

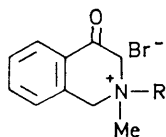
Effect of Transition-state Geometry on the [2,3]-Sigmatropic Rearrangements of Ammonium Ylides

By S. MAGESWARAN, W. D. OLLIS,* I. O. SUTHERLAND, and Y. THEBTARANONTH

(Department of Chemistry, The University, Sheffield S3 7HF)

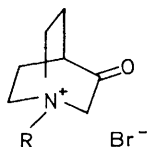
Summary The normally rapid [2,3]-sigmatropic rearrangement of allylic ammonium ylides may be slowed down or prevented by unfavourable transition-state geometry

ORBITAL symmetry relationships provide a satisfying general way of predicting whether pericyclic reactions are allowed as concerted processes,¹ and interest is now being focussed upon the effects of bending and torsional distortions in the transition states for these reactions. In this communication we discuss the effects of torsional strain upon the rates of the [2,3]-sigmatropic rearrangements of allylic ammonium ylides. Although the effects of torsional strain have previously been the subject of comment, particularly for reactions involving antarafacial π -components,² these comments have been concerned with isolated examples rather than a systematic study of structurally related systems in which torsional strain can be varied.



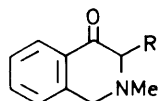
(1) R = CH₂CH=CHPh

(3) R = CH₂Ph



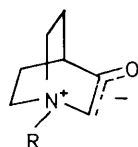
(5) R = CH₂Ph

(6) R = CH₂CH=CHPh



(2) R = CHPh·CH=CH₂

(4) R = CH₂Ph



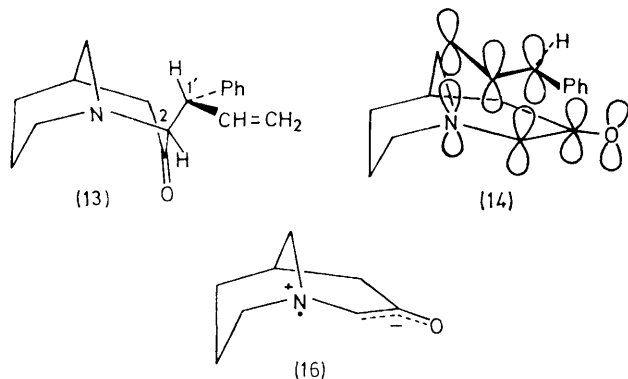
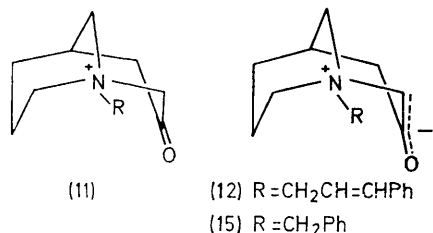
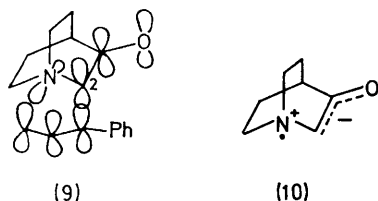
(7) R = CH₂Ph

(8) R = CH₂CH=CHPh

The *N*-cinnamylisoquinolinium derivative (1) rearranges rapidly (*ca* 20 min at -50°) on treatment with methanolic 0.5 M-sodium methoxide to give the product (2) (88%) of the allowed [2,3]-sigmatropic rearrangement.³ The analogous *N*-benzyl salt (3) also rearranges (*ca* 60 min at 20°) on treatment with methanolic sodium methoxide to give the Stevens rearrangement product (4) (60%) presumably by a radical-pair mechanism.⁴ In contrast both the *N*-benzyl (5) and *N*-cinnamyl (6) ammonium salts derived from 1-azabicyclo[2,2,2]octan-3-one give stable ylides (7) and (8) on treatment with aqueous sodium hydroxide. The ylides (7) and (8) gave very complex mixtures on heating. The formation of the *N*-cinnamylammonium ylide (8) is particularly noteworthy because it is the first carbonyl-stabilised ammonium ylide to be described bearing an allylic substituent which does not rearrange rapidly. This failure of the ylides (7) and (8) to rearrange cleanly is presumably a consequence of the prevention of good bonding, involving the indicated atomic orbitals, in the transition state (9) by the steric requirements of the bridged ring system. In particular, the torsion angle ω between the *p*-orbital at C(2) and the participating nitrogen orbital is *ca* 90° , and some of this twisting would also be imparted to the migrating allyl unit. The possibility of the rearrangement of ylides (7) and (8) by a radical pair mechanism involving the radical (10) is also ruled out by the lack of conjugation between the nitrogen orbital containing the unpaired electron and the π -orbitals of the enolate anion system.

The twisting of the π -system in the transition state (9) and the inhibition of conjugation in the radical (10) is maximised (ω *ca* 90°) by the geometry of the azabicyclo[2,2,2]octane system, whereas it would be expected to be less severe (ω *ca* 30°) in the azabicyclo[3,3,1]nonane system by analogy with the recent modification⁵ of Bredt's rule. In

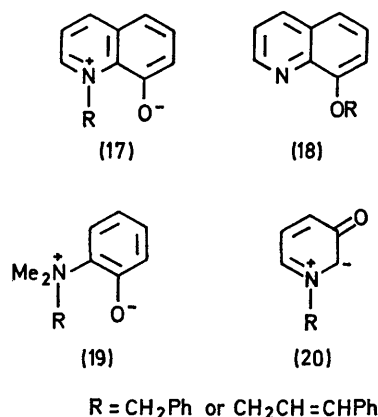
accord with this expectation, the cinnamyl ylide (**12**), generated from the salt (**11**), rearranged smoothly at 120° to give a good yield [85% based on the salt (**11**)] of the single



[2,3]-sigmatropic rearrangement product (**13**). The stereochemistry of compound (**13**) is proposed on the basis of maximum orbital overlap and minimum non-bonded interactions in the transition state (**14**). The axial orientation of the α -phenylallyl group is deduced from the small $\text{NH-C}(2)\text{H}$ coupling constant in the n.m.r. spectrum of compound (**13**) in trifluoroacetic acid. The relative configuration of the other chiral centre (1') of the α -phenylallyl unit is based only upon the transition state geometry (**14**). The *N*-benzyl ylide (**15**) failed to rearrange cleanly by the radical pair mechanism and on heating (160—175°) decomposed to

give a complex mixture of products. Thus, in the case of the azabicyclo[3,3,1]nonane system, orbital overlap is adequate to permit rearrangement by way of the homoaromatic transition state (**14**), although the rearrangement only proceeds at a temperature at least 170° higher than for the ylide derived from the isoquinoline (**1**); the conjugative stabilisation of the radical (**16**) is not, however, adequate to permit a clean Stevens rearrangement of the ylide (**15**).

These principles are also illustrated by the failure of the betaines (**17**) to rearrange thermally by a formally allowed



[1,4]-sigmatropic rearrangement to the ethers (**18**). This result is in contrast to the ready [1,4]-sigmatropic rearrangement⁶ of the rather similar betaines (**19**) in which the N-R bond can adopt a conformation suitable for the development of good bonding in the transition state. The betaines (**17**) are also unable to rearrange to the ether (**18**) by an $\text{S}_{\text{N}}1$ mechanism, since substitution of the group at the carbon atom R necessarily involves endocyclic⁷ stereochemistry. The thermal stability of the pyridinium betaines (**20**) is another illustration of the same principle.

We conclude that apparent sigmatropic rearrangements which involve considerable twisting of the π -system in the transition state, for example, the [3,3]-rearrangement with two antarafacial units,^{2,8} are likely to involve alternative pathways.

(Received, July 27th, 1971; Com. 1309.)

¹ R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 827.

² J. E. Baldwin and M. S. Kaplan, *Chem. Comm.*, 1969, 1354.

³ R. W. Jemison and W. D. Ollis, *Chem. Comm.*, 1969, 294.

⁴ U. Schöllkopf, U. Ludwig, G. Ostermann, and M. Patsch, *Tetrahedron Letters*, 1969, 3415; R. W. Jemison, S. Mageswaran, W. D. Ollis, S. E. Potter, A. J. Pretty, I. O. Sutherland, and Y. Thebtaranonth, *Chem. Comm.*, 1970, 1201.

⁵ J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, 1970, **92**, 948; J. R. Wiseman and W. A. Pletcher, *ibid.*, 1970, **92**, 956; R. Keese and E.-P. Krebs, *Angew. Chem. Internat. Edn.*, 1971, **10**, 262.

⁶ S. Mageswaran, W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, forthcoming publication. For an account of [1,4]-sigmatropic rearrangements in a related system see U. Schöllkopf and I. Hoppe, *Tetrahedron Letters*, 1970, 4527 and references therein.

⁷ L. Tenud, S. Farooq, J. Seibl, and A. Eschenmoser, *Helv. Chim. Acta*, 1970, **53**, 2059.

⁸ T. Miyashi, M. Nitta, and T. Mukai, *Tetrahedron Letters*, 1967, 3433.