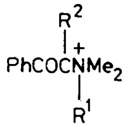
Limited Rotational Equilibration in Reactions involving Diradical Intermediates

By W. David Ollis,* Max Rey, and Ian O. Sutherland
(*Department of Chemistry, The University, Sheffield* S3 7HF)

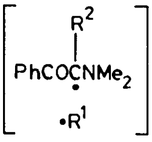
Summary The thermal rearrangements of the ylides (**4**) and (**8**) give the products of competing [1,2] and [3,2] processes; the observed product ratios are consistent with limited rotational equilibration of diradical intermediates.

The [1,2] Stevens rearrangement of ammonium ylides (**1**) → (**3**) has been shown[1] to involve initial homolysis to



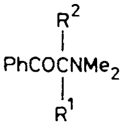
$\mathrm{PhCOC}\underset{R^1}{\overset{R^2}{\overset{+}{N}}}\mathrm{Me}_2$

(**1**)



$\left[\begin{matrix}\mathrm{PhCO}\underset{\bullet}{\overset{R^2}{C}}\mathrm{NMe}_2\\ \bullet R^1\end{matrix}\right]$

(**2**)

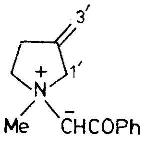


$\mathrm{PhCO}\underset{R^1}{\overset{R^2}{C}}\mathrm{NMe}_2$

(**3**)

give a radical pair (**2**) with radical pair recombination giving rise to the product (**3**). The radical pair recombination (**2**) → (**3**) is fast, and leads to the observed intramolecularity and stereoselectivity. It was therefore of interest to examine the intramolecular [1,2] rearrangement of the ylide (**4**) to determine whether the intermediate diradical (**5**) could undergo rotational equilibration before recombination, giving rise to the products (**6**) and (**7**) involving coupling at positions 1′ and 3′ of the allyl system.

The stable crystalline ylide (**4**), m.p. 120—122 °C, was synthesised by treating the corresponding quaternary ammonium bromide with aqueous sodium hydroxide. The ylide (**4**) rearranged on heating (100—110 °C) giving the products (**6**) and (**7**) in good yield, and repetition of this experiment using the ylide (**4**) labelled with ^{13}C in the exocyclic methylene group, C-3′, gave (**6**) and (**7**) in proportions that could be determined either directly by ^{13}C n.m.r. spectroscopy or by ^{1}H n.m.r. spectroscopy, using the ^{13}C satellite spectrum. The results of this study are summarised in the Table and it is evident that the diradical (**5**) couples preferentially to give (**7**), the product of a formal 'allowed' [3,2] rearrangement, rather than (**6**), which formally results from a 'forbidden' [1,2] rearrangement.



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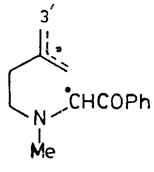
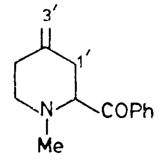
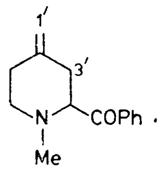


(5)



(6)



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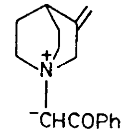

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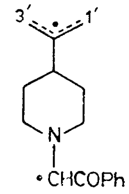

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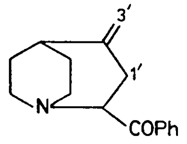
Table. ^{13}C distribution in the rearrangement products of the ylides (**4**) and (**8**).

Compound	Conditions	Product	Yield	^{13}C Distribution[a]	
			%	Exocyclic =CH_2 %	Endocyclic >CH_2 %
(**4**)[d]	100—110 °C, neat	(**6**) + (**7**)	83	14 (**6**)[b]	86 (**7**)[c]
	60 °C in dimethoxyethane	(**6**) + (**7**)	45	10 (**6**)[b]	90 (**7**)[c]
(**8**)[d]	120—130 °C, neat	(**10**) + (**11**)	24	67 (**10**)[b]	33 (**11**)[c]
		+ (**12**)	56	100	0

[a] As determined by ^{13}C or ^{1}H n.m.r. spectroscopy. [b] Corresponding to a formal [1,2] rearrangement. [c] Corresponding to a formal [3,2] rearrangement. [d] Labelled with ^{13}C at the exocyclic methylene carbon, C-3′.

Thus the diradical (**5**), derived from the ylide (**4**), couples preferentially (86:14 or 90:10) at C-3′, a result which is in interesting contrast to the more nearly random coupling observable[2] for the diradical (**13**) generated by pyrolysis of the hydrocarbon (**14**). The symmetrical diradical (**15**), generated from the hydrocarbon (**16**), gives virtually random coupling[3] as expected from the high symmetry of (**15**). It was therefore of interest to examine an ylide system with greater symmetry than (**4**).



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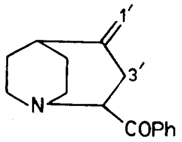

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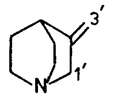

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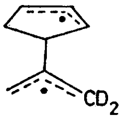

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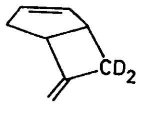
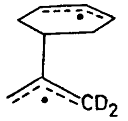


(14)



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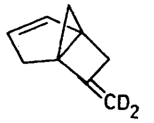

(16)

The bicyclic ylide (**8**), m.p. 147—150 °C, gave the rearrangement products (**10**) and (**11**) on heating at 120—130 °C in rather low yield (24%) together with the fragmentation product (**12**) (56%). Examination of the ^{13}C distribution in the rearrangement product derived from the ylide (**8**) having a ^{13}C label at the exocyclic methylene carbon C-3′ gave the results summarised in the Table. In this case the diradical intermediate (**9**) is more completely equilibrated before coupling occurs and the [1,2] rearrangement product (**10**) predominates.

The incomplete equilibration of the diradicals (**5**) and (**9**) before radical coupling occurs may be a result of steric or electronic[4] hindrance to equilibration. Alternative explanations of our observations in the terms of competing concerted and non-concerted rearrangement mechanisms are possible,[5] but the distinction between intermediates or transition states involving interacting diradicals and those involving pericyclic bonding is not possible on the basis of any experimental results that we have obtained. The reversal of product ratios for the two cases (**4**) and (**8**) is most easily explained on the basis of incomplete rotational equilibration in diradical intermediates.

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[1] W. D. Ollis, M. Rey, I. O. Sutherland, and G. L. Closs, *J.C.S. Chem. Comm.*, 1975, 543; K. Chantrapromma, W. D. Ollis, and I. O. Sutherland, *J.C.S. Chem. Comm.*, 1978, 670 (accompanying communication).

[2] D. Hasselmann, *Tetrahedron Letters*, 1972, 3465; 1973, 3739.

[3] J. A. Berson and J. M. Janusz, *J. Amer. Chem. Soc.*, 1974, **96**, 5939.

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

[5] For examples, see papers cited in ref. 1.