The Apparent [2,3] Sigmatropic Rearrangements of Acetylenic Ammonium Ylides

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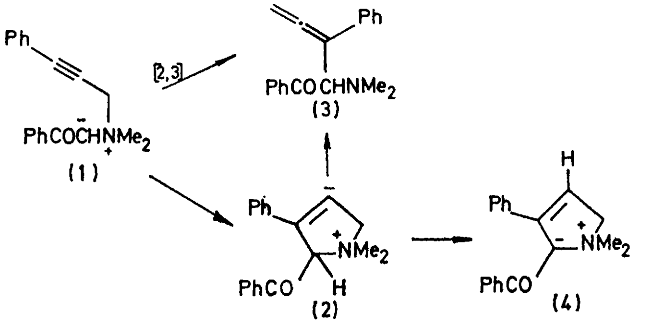
Summary The rearrangement reactions of acetylenic ammonium ylides are not inhibited by the steric requirements of the bicyclic systems of (**7a**) and (**10a**); accordingly a non-concerted mechanism analogous to (**1**) → (**2**) → (**3**) is proposed for these reactions, rather than the [2,3] concerted sigmatropic mechanism.

We have shown[1] that the phenylpropynyl ylide (**1**) rearranges at 0° either by the apparent [2,3] sigmatropic process (**1**) → (**3**) or by an intramolecular cyclisation process to give first the betaine (**2**) which then undergoes a prototropic shift giving the isolable ylide (**4**). Since the process (**1**) → (**3**) might in fact involve the non-concerted mechanism (**1**) → (**2**) → (**3**) indicated in the Scheme, we have further investigated the rearrangement reactions of acetylenic ylides using the steric requirements of bicyclic systems[2] as a probe into reaction mechanism.

The prototropic rearrangement (**2**) → (**4**) can be prevented by carrying out the rearrangement in an aprotic solvent using the quaternary salt with sodium hydride in dimethyl sulphoxide at room temperature. Under these conditions (10 h) the tetrahydro-isoquinoline derivative (**5**) gives the unstable allene (**6**) in good yield. The bicyclic quaternary salt (**7a**) also rearranges using the *same reaction conditions* to give initially the allene (**8**) which may be isolated under controlled conditions. The allene (**8**) may also undergo further base-catalysed rearrangement giving a mixture (1 : 1) of the diastereomeric dienes (**9a** and **b**) (76% yield). This result contrasts with the failure of the ylide from the corresponding *N*-cinnamyl salt (**7b**) to rearrange cleanly, even at elevated temperatures (80°).



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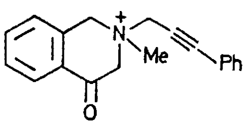
The bicyclic quaternary salt (**10a**) also rearranges readily (12 h) to give the allene (**11**), which again is isolable under controlled conditions but also reacts further to give the stable furan derivative (**12**) (99% yield). This result again contrasts with the rearrangement of the ylide from the corresponding cinnamyl salt (**10b**) which is considerably retarded by the bicyclic system.[2] The ylide derived from the salt (**13**) fails to rearrange at room temperature, and at higher temperatures (80—90°) it gives a complex mixture of products from which no pure compounds could be isolated.

The similarity of the reaction conditions required for the rearrangements of the salts (**5**), (**7a**), and (**10a**) indicates that the rearrangement of acetylenic ylide derivatives is not retarded by the bicyclic systems of (**7**) and (**10**). We therefore propose that the apparent [2,3] sigmatropic rearrangement of acetylenic ylide derivatives does not occur by a concerted process but is replaced by a non-concerted pathway analogous to (**1**) → (**2**) → (**3**). The comparatively faster rearrangement of acetylenic as compared with olefinic ylide derivatives can then be understood, because a route involving a σ-bonded intermediate [*cf.* (**2**)] would have less rigorous steric requirements than those of the concerted process analogous to (**1**) → (**3**). The participation of triple bonds in concerted anionic [2,3] sigmatropic rearrangements, previously a generally accepted process,[3] is considered on the basis of these results and those reported previously,[1] to be an unlikely event.



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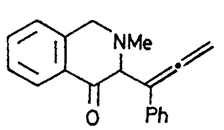

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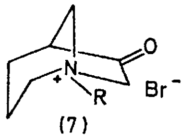
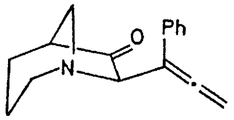


(7)

a; R = CH$_2$C≡CPh

b; R = CH$_2$CH=CHPh



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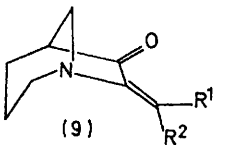

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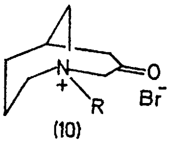
a; R^1 = Ph, R^2 = CH=CH$_2$

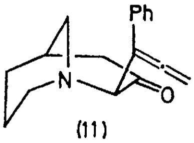
b; R^1 = CH=CH$_2$, R^2 = Ph



(10)

a; R = CH$_2$C≡CPh

b; R = CH$_2$CH=CHPh



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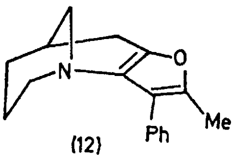

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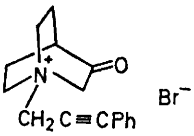

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[1] S. Mageswaran, W. D. Ollis, and I. O. Sutherland, *Chem. Comm.*, 1971, 1493.

[2] S. Mageswaran, W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, *Chem. Comm.*, 1971, 1494; C. J. Dixie and I. O. Sutherland, *J.C.S. Chem. Comm.*, 1972, 646, and references cited therein.

[3] I. Iwai in 'Mechanisms of Molecular Migration, Vol. 2,' ed. B. S. Thyagarajan, Interscience, New York, 1969, p. 105; J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Comm.*, 1968 ,1083; U. Schöllkopf and M. Rizk, *Angew. Chem. Internat. Edn.*, 1965, 4, 957.