The Thermal Rearrangement of Allyl- and Pentadienyl-ammonio-amidates. Evidence for Competing but Distinct Concerted and Radical Mechanisms

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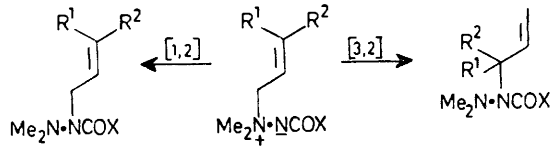
Summary The allyl-*N*-acylammonio-amidates (**1**) rearrange by competing [1,2] and [3,2] shifts and the reactions show similar solvent and substituent effects; nevertheless, the rearrangement reactions of pentadienyl-*N*-acylammonio-amidates (**4**) show that the [1,2] rearrangement proceeds entirely by a non-concerted process involving radicals, whereas the [3,2] rearrangement involves a different mechanism which could be a concerted pericyclic process.

The reported[1] [1,2], rather than [3,2], anionic rearrangement of allyl-*N*-acylammonio-amidates (**1**; R^1 = R^2 = Me or R^1 = H, R^2 = Ph) is unexpected.[2–4] We now find that the thermal rearrangement of the ylides (**1**) gives a mixture of [1,2] and [3,2] products (**2**) and (**3**) in a ratio that depends upon the ylide structure and the reaction conditions (see Table 1). An examination of the relative rates of formation of the products (**2**) and (**3**) shows that substituent effects for a range of groups X are similar for both rearrangements and result in a wide range of rate constants (rates change by a factor of up to nearly 10^4 and increase in the order X = Ph, Me < OEt < NHMe).



(**2**) (**1**) (**3**)

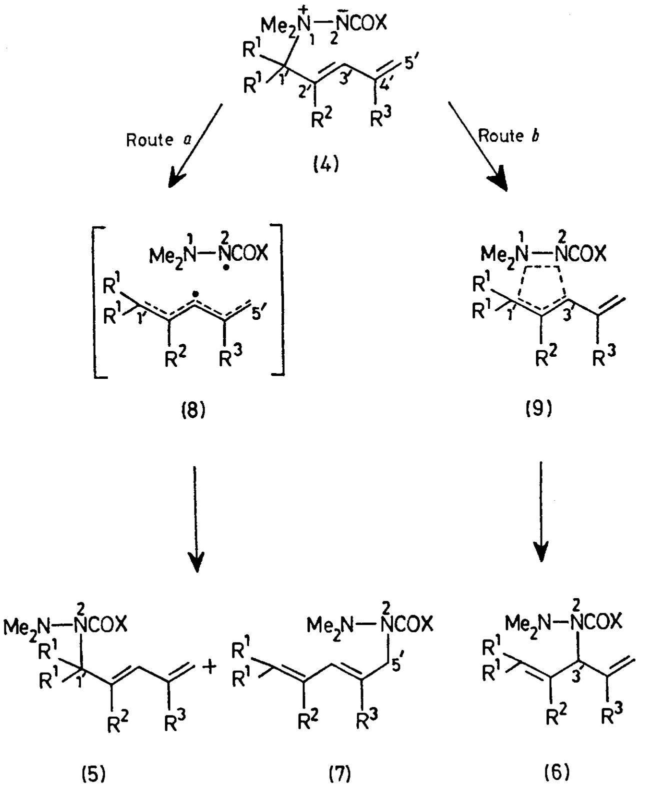
Two possible mechanisms have been considered[2,4] for reactions of this type: a concerted mechanism in which bond making and breaking proceed simultaneously and a two-stage mechanism in which bond making and breaking occur at different stages in the reaction pathway. Studies based upon the observation of CIDNP[6] and free radical trapping[7] have supported a radical pair mechanism for the [1,2] rearrangement, but it has not been possible to rule out a contribution from a competing concerted [1,2] sigmatropic pathway. The study of solvent and substituent effects summarised above and in Table 1 suggests that both reactions associated with competing [1,2] and [3,2] rearrangements involve similar mechanisms, with relatively small changes in dipole moment in the transition states as compared with the ylide (**1**). This result is consistent with either concerted or radical mechanisms for the formation of both products, and a further series of experiments was therefore devised to probe for the expected mechanistic distinction.

Table 1. Solvent effects in the rearrangement of the ylide (**1**; R^1 = H, R^2 = Ph, X = OEt) at 79 °C

Solvent	E_T[a]	$k_{1,2}$[b] $\times 10^{-4}$/s^{-1}	$k_{3,2}$[b] $\times 10^{-4}$/s^{-1}	Product ratio (**3**)/(**2**)[c]
CCl$_4$	32·5	1·27	2·32	1·83
C$_6$H$_6$	34·5	1·04	1·33	1·28
Dioxan	36·0	0·45	0·51	1·13
EtOAc	38·1	0·47	0·58	1·23
MeCN	46·0	0·19	0·13	0·68

[a] E_T is an empirical solvent parameter (ref. 5). [b] $k_{1,2}$ refers to the [1,2] rearrangement (**1**) → (**2**) and $k_{3,2}$ refers to the [3,2] rearrangement (**1**) → (**3**). [c] These results are not affected by the [1,3] rearrangement (**3**) → (**2**) (ref. 3) which only occurs at significant rates at higher temperatures (*ca.* 150 °C).

The rearrangement reactions of the pentadienyl ylides (**4**)† gave mixtures of the rearrangement products (**5**),† (**6**), and (**7**)† resulting from formal [1,2], [3,2], and [5,2] sigmatropic rearrangements in ratios that depended upon the nature of the substituents X, R^1, R^2, and R^3 (Table 2). The results of this study are consistent with the following mechanistic conclusions. (a) The ratio of coupling at positions 1′ and 5′ of the pentadienyl side chain depends upon product, rather than reactant structure, and coupling occurs preferentially from both 2′- and 4′-methylpentadienyl precursors at the terminal carbon atom of the pentadienyl system remote from the methyl substituent, whereas a 1 : 1 product ratio is obtained using 1′,1′-dideuteriopentadienyl ylides. This result is consistent with radical coupling involving the radical pair (**8**) (see Scheme, Route *a*) in which translational motion, permitting 1′–2 and 5′–2 coupling, is fast relative to the rate of radical pair recombination. (b) The extent of 3′–2 coupling varies in a manner that is consistent with a concerted rearrangement pathway by way of the transition state (**9**) (see Scheme, Route *b*). Thus, the extent of 3′–2 coupling is greater from a 4′-methylpentadienyl ylide than from a 2′-methylpentadienyl ylide, and in addition it depends upon the nature of the group X (see Table 2). These results also indicate that radical coupling is an improbable pathway for the formation of this rearrangement product (**6**). The [1,3] rearrangement of the product (**6**) is too slow, under the conditions used for the rearrangement of the ylides (**4**), to have any effect upon the observed ratios of the products (**5**), (**6**), and (**7**).



Scheme.

Pathway *a* is intended to refer not only to intramolecular radical recombination yielding the products (**5**) and (**7**), but also to intermolecular recombination (*cf.* ref. 9).

This clear mechanistic distinction between the formation of the products (**5**) and (**7**) by a radical process and the

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† The ylides (**4**) and the products (**5**) and (**7**) have the *E*-stereochemistry about the 2′,3′-double bond shown in the formulae; products (**5**) and (**7**) having *Z*-stereochemistry were not detectable.

Table 2. Rearrangement reactions of the pentadienyl ylides (**4**) at 80 °C in benzene

X	R^1	R^2	R^3	Product ratios[b,c]		
				[1,2]	[3,2]	[5,2]
Me	H	Me	H	1·0	—[a]	2·0
Me	H	H	Me	2·0	—[a]	1·0
EtO	H	Me	H	1·0	0·5	2·0
EtO	H	H	Me	2·0	0·8	1·0
MeNH	H	Me	H	1·0	0·8	2·0
MeNH	H	H	Me	2·0	1·5	1·0
Me	D	H	H	1·0	—[a]	1·0
EtO	D	H	H	1·0	0·3	1·0
MeNH	D	H	H	1·0	0·6	1·0

[a] Insufficient [3,2] rearrangement product was formed for isolation. [b] Product ratios are derived from n.m.r. analysis of the total reaction product. They are accurate either to ±0·1 or to ±10%, whichever is the larger. [c] Recombination of the radical pair (8) involving positions C-1′ and C-5′ to regenerate the ylide (**4**) leads to some scrambling of the pentadienyl fragment. Such scrambling is slow compared with the rate of overall rearrangement and the qualitative significance of these ratios is unchanged.

product (**6**) by an allowed concerted process is of considerable interest when viewed in the light of orbital symmetry considerations.[8] The *concerted non-allowed* pathway to the product (**5**) does not seem to be of importance and we note that product (**7**) is formed with *trans*-stereochemistry inconsistent with an origin in a concerted [5,2] rearrangement. By analogy with this conclusion, it is very unlikely that other [1,2] anionic rearrangements[4,9] involve any contribution from the concerted pathway. The transition state (**9**) is a lumomer[10] of the radical pair (**8**) with the correct orbital arrangement for transformation into the products (**5**) and (**7**). Even if (**9**) were a radical pair, it is possible that separate and distinct pathways would be observable for the pair of products (**5**) and (**7**) and the single product (**6**). The distinction between interacting radical pairs and pericyclic transition states such as (**9**) is, however, difficult to make on other than a theoretical basis.

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