Reversibility of Nitrogen Ylide Formation with Quaternary Ammonium Salts

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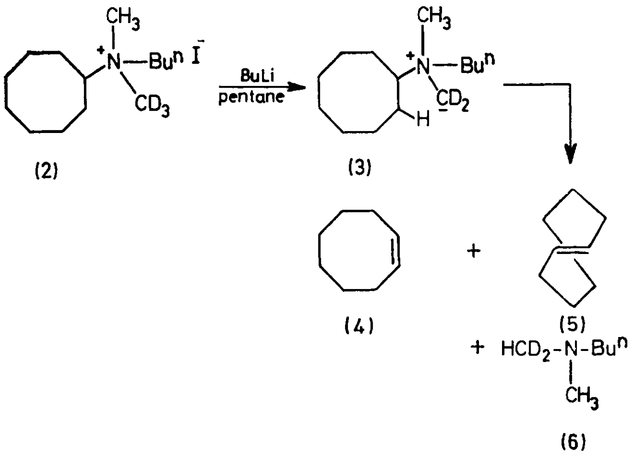
Summary Deuterium labelling experiments have established that nitrogen ylides derived from quaternary ammonium halides are formed reversibly with $-NH_3{}^-NH_2$ and irreversibly with alkyl-lithium compounds in pentane.

Although the literature on the mechanism of elimination reactions is voluminous, there have been only limited reports on elimination reactions that involve a *syn* $\alpha'\beta$ (ylide) mechanism. The ylide mechanism has been unequivocally established to be a *syn* elimination by Weygand[1] and Cope[2] on the basis of specific isotope labelling experiments. More recently, we have reported[3] deuterium labelling experiments that established that both *cis*- and *trans*-cyclo-octene are formed by an ylide mechanism when *N*-n-butyl-*NN*-dimethylcyclo-octylammonium iodide (**1**) is treated with either KNH_2 or $LiNH_2$ in liquid ammonia. Similarly, formation of an ylide intermediate followed by intramolecular abstraction of the β-hydrogen was observed



in reactions of compound (**1**) with alkyl-lithium reagents in pentane.[4] Elimination of (**1**) with amide ion in liquid NH_3 resulted in a different ratio of *cis*-and *trans*-cyclo-octene from that observed with RLi in pentane,[4] which was surprising since we had initially assumed that the *cis–trans* ratio of alkenes should be independent of the base that is used to generate the ylide intermediate (**3**). We suggested[4] that these findings could be attributed in part to the formation of a heterogeneous aggregate with the alkyl-lithium reagents.

We now report that the ylide intermediate (**3**) is formed irreversibly with n-butyl-lithium as the base in pentane. However, rapid exchange of the α'-hydrogen, with complete loss of the deuterium label in (**3**), occurs with NH_2^- in liquid NH_3. The labelled iodide (**2**), prepared from *N*-n-butyl-*N*-methylcyclo-octylamine[5] and CD_3I in Et_2O, reacted with BuLi in pentane to afford *cis*- and *trans*-cyclo-octene in a 70:30 ratio (Scheme). The butylamine (**6**) was isolated by g.l.c. and mass spectral analysis showed it to have lost 2·0% of the deuterium initially present in (**2**) (Table). This represents less than a statistical loss of deuterium and probably reflects a substantial isotope effect. More significantly, these data preclude extensive exchange of the α'-hydrogen in the tetra-alkylammonium salt (**2**).

TABLE. Products from the labelled quaternary ammonium salt (**2**).

Base–solvent	*cis*-Cyclo-octene[c] (**4**) (%)	*trans*-Cyclo-octene (**5**) (%)	*NN*-Dimethyl-n-butylamine[e] (**6**)
KNH_2–NH_3[a]	31·6[d]	68·4[d]	97·1% $^2H_0$ 2·9% $^2H_1$
$LiNH_2$–NH_3[a]	31·5[d]	68·5[d]	97·8% $^2H_0$ 2·2% $_2H_1$
Bu^nLi–pentane[b]	70·1[d]	29·9[d]	98% $^2H_3$ 4% $^2H_2$

[a] Reaction time 5 h at −33°. [b] Reaction time 24 h at room temperature. [c] All values are an average of two or more experiments. [d] 100% $^2H_0$; 0% $^2H_1$. [e] Amine was analysed at 11 eV where there was no contribution of the $M - 1$ peak. The values are accurate to within ±1·5%. The initial deuterium content of the CD_3I was 89% $^2H_3$, and the values given are corrected for the initial deuterium content.

In marked contrast to the above results, the reaction of (**2**) with KNH_2 in liquid NH_3 afforded a *cis-trans* ratio of 32:68 and the isolated amine (**6**) had lost essentially all its deuterium. Since control experiments have established that the tertiary amine (**6**) does not undergo hydrogen exchange under the reaction conditions, the α'-hydrogens in (**2**) are being completely exchanged prior to elimination. The rapid reversible formation of the ylide intermediate (**3**) is also occurring with $LiNH_2$ in liquid NH_3 as evidenced by the total exchange of the α'-deuterium.

Since the same product ratio was obtained with KNH_2 and $LiNH_2$, the complexation of the carbanion base centre of the ylide with the metal cation in liquid NH_3 does not seem to affect its relative basicity. Even though an ylide mechanism is operating with both base–solvent systems,[3,4] the difference in the ratio of (**4**) to (**5**) is apparently influenced by the reversibility of the ylide formation. We have previously argued[6] that the exclusive formation of *cis*-cyclo-octene in the Cope elimination, where *syn* elimination is affected by an oxy-anion in a manner analogous to the ylide mechanism, is due to the selectivity of the weakly basic oxyanion. Consistent with this suggestion, stabilized benzyl ylides also afford the thermodynamically favoured *cis*-cyclo-octene. Thus, in RLi–pentane the carbanionic centre of the ylide is more highly co-ordinated with Li^+ and is a more selective base affording a higher percentage of *cis*-stereoisomer.

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