[4,5] Anionic Sigmatropic Rearrangements

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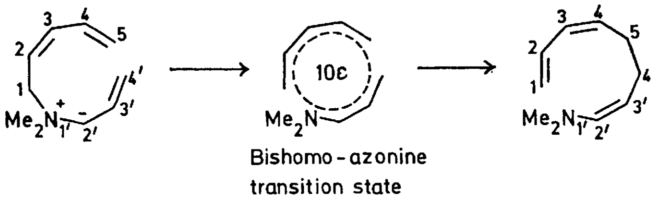
Summary Allyl(pentadienyl)ammonium ylides (VII) rearrange to the enamines (III) at room temperature; the reaction is shown to be a concerted [4,5] sigmatropic rearrangement proceeding *via* a nine-membered transition state involving 10π electrons.

Although the Woodward–Hoffmann rules[1] have predicted that high-order sigmatropic rearrangements should be feasible in suitable systems, the first examples of the thermal [5,5][2] and cationic [3,4][3] rearrangements have been reported only recently.[2,3] We now describe the first examples of long-range concerted anionic rearrangements—[4,5] sigmatropic rearrangements.† These may be represented without stereochemical implication as shown in Scheme 1.

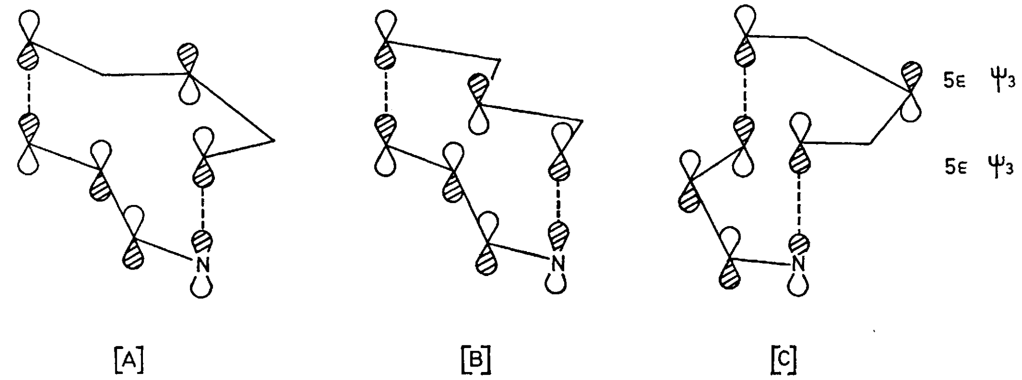


Scheme 1.

The Z-penta-2,4-dienylamines (Ia—d) were prepared from the appropriate 3- or 4-substituted pyridine methiodides by (i) reduction with aqueous alkaline sodium borohydride, (ii) quaternisation with methyl iodide, and (iii) Hofmann elimination using sodium methoxide–dimethyl sulphoxide. Z-(N-2-Methylpenta-2,4-dienyl)-NN-dimethylamine (Ia)[5] and cinnamyl bromide gave the salt (IIa) which on treatment with sodium methoxide–dimethyl sulphoxide at room temperature gave the enamine (IIIa) (*ca.* 60%). In addition, the amines (IVa) (*ca.* 5%) and (Va) (*ca.* 5%) were obtained as by-products; they are presumably formed from radical-pair intermediates. The enamine (IIIa) on mild acid hydrolysis gave the aldehyde (VIa). During this work, all the enamines (IIIa—e) and (XV) were characterised as their corresponding aldehydes.‡

The reaction (IIa → IIIa) certainly involves the ylide (VIIa) which undergoes a [4,5] sigmatropic rearrangement (VII, see arrows) *via* a bishomo-azonine 'aromatic' transition state involving 10π electrons.[6] In the transition state (see Scheme 1), the pentadienyl fragment will adopt a transoid configuration for effective orbital overlap and this determines the stereochemistry of the enamine (IIIa). In spite of the nine-membered transition state, the reaction (IIa → IIIa) proceeds in an impressive yield.

In a similar manner, the salts (IIb and c) were transformed by [4,5] sigmatropic rearrangement into the enamines (IIIb and c) (50—60%) respectively. The by-product (VIIIb) (3%) arises by a [2,3] sigmatropic rearrangement of the alternative ylide (IXb) formed from the salt (IIb). In the case of the salt (IId), the major product (VIIId) (50%) was formed by a [2,3] sigmatropic rearrangement and the enamine (IIId) (30%) in somewhat lower yield by a [4,5] sigmatropic rearrangement. Rearrangement of the salt (IIe) yielded only 5% of the [4,5] rearrangement product (IIIe); the alternative symmetry-allowed and sterically acceptable [6,3] rearrangement might have occurred, but was not observed. The major component isolated was the aldehyde (X, mixture of diastereomers in the ratio 1:1) (20%). This aldehyde (X) can arise by isomerisation of the allyl salt (IIe) to its prop-1-enyl isomer (XI), followed by [3,3] rearrangement[7] to the ene-ammonium cation (XII) and hydrolysis to aldehyde (X). This pathway has been observed previously[7] for allylic and acetylenic ammonium salts, but normally occurs only in protic solvents.[8]



Scheme 2. *Three of the eight possible transition state geometries associated with suprafacial-suprafacial* [4,5] *sigmatropic rearrangements.*

The geometry of the transition state (Scheme 2) which is associated with the observed anionic [4,5] sigmatropic rearrangement (II → III) is [A] rather than [B] or [C].

An alternative, but less likely, mechanism for the transformation (II → III) involves a [2,3] rearrangement of the ylide (VII) to amine (XIII) followed by a [3,3] rearrangement of amine (XIII) to the enamine (III). This possible mechanism (II → VII → XIII → III) is excluded by the rearrangements of salt (XIV; X = H, Y = Me) to enamine (XV; X = H, Y = Me) (15%) and salt (XIV; X = Me, Y = H) to isomeric enamine (XV; X = Me, Y = H) (15%); the formation of two different enamines definitely excludes the possibility of a sequence of a [2,3] followed by a [3,3] rearrangement and clearly supports the view that the [4,5] rearrangement occurs directly in a concerted fashion.

The transformations (XIV → XV) can therefore be formulated as [4,5] sigmatropic rearrangements proceeding *via* a transition state of type [B] (Scheme 2) in which the *trans*-pentadienyl unit adopts a transoid configuration. The relatively low yield of [4,5] rearrangement product in these cases may be an indication that orbital overlap in

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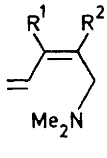
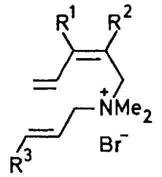
† The formation of 1-methylthio-3-(p-tolyl)-*trans*-prop-1-ene as a minor product in the base-induced rearrangement of allyl benzyl sulphide[4] could be formally considered as a [4,5] rearrangement although other pathways have not been excluded.

‡ All new compounds were fully characterised by spectroscopic methods, analysis and/or high resolution mass spectrometry.

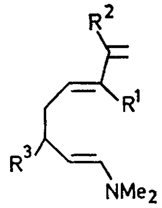
transition state [B] is less effective than in transition state [A]. [4,5] Rearrangements involving transition states of type [B] have been observed in different systems.[9]



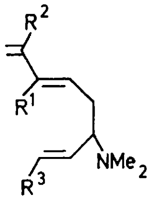
(I)



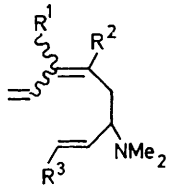
(II)



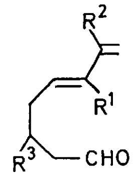
(III)



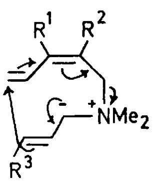
(IV)



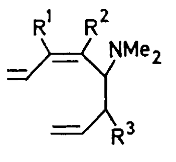
(V)



(VI)



(VII)



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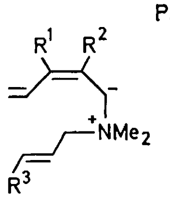
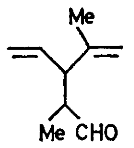
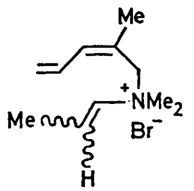


(IX)

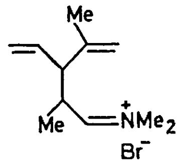
In formulae (I)—(IX) and (XIII)	R^1	R^2	R^3
(a)	H	Me	Ph
(b)	Me	H	Ph
(c)	Me	Me	Ph
(d)	H	H	Ph
(e)	H	Me	H



(X)



(XI)



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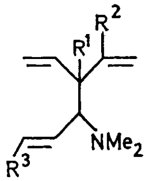

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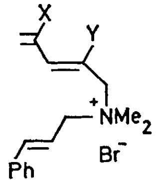

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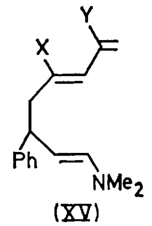

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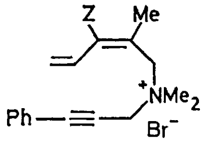
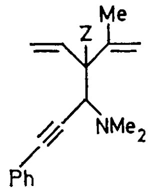
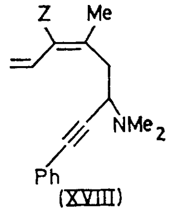


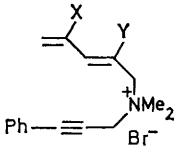
(XVI)



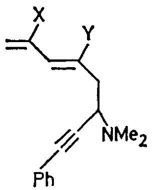
(XVII)



(XVIII)



(XIX)



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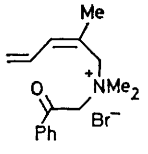
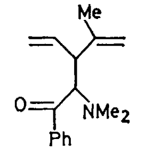


(XXI)



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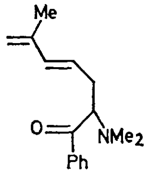

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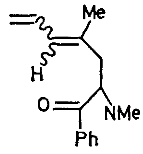

(XXIV)

The acetylenic analogue of a [4,5] anionic sigmatropic rearrangement in the base-catalysed transformation of the acetylenic salts (XVI; Z = H or Me) is not observed.[10] The major products (XVII; Z = H or Me, mixture of diastereomers) (80—90%) arise from a [2,3] rearrangement (without participation by the triple bond), whereas the minor products (XVIII; Z = H or Me) (5—10%) arise from a Stevens [1,2] rearrangement. Similarly, the salts (XIX; X = H, Y = Me) and (XIX; X = Me, Y = H) lead to the [2,3] sigmatropic rearrangement product (XVII; Z = H, diastereomeric mixture) (*ca.* 80%); the minor products (XX; X = H, Y = Me) and (XX; X = Me, Y = H) (5—10%) in both cases are formed by a Stevens [1,2] rearrangement. The salt (XXI) with base gave the amine (XXII, diastereomeric mixture) (90%) which on heating yielded the amines (XXIII) (50%) and (XXIV) (50%) by a [1,3] shift.[11]

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