in an acidic solution of potassium perchromate, 1,2-dichloropropane was obtained in a low yield, besides several unidentified compounds.

The tellurium-carbon bond of the adduct was cleaved by the action of bromine. III yielded a mixture of dihalopropanes.

$$\text{III} \xrightarrow{Br_2} CH_2Br\text{-}CHBr\text{-}CH_3 + CH_2Cl\text{-}CHBr\text{-}CH_3 + CH_2Br\text{-}CHCl\text{-}CH_3 + CH_2Cl\text{-}CHCl\text{-}CH_3 \quad (3)$$

Under the same conditions, the chlorine atom in 1,2-dichloropropane or bromochloropropane was not replaced by bromine. This indicates that the chlorine atom in the alkyl remainder of the adduct was activated toward substitution by a neighboring tellurium atom. The activation of the chlorine and the products in Eq. (3) were interpreted in terms of the cyclic tellurium-ion intermediate (V), which had previously been postulated by De Moura Campos and Petragnani[5] in analogy to the episulfonium ion considered in the behavior of the sulfenyl chloride-olefin adduct.[7,12]



(V) X: Cl or Br

Pyrolysis of the TTC-Propylene Adduct. The pyrolysis of the adducts afforded allyl chloride, isopropyl chloride, 1,2-dichloropropane, and hydrogen chloride as well as inorganic telluride and propylene. It is likely that the adduct was of the Markownikoff type, for if it were of the anti-Markownikoff type *n*-propyl chloride, instead of isopropyl chloride, would be produced by hydrogen transfer at the pyrolysis.

The effect of the temperature on the yield of organic chloride (based on tellurium, mol/atom $\times 100$) was studied by using the adduct obtained from the reaction in an acetonitrile solvent (III 56%, IV 44%).

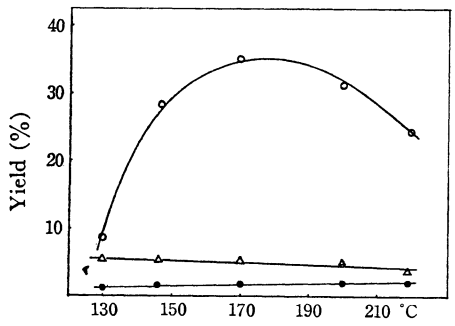


Fig. 1. Effect of temperature on the pyrolysis.
○: Allyl chloride, △: Isopropyl chloride,
●: 1,2-dichloropropane

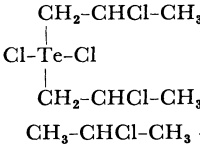
At a low temperature, the decomposition was incomplete and the residue contained organic tellurides. At a higher temperature, the dissociation (Eq. (8)) predominated over the chlorination. Therefore, the optimum temperature appears in Fig. 1.

The relation between the yield of organic chlorides and the ratio of III and IV in the adduct is shown in Table 3.

Table 3. Pyrolysis of III and IV
170°C, 5 mmHg

III (%)	IV	Isopropyl chloride (%)	Allyl chloride (%)	1,2-dichloropropane (%)
98	2	<1	11	1.2
83	17	1.6	19.9	2.7
81	19	6.0	25.3	2.4
56	44	5.0	34.9	1.7
32	68	9.9	49.0	3.0

Table 3 shows that isopropyl chloride was mainly produced from IV, indicating that intramolecular hydrogen transfer was operating and that intermolecular hydrogen transfer was not important in this case.



$$CH_3\text{-}CHCl\text{-}CH_3 + CH_2{=}CH\text{-}CH_2Cl + TeCl_2 \quad (4)$$

The formation of allyl chloride from III and IV is thought to require some type of allylic intermediate, which may be stabilized by the tellurium atom.

$$\text{III, IV} \xrightarrow{-HCl} \text{allylic intermediate} \xrightarrow{-Te} CH_2{=}CH\text{-}CH_2Cl \quad (5)$$

The allylic intermediate illustrates how 3-chloro-1-butene and 1-chloro-2-butene were formed, along with isomeric butenes, from the TTC-butene-1 adduct,[1] and also from the TTC-butene-2[13] adduct.

In this thermal decomposition, the elimination of hydrogen from the carbon bearing both hydrogen and chlorine or the preliminary development of the carbonium ion at the α to tellurium carbon is excluded, because no vinylic chlorides were found in the pyrolysate.

The adduct would give 1,2-dichloropropane by either Eq. (6) or (7), though it is uncertain which process prevails:

12) N. Kharasch, "Organic Sulfur Compounds," Vol. 1, Pergamon Press, New York (1961), p. 382.

13) Unpublished work.

$$\text{III, IV} \longrightarrow \begin{cases} \rightarrow CH_2Cl\text{-}CHCl\text{-}CH_3 + Te & (6) \\ \rightarrow CH_2Cl\text{-}CHCl\text{-}CH_3 + CH_2{=}CH\text{-}CH_3 + TeCl_2 & (7) \end{cases}$$

All these reaction, Eqs. (4)—(7), compete in the rather fast dissociation of the adduct to regenerate TTC and propylene.

$$\text{III, IV} \rightarrow CH_2{=}CH\text{-}CH_3 + TeCl_4 \quad (8)$$

This reaction may be partly responsible for the absence of vinylic chlorides in the pyrolysate.

The results with propylene, described here, can be applied to the study of the behavior of other linear olefins.

Experimental

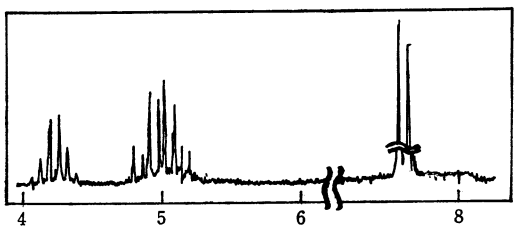
The IR spectrum was measured using a Nippon Bunko DS-401G-type spectrophotometer. The NMR spectra were recorded on a Japan Electron Optics H-100 spectrometer (100MHz), with benzene as the internal standard. TMS was not used, because it caused precipitation with the organic tellurium compounds described in this report. As has been shown previously,[14] the isotopes of tellurium (^{123}Te and ^{125}Te; nuclear spin, 1/2; natural abundance, *ca.* 25%) hardly affected the NMR spectrum.

The chlorinated organic compounds were analyzed by gas chromatography, using a Carbowax column (at 60°C and 110°C) or a tricresylphosphate column (at 60°C).

2-Chlorocyclohexyl Trichloride (I).[15] Mp 112—113°C (decomp.), Found: C, 20.5; H, 3.8; Cl, 40.0%, mol. wt (cryoscopic), 360.

Addition of TTC to Propylene. Two grams (7.4 mmol) of TTC in 20 m*l* of acetonitrile were mixed with 0.45 m*l* (*ca.* 7.4 mmol) of liquid propylene in a sealed tube. The mixture was then left standing for 2 hr at at room temperature. On removing the solvent *in vacuo*, chloro-*n*-propyltellurium trichloride (III) was obtained as a viscous oil. The characteristics in the NMR spectrum of III (Fig. 2) in deuteriochloroform were similar to those of the sulfenyl chloride-propylene adduct.[7] The terminal methylene and the methine protons form an ABX-type spin system: a double quartet for the methylene protons ($J_{gem} \simeq 12$Hz, $\Delta\nu \simeq$ 22Hz) and six symmetrical lines for the methine protons.

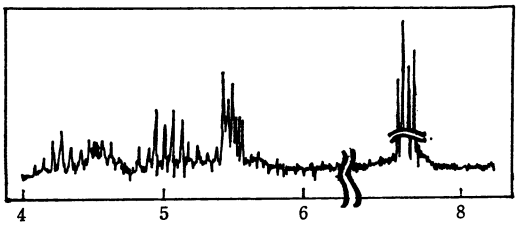
The same procedure was repeated using 3.7 mmol of TTC and 77 mmol of propylene. The NMR spectrum



ppm from benzene

Fig. 2. NMR spectrum of III.

of the resulting oil (Fig. 3) suggested that bis(chloro-*n*-propyl)tellurium dichloride (IV) was formed in addition to III. The absorptions that represent the methylene and methine protons also show the features of an ABX-type spin system, though the band for the former protons is distorted and that for the latter is broadened.



ppm from benzene

Fig. 3. NMR spectrum of III and IV.

Small percentages of impurities, depending on the solvent used in the addition reaction, were also observed in the higher field of the NMR spectra, but they are omitted in the figures cited above.

Attempt to distill or recrystallize the adduct resulted in failure.

The experiments for Table 2 were carried out as follows: two grams of TTC in 20 m*l* of a solvent were transferred to a three-necked flask fitted with a magnetic stirrer, a gas inlet, and an ice-water cooled condenser. After replacing the air with a stream of nitrogen, propylene was bubbled in under vigorous stirring at room temperature for an hour. The solvent was then removed under reduced pressure and a part of the adduct was dissolved in deuteriochloroform in order to measure the NMR spectrum.

The Reaction of the TTC-propylene Adduct with Bromine. One gram of III was dissolved in 10 m*l* of methanol containing 7.0 g of bromine and 1.5 g of potassium bromide. The mixture was warmed at 50°C for 4hr, washed with aqueous potassium hydroxide to remove the excess bromine, and filtered from inorganic tellurium compounds. A mixture of dihalopropanes and unreacted organotellurium compound separated as an oily layer. The dihalopropanes obtained by the distillation of the oil under reduced pressure gave three peaks on gas chromatography; each of them was then separated. By comparing the IR spectra with Sadtler's standard ones, the first and the third fraction, in order of elution, were found to be 1,2-dichloropropane and 1,2-dibromopropane respectively. The second fraction was a mixture of 1-bromo-2-chloropropane and 1-chloro-2-bromopropane, the ratio of which was determined from the NMR spectra. The authentic sample of the bromochloropropanes, in which 1-chloro-2-bromopropane predominates, was prepared from propylene oxide by ring closure with hydrogen chloride, followed by bromination with phosphorus pentabromide. In the NMR spectrum, the doublets for the methyl protons of 1-chloro-2-bromopropane and 1-bromo-2-chloropropane appeared at δ 1.79 (from TMS) and at δ 1.65 respectively. These signals were used to calculate the ratio of the isomers. The composition of the dihalopropanes formed by the reaction of III with bromine was approximately as follows: $CH_3CHCl\text{-}CH_2Cl$ 5%, $CH_3\text{-}CHCl\text{-}CH_2Br$ 6%, $CH_3\text{-}CHBr\text{-}CH_2Cl$ 18%, and $CH_3\text{-}CHBr\text{-}CH_2Br$ 71%. When one gram of III

14) Von Gotthard Klose, *Z. Naturforsch.*, *A*, **16**, 528 (1961).

15) M. De Moura Compos and N. Petragnani, *Tetrahedron Lett.*, **1959**, 11.

was refluxed with 2 g of bromine in methylene dichloride for 10 hr and then worked up as has been described above, the following product distribution was observed: CH_3–CHCl–CH_2Cl 11%, CH_3–CHCl–CH_2Br 20%, CH_3–CHBr–CH_2Cl 38%, and CH_3–CHBr–CH_2Br 31%.

Pyrolysis of the Adducts. Pyrolysis was conducted under a pressure of 1—5 mmHg. About one gram of the adduct in a 25-m*l* flask was immersed into an oil bath maintained at a desired temperature. The decomposition occurred immediately. The products were inorganic tellurium compounds (residue), hydrogen chloride, and organic compounds, the last of which were collected in a dry ice-methanol trap. When necessary, the trap contained a weighed amount of chloroform as an internal standard for gaschromatography. It was ascertained that the simple addition of hydrogen chloride to the olefins did not occur in the cold trap. Each of the organic products from the pyrolysis was separated by distillation or by gas chromatography and was identified by comparing the IR spectrum with that of the authentic sample or with Sadler's standard spectrum.

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