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THE ACTION OF SODIUM HYDROGEN TELLURIDE ON OLEFINS

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Abstract - The action of sodium hydrogen telluride, NaTeH, on non electrophilic carbon-carbon double bonds has been investigated. The reaction is found to be very sensitive to the substituents on the ethylenic linkage. Whereas phenyl conjugated olefins are reduced to alkylbenzenes, the reagent adds to isolated mono and disubstituted double bonds leading to organotellurium derivatives and with gem-disubstituted ones it leads to a mixture of reduction and addition products. These results are interpreted in terms of a radical pair mechanism involving hydrogen atom transfer from hydrogen telluride, HTe^- to the double bond.

Sodium hydrogen telluride[1] (NaTeH) has been in recent years the subject of numerous studies with the aim of exploring its synthetic potentialities. It is apparent from this work that this reagent may behave either as a nucleophile or as a reducing agent. Thus, organotellurium compounds are obtained from alkyl halides[2], epoxides[3], ammonium salts[3] and Vilsmeier salts[4], but, on the other hand, imines[5], immonium salts[5], N-oxides[6], nitrones[6] and double bonds in α,β unsaturated carbonyl compounds[7] are reduced.

Studies on the mechanisms of these reactions are scarce. It has been proposed[7b] that reduction could result from electron transfer, hydride transfer or hydrogen atom transfer. In this article we present the experimental facts and a full discussion of the various mechanisms for reduction of the olefinic bond.

The nature of the products obtained in a given reaction as a function of the substrate may provide valuable information about its mechanism.

We have recently shown[5b] that both reactivities could be observed in the action of sodium hydrogen telluride on a definite function, i.e., the reduction of imines into amines is accompanied in some cases by the addition of the reagent leading to organotellurium compounds. We are now able to show that non-electrophilic, ethylenic double bonds also react in both ways.

It is known that sodium hydrogen telluride reduces the carbon-carbon double bonds conjugated to aromatic rings[7]. On the other hand, the inertness of sodium hydrogen telluride towards the isolated double bonds has often been pointed out. However, we have found that hydrogen telluride can actually react with simple olefins, which leads to no reduction of the isolated double bond but addition of the reagent to give organotellurium derivatives. The transition from reduction to addition accordingly as the non-electrophilic double bond is conjugated to an aromatic ring or not allows us to make an approach to the mechanism of action of the reagent.

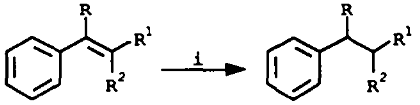
RESULTS

Carbon-carbon double bonds conjugated to an aromatic ring.

Some examples of the reduction of such double bonds by sodium hydrogen telluride have been previously reported[7b]. The reaction rate, which is slow at room temperature, becomes appreciable in refluxing ethanol and only reduction products are observed (no organotellurium compounds are obtained).

The relative rates of reduction of several styrenes are depicted in table 1. Methyl substitution on the double bond, and specially at the β position, slows down the reaction. The runs performed with the more hindered styrenes (entries 4-6) show that steric hindrance can inhibit the reaction.

Table 1



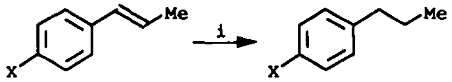
1 2

Entry	Substrate			Yield %^{a}	
	R	R^1	R^2	1	2
1	H	H	H	—	100
2	Me	H	H	—	100
3	H	Me	H	43	57
4^b	Me	(Me,H)		87^c	13
5	H	Me	Me	100	—
6	Me	Me	Me	100	—

i) NaTeH (2.5mM per mM of 1), EtOH, reflux, 2.5 h.
a) determined by ^{1}H NMR. b) 67%E, 33%Z. c) 33%E, 67%Z.

The effect of substituents in the para position of the benzene ring is shown in table 2. A moderate acceleration of the reaction for the substituted styrenes is observed regardless of whether the group is electron donating (entry 1) or electron withdrawing (entry 3). Moreover, we find little difference in rate for the reduction of the p-methoxy 3 (X= -OMe) and the p-cyano 3 (X= -C≡N) derivatives.

Table 2

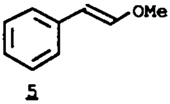


3 4

Entry	Substrate	Yield %^{a}	
	X	3	4
1	-OMe^b	30	70
2	-H^b	43	57
3	-C≡N^c	28^d	72

i) NaTeH (2.5mM per mM of 3), EtOH, reflux, 2.5h.
a) determined by NMR. b) 100%E. c) 35%E, 65%Z. d) 25%E, 75%Z.

A different reactivity is observed towards the methoxystyrenes as a function of the position of the methoxy group. Whereas the β-methoxystyrene **5** is recovered unchanged after treatment with excess of sodium hydrogen telluride in refluxing ethanol for 2.5 h, the α-methoxystyrene **6** reacts even at room temperature to give the dihydroderivative **7** (84%) as well as 12% of acetophenone **8** and 4% of unchanged **6**.



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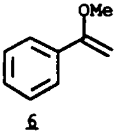

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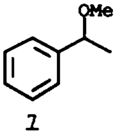

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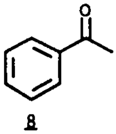

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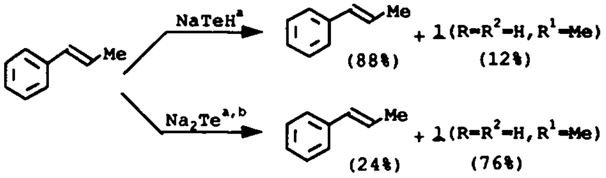
Finally, the reducing activities of sodium hydrogen telluride, NaTeH, and sodium telluride[8], Na_2Te, towards β-methylstyrene (**1**, $R{=}R^2{=}H, R^1{=}Me$) are presented in scheme 1. It shows that $Te^=$ is a less efective reducing agent in this family of reactions.

Scheme 1



a) 2.5mM per mM of β-methylstyrene (**1**, $R{=}R^2{=}H, R^1{=}Me$), EtOH, reflux, 6h.
b) obtained by addition of alkali to a solution of NaTeH.

Isolated double bonds.

It has often been pointed out that NaTeH is inert towards isolated double bonds[7a,9]. Nevertheless, simple non-hindered olefins react with NaTeH in refluxing ethanol.

Thus, from undecylenic acid **9** a mixture of secondary telluride **10**, secondary ditelluride **11** and primary ditelluride **12** is obtained (scheme 2), where the secondary derivatives **10** and **11** are predominant (ratio of secondary to primary products: 11.5/1) The reaction products have been identified as follows: a) an authentic sample of telluride **10**, which is the major product, was prepared from 10-bromoundecanoic acid **14** (scheme 2); b) the reductive detelluration of derivatives **10**-**12** with nickel boride[10] leads quantitatively to undecanoic acid **13** as the only reaction product (the use of Ni_2B as a detelluration agent is well known[3]); c) the NMR spectra are in full accord with the structures proposed.

Scheme 2

$$\underset{\mathbf{9}}{CH_2{=}CH{-}R} \xrightarrow[\text{EtOH, reflux.}]{\text{NaTeH (3eq)}} R(Me)CH{-}Te_n{-}CH(Me)R + \underset{\mathbf{12}\ (8\%)}{RCH_2{-}CH_2{-}Te_2{-}CH_2{-}CH_2R}$$

n=1, **10** (79%)
n=2, **11** (13%)

$$\downarrow \begin{array}{l} Ni_2B \\ \text{EtOH, r.t.} \end{array}$$

$$\underset{\mathbf{13}}{CH_3{-}CH_2{-}R}$$

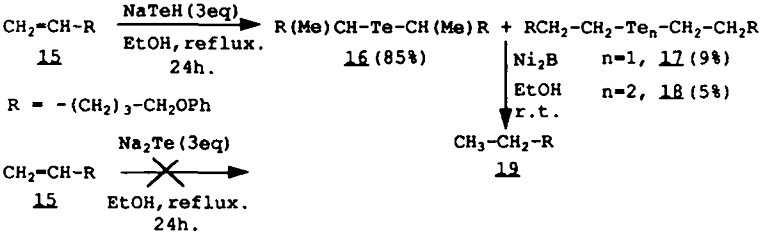
$R = -(CH_2)_8{-}CO_2H$

$$\underset{\mathbf{9}}{2CH_2{=}CH{-}R} \xrightarrow[\text{AcOH}]{\text{BrH}} \underset{\mathbf{14}}{2CH_3{-}CH(Br){-}R} \xrightarrow[\text{EtOH, r.t.}]{\text{NaTeH (1eq)}} \underset{\mathbf{10}}{R(Me)CH{-}Te{-}CH(Me)R}$$

Similarly, 6-phenoxy-1-hexene 15 leads to the organotellurium derivatives 16-18 after 24 h. of reaction in refluxing ethanol.Upon treatment of the mixture of 16-18 with Ni_2B, 1-phenoxyhexane 19 is obtained as the sole reaction product.

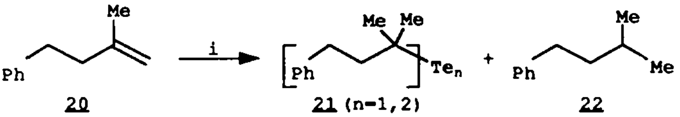
On the other hand, contrary to the conjugated double bonds (scheme 1), sodium telluride (obtained by the addition of alkali to a solution of sodium hydrogen telluride) is found to be inactive towards 15 (scheme 3).

Scheme 3



In both these cases only addition products are observed to the exclusion of the corresponding reduction products (13 and 19). In contrast, the reaction of NaTeH with 4-phenyl-2-methyl-1-butene 20 resulted in partial reduction of the carbon-carbon double bond (table 3), producing substantial quantities of isoamylbenzene 22 in addition to the organotellurium derivatives 21 (addition products).

Table 3



Entry	HTe^-/20[a]	time(h)	Yield %[b] 20	21	22
1	3/1	24	77	11	12
2	6/1	72	50	14	36

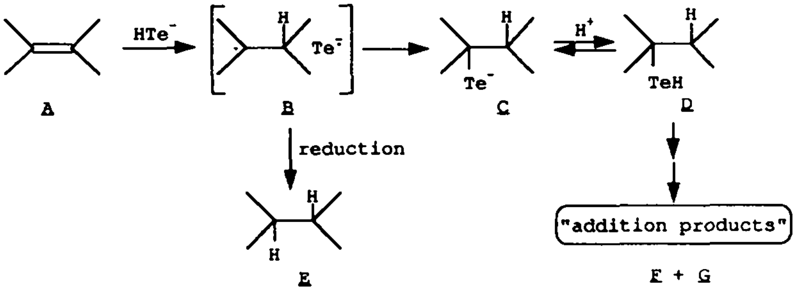
i) NaTeH, EtOH, reflux. a) molar ratio. b) determined by ^1H NMR.

COMMENTS

In the experiments described above two of the possible mechanisms of action of NaTeH may be rapidly eliminated, i.e. nucleophilic addition of hydrogen telluride, HTe^-, to the double bond and hydride transfer from HTe^- to the double bond. This is because not only an ethylenic double bond is non-electrophilic but also because an activation in that direction by protonation is not favoured at the essentially neutral pH of the reaction medium. Moreover, hydride transfer is not compatible with the acceleration in the reduction rate of styrenes (table 2) substituted in *para* by an electron donating group (-OMe). Finally, these hypotheses do not account for the transition from reduction to addition accordingly as the double bond is phenyl conjugated or not.

In consequence, the hypotheses of hydrogen atom transfer or electron transfer associated to proton transfer are to be examined. Both of which lead to the formation of radical B (scheme 4).

Scheme 4



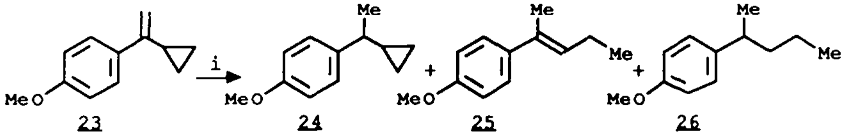
From scheme 4,an orientation of the reaction as a function of the radical B formed may be proposed. It is known that the electron affinity of a radical and consequently its reduction rate are increased when the radical center is conjugated to π bonds[11]. The formation of a benzylic radical from styrenes would therefore favour the reduction (B→E) with respect to coupling (B→C).

On the other hand, the fact that an acceleration in the rate of reduction of p-substituted styrenes is observed as well with electron donating groups as with electron withdrawing groups is in agreement with the known acceleration in the rate of formation of a more stable radical.The formation of the intermediate radical (A→B,scheme 4) being considered as the rate determining step.

The formation of a radical in the reaction of olefins with hydrogen telluride,HTe^-, is also in agreement with three observations concerning the relative reactivities of:a) α-cyclopropylstyrene 23 and β-cyclopropylstyrene 27, b) β-methoxystyrene 5 and α-methoxystyrene 6, and c) the simple monosubstituted olefins 9 and 15 and the gem-disubstituted olefin 20.

a) The treatment of α-cyclopropylstyrene 23 with ethanolic NaTeH(2.5mM per mM of 23) under reflux gives a mixture of products 24, 25 and 26 (table 4), where the last two arise from the opening of the cyclopropyl group.

Table 4



Entry	time(h)	Yield %[a]			
		23	24	25	26
1	2.5	-	42	50	8
2	18	-	40	20	40

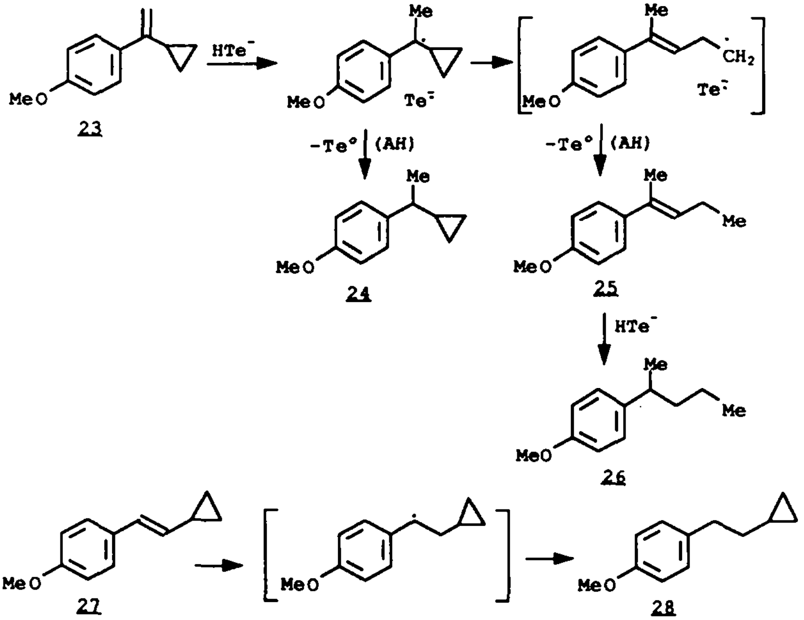
i)NaTeH(2.5mM per mM of 20),EtOH;reflux.a)determined by ^1H NMR

The comparison between entries 1 and 2 shows that initially formed **25** is slowly reduced by HTe^- to **26**. The amount of unrearrenged product, 4-(1-cyclopropylethyl)anisole **24**, remains unchanged when the reaction time is prolonged.

On the contrary, the reduction of β-cyclopropylstyrene **27** by HTe^- (2.5mM per mM of **27**, EtOH, reflx, 18h.) does not give rise to the opening of the cyclopropyl group and only **28** is formed.

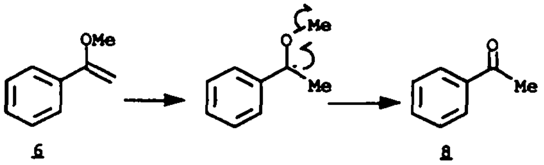
The opening of a cyclopropyl group in a cyclopropylmethyl radical leading to an homoallylic radical is well documented[12] and is characteristic of such radicals. Therefore, the reduction of α-cyclopropylstyrene **23** leading to 58-60% of rearrenged products and of β-cyclopropylstyrene **27** without rearrengement, stands for the formation of an intermediate radical, benzylic in this case (scheme 5).

Scheme 5



b) The fact that α-methoxystyrene **6** reacts readily at room temperature is in agreement with the formation of a benzylic radical stabilized by the methoxy group. The obtention of acetophenone **8** as by-product is also in favour of the formation of an α-alkoxybenzylic radical whose fragmentation according to scheme 6 is known[13].

Scheme 6

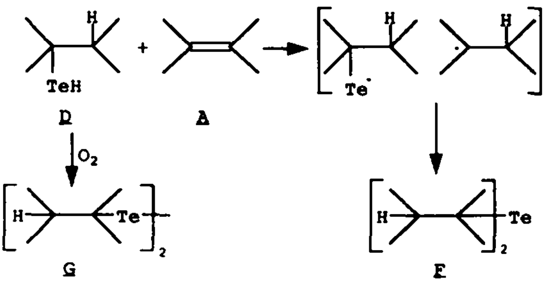


It is noteworthy that the β-isomer 5 is not affected even under reflux,whereas 57% of n-propylbenzene is obtained from β-methylstyrene 1(R=R^2=H,R^1=Me) under the same conditions(table 1). It appears from table 1 that the action of HTe$^-$ is considerably slowed down by steric hindrance. It is possible that in the case of β-methoxystyrene 5, in addition to the steric hindrance, the enhanced electronic density of the methoxy group makes the approach of the negatively charged reagent more difficult.

c) Whereas with the terminal monosubstituted double bonds of compounds 9 and 15 only the addition of HTe$^-$ is observed (schemes 2 and 3), the gem-disubstituted olefin 20,4-phenyl-2-methyl-1-butene,is partially reduced (table 3). In the last case a tertiary radical,which is easily reducible, is formed.

According to scheme 4, the formation of organotellurium compounds from the isolated double bonds results from a secondary reaction of the initially produced tellurol D .

Scheme 7

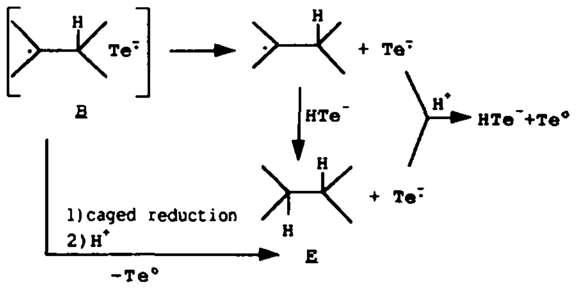


The obtention of tellurides (E,scheme 7) as principal products suggests that a tellurol, like hydrogen telluride, can transfer its hydrogen atom to the double bond,which is followed by a coupling step. The ditellurides G, minor products, may arise from the oxidation of non reacted tellurol during work up (scheme 7).

In consequence, the hypothesis involving the formation of the radical pair B (scheme 4) allows a consistent explanation of the experimental facts.

However,more precise details concerning the reduction(B→E) of the intermediate radical as well as the formation(A→B) of the pair B in scheme 4 are to be discussed.

Scheme 8

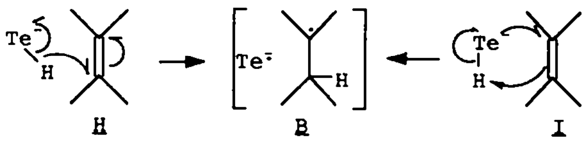


The oxido-reduction (B→E) of the radical pair B in a caged process competing with the coupling (B→C) may be considered,but more probable is the transfer of a further atom of hydrogen from a second mol of reagent out of the cage (scheme 8).It is known that the last process is favoured for long-lived radicals, which is the case of stabilized radicals such as benzylic ones (case of styrenes).

In this case, the reduction may be performed by the excess of hydrogen telluride,HTe$^-$, and so it is favoured with respect to coupling.This interpretation may also account for the relative augmentation of reduction product 22 when the molar ratio HTe^-/substrat is increased (case of olefin 20, table 3), although the fragmentation of a tertiary carbon-tellurium bond is also likely (see below).

Concerning the first step of scheme 4, the hydrogen atom comes from hydrogen telluride, HTe^-. The fact that sodium telluride, Na_2Te, is inactive towards an isolated double bond seems to confirm such an hypothesis.

Scheme 9



The hydrogen atom transfer process may result from a direct transfer of a hydrogen atom (H→B) or from an electron transfer assisted by a proton transfer from the reagent (I→B), which is formally equivalent (scheme 9).

It is, however, to be noted that if the telluride $Te^=$ is inactive towards an isolated double bond, it reduces styrenes, most probably by electron transfer to give a radical anion followed by protonation (a Birch[14]-like reduction).

Another way to consider the reaction of HTe^- with an isolated double bond as in 9, 15 and 20 is to postulate a concerted molecular type addition. In this case the partial reduction of 20 into 22 should arrise from homolysis of the weak tertiary carbon-tellurium bond leading to a carbon radical which is easily reduced. A suitable multiply labelled (H, D, T) experiment would demonstrate the *cis* addition resulting from a molecular type mechanism.

Coda.

The solutions of NaTeH used by several authors are sometimes referred to as being red. This indicates that HTe^- is not the single tellurium-containing reagent present in such solutions. A precise definition of the reagent seems therefore necessary for a mechanistic approach to its action on a particular functional group.

Sodium hydrogen telluride cannot be obtained directly by reducing elemental tellurium with sodium borohydride in ethanol according to: $Te^0 + NaBH_4 + 3EtOH \rightarrow NaTeH + B(OEt)_3 + 3H_2$

Under such conditions the reduction leads to the colourless sodium telluride Na_2Te according to: $Te^0 + 2NaBH_4 + 6EtOH \rightarrow Na_2Te + 2B(OEt)_3 + 7H_2$.

It is to be noted that, as it has been shown by L.Tschugaeff and W.Chlopin[8], the still unreacted tellurium reacts with the formed telluride $Te^=$ to give the red ditelluride ($Na_2Te + Te^0 \rightarrow Na_2Te_2$). This red colour is observed as the reaction progresses. The ditelluride thus formed is reducible to telluride in the reaction mixture. The reduction has to be continued until there is no further evolution of hydrogen.

Under the actual reduction conditions (refluxing ethanol), $NaBH_4$ is in part decomposed ($NaBH_4 + 4EtOH \rightarrow B(OEt)_3 + NaOEt + 4H_2$). It is therefore necessary to use an excess of $NaBH_4$ which is then destroyed by refluxing up to the hydrogen evolution sets off.

A colourless ethanolic solution of NaTeH is obtained by adding acetic acid to the solution of Na_2Te, which is also colourless. On account of the respective Ka[15] of H_2Te (2.3×10^{-3}), HTe^- (1.6×10^{-11}) and AcOH (2×10^{-5}), only the first acidity of H_2Te is neutralized. The NaOEt is also neutralized and the excess $NaBH_4$ eventually present is destroyed. An ethanolic solution of NaTeH is thus obtained, whose concentration is determined as a function of the weight of tellurium reduced and whose pH is kept near the neutrality by the buffer AcOH/NaOAc.

EXPERIMENTAL

General Comments.- NMR spectra were determined for solutions in deuteriochloroform using tetramethylsilane as an internal reference at 60 MHz, 80 MHz and 200 MHz on a Varian T 60, on a Bruker WP 80 and on a Bruker WP 200 SY spectrometer respectively. The chemical shifts, reported in parts per million, are followed by the splitting pattern (m= multiplet;

q=quartet;t=triplet;d=doublet;s=singlet),the coupling constant J in Hz,the number of protons found by integration,and the assignment of the resonance signal.Mass spectral analyses were performed on an AEI MS 50 instrument operating in the electron impact mode at 70 eV.The organotellurium compounds derived from simple olefins were obtained as mixtures of a principal product accompanied by secondary ones.These products have not been isolated,and thus tentatively identified in the mixtures according to their ^{1}H NMR and mass spectra which presented the characteristic chemical shifts for protons α to tellurium[30] and the characteristic isotope clusters typical of tellurium-containing ions[30].All tellurium containing mass peaks are reported for ^{130}Te.All reactions involving the tellurium reagents NaTeH and Na$_2$Te were performed under argon atmosphere and using deoxygenated solvents according to the standard techniques for the manipulation of air sensitive compounds[16].

Preparation of Sodium Hydrogen Telluride.Typical procedure.- A mixture of powdered tellurium(0.51g,4mgat),sodium borohydride(0.45g,12mM) and deoxygenated ethanol(35ml) was refluxed under argon.After a short time,a vigorous evolution of hydrogen set in.As tellurium dissolved the solution became red-purple in colour.After 30 minutes,all tellurium was dissolved and the solution began to decolourize.After 40-45 minutes of reaction the solution became colourless and the hydrogen evolution stopped.The solution was allowed to cool to room temperature and deoxygenated acetic acid(0.69ml,12mM) was slowly added.The colourless solution of sodium hydrogen telluride,NaTeH, obtained was immediately used.

If the solution of sodium telluride,Na$_2$Te,was still coloured(residual oligotellurides, Na$_2$Te$_n$) when the evolution of hydrogen stopped,after cooling to room temperature,sodium borohydride(0.038g,1mM) was added under argon.On stirring at room temperature the colour progressively faded as hydrogen was evolved.After 15 minutes a colourless solution (complete reduction) of Na$_2$Te was obtained.Then,deoxygenated acetic acid(0.75ml,13mM) was added as above.

Materials.- Styrene, α-Methylstyrene(1,R=Me,R^1=R^2=H), β-Methylstyrene(1,R=R^2=H,R^1=Me), Anethole(3,X=Me), β-Methoxystyrene 5,and Undecylenic acid 9 were commercially available.

The olefins 1(R=Me,R^1,R^2=Me,H),1(R=H,R^1=R^2=Me),3(X= -C≡N),20 and 23 were prepared by the Wittig reaction according to the following general method: to a suspension of the appropriate phosphonium salt(20mM) in anhydrous ether was added butyllithium (20mM, solution in hexanes).The reaction mixture was stirred until dissolution of the phosphonium salt(red-orange solution)Then,a solution of the appropriate aldehyde or ketone(20mM) in anhydrous ether was added,and after a period of stirring at room temperature or under reflux of the solvent,the reaction mixture was filtered through celite.The solvent was evaporated and the residue was taken in pentane and filtered.After concentration,the residue was chromatographed on silica gel(eluant pentane)

α,β-Dimethylstyrene[19](66%E,33%Z) was obtained(62% yield) from acetophenone and triphenylmethyl phosphonium bromide.^{1}H NMR(200MHz):7.17-7.43(m 5H Ph-H),5.88(q J=7 1H(Z)) 5.58(q J=7 1H(E)),2.02(s 3H Me$_\alpha$),1.79(d J=7 3H Me$_\beta$(Z)),1.59(d J=7 3H Me$_\beta$(E)). β,β-Dimethylstyrene was obtained(77% yield) from benzaldehyde and triphenylisopropyl phosphonium bromide[21].bp:80-81°C/18mmHg(lit[20].76-77°C/11mmHg);^{1}H NMR(60MHz):7.13(m 5H Ph-H),6.2(m 1H vinyl),1.8-1.9(m 6H =CMe$_2$). *p*-Cyano-β-Methylstyrene[22](35%E,65%Z) was obtained (69% yield) from *p*-cyano-benzaldehyde and triphenylethyl phosphonium bromide MS: 143 (100%),142(68%),116(47%);^{1}H NMR(200MHz):7.67 and 7.43(d J=8 and d J=8 4H Ph-H(Z)),7.62 and 7.45(d J=8 and d J=8 4H Ph-H(E)),6.49(d J=12 1H H$_\alpha$(Z)),6.42-6.48(2H H$_\alpha$ et H$_\beta$(E)),6.05(dq J=12 J=7.5 1H H$_\beta$(Z)),1.91-1.95(3H Me(Z)),1.91(d J=7.5 3H Me(E)). 4-Phenyl-2-methyl-1-butene 20 was obtained(73% yield) from 4-phenyl-2-butanone and triphenylmethyl phosphonium bromide.bp:140°C/22mmHg(lit[24].130-135°C/15 mmHg);^{1}H NMR(80MHz):7.23(m 5H Ph-H),4.74(m 2H =CH$_2$),2.60-2.92(m 2H Ph-CH$_2$),2.1-2.5(m 2H =CH-CH$_2$),1.76(m 3H =CH-Me). *p*-Methoxy-α-cyclopropylstyrene 23 was obtained(59% yield) from anisyl-cyclopropylketone and triphenylmethyl phosphonium bromide.bp:129-131°C/23mmHg(lit.74°C/0.3mmHg[25a],116°C/ 50 mmHg[25b]);^{1}H NMR[25b](200MHz):7.51(d J=9 2H Ph-H),6.82(d J=9 2H Ph-H),5.18 and 4.79(m 1H and m 1H vinyl-H),3.79(s 3H -OMe),1.40-1.79(m 1H cyclopropyl C-H),0.4-0.94(m 4H cyclopropyl).

The olefins 1(R=R^1=R^2=Me) and 6 were prepared by literature methods. α,β,β-Trimethylstyrene[17](67% yield from acetophenone).bp:86-87°C/23mmHg(lit[17]·191-192°C/760 mmHg);^{1}H NMR(80MHz):7.12(m 5H Ph-H),1.94(s 3H Me$_\alpha$),1.78(s 3H Me$_\beta$(trans)),1.56(s 3H Me$_\beta$(cis)).α-Methoxystyrene 6[18](70% yield from styrene).bp:90-91°C/22mmHg(lit[18].88-89°C/ 20mmHg);^{1}HNMR(80MHz):7.2-7.7(m 5H Ph-H),4.61 and 4.17(d J=2.5 and d J=2.5 2H vinyl protons),3.69(s 3H -OMe).

6-Phenoxy-1-hexene 15.- Phenol(2.35g,25mM) was added to a solution of sodium ethoxide(25mM) in ethanol(15ml) and the reaction mixture was stirred 0.5h at room temperature.Then,6-bromo-1-hexene(4.1g,25mM) was added and the reaction mixture was stirred overnigth at 70°C.After cooling to room temperature,dilution with water,extraction with dichloromethane,washing the organic phase with water,drying over magnesium sulfate and evaporation of the solvent,the crude product which resulted was distilled yielding 3.6g(81%) of 15 bp:122-123°C/20mmHg (lit[23].69°C/0.2mmHg);^1H NMR (80MHz):7.1-7.37(m 2H Ph-H),6.72-7(m 3H Ph-H),5.77(m 1H $-CH=CH_2$),4.82-5.15(m 2H $=CH_2$),3.92(t 2H $-OCH_2-$),2.11(m 2H $-CH_2-CH=$),1.35-2(m 4H $-OCH_2-(CH_2)_2$).

p-Methoxy-β-Cyclopropylstyrene 27.- To a solution of triphenylcyclopropyl phosphonium bromide(3.97g,10mM) in DMF(10ml),cooled to 0°C,was added 1ml of a 1M solution of potassium tert-butoxide in dry DMF.A red colour immediately appeared.An aliquot of a solution of anisaldehyde(1.36g,10mM) in DMF(5ml) was added until the red colour dissapeared.Then,the solutions of base and aldehyde were alternatively added until all anisaldehyde was used.The solution was allowed to warm to room temperature with stirring,poured into water,neutralized with diluted aqueous HCl,and extracted with pentane.The organic phase was washed with water,dried over magnesium sulfate,and the solvent evaporated.The residue was chromatographed on silica gel yielding 1.46g(84%) of 27(22%E,78%Z) MS:174(100%),173(43%),159(31%),143(25%);^1H NMR(200MHz) (from the mixture of isomers) E-27: 7.22-6,81(d J=9 and d J=9 Ph-H), 6.41(d J=16 =CH-Ph), 5.59(dd J=16 J=9 $=CH-C_3H_5$), 3.78(s -OMe)1.46-1.57(m 1H cyclopropyl C-H),0.82 and 0.43 (m 2H and m 2H cyclopropyl methylenes). Z-27:7.37 and 6.87(d J=9 and d J=9 Ph-H),6.29(d J=12 =CH Ph), 4.99(dd J=12 J=10 $=CH-C_3H_5$),3.80(s -OMe),1.84(m 1H cyclopropyl C-H),0.82 and 0.43(m 2H and m 2H cyclopropyl methylenes).

Reaction of NaTeH with styrenes

General Procedure.- A solution of the appropriate styrene(1.5mM) in ethanol(1ml) was added to a freshly prepared solution of NaTeH(4mM) in ethanol(35mL) under reflux.The reaction mixture was stirred under reflux for 2.5h.,during which time a precipitation of elemental tellurium was observed when reduction had taken place.The reaction mixture was then cooled to room temperature and left open to air with stirring for 0.5h. to destroy the excess of NaTeH. The mixture was filtered through celite(washing with Cl_2CH_2). The filtrate was washed with water,dried over $MgSO_4$,and the solvent was evaporated.When necessary,the products were isolated by chromatography on silica gel.

- Styrene(0.157g,1.5mM) gave ethylbenzene(0.146g,91%) as a single product,identical with authentic material.^1H NMR(80MHz):7.25(m 5H Ph-H),2.68(q J=7.5 2H CH_2),1.29(t J=7.5 3H Me). - α-Methylstyrene(0.180g,1.52mM) gave isopropylbenzene(0.167g,92%) as a single product,identical with authentic material.^1H NMR(80MHz):7.23(m 5H Ph-H),2.90(m 1H $CH(Me)_2$),1.26(d J=7 $CH(Me)_2$). - β-Methylstyrene(0.176g,1.49mM) gave a mixture(0.161g) of propylbenzene and starting material in the molar ratio 1.3/1 (NMR).A similar experience(0.176g,1.52mM),but pursued overnight gave propylbenzene(0.163g,91%) identical with authentic material as a single product.^1H NMR(80MHz):7.17(m 5H Ph-H),2.56(t J=7.5 2H $Ph-CH_2$),1.63(m 2H $Ph-CH_2-CH_2$), 0.93(t J=7.5 3H Me). - α,β-Dimethylstyrene(67%E,33%Z) (0.200g,1.51mM) gave a mixture of starting material (63%E,37%Z) and s-butylbenzene in the molar ratio 6.7/1(NMR).In another experience carried out with a molar ratio NaTeH/α,β-Dimethylstyrene = 4/1 instead of 2.5/1,and a refluxing time of 48h instead of 2.5h. α,β-Dimethylstyrene(0.130g,0.98mM) gave s-butylbenzene as single product(0.124g,94%) identical with authentic material.^1H NMR(200 MHz):7.25 (m 5H Ph-H),2.58(m 1H Ph-CH),1.60(m 2H $-CH-CH_2$),1.22(d J=7 3H -CHMe),0.81(t J=7 3H $-CH_2-Me$). - Anethole(0.225g, 1.5mM) gave a mixture(0.211g) of *p*-propylanisole[26] and starting material in the molar ratio 2.3/1(NMR).A similar experience(0.231g,1.54mM),but pursued overnight gave n-propylanisole(0.220g,94%) as a single product.^1H NMR(80MHz):7.04(d J=9 2H Ph-H),6.75(d J=9 2H Ph-H),3.71(s 3H OMe),2.51(t J=7.5 2H $PhCH_2$),1.60(m 2H $Ph-CH_2-CH_2$), 0.90(t J=7.5 3H CH_2-Me). -.p-Cyano-β-Methylstyrene(35%E,65%Z) (0.225g,1.57mM) gave a mixture (0.213g) of p-propylbenzonitrile and starting material(25%E,75%Z) in the molar ratio 2.6/1(NMR).A similar experience(0.200g,1.40mM of 3(X= -CN)),but pursued overnight gave 4 X= -CN (0.185g,91%) as a single product.MS:145(M,70%),116(100%).^1H NMR(200MHz):7.63(d J=8 2H Ph-H),7.30(d J=8 2H Ph-H),2.67(t J=7.5 2H $PhCH_2$),1.66(m 2H $PhCH_2CH_2$),0.94(t J=7.5 3H CH_2Me). -.p-Methoxy-α-Cyclopropylstyrene 23(0.261g,1.50mM) gave a mixture(0.253g) of compounds 24[25a,27],25[28],and 26[28] in the molar ratio 1/1.2/0.2(NMR).In a similar experience (0.265g,1.52mM of 23) where the refluxing period was 18h. instead of 2.5h.,a mixture (0.251g) of compounds 24,25,and 26 in the molar ratio 1/0.5/1 was obtained.^1H NMR (200MHz);24:7.16(d J=9 2H Ph-H),6.83(d J=9 2H Ph-H),3.73(s 3H OMe),1.88(m 1H Ph-CH), 1.24(d J=7 3H Ph-CHMe),0.82(m 1H cyclopropyl C-H),0-0.53(m 4H cyclopropyl).;25:7.31(d J=9 2H Ph-H),6.82(d J=9 2H Ph-H),5.67(t J=7 of q J=1.5 1H vinyl-H),3.74(s 3H -OMe),2.12(m 2H =CH-CH_2-Me),1.94(d J=1.5 3H -CH=CMe),0.97(t J=7.5 3H CH_2-Me).;26:7.08(d J=9 2H Ph-H), 6.81(d J=9 2H Ph-H),3.73(s 3H OMe),2.59(m 1H PhCH),1.45(m 2H CH_2Me),1.14(m 2H CH-CH_2Me), 1.13(d J=7 3H Ph-CH-Me),0.79(t J=7,3H CH_2-Me). -.p-Methoxy-β-Cyclopropylstyrene 27 (22%E,78%Z)(0.26g,1.49mM).The refluxing period was 18h.instead of 2.5h. A mixture(0.239g) of starting material 27(10%E,90%Z) and 1-phenyl-2-cyclopropyl-ethane 28 in the molar ratio 2.1/1 was obtained.^{1}H NMR(200MHz):7.22(d J=9 2H Ph-H),6.81(d J=9 2H Ph-H),2.65(t 2H Ph-CH_2),1.47(m 2H Ph-CH_2-CH_2),0.69(m 1H cyclopropyl C-H),0.45(m 2H cyclopropyl),0.03(m 2H cyclopropyl). -.α-Methoxystyrene 6(0.200g,1.49mM) in ethanol(1ml) was added to a solution of NaTeH(4mM) in ethanol(35ml) at room temperature and the reaction mixture was stirred at room temperature for 2.5h.After work up as in the general procedure,a mixture(0.187g) of the ether 7,acetophenone 8 and starting material in the molar ratio 21/3/1(NMR) was obtained.The crude product was chromatographed on silica gel.Gradient elution with pentane containing increasing amounts of ethyl ether gave methyl-α-phenethyl-ether 7[29](0.160g,79%).^{1}H NMR(80MHz):7.27(m 5H Ph-H),4.25(q J=6.5 1H CH-Me),3.20(s 3H -OMe), 1.42(d J=6.5 3H CH-Me);and acetophenone 8(0.018g,10%) identical with authentic material.

Relative reactivities of NaTeH and Na_2Te towards β-Methylstyrene.

-.Sodium Hydrogen Telluride:β-methylstyrene (0.177g,1.5mM) in ethanol(1ml) was added to a solution of NaTeH(4mM) in ethanol(35ml) under reflux.The reaction mixture was refluxed for 6h,and then,worked up as in the general procedure gave a mixture(0.165g) of n-propylbenzene and starting material in the molar ratio 7.3/1(NMR).

-.Sodium Telluride:A solution of NaTeH(4mM) in ethanol(35ml) was made alkaline by the addition,at room temperature,of concentrated(30%) aqueous sodium hydroxide(1.2ml).Then, β-methylstyrene(0.171g,1.48ml) was added under reflux.The reaction mixture was refluxed for 6h.,and worked up as above gave 0.161g of a mixture of n-propylbenzene and starting material in the molar ratio 0.32/1(NMR).

Reaction of NaTeH with simple olefins.

-.Undecylenic acid 9:To a solution of NaTeH(6mM) in ethanol(40ml) was added 0.37g(2mM) of acid 9.The reaction mixture was refluxed for 24h.,and then cooled to room temperature.Acetic acid(2ml) was added and the reaction mixture was left open to air with stirring for 0.5h.The mixture was filtered through celite(washing with Cl_2CH_2).The filtrate was washed with water,and dried over $MgSO_4$.Evaporation of the solvent gave 0.48g of crude product,mixture of compounds 10,11,and 12 in the molar ratio 9.9/1.6/1,which was determined by integration of the NMR signals of the protons α to tellurium[30].^{1}H NMR (200MHz):3.67(m 2H(of 11) CH-Te-Te),3.24(m 2H(of 10) CH-Te),3.04(t J=7 4H(of 12) CH_2-Te-Te),2.33(t J=7 4H(of 10-12) CH_2-COOH).The mass spectra of the crude product showed the molecular peaks m/z 630(R_2Te_2),and m/z 500(R_2Te);R=$C_{11}H_{21}O_2$.-Detelluration:The crude product(0.265g) was added,under argon,to a suspension of nickel boride,Ni_2B,prepared from $NiCl_2.6H_2O$(4g) and $NaBH_4$(2g) in ethanol(75ml).The reaction mixture was stirred overnight at room temperature and then filtered through celite(washing with Cl_2CH_2).The filtrate was washed with water,and dried over $MgSO_4$.Evaporation of the solvent gave undecanoic acid 13 as a single product(0.181g) identical with authentic material.^{1}H NMR(80MHz): 2.34(t J=7.5 2H -CH_2-COOH),1.1-2(m 16H -$(CH_2)_8$-),0.89(t J=7.5 3H -CH_2-Me).-Preparation of telluride 10 from acid 14:To a solution of NaTeH(1mM) in ethanol(40ml) was added 10-Bromoundecanoic acid 14[31](0.53g,2mM) and the reaction mixture was stirred at room temperature for 2h.Usual work up gave telluride10(0.443g,89%) as a ligth yellow oil.MS: 500(R_2Te,10%);298(RTe-17,21%);185(R,12%);167(R-18,27%);149(18%);83(52%);69(73%) 55(100%); 41(38%).R=$C_{11}H_{21}O_2$.^{1}H NMR(200MHz):3.24(m 2H CH-Te),2.33(t 2H CH_2-COOH),1.55-1.80(m 10H Me-CHTe-CH_2-),1.30(m 24H -$(CH_2)_6$-).

-.6-Phenoxy-1-Hexene 15:The procedure described for Undecylenic acid 9 was followed.The crude product(0.446g,from 0.35g of 15) was a mixture of compounds 16,17,and 18 in the molar ratio 17/1.8/1,determined by NMR as above.^{1}H NMR(200MHz):7.31(m 4H (of 16-18) Ph-H),6.94(m 6H(of 16-18) Ph-H),3.92(t 4H(of 16-18) PhOCH_2),3.25(m 2H(of 16) CH-Te),3.04(t J=7 4H(of 18) CH_2-Te-Te),2.67(t J=7 4H(of 17) CH_2-Te),1.21-2(m 8H(of 16-18) Ph$OCH_2(CH_2)_2$) The mass spectra of the crude product showed the ions m/z 614(R_2Te_2),m/z 484(R_2Te),and m/z 177(R);R=$C_{12}H_{17}O$.Detelluration was also performed following the procedure above described.From 0.22g of crude product 16-18,1-phenoxyhexane 19(0.157g) was obtained as single product.^{1}H NMR(80MHz):7.1-7.35(m 2H Ph-H),6.75-7(m 3H Ph-H),3.92(t J=7 2H PhOCH_2), 1.1-1.95(m 8H -$(CH_2)_4$-),0.9(t J=7 3H CH_2-Me).

- 4-Phenoxy-2-Methyl-1-Butene 20:The procedure described for undecylenic acid 9 was followed(0.25g,2mM of 20;molar ratio NaTeH/20 =3/1;EtOH;reflux;24h) and gave 0.278g of crude product which was a mixture of starting material,isoamylbenzene 22,and tellurium derivatives 21 in the molar ratio 14/2.2/1(NMR).The crude product was chromatographed on silica gel.Gradient elution with pentane containing increasing amounts of ethyl ether gave:-Isoamylbenzene 22(0.025g,10%) which was identical with authentic material.^{1}H NMR (80MHz):7.21(m 5H Ph-H),2.59(m 2H $PhC\underline{H}_2$),1.45-1.71(m 3H $C\underline{H}_2C\underline{H}(Me)_2$),0.92(d J=7 6H $CH(\underline{Me})_2$).-Starting material 20(0.163g,65%);and -A mixture of telluride 21(n=1) and ditelluride 21(n=2) in the molar ratio 2.6/1;MS:554(R_2Te_2),424(R_2Te),408(RTe_2H),147(R); $R=C_{11}H_{15}$;^{1}H NMR(200MHz):7.37(m 10H Ph-H),2.76(m 4H $PhC\underline{H}_2$),1.93(m 4H $PhCH_2C\underline{H}_2$),1.72(s 12H $C\underline{Me}_2$ of 21(n=2)),1.67(s 12H $C\underline{Me}_2$ of 21(n=1)).Althouh the work up was carried out under diminished light,a black residue on silica gel indicated partial decomposition of organotellurium compounds 21 during chromatography.In another experience,the molar ratio NaTeH/20 was 6/1 instead of 3/1 and the refluxing period was 72h. instead of 24h. After a similar work up a mixture of starting material,and compounds 22 and 21 in the molar ratio 7.1/5.1/1 was obtained.

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