

Nitrogen Ylide Intermediates in Elimination Reactions of Quaternary Ammonium Salts

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Summary Specific deuterium labelling experiments have established that an $\alpha'\beta$ (ylide) mechanism is involved in the elimination reaction of quaternary ammonium halides when RLi is used as the base.

THERE are few authentic cases involving deuterium labelling studies where elimination reactions of quaternary ammonium compounds have been shown to involve a *syn* $\alpha'\beta$ (ylide) mechanism [equation (1)]. For example, the

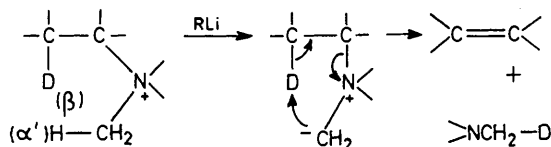
pyrolysis of a highly branched quaternary ammonium hydroxide, where an E_2 elimination was precluded for steric reasons, has been shown to proceed principally by an ylide mechanism.¹ The elimination reactions of [β -²H₂]cyclohexylmethyltrimethylammonium bromide and [β -²H₂]octyltrimethylammonium bromide with PhLi in Et₂O have also been established as involving ylide intermediates.² More recently we have shown that *N*-*n*-butyl-*NN*-dimethylcyclooctylammonium iodide affords both *cis*- and *trans*-cyclo-

TABLE

Quaternary ammonium iodide	Base-solvent	Alkene	<i>NN</i> -Dimethyl- <i>n</i> -butylamine
(1)	$\text{KNH}_2\text{-NH}_3^a$	(2) 0.0% $^2\text{H}_1^e$ 100.0% $^2\text{H}_0$	15.5% $^2\text{H}_1$ 84.5% $^2\text{H}_0$
(1)	$\text{LiNH}_2\text{-NH}_3^f$	(2) 2.3% $^2\text{H}_1$ 97.7% $^2\text{H}_0$	6.7% $^2\text{H}_1$ 93.3% $^2\text{H}_0$
(1)	$\text{Bu}^n\text{Li-Et}_2\text{O}^b$	(2) 0.0% $^2\text{H}_1$ 100.0% $^2\text{H}_0$	99.0% $^2\text{H}_1$ 1.0% $^2\text{H}_0$
(1)	$\text{Bu}^n\text{Li-pentane}^b$	(2) 0.0% $^2\text{H}_1$ 100.0% $^2\text{H}_0$	99.4% $^2\text{H}_1$ 0.6% $^2\text{H}_0$
(3)	$\text{KNH}_2\text{-NH}_3^d$	(4) 1.8% $^2\text{H}_1$ 98.2% $^2\text{H}_0$	88.6% $^2\text{H}_1$ 11.4% $^2\text{H}_0$
(3)	$\text{LiNH}_2\text{-NH}_3^d$	(4) 3.9% $^2\text{H}_1$ 96.1% $^2\text{H}_0$	44.9% $^2\text{H}_1$ 55.1% $^2\text{H}_0$
(3)	$\text{Bu}^n\text{Li-pentane}^b$	(4) 0.3% $^2\text{H}_1$ 99.7% $^2\text{H}_0$	93.3% $^2\text{H}_1$ 6.7% $^2\text{H}_0$
(5)	$\text{Bu}^n\text{Li-pentene}^b$	(6) 56.4% $^2\text{H}_1$ 43.6% $^2\text{H}_0$	40.9% $^2\text{H}_1$ 59.1% $^2\text{H}_0$
(5)	$\text{KNH}_2\text{-NH}_3^d$	(6) 88.2% $^2\text{H}_1$ 11.8% $^2\text{H}_0$	10.2% $^2\text{H}_1$ 89.8% $^2\text{H}_0$

^a Reaction time 5 h. ^b Reaction time 24 h at room temperature. ^c Syntheses and deuterium analyses were carried out as described previously.^{3,4} ^d Reaction time 16 h. ^e The $^2\text{H}_1$ represents a weighted average based upon 32.7% oct-1-ene, 8.9% *trans*-oct-2-ene, 58.4% *cis*-oct-2-ene formed from (5) under these conditions. ^f Reaction time was 10 h.

octene by a *syn* α/β pathway with either KNH_2 or LiNH_2 in liquid ammonia,³ or with alkyl- or aryl-lithium reagents in either pentane or Et_2O .⁴ These data corroborated earlier suggestions that ylide mechanisms were involved in elimination of quaternary ammonium halides with PhLi as the base.⁵

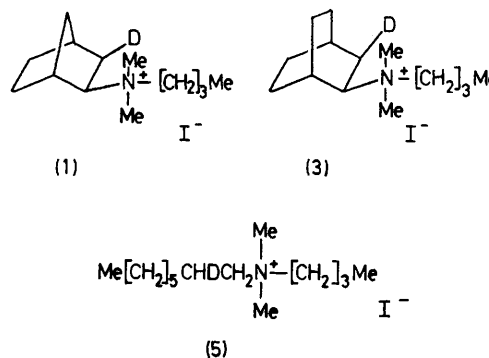


Our observation of an ylide mechanism operating in the cyclo-octyl system and the striking difference in the reversibility of ylide formation⁶ under different reaction conditions prompted us to examine more rigid bicyclic quaternary ammonium salts where the proton and the leaving group are held coplanar and could favour an intramolecular *syn* elimination. We now report that the ylide mechanism appears to be the principle mechanism operating with all quaternary ammonium salts when alkyl- or aryl-lithium reagents are used as the base. However, the mode of elimination with NH_2^- in liquid NH_3 is dependent upon the substrate involved.

The reaction of the quaternary ammonium iodide (1) with KNH_2 in liquid NH_3 resulted in a 100% *syn* elimination. Norbornene (2) produced contained no deuterium while the dimethyl-*n*-butylamine contained 15% of the deuterium initially present in (1). Hydrogen exchange in the dimethyl-*n*-butylamine does not occur under these conditions.³ Thus, only 15% of the elimination proceeded by the expected ylide pathway with the remainder of the alkene being formed by an E_2 type of mechanism (Table). The reaction of (1) with $\text{LiNH}_2\text{-NH}_3$ also proceeded by a *syn* elimination (97.7%) with an E_2 type elimination dominating the reaction, with only 6.7% reaction by an ylide intermediate. Hofmann elimination of (1) has also been shown to proceed by >94% E_2 elimination.⁷ Our results stand in marked

contrast to the elimination of cyclo-octylammonium salts where under otherwise identical conditions an exclusive α/β pathway was observed.³

A reversal in mechanisms was observed with the reaction of (1) with Bu^nLi in either ether or pentane. These reactions afforded norbornene by a 100% (within experimental error) *syn* α/β mechanism. The dimethyl-*n*-butylamine contained 99% of the deuterium initially present in (1). This is compelling evidence for an intramolecular ylide mechanism and precludes an α -elimination,⁸ an E_1cb



intermediate with hydrogen exchange, both E_1 and E_2 reaction pathways, and the exchange of hydrogen in the liberated dimethylbutylamine with solvent. An intermolecular ylide mechanism can also be excluded since this pathway should give a complex (near-statistical) distribution of $^2\text{H}_1$, $^2\text{H}_2$, and higher deuteriated amine upon elimination (Table).

The reaction of the quaternary ammonium iodide (3) with Bu^nLi in pentane also afforded bicyclo[2,2,2]oct-2-ene (4) by a 100% *syn* pathway. Only 6.7% of the reaction involved an E_2 pathway. Similarly elimination of (3) with $\text{KNH}_2\text{-NH}_3$ involved essentially a 100% *syn* pathway. However, this reaction more closely resembled our results with the cyclo-octyl system and formation of (4) proceeded

by an 88.6% ylide elimination. The reaction of (3) with $\text{LiNH}_2\text{-NH}_3$ involved some *anti* E_2 elimination (*ca.* 3.9%) and an ylide intermediate accounted for only 44.9% of the reaction. Compound (3) is considerably more flexible than (1) and affords a less strained alkene on elimination. Thus, elimination reactions with NH_2^- in liquid NH_3 appear to be dependent upon the strain energy of the alkene being formed. This difference in mechanistic pathways is also very likely a manifestation of the relative basicity of the ylide which is influenced by the reversibility of its formation.

An intramolecular ylide pathway was also established for elimination of the acyclic iodide (5) with Bu^nLi as the base. The oct-1-ene formed contained 56.4% $^2\text{H}_1$ and the liberated amine contained 40.9% $^2\text{H}_1$. Thus, the reaction proceeded by an $\alpha'\beta$ elimination to the extent of at least

93.8% with an isotope effect $k_{\text{H}}/k_{\text{D}}$ of 1.3. Comparable isotope effects have been observed in the formation of cyclo-octene under these conditions.^{3,4} Reaction of (5) with $\text{KNH}_2\text{-NH}_3$ also proceeded by at least an 86.4% ylide mechanism affording (6) and a mixture of *cis*- and *trans*-oct-2-ene. In this case $k_{\text{H}}/k_{\text{D}}$ was *ca.* 7.

Thus, we may conclude that the formation of cyclic, strained bicyclic, bicyclic, and terminal alkenes by elimination of a quaternary ammonium iodide with strong bases like alkyl- and aryl-lithium reagents will most likely involve an ylide intermediate. In contrast, the mechanism for elimination reactions with the $\text{KNH}_2\text{-NH}_3$ system appears to be dependent upon the alkene formed.

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