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$TeCl_4$ in organic synthesis. Elimination reactions

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Abstract

$TeCl_4$ has been shown to react smoothly with unsaturated or halogenated cyclohydrocarbons. With cyclohexene, alkylcyclohexenes, halogenocyclohexenes, halogenocyclohexanes or unsaturated polycyclic compounds at elevated temperatures (ca 80 °C), aromatization takes place as the only process, whereas at room temperature, addition products of halogenation or halogenotelluration are also formed. With conjugated dienes only chlorine-containing products are obtained with $TeCl_4$, whereas dienes with separated double bonds undergo addition of $TeCl_4$ to the double bond. An ionic pathway for the addition and aromatization reactions is suggested.

Introduction

Synthetic methods based on tellurium salts and organotellurium compounds have been described [1]. Eliminations of a tellurium moiety from some organotellurium compounds were described by Uemura and coworkers [2]. The decomposition of organotelluroxides to yield olefins and the corresponding telluroxides were studied by Sharpless et al. [3], Cava et al. [4] and Uemura et al. [5]. Reactions between several olefines and $TeCl_4$ to yield products of addition of the $TeCl_4$ across the double bond have been reported [6–9]. In a recent review [10] of the synthetic application of organotellurium compounds, the elimination reactions of *vic*-halogenoorganotellurium compounds to give the corresponding olefinic species are described. Aromatization of 1-tetraloneethylenedithioacetal to naphthol-[1,2-*b*]dihydro-1,4-dithiin by $TeCl_4$ was mentioned by Tani et al. [11]. We have previously reported the aromatization of unsaturated or halogenocyclohydrocarbons by tellurium tetrachloride [12].

We describe below the addition–elimination reactions of tellurium salts with unsaturated or halogenated cyclic hydrocarbons to yield the corresponding aromatic compounds or species containing new double-bonds.

Results and discussion

Reactions of $TeCl_4$ with cyclohexenes, halogenocyclohexanes (Table 1), dienes, cyclodienes (Table 2) and saturated as well as unsaturated polycyclic compounds

Table 1

Reactions of cyclohexenes and halocyclohexanes with $TeCl_4$. Reaction time 20 h

Reagent	Solvent	T (°C)	Products	Yield (%)
cyclohexene	CCl_4, $CHCl_3$ CH_3CN	Reflux	benzene	71
cyclohexene	CCl_4, $CHCl_3$ CH_3CN	25	2-chlorocyclohexyl-tellurium trichloride	–
4-methylcyclohexene	$CHCl_3$, CCl_4 benzene	Reflux	toluene	65
4-methylcyclohexene	CH_3CN, CCl_4 benzene	25	2-chloro-4-methyl cyclohexyltellurium trichloride	–
1-methylcyclohexene	CCl_4	76	toluene	78
1,2-dimethylcyclohexene	CCl_4, $CHCl_3$	Reflux	*o*-xylene	68
3-chlorocyclohexene	CH_3CN, CCl_4	Reflux	benzene	58
3-chlorocyclohexene	CH_3CN, CCl_4	25	dichlorocyclo-hexene [a]	–
Limonene	CCl_4	78	*p*-cymene	69
cyclohexyl chloride	CCl_4	78	benzene	75
cyclohexyl bromide	CCl_4	78	benzene	38

[a] 4 Isomers.

were studied (Table 3). In all the addition reactions at higher temperatures (refluxing CCl_4, $CHCl_3$, CH_3CN) no telluration, i.e. no addition of the tellurium halide across the double bond, was observed. With cyclohexyl chloride (Table 1), after 1 h the major product was cyclohexene (ratio of cyclohexene to benzene 2.3 : 1), whereas after 8 h only benzene was present (yield 75%). With cyclohexyl bromide no reaction had occurred after 1 h, but after 5 h only cyclohexene was present, and after 8 h only benzene was present (yield 38%).

The reaction of cyclohexene with $TeBr_4$ at 67 °C gave benzene only, 3-bromocyclohexene gave (70 °C) benzene together with dibromocyclohexenes (4 isomers),

Table 2

Reactions of dienes and cyclodienes with $TeCl_4$

Reagent	Solvent	T (°C)	Products	Yield (% of aromatic product)	t (h)
1,3-cyclohexadiene [a]	CCl_4, $CHCl_3$	reflux	benzene, dichloro-cyclohexene [b]	83	8
1,4-cyclohexadiene	CCl_4	78	benzene, 4-chloro-5-trichlorotellyl cyclohexene	75	8
1,5-cyclooctadiene	CCl_4, neat	78	5-chloro-6-trichloro-tellylcyclooctene		25
1,3-cyclooctadiene	CCl_4	78	2,8-dichlorocyclooctene		25
2,3-dimethyl-1,3-butadiene	CCl_4, $CHCl_3$	reflux	2,3-dimethyldichloro-butene		20

[a] The same reagent with $TeBr_4$ at 70 °C gave benzene and the 4 isomers of dibromocyclohexene. In general, the reactivity of $TeBr_4$ in these reactions is lower than that of the $TeCl_4$. [b] 4 Isomers: *cis* and *trans* 3,6-dichlorocyclohexene, *cis* and *trans* 3,4-dichlorocyclohexene.

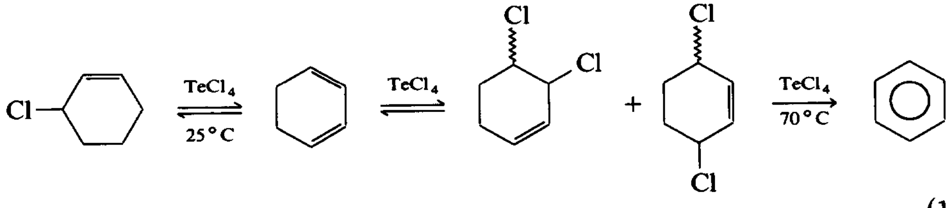
Table 3

Reactions of saturated and unsaturated polycyclic compounds with $TeCl_4$

Reagent	Solvent	T (°C)	Products	Total yield (%)	t (h)
tetralin	neat	100	naphthalene chloronaphthalene	35	30
decalin	neat	190	naphthalene, chloronaphthalene	28	48
9,10-dihydroanthracene	$CHCl_3$	25	anthracene, 9-chloroanthracene 9,10-dichloroanthracene	96	2
2,2′-bicyclohexene	$CHCl_3$	65	biphenyl (μ-2,2′-dichlorotellyl-3,3′-dichloro) bicyclohexane	72	10
1,1′-bicyclohexene	$CHCl_3$	60	biphenyl, 2,2′-dichlorobi(cyclohexyl hexane)	66	10
2,2′-bicyclopentene	CCl_4	70	(μ-2,2′-dichlorotellyl--3,3-dichloro) bycyclopentane		10

whereas there was no reaction between cyclohexyl chloride or cyclohexyl bromide and $TeBr_4$ at 80 °C. As can be seen from Table 1, in the reactions of $TeCl_4$ with cyclohexene and methylcyclohexene in a temperature range of 20–60 °C the addition predominates, whereas at temperatures > 60 °C aromatization is favoured. The addition products formed at temperatures below 60 °C are transformed to the corresponding aromatic species when treated with additional $TeCl_4$ at temperatures > 60 °C.

In the reaction of 3-chlorocyclohexene with $TeCl_4$ the first step is the elimination of HCl to yield 1,3-cyclohexadiene, which is then chlorinated by the $TeCl_4$ in the mixture to give the four addition products of chlorine (products of *cis* and *trans* 1,2-addition and *cis* and *trans* 1,4-addition of chlorine). These addition products react with $TeCl_4$ by an elimination reaction at higher temperatures to give benzene (eq. 1):



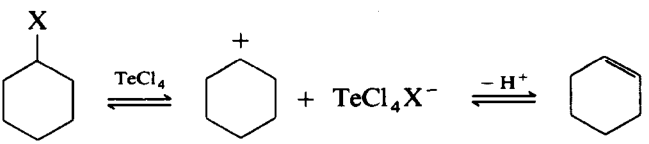
(1)

No telluration products were observed in these reactions. We suggest that the dichloro-addition products were formed, since they were isolated from the reaction of 3-chlorocyclohexene with $TeCl_4$. It was also found that chlorocyclohexene reacts faster with $TeCl_4$ than cyclohexene to yield benzene (with 3-chlorocyclohexene benzene was formed after $\frac{1}{2}$ h, but only after 2 h with cyclohexene under the same conditions).

The duality of behaviour of $TeCl_4$ (telluration and chlorination) can be seen from the results of the reaction of $TeCl_4$ with cyclodienes (Table 2). With conjugated dienes only chlorination products are obtained, whereas dienes with separated double bonds, such as 1,4-cyclohexadiene or 1,5-cyclooctadiene [13], undergo addition of $TeCl_4$ to the double bond (telluration). In the reaction of $TeCl_4$ with 1,4-cyclohexadiene in our work and also with 1,5-cyclooctadiene [13], the $TeCl_4$ add to only one double bond, and even use of a large excess of $TeCl_4$ or doubling of the reaction time does not result in a second addition.

In the $TeCl_3{}^+$ moiety the positive charge is mainly on the tellurium, and telluration should predominate in charge-controlled reactions whereas chlorination should predominate in orbital-controlled reactions. In addition, since the tellurium atom is more hindered than the chlorine atom, it is to be expected that chlorination will be favoured with increasing size of nucleophile. In a single double bond the charge is more localized than in a conjugated one, and its HOMO energy is smaller (-10.4 eV in ethylene compared to -9.1 eV in butadiene [14]), resulting in a charge-controlled reaction with $TeCl_4$ for the single bonds and orbital-controlled reaction for the conjugated double bond.

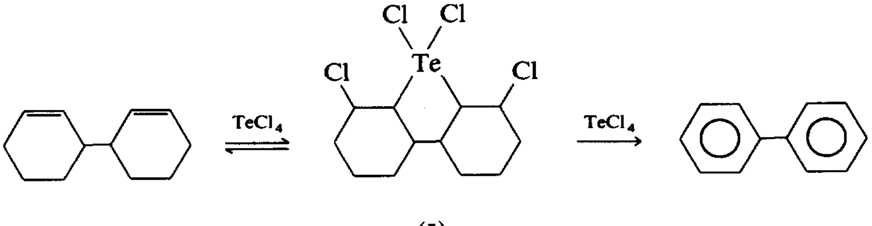
The first stage in the aromatization of halogenocycloalkanes is the removal of HX (X = Cl, Br) by the $TeCl_4$ to yield the cycloalkene, which reacts with $TeCl_4$ to give the aromatic products (eqs. 2 and 4).



(2)

It is because the $TeCl_5{}^-$ anion is more stable than $TeCl_4Br^-$, that aromatization of chlorocyclohexane is faster than that of bromocyclohexane.

The results of aromatization of polycyclic species by $TeCl_4$ are shown in Table 3. Like the monocyclic polyene, the polycyclic conjugated enes (e.g. 1,1′-bicyclohexene) undergo chlorination with $TeCl_4$, whereas the separated enes (e.g. 2,2′-bicyclohexene) undergo telluration. The reaction of 2,2′-bicyclohexene with $TeCl_4$ yields initially the addition product I, (μ-2,2′-dichlorotellyl-3,3′-dichloro)bicyclohexane (eq. 3), (the identity of which was confirmed by a single crystal X-ray diffraction study) compound I reacts with $TeCl_4$ to give biphenyl.



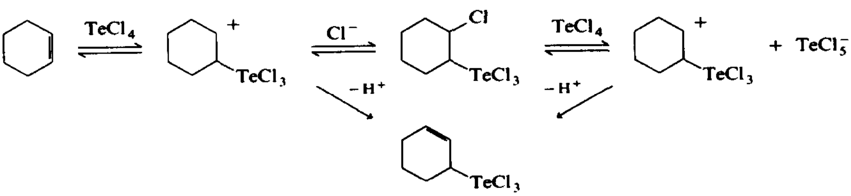
(3)

(I)

The addition product I is assumed to be the intermediate in the aromatization of 2,2′-bicyclohexene since it reacts faster with $TeCl_4$ to give biphenyl (48% yield after

7 min reflux in $CHCl_3$) than does 2,2′-bicyclohexene (13% yield after 10 min reflux in $CHCl_3$). Compound I reacts readily with reducing agents such as Na_2S, hydrolysing reagents (NaOH) or halogen-displacing halides such as KI, NaI or NaBr to give 2,2′-bicyclohexene. The ready aromatization of 9,10-dihydroanthracene in the presence of $TeCl_4$ (at room temperature) is attributed to the additional stability of the ion formed at position 9 or 10 during the reaction. Decalin reacts with $TeCl_4$ to give naphthalene only at elevated temperatures (190 °C). At this temperature the decalin is chlorinated by $TeCl_4$, and the chlorodecalin formed reacts readily with the remaining $TeCl_4$ to yield octahydronaphthalene, which reacts with further $TeCl_4$ to give naphthalene. The naphthalene formed can react with $TeCl_4$ to give chloronaphthalene (Table 3).

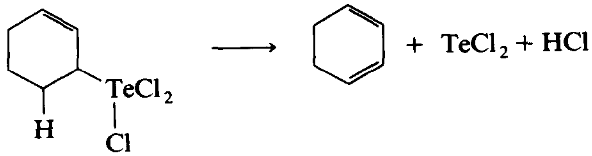
An outline of the suggested course of the aromatization of cyclohexenes and cyclohexadienes is shown in eq. 4:



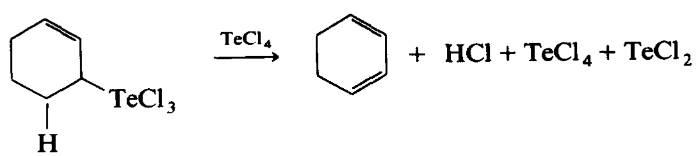
(II)

(4)

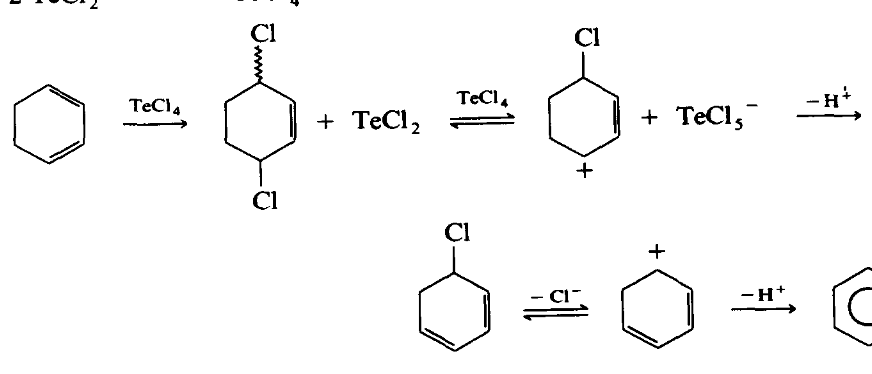
3-(trichlorotellyl)cyclohexene (II) can lose a hydrogen atom and the $TeCl_3$ moiety to yield the corresponding diene in an intra- or inter-molecular process ($TeCl_2$ is a good leaving group):



or



$$2\,TeCl_2 \longrightarrow TeCl_4 + Te$$



(5)

Table 4

Chlorinating agent	Mode of reaction	Isomer ratios			
		1,2-*cis*	1,4-*cis*	1,2-*trans*	1,4-*trans*
$TeCl_4$	ionic	1	5	11	16
$SbCl_5$ [16]	ionic	1	8	20	22
NCl_3 [16]	radical [16]	1	3	8	5
$PhICl_2$	radical [16]	1	13	49	37

Compound II could not be isolated, and it is well known that alkyltellurium trichlorides (in contrast to aryltellurium trichlorides) are unstable [15].

1,3-Cyclohexadiene reacts with $TeCl_4$ at room temperature to give the dichloro-products, which can be isolated, but at higher temperatures ($\sim 70\,°C$) it is converted rapidly into benzene.

An ionic rather than a radical mechanism is suggested for these reactions for the following reasons:

(a) Addition of $TeCl_4$ to 1,3-cyclohexadiene gives the isomer ratio shown in Table 4, which includes data for reactions with other chlorinating agents.

For the radical chlorination of cyclohexadiene with NCl_3 [16] or $PhICl_2$ [17] the major product is the 1,2-*trans* isomer, whereas in an ionic chlorination [17] in which the anion formed is bulky, 1,2-addition is hindered and the 1,4-*trans* isomer is the major product. In the ionic chlorination with Cl_2 [16], in which steric hindrance is small, the 1,2-*trans* isomer predominates.

$SbCl_5$ has a trigonal bipyramidal structure, as does $TeCl_4$, and is an ionic chlorinating agent [16]. The isomer ratio from the chlorination of 1,3-cyclohexadiene with $SbCl_5$ is similar to that from the $TeCl_4$ chlorination (Table 4).

(b) When 2,6-di(t-butyl)-*p*-cresol and 2,4-di(t-butyl)phenol, which are radical scavengers, were present during the reaction of $TeCl_4$ with cyclohexene or with 9,10-dihydroanthracene there was no change in the rate of reaction, or the nature of the products.

(c) The rate of the aromatization of 9,10-dihydroanthracene is related to the polarity of the solvent used, increasing in the sequence $C_6H_6 < CHCl_3 < ClC_6H_5 < o\text{-}Cl_2C_6H_4$. The chlorination of anthracene with $TeCl_4$ showed a similar increase in the rate of chlorination with the polarity of the solvent [18].

(d) Macrocyclic polyethers ("crown ethers") give stable complexes with many cations [19], leaving the corresponding "gegen anions" more available as nucleophiles. When 18-crown-6 ether was present in the mixture of $TeCl_4$ (1:1 molar ratio $TeCl_4$ to crown ether) with cyclohexene, 3-chlorocyclohexene, or 9,10-dihydroanthracene there was complete inhibition of the reaction. We thus suggest that the incipient $TeCl_3^+$ ions is the reactive species in these reactions.

Oxidation of saturated and unsaturated cyclic hydrocarbons to give complete unsaturation is known in only a few cases [10]. Such reactions are carried out catalytically and at high pressure and temperature; for example, 9,10-dihydroanthracene is converted into anthracene after reflux for 24 h with $CuCl_2$ [21]. Tellurium metal oxidizes polycyclic hydrocarbons [22] such as tetralin, indene, or anthracene at high temperatures (molten tellurium). In the work described here the oxidation of the cyclohydrocarbons (saturated or unsaturated) to the corresponding aromatic compounds was carried out under atmospheric pressure and at relatively low temperatures and yet high yields are obtained. Usually only one product is obtained, which is the corresponding aromatic species.

Experimental

All reagents were of commerical grades. $TeCl_4$ and $TeBr_4$ (Aldrich USA) were used without further purification. Melting points are uncorrected (Fisher–Johns Melting Point apparatus). IR Spectra were recorded on a Perkin–Elmer grating IR 177 spectrometer. Mass spectra were obtained with a Hitachi–Perkin–Elmer RMU6 spectrometer. ^{1}H NMR spectra were recorded on a Varian HA-100 spectrometer, and ^{13}C NMR spectra on a Varian CFT-20 NMR spectrometer.

The reactions were monitored by GLC (Packard–824 and Varian Aerograph 920 models).

Synthesis of the addition product (μ-2,2′-dichlorotellyl-3,3′-dichloro)bicyclohexane(I)

2,2′-Bicyclohexene (1.62 g, 0.01 mole) and $TeCl_4$ (2.7 g, 0.01 mole) were added to 25 ml of dry toluene. The solution was stirred for 5 h at room temperature. The white solid obtained after the evaporation of the solvent under vacuum was washed with ethanol and recrystallized from CCl_4. M.p. 157–159 °C, yield 51%.

Analysis. Found: C, 33.20; H, 3.79; Cl, 33.03; Te, 29.01. $C_{12}H_{18}Cl_4Te$ calc.: C, 33.56; H, 4.16; Cl, 32.89; Te, 29.62%. ^{1}H-NMR ($CDCl_3$): δ 1.6 (8H, m); 2.4 (4H, m); 2.84 (2H, m); 4.5 (4H, m). ^{13}C-NMR ($CDCl_3$); δ 20.38 (C5,C5′); 27.68 (C6,C6′); 37.27 (C4,C4′); 44.16 (C1,C1′); 57.04 (C3,C3′); 75.56 (C2,C2′).

Expulsion of $TeCl_4$ from the addition product (μ-2,2′-dichlorotellyl-3,3′-dichloro)bicyclohexane(I)

1. Na_2S. Compound *I* (0.01 mole) was added to molten (0.03 *M*) $Na_2S \cdot 9H_2O$ and the mixture was stirred for 20 min. The yellow solid formed was washed with water and the aqueous phase was extracted with $CHCl_3$. Evaporation of the $CHCl_3$ and distillation of the remaining liquid at 50 °C/0.2 mmHg gave 2,2′-bicyclohexene.

2. KI in acetone. A mixture of I (0.01 mole) and KI (excess) in acetone was stirred for 1 h at room temperature during which the solution turned purple (formation of I_2). After evaporation of the solvent and washing of the residue with $CHCl_3$, the remaining liquid was distilled at 52 °C/0.2 mmHg and shown to be 2,2′-bicyclohexene.

3. 1 *N* NaOH. Compound I was stirred with an excess of 1 *N* NaOH for 2 h. Distillation gave 2,2′-bicyclohexene.

4-Trichlorotellurio-5-chlorocyclohexene

A mixture of 0.8 g (0.01 mole) of 1,4-cyclohexadiene and 2.7 g (0.01 mole) of $TeCl_4$ in 20 ml of dry $CHCl_3$ was stirred at room temperature for 1 h. Evaporation of the solvent and recrystallization of the residue from CCl_4 gave white crystals. M.p. 82–85 °C, yield 49%.

^{1}H-NMR ($CDCl_3$): δ 3.0 (4H, m); 5.08 (2H, m); 5.9 (2H, m). ^{13}C-NMR ($CDCl_3$): δ 28.21 (C-6); 37.02 (C-3); 58.79 (C-5), 78.40 (C-4), 123.97 (C-1); 126.10 (C-2).

Reaction between 2,2′-bicyclopentene and $TeCl_4$

A mixture of 1.63 g (1.3×10^{-2} mole) of 2,2′-bicyclopentene and 3.2 g (1.2×10^{-2} mole) of $TeCl_4$ in 25 ml of dry $CHCl_3$ was stirred for 3 h at room temperature. Evaporation of the solvent left a white solid, which was recrystallized from CCl_4, m.p. 116–120 °C, yield 57%. Analysis. Found: C, 29.71; H, 3.46; Cl, 34.99; Te, 31.73. $C_{10}H_{14}TeCl_4$ calc.: C, 29.70; H, 3.46; Cl, 35.14; Te, 31.68%. ^{13}C-NMR ($CDCl_3$): δ 28.49 (C5, C5′); 36.67 (C4, C4′); 58.92 (C1, C1′); 59.72 (C3, C3′); 77.43 (C2, C2′).

Dichlorocyclohexene (4 isomers)

To a solution of 0.01 mole of 1,3-cyclohexadiene in 20 ml of $CHCl_3$ was added 0.01 mole of $TeCl_4$. The solution turned black (precipitation of Te^0). It was stirred at room temperature for 4 h then filtered to remove the inorganic products. The products in the filtrate were separated by GLC (XE60 7–8% on chrom. w at 100 °C) and 4 isomers were isolated.

Melting points and ^1H NMR data were in accord with those in the literature [23].

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