The Role of Cyclohexadienones in the Thermal Sigmatropic Rearrangements of 2-Oxidoanilinium Ylides

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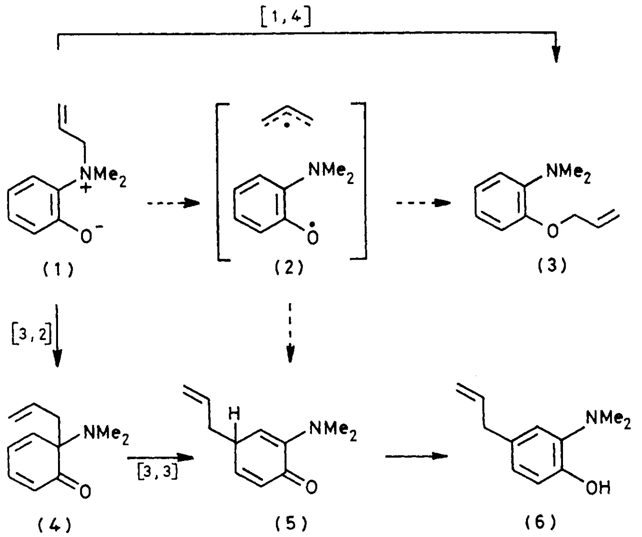
Summary Thermal isomerisation of *N*-allyl-2-oxidoanilinium ylides under mild conditions yields three products which are each formed by two types of competitive pathways; the minor pathway involves a radical pair intermediate and three modes of coupling, and the major pathway involves a collection of concerted sigmatropic rearrangements.

The simultaneous operation of symmetry-allowed and symmetry-forbidden processes in certain thermal rearrangements is of general interest[1] and we have made considerable progress in the experimental examination[2] of factors which influence the competition between (i) concerted transformations and (ii) non-concerted processes involving radical pair intermediates. Quantitative distinction between these two pathways has been firmly established for the thermal rearrangement of *N*-allyl-2-oxidoanilinium ylides (Scheme) using specifically deuteriated *N*-allyl derivatives (**1**).[2] The operation of concerted [1,4], [3,2], and [3,3] sigmatropic rearrangements [(**1**) → (**3**), (**1**) → (**4**), and (**4**) → (**5**), respectively], as well as the role of the radical pair (**2**) as an intermediate, has been revealed by a combination of mass spectrometry, ^{1}H n.m.r. spectrometry, and CIDNP studies.[3] We now report developments from these earlier investigations which have led to (a) the isolation of appropriately substituted cyclohexadienones postulated as reaction intermediates in the Scheme, (b) the identification of three out of the four possible modes of radical coupling, and (c) the involvement of sigmatropic rearrangements in addition to those depicted in the Scheme.

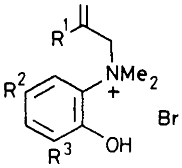


Scheme. Mechanisms for the thermal rearrangement of *N*-allyl-*NN*-dimethylanilinium-2-olate (**1**). Dashed arrows correspond either to homolytic reactions or to established radical pair recombination processes.

Quaternisation in acetonitrile of suitably substituted 2-dimethylaminophenols with various allyl bromides gave the salts (**7**) which were transformed into the ylides (**8**) by treatment (0 °C) with methanolic sodium methoxide. The ylides (**8a**—**g**) were reasonably stable at 0 °C, but on heating (C_6H_6; 40 °C; 6—14 h) expected and novel isomerisations were observed. The ylides (**8a**—**e**) yielded the ethers (**10a**—**e**), the cyclohexa-2,5-dienones (**12a**—**e**), and the phenols (**14a**—**e**): the formation of the phenols was not expected. The phenols (**14a**—**e**) could have been produced either by a [3,3] Claisen rearrangement of the allyl ethers (**10a**—**e**)[4] or by a [3,3] Cope rearrangement of the cyclohexa-2,5-dienones (**12a**—**e**).[4,5] However, appropriate experiments demonstrated that neither of these rearrangements was involved because the allyl ethers (**10**) and the cyclohexa-2,5-dienones (**12**) were both shown to be unchanged under the conditions (C_6H_6; 40 °C) which promoted the thermal isomerisation of the ylides (**8**). Alternative routes to the phenols (**14**) had therefore to be considered and the obvious immediate precursors of the phenols (**14a**—**e**) were the corresponding cyclohexa-2,4-dienones (**13a**—**e**) in which R^3 = H. The prototropic aromatisation (**13a**—**e**) → (**14a**—**e**) could not occur for the cyclohexadienones (**13**; R^3 = alkyl). Hence, for this reason and for the additional reason that the cyclohexadienones (**11**; R^3 = alkyl) might also be isolable, we embarked upon the synthesis and examination of the thermal isomerisation (C_6H_6; 40 °C; 14 h) of the ylides (**8f**) and (**8g**).

The ylide (**8f**) gave the ether (**10f**; low yield), the cyclohexa-2,5-dienone (**12f**; 62%), and the cyclohexa-2,4-dienone (**13f**; 15%). Similarly, the ylide (**8g**) gave the products (**10g**; 10%), (**12g**; 34%), and (**13g**; 12%). The structures of the three products isolated from the thermal isomerisations (**8f**) → (**10f**) + (**12f**) + (**13f**) and (**8g**) → (**10g**) + (**12g**) + (**13g**) correspond, in each case, to three of the four possible modes of radical coupling of the radical pairs (**9f**) or (**9g**). Our earlier experiments[2] on the mechanism of the thermal rearrangement of *N*-allyl-*NN*-dimethylanilinium-2-olate (**1**) firmly established (Scheme) that although the cyclohexadienone (**4**) was definitely involved as an intermediate, it was formed only by the [3,2] rearrangement (**1**) → (**4**), and that it was not formed by radical pair recombination (**2**) → (**4**). The corresponding cyclohexadienones (**11f**) and (**11g**) were not detected among the thermal products from the ylides (**8f**) and (**8g**) because they participate in further sigmatropic rearrangements.

The extent to which radical pair (**9**) formation and recombination are involved in the thermal rearrangements of the ylides (**8**) may be inferred from the quantitative results recorded in the Table. These results were obtained using the specifically dideuteriated ylides (**15a**) and (**15b**) which were heated in benzene either at 40 °C or at 80 °C. The rearrangements which were observed are of the type {(**15**) → [$^2H_2$] (**10**) + [$^2H_2$] (**12**) + [$^2H_2$] (**14**)}. The products (**10**), (**12**), and (**14**) were shown by ^1H n.m.r. and mass spectral analysis to be specifically dideuteriated either in position 1′ or in position 3′ of their allyl groups. Using our previously described methods,[2] quantitative determination can be made of the extent to which the products (**10**), (**12**), and (**14**) are formed by radical pair recombination. The results (Table) show that (i) radical pair recombination is a significant but *minor* pathway in the thermal rearrangements of the ylides (**8** ≡ **15**) and (ii) radical pair pathways are encouraged at higher temperatures.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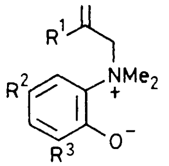
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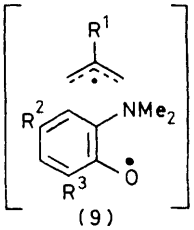
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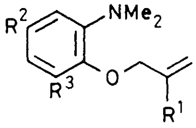
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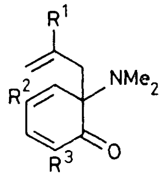
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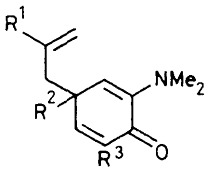
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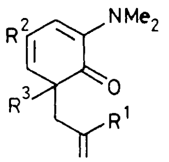
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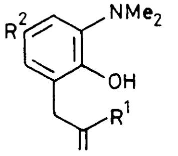
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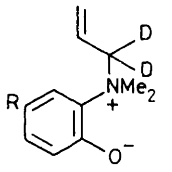
(15)

(a) R = Me

(b) R = Me_3C

		R^1	R^2	R^3
In (**7**)—(**14**)	(a)	H	Me	H
	(b)	Me	Me	H
	(c)	Me_3C	Me	H
	(d)	H	Me_3C	H
	(e)	Me	Me_3C	H
	(f)	H	Me	Me
	(g)	Me	Me	Me

TABLE

Starting ylide	Reaction temperature/°C	The extent of radical pair coupling leading to $^2H_2$ derivatives of the products[a]		
(**15a**)	40	(**10a**), 12%	(**12a**), 20%	(**14a**), 34%
(**15a**)	80	(**10a**), 14%	(**12a**), 30%	(**14a**), 41%
(**15b**)	40	(**10d**), 16%	(**12d**), 28%	(**14d**), 49%
(**15b**)	80	(**10d**), 17%	(**12d**), 20%	(**14d**), 55%

[a] The products are mixtures of two dideuterio-derivatives. Their constitution and the determination of their relative proportions are discussed in the text.

The results (Table) require that the thermal rearrangement of ylides (**8**) → (**10**) + (**12**) + (**13**) or (**14**) involves sequences of concerted sigmatropic rearrangements as the *major* reaction pathways. The routes to the ethers (**10**) and the cyclohexadienones (**12**) are well established (Scheme), but the formation of the cyclohexadienones (**13f**) and (**13g**) or the tautomerically equivalent phenols (**14a**—**e**) as rearrangement products is novel. As a route to these compounds (**13**) or (**14**), we do not favour[6] the direct [3,6] sigmatropic rearrangement (**8**) → (**13**). However, the sequence of a [3,2] followed by a [1,5] sigmatropic rearrangement (**8**) → (**11**) → (**13**) has excellent precedents.[7] Reference has already been made to the thermal stability (C_6H_6; 40 °C;

48 h) of the cyclohexa-2,5-dienones (**12**) under the conditions (C_6H_6; 40 °C; 12—18 h) under which they are formed from the ylides (**8**). However, under rather more vigorous conditions (C_6H_6; 80 °C; 12—18 h), the following relevant thermal isomerisations have been observed: (**12b**) → (**14b**), (**12f**) → (**10f**) + (**13f**), and (**12g**) → (**10g**) + (**13g**).

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