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THE ADDITION OF SODIUM HYDROGEN TELLURIDE TO UNACTIVATED CARBON-CARBON DOUBLE BONDS

Derek H.R.Barton*, Luis Bohé and Xavier Lusinchi

Institut de Chimie des Substances Naturelles, C.N.R.S.,
91198 Gif-sur-Yvette, France

Abstract - The reaction of unhindered olefins with sodium hydrogen telluride in refluxing ethanol produces dialkyltellurides by an addition process which shows prominent Markownikov selectivity.

Owing to its utility in organic synthesis, the action of sodium hydrogen telluride[1], NaTeH, on a variety of functional groups[2a-j] has attracted considerable interest in the last few years.

Carbon-carbon double bonds, when conjugated with carbonyl groups[3a,b] or with aromatic rings[4], are reduced by NaTeH, but isolated double bonds are stated not to react.

Here we wish to report that NaTeH does, in fact, react smoothly with unhindered olefins to afford products containing well defined carbon-tellurium bonds. These products are dialkyltellurides, sometimes accompanied by the corresponding ditellurides.

For example, when monosubstituted olefins 1 and 2 were reacted with excess NaTeH in ethanol under reflux for 24 h., mixtures of tellurium containing derivatives 3,4 and 7,8 were respectively obtained in 92% and 96% yields after usual work up[5].

As shown by ^1H NMR analysis, the relative ratio of products derived from undecylenic acid 1 was 10,10-telluride 3a[6] 79%, 10,10-ditelluride 3b[6] 13% and 11,11-ditelluride 4[6] 8%. The main product 3a was identical with that obtained by reacting 10-bromo-undecanoic acid 5[7] with one equivalent of NaTeH in ethanol at room temperature. Furthermore, treatment of the mixture of products 3 and 4 with nickel boride[2j] at room temperature afforded undecanoic acid 6 in 90% global yield from 1.

In the same way, 6-phenoxy-1-hexene 2[8a] was found to give 85% of secondary telluride 7, 9% of primary telluride 8a and 5% of primary ditelluride 8b[9]. Complete detelluration was also achieved by means of nickel boride to obtain 1-phenoxyhexane 9 in 92% global yield from 2.

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* Present address : Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.

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

1

$Te_n\left[CH(Me)-(CH_2)_8-CO_2H\right]_2$

3a n=1

3b n=2

$Te_2\left[CH_2-(CH_2)_9-CO_2H\right]_2$

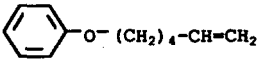
4

$CH_3-CHBr-(CH_2)_8-CO_2H$

5

$CH_3-(CH_2)_9-CO_2H$

6



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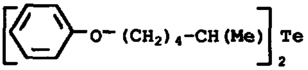

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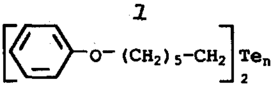
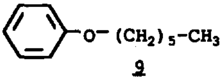


8a n=1

8b n=2



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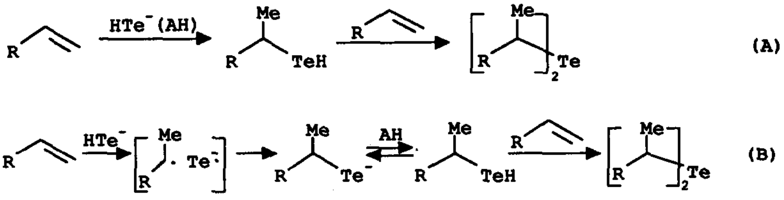
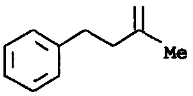
In both cases prominent Markovnikov type regioselectivity is observed (92% and 85% of secondary derivatives are respectively obtained) suggesting two possible mechanisms. Either (A, scheme 1) a nucleophilic attack of HTe^- (which should be promoted by general acid catalysis) or an hydrogen atom transfer from HTe^- to the double bond (B, scheme 1).

Scheme 1



Both hypotheses are consistent with the fact that after treatment of olefin 2 with Na_2Te[5] in the same conditions as for reaction with NaTeH (i.e. 3mM per mM, EtOH, reflux, 24 h), the starting material was quantitatively recovered.

In order to determine the scope of this addition, disubstituted olefins 10-13 were also reacted with NaTeH in the conditions above described for monosubstituted ones.



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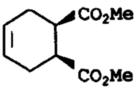

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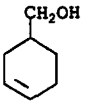

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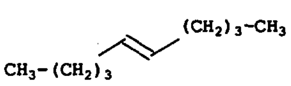

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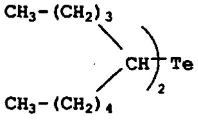

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Interestingly, gem disubstituted olefin 10[8b] afforded only 11% of addition products, mainly telluride 15[10] accompanied by little primary isomer and ditelluride, 12% of the unexpexted reduction product 17 and 77% of unchanged substrate (table,entry 1). On extended reaction period (entry 2) the yield of addition products was practically unchanged (14% vs 11%) while a three-fold increment was observed for the reduction product.

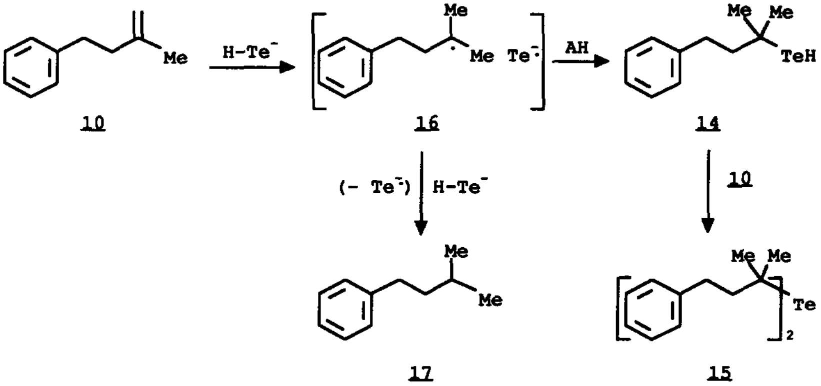
Table

Entry	Time (hr)	Yield %[c] 10	 15	 17
1	24[a]	77	11	12
2	72[b]	51	14	36

a) NaTeH 3mM per mM,EtOH,reflux.b) NaTeH 3mM per mM,EtOH,reflux.
c) determined by ^{1}H NMR.

This result may be better explained in terms of the hydrogen atom mechanism, by considering that both the addition product 15 and the reduction product 17 come from radical 16 (scheme 2).Whereas a second hydrogen atom transfer (after diffusion) would lead to 17, the coupling of radicals in 16 would lead (after protonation) to tellurol 14.Further attack of 14 on unreacted 10 leads to 15.

Scheme 2



The hypothesis depicted in scheme 2 accounts not only for the formation of more reduction product 17 from olefin 10 when the concentration of NaTeH is increased, but also for the regioselectivity of the additions as the more substituted, more stable radical would be formed in preference to the less substituted one.

The attack of HTe⁻ and particularly that of the bulky tellurol 14 on olefin 10 are considerably inhibited by steric hindrance as shown by the sluggishness of the global reaction and the low yield of telluride when compared with those obtained from olefins 1 and 2.

By contrast, trans-5-decene 13 gave only 16% of addition products, mainly telluride 18[11] and some ditelluride, and 84% of unreacted substrate.No reduction by NaTeH is observed. The mixture of telluride 18 and the corresponding ditelluride was quantitatively detellurated by nickel boride to n-decane. Cyclic olefins 11[8c] and 12 were not affected by NaTeH.

Thus NaTeH continues to justify its reputation as a mechanistic chameleon[12].

References and Notes

1. D.H.R. Barton and S.W. Mc Combie, *J. Chem. Soc., Perkin Trans.I.*, 1574 (1975).
2. a) K. Ramasamy, K.S. Kalyanasundaran and P. Shanmugan, *Synthesis*, 311 (1978). b) A.G.M. Barett, R.W. Read and D.H.R. Barton, *J. Chem. Soc., Perkin Trans.I*, 2184 (1980); c) idem, *ibid.*, 2191 (1980); d) A. Osuka and H. Susuki, *Chem Lett.*, 119, (1983); e) A. Osuka K. Takaoka and H. Susuki, *Chem Lett.*, 1373 (1983) ; f) idem, *ibid.*, 271 (1984); g) H. Susuki and K. Takaoka, *Chem Lett.*, 1733 (1984); h) D.H.R. Barton, A. Fekih and X. Lusinchi, *Tetrahedron Lett.*, 26, 3693 (1985); i) idem, *ibid.*, 26, 4603 (1985); j) idem, *ibid.*, 26, 6197 (1985).
3. a) M. Yamashita, Y. Kato and R. Suemitsu, *Chem Lett.*, 847 (1980); b) T. Murae, M. Sasaki, T.Konosu, H. Matsuo and T. Takahashi, *Tetrahedron Lett.*, 27, 3411 (1986).
4. K. Ramasamy, K.S. Kalyanasundaran and P. Shanmugan, *Synthesis*, 545 (1978).
5. General procedure: Tellurium powder (381mg, 3mM) and $NaBH_4$ (340mg, 9mM) in 20ml of deoxygenated EtOH are refluxed under argon. Tellurium completely dissolves and when evolution of H_2 sets off the solution is still purple(residual oligotellurides) After cooling at r.t., $NaBH_4$ (38mg, 1mM) is added under argon.On stirring for a few minutes a colourless solution (complete reduction) of Na_2Te is obtained. AcOH (0.525ml) is slowly added at r.t. and to this solution of NaTeH, under reflux, olefin (1mM) is added and stirring continued. After 24 h., the excess of NaTeH is destroyed by exposure to air. The reaction mixture is filtered through celite, the filtrate is poured into water and products are extracted with CH_2Cl_2.The extract is dried and evaporated to give products.
6. ^1H NMR (200 MHz) Cl_3CD, δ (ppm), 3a: 3.24 (m, 2H, CH-Te), 2.33 (t, J 7Hz, CH_2CO_2H), 1.56-1.81 (m, 10H, $TeCH(CH_3)CH_2$); 3b: 3.67 (m, 2H, CH-Te-Te); 4: 2.66 (t, J 7Hz, 4H, CH_2-Te).
7. P. Chuit, F. Boelsing, J. Hausser and G. Malet, *Helv. Chim. Acta*, 9, 1074 (1926).
8. a) D. Mansuy, J. Leclaire, M. Fontecave and P. Dansette, *Tetrahedron*, 40, 2847, (1984); b) J.L. Charlton, G.C. Williams and G.N. Lypka, *Can. J. Chem.*, 58, 1271, (1980); c) A.C. Cope and E.C. Herrick, *Org. Synth. Coll. Vol. 4*, 304, (1963)
9. ^1H NMR (200 MHz) Cl_3CD, δ (ppm), 7: 3.90 (t, J 6Hz, 4H, $PhOCH_2$), 3.25 (m, 2H, CH-Te), 1.21-2 (m, 10H, $TeCH(CH_3)CH_2$); 8a: 2.64 (t, J 7.5 Hz, 4H, CH_2-Te); 8b: 3.03 (t, J 7.5 Hz, 4H, CH_2-Te-Te).
10. ^1H NMR (200 MHz) Cl_3CD, δ (ppm), 7.37 (s, 10H, aromatic), 2.76 (t, 9Hz, 4H, $PhCH_2$), 1.93 (t, J 9Hz, 4H, Ph-C-CH_2), 1.73 (s, 12H, Me).
11. ^1H NMR (200 MHz) Cl_3CD, δ (ppm), 3.20 (m, 2H, CH-Te), 1.64 (m, 8H, CH_2-CHTe-CH_2), 1.30 m, 10H, methylenes), 0.91 (t, 3H, CH_3), 0.89 (t, 3H, CH_3).
12. a) D.H.R. Barton, L. Bohé and X. Lusinchi, *Tetrahedron Lett.*, 28, 6609 (1987); b) idem, *ibid.*, 29, 2571 (1988).

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