CIDNP in the Rearrangement of 2-Oxyanilinium Ylides. Simultaneous Concerted and Non-concerted Reactions

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Summary The thermal rearrangement of the 2-oxyanilinium ylide (**1**) is shown to involve competing, but distinct, concerted and radical-pair processes.

THE thermal rearrangement ($CHCl_3$; 60°) of the allylic anilinium ylide (**1**) gives, as the major reaction products, the allylphenol (**2**) and the ether (**3**), and on the basis of deuteriation studies previously reported[1] these products are principally formed by the concerted sigmatropic rearrangements indicated in the Scheme. When the reaction (**1**) $\rightarrow$ (**2**) + (**3**) is carried out in nitrobenzene at 110—120° in the probe of an n.m.r. spectrometer the spectrum of the freshly formed phenol (**2**) shows strong emission signals associated with the protons at the 1'- and 3'-positions of the allyl side chain (Figure A). These signals decay rapidly (2—3 min) and are replaced by the normal absorption signals of the allylphenol (**2**). This observation of CIDNP[2] during the rearrangement of the ylide (**1**) suggests that the product (**2**) is formed, at least in part, by homolysis of the ylide (**1**), or the intermediate dienone (**4**), to give a radical pair followed by recombination to give the phenol (**2**).

The thermal rearrangements of the deuteriated ylides (**1a**), (**1c**), and (**1e**), prepared from the corresponding quaternary salts (**5**), indicate clearly the significance of the results described above. The quaternary salts (**5a**) and (**5d**) were prepared by the reaction of *o*-dimethylaminophenol with the corresponding deuteriated allyl toluene-*p*-sulphonate,[3] and the salt (**5c**) was prepared by the reduction

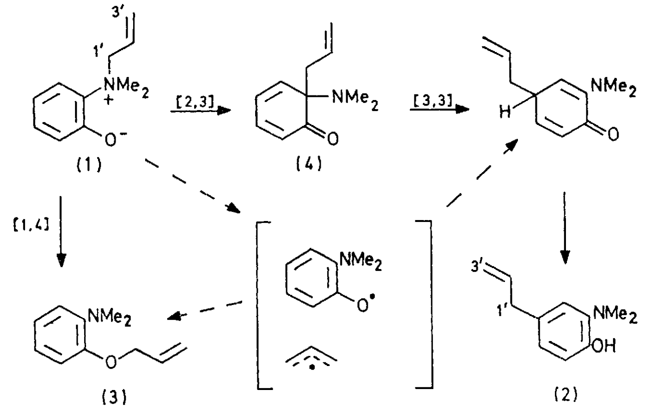
TABLE

Deuterium distribution[a] in ylide (**1**) and the rearrangement products (**2**) and (**3**)

	Starting ylide		Reaction[b]	Phenol (**2**)[c]		Ether (**3**)[d]		% Radical
	1′	3′	temperature	1′	3′	1′	3′	pair mechanism
(**1a**)	1·95	0	60°	1·78	0·17	1·79	0·16	17
(**1a**)	1·95	0	110—120°	1·59	0·36			37
(**1c**)	0	1·96	60°	0·25	1·71	0·19	1·77	22
(**1c**)	0	1·96	110—120°	0·35	1·61			36
(**1e**)	1·90	0·95	60°	1·73	1·12	1·79	1·06	15
(**1e**)	1·90	0·95	110—120°	1·53	1·32			39

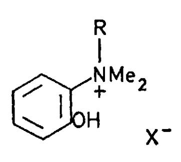
[a] The numbers refer to the average number of deuterium atoms (±0·03) at positions 1′ and 3′ of the allyl side chain based upon the n.m.r. spectra of (**1**) and the methiodides of (**2**) and (**3**) and the mass spectra of (**1**), (**2**), and (**3**). [b] At 60° in $CHCl_3$ or 110—120° in $PhNO_2$. [c] Formed in 45—47% yield. [d] Formed in 19% yield.

of the salt (**5b**) with deuterium (Pd–$BaSO_4$ in MeOD). The n.m.r. spectra of the deuteriated allylphenol (**2**) formed from each of the three deuteriated ylides (**1a**), (**1c**), and (**1e**) in nitrobenzene at 110—120° showed effects due to CIDNP (Figure, B, C, and D). The relationships between these emission signals and the absorption signals observable after the polarisation had decayed (Figure) indicate that the allyl residue in the phenol (**2**) giving rise to CIDNP has undergone apparently complete 1′,3′-allylic scrambling of the deuterium label but no *cis–trans* scrambling [*i.e.* (**1a**) → (**2a**) + (**2b**); (**1c**) → (**2c**) + (**2d**); and (**1e**) → (**2e**) + (**2g**)].



In (**1**)—(**3**) the allyl group is deuteriated as follows: (a)-CD_2-$CH{=}CH_2$, (b)-$CH_2CH{=}CD_2$, (c)-$CH_2CD{=}CD_2$, (d)-$CD_2CD{=}CH_2$ (e)-$CD_2CHC\overset{Z}{=}HD$, (f)-$CD_2CH\overset{E}{=}CHD$, (g)-$CHDCH{=}CD_2$.

SCHEME. *Thermal rearrangement of the ylide* (**1**). *The broken arrows refer to radical pair pathways and the full arrows to concerted sigmatropic pathways.*



(5)

(**a**) R = $CD_2CH{=}CH_2$, X = p-$MeC_6H_4SO_2{\cdot}O$
(**b**) R = $CH_2C{\equiv}CD$, X = Br
(**c**) R = $CH_2CD{=}CD_2$, X = Br
(**d**) R = $CD_2CH\overset{Z}{=}CHD$, X = p-$MeC_6H_4SO_2{\cdot}O$

However only limited 1′,3′-scrambling is observable in the final spectrum of the unpolarised phenol (**2**), but *cis–trans* scrambling is almost complete [the major reaction pathways are therefore (**1a**) → (**2a**); (**1c**) → (**2c**); and (**1e**) → (**2e**) + (**2f**)]. Deuterium analyses (n.m.r. and mass spectra) of the ylides (**1**) and the phenols (**2**) are given in the Table for the reaction at 110—120°, together with results for both the phenol (**2**) and the ether (**3**) for the reaction carried out at 60°. From these results we conclude that both (**2**) and (**3**) are formed principally by concerted processes[1] [no 1′,3′-scrambling but complete *cis–trans* scrambling in (**2**)], and also, to a lesser but significant extent, by homolysis of the ylide (**1**) to give a radical pair followed by recombination to give both (**2**) and (**3**) [complete 1′,3′-scrambling but no *cis-trans* scrambling in (**2**) and (**3**)]. These processes are summarised in the Scheme. From the Table it follows that the thermal transformation (**1**) → (**2**) + (**3**) proceeds simultaneously by minor radical pair and major concerted processes. The relative extents of the *minor* process involving radical pairs are *ca.* 20% at 60° and *ca.* 35% at 110—120°: this is the process *detectable* by CIDNP studies.

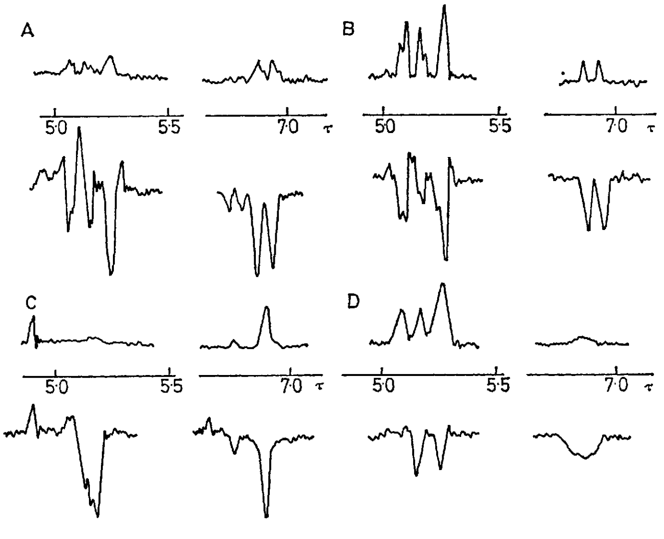


FIGURE. *N.m.r. spectra of allylphenol* (**3**) *in* $PhNO_2$ (1′ *and* 3′ *protons only*). *The lower trace shows the spectrum of freshly formed product* (0·5—1·5 *min*) *and the upper trace the spectrum after* ca. 10 *min. The spectra are obtained from the rearrangement products of the following ylides: A, undeuteriated; B,* 1′,1′-*dideuterio*-(**1a**); *C,* 2′,3′,3′-*trideuterio*-(**1c**); *D,* 1′,1′,3′-*trideuterio*-(**1e**).

These conclusions demonstrate that the observation of CIDNP does not rule out the existence of a concerted mechanism for product formation, which may even be the major reaction pathway. In view of the conclusions that have been drawn concerning the radical-pair mechanism of a number of [1,2] anionic rearrangements (for reviews see ref. 4), often based to a large extent upon the observation of CIDNP (for a summary and criticism see ref. 5), we *point out* that the mechanism of these reactions remains uncertain in the absence of more compelling evidence (*e.g.* ref. 6) for an exclusive radical-pair mechanism. Recent comments[7] concerning the relationship between the 'concerted–forbidden' and radical-pair pathways for other pericyclic processes may also be relevant in view of the observed retention of configuration in the Stevens rearrangement and related reactions.[4] Experiments are in progress[8] designed to determine quantitatively the extent to which this [1,2] rearrangement is a 'concerted-forbidden' process.

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[8] Unpublished results of experiments in progress with Professor G. Closs, University of Chicago.