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A MECHANISTIC APPROACH TO THE REACTION BETWEEN IMINES AND SODIUM HYDROGEN TELLURIDE

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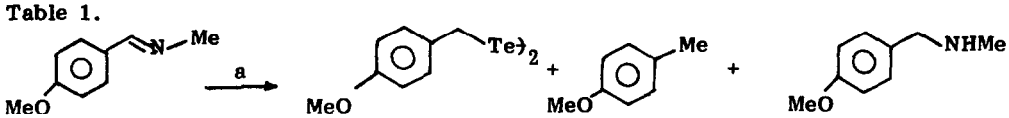
Abstract - A study of the mechanism of the action of sodium hydrogen telluride on imines is presented. It accounts for the observed reduction of the imine function to secondary amino or methylene groups depending on the structure of the substrate.

Sodium hydrogen telluride,[1] NaTeH, has been described as a nucleophilic[2a] or as a reducing reagent.[2b,3] Most of the published work deals with its use as a valuable synthetic reagent. It is, however, a true mechanistic chameleon.[4]

The study of the reduction of suitably activated double bonds shows both $H^{\ominus}$ and H· mechanisms which are reasonably understood. The mechanism for the reduction of Vilsmeier derivatives has also been clarified. It involves tellurocarbonyl esters, some of which have been isolated and fully characterised.

Concerning the action of sodium hydrogen telluride on imines, only reduction to amines has been reported[6]. Also, reductive amination of carbonyl compounds[7] has been performed in the presence of this reagent.

Table 1.



1 2 3 4

Entry	Time (hr)	Temp.	Yield[b] (%)			
			1	2	3	4
1	24	r.t.	-	60	18	22
2	12	reflux	-	-	75	25

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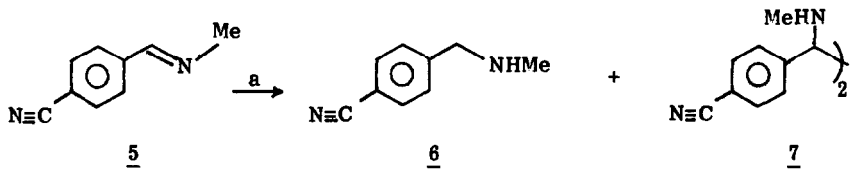
The results now obtained in reduction of imines 1 and 5, differently substituted in the aromatic ring, with NaTeH allow us to conclude that, as has already been demonstrated for Vilsmeier derivatives, reduction begins by addition of HTe^- on to the substrate.

Imine 1[8a] derived from p-methoxybenzaldehyde and methylamine afforded (Table 1) only 22-25% of secondary amine 4[9] and 75-78% of products 2, 3 arising from elimination of methylamine. Entry 2 shows that p-methylanisole 3 comes from ditelluride 2[10] which is further reduced.

Table 2.

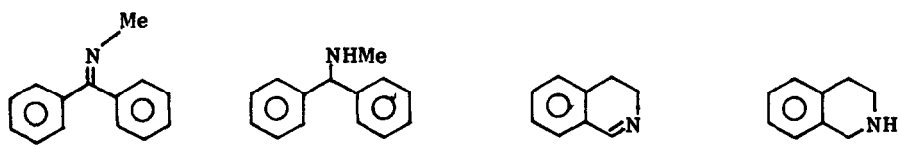


5 6 7

Time (hr)	Yield (%)[b]		
	5	6	7
0,5	-	85	15
12	-	83	17

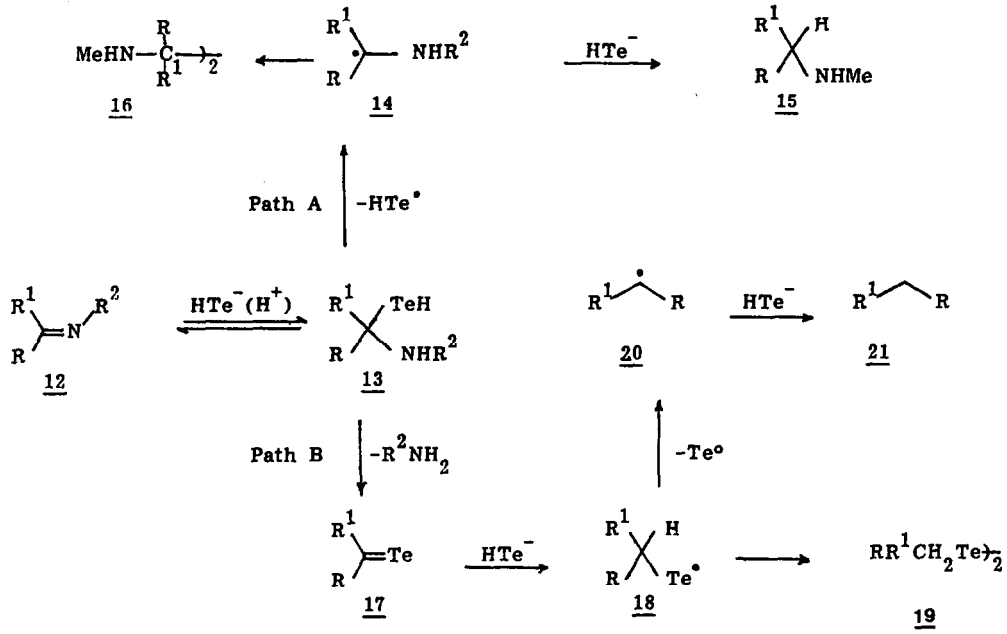
[a] HTeNa (3 mM per mM), EtOH, r.t. [b] Yields determined by ^1H NMR.

On the other hand, when the imine 5[8b], derived from p-cyanobenzaldehyde and methylamine, was reduced by NaTeH, it gave 83-85% of amine 6[9] and 15-17% of dimeric product 7.[11] Here, the methylamino group was completly retained in the products and neither ditelluride nor p-methylbenzonitrile were observed. Beside these results, imines 8[8c] and 10[8b] were quantitatively reduced into amines 9[9] and 11[9] when treated at room temperature by NaTeH (3 mM per mM, EtOH, 0.5 h)



8 9 10 11

To account for these facts, the mechanism given in Scheme 1 may be reasonably proposed.



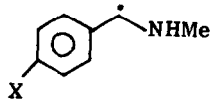
Scheme 1

The addition of HTe^- to the iminic double bond[12] in 12 in a first step gives the intermediate tellurium-containing derivative 13 which may evolve by two different pathways.

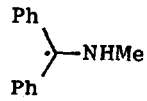
It may lose a primary amine, R^2NH_2, leading to tellurocarbonyl compound 17 which is further reduced according to path B, where the tellurium-centered radical 18 accounts for the formation of ditelluride 19. This interpretation is essentially in agreement with that given for the related reduction of Vilsmeier derivatives, $R(OR^1)C=\overset{+}{N}Me_2Cl^-$ by HTeNa where telluroesters, $R(OR^1)C=Te$, have been isolated and shown to be intermediates.[5] On the other hand, reduction into amine 15 may be explained by homolysis of the carbon-tellurium bond of 13 to give radical 14 which may be reduced as described in path A. The presence of this radical is indicated by the formation of dimer 16. According to this approach, products would result from competition between path A and B. Stabilisation of radical 14 would accelerate path A. This may account for the fact that imine 5 reacts exclusively by this path, radical 22 (X= -C≡N) being stabilised by a phenylogous captodative effect.[13a]

For imine 1, a phenylogous didonor radical 22 (X = -OMe) is produced in path A. This radical, less stabilised, is known to be formed at a lower rate,[13b] and thus, the polar elimination, path B, becomes competitive and products from both pathways are obtained.

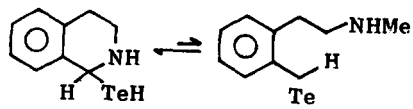
The quantitative reduction of ketimine 8 into amine 9 confirms that when a highly stabilised α-alkylamino radical, like 23, can be formed, homolytic cleavage of the intermediate 13 prevails.



22



23



24

For imine 10, the cyclic form 24 of the tellurium-containing intermediate is clearly favoured. Thus, only the irreversible homolytic path is followed.

In conclusion the action of sodium hydrogen telluride on the imine function may be consistently explained in terms of a nucleophilic addition to form a tellurium-containing intermediate, which eventually undergoes either homolysis of the carbon-tellurium bond leading to secondary amine, or polar elimination of a primary amine, in which case the imino group is reduced into methylene through a tellurocarbonyl compound. Homolysis prevails when a highly stabilised radical can be formed.

References and notes

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9. Secondary amines 4, 6, 9 and 11 were identified by comparison with authentic samples obtained by reduction of imines 1, 5, 8 and 10 with $NaBH_4$.
10. H. Suzuki, K. Miyoshi, A. Osuka, Nippon Kagaku Kaishi, 3, 472, 1981.
11. Two diasteroisomers isolated by T.L.C. One of mp = 119-120°C, ^{1}H NMR (200 MHz), Cl_3CD, δ (ppm) 7.54 (d, J_{AB} 8.5 Hz, 4H), 7.18 (d, J_{AB} 8.5 Hz, 4H), 3.56 (s, 2H), 2.25 (s, 6H), 1.96 (s, 2H); MS (FAB) 291 $(M+1)^+$ and the other of mp = 180-184°C (d), ^{1}H NMR (200 MHz), Cl_3CD, δ(ppm) 7.64 (d, J_{AB} 8.5 Hz, 4H), 7.30 (d, J_{AB} 8.5 Hz, 4H), 3.81 (s, 2H), 2.21 (s, 6H), 1.60 (s, 2H). MS (FAB) 291 $(M+A)^+$.
12. This addition at pH≈6 depends, very likely, on acid catalysis. $TeNa_2$ does not add to imines.
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