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SODIUM HYDROGEN TELLURIDE AS A USEFUL NUCLEOPHILIC REAGENT FOR THE CLEAVAGE OF EPOXIDES AND OF QUATERNARY AMMONIUM SALTS

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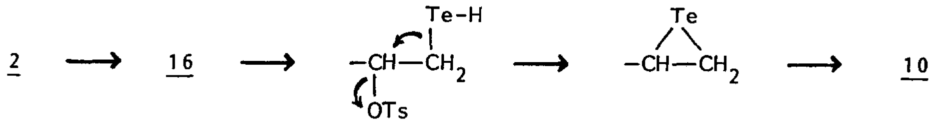
Abstract.- Sodium hydrogen telluride opens many epoxides cleanly by an SN_2 *process to give telluro-alcohols, which by reduction with nickel boride afford alcohols. An intermediate telluro-alcohol was converted to olefin in high yield by treatment with p-toluenesulphonyl chloride in pyridine. Quaternary ammonium salt are also cleaved efficiently by sodium hydrogen telluride.*

Sodium hydrogen telluride, which is easily prepared,[1] is a useful reducing agent in organic synthesis.[2,3] The mechanisms by which this reagent reduces organic compounds appears to be by electron transfer[3,4,5] or by the formation of a carbon-tellurium bond.[6] We now report two useful reactions with this reagent where the products contain a well-defined carbon-tellurium bond.

We find that the addition of many 1,2-epoxides to solution of sodium hydrogen telluride in ethanol under reflux gives high yields of telluro-alcohols with a regiospecificity corresponding to an SN_2 opening. After destruction of the excess reductant with 1,2-dibromoethane,[5] treatment with nickel boride[7] at room temperature removes all tellurium very smoothly and affords the expected alcohols contaminated with (for secondary alcohols) a small amount of the corresponding ketone. Oxidation with pyridine dichromate converted the secondary alcohols quantitatively to ketones. Some results are shown in Table 1.

The intermediate telluro-alcohols do not eliminate tellurium spontaneously and do not evolve into tellurium free products without treatment with nickel boride. Before reaction with the nickel boride ketones are not present, so they are formed in the detelluration step.

The formation of telluro-alcohols in good yield also permits a new and high yielding conversion of epoxide into olefin. Thus treatment of the telluro-alcohol 16, obtained from the epoxide 2, after removal of tellurium by filtration and of ethanol by evaporation, with pyridine (deoxygenated) and toluene-p-sulphonyl chloride (2.3 equiv.) gives the olefin 10 nearly quantitatively (92%). The mechanism of olefin formation is probably as shown in Scheme 1.



Scheme 1

The spontaneous conversion of epi-telluride into olefin is already a known reaction.[8]

Sodium hydrogen telluride is also an efficient reagent for the dealkylation of quaternary ammonium salts. It is used in the same way as for epoxide opening. Examples are given in Table 2.

Table 1

Epoxide	Procedure	Alcohol (%)	Ketone (%)
1	A	6 (75)	8 (13)
	B		8 (88)
2	A	7 (78)	9 (11)
	B		9 (89)
3	A	11 (74)	12 (12)
	B		12 (86)
4	A	13 (99)	—
5	A	14 (77)	15 (13)
	B		15 (90)

Procedure A: After opening of the epoxide with sodium hydrogen telluride and treatment with nickel boride. Composition analysed by N.M.R.
Procedure B: Ketone obtained after oxidation of total product isolated as under A.

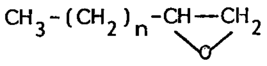
Table 2

Quaternary Ammonium	Tertiary Amine (%)	Tellurol
17	—	$PhCH_2TeH$[a]
17	—	$PhCH_2TeH$[b]
18	$PhNMe_2$ (97)	—
19	—	MeTeH[c]
20	24 (94)	—
21	25 (96)	—
22	26 (94)	
23	DesMe 23 (87)	

a) Characterised by air oxidation to $(PhCH_2Te)_2$ (88%).
b) Characterised by Nickel Boride reduction to toluene (97%).
c) Characterised by air oxidation to $(MeTeO)_2O$ (83%).

We also showed that trimethylsulphonium iodide was smoothly reduced to Me_2S and MeTeH (characterised as $(MeTeO)_2O$).

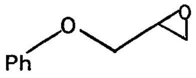
These results show that the reaction with onium salts is a normal SN_2 reaction. This process complements very well the classical Emde cleavage of quaternary ammonium salts[9] and has the advantage that the two cleavage products have functionality. It is also easier to carry out experimentally.



$CH_3\text{-}(CH_2)_n\text{-}CH\text{—}CH_2$

1 n = 5

2 n = 15



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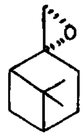

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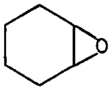

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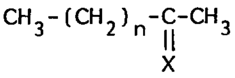


$CH_3\text{-}(CH_2)_n\text{-}\underset{\underset{X}{\|}}{C}\text{-}CH_3$

6 n = 5 , X = H, OH

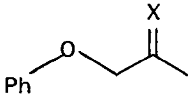
7 n = 15, X = H, OH

8 n = 5 , X = O

9 n = 15, X = O

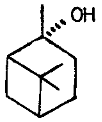
$CH_3\text{-}(CH_2)_{15}\text{-}CH{=}CH_2$

10



11 X = H, OH

12 X = O



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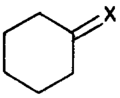
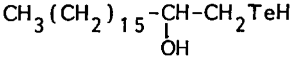


14 X = H, OH

15 X = O



$CH_3(CH_2)_{15}\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_2TeH$

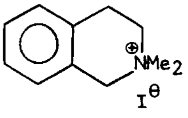
16

$R\text{-}N^{\oplus}Me_3$

17 R = $PhCH_2$, $OH^{\ominus}$

18 R = Ph, $I^{\ominus}$

19 R = Me, $OH^{\ominus}$



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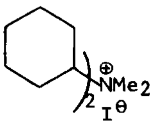

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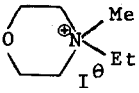

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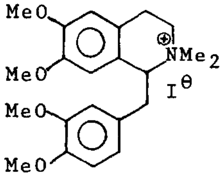

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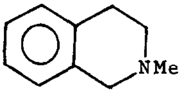

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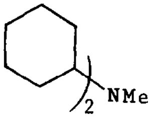

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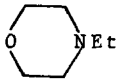

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