Orbital Symmetry Control in the Rearrangements of Allylic Ammonium Ylides and a Novel Related Thermal Rearrangement

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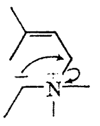
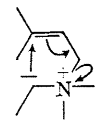
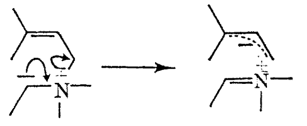
IN the preceding Communication, reference is made to the possibility that the intermediate sulphonium ylides produced by deprotonation of sulphonium cations could well be stabilised by d_π–p_π orbital interaction. This circumstance, which is provided by the sulphur atom, is not available for ylids derived from quaternary ammonium cations, and possible consequences of this difference have now been examined. At least three types of reaction mechanism[1] formally represented by (I), (II), and (IIIa → IIIb) can be envisaged for ylides derived from ammonium cations.



(I)



(II)



(IIIa) (IIIb)

In an earlier study[2] of the base-catalysed rearrangement of cations of the type (IV), support for the operation of the formally symmetry-forbidden Stevens rearrangement [(I); with retention of configuration at the terminus of the migrating group] was apparently provided by the observation that some rearrangements [(IVb) → (Vb) + (VIb) and (IVc) → (Vc) + (VIc)] gave mixtures of products, whereas others [(IVa) → (Va), (IVd) → (Vd), and (IVe) → (Ve)] gave one product exclusively. This difference was puzzling,[2] but re-investigation of these reactions shows that the base-catalysed rearrangement of the ammonium cations (IV) gives *only* the symmetry-allowed products (V) which, in those cases where $R^1 \neq R^2$, are mixtures of two diastereomeric racemates. The base-catalysed reactions (IVb) → (VIb) and (IVc) → (VIc) do not occur.

There is an identity of reaction type shown by ammonium cations[2,3] (IV) and the corresponding sulphonium cations,† but there are interesting differences between the base-catalysed reactions of bis-allylammonium cations (VII; $X = NMe_2$) and sulphonium cations (VII; $X = SR$). Four possible products [(VIII and (IX), symmetry-allowed; and (X) and (XI) symmetry-forbidden] can be recognised.[4a] For base-catalysed reactions, only the symmetry-allowed process [(VII) → (VIII) 90—95%] has been observed when $X = SMe$ or SEt,[4] but when $X = NMe_2$ then the alternative symmetry-allowed process [(VII) → (IX)] does take place. Thus, the bis-3,3-dimethylallylammonium cation (VIIf;

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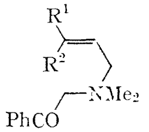
† Preceding Communication.

X = NMe_2) with phenyl-lithium eventually gives the aldehyde (XII; 15%), presumably formed *via* the enamine intermediate (IXf; X = NMe_2). Similarly, the bis-cinnamyl compound[5] (VIIb; X = NMe_2) gives the aldehyde [(XIII) yield 25%)] *via* the enamine (IXb; X = NMe_2). Other products are also formed from the rearrangements of ammonium cations (VII; X = NMe_2) and their constitutions are under investigation. The generalisations [(VII) → (VIII) when X = SR] and [(VII) → (IX) when X = NMe_2] are limited to the present results and refer only to base-catalysed processes; they are not intended to include the related benzyne-promoted reactions.[4a,d,f] The differences and similarities between the behaviour of allylic ylid intermediates derived from sulphonium and ammonium cations is clear, but further studies are necessary before a choice can be made between alternative mechanistic possibilities such as (II) or (III).

During these studies, an interesting *general* thermal rearrangement has been encountered which is exemplified by the transformation (Vf) → (VIf) (yield *ca.* 100%). This isomerisation takes place at 180°. The mechanism and generality of this reaction is under investigation, but it will be clear that it has implications so far as the mechanism of the Stevens' rearrangement[1] (I) is concerned. Thus, although the concerted reaction (IVf) → (VIf) is not symmetry-allowed (with retention of configuration at the terminus of the migrating group), and this reaction (IVf) → (VIf) is not in fact observed, this transformation can be achieved by a sequence of two reactions (IVf) → (Vf) → (VIf).

The thermal transformation (V) → (VI) is unusual in several respects, although it may be compared with other thermally promoted allylic rearrangements.[6] This new reaction may be regarded as a 1,3-sigmatropic reaction[7] which proceeds thermally under unusually mild conditions. The description as a thermal 1,3-sigmatropic reaction has stereochemical implications associated with inversion[7,8] which are now being scrutinised experimentally. Mechanistically related reactions are rare, but thermal processes showing some similarity, including C–C bond cleavage, are (XIV) → (XVI),[9] (XV) → (XVII),[10] and (XVIII) → (XIX).[11] The general aspects of these and other 1,3-sigmatropic reactions are also under investigation including the possibility that the observed formation of some symmetry-forbidden Stevens rearrangement products involves a hitherto unrecognised reaction sequence which includes a thermal isomerisation as the last step.



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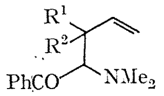
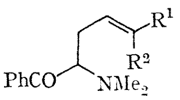


(V)



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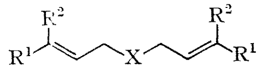
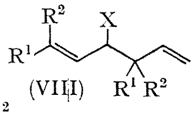


(VII)



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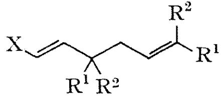

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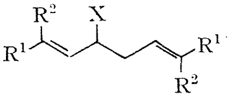
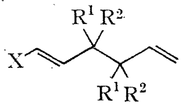
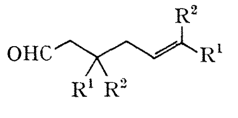


(X)

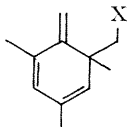


(XI)

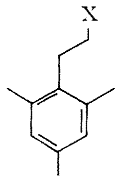
	R^1	R^2
(a)	Me	H
(b)	Ph	H
(c)	o-$Me{\cdot}C_6H_4$	H
(d)	p-$MeO{\cdot}C_6H_4$	H
(e)	o-$O_2N{\cdot}C_6H_4$	H
(f)	Me	Me



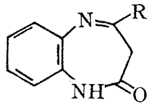
(XII) $R^1 = R^2 = Me$
(XIII) $R^1 = Ph$; $R^2 = H$



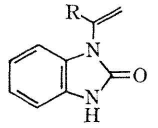
(XIV) X = NMe_2
(XV) X = SMe



(XVI) X = NMe_2
(XVII) X = SMe



(XVIII)



(XIX)

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