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USE OF SODIUM HYDROGEN TELLURIDE IN ORGANIC SYNTHESIS

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The utility of sodium hydrogen telluride for various synthetic purposes and the mechanistic variations observed are discussed.

TELLURIUM reagents find increasing uses in Organic Synthesis. Among these, sodium hydrogen telluride has proven to be a selective reagent for the reduction of a wide variety of organic molecules. Sodium hydrogen telluride was originally prepared by Klayman and Griffin[1] in water and later by Barton *et al.*[2] in ethanol medium. Its utility as a reducing agent was first recognised serendipitously (1978) by Shanmugam *et al.*[3] who have found it to be a very convenient reagent for the hydrogenation of 3-vinylquinolines (*1*) as well as cinnamic acid derivatives (*3*) (Fig. 1). A similar application was later (1980) reported by Yamashita *et al.*[4] (Fig. 2). The reducing action of the reagent has been shown recently by Barton

$$X = Cl \text{ or } OH$$

$$C_6H_5-CH=CH-COX \xrightarrow{HTe^-} C_6H_5-CH_2-CH_2-COX$$

$$\underline{3} \qquad\qquad\qquad \underline{4}$$
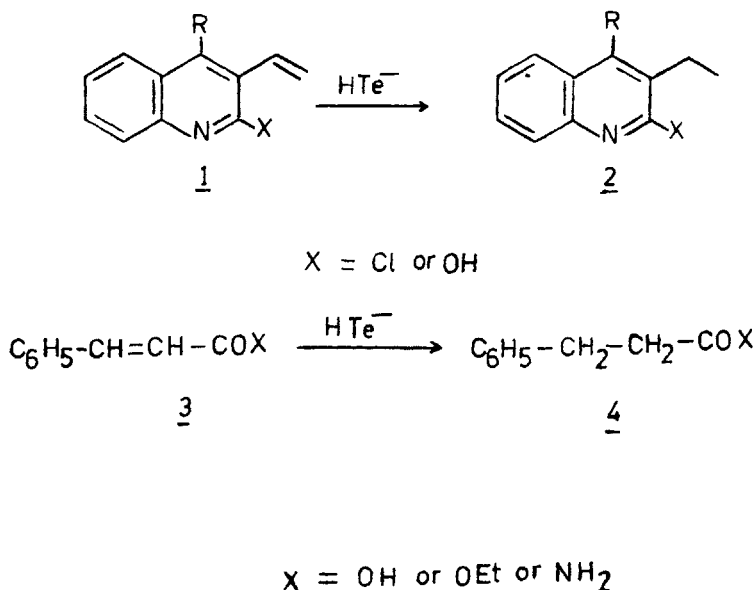
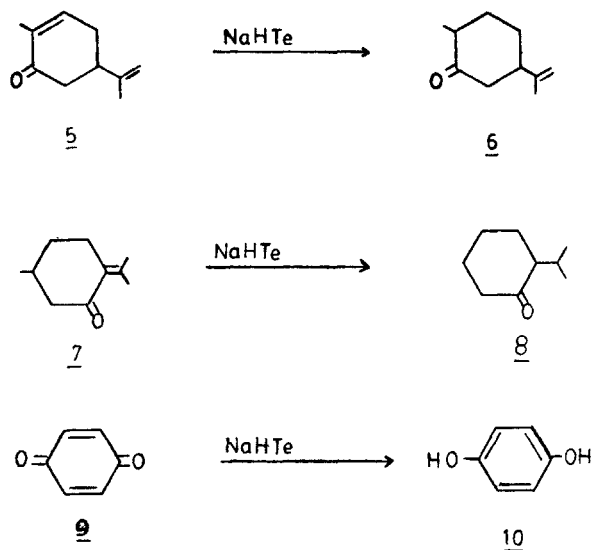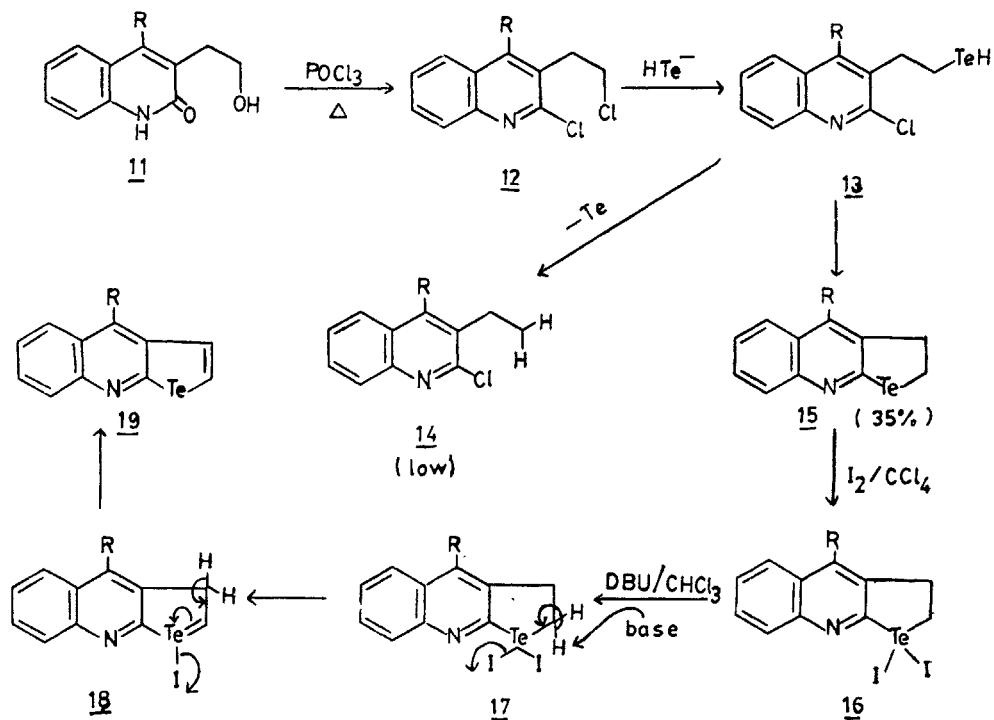$$X = OH \text{ or } OEt \text{ or } NH_2$$

FIG 1

FIG 2

FIG 3

et al.[5] to operate in four different methanistic ways. They include : (*i*) a nucleo-philic reaction; (*ii*) a hydride transfer; (*iii*) a hydrogen atom transfer; and (*iv*) an electron transfer.

FORMATION OF CARBON-TELLURIUM BOND

A typical example[6] of the first category of the mechanisms is the synthesis of telluroloquinoline systems (Fig. 3).

Another example[7] of the carbon-tellurium bond formation is the transforma-tion of cholest-5-en-3β-yloxy (Phenylmethylene) dimethylammonium chloride *20* to its benzyl ether *26* when treated with sodium hydrogen telluride (Fig. 4). Other examples in which the carbon-tellurium bond formation occurs are (*i*) reaction[8] of epoxide *27* with sodium hydrogen telluride : the telluro alcohol *28* formed by the nucleophilic opening of the epoxide, when treated with nickel boride gave an alcohol *29*, while treatment with tosylchloride and pyridine gave the olefin *32* (Fig. 5).
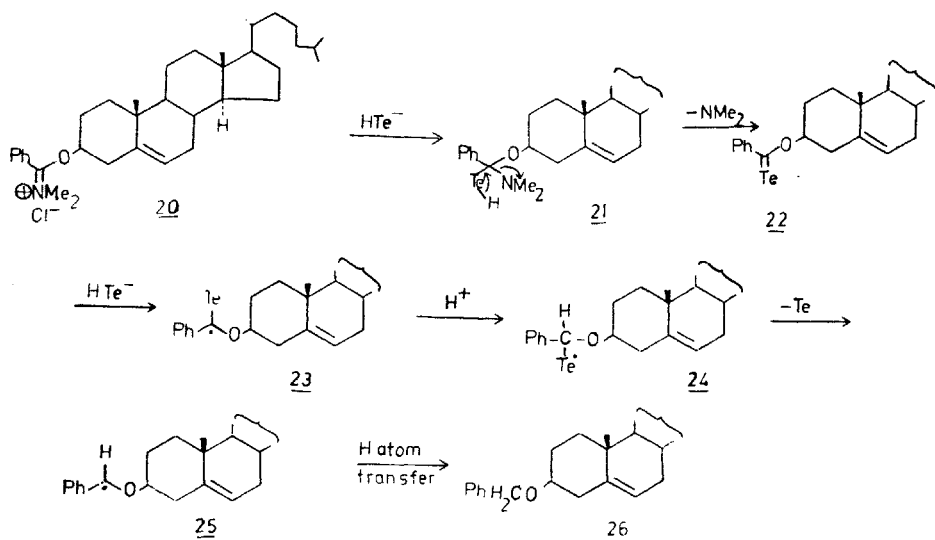

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Reduction of Immonium Salts

Immonium salts *33* were reduced[9] to their dihydro derivatives *35* when treated with sodium hydrogen telluride (Fig. 6).

Reduction of Nitrones

Nitrones *36* were reduced[10] to imines *39* with the reagent under basic pH (Fig. 7).
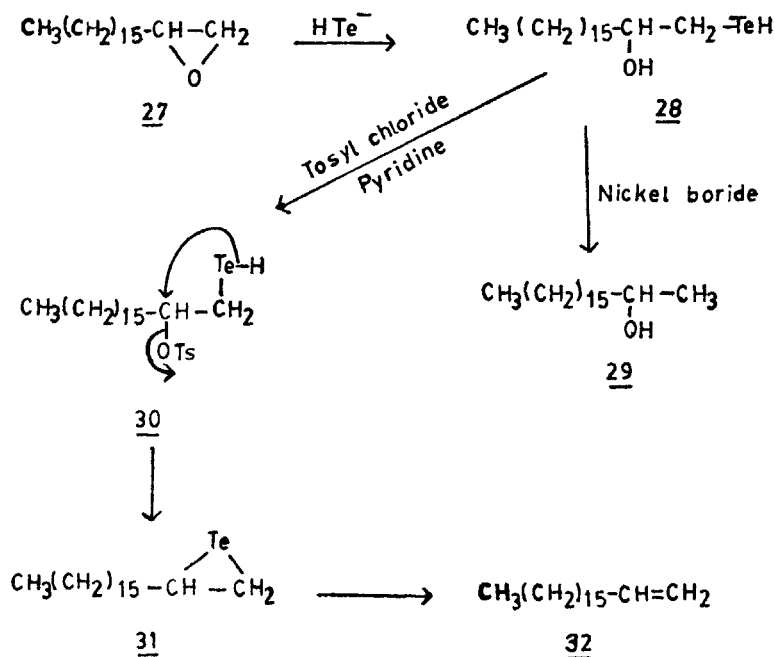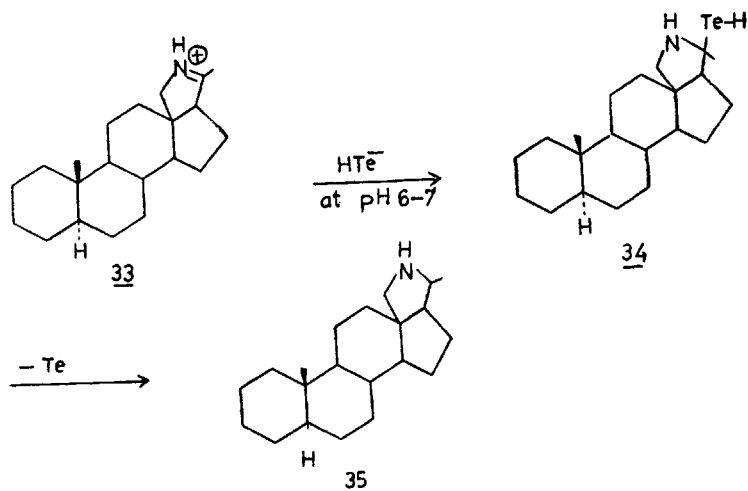
FIG 5

FIG 6

Reduction of α, β-epoxy ketones to β-hydroxyketones

Suzuki *et al.*[11] utilised the titled reagent for the reduction of α, β-epoxy ketones *40* to β-hydroxyketones *43*. This reaction also involves a nucleophilic ring opening of the epoxide (Fig. 8).
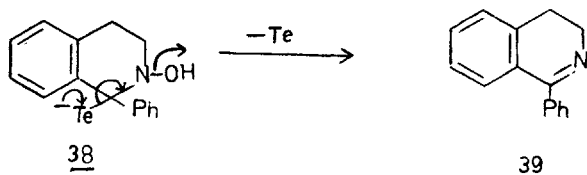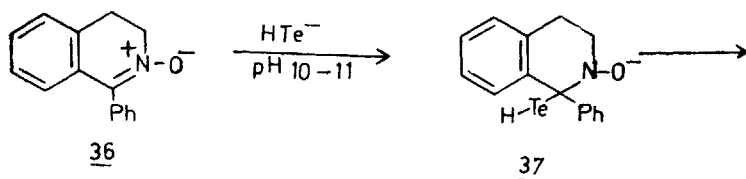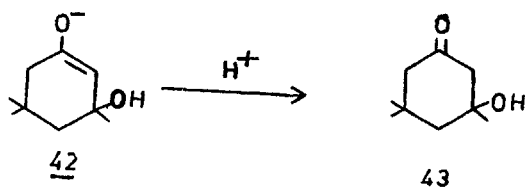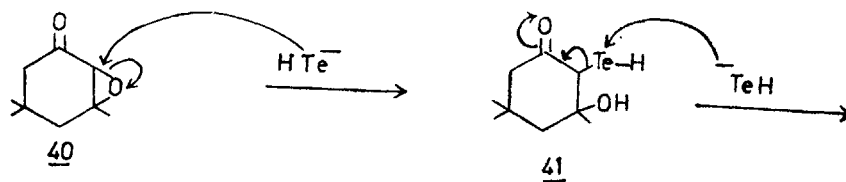
FIG 7

FIG 8

Hydrogenolysis[12] of α-halocarbonyl compounds *44* is another reaction which is presumed to proceed through a nucleophilic reaction (Fig. 9).

HYDRIDE TRANSFER REACTION

Reduction of double bonds conjugated with a carbonyl group by sodium hydrogen telluride falls into this category. An example[13] is the reduction of flavones *46* to flavanones *47*. No reagent which has general applicability has hitherto been reported for this conversion. Flavones *46* when treated with sodium hydrogen telluride underwent reduction of the C_2-C_3 bond to give the corresponding flavanones *47* (Insert Fig. 10 and 11).
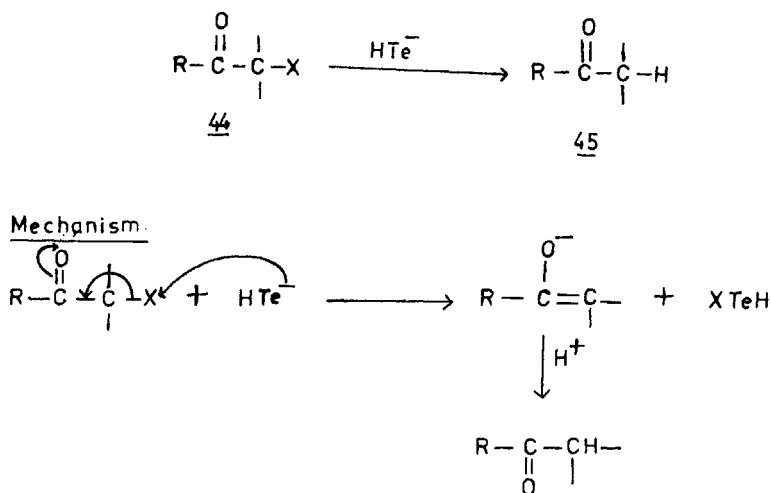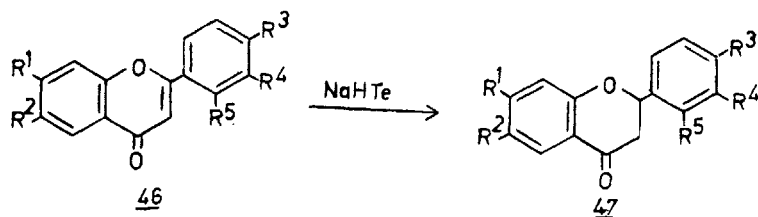
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle |}{}}{\underset{|}{C}}-X \quad \xrightarrow{\;HTe^{-}\;} \quad R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle |}{}}{\underset{|}{C}}-H$$

$$\underset{\underline{44}}{} \qquad\qquad\qquad\qquad\qquad \underset{\underline{45}}{}$$

Mechanism.

$$R-\overset{\overset{\displaystyle O}{\|}}{C} \overset{\frown}{\longleftarrow} \overset{+}{\underset{|}{C}} \overset{\frown}{\smile} X \quad + \quad H Te^{-} \quad \longrightarrow \quad R-\overset{\overset{\displaystyle O^{-}}{|}}{C} = \overset{}{\underset{|}{C}}- \quad + \quad XTeH$$

$$\Big\downarrow H^{+}$$

$$R-\overset{}{\underset{\overset{\displaystyle \|}{O}}{C}}-\overset{}{\underset{|}{C}}H-$$

FIG 9

(a) : $R^1 = R^2 = R^3 = R^4 = R^5 = H.$

(b) : $R^1 = OCH_3, R^2 = R^3 = R^4 R^5 = H.$

(c) : $R^1 = R^3 = R^4 = R^5 = H, R^2 = OCH_3.$

(d) : $R^1 = R^2 = R^4 = R^5 = H, R^3 = OCH_3.$

(e) : $R^1 = R^2 - R^5 = H, R^3 = R^4 = OCH_3.$

(f) : $R^1 = R^2 = R^5 = H, R^3 = R^4 = -OCH_2-O-$

(g) : $R^2 = R^5 = H, R^1 = R^3 = R^4 = OCH_3.$

(h) : $R^1 = R^2 = R^3 = H, R^4 = R^5 = OCH_3.$

FIG 10

HYDROGEN ATOM TRANSFER REACTION

Reduction of double bonds conjugated with an aromatic ring is an example of hydrogen atom transfer reaction. The fact that the titled reagent reduces only conjugated double bonds and not isolated ones is made use of in the distinction[14] between 3-vinylquinolones *49* and 3-prenylquinolones *50* that are obtained as intermediates, in the synthesis of atanine and its analogues. In the case of 3-vinylquinolones *49* the radical formed by hydrogen atom addition is stabilised by resonance whereas no such stabilisation is possible in 3-prenylquinolones *50* (Fig. 12).
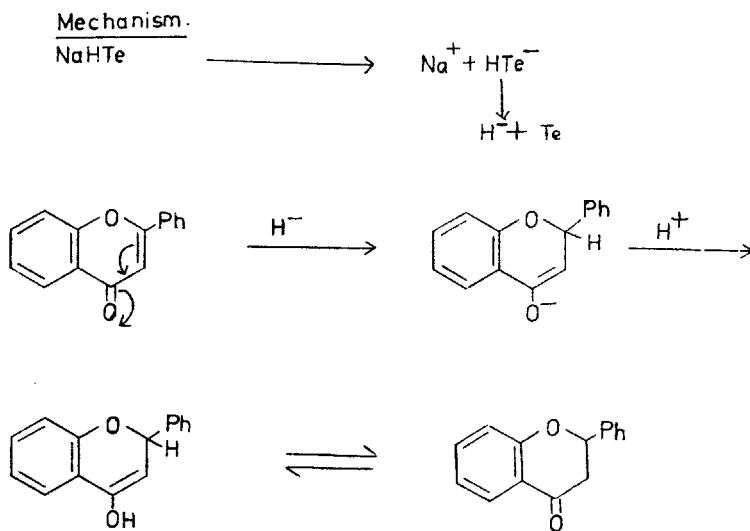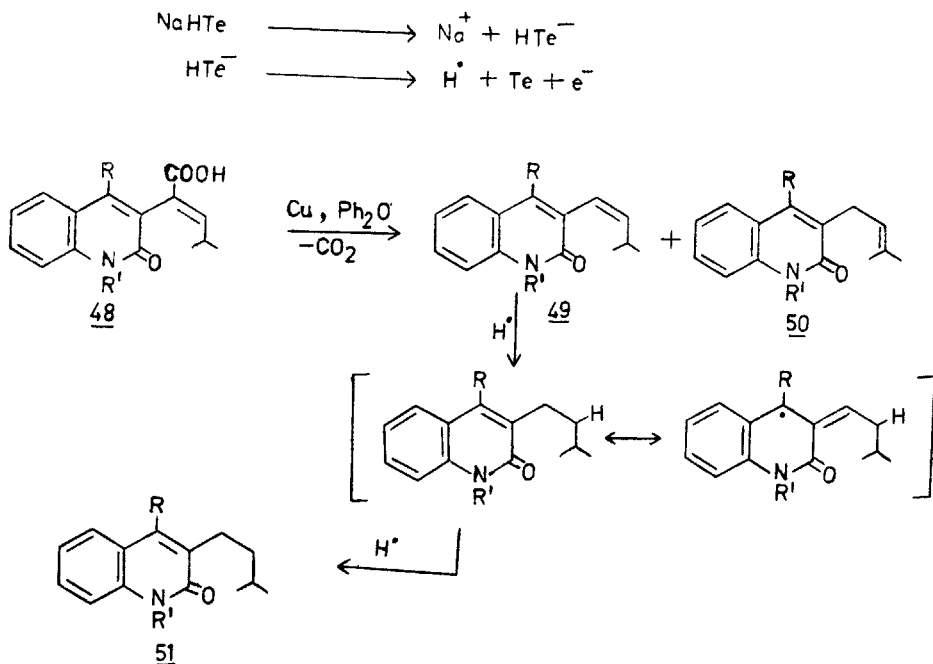
Mechanism.

NaHTe $\longrightarrow$ Na$^+$ + HTe$^-$

$\downarrow$

H$^+$ + Te

FIG 11

NaHTe $\longrightarrow$ Na$^+$ + HTe$^-$

HTe$^-$ $\longrightarrow$ H$^\cdot$ + Te + e$^-$

FIG 12

Another example of this type of reaction is the reductive amination[15] of carbonyl compounds *52*. Here Schiff's base *53* is thought to be an intermediate, which then undergoes hydrogen atom abstraction (Fig. 13).

$$HTe^- \longrightarrow H^\cdot + Te + e^-$$

52   53

54

FIG 13

55   56

57   58

No reaction

59   60   61
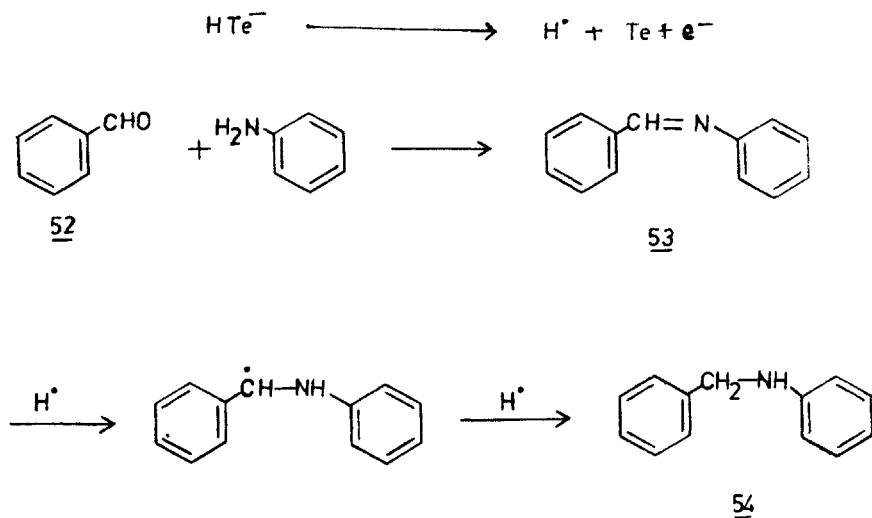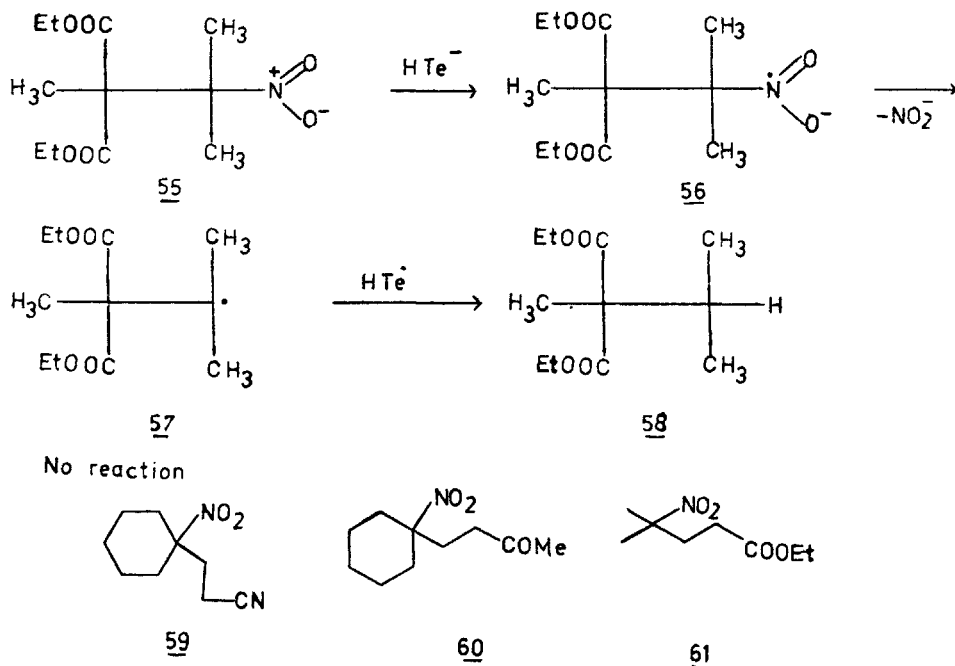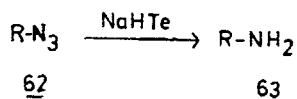
FIG 14

ELECTRON TRANSFER REACTIONS

A typical example of this type is the displacement[16] of tertiary nitro groups by hydrogen. The mechanism involves an one electron transfer to the nitro compound 55 from sodium hydrogen telluride and subsequent detachment of the

nitrite anion from the resulting nitro compound anion radical *56*. Tertiary nitro groups at α or β position of a ketone or ester were found to be readily displaced, while those situated or γ-position of ketone, ester or nitrile e.g., *59* to *61* remained inert to sodium hydrogen telluride treatment (Fig. 14).

Another example of this type of reaction is the reduction of alkyl, aryl azide[17] *62* to amines *63* and azidoketones[18] to aminoketones (Fig. 15).

$$R\text{-}N_3 \xrightarrow{\text{NaHTe}} R\text{-}NH_2$$

$$\underline{62} \qquad\qquad \underline{63}$$

Mechanism

$$TeH^- \longrightarrow TeH^{\cdot} + e^-$$

$$\left[R - N \overset{+}{=} \overset{+}{N} = \bar{N} \longleftrightarrow R - \bar{N} - \overset{+}{N} \equiv N \right] \xrightarrow{e^-} R - \bar{N} - N = N^{\cdot}$$

$$\downarrow H^+$$

$$R\text{-}\overset{\cdot}{N}H + N_2 \longleftarrow R - NH\text{-}N\equiv N$$

$$\downarrow H\overset{\cdot}{T}e$$

$$R\ NH_2 + Te$$
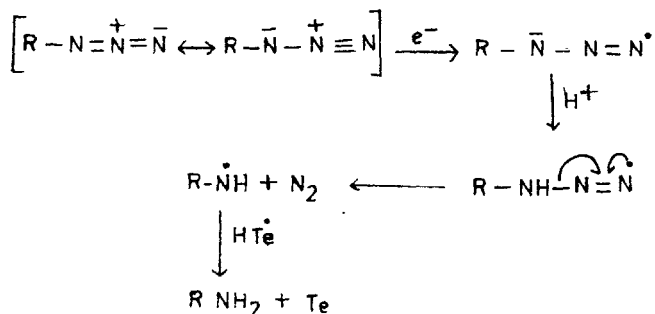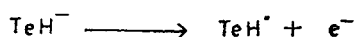
<div align="center">FIG 15</div>
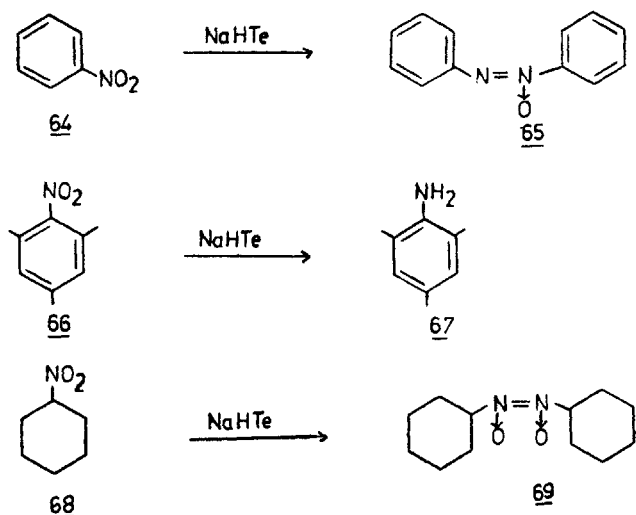

<div align="center">FIG 16</div>

Reduction of aromatic and aliphatic nitro compounds reported by Suzuki *et al.*[19] also belongs to this class. He found that unhindered nitro compounds like nitrobenzene *64* was reduced to azoxy benzene *65*, while sterically hindered nitrobenzenes *66* were reduced to anilines *67*. Nitro alkanes such as nitro cyclohexane *68* was reduced to dimer of nitroso alkane *69* (Fig. 16).
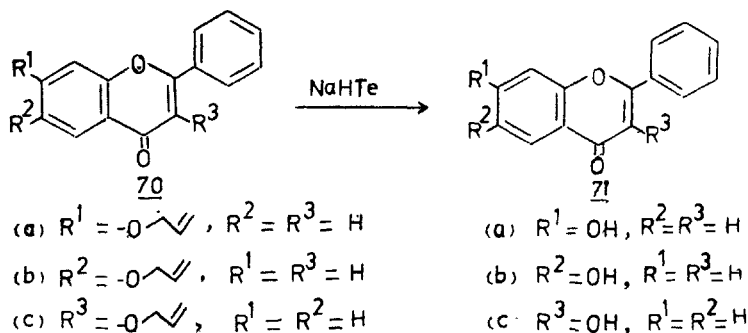
Recently, a few reactions have been accomplished using the titled reagent and they are as enumerated below:

Deallylation of Allyl Phenyl Ethers

Allyl phenyl ethers *70* were found to undergo deallylation[20] when treated with sodium hydrogen telluride even under almost neutral conditions. The mechanism is thought to involve a simultaneous electron transfer as well as hydrogen atom capture (Fig. 17). Just as the allyl ethers, the prenyl ethers *72, 74* also underwent deprenylation when treated with the reagent. This finding is considered of value in natural product chemistry for prenyloxy grouping occurs in several products isolated from the plants of retaceous family. Examples are Bucharine *76* and Ravenine *77*. (Fig. 18).

Deallylation of Allylcarboxylates

Extension of the deallylation reaction[20] to allylcarboxylates *78* proved fruitful, as they also underwent deallylation on treatment with the reagent. Here also as
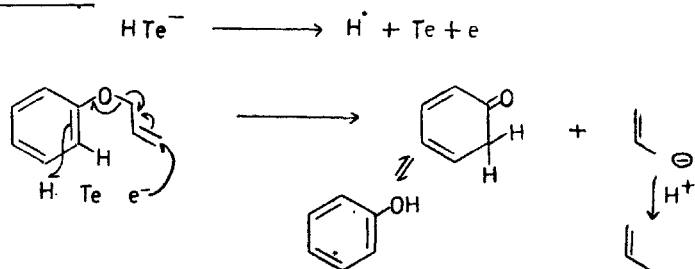

Mechanism.

$$HTe^- \longrightarrow H^\cdot + Te + e$$

Fɪɢ 17

FIG 18

(a) $R^1 = R^2 = R^3 = H$

(b) $R^1 = OMe, R^2 = R^3 = H$

(c) $R^1 = R^2 = -O-CH_2-O-, R^3 = H$

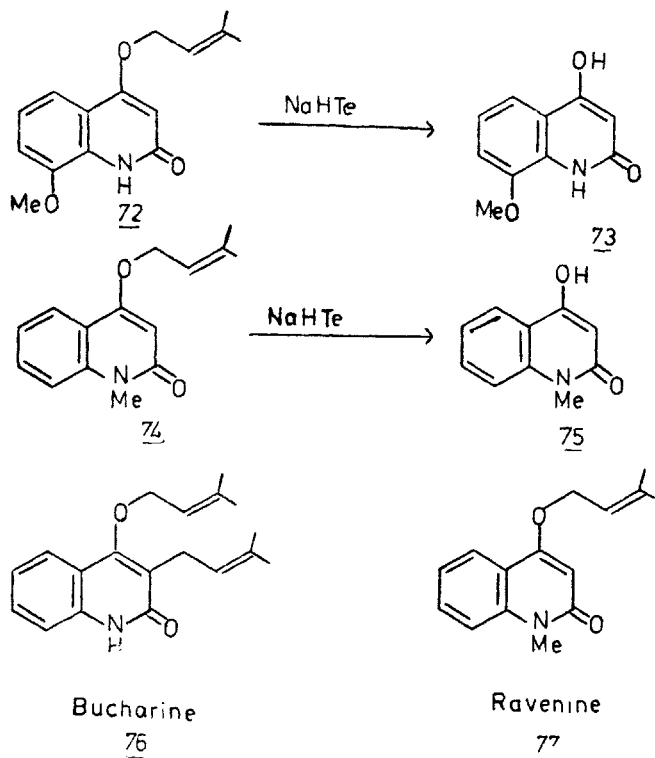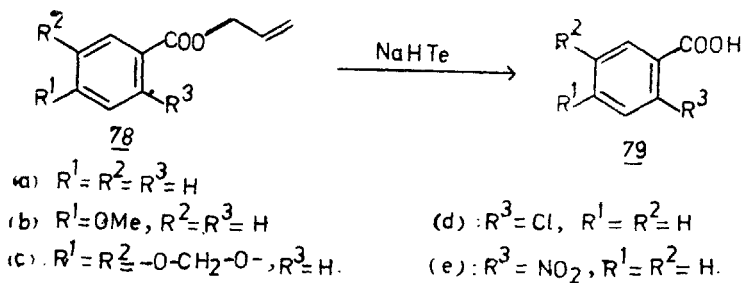(d) $R^3 = Cl, R^1 = R^2 = H$
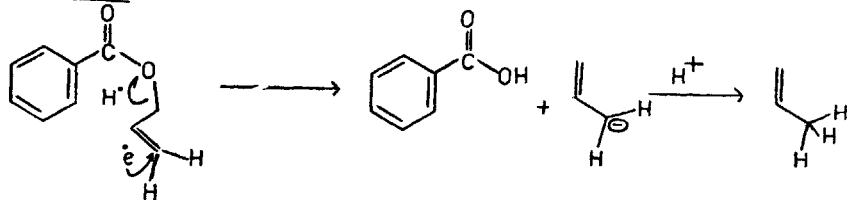
(e) $R^3 = NO_2, R^1 = R^2 = H$

Mechanism:

FIG 19

in the previous case the mechanism is thought to involve an electron transfer and a hydrogen atom capture simultaneously (Fig. 19).

Partial Deallylation of 3,3-Diallyl-1,2,3,4-tetrahydroquinolin-2,4-diones

Another important reaction that was encountered with sodium hydrogen telluride was the partial deallylation[21] of 3,3-diallyl-1,2,3,4-tetrahydroquinolin-2, 4-diones *80* to give the monoallyl-2-quinolones *81*. The mechanism is envisaged to proceed by an electron transfer from HTe⁻ (Fig. 20).

This partial deallylation reaction is considered worthwhile since prenylquinolones for example 3-prenyl-4-hydroxyquinolin-2 (*1*H) one (*81*b) as well as its derivatives have been recognised[22] as precursors both in organic synthesis and biosynthesis to a number of prenyl-, furo-, and pyrano-quinoline alkaloids (Fig. 21).

Deblocking of 2-Bromoethyl Phenyl Ethers

2-bromoethyl phenyl ethers[23] *82* when treated with the titled reagent underwent cleavage of the 2-bromoethyl grouping, giving the respective phenol *83*. The mechanism is considered to consist of an electron transfer and simultaneous halogen atom capture by TeH. (Fig. 22).
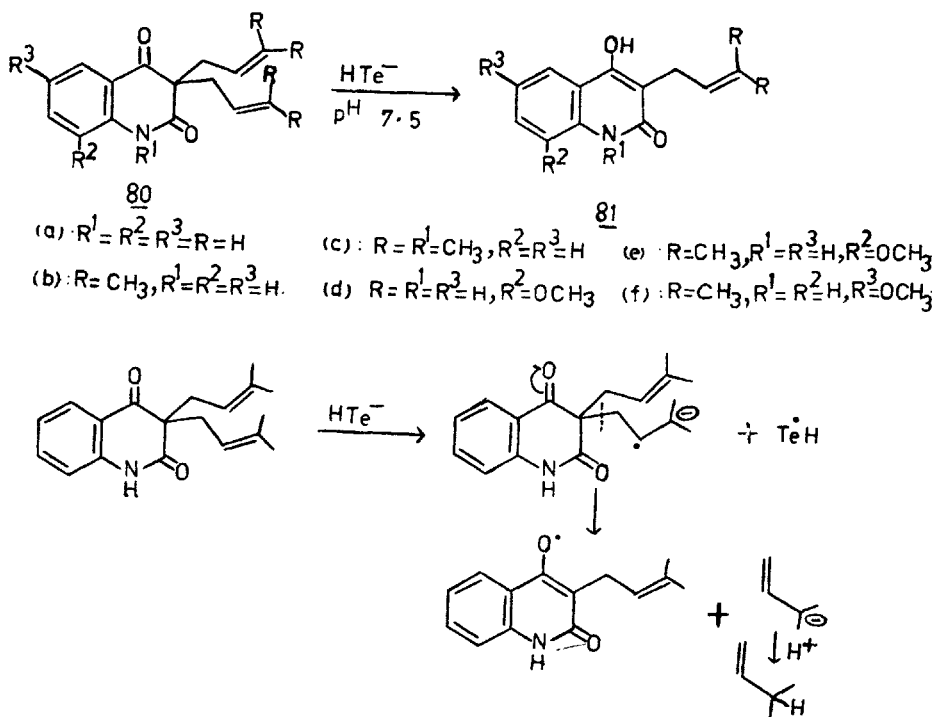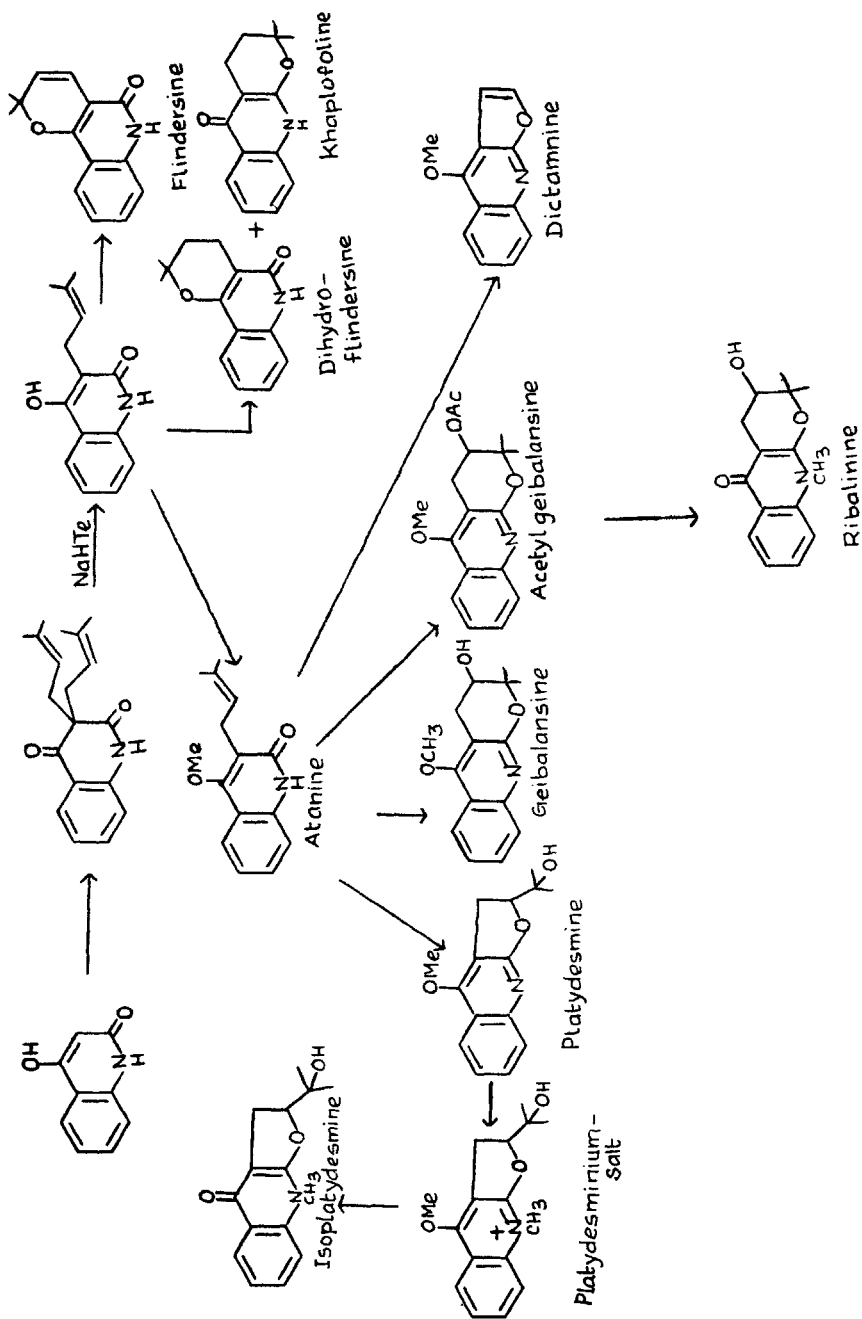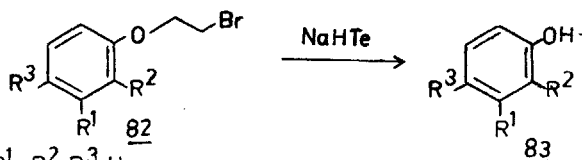

FIG 20

FIG 21
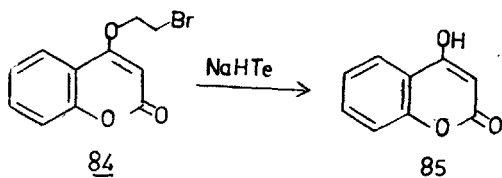
(a) $R^1 = R^2 = R^3 = H$,

(b) $R^1 = CH_3, R^2 = R^3 = H$; (c) $R^3 = CH_3, R^1 = R^2 = H$;(d) $R^2 = NO_2, R^1 = R^3 = H$;(e) $R^2 = COCH_3, R^1 = R^3 = H$.

82

83

84   85

Mechanism·

$HTe^- \longrightarrow HTe^· + e^-$

$+ HTeBr$

$\downarrow H^+$
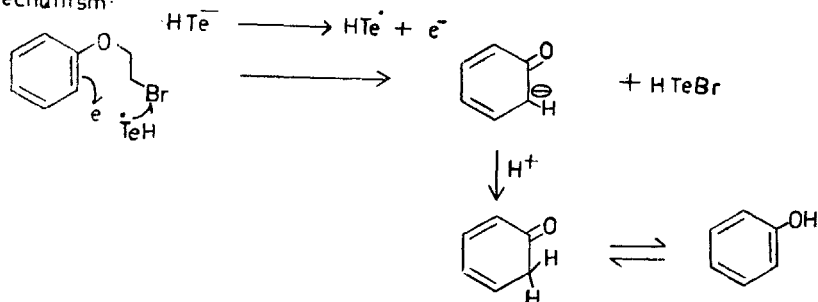
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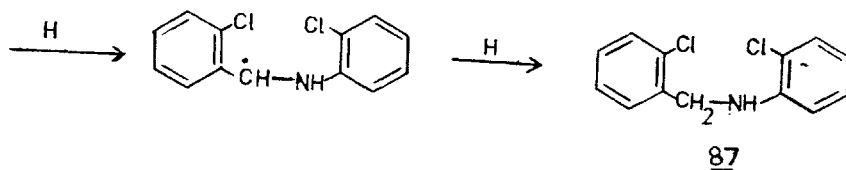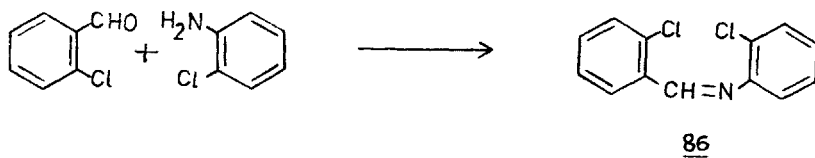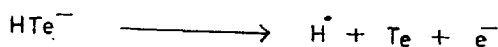
FIG 22

$HTe^- \longrightarrow H^· + Te + e^-$

86

87

FIG 23

Reduction of Schiff's Base

Shiff's base *86* formed from aniline and O-chlorobenzaldehyde was found to undergo reduction[24] giving the secondary amine *87* on treatment with the reagent (Fig. 23).

Here the reaction is thought to proceed by hydrogen atom transfer.

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