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AN OLEFIN INVERSION VIA *cis*-CHLOROTELLURATION-*trans*-DECHLOROTELLURATION

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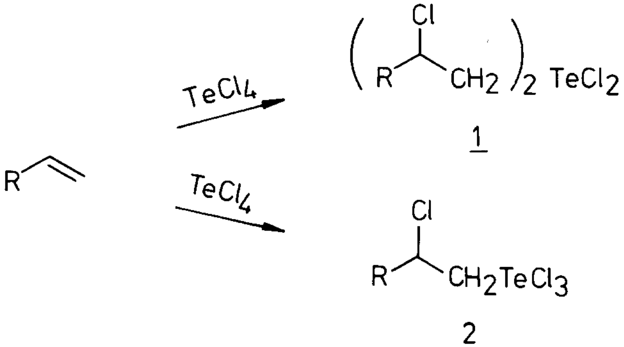
Summary: Tellurium tetrachloride addition to olefins, followed by treatment of the 2-chloroalkyltellurium trichloride adduct with aqueous Na_2S, results in separation of elemental tellurium and formation of the inverted olefin.

The addition of one mole of tellurium tetrachloride to two moles of an alkene is known to produce a bis(2-chloroalkyl)tellurium dichloride (1).[1,2] Equimolar quantities of alkene and tellurium tetrachloride similarly yield a 2-chloroalkyltellurium trichloride (2).[1,3] Very little work has been aimed at elucidating the mechanism of these reactions[4] and to our knowledge their steric course is unknown.



During work on the mechanism of chlorotelluration of olefins we observed that 1:1 adducts 2 are readily reduced by sodium sulfide to yield olefin and elemental tellurium. It occurred to us that a chlorotelluration-reduction sequence might constitute an olefin inversion reaction, provided the addition and elimination reactions have opposite stereochemistry. We therefore studied the stereochemistry of the addition-elimination and now report that olefins may be inverted in a one-pot procedure by a *cis*-chlorotelluration-*trans*-dechlorotelluration sequence.

Reaction of the appropriate alkene with one equivalent of $TeCl_4$ in chloroform or acetonitrile gave a 2-chloroalkyltellurium trichloride adduct in high yield. Reduction of this adduct with

Table 1. Olefin Inversion *via* chlorotelluration-Na_2S-reduction[a]

Reactant	solvent[b]	adduct	product[c] *E*:*Z*
E-1-deuterio-1-decene	$CHCl_3$	3b	15:85[d]
"-	CH_3CN	"	26:74
Z-2-butene	$CHCl_3$	3c	25:75
"-	CH_3CN	"	81:19
E-2-butene	$CHCl_3$	"	13:87
"-	$CHCl_3$[e]	"	20:80
"-	CH_3CN	"	3:97

a. Unless otherwise noted the chlorotelluration was performed at 0°C.

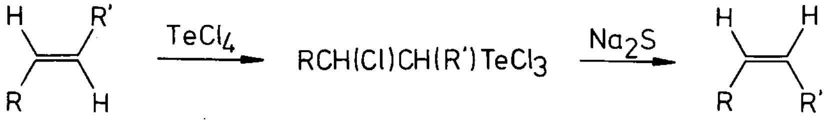
b. All sovents used in the chlorotelluration were dried by conventional methods.

c. Absolute yields of recovered olefin were determined only for the 1-decene case and were > 80 %. Analyses of the product 2-butenes were carried out with a 15' x 1/8" column packed with 15 % dimethylsulfolane on Gaschrom RZ 60/80 mesh.

d. For some unknown reason these experiments sometimes yielded a lower stereoselectivity, with *E*:*Z* as high as 40:60.

e. Chlorotelluration performed at 25°C.

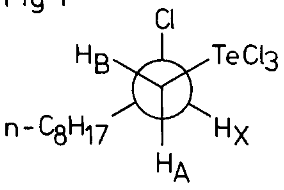
aqueous Na_2S resulted in immediate separation of elemental tellurium and formation of the starting alkene as a mixture of *E*-*Z* isomers. The product alkene mixture was analyzed by glc or by NMR to give the *E*:*Z* ratio. Stereochemical results from reaction of some alkenes are given in Table 1. In most cases studied, an inversion of the olefin predominates, but there are considerable variations depending on the solvent and the substrate used. In a typical procedure, *E*-2-butene (38 mg) was added to a solution of $TeCl_4$ (220 mg, freshly sublimed) in acetonitrile (5 ml) in a 2-necked 25 ml flask. The mixture was stirred for 3 hours at 0°C, evaporated at room temperature under *vacuo* and the flask fitted with a septum and a dropping funnel containing $Na_2S \cdot 9H_2O$ (10 ml of a 14 % aqueous solution). The pressure was lowered in the flask and the Na_2S solution introduced dropwise, producing an evolution of gas and a precipitation of elemental tellurium. Analysis of the gaseous 2-butene by glc showed that the ratio *Z*:*E* was 97:3.



3a $R = n\text{-}C_8H_{17}, R' = H$
b $R = n\text{-}C_8H_{17}, R' = D$
c $R = CH_3, R' = CH_3$

In order to gain some insight into the mechanism of the reaction we isolated the adduct 3b from chlorotelluration of *E*-1-deuterio-1-decene.[5] NMR analysis of the adduct 3a from undeuterated 1-decene showed that the terminal methylene group (H_A, H_B) gives an AB part

Fig 1



3a

NMR-data for 3a ($CDCl_3$)

$\delta_A = 4.42$, $\delta_B = 4.62$

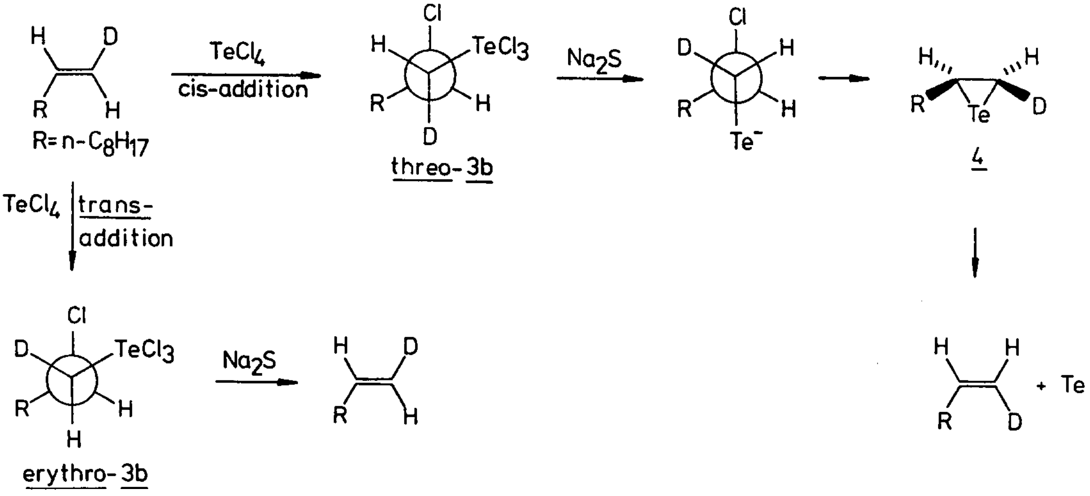
$\delta_X = 5.08$ ppm

$J_{AB} = 11.1$, $J_{AX} = 4.9$

$J_{BX} = 10.4$ Hz

of an ABX system, with one small (J_{AX} = 4.9 Hz) and one large (J_{BX} = 10.4 Hz) vicinal coupling constant. These values[6] are consistent with the expected conformation in which the $TeCl_3$-moiety is *gauche* to the chlorine atom but *anti* to the alkyl group. The electron rich β-chlorine atom is probably loosely coordinated in solution to the electron deficient tellurium atom, a phenomenon previously observed for the oxygen atom in 8-ethoxy-4-cyclooctenyltellurium trichloride in the solid state.[7] Thus we have made the assignment of terminal protons of 3a as shown in fig 1. The proton NMR-spectrum of the adduct 3b from $TeCl_4$-addition to *E*-1-deuterio-1-decene in chloroform showed two doublets appearing at δ = 4.62 ppm (J = 10.4 Hz) and 4.42 ppm (J = 4.9 Hz) with a relative area of 85:15, indicating a ratio *threo:erythro*-3b of 85:15. Thus there is a predominant *cis*-addition in the $TeCl_4$-addition to this olefin. The reduction of the 85/15 mixture of *threo*- and *erythro*-3b by Na_2S gave a 85/15 mixture of *Z*- and *E*-1-deuterio-1-decene in accordance with a completely stereospecific *trans*-elimination via an epitelluride 4. Epitellurides have previously been postulated as intermediates in similar reactions.[7,8]

Scheme 1



A reasonable explanation of the stereochemical results in Table 1 is that there is a competition between two reaction mechanisms in the chlorotelluration; one conventional *trans*-addition due to electrophilic attack of $TeCl_3^+/Cl^-$ to the alkene and one concerted [2+2] *cis*-addition of tellurium and coordinated chloride to the double bond (Scheme 1).[9] Radicals may also be involved in some of the additions. A study on the mechanism of $TeCl_4$ addition to olefins will be presented in a forthcoming publication.[10]

Numerous procedures have been reported for inversion of olefins.[11] The one described here is a simple, mild one-pot procedure involving a *cis*-addition of $TeCl_4$ followed by a Na_2S-induced *trans*-elimination. We are presently trying to change the reaction conditions in order to increase the stereospecificity of the reaction and we also wish to test it on a wider range of substrates to evaluate its scope and limitations.

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