

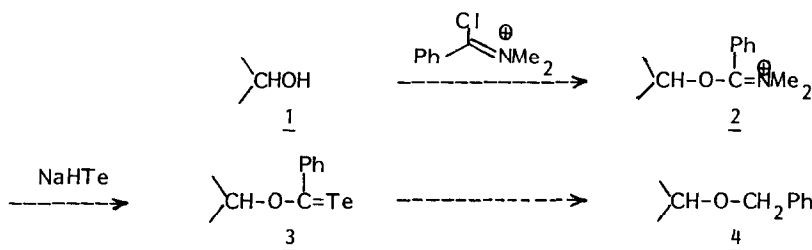
SELECTIVE REDUCTION OF IMONIUM SALTS BY SODIUM HYDROGEN TELLURIDE

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Abstract. Sodium hydrogen telluride reduces imonium salts efficiently at room temperature in ethanol. The products of the reaction depend upon the pH. Under alkaline pH only dihydro-derivatives are formed. Under acid pH (6-7) the products depend on the structure of the salt. The tellurium can be recovered quantitatively.

Some years ago we reported a facile procedure for the preparation of sodium hydrogen telluride in ethanol solution.¹ This reagent was shown to be an interesting reductant giving in good yield benzyl ethers 4 from unhindered alcohols 1 and a phenyl Vilsmeier reagent 2 as indicated in Scheme 1.



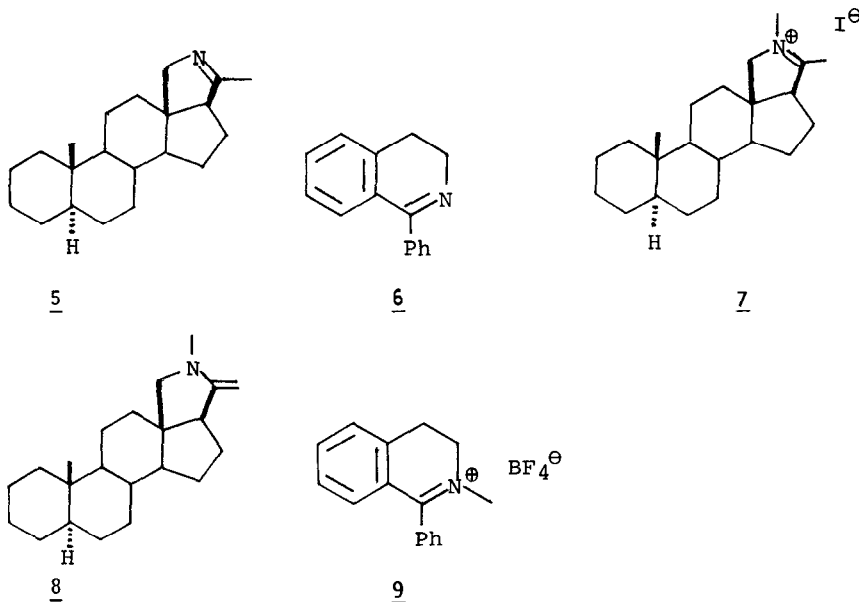
Scheme 1

Further study^{1,2} suggested that tellurono-esters 3 were intermediates and in a related investigation using a *t*-butyl Vilsmeier reagent several tellurono-esters of the pivaloyl type were isolated for the first time and completely characterised.³

Sodium hydrogen telluride has been shown to be a convenient reagent for the reduction of unsaturated to saturated carbonyl compounds,⁴ for the removal of halogen from α -halo-carbonyl compounds,⁵ for the reduction of nitro-compounds⁶ and for the cleavage of α,β -epoxy-carbonyl groups at the α -position.⁷ Other selective reductions of bromo-compounds and of azides have also been described.⁸ The recent report⁹ of the reductive amination of carbonyl compounds using sodium hydrogen

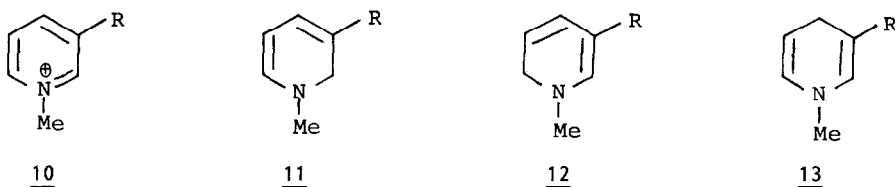
telluride prompts us to communicate our own observations, on similar reactions of interest in alkaloid chemistry. Our experiments have shown the interest and importance of pH control with the reagent.

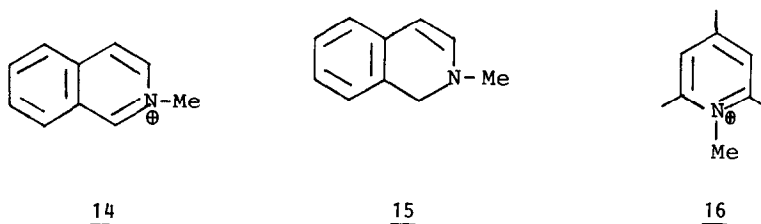
Under the usual conditions¹ (in ethanol at room temperature at pH 6-7 under argon) the imines 5¹⁰ and 6¹¹ were smoothly reduced, but at pH 10-11 no reaction occurred. We conclude that it is the protonated imine that is being reduced. In agreement, the reduction of the salt 7 at pH 6-7 is quantitative, whereas at alkaline pH a mixture of the reduction product and of the enamine 8 is formed. On the other hand the salt 9 is quantitatively reduced at all pH to the saturated derivative. It is, therefore, the iminium salt that is reduced.



At pH 10-11 N-methylpyridinium iodide (10, R = H) gave quantitatively a mixture of (11 and 12, R = H) as well as the 1,4-dihydro- derivative (13, R = H) in the proportion of 2:1. At pH 6 the reduction was complete to give N-methylpiperidine and polymeric material. Similarly 1,3-dimethylpyridinium iodide and 1-methyl-3-acetylpyridinium iodide gave at pH 10-11 a mixture of dihydro- derivatives (11, 12, 13, R = CH₃, 4:4:1 and R = COCH₃, 2:2:1)¹³

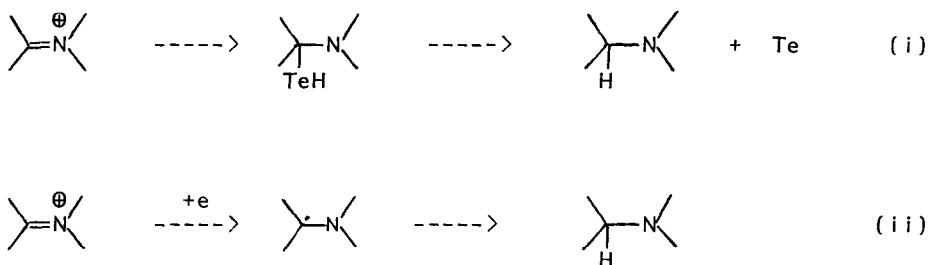
Likewise N-methylisoquinolinium iodide 14 gave N-methyltetrahydroquinoline at pH 6 and under basic conditions the dihydro- derivative 15.





Two mechanisms would seem probable for reduction by sodium hydrogen telluride.

The first mechanism (i) is the formation of a covalent carbon-tellurium bond which then fragments to give a radical which is reduced by hydrogen atom transfer to give product. This kind of mechanism has already been demonstrated.^{2,3} The second mechanism (ii) is a transfer of electron to form a radical which is then quenched by hydrogen atom transfer. This undoubtedly exists for the reduction of nitro-compounds⁶ and of azides.⁸



In principle, process (i) is far more liable to steric retardation than process (ii). We therefore made a competitive reduction between the collidine methiodide 16 and pyridine methiodide (10, R = H) at pH 10-11 at room temperature. After 6 hours the methiodide (10, R = H) was 96% reduced but there remained 40% of 16. This result supports mechanism (i).

One of the advantages of working with NaHTe is that at the end of the reaction the excess of reductant is quantitatively converted to metallic tellurium by a stream of air, or the addition of dibromo-1,2 ethane under argon, if the products are air-sensitive. The reactions are, therefore, quantitative in tellurium.

References

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