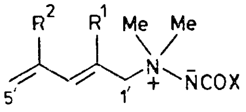
The Thermal Rearrangements of Pentadienylammonium Ylides. Competing [1,2], [3,2], and [5,2] Rearrangements

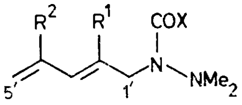
By KAN CHANTRAPROMMA, W. DAVID OLLIS,* and IAN O. SUTHERLAND
(*Department of Chemistry, The University, Sheffield* S3 7HF)

Summary The pentadienylammonium ylides (**9**) rearrange thermally to give the products (**14**), (**15**), (**16**), and (**17**) by two distinct reaction pathways; the first is formally a forbidden sigmatropic rearrangement and it involves an interacting radical pair having some translational freedom giving predominantly the products of [1,2] and [5,2] rearrangements, and the second is formally an allowed [3,2] sigmatropic rearrangement which involves an interacting radical pair indistinguishable from the transition state of a concerted pericyclic process.

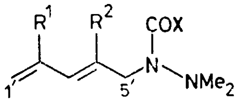
THE [1,2] Stevens rearrangement of pentadienyl ammonioamidates (**1**) gives[1] the rearrangement products (**2**) and (**3**) in which the pentadienyl fragment couples at positions 1′ and 5′ respectively. This result clearly demonstrates that the [1,2] rearrangement of the ylides (**1**) proceeds totally by a radical mechanism. It was of interest to discover whether the [1,2] Stevens rearrangement of pentadienylammonium ylides (**9**) showed similar characteristics: earlier evidence,[2] based upon CIDNP, was consistent with either competing radical and concerted processes or a radical process in which only a small proportion of the reaction gave rise to CIDNP.



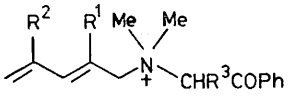
(1)



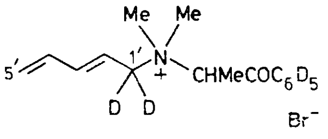
(2)



(3)



(4) Br⁻



(5)

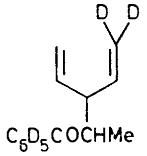
In (**1**), (**2**), and (**3**), R^1 or R^2 = Me or H, X = Ph, Me, OEt, or NHMe

The base catalysed rearrangement of the pentadienylammonium salt (**4a**)† gave only the product (**16a**) of a [3,2] sigmatropic rearrangement, but the methyl substituted salt (**4b**) with aqueous sodium hydroxide at room temperature gave the products of [1,2] (**14b**) and [3,2]

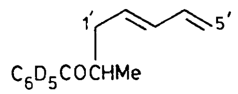
---

† The pentadienylammonium ylides (5) were not isolable and rearrangements were carried out by treating the corresponding quaternary ammonium salts (4) with base.

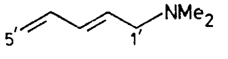
(**16b**) rearrangements in a 1:3 ratio, together with minor amounts of the products of [1,3] and [3,3] rearrangements.[3] A repetition of this experiment using an equimolecular mixture of the salt (**4b**) and the heptadeuterio-salt (**5**) showed that at 0 °C, using both aqueous sodium hydroxide and methanolic sodium methoxide, the products (**14b**) and (**16b**) were both formed by an intramolecular rearrangement ($^2H_0$ and $^2H_7$ products only with no detectable $^2H_2$ and $^2H_5$ products within the limits of experimental error).



(6)



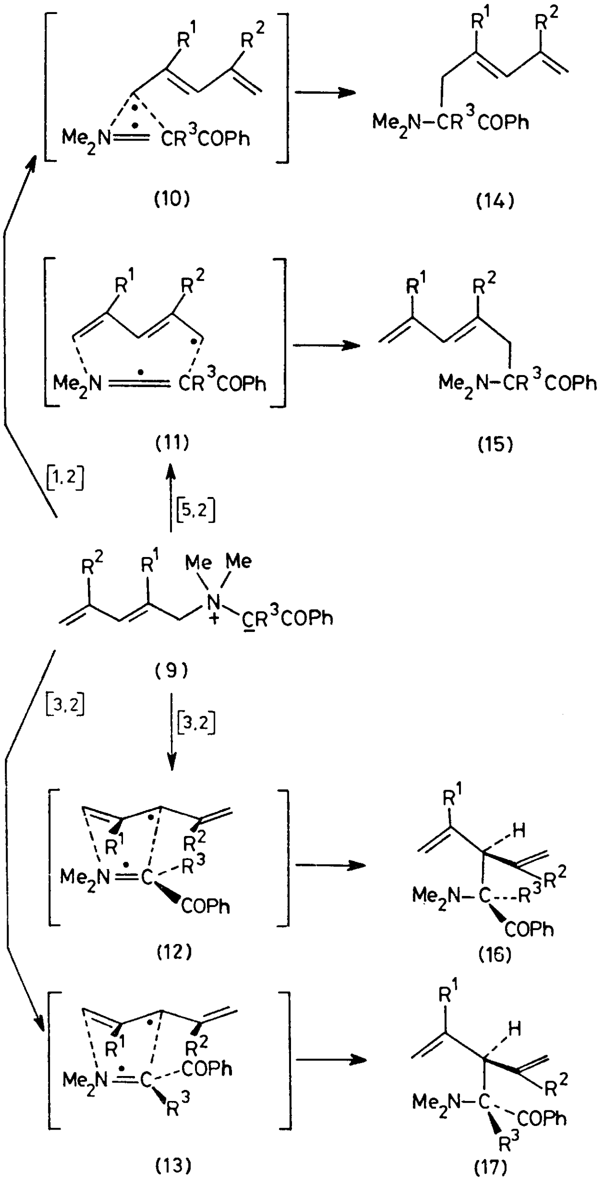
(7); 1′-CD$_2$, 5′-CH$_2$ or 1′-CH$_2$,5′-CD$_2$



(8); 1′-CD$_2$,5′-CH$_2$ or 1′-CH$_2$,5′-CD$_2$

At 50 °C using methanolic sodium methoxide, the [3,2] rearrangement (**9b**) → (**16b**) was again intramolecular, but the [1,2] rearrangement (**9b**) → (**14b**) was intermolecular ($^2H_2$ and $^2H_5$ products) to the extent of 21 ± 2%. The rearrangement of the heptadeuterio-salt (**5**) also allowed the estimation of the relative amounts of coupling at positions 3′, 1′, and 5′ of the pentadienyl unit to give the heptadeuterio-products (**16b** + **17b**), (**14b**), and (**15b**) respectively. The products were separated after reduction (Zn–AcOH) to give the deuteriated ketones (**6**) and (**7**), and the estimation of the extent of deuteriation at positions 1′ and 5′ of (**7**) was carried out by n.m.r. analysis. The results of this study are summarised in the Table and two general points should be noted: (i) the ratio of coupling at position 3′ to the coupling at positions 1′ and 5′ is highly dependent upon reaction conditions and (ii) the ratio of coupling at positions 1′ and 5′ is only 1:1, as expected for an equilibrated radical pair intermediate, for the reaction in water at 0 °C, whereas in methanol at 0 and 50 °C coupling at position 5′ predominates.

These two general conclusions received further support from a study of the base catalysed rearrangements of the salts (**4c**) and (**4d**). The results of this study, which are summarised in the Table, show one further general feature of the rearrangement reactions: (iii) coupling at position 3′ leads to two diastereomeric products, (**16**) and (**17**), in a ratio that depends upon the structure of the starting ammonium salt indicating that the [3,2] rearrangement is a stereoselective process.



In formula (**4**) and formulae in this Scheme: **a**, R^1 = R^2 = R^3 = H; **b**, R^1 = R^2 = H, R^3 = Me; **c**, R^1 = R^3 = Me, R^2 = H; **d**, R^1 = H, R^2 = R^3 = Me.

Scheme. Competing interacting radical pair pathways for the rearrangement of pentadienylammonium ylides. This scheme has no implications regarding the extent of bonding between the two components of the radical pairs (**10**), (**11**), (**12**), and (**13**). The broken lines represent electronic interactions between the indicated atoms, and it is not intended to represent the interconversions (**9**) → (**14**), (**9**) → (**15**), (**9**) → (**16**), and (**9**) → (**17**) as either concerted or non-concerted processes.

All the above observations (i), (ii), and (iii) are consistent with rearrangement processes involving interacting radical pair intermediates or transition states, as outlined in the Scheme. The radical pairs (**10**) and (**11**) leading to 1′–2 and 5′–2 coupling respectively, are either formed directly from the ylide (**9**) with the appropriate geometry to generate the indicated (broken lines) interactions or, more probably, the initially formed radical pair, which would have a geometry related to (**10**), undergoes translational movement in solvents of low viscosity to give the radical pair (**11**). The latter (**11**) is evidently of lower energy than the former (**10**), possibly because the destabilising 1,1′ interaction in (**10**) is weaker in (**11**), and this leads to a definite preference for 5′–2 coupling rather than 1′–2 coupling. These two interacting radical pairs (**10**) and (**11**) are quite distinct from the diastereomeric interacting radical pairs‡ (**12**) and (**13**) which lead to [3,2] rearrangement

‡ The description 'interacting radical pair' for (**12**) and (**13**) is not intended to exclude the type of transition state for allowed pericyclic processes, usually discussed in connection with orbital symmetry relationships (ref. 4).

Table. Rearrangement reactions[a] of pentadienylammonium ylides (**9**).

Ylide	Reaction conditions	Ratio of [3,2] to [1,2] + [5,2] processes	Ratio of [5,2] to [1,2] processes	% Yield of [1,2] + [3,2] + [5,2] products
(**5**)[b,c]	NaOH–H_2O, 0 °C	6·5[d]:1	1·0[e] (1·0)[c]:1	56
	NaOMe–MeOH, 0 °C	3·0[d]:1	1·4[e] (1·7)[c]:1	79
	NaOMe–MeOH, 50 °C	1·0[d]:1	1·4[e] (1·7)[c]:1	68
(**9c**)	NaOH–H_2O, 0 °C	0·74 (0·33)[f]:1	1·35:1	75
	NaOMe–MeOH, 0 °C	0·14 (0·33)[f]:1	1·90:1	73
	NaOMe–MeOH, 50 °C	0·06 (0·56)[f]:1	1·60:1	72
(**9d**)	NaOH–H_2O, 0 °C	1·06 (3·0)[f]:1	1·13:1	
	NaOMe–MeOH, 0 °C	0·25 (3·5)[f]:1	1·40:1	

[a] The rearrangement (**9**) → (**14**) is formally a [1,2] sigmatropic process, (**9**) → (**15**) is a [5,2] process, and (**9**) → (**16**) + (**17**) is a [3,2] process. [b] The ylide (**5**), recovered after partial rearrangement, showed no further scrambling of the deuterium label (footnote c). [c] Corrected for deuterium distribution in the salt corresponding to the ylide (**5**) (1·70D at position 1′ and 0·30D at position 5′) as measured by the ^{1}H n.m.r. spectrum of the reduction product (Zn–HOAc) (**8**). [d] Based upon g.l.c. analysis of the mixture of ketones (**6**) and (**7**). [e] Based upon deuterium distribution in the ketone (**7**). [f] Ratio of diastereomer A to diastereomer B in the [3,2] products (**16**) + (**17**).

products and are favoured by low reaction temperatures and by water, rather than methanol, as the reaction medium. The reversal of the ratio of the diastereomeric reaction products (**16**) and (**17**) when the starting ammonium salt has a 2′- or 4′-methyl substituent is consistent with the expected lack of rotational equilibration of the two interacting radical pairs (**12**) and (**13**). It is also probable that there is little or no translational equilibration between the two interacting radical pairs (**12**) and (**13**) and the two interacting radical pairs (**10**) and (**11**) since intermolecular coupling of the radicals derived from the ylide (**9b**) gives only the reaction products (**14b**) and (**15b**).

The rearrangement reactions of ammonium ylides may therefore be conveniently discussed in the terms of interacting radical pair intermediates or transition states, in which radical coupling to give products is fast compared with rotation and diffusion. The translational interconversion of radical pairs is possible to a limited extent before radical coupling, but it may be restricted to the interconversion of radical pairs that are homomeric.[5] Interacting radical pairs, such as (**12**) and (**13**), leading to symmetry allowed reactions are not distinguishable, on the basis of the results reported in this paper, from the transition states of concerted§ pericyclic processes. However, they are clearly distinct from the interacting radical pairs leading to symmetry forbidden reaction products.

(*Received*, 13*th March* 1978; *Com.* 275.)

§ The recent description of the Wittig [1,2] rearrangement as a radical-concerted process (ref. 6) illustrates the difficulty inherent in the use of the term 'concerted' and attempting to make a distinction between concerted processes and primary radical pair recombination.

[1] K. Chantrapromma, W. D. Ollis, and I. O. Sutherland, *J.C.S. Chem. Comm.*, 1977, 97.

[2] U. H. Dolling, G. L. Closs, A. H. Cohen, and W. D. Ollis, *J.C.S. Chem. Comm.*, 1975, 546.

[3] K. Chantrapromma, W. D. Ollis, and I. O. Sutherland, *J.C.S. Chem. Comm.*, 1978, 670 (accompanying communication).

[4] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781; M. J. S. Dewar, *ibid.*, 1971, **10**, 761; H. E. Zimmerman, *Accounts Chem. Res.*, 1971, **4**, 272; 1972, **5**, 393.

[5] M. J. S. Dewar, S. Kirschner, H. W. Kollmar, and L. E. Wade, *J. Amer. Chem. Soc.*, 1974, **96**, 5242.

[6] J. F. Garst and C. D. Smith, *J. Amer. Chem. Soc.*, 1976, **98**, 1526.