

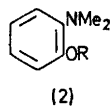
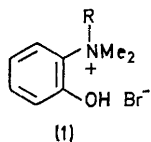
The Sigmatropic Rearrangements of 2-Oxyanilinium Ylides

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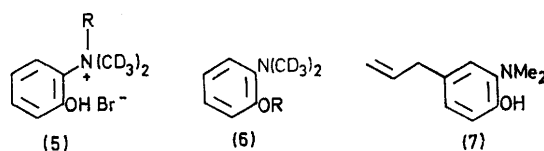
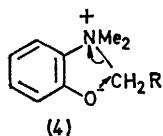
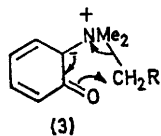
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Summary The [1,4] sigmatropic rearrangement of the anilinium ylides derived from the salts (1) is an intramolecular process, (1) → (2); the *N*-allyl ylide (8) reacts, in addition, by a sequence of [2,3] and [3,3] sigmatropic rearrangements to give the allyl phenol (10).

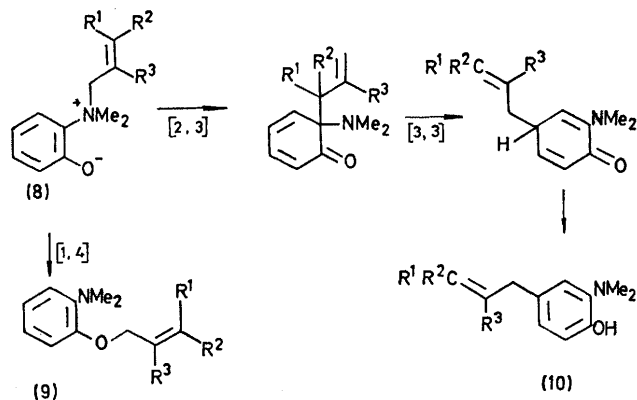
THE [1,4] rearrangement of the ylides derived from 2-hydroxyanilinium salts (1) gives¹ variable yields of the 2-alkoxyaniline derivatives (2). For a reaction of this type it has been pointed out² that the participation of the additional π -electrons [see arrows in (3)] would transform the stereo-electronically forbidden endocyclic nucleophilic displacement [see arrows in (4)] into a symmetry-allowed [1,4] sigmatropic process.³ In spite of these considerations additional products formed¹ in the rearrangements of (1a) and (1b) required that the reaction mechanism should be further scrutinised before the reaction (1) → (2) could be reliably regarded as a [1,4] sigmatropic reaction.



In (1) and (2) (a) R = CH₂Ph (b) R = CH₂CH=CHPh (*trans*)
(c) R = CH₂C≡CH (d) R = CH₂C≡CD (e) R = CH₂CH=CH₂



In (5) and (6) (a) R = CD₂Ph (b) R = CD₂CH=CHPh (*trans*)



SCHEME. Sigmatropic rearrangements of *N*-allyl-*N,N*-dimethyl-2-oxyanilinium ylide (8).

The deuteriated salts† (5a and b) were prepared by the alkylation of *o*-aminophenol hydrochloride with [²H₄]methanol at 180° to give *o*-di[²H₃]methylaminophenol, followed by alkylation with 1,1-dideuteriobenzyl bromide⁴ or dideuteriocinnamyl bromide.⁵ The pyrolysis of a mixture (1:1) of the crystalline ylides derived from the undeuteriated salt

† The ¹H n.m.r. spectra of all deuteriated compounds discussed in this communication are consistent with the indicated locations of the deuterium atoms. Deuterium analyses are also based upon mass spectra.

(1a) and the octadeuteriated salt (5a) gave only the undeuteriated (2a) and octadeuteriated (6a) ethers; no products from intermolecular reactions were detectable by mass spectrometry (< 7%). A similar result (< 5% mixing) was obtained for the mixture of crystalline ylides derived from the salts (1b) and (5b) and we conclude that the rearrangement of the ylides derived from (1) to give the ethers (2) is an intramolecular process. The simplest mechanism would be a [1,4] sigmatropic rearrangement and we present further evidence for this mechanism in the case of the *N*-allyl ylide derived from the salt (1e).

The thermal rearrangement (60°) of the crystalline ylide derived from the salt (1e) gives two reaction products: the major product (49% yield) is the allylphenol (7), and the ether (2e) is the minor product (25% yield). The formation of the phenol (7) suggested that in this case other symmetry-allowed reactions were competing with the [1,4] rearrangement, and on the basis of the following deuteration studies these have been shown to be consecutive [2,3] and [3,3] sigmatropic rearrangements (Scheme).

Reduction of the salt (1c) with deuterium (Pd-BaSO₄ in MeOD) gave the dideuteriated salt [cf. (1e)] which gave the ylide (8; R¹ = H, R² = R³ = D; 1.64 ± 0.03D);[‡] thermal rearrangement of this ylide gave the phenol (10) in which the deuterium could be detected only at the 2'- and 3'-positions of the allyl residue, but the stereochemistry of the deuterium label could not be determined. The ylide (8; R¹ = D, R² = R³ = H; 0.80 ± 0.03D)[‡] was prepared by hydrogenation (Pd-BaSO₄ in MeOH) of the salt (1d) followed by ylide formation; the rearrangement of this ylide at 60° gave the allylphenol (10; 0.80 D)[‡], in which the

deuterium label was equally distributed between both of the 3'-positions of the allyl group, together with the ether (9; R¹ = D, R² = R³ = H, 0.80D)[‡] in which the deuterium label had retained its stereochemical identity (cf. ref. 6).

Thus the phenol (10) is formed with total *cis-trans* scrambling of the deuterium label, whereas the stereochemical identity of the label is retained in the formation of the ether (9). This result is consistent with the reaction mechanism shown in the Scheme, and by analogy we regard the other [1,4] rearrangements as proceeding by a similar concerted mechanism. The rearrangement reactions shown in the Scheme are formally symmetry allowed³ but the evident similarity between the activation energies associated with the [1,4] and [2,3] rearrangements is striking since aromatic character is lost in the latter process. This result, together with the surprising rarity of simple anionic [1,4] sigmatropic rearrangements (cf. ref. 7) suggests that the inherent S_Ni character of this process results in a relatively high activation energy. The formation of the allylphenol (7) is accompanied by a CIDNP effect, involving emission signals from the 1'- and 3'-allyl methylene groups, when the rearrangement is carried out in nitrobenzene at 110–120°. The implications of this, and similar results, will be discussed in a future publication; we note that the studies described in this communication do not rule out the occurrence of non-concerted processes to a minor degree in the formation of the ethers (9) and the phenols (10) [the n.m.r. method used to locate deuterium in the products (9) and (10) would not detect up to 10–20% of 1',3'-scrambling].

(Received, 3rd April 1973; Com. 473.)

[‡] The location of deuterium and the extent of actual incorporation are as indicated.

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