Base-catalysed Rearrangement of Allyl–Propynyl Ammonium Cations in Protic Media

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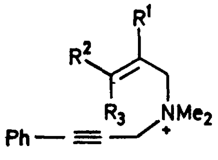
Summary The base-catalysed rearrangement of the allyl–propynyl ammonium cations (I) in aqueous solution yields either the isomeric cations (II) or the aldehydes (III) and (IV), or mixtures of (II), (III), and (IV); this result contrasts dramatically with the transformations of (I) observed in aprotic solvents.

In the preceding communication,[1] the base-catalysed rearrangement of allyl–propynyl ammonium cations (I) in aprotic media (MeONa–Me_2SO) has been described. It is now reported that the ammonium cations (I) exhibit a completely different sequence of reactions under conditions of base-catalysed equilibration using a trace of sodium hydroxide in boiling water. Depending upon the nature of

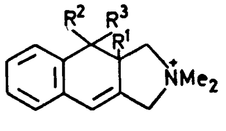
Table

	Reactants (I)			Product yields (%)		
	R^1	R^2	R^3	(II)	(III)	(IV)
(a)	H	H	H	65	33	
(b)	H	Me (H)[a]	H (Me)[a]	*ca.* 80	16	4
(c)	H	Me	Me	45		20
(d)	H	Ph	H	100		
(e)	Me	H	H		76	
(f)	Ph	H	H		70	6

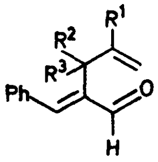
[a] The reactant (Ib) was a mixture of *trans*- and *cis*-crotyl derivatives.



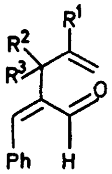
(I)



(II)



(III)



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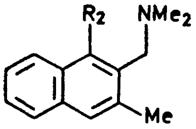

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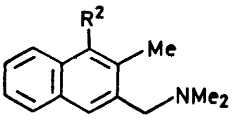
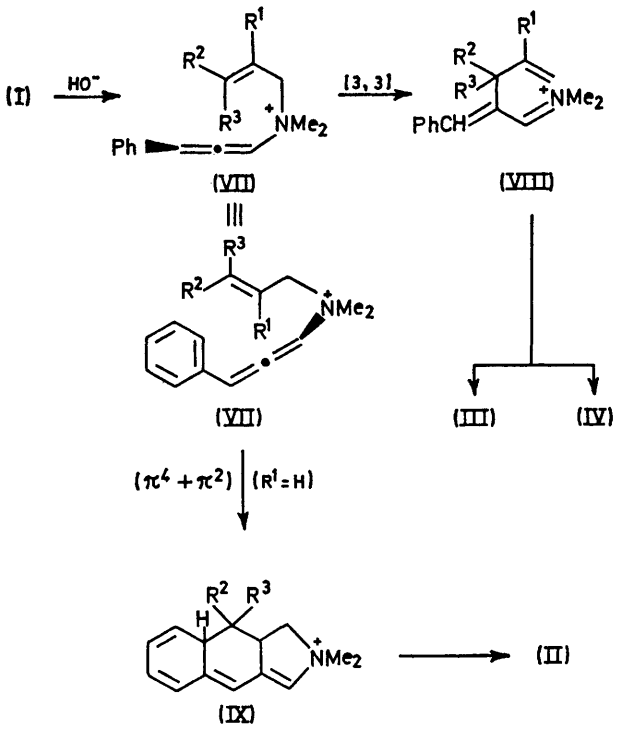


(VI)

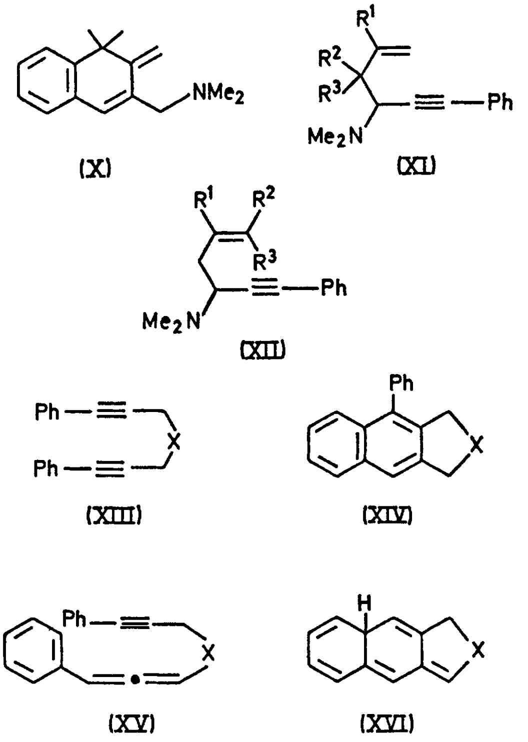
the substituents R^1, R^2, and R^3 [see (I)], the products include the isomeric cations (II) and the *cis*- and *trans*-diastereomeric aldehydes (III) and (IV). The results are summarised in the Table.

The constitutions (II) were established by analytical and spectroscopic data and they were confirmed by the following transformations. The product (IIa) with hot 25% aqueous sodium hydroxide gave the naphthalene (Va) (80%) which, by an Emde Reduction (Na–Hg/H_2O) yielded 2,3-dimethylnaphthalene (95%). The dihydronaphthalenes (IIb) and (IId) similarly yielded a mixture of the naphthalenes (Vb + VIb) and (Vd + VId) respectively, which were separated chromatographically. The configurations assigned in the Table to the aldehydic products (III) and (IV) are provisional and their relation to the transition state associated with the [3,3]-sigmatropic rearrangement (VII) → (VIII) is being investigated.



SCHEME

The mechanisms which are proposed for the transformations (I) → (II) and/or (III) + (IV) are given in the Scheme. The acetylenic ammonium cation (I) first undergoes a base-catalysed prototropic isomerisation[2-4] yielding the allenic ammonium cation (VII). This allene (VII) may then participate in a [3,3]-sigmatropic rearrangement[5] yielding the ene-ammonium cation (VIII) which by hydrolysis gives the diastereomeric aldehydes (III) and (IV); the corresponding [3,3]-rearrangement of allyl-vinyl-ammonium cations is known.[6] Alternatively, the allene (VII) by an intramolecular $[_{\pi}4 + _{\pi}2]$-cycloaddition[7] can give the intermediate (IX) which by a [1,5]-shift (unconcerted or two 1,3-sigmatropic shifts) of hydrogen could lead to isolated product (II). The $[_{\pi}4 + _{\pi}2]$-cycloaddition is not observed in those cases (II e and f) in which R^1 = Me or Ph, presumably because the transition state required for the $[_{\pi}4 + _{\pi}2]$-cycloaddition is too sterically hindered.



In (XIII) - (XVI) (a) X = CH_2;
(b) X = O;
(c) X = S;
(d) X = NMe;
(e) X = $\overset{+}{N}Me_2$

The difference between the results described in this and the preceding communication[1] is remarkable particularly as the ylides derived from the cations (I) are common intermediates. Related reactions are observed in concentrated aqueous sodium hydroxide; for example, the cation (Ic) yields the products (IVc) (12%), (X) (17%), (XI; R^1 = H, R^2 = R^3 = Me) (46%), and (XII; R^1 = H, R^2 = R^3 = Me) (9%).

The remarkably smooth base-catalysed transformation[2,8] of the bis-(3-phenylprop-2-ynyl)-derivatives (XIII a—d) into the naphthalenes (XIV a—d) also presumably involves a $[_{\pi}4 + _{\pi}2]$-cycloaddition of the allenic isomer (XV) giving the intermediate (XVI) which then yields the product (XIV).

On this basis, the claim[2,9] that the ammonium cation (XIIIe) did not react similarly seems peculiar. We now find that addition of a trace of sodium hydroxide to an aqueous solution of the cation (XIIIe) gives the isomer (XIVe) (96%) exothermically.

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[1] R. W. Jemison, T. Laird, and W. D. Ollis, preceding communication.

[2] I. Iwai in 'Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, Interscience, New York, 1969, vol. 2, pp. 73—116.

[3] G. D. Appleyard and C. J. M. Stirling, *J. Chem. Soc.* (*C*), 1969, 1904.

[4] R. J. Bushby, *Quart. Rev.*, 1970, **24**, 585.

[5] L. Skattebøl and S. Solomon, *J. Amer. Chem. Soc.*, 1965, **87**, 4506; H. M. Frey and D. M. Lister, *J. Chem. Soc.* (*A*), 1967, 26; H. M. Frey and A. M. Lamont, *ibid.*, 1969, 1592.

[6] E. Elkik, *Bull. Soc. chim. France*, 1960, 972; 1969, 903; K. C. Brannock and R. D. Burpitt, *J. Org. Chem.*, 1961, **26**, 3576; G. Opitz, *Annalen*, 1961, **650**, 122; A. T. Babayan, *Tetrahedron*, 1964, **20**, 1371; J. Corbier, *Compt. rend.*, 1969, **268C**, 1614; 1970, **270C**, 2077.

[7] C. Dufraisse, J. Mathieu, and J. Valls, *Compt. rend.*, 1958, **246**, 661; K. Alder, U. Dölling, W. Schröder, and W. Spanke, *Chem. Ber.*, 1959, **92**, 99; E. R. H. Jones, H. H. Lee, and M. C. Whiting, *J. Chem. Soc.*, 1960, 341; J. E. Baldwin and L. E. Walker, *J. Org. Chem.*, 1971, **36**, 1440.

[8] I. Iwai and J. Ide, *Chem. and Pharm. Bull.* (*Japan*), 1964, **12**, 1094.

[9] I. Iwai and T. Hiroaka, *Chem. and Pharm. Bull.* (*Japan*), 1963, **11**, 1556, 1564.