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ELIMINATION AND EXCHANGE IN
SUBSTITUTED TETRAHYDROPYRIDINES
1,2 vs 1,4 ELIMINATION

George R. Wenzinger & J. A. Williams

Chemistry Department
University of South Florida
Tampa, Florida 33620

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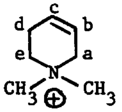
The recent reviews on elimination reactions,[1,2] both 1,2 and 1,4 conjugate eliminations, indicate a continued interest in elimination reactions and specifically in a carbanion mechanism for base induced eliminations. This prompts us to report the following data on tetrahydropyridinium salts, II, IV, and VI.

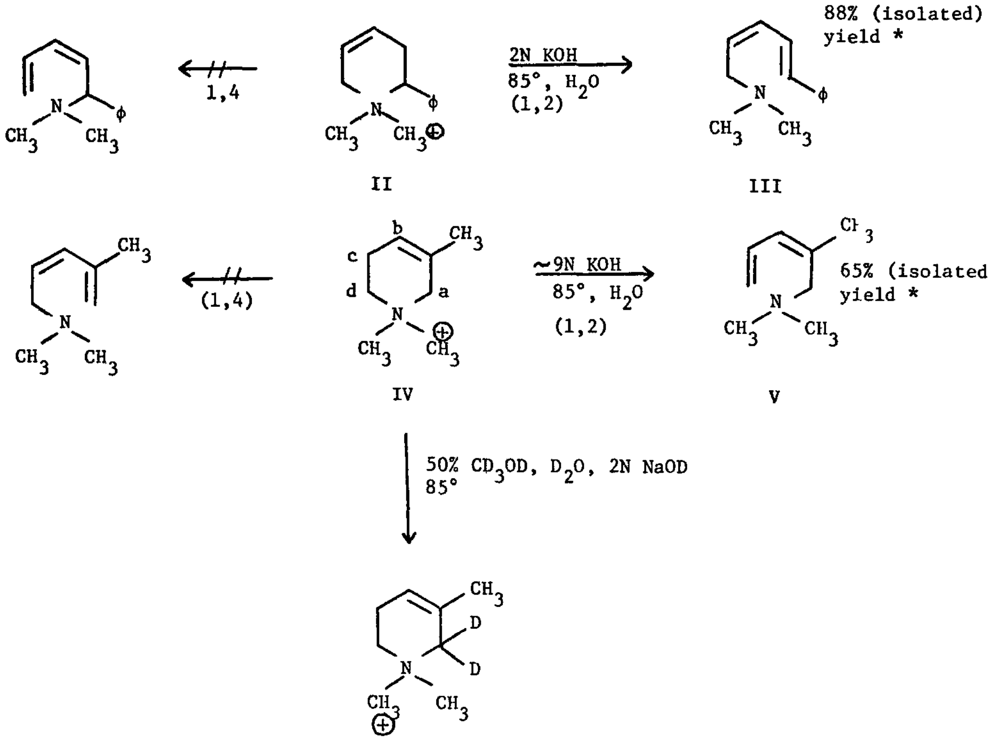
Saunders, in 1966, reported on the deuterium exchange of I[3] in which protons a-e all exchange in D_2O, NaOD solutions at 100°C. with the rate of exchange of a being about four times that of d. A concurrent elimination was reported. Since this elimination could occur in either a 1,2 or a 1,4 sense we choose to observe the exchange and elimination behavior of II and IV so as to distinguish between 1,2 and 1,4 elimination in a system which might also be activated enough to observe carbanionic eliminations. The products of these eliminations are presented in Scheme I.



I

It is quite clear that only 1,2 elimination processes occur with both II and IV for II leads to III as the lone dienic product and IV produces only V (glpc). Clearly 1,4 elimination

Scheme I



*The preparations of III and V were run in H_2O. However, glpc analysis of the products obtained from II and IV using 50% methanol/water indicated the same products as in H_2O.

processes[1] do not compete with standard 1,2 eliminations in these systems.

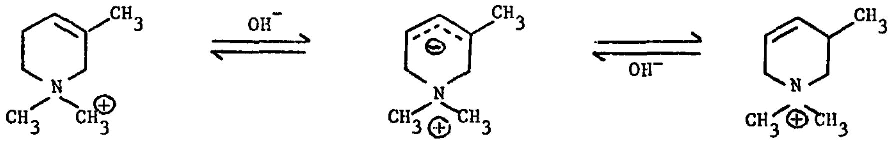
Models indicate that both II and IV can adopt geometries favorable for trans 1,2 elimination reactions which appear to be the favored path of such eliminations in most cases.[4] The stereopathways open to the 1,4 elimination are neither clearly _trans_ nor clearly _cis_. Although the stereochemistry of 1,4 elimination reactions is not yet clearly understood,[1,5] there are indication that _cis_ (syn) eliminations are favored over _trans_ (anti) eliminations.[5] Since neither pure _cis_ or _trans_ 1,4 seems possible in these systems it may be that 1,2 eliminations dominate for 1,4 elimination may be quite sensitive to maintenance of a degree of coplanarity between the C-H bond, the π orbitals of the double bond and the $\mathrm{C{-}\overset{|}{\underset{|}{N}}{-}}$ bond. If so the dominance of 1,2 eliminations is clear. (Entropic factors may be the critical factor in 1,2 vs 1,4 comparions.)$^{\text{see ref. 6 for 1,2}}$ vs 1,4 competition

Exchange-Anions:

Exchange work on IV at 85° in 50% CH_3OD/D_2O indicate that H_a is 100% exchangd at the time elimination is 30% complete. More interesting is the fact that we have not been able to detect exchange at H_c up to 40% elimination of IV. The ability to detect small amounts of exchange in the nmr is somewhat limited by the instrumentation available to us, however, it is clear that 10% exchange would be readily picked up and that 5% exchange represents the largest amount of exchange that could go undetected. This implies that the rate of exchange at H_c is approximately twenty times slower than at H_a. This contrasts with a factor of four in rate for Ha vs H_d in I[3]. This is not unexpected for the effect of a methyl group on the rate exchange of allylic hydrogens.[7]

Isomerizations:

The possible equilibrium IV $\rightleftarrows$ VI has also been looked for from both directions under the same conditions that elimination and exchange occurs. It is clear that IV $\rightleftarrows$ VI does not occur to any significant extent for the VI → IV conversion is easily detected in the nmr and if equilibrium existed IV would be expected to predominate from data on alkene equilibrium.[8] Less than 5% isomerization to IV could be detected, hence the IV $\rightleftarrows$ VI equilibrium is not present in this system via way of the anion IVa. (This assumes that the rate of proton removal from VI is not less than 1/5 the rate of elimination from IV. This assumption is presently being investigated.)



IV IVa VI

Thus it appears that if anions are formed, as might be possible from Saunders[3] data, they are transformed immediately into elimination products which are clearly 1,2 and not 1,4 conjugate in nature.

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