Base Catalysed Rearrangements Involving Ylide Intermediates. Part 12.[1] The Preparation and Reactions of 2-Oxidoanilinium Ylides

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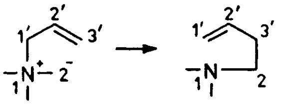
2-Oxidoanilinium ylides (22) may be prepared from the corresponding quaternary salts (21) by reaction with aqueous sodium hydroxide. The ylides (22) rearrange on heating to give the products (23) of [1,4] rearrangements which, on the basis of mixing experiments, are intramolecular processes. The *N*-allyl ylide (22c) rearranges to give both the ether (23c) and the allylphenol (30); a study of the rearrangements of specifically deuteriated ylides (41) shows that these reactions involve competing concerted and radical pair processes. The observation of CIDNP during the formation of the allylphenol (30) is shown to be associated with the minor radical pair pathway for the formation of this product.

THERE are two orbital symmetry-allowed[2] and geometrically favourable sigmatropic rearrangements of allylic ammonium ylides that involve six participating electrons.[3,4] These are the widely recognised [3,2] sigmatropic rearrangement (1) ⟶ (2) with suprafacial geometry[5] and the rarely encountered [1,4] sigmatropic rearrangement (3) ⟶ (4) with suprafacial geometry of the π-electron system and retention of configuration of the migrating group.[6]



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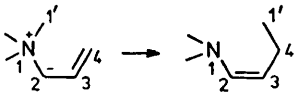
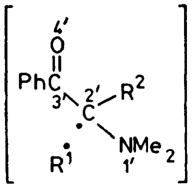


(3) (4)

Many examples of the [3,2] sigmatropic rearrangement have been discussed in this series of papers[1] and similar reactions occur in a wide range of ylide and anionic systems. The [1,4] rearrangement has been observed on a number of occasions as a reaction that competes with the Stevens [1,2] rearrangement[4] when the latter involves a radical pair in which there are appropriate alternative possibilities for coupling. Examples of this type include the radical pair (5), derived from the ylide (6), in which coupling[7] can occur at positions 2′, 3′, and 4′ [see (5)] and the rearrangement reactions[6,8] of the allylammonium ylides (7) which give the products (8) and (9) of competing [1,2] and [1,4] rearrangements.



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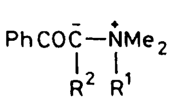

$\mathrm{PhCO}\underset{R^2}{\bar{C}}-\underset{R^1}{\overset{+}{N}}\mathrm{Me_2}$

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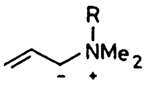

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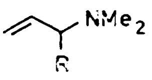

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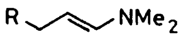
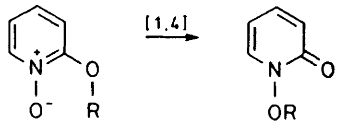


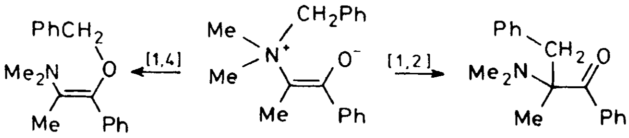
(9)

A number of [1,4] rearrangements have been reported in systems that are related to the ammonium ylides, as for example the 10-thia-anthracenes,[9] but the extensively studied [1,4] rearrangement (10) ⟶ (11) of 2-alkoxypyridine *N*-oxides is the best known example of this reaction.[10-13] The reaction (10) ⟶ (11) appears to be virtually the only example of an anionic [1,4] rearrangement, with carbon as a migrating centre, which shows the normal features of an allowed sigmatropic process. Thus when the migrating group R is an allyl group there is no detectable [3,4] rearrangement (allyl inversion) accompanying the [1,4] process, and only in extreme cases does the reaction (10) ⟶ (11) appear to have a radical pair mechanism.[11,12,13]



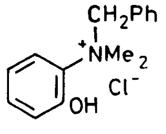
(10) (11)

R = alkyl, benzyl, allyl



(13) (12) (14)

The [1,4] rearrangement of the *cisoid*[14] carbonyl-stabilised ammonium ylide (12) ⟶ (13) is formally analogous to the reaction (10) ⟶ (11) but this reaction, which has only recently been recognised,[7] is only a minor rearrangement pathway, the major reaction (12) ⟶ (14) being a Stevens [1,2] rearrangement which involves a radical pair mechanism.[7,15] The incorporation of the enolate anion system of (12) into an aromatic system might be expected to favour the [1,4] rearrangement, resulting in the formation of a phenol ether, rather than the [1,2] rearrangement, which would lead to a cyclohexadienone, and a report[16] that the base catalysed rearrangement of the phenolic ammonium salt (15) yielded the amino-ether (16) supported this view. Furthermore the analogous base-catalysed rearrangement of the salt (17) has been reported[17] to yield the product (18). Both of these rearrangements can be regarded as [1,4] sigmatropic rearrangements of the intermediate ylides * (19) and (20).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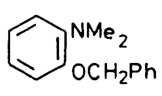
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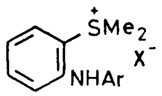
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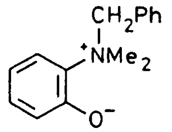
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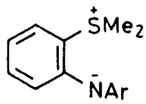
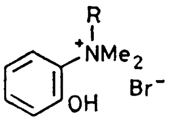

(20)

The base catalysed rearrangement of the *ortho*-hydroxyanilinium salts [*cf.* (15)] was re-investigated[18] in order to establish the generality of this [1,4] rearrangement and to determine the mechanism of the reaction (19) ⟶ (16). The salts (15) and (21b—d) were prepared by the reaction of 2-dimethylaminophenol with the appropriate alkyl halides. On treating aqueous solutions of the salts (15) and (21b—d) with aqueous sodium hydroxide at 0 °C the 2-oxidoanilinium ylides (22a—d) were obtained as colourless solids. The structures (22a—d) were established by the n.m.r. spectra of the ylides and by the regeneration of the salts (21a—d) by treatment of the ylides (22a—d) with hydrobromic acid.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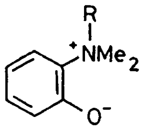
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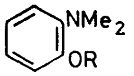
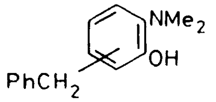

(23)

a, R = CH_2Ph
b, R = (*E*) - $CH_2CH{=}CHPh$
c, R = $CH_2CH{=}CH_2$
d, R = $CH_2CH{=}CMe_2$
e, R = $CH_2C{\equiv}CPh$
f, R = (*Z*) - $CH_2CH{=}CHPh$
g, R = $CH_2C{\equiv}CH$
h, R = $CH_2C{\equiv}CD$

The ylide (22a) rearranged on heating at 110 °C to give a low yield (32%) of the product (23a) of a [1,4] rearrangement. Three other products were isolated in very low yield. One of these (5.5% yield) had the spectral properties of the benzyl-2-dimethylaminophenol (24) but the n.m.r. spectrum did not define the position of attachment of the benzyl group to the aromatic ring. The other two products, (25) (2.5% yield) and (26) (12% yield), each contained two benzyl groups and their structures were readily derived from their n.m.r. spectra; these products evidently result from intermolecular nucleophilic displacement reactions of the ylide (22a). Thus the [1,4] rearrangement (22a) ⟶ (23a) is accompanied by intermolecular reactions and possibly by an alternative mode of intramolecular rearrangement to give (24). The *N*-cinnamyl ylide (22b) rearranged more cleanly at 80 °C to give the ether (23b) (79% yield) and a second product, identified on the basis of its n.m.r. spectrum as the 4-(1-phenylallyl)phenol (27). The formation of (27) is difficult to rationalise since it cannot arise from a sequence of allowed, concerted † rearrangements. The ether (23b) is stable under the conditions of the rearrangement but at 110 °C it gives a low yield of the Claisen [**3,3**] rearrangement product (28), which has an n.m.r. spectrum quite distinct from that of the product (27). In view of the reaction schemes reported below it seems probable that the product (27) is formed from (22b) by an initial [1,2] rearrangement to give the dienone (29) which subsequently undergoes [3,3] rearrangement to give (27).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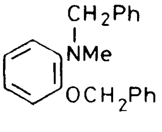
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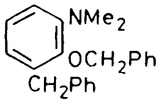
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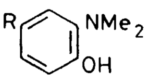

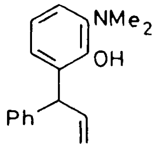

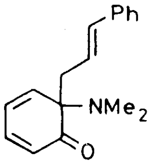

(27) R = $CHPhCH{=}CH_2$ (28) (29)
(30) R = $CH_2CH{=}CH_2$

The *N*-allyl ylide (22c) rearranged when heated in chloroform at 60 °C to give two major products, the ether (23c) (24% yield) and the allylphenol (30) (50% yield). The allylphenol (30) does not arise from the ether (23c) since the latter is stable at 60 °C although at higher temperatures it reacts to give a complex mixture of products. The *N*-(3,3-dimethylallyl) ylide (22d) rearranged on heating at 80 °C to give the ether (23d) (55% yield) as the only isolable product.

The ethers (23a—d) are the expected products of [1,4] rearrangements of the ylides (22a—d) but the yields are surprisingly low for what appears to be a simple, ' allowed ' pericyclic process, and these yields may be compared with the rather higher yields obtained, for example, in Claisen and Cope [3,3] rearrangements. It therefore appeared necessary to determine whether these [1,4] rearrangements (22) ⟶ (23) are concerted, intramolecular processes.

A concerted [1,4] rearrangement of an *N*-allyl ylide

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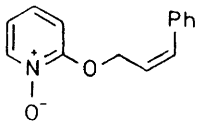
* Compounds of this type are described as ylides, rather than betaines, to stress the formal relationship with the carbonyl stabilised onium ylides [*e.g.* (12)].

† The term ' concerted ' is used throughout this paper in the sense indicated in Part 1 of this series.[3]

[*e.g.* (22b—d) ⟶ (23b—d)] would be expected to occur without the possibility of loss of configuration of the double bond of the migrating allyl group. This hypothesis was tested by examining [19] the rearrangement of the *cis*-cinnamyl *N*-oxide (31); at 52 °C the *cis*-cinnamyloxypyridone (32a) was obtained in high yield (80%) and the corresponding *trans*-cinnamyloxypyridone (32b) could not be detected in the reaction product. In contrast with this result the rearrangement of the *cis*-cinnamyl ylide (22f) proved to be complex. The *cis*-cinnamyl salt (21f) was prepared by catalytic hydrogenation of the 3-phenylprop-2-ynyl salt (21e) using a palladium–barium sulphate catalyst. At 80 °C the rearrangement of the ylide (22f) gave no isolable reaction products but when an ethereal solution of the ylide (22f) was heated under reflux a moderate yield (45%) of the products of [1,4] rearrangement could be obtained. This product was shown by its n.m.r. spectrum to consist of a mixture of the *cis*-cinnamyl ether (23f) and the *trans*-cinnamyl ether (23b) in a 3 : 1 ratio; the methiodides of these two ethers could be separated by fractional crystallisation and their structures established. The formation of these two ethers (23f) and (23b) indicates that the rearrangement (22f) ⟶ (23f) is accompanied by some loss of the configuration of the migrating allyl group and therefore it is not entirely a concerted [1,4] sigmatropic process. This result encouraged further scrutiny of the mechanism of other apparent [1,4] sigmatropic rearrangements of the type (22) ⟶ (23).



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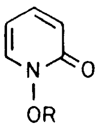
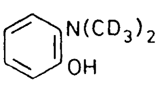


(32)

a, R = (*Z*)- $CH_2CH{=}CHPh$

b, R = (*E*)- $CH_2CH{=}CHPh$

The intramolecularity of the rearrangements (22a) ⟶ (23a) and (22b) ⟶ (23b) was selected as the next topic for study using isotopically labelled ylides in the usual type of ' cross-over ' experiments. The deuteriated dimethylaminophenol (33) was prepared by the reaction of *o*-aminophenol hydrochloride with [$^2H_4$]methanol; reaction of (33) with appropriately deuteriated benzyl bromide and cinnamyl bromide gave the [$^2H_8$]-salts (34) and hence the [$^2H_8$]-ylides (35). The ^1H n.m.r. spectra of the salts (34) and the ylides (35) showed a complete lack of signals assignable to -$\overset{+}{N}CH_3$ and -$\overset{+}{N}CH_2$- groups in accord with the expected positions of deuterium substitution. The rearrangement of an equimolecular mixture of the [$^2H_0$]-ylide (22a) and the [$^2H_8$]-ylide (35a) gave a crude reaction product which contained the [$^2H_0$]-ether (23a) and the [$^2H_8$]-ether (36a) as major reaction products with no detectable amount of the cross-over products, the [$^2H_2$]-ether (37a) and the [$^2H_6$]-ether (38a). A similar result was obtained using a mixture of the [$^2H_0$]cinnamyl ylide (22b) and the [$^2H_8$]cinnamyl ylide (35b). Thus the rearrangements (22a) ⟶ (23a) and (22b) ⟶ (23b) are intramolecular processes and by analogy it is probable that other [1,4] rearrangements of the type (22) ⟶ (23) are also intramolecular.*



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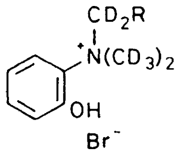

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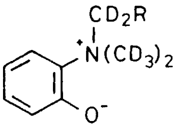

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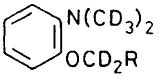

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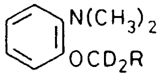

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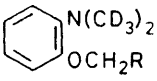

(38)

a ; R = Ph ; b, R = (*E*)- $CH{=}CHPh$

The formation of the allylphenol (30) as the major rearrangement product from the ylide (22c) was unexpected since the formation of this product must involve loss of aromaticity, for example, in the dienone (39) which must be the immediate precursor of the allylphenol (30). The mechanism of the rearrangement (22c) ⟶ (23c) + (30) was therefore investigated in more detail. The regioselectivity of the rearrangement was investigated initially using the deuterium-labelled salts (40a) and (40c) (*cf.* ref. 20) which were converted into the corresponding ylides (41a) and (41c). The salt (40a) was prepared by catalytic reduction of the *N*-propynyl salt (21g) using deuterium and a palladium–barium sulphate catalyst (*cf.* ref. 20). The n.m.r. spectrum of (40a) provided evidence for the $\overset{+}{N}CH_2CD{=}CHD$ grouping (τ 5.23, s, $\overset{+}{N}CH_2CD{=}$ and τ 4.36, br s, $CD{=}CDH$). The salt (40c) was prepared by catalytic hydrogenation of the *N*-[3-^{2}H]propynyl salt (21h) using a palladium–barium sulphate catalyst; the n.m.r. spectrum of (40c) (τ 5.27, m, $\overset{+}{N}CH_2CH{=}$ and τ 4.38—4.43, m, $CH{=}CHD$) was consistent with the position of the deuterium label and the mass spectrum of the corresponding ylide (41c) indicated an average deuterium content of 0.80 ± 0.03 atoms per molecule. Thermal rearrangement of the ylide (41a) gave the allylphenol (42a + b) in which the deuterium labels appeared to be associated with positions 2 and 3 of the allyl group (n.m.r., τ 6.70, s, $ArCH_2CD{=}$ and τ 4.98, br s, $CD{=}CDH$) but unfortunately, although this result indicated an apparent regioselectivity for the rearrangement (41a) ⟶ (42a and b), no information was provided regarding the stereochemical course of the reaction. The rearrangement of the ylide (41c) was more informative and the two major reaction

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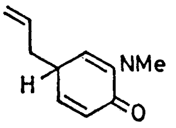
* These results may be compared with the results of a similar examination of the Stevens [1,2] rearrangement (ref. 15) in which substantial amounts of cross-over products may be formed under some reaction conditions.

products, the allylphenol (30; 0.80 D) and the ether (22c; 0.80 D), were converted into crystalline methiodides. The n.m.r. spectrum of the methiodide of the ether indicated that it had the deuterium label located as in (43c) [AMX_2 system, τ_A 3.73, τ_M 4.59, τ_X 5.04, J_{AM} 10, J_{AX} 5.5, J_{MX} 1.5 Hz, with H_A additionally split into triplets J 2.5 Hz by *trans*-CH_A=CD coupling, (*Z*)-ArC-$(H_X)_2CH_A$=CH_MD]. Thus the allyl group participates in the [1,4] rearrangement with retention of the stereochemistry of the allylic double bond. The n.m.r. spectrum of the methiodide of the phenol indicated that it was a mixture of the stereoisomers (44c) and (44d) (AMX_2 + ANX_2 systems, τ_A 4.02, τ_M 4.83, τ_N 4.89, τ_X 6.58, J_{AM} 10, J_{AN} 18, J_{AX} 7 Hz).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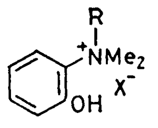
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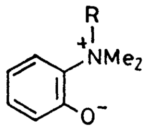
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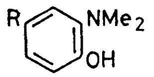
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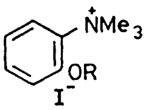
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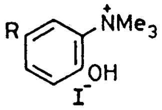
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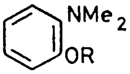
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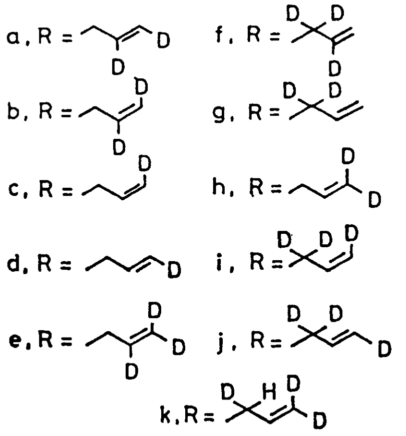
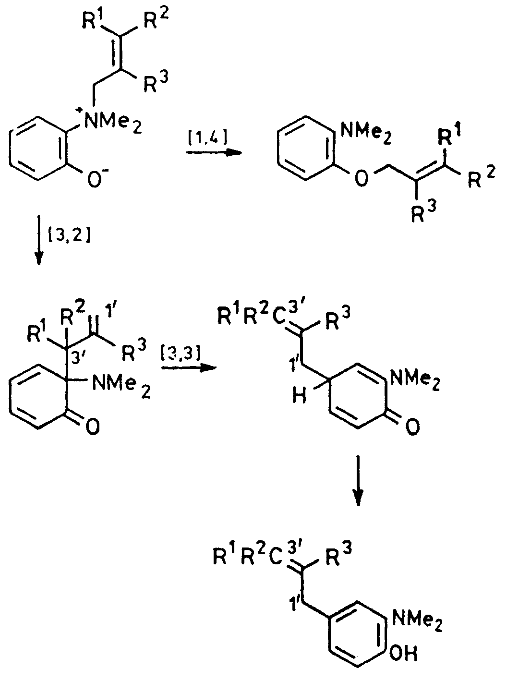


The results of this initial mechanistic investigation are compatible with the formation of the ether (23c) by [1,4] sigmatropic rearrangement of the ylide (22c) and the formation of the allylphenol (30) from the ylide (22c) by a sequence of allowed [3,2] and [3,3] sigmatropic rearrangements. This conclusion is summarised in Scheme 1. It should be noted that the deuterium labels used in the cases of (41a) and (41c) do not provide precise estimation of 1,3-scrambling within the allyl group (see labelling in the Scheme) and Scheme 1 therefore represents only the major mechanistic pathway (see below and Scheme 2).

The results reported above appear to indicate that the rearrangement (22c) ⟶ (23c) + (30) involves only allowed and concerted sigmatropic rearrangements. It was therefore surprising to find that the n.m.r. spectrum of the freshly formed phenol (30) showed strong emission signals associated with the protons at the 1′- and 3′-positions in the allyl side chain (Figure 1) when the rearrangement was carried out in nitrobenzene at 110—120 °C in the probe of an n.m.r. spectrometer. These signals decayed rapidly (2—3 min) and were replaced by



SCHEME 1 Sigmatropic rearrangements of *N*-allyl-*NN*-dimethylanilinium-2-olate (22c). In (41a) R^1 = H, R^2 = R^3 = D and in (41c) R^1 = D, R^2 = R^3 = H

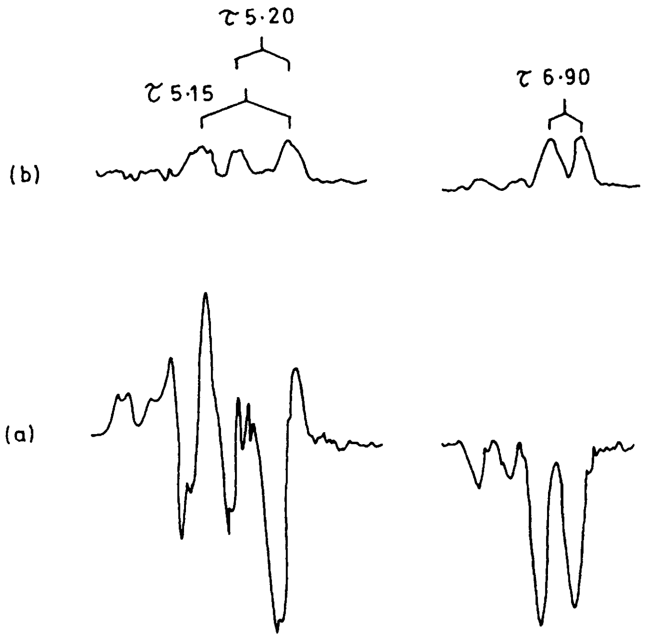


FIGURE 1 ^1H N.m.r. spectrum (100 MHz) of =CH_2 (τ 5.15, 5.20) and ArCH_2 (τ 6.90) of the phenol (30) formed from the ylide (22c) in nitrobenzene at 110—120 °C; (a) after *ca.* 1 min, (b) after 5 min the normal absorption signals of the allylphenol (30). The observation of CIDNP in the product of a reaction provides evidence that the product is derived directly or indirectly from a radical pair [21-24] and it was therefore clear that, under these reaction conditions, at least some of the allylphenol (30) was formed by a reaction sequence including at least one non-concerted process involving homolysis and radical pair recombination. This apparent derivation of the allylphenol (30) by two different pathways was investigated more fully by experiments using appropriate deuteriated ylides.

Reduction of the *N*-[3-^{2}H]propynyl salt (21h) with deuterium and a palladium–barium sulphate catalyst gave the *N*-[2,3,3-$^2H_3$]allyl salt (40e) in which the expected positions of the deuterium labels were consistent with the n.m.r. spectrum (τ 5.25, s, $\overset{+}{N}CH_2CD{=}CD_2$) which indicated an average deuterium content of 2.86 ± 0.1 atoms per molecule. The corresponding ylide (41e; 2.93 ± 0.03 D by mass spectrometry) rearranged at 60 °C in chloroform to give the ether (23c; 2.93 ± 0.03 D) and phenol (30; 2.93 ± 0.03 D). The n.m.r. spectrum of the methiodide of the ether showed that it consisted of the *N*-[2,3,3-$^2H_3$]-salt (43e) and the *N*-[1,1,2-$^2H_3$]-salt (43f) in the ratio indicated in the Table. The n.m.r. spectrum of the methiodide of the phenol showed that it was a mixture of the [2,3,3-$^2H_3$]allylphenol methiodide (44e) and the [1,1,2-$^2H_3$]allylphenol methiodide (44f) (Table). Thus at 60 °C the rearrangement of (41e) involves a concerted [1,4] sigmatropic process to give only the ether (45e) (81%) and a random coupling of the allyl–dimethylaminophenoxy radical pair (46) (Scheme 2) at phenolic oxygen to give a 1 : 1 mixture of (45e) and (45f) (19%). Similarly the allylphenol (30) is formed by a sequence of concerted [3,2] and [3,3] sigmatropic rearrangements to give only (42e) (75%) and by a process that at some stage involves random coupling of the allyl–dimethylaminophenoxy radical pair (46) at a ring carbon atom to give, ultimately, a 1 : 1 mixture of (42e) and (42f) (25%). This process could either be coupling at C-2 followed by a concerted [3,3] rearrangement and aromatisation or coupling at C-5 followed by aromatisation; the above results do not distinguish between these two possibilities. The rearrangement of the ylide (41e) was repeated in nitrobenzene at 110 °C and the CIDNP associated with the freshly formed product was recorded (Figure 2); it was noted that the emission spectrum showed signals assignable to 1-H_2 and 3-H_2 of the allylphenol (30) of apparently equal intensity whereas the eventual absorption spectrum associated with the allylphenol showed a signal of much higher intensity for 3-H_2. Thus the allylphenol giving rise to CIDNP showed complete 1,3-scrambling of the hydrogen label in the allyl group whereas the n.m.r. spectrum of the isolated allylphenol (30; 2.93 ± 0.03 D) showed that it was a mixture of the [2,3,3-$^2H_3$]allylphenol (42e) and the [1,1,2-$^2H_3$]allylphenol (42f) in the ratio indicated in the Table. Thus under the more drastic reaction conditions required for the observation of CIDNP the formation of the allylphenol (30) involves primarily a concerted reaction sequence (64%) together with a process involving a random radical coupling (36%).

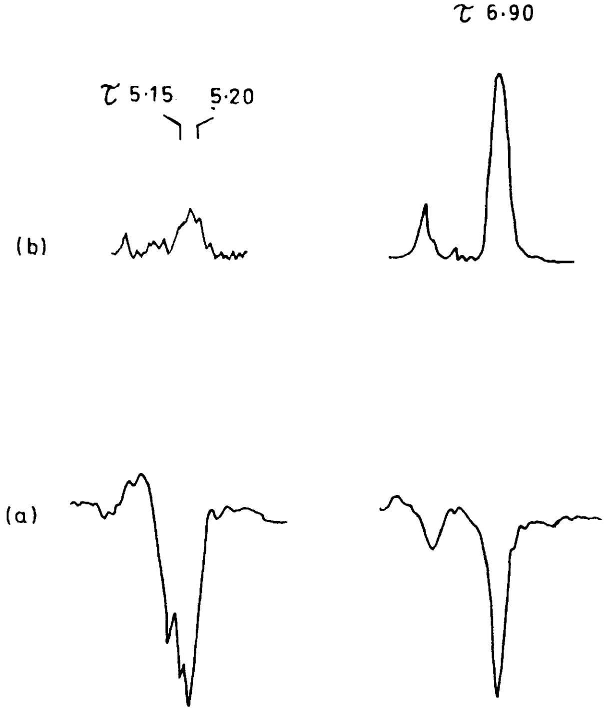


FIGURE 2 ^{1}H N.m.r. spectrum (100 MHz) of $=CH_2$ (τ 5.15, 5.20) and $ArCH_2$ (τ 6.90) of the deuteriated phenols (42e and f) formed from the ylide (41e) in nitrobenzene at 110 °C; (a) after *ca.* 1 min, (b) after 5 min

Deuterium distribution [a] in ylide (22c) and the rearrangement products (23c) and (30)

Starting ylide	C(1)	C(3)	Reaction [b] temperature/°C	Phenol C(1)	Phenol C(3)	Ether C(1)	Ether C(3)	% Radical pair mechansm [c]	
(41e)	0	1.96	60	0.25	1.71	0.19	1.77	25	19
			110	0.35	1.61			36	
(41g)	1.95	0	60	1.78	0.17	1.79	0.16	17	16
			110	1.59	0.36			37	
(41i)	1.90	0.95	60	1.73	1.12	1.79	1.06	18	12
			115	1.53	1.32			39	

[a] Total deuterium content based upon mass spectra of (22c), (23c), and (30). Deuterium distribution based upon the n.m.r. spectra of the ylide (22c) and the methiodides of (23c) and (30). The numbers refer to the average number of deuterium atoms (±0.03) at positions 1 and 3 of the allyl side chain. [b] At 60 °C in $CHCl_3$ and at 110—120 °C in $PhNO_2$. [c] The first number refers to formation of the phenol (30) and the second number to the ether (23c).

This examination of 1,3-allylic scrambling during the formation of the ether (23c) and the phenol (30) was repeated using the [1,1-^{2}H$_{2}$]allyl ylide (41g) which was prepared from the salt (40g; X = p-MeC$_{6}$H$_{4}$SO$_{3}$). The required [1,1-^{2}H$_{2}$]-salt was prepared by the direct alkylation of *o*-dimethylaminophenol with [1,1-^{2}H$_{2}$]allyl toluene-*p*-sulphonate; 1,3-allylic scrambling of the deuterium label was not detectable in this reaction. Thermal rearrangement of the [1,1-^{2}H$_{2}$]allyl ylide (41g; 1.95 D) at 60 °C in chloroform gave the ether (23c; 1.95 D) and the allylphenol (30; 1.95 D) which were converted into the corresponding methiodides. The n.m.r. spectra of the methiodides indicated that in each case they were mixtures of the [1,1-^{2}H$_{2}$]-salt, (43g) or (44g), and the [3,3-^{2}H$_{2}$]-salt, (43h) or (44h), in the ratios indicated in the Table. Thus this second experiment gave results agreeing closely with those of the previous experiment and at 60 °C the [1,4] rearrangement (22c) ⟶ (23c) involves a concerted process (84%) and a random radical coupling (16%) and the formation of the allylphenol (30) involves a sequence of concerted reactions (83%) and a reaction sequence involving a random radical coupling (17%). An examination of the CIDNP that accompanies the formation of the allylphenol from the [1,1-^{2}H$_{2}$]allyl ylide (41g) at 110 °C in nitrobenzene shows that it is associated with 1,3-allylic scrambling of the deuterium label (Figure 3). The n.m.r. spectrum of the isolated allylphenol (23c; 1.95 D) formed under these conditions shows that its formation is associated with concerted and specific allylic coupling (63%) and a process involving random allylic coupling (37%).

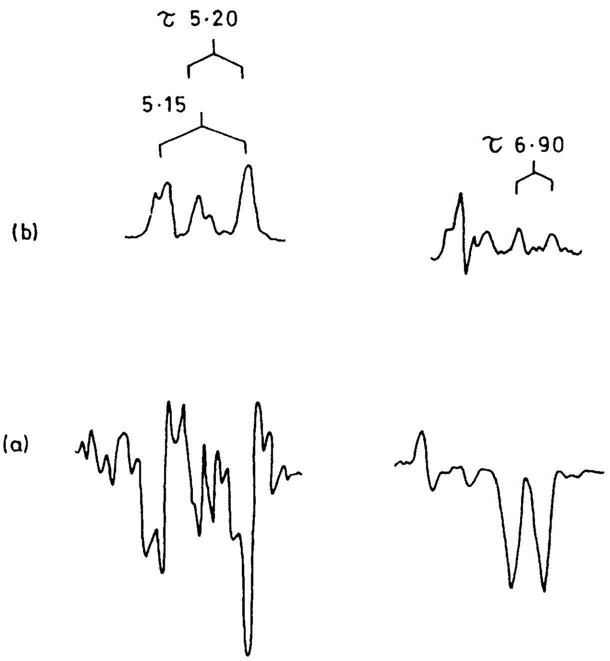


FIGURE 3 ^{1}H N.m.r. spectrum (100 MHz) of =CH_{2} (τ 5.15, 5.20) and ArCH_{2} (τ 6.90) of the deuteriated phenols (42g and h) formed from the ylide (41g) in nitrobenzene at 110 °C; (a) after *ca*. 1 min, (b) after 5 min

Thus the above examination of the fate of the deuterium labels during the rearrangement of the ylides (41e) and (41g) shows that the formation of the ether (23c) and the allylphenol (30) are partly concerted processes involving specific rearrangements of the allyl group and partly processes involving random coupling of the allyl component of the radical pair (46) at some stage in the reaction pathway. This formation and recombination of the radical pair (46) to give the products (23c) and (30) could be associated with homolysis of the ylide (22c) or either of the dienones shown in Scheme 1 and identification of the homolysis step required additional labelling experiments. Thus an allyl radical generated from the ylide (22c) would be expected to retain the original configuration of the allylic double bond * (as indicated by a suitable deuterium label) during radical coupling processes leading *directly* to the ether (23c) and the allylphenol (30). If a [3,2] rearrangement of the ylide (22c) occurs prior to the homolysis the configuration of the allylic double bond would be lost (see Scheme 1) and if the allylphenol (30) results from a sequence of homolysis and recombination to give an *ortho*-dienone followed by [3,3] rearrangement this would also lead to loss of configuration of the allylic double bond. The rearrangement of the [1,1,3-^{2}H$_{3}$] ylide (41i) was therefore investigated since this pattern of deuterium labelling is adequate to check both the regio- and stereo-selectivity of the rearrangement.

The salt (40i; X = p-MeC$_{6}$H$_{4}$SO$_{3}$), required as a precursor of the ylide (41i), was prepared by the reaction of (*Z*)-[1,1,3-^{2}H$_{3}$]allyl toluene-*p*-sulphonate with *o*-dimethylaminophenol. The required (*Z*)-[1,1,3-^{2}H$_{3}$]allyl alcohol was prepared by a modification of the elegant procedure used by Majerski and Schleyer[25] for the preparation of (*Z*)-[1,1,2,3-^{2}H$_{4}$]allyl alcohol. Rearrangement of the ylide (41i; 2.85 D) in chloroform at 60 °C gave the ether (23c; 2.85 D) and the allylphenol (30; 2.85 D). Examination of the n.m.r. spectrum of the methiodide of the ether showed that the compound was formed by a concerted process to give (45i) (88%) and random allylic coupling to give a 1 : 1 mixture of (45i) and (45k) (12%). A similar examination of the n.m.r. spectrum of the methiodide of the phenol showed that it was formed by a concerted reaction sequence to give a 1 : 1 mixture of (42i) and (42j) (82%) and by a process involving a random allylic coupling to give a 1 : 1 mixture of (42i) and (42k) † (18%). The examination of the CIDNP associated with the formation of the allylphenol from the ylide (41i) at 115 °C in nitrobenzene (Figure 4) showed that the stereochemistry of the allyl label was retained in the product giving rise to an emission spectrum. Thus the allylphenol (30) is formed by a minor homolytic pathway from the ylide (22c) with retention of the configuration of the allylic double bond. This pathway must therefore involve homolysis of the ylide (22c) followed by radical pair (46) recombination to give the *para*-dienone (47). The n.m.r. spectrum of the allylphenol (30; 2.85 D) derived from the ylide (22c)

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* This expectation is based upon the substantial barrier to rotation in a delocalised allyl radical.

† The absence of (42j) in the products of the radical coupling is assumed on the basis of the CIDNP study.

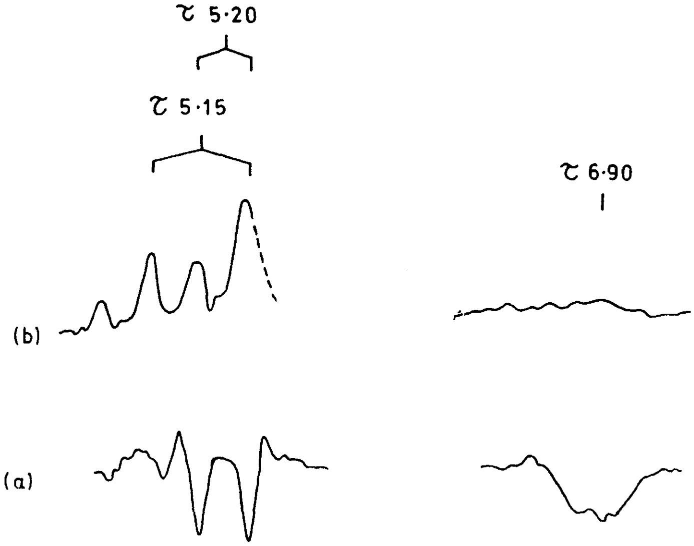
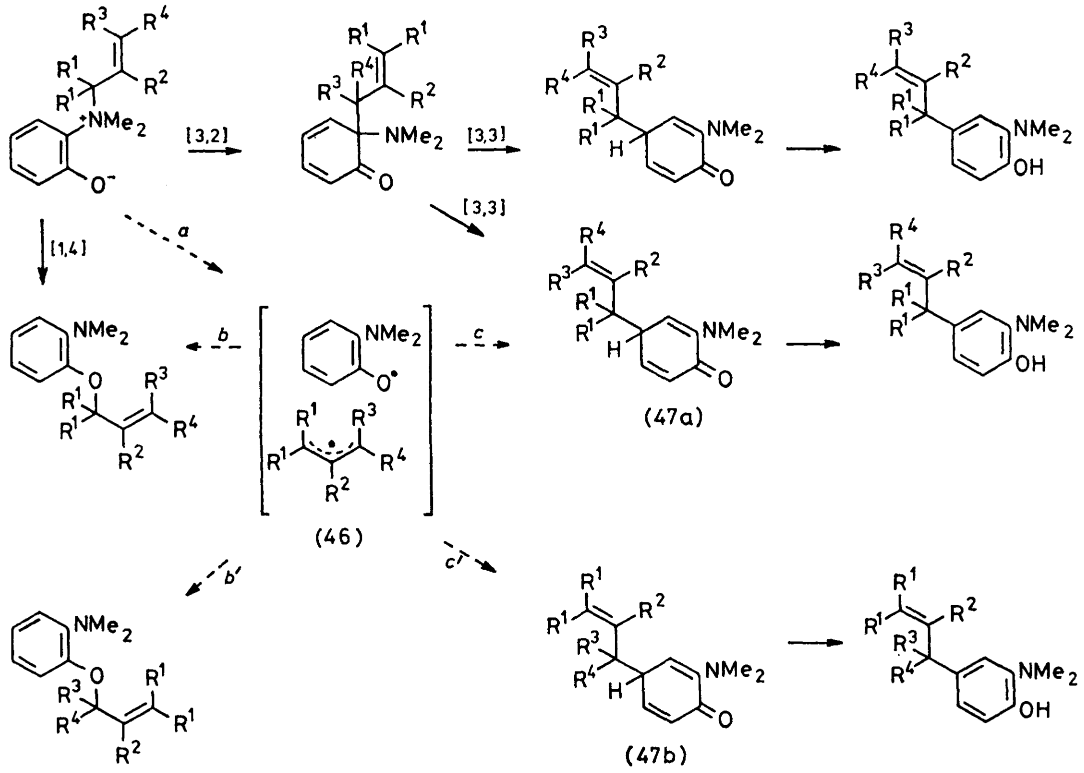


FIGURE 4 ^{1}H N.m.r. spectrum (100 MHz) of $=CH_2$ (τ 5.15, 5.20) and $ArCH_2$ (τ 6.90) of the deuteriated phenols (42i—k) formed from the ylide (41i) in nitrobenzene at 115 °C; (a) after *ca.* 1 min, (b) after 5 min

under these more vigorous rearrangement conditions indicated that considerable stereochemical scrambling had occurred. A careful examination of the n.m.r. spectrum of the methiodide of the allylphenol showed that its formation from (41i) involved a concerted sequence of reactions to give (42i and j) (61%) and a random radical coupling to give (42i and k) (39%).

The results described above and summarised in the Table are consistent with the formation of the ether (23c) and the allylphenol (30) from the ylide (22c) by the competing sigmatropic rearrangements and radical pair processes summarised in Scheme 2. In particular it can be seen from Scheme 2 that the formation of the ether (23c) and the allylphenol (30) by the radical pair routes (step *a* + steps *b* or *b*′ or step *a* + steps *c* or *c*′) leads to retention of the stereochemistry of the allylic double bond but complete randomisation of positions 1 and 3 of the allyl grouping. In contrast, formation of the ether (23c) by a [1,4] sigmatropic rearrangement does not result in either loss of the stereochemistry of the allylic double bond or 1,3-allyl scrambling but formation of the allylphenol (30) by a sequence of [3,2] and [3,3] sigmatropic rearrangements results in loss of the stereochemistry of the allylic double bond but no 1,3-allyl scrambling.

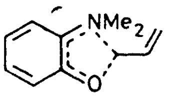
A number of conclusions that have general implications for the mechanism of sigmatropic rearrangements follow from these results. The observation of CIDNP during product formation does not rule out the simultaneous formation of products by concerted and radical pair processes, a conclusion that is related to an interesting study of the [1,4] rearrangement of 2-alkoxypyridine *N*-oxides [12] and our earlier studies of the Stevens [1,2] rearrangement [15,26] carried out in collaboration with



SCHEME 2 Concerted and radical pair rearrangements of *N*-allyl-*NN*-dimethyl-2-oxidoanilinium ylide (22c). In (41e) $R^1 = H$, $R^2 = R^3 = R^4 = D$; in (41g) $R^1 = D$, $R^2 = R^3 = R^4 = H$; in (41i) $R^1 = R^3 = D$, $R^2 = R^4 = H$

Professor G. L. Closs. Furthermore, we note that the rather drastic conditions frequently required for the observation of CIDNP in thermal rearrangement reactions may favour radical pair processes (see results in Table and refs. 12, 15, and 27). The caveat that radical reactions, identified on the basis of CIDNP, may represent only minor side reactions associated with more important non-radical processes has long been recognised.[28] These limitations in the conclusions that can be drawn from the observation of CIDNP during product formation in thermal rearrangements require that additional tests should be applied to check the involvement of radicals in the reaction pathway. Such tests may involve trapping procedures,[29] studies of racemisation and intermolecularity [15] and, as in the present case, an examination of the regioselectivity of allylic rearrangements. These tests are able to detect phenomena associated with radical pairs that may have significantly shorter lifetimes than that required (>*ca.* 10^{-9} s) [21,22] for the mixing of singlet and triplet states leading to the development of spin polarisation in reaction products.

The close relationship between the radical pair (46) and the transition states (48), (49), and (50) for concerted [1,4], [3,2], and [3,3] rearrangements, that may be derived [2] by appropriate interaction between the components of the radical pair (46), is emphasized by the competition between the reactions in which they are involved (Scheme 2). This suggests that the change in free energy associated with the interaction between the two components of the radical pair (46) is small in spite of the favourable orbital-symmetry relationships. This similarity in the free energies of radical pairs and the transition states for related allowed sigmatropic rearrangements is a general characteristic of many of the radical pairs derived from ylide homolysis and is consistent with the competition between symmetry-allowed and symmetry-forbidden processes that is often noted in ylide rearrangements. Nevertheless regio- and stereoselectivity [30,31] are frequently encountered in the rearrangements of ylides and related compounds when an allowed [3,2] or [5,4] sigmatropic pathway is available.



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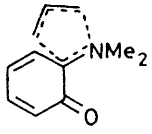

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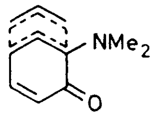

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EXPERIMENTAL

For general directions see Part 1.[3] Spectra showing CIDNP effects were recorded using a Varian HA 100 spectrometer, the sample being placed in a preheated probe and spectra being recorded using a 100-s scan rate.

2-*Hydroxy*-NN-*dimethylanilinium Salts* (15) *and* (21).—An equimolecular mixture of 2-dimethylaminophenol [32] and the alkyl halide in methyl cyanide was left at room temperature for 48 h. The solvent was evaporated off and the quaternary salt recrystallised from ethanol–ether. The following salts were prepared: *N*-benzyl-2-hydroxy-*NN*-dimethylanilinium chloride (15) (87%), m.p. 148—149 °C (lit.,[16] 115—116 °C), τ (CF_3CO_2H) 2.52—3.14 (m, 9 aryl H), 4.76 (s, $\overset{+}{N}CH_2Ph$), and 6.27 (s, $\overset{+}{N}Me_2$); N-*cinnamyl*-2-*hydroxy*-NN-*dimethylanilinium bromide* (21b) (93%) as prisms, m.p. 150—151 °C (Found: C, 60.8; H, 6.2; N, 4.3; Br, 24.2. $C_{17}H_{20}BrNO$ requires C, 61.6; H, 6.0; N, 4.2; Br, 23.95%); τ (CF_3CO_2H) 2.44—2.99 (m, 9 aryl H), ABX_2 system, τ_A 3.12, τ_B 4.08, τ_X 5.15 [J_{AB} 16, J_{BX} 8 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_APh$], and 6.31 (s, $\overset{+}{N}Me_2$); N-*allyl*-2-*hydroxy*-NN-*dimethylanilinium bromide* (21c) (89%) as prisms, m.p. 155 °C (Found: C, 51.15; H, 6.3; N, 5.4; Br, 30.95. $C_{11}H_{16}BrNO$ requires C, 51.2; H, 6.2; N, 5.4; Br, 31.0%); τ (CF_3CO_2H); 2.47—2.98 (m, 4 aryl H), 4.36—4.40 (m, $CH{=}CH_2$), 5.24 (d, *J* 5 Hz, $\overset{+}{N}CH_2$), and 6.28 (s, $\overset{+}{N}Me_2$); N-(3,3-*dimethylallyl*)-2-*hydroxy*-NN-*dimethylanilinium bromide* (21d) (92%), m.p. 139 °C (Found: C, 54.5; H, 6.9; N, 5.0; Br, 28.3. $C_{13}H_{20}BrNO$ requires C, 54.55; H, 7.0; N, 4.9; Br, 28.0%); τ (CF_3CO_2H) 2.46—2.98 (m, 4 aryl H), 4.87 (t, *J* 8 Hz, $CH_2{-}CH{=}$), 5.28 (d, *J* 8 Hz, $\overset{+}{N}CH_2$), 6.36 (s, $\overset{+}{N}Me_2$), and 8.21 (s, CMe_2); and 2-*hydroxy*-NN-*dimethyl*-N-(3-*phenylprop*-2-*ynyl*)*anilinium bromide* (21e) (90%) as rhombic crystals, m.p. 150 °C (Found: C, 61.2; H, 5.5; N, 4.1; Br, 24.4. $C_{17}H_{18}BrNO$ requires C, 61.45; H, 5.4; N, 4.2; Br, 24.1%); $\nu_{max.}$ 2 240 cm^{-1}; τ (CF_3CO_2H) 2.36—2.98 (m, 9 aryl H), 4.85 (s, $\overset{+}{N}CH_2$), and 6.17 (s, $\overset{+}{N}Me_2$).

NN-*Dimethylanilinium*-2-*olates* (22).—An aqueous solution of the anilinium salt (21) was treated with an excess of 50% aqueous sodium hydroxide at 0 °C and the mixture left overnight at 0 °C. The ylide (22) which separated was extracted into dichloromethane and the extract dried and evaporated at room temperature to give a sample which could be used without further purification. The following ylides were prepared: N-*benzyl*-NN-*dimethylanilinium*-2-*olate* (22a) (80%), m.p. 95—97 °C (Found: *M*, 227.1310. $C_{15}H_{17}NO$ requires *M*, 227.1310); τ 2.70—3.02 (m, 6 aryl H), 3.16 (dd, *J* 8 and 2 Hz, 6-H), 3.37br (d, *J* 8 Hz, 3-H), 3.96 (ddd, *J* 8, 9, and 2 Hz, 5-H), 4.58 (s, $\overset{+}{N}CH_2$), and 6.54 (s, $\overset{+}{N}Me_2$); N-*cinnamyl*-NN-*dimethylanilinium*-2-*olate* (22b) (79%), m.p. 64 °C (Found: *M*, 253.1469. $C_{17}H_{19}NO$ requires *M*, 253.1467); τ 2.75 (s, C_6H_5), 2.88 (t, *J* 8 Hz, 4-H), 3.08 (d, *J* 8 Hz, 6-H), 3.16 (d, *J* 8 Hz, 3-H), 3.83 (t, *J* 8 Hz, 5-H), ABX_2 system, τ_A 3.30, τ_B 4.07, τ_X 4.93 [J_{AB} 16, J_{BX} 7 Hz, $\overset{+}{N}(CH_X)_2CH_B{=}CH_APh$], and 6.50 (s, $\overset{+}{N}Me_2$); N-*allyl*-NN-*dimethylanilinium*-2-*olate* (22c) (80%), m.p. 80—83 °C (Found: *M*, 177.1153. $C_{11}H_{15}NO$ requires *M*, 177.1153); ABCX system, τ_A 2.92, τ_B 3.09, τ_C 3.24, τ_X 3.88 (J_{AB} 1.5, J_{AC} 8.5, J_{AX} 7, J_{BX} 8.5, J_{CX} 1.5 Hz, 4-H_A + 6-H_B + 3-H_C + 5-H_X), 4.38—4.70 (m, $CH{=}CH_2$), 5.07 (d, *J* 6 Hz, $\overset{+}{N}CH_2$), and 6.49 (s, $\overset{+}{N}Me_2$); and N-(3,3-*dimethylallyl*)-NN-*dimethylanilinium*-2-*olate* (22d) (68%), m.p. 106—107 °C (Found: *M*, 205.1456. $C_{13}H_{19}NO$ requires *M*, 205.1467); τ 2.93 (t, *J* 8 Hz, 4-H), 3.06 (d, *J* 8 Hz, 6-H), 3.26 (d, *J* 8 Hz, 3-H), 3.88 (t, *J* 8 Hz, 5-H), 4.84br (t, *J* 7 Hz, $CH_2CH{=}$), 5.12 (d, *J* 7 Hz, $\overset{+}{N}CH_2CH$), 6.54 (s, $\overset{+}{N}Me_2$), and 8.22 (s, $={CMe_2}$).

Thermal Rearrangement of N-*Benzyl*-NN-*dimethylanilinium*-2-*olate* (22a). *Formation of* 3-*Benzyl*-2-*benzyloxy*-NN-*dimethylaniline* (26), N-*Benzyl*-2-*benzyloxy*-N-*methylaniline* (25), *Benzyl*-2-*hydroxy*-NN-*dimethylaniline* (24), *and*

2-Benzyloxy-NN-*dimethylaniline* (23a).—The ylide (22a) (2.0 g) was heated in a sealed tube at 110 °C for 2 h (N_2 atmosphere). The reaction product was separated into four components by chromatography on silica using light petroleum–ethyl acetate (9 : 1 v/v) as the eluant. (i) *3-Benzyl-2-benzyloxy*-NN-*dimethylaniline* (26) (250 mg, 12%) was obtained as a pale yellow oil (Found: *M*, 317.1765. $C_{22}H_{23}NO$ requires *M*, 317.1780); τ 2.72—2.96 (m, 10 aryl H), ABC system, τ_A 3.03, τ_B 3.14, τ_C 3.31 (J_{AB} 8, J_{AC} 7, J_{BC} 2.5 Hz, 4-H_B, 5-H_A, 6-H_C), 5.16 (s, OCH_2Ph), 6.08 (s, $ArCH_2Ph$), and 7.22 (s, NMe_2); the *methiodide* had m.p. 138 °C (Found: C, 60.3; H, 5.5; N, 3.0; I, 28.0. $C_{23}H_{26}INO$ requires C, 60.1; H, 5.7; N, 3.05; I, 27.7%); τ [$(CD_3)_2CO$] 2.00—2.76 (m, 13 aryl H), 4.66 (s, OCH_2Ph), 5.70 (s, $ArCH_2Ph$), and 6.01 (s, $\overset{+}{N}Me_3$). (ii) N-*Benzyl-2-benzyloxy*-N-*methylaniline* (25) was obtained as a yellow oil (50 mg, 2.5%) (Found: *M*, 303.1625. $C_{21}H_{21}NO$ requires *M*, 303.1623); τ 2.59—3.14 (m, 14 aryl H), 4.92 (s, OCH_2Ph), 5.80 (s, NCH_2Ph), and 7.38 (s, NMe). (iii) Benzyl-2-hydroxy-*NN*-dimethylaniline (24) was obtained as pale yellow needles (110 mg, 5.5%), m.p. 173 °C, from ethanol (Found: *M*, 227.1316. $C_{15}H_{17}NO$ requires *M*, 227.1310); τ 2.76—3.37 (m, 9 aryl H + OH), 6.02 (s, $ArCH_2Ph$), and 7.43 (s, NMe_2). (iv) *2-Benzyloxy*-NN-*dimethylaniline* (23a) was obtained as a yellow oil (630 mg, 32%) (Found: *M*, 227.1316. $C_{15}H_{17}NO$ requires *M*, 227.1310); τ 2.62—3.13 (m, 9 aryl H), 4.90 (s, OCH_2Ph), and 7.20 (s, NMe_2); the methiodide had m.p. 165 °C (lit.,[16] 158—159 °C) (Found: C, 51.7; H, 5.1; N, 3.8; I, 34.3. Calc. for $C_{16}H_{20}INO$: C, 52.0; H, 5.4; N, 3.8; I, 34.4%); τ (D_2O) 2.25—2.68 (m, 9 aryl H), 4.43 (s, OCH_2Ph), and 6.15 (s, $\overset{+}{N}Me_3$).

Thermal Rearrangement of N-*Cinnamyl*-NN-*dimethylanilinium-2-olate* (22b). *Formation of 2-Cinnamyloxy*-NN-*dimethylaniline* (23b) *and 2-Hydroxy*-NN-*dimethyl*-5-(1-*phenylallyl*)*aniline* (27).—The ylide (22b) (2.0 g) was heated in a sealed tube at 80 °C for 15 min (N_2 atmosphere). The product was separated by chromatography on silica, using light petroleum–ethyl acetate (9 : 1 v/v) as the eluant, to give two compounds: (i) *2-cinnamyloxy*-NN-*dimethylaniline* (23b) as plates, m.p. 46 °C (1.58 g, 79%) by crystallisation from pentane (Found: C, 80.9; H, 7.5; N, 5.4; *M*, 253. $C_{17}H_{19}NO$ requires C, 80.6; H, 7.5; N, 5.5%; *M*, 253); τ 2.63—2.86 (m, 5 aryl H), 3.13 (s, 4 aryl H), ABX_2 system, τ_A 3.28, τ_B 3.59, τ_X 5.28 [J_{AB} 16, J_{BX} 5 Hz, $OC(H_X)_2CH_B{=}CH_A$-Ph], and 7.21 (s, NMe_2); the *methiodide* had m.p. 165—167 °C (from ethanol–diethyl ether) (Found: C, 54.5; H, 5.8; N, 3.5; I, 32.0. $C_{18}H_{22}INO$ requires C, 54.7; H, 5.6; N, 3.5; I, 32.15%); τ [$(CD_3)_2SO$] 2.35—3.11 (m, 9 aryl H), ABX_2 system, τ_A 3.27, τ_B 3.56, τ_X 4.98 [J_{AB} 16, J_{BX} 5 Hz, $OC(H_X)_2CH_B{=}CH_APh$], and 6.10 (s, $\overset{+}{N}Me_3$); and (ii) *2-hydroxy*-NN-*dimethyl*-5-(1-*phenylallyl*)*aniline* (27), a yellow oil (220 mg, 11%) (Found: *M*, 253.1466. $C_{17}H_{19}NO$ requires *M*, 253.1467); $\nu_{max.}$ 3 300 cm^{-1}; τ 2.77—3.19 (m, 8 aryl H), 3.53br (s, OH), ABCX system, τ_A 4.86, τ_B 5.08, τ_C 5.38, τ_X 3.77 (J_{AB} 1.5, J_{AX} 10, J_{BX} 17, J_{CX} 7 Hz, $CH_CCH_X{=}CH_AH_B$), and 7.44 (s, NMe_2); τ ($CDCl_3$–C_6F_6, 1 : 1 v/v) ABC system, τ_A 2.96, τ_B 3.18, τ_C 3.28 (J_{AB} 2, J_{BC} 8 Hz, 6-H_A, 4-H_B, 3-H_C); the *methiodide* had m.p. 179 °C (from ethanol–diethyl ether) (Found: C, 54.7; H, 5.9; N, 3.4; I, 32.2. $C_{18}H_{22}INO$ requires C, 54.7; H, 5.6; N, 3.5; I, 32.15%); τ (CF_3CO_2H) 2.63—2.72 (m, 8 aryl H), ABCX system, τ_A 4.70, τ_B 4.99, τ_C 5.29, τ_X 3.72 (J_{AB} 1.5, J_{AX} 10, J_{BX} 17, J_{CX} 7 Hz, $CH_CCH_X{=}CH_AH_B$), and 6.32 (s, $\overset{+}{N}Me_3$).

Thermal Rearrangement of 2-Cinnamyloxy-NN-*dimethylaniline* (23b). *Formation of 2-Dimethylamino*-6-(1-*phenylallyl*)*phenol* (28).—The amine (23b) (300 mg) was heated at 110 °C for 4 h in a sealed tube (N_2 atmosphere). The product was a complex mixture (t.l.c.); the only product isolated after chromatography on silica, using light petroleum–ethyl acetate as the eluant, was identified as the *aminophenol* (28) (55 mg, 18%), a pale yellow oil (Found: *M*, 253.1468. $C_{17}H_{19}NO$ requires *M*, 253.1467); $\nu_{max.}$ 3 300 cm^{-1}; τ 2.71—2.86 (m, C_6H_5), ABC system, τ_A 2.97, τ_B 3.08, τ_C 3.23 (J_{AB} 2, J_{AC} 7.5, J_{BC} 8 Hz, 4-H_A, 5-H_C, 6-H_B), 3.19br (s, OH), ABCX system, τ_A 4.81, τ_B 4.88, τ_C 5.05, τ_X 3.68 (J_{AC} 1.5, J_{AX} 10, J_{BX} 7, J_{CX} 17, J_{AB} 1.5, J_{BC} 1.5 Hz, $CH_BCH_X{=}CH_AH_C$), and 7.40 (s, NMe_2).

Thermal Rearrangement of N-*Allyl*-NN-*dimethylanilinium-2-olate* (22c). *Formation of 2-Allyloxy*-NN-*dimethylaniline* (23c) *and 4-Allyl-2-dimethylaminophenol* (30).—A solution of the ylide (22c) (1.00 g) in chloroform (5 ml) was heated under reflux for 2 h (N_2 atmosphere). The reaction product was purified by chromatography on silica, using light petroleum–ethyl acetate (9 : 1 v/v) as the eluant, to give two major fractions: (i) *2-allyloxy*-NN-*dimethylaniline* (23c), a pale yellow oil (240 mg, 24%) (Found: *M*, 177.1156. $C_{11}H_{15}NO$ requires *M*, 177.1153); τ 3.09—3.28 (m, 4 aryl H), $ABCX_2$ system, τ_A 3.97, τ_B 4.62, τ_C 4.78, τ_X 5.43 [J_{AB} 17, J_{AC} 10, J_{AX} 5, J_{BC} 1.5, J_{BX} 1.5, J_{CX} 1.5 Hz, $OC(H_X)_2CH_A{=}CH_BH_C$], and 7.22 (s, NMe_2); the *methiodide* had m.p. 175—178 °C (from ethanol–diethyl ether) (Found: C, 45.1; H, 5.8; N, 4.2; I, 39.95. $C_{12}H_{18}INO$ requires C, 45.1; H, 5.6; N, 4.4; I, 39.8%); τ (D_2O) 2.50—2.73 (m, 4 aryl H), $ABCX_2$ system, τ_A 3.62, τ_B 4.37, τ_C 4.44, τ_X 4.98 [J_{AB} 17, J_{AC} 10, J_{AX} 5.5, J_{BC} 1.5 Hz, $OC(H_X)_2CH_A{=}CH_BH_C$], and 6.12 (s, $\overset{+}{N}Me_3$); and (ii) *4-allyl-2-dimethylaminophenol* (30), a pale yellow oil (495 mg, 50%) (Found: *M*, 177.1148. $C_{11}H_{15}NO$ requires *M*, 177.1153); $\nu_{max.}$ 3 300 cm^{-1}; τ 3.06—3.18 (m, 3 aryl H), 3.42br (s, OH), $AMNX_2$ system, τ_A 4.09, τ_M 4.98, τ_N 5.00, τ_X 6.72 [J_{AM} 17, J_{AN} 10, J_{AX} 6, J_{MN} 2, J_{MX} 1.5, J_{NX} 1.5 Hz, $C(H_X)_2CH_A{=}CH_MH_N$], and 7.39 (s, NMe_2); τ (C_6F_6) ABC system, τ_A 3.09, τ_B 3.40, τ_C 3.64 (J_{AB} 2, J_{BC} 8 Hz, 3-H_C + 4-H_B + 6-H_A); the *methiodide* had m.p. 185—187 °C (decomp.) (from ethanol–diethyl ether) (Found: C, 45.0; H, 5.7; N, 4.4; I, 39.8. $C_{12}H_{18}INO$ requires C, 45.1; H, 5.6; N, 4.4; I, 39.8%); $\nu_{max.}$ 3 100 cm^{-1}; τ (CF_3CO_2H) 2.44—2.82 (m, 3 aryl H), $AMNX_2$ system, τ_A 4.02, τ_M 4.83, τ_N 4.89, τ_X 6.58 [J_{AM} 10, J_{AN} 18, J_{AX} 7, J_{MN} 2 Hz, $(CH_X)_2CH_A{=}CH_MH_N$], and 6.21 (s, $\overset{+}{N}Me_3$).

Thermal Rearrangement of N-(3,3-*Dimethylallyl*)-NN-*dimethylanilinium-2-olate* (22d). *Formation of 2-*(3,3-*Dimethylallyloxy*)-NN-*dimethylaniline* (23d).—The ylide (22d) (1.0 g) was heated in benzene at 80 °C for 1 h (N_2 atmosphere). The product was purified by chromatography (silica; light petroleum–ethyl acetate) to give the *ether* (23d) (550 mg, 55%) (Found: *M*, 205.1468. $C_{13}H_{19}NO$ requires *M*, 205.1467); τ 3.08—3.21 (m, 4 aryl H), 4.49 (t, *J* 6.5 Hz, $CH_2CH{=}$), 5.45 (d, *J* 6.5 Hz, OCH_2CH), 7.23 (s, NMe_2), 8.26 (s, =CMe), and 8.31 (s, =CMe). The *methiodide* had m.p. 175—180 °C (decomp.) (from ethanol–diethyl ether) (Found: C, 48.2; H, 6.5; N, 3.9; I, 36.3. $C_{14}H_{22}INO$ requires C, 48.4; H, 6.3; N, 4.0; I, 36.6%); τ (CF_3CO_2H–D_2O) 3.28—3.62 (m, 4 aryl H), 4.63 (t, *J* 6 Hz, $CH_2CH{=}$), 5.40 (d, *J* 6 Hz, OCH_2CH), 6.50 (s, $\overset{+}{N}Me_3$), and 8.42 (s, $=CMe_2$).

N-(Z)-*Cinnamyl-2-hydroxy*-NN-*dimethylanilinium Bromide* (21f).—The phenylpropynyl salt (21e) (4.0 g) in methanol (250 ml) was hydrogenated at room temperature and atmospheric pressure using a 5% palladium–barium sulphate catalyst (300 mg). The reaction was stopped when hydrogen uptake had reached 1.1 mol. equiv., the mixture was filtered and the filtrate evaporated. The residual solid crystallised from ethanol–diethyl ether to give the (Z)-*cinnamyl salt* (21f) (3.6 g, 89%) as plates, m.p. 138 °C (Found: C, 61.2; H, 6.1; N, 4.2; Br, 23.9. $C_{17}H_{20}BrNO$ requires C, 61.1; H, 6.0; N, 4.2; Br, 23.95%); τ (CF_3CO_2H) 2.50—2.92 (m, 9 aryl H), ABX_2 system, τ_A 2.97, τ_B 4.56, τ_X 5.00 [J_{AB} 11, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_APh$], and 6.43 (s, $\overset{+}{N}Me_2$).

N-(Z)-*Cinnamyl*-NN-*dimethylanilinium*-2-*olate* (22f).—The (*Z*)-cinnamyl salt (21f) was treated with aqueous sodium hydroxide to give the *ylide* (22f) (75%) as a hygroscopic solid (Found: *M*, 253.1478. $C_{17}H_{19}NO$ requires *M*, 253.1467); τ 2.64—3.30 (m, 8 aryl H), 3.84 (dt, *J* 8 and 2 Hz, 5-H), ABX_2 system, τ_A 3.00—3.30, τ_B 4.57, τ_X 4.71 [J_{AB} *ca.* 12, J_{BX} 7 Hz, $\overset{+}{N}C(H_X)_2CH_B{=}CH_APh$], and 6.63 (s, $\overset{+}{N}Me_2$).

Thermal Rearrangement of N-(Z)-*Cinnamyl*-NN-*dimethylanilinium*-2-*olate* (22f). *Formation of* Z- *and* E-*Isomers of* 2-*Cinnamyloxy*-NN-*dimethylaniline* (23f) *and* (23b).—The (*Z*)-cinnamyl ylide (22f) (2.00 g) was heated at 35—40 °C for 5 h (N_2 atmosphere) to give a complex mixture of products which was separated by chromatography to give a mixture of (*Z*)- and (*E*)-2-cinnamyloxy-*NN*-dimethylaniline (23f) and (23b) (900 mg, 45%) in a 3 : 1 ratio (n.m.r.). This mixture of isomers gave methiodides which could be separated by fractional crystallisation from ethanol. The major isomer was identified as the (*Z*)-*cinnamyl salt* (750 mg); plates, m.p. 192—193 °C (Found: C, 54.4; H, 5.6; N, 3.6; I, 32.1. $C_{18}H_{22}INO$ requires C, 54.7; H, 5.6; N, 3.5; I, 32.15%); τ [$(CD_3)_2SO$] 2.18—2.39 (m, 9 aryl H), ABX_2 system, τ_A 3.21, τ_B 4.22, τ_X 4.88 [J_{AB} 12, J_{BX} 6 Hz, $OC(H_X)_2CH_B{=}CH_APh$], and 6.30 (s, $\overset{+}{N}Me_3$). The minor isomer (210 mg) was identified as the (*E*)-cinnamyl salt by comparison with an authentic sample.

Preparation and Reactions of Deuteriated Ylides

[$\alpha\alpha$-$^2H_2$]*Benzyl Bromide*.—[$\alpha\alpha$-$^2H_2$]Benzyl alcohol[33] (1.5 g) in anhydrous ether (10 ml) and pyridine (0.6 ml) was treated with phosphorus tribromide (2.4 g). The mixture was stirred at room temperature for 2 h, and poured onto ice (10 g). The organic layer and ethereal extracts of the aqueous layer were dried and evaporated to give [$\alpha\alpha$-$^2H_2$]benzyl bromide (1.8 g, 76%), b.p. 38 °C at 0.5 mmHg. Mass spectrometric analysis indicated that this product contained 1.9 ± 0.03 atoms of deuterium per molecule.

2-*Di*([$^2H_3$]*methyl*)*aminophenol* (33).—Compound (33), prepared[32] using 2-hydroxyaniline hydrochloride and [$^2H_4$]-methanol, had m.p. 46—47 °C, *m/e* 143 (*M*); τ 2.62—2.80 (m, 5 aryl H) only.

2-*Hydroxy*-N-([$\alpha\alpha$-$^2H_2$]*benzyl*)-NN-*di*([$^2H_3$]*methyl*)-*anilinium Bromide* (34a).— Compound (34a) was prepared as for the non-deuteriated compound. The *product* had m.p. 170—171 °C (from ethanol–diethyl ether) (Found: C, 57.2; H, 5.9[*]; N, 4.3; Br, 25.2. $C_{15}H_{10}D_8BrNO$ requires C, 57.0; H, 5.7; N, 4.4; Br, 25.3%); τ (CF_3CO_2H) 2.70—3.40 (m, 9 aryl H) only.

N-([$\alpha\alpha$-$^2H_2$]*Benzyl*)-NN-*di*([$^2H_3$]*methyl*)*anilinium*-2-*olate* (35a).—The *ylide* (35a) had m.p. 95 °C (Found: *M*, 235. $C_{15}H_9D_8NO$ requires *M*, 235); τ 2.78—3.47 (m, 8 aryl H) and 3.99 (m, 5-H). A 1 : 1 mixture of the deuteriated ylide (35a) and the non-deuteriated ylide (22a) was heated under nitrogen at 110 °C for 2 h. The mass spectrum of the product showed ions at *m/e* 227 and 235 corresponding to [$^2H_0$] and [$^2H_8$] products.

[$\alpha\alpha$-$^2H_2$]*Cinnamyl Alcohol*.—Ethyl cinnamate (4.2 g) in diethyl ether (25 ml) was slowly added to a cold, stirred suspension of lithium aluminium deuteride (600 mg) in ether (75 ml). The mixture was stirred for 2 h, excess of lithium aluminium deuteride destroyed by the addition of water, and the ethereal solution dried and evaporated. The residual oil was distilled to give the deuteriated alcohol (2.4 g, 74%), b.p. 105—106 °C at 1 mmHg (lit.,[34] 156—162 °C at 70 mmHg); τ 2.66—2.84 (m, 5 aryl H), AB system, τ_A 3.44, τ_B 3.74 (J_{AB} 16 Hz, $PhCH_A{=}CH_BCD_2$), and 7.70br (s, OH). [$\alpha\alpha$-$^2H_2$]Cinnamyl bromide was prepared from the deuteriated alcohol by a method analogous to that used for [$\alpha\alpha$-$^2H_2$]benzyl bromide. The product (89% yield) had b.p. 75 °C at 0.3 mmHg. Mass spectrometric analysis indicated a deuterium content of 1.92 ± 0.03 atoms of deuterium per molecule; τ 2.64—2.84 (m, 5 aryl H), and AB system, τ_A 3.41, τ_B 3.70 (J_{AB} 16 Hz, $PhCH_A{=}CH_BCD_2$).

N-([$\alpha\alpha$-$^2H_2$]*Cinnamyl*)-2-*hydroxy*-NN-*di*([$^2H_3$]*methyl*)-*anilinium Bromide* (34b).—The *bromide* (34b) was obtained in 84% yield, m.p. 148—151 °C (Found: C, 59.4; H, 6.1; N, 3.95; Br, 23.3. $C_{17}H_{12}D_8BrNO$ requires C, 59.65; H, 5.8; N, 4.1; Br, 23.4%); τ (CF_3CO_2H) 2.99—3.43 (m, 9 aryl H), and AB system, τ_A 3.88, τ_B 4.53 (*J* 16 Hz, $PhCH_A{=}CH_BCD_2$).

N-([$\alpha\alpha$-$^2H_2$]*Cinnamyl*)-NN-*di*([$^2H_3$]*methyl*)*anilinium*-2-*olate* (35b).—The *ylide* (35b) was obtained in 81% yield, m.p. 69—70 °C (Found: *M*, 261. $C_{17}H_{11}D_8NO$ requires *M*, 261); τ 2.76—3.16 (m, 8 aryl H), 3.83 (m, 5-H), and AB system, τ_A 3.29, τ_B 4.09 (J_{AB} 16 Hz, $PhCH_A{=}CH_BCD_2$). A 1 : 1 mixture of this product and the non-deuteriated ylide (22b) was heated at 80 °C for 15 min. The mass spectrum of the product showed ions at *m/e* 253 and 261 corresponding to [$^2H_0$] and [$^2H_8$] products.

N-{(E)-[2,3-$^2H_2$]*Allyl*)}2-*hydroxy*-NN-*dimethylanilinium Bromide* (40a; X = Br).—The reaction of 2-dimethylaminophenol with prop-2-ynyl bromide in methyl cyanide gave 2-*hydroxy*-NN-*dimethyl*-N-*prop*-2-*ynylanilinium bromide* (21g) (89%), m.p. 150 °C (decomp.) (from ethanol–diethyl ether) (Found: C, 51.4; H, 5.6; N, 5.4; Br, 31.1. $C_{11}H_{14}BrNO$ requires C, 51.6; H, 5.5; N, 5.5; Br, 31.25%); $\nu_{max.}$ 3 200, 2 130 cm^{-1}; τ (CF_3CO_2H) 2.30—3.00 (m, 4 aryl H), 4.98 (d, *J* 3 Hz, $\overset{+}{N}CH_2C{\equiv}CH$), 6.13 (s, $\overset{+}{N}Me_2$), and 7.23 (t, *J* 3 Hz, $CH_2C{\equiv}CH$). The salt (21 g) (1.0 g) in [$^2H_4$]methanol (5 ml) was reduced using deuterium and a 5% palladium–barium sulphate catalyst. After the theoretical uptake of deuterium the solution was filtered and evaporated and the residual gum crystallised from ethanol–diethyl ether to give a 3 : 1 mixture (n.m.r.) of the deuteriated salt (40a; X = Br) and the starting salt (21 g); τ (CF_3CO_2H) 2.38—2.96 (m, 4 aryl H), 4.36br (s, CD=CDH), 5.23 (s, $\overset{+}{N}CH_2CD{=}$), and 6.27 (s, $\overset{+}{N}Me_2$) together with signals assignable to the salt (21g). This salt was converted into the corresponding ylide (41a) without further purification.

Thermal Rearrangement of N-{(E)-[2,3-$^2H_2$]*allyl*}-NN-*dimethylanilinium*-2-*olate* (41a). *Formation of* 4-([2,3-$^2H_2$]-*Allyl*)-2-*dimethylaminophenol* (42a *and* b).—The ylide (41a)

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[*] The figure given for H for this and other deuteriated compounds corresponds to the combined H and D composition calculated as for H.

(200 mg) in chloroform was heated under reflux for 2 h. The only product isolable by t.l.c. was obtained as a pale yellow oil, identified as 4-([2,3-$^{2}H_2$]allyl)-2-dimethylaminophenol (90 mg, 45%); τ 3.06—3.18 (m, 3 aryl H), 3.42br (s, OH), 4.98br (s, CD=CHD), 6.70 (s, ArC*H*$_2$CD=), and 7.38 (s, NMe$_2$). The mass spectrum indicated that this product contained an average of 1.64 ± 0.03 atoms of deuterium per molecule.

[3-^{2}H]*Prop-2-ynyl Bromide.*[35]—A mixture of prop-2-ynyl bromide (4.0 g), deuterium oxide (5.0 g), and anhydrous potassium carbonate (10 mg) was shaken at room temperature for 12 h. The organic layer was separated, dried, and distilled (N$_2$ atmosphere) to give [3-^{2}H]prop-2-ynyl bromide (3.7 g, 92%), b.p. 83—84 °C at 760 mmHg (lit.,[1] 83—84 °C at 760 mmHg), $\nu_{max.}$ 2 600 and 1 980 cm^{-1}. The n.m.r. spectrum (τ 6.19 and τ 7.55) indicated that this product contained an average of 0.93 ± 0.01 deuterium atoms (as C≡CD) per molecule.

2-*Hydroxy*-NN-*dimethyl*-N-([3-^{2}H]*prop-2-ynyl)anilinium Bromide* (21h).—A solution of 2-dimethylaminophenol (1.0 g) in deuteriochloroform (3 ml) was stirred with deuterium oxide (3 ml) for 1 h (N$_2$ atmosphere). The mixture was evaporated to dryness, the residue dissolved in methyl cyanide (5 ml) and [3-^{2}H]prop-2-ynyl bromide (1.0 g) added. The precipitate was collected and recrystallised from ethanol–diethyl ether to give the [3-^{2}H]*prop-2-ynyl salt* (21h) (1.4 g, 75%) as rhombic crystals, m.p. 149 °C (decomp.) (Found: C, 51.6; H, 5.6; N, 5.4; Br, 31.0. $C_{11}H_{13}DBrNO$ requires C, 51.4; H, 5.45; N, 5.45; Br, 31.1%); $\nu_{max.}$ 2 500 and 1 970 cm^{-1}; τ (CF$_3$CO$_2$H) 2.40—3.00 (m, 4 aryl H), 4.98 (s, $\overset{+}{N}CH_2C{\equiv}CD$), 6.14 (s, $\overset{+}{N}Me_2$), and 7.23 (t, *J* 3 Hz, residual C≡CH). The n.m.r. spectrum (τ 4.98 and 7.23) indicated an average deuterium content of 0.90 ± 0.01 atoms (as C≡CD) per molecule.

N{(Z)-[3-^{2}H]*Allyl*}-2-*hydroxy*-NN-*dimethylanilinium Bromide* (40c; X = Br).—The salt (21h) (2.0 g) in ethanol (10 ml) was hydrogenated at atmospheric pressure using a 5% palladium-barium sulphate catalyst (100 mg). The (Z)-[3-^{2}H]*allyl salt* (40c; X = Br) (840 mg, 42%) was obtained as prisms, m.p. 154—155 °C (Found: C, 50.75; H, 6.25; N, 5.4; Br, 30.7. $C_{11}H_{15}DBrNO$ requires C, 51.0; H, 6.2; N, 5.1; Br, 30.9%); τ (CF$_3$CO$_2$H) 2.53—2.98 (m, 4 aryl H), 4.38—4.43 (m, CH=CHD), 5.27 (m, $\overset{+}{N}CH_2$), and 6.30 (s, $\overset{+}{N}Me_2$). The n.m.r. spectrum (τ 4.38—4.43 and 5.27) indicated an average deuterium content of 0.82 ± 0.1 atoms (as C=CD) per molecule.

N-{(Z)-[3-^{2}H]*Allyl*}-NN-*dimethylanilinium-2-olate* (41c).—The *ylide* (41c), obtained by treating the [3-^{2}H]-quaternary salt (40c; X = Br) with aqueous sodium hydroxide, had m.p. 80—82 °C; τ ABCX system, τ_A 2.95, τ_B 3.08, τ_C 3.31, τ_X 3.89 (J_{AB} 1.5, J_{AC} 8, J_{AX} 7, J_{BX} 8, J_{CX} 1.5 Hz, 3-H$_C$ + 4-H$_A$ + 5-H$_X$ + 6-H$_B$), ABX$_2$ system, τ_A 4.46, τ_B 4.65, τ_X 5.03 [J_{AB} 10, J_{AX} 7 Hz, (*Z*)-$\overset{+}{N}C(H_X)_2CH_A{=}CH_BD$, the signal assigned to H$_A$ is broadened by residual H–D coupling], and τ 6.49 (s, $\overset{+}{N}Me_2$). The mass spectrum indicated an average deuterium content of 0.80 ± 0.03 atoms per molecule.

Thermal Rearrangement of N-{(Z)-[3-^{2}H]*allyl*}-NN-*dimethylanilinium-2-olate* (41c). *Formation of* 2-{(Z)-[3-^{2}H]-*allyloxy*}-NN-*dimethylaniline* (45c) *and* 4-{(Z-) and (E)-[3-^{2}H]*allyl*}-2-*dimethylaminophenol* (42c *and* d).—The ylide (41c) (300 mg) was heated under reflux in chloroform for 2 h and the reaction products separated by t.l.c. to give two pure components. (i) The (*Z*)-3-deuterioallyl ether (45c) was obtained as a pale yellow oil (54 mg, 18%). The mass spectrum indicated an average deuterium content of 0.80 ± 0.03 atoms per molecule. The *methiodide* (43c) was obtained as prisms, m.p. 175—178 °C (Found: C, 44.7; H, 5.8; N, 4.2; I, 39.9. $C_{12}H_{17}DINO$ requires C, 45.0; H, 5.6; N, 4.4; I, 39.7%); τ [(CD$_3$)$_2$CO–D$_2$O] ABCD system, τ_A 2.08, τ_B 2.37, τ_C 2.56, τ_D 2.77 (J_{AB} 1.5, J_{AD} 8, J_{BC} 8, J_{BD} 7, J_{CD} 1.5 Hz, 3-H$_C$ + 4-H$_B$ + 5-H$_D$ + 6-H$_A$), AMX$_2$ system, τ_A 3.73, τ_M 4.59, τ_X 5.04 [J_{AM} 10, J_{AX} 5.5, J_{MX} 1.5 Hz, OC(H$_X$)$_2$CH$_A$=CH$_M$D, the signal assigned to H$_A$ is additionally split into 1 : 1 : 1 triplets, *J* 2.5 Hz by (*E*)-HC=CD coupling], 6.12 (s, $\overset{+}{N}Me_3$), and 4.46br (d, *J ca.* 17 Hz, residual (*E*)-HC=C*H*H). The n.m.r. spectrum (τ 3.73, 4.46 and 4.59) indicated an average deuterium content of *ca.* 0.8 atoms (as HC=CHD) per molecule. (ii) The [3-^{2}H]allylphenol (42c and d) was obtained as an oil (132 mg, 44%). The mass spectrum indicated an average deuterium content of 0.80 ± 0.03 atoms per molecule. The *methiodide* (44c and d) had m.p. 185—186° (decomp.) (from ethanol–diethyl ether) (Found: C, 44.7; H, 5.7; N, 4.2; I, 39.55. $C_{12}H_{17}DINO$ requires C, 45.0; H, 5.6; N, 4.4; I, 39.7%); τ (CF$_3$CO$_2$H) 2.44—2.82 (m, 4 aryl H), AMX$_2$ + ANX$_2$ systems, τ_A 4.02, τ_M 4.83, τ_N 4.89, τ_X 6.58 [J_{AN} 18, J_{AM} 10, J_{AX} 7 Hz, (*Z*)-C(H$_X$)$_2$-CH$_A$=CH$_M$D + (*E*)-C(H$_X$)$_2$CH$_A$=CH$_N$D], and 6.21 (s, $\overset{+}{N}Me_3$).

N-([2,3,3-$^{2}H_3$]*Allyl*)-2-*hydroxy*-NN-*dimethylanilinium Bromide* (40e; X = Br).—The monodeuteriated propynyl salt (21h) (2.0 g) in [$^{2}H_4$]methanol (10 ml) was reduced using deuterium and a 5% palladium–barium sulphate catalyst (100 mg). The product crystallised from ethanol–diethyl ether to give the [2,3,3-$^{2}H_3$]-*salt* (40e; X = Br) (1.3 g, 64%), m.p. 155—156 °C (Found: C, 50.7; H, 6.3; N, 5.5; Br, 30.6. $C_{11}H_{13}D_3BrNO$ requires C, 50.6; H, 6.1; N, 5.4; Br, 30.65%); τ (CF$_3$CO$_2$H) 2.44—2.98 (m, 4 aryl H), 5.25 (s, $\overset{+}{N}CH_2CD{=}CD_2$), and 6.28 (s, $\overset{+}{N}Me_2$). The n.m.r. spectrum indicated an average deuterium content of 2.86 ± 0.1 atoms per molecule.

N-([2,3,3-$^{2}H_3$]*Allyl*)-NN-*dimethylanilinium-2-olate* (41e).—The reaction of the [2,3,3-$^{2}H_3$]-salt (40e; X = Br) with aqueous sodium hydroxide gave the [2,3,3-$^{2}H_3$]-ylide (41e) (82%), m.p. 80—82 °C τ ABCD system, τ_A 2.93, τ_B 3.09, τ_C 3.25, τ_D 3.86 (J_{AB} 1.5, J_{AC} 8, J_{AD} 7, J_{BD} 8, J_{CD} 1.5 Hz, 4-H$_A$ + 6-H$_B$ + 3-H$_C$ + 5-H$_D$), 5.06br (s, $\overset{+}{N}CH_2CD{=}CD_2$), and τ 6.49 (s, $\overset{+}{N}Me_2$). The mass spectrum indicated an average deuterium content of 2.93 ± 0.03 atoms per molecule.

Thermal Rearrangement of N-([2,3,3-$^{2}H_3$]*Allyl*)-NN-*dimethylanilinium-2-olate* (41e). *Formation of* 4-[$^{2}H_3$]*Allyl-2-dimethylaminophenol* (42e *and* f) *and* 2-[$^{2}H_3$]*Allyloxy*-NN-*dimethylaniline* (45e and f).—(*a*) The ylide (41e) (300 mg) was heated under reflux in chloroform for 2 h to give two isolated products. (i) 2-[$^{2}H_3$]*Allyloxy*-NN-*dimethylaniline* (45e and f) (57 mg, 19%) was shown by mass spectrometry to have an average deuterium content of 2.93 ± 0.03 atoms per molecule. The *methiodide* (43e and f) had m.p. 175—177 °C (decomp.) (Found: C, 44.8; H, 5.8; N, 4.1; I, 39.7. $C_{12}H_{15}D_3INO$ requires C, 44.7; H, 5.6; N, 4.35; I, 39.4%). The n.m.r. spectrum showed that this product consisted of 2-([2,3,3-$^{2}H_3$]allyloxy)-*NNN*-trimethylanilinium iodide (43e) (90.3%) and 2-([1,1,2-$^{2}H_3$]allyloxy)-*NNN*-trimethylanilinium iodide (43f) (9.7%). (ii) 4-[$^{2}H_3$]*Allyl-2-dimethylaminophenol* (42e and f) (137 mg, 46%) was shown by mass spectrometry to have an average deuterium content of 2.93 ± 0.03 atoms per molecule. The *methiodide* (44e and f) had m.p. 185 °C (decomp.) (Found: C, 44.5; H, 5.7; N, 4.2; I, 39.4. $C_{12}H_{15}D_3INO$ requires C, 44.7; H, 5.6; N, 4.35; I, 39.4%). The n.m.r. spectrum showed that this product consisted of 5-([2,3,3-$^2H_3$]allyl)-2-hydroxy-*NNN*-trimethylanilinium iodide (44e) (87%) and 5-([1,1,2-$^2H_3$]allyl)-2-hydroxy-*NNN*-trimethylanilinium iodide (44f) (13%).

(*b*) The ylide (41e) was heated in nitrobenzene at 110 °C in an n.m.r. tube and the resulting CIDNP studied. The crude product was purified by t.l.c. to give 4-[$^2H_3$]allyl-2-dimethylaminophenol (42e and f), shown by mass spectrometry to have an average deuterium content of 2.93 ± 0.03 atoms per molecule. The n.m.r. spectrum showed that this product was a mixture of 4-([2,3,3-$^2H_3$]allyl)-2-dimethylaminophenol (42e) (82%) and 4-([1,1,2-$^2H_3$]allyl)-2-dimethylaminophenol (42f) (18%).

N-([1,1-$^2H_2$]*Allyl*)-2-*hydroxy*-NN-*dimethylanilinium Toluene*-p-*sulphonate* (40g; X = *p*-$MeC_6H_4SO_3$).—[1,1-$^2H_2$]Allyl alcohol was prepared by the reduction [36] of acrylyl chloride with lithium aluminium deuteride in ether. The alcohol had b.p. 90—99 °C at 760 mmHg (lit.,[36] 95—98 °C at 760 mmHg); τ ABX system, τ_A 4.79, τ_B 4.92, τ_X 4.05 (J_{AB} 2, J_{AX} 18, J_{BX} 10 Hz, $CD_2CH_X{=}CH_AH_B$), and 6.82 (s, OH). The [1,1-$^2H_2$]-alcohol (1.1 g) in anhydrous ether (20 ml) reacted with toluene-*p*-sulphonyl chloride (3.8 g) and powdered sodium hydroxide (2.2 g) at 0 °C for 1 h. The reaction mixture was poured onto ice and the product extracted with ether. The ethereal extract was dried and evaporated to give [1,1-$^2H_2$]allyl toluene-*p*-sulphonate (4.1 g, 91%) as a viscous liquid which was used without further purification. A solution of the toluene-*p*-sulphonate (2.7 g) in methyl cyanide (5 ml) was added to a stirred solution of 2-dimethylaminophenol (1.5 g) in methyl cyanide (5 ml) and the mixture left overnight at room temperature. The solvent was evaporated off and the residue washed with ether to give the *salt* (40g; X = *p*-$MeC_6H_4SO_3$) as an ether-insoluble gum (3.7 g, 89%) which solidified after prolonged drying *in vacuo*; τ AA′BB′ system, τ_A 2.37, τ_B 3.01 ($J_{AB} = J_{A'B'}$ = 8 Hz, 4 aryl H), 2.65—3.37 (m, 4 aryl H), 4.61—4.89 (m, $CH{=}CH_2$), 6.53 (s, $\overset{+}{N}Me_2$), and 7.82 (s, Ar*Me*).

N-([1,1-$^2H_2$]*Allyl*)-NN-*dimethylanilinium*-2-*olate* (41g).—The toluene-*p*-sulphonate (40g; X = *p*-$MeC_6H_4SO_3$) (3.0 g) in water (10 ml) reacted with an excess of aqueous sodium hydroxide (3 ml; 50%) to give the [1,1-$^2H_2$]*allyl ylide* (41g) (1.05 g, 76%), m.p. 80—81 °C. The mass spectrum indicated an average deuterium content of 1.95 ± 0.03 atoms per molecule; τ ABCX system, τ_A 2.95, τ_B 3.10, τ_C 3.27, τ_X 3.90 (J_{AB} 1.5, J_{AC} 8, J_{AX} 7, J_{BX} 8, J_{CX} 1.5 Hz, 4-H_A + 6-H_B + 3-H_C + 5-H_X), 4.37—4.73 (m, $CD_2CH{=}CH_2$), and 6.48 (s, NMe_2).

Thermal Rearrangement of N-([1,1-$^2H_2$]*Allyl*)-NN-*dimethylanilinium*-2-*olate*] (41g). *Formation of* 4-[$^2H_2$]*Allyl*-2-*dimethylaminophenol* (42g *and* h) *and* 2-[$^2H_2$]*Allyloxy*-NN-*dimethylaniline* (45g *and* h).—(*a*) The [1,1-$^2H_2$]allyl ylide (41g) was heated under reflux in chloroform for 2 h to give two isolated products. (i) 2-[$^2H_2$]Allyloxy-*NN*-dimethylaniline (45g and h) (19%), isolated as a pale yellow oil, was shown by mass spectrometry to have an average deuterium content of 1.95 ± 0.03 atoms per molecule. The *methiodide* (43g and h) had m.p. 176—178 °C (decomp.) (Found: C, 44.7; H, 5.5; N, 4.1; I, 39.4. $C_{12}H_{16}D_2INO$ requires C, 44.9; H, 5.6; N, 4.4; I, 39.6%). The n.m.r. spectrum showed that this product consisted of 2-([1,1-$^2H_2$]allyloxy)-*NNN*-trimethylanilinium iodide (43g) (91.7%) and 2-([3,3-$^2H_2$]allyloxy)-*NNN*-trimethylanilinium iodide (43h) (8.3%). (ii) 4-[$^2H_2$]Allyl-2-dimethylaminophenol (42g and h) (47%) was shown by mass spectrometry to have an average deuterium content of 1.95 ± 0.03 atoms per molecule. The *methiodide* (44g and h) had m.p. 185 °C (decomp.) (Found: C, 44.6; H, 5.82; N, 4.4; I, 39.7. $C_{12}H_{16}D_2INO$ requires C, 44.9; H, 5.6; N, 4.4; I, 39.6%). The n.m.r. spectrum showed that this product consisted of 5-([1,1-$^2H_2$]allyl)-2-hydroxy-*NNN*-trimethylanilinium iodide (44g) (91.1%) and 5-([3,3-$^2H_2$]allyl)-2-hydroxy-*NNN*-trimethylanilinium iodide (44h) 8.9%).

(*b*) The ylide (41g) was heated in nitrobenzene at 110 °C in an n.m.r. tube and the resulting CIDNP studied. The crude product was purified by t.l.c. to give 4-[$^2H_2$]allyl-2-dimethylaminophenol (42g and h). Mass spectrometry indicated an average deuterium content of 1.95 ± 0.03 atoms per molecule. The n.m.r. spectrum showed that this product was a mixture of 4-([1,1-$^2H_2$]allyl)-2-dimethylaminophenol (42g) (81.5%) and 4-([3,3-$^2H_2$]allyl)-2-dimethylaminophenol (42h) (18.5%).

(Z)-[1,1,3-$^2H_3$]*Allyl Alcohol*.—This was prepared by an adaptation of the procedure used by Majerski and Schleyer [25] for the preparation of (Z)-[1,1,2,3-$^2H_4$]allyl alcohol. Ethyl propiolate (25 g), deuterium oxide (40 g), and anhydrous potassium carbonate (3 g) were shaken at room temperature for 24 h. The organic layer was separated, dried, and distilled to give ethyl [3-^2H]propiolate (23 g, 91%), b.p. 121 °C; $\nu_{max.}$ 1 970 and 1 720 cm^{-1}; τ A_2X_3 system, τ_A 5.78, τ_X 8.70 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$] only. The adduct of the above ester (22 g) and anthracene (39.7 g) was obtained as pale yellow prisms (38.8 g, 65%), m.p. 109—111 °C (Found: *M*, 277. $C_{19}H_{15}DO_2$ requires *M*, 277); τ 2.61—3.12 (m, 8 aryl H), 4.31 (s, ArC*H*Ar), 4.82 (s, ArC*H*Ar), A_2X_3 system, τ_A 5.85, τ_X 8.78 [J_{AX} 7 Hz, $OC(H_A)_2C(H_X)_3$]. The adduct (38 g) in ethyl acetate (750 ml) was hydrogenated using 10% palladium–charcoal as catalyst (1.0 g). When the theoretical quantity of hydrogen had been absorbed the reaction mixture was filtered and evaporated and the residual solid recrystallised from ethanol to give *ethyl* cis-[11-$^2H_2$]-9,10-*ethano*-9,10-*dihydroanthracene*-12-*carboxylate* (36 g), 94%) as prisms, m.p. 103—104 °C (Found: *M*, 279. $C_{19}H_{17}O_2D$ requires *M*, 279); τ 2.71—3.03 (m, 8 aryl H), 5.36 (d, *J* 3 Hz, $Ar_2C\mathit{H}CHCO_2Et$), 5.74 (d, *J* 3 Hz, $Ar_2C\mathit{H}CHD$), 6.03 (m, AB of ABX_3 system, OCH_AH_B), 7.20 (dd, *J* 3, 10 Hz, $CDHC\mathit{H}CO_2Et$), 8.11br (dd, *J* 3, 10 Hz, $CHCD\mathit{H}CH$), and 8.88 [t, *J* 7 Hz, X of ABX_3 system, $C(H_X)_3$]. The above ester (35 g) in ether (1 l) was reduced using lithium aluminium deuteride (4 g). The product (28.5 g, 95%) was obtained as needles, m.p. 108—110 °C (lit.,[1] 108—110 °C) (Found: *M*, 239. Calc. for $C_{17}H_{13}D_3O$: *M*, 239); τ 2.72—3.01 (m, 8 aryl H), ABXY system, τ_A 5.68, τ_B 5.84, τ_X 8.00, τ_Y 8.24 ($J_{AX} = J_{BY}$ = 2.5, J_{XY} 10.5 Hz, $Ar_2CH_ACH_XCH_YCH_BAr_2$), and 8.62 (s, OH). The above alcohol was heated at 320 °C to give, in quantitative yield, a distillate which was identified as (*Z*)-[1,1,3-$^2H_3$]allyl alcohol. Redistillation gave the pure alcohol, b.p. 97—100 °C (Found: *M*, 61. Calc. for $C_3H_3D_3O$: *M*, 61); AB system, τ_A 4.08, τ_B 4.92 (J_{AB} 10.5 Hz, (*Z*)-$CH_BD{=}CH_ACD_2$, H_A broadened by H–D coupling), and 6.11 (s, OH).

N-{(Z)-[1,1,3-$^2H_3$]*Allyl*}-2-*hydroxy*-NN-*dimethylanilinium Toluene*-p-*sulphonate* (40i; X = *p*-$MeC_6H_4SO_3$).—The [$^2H_3$]-allyl alcohol (2.2 g) reacted with toluene-*p*-sulphonyl chloride (6.8 g) and sodium hydroxide (4.2 g) in anhydrous ether (50 ml) to give (*Z*)-[1,1,3-$^2H_3$]allyl toluene-*p*-sulphonate which was used without further purification. The crude toluene-*p*-sulphonate reacted with 2-dimethylaminophenol (4.7 g) to give the (*Z*)-[1,1,3-$^2H_3$]allyl salt (40i; X = *p*-$MeC_6H_4SO_3$) (9.6 g, 97%) as a hygroscopic solid; τ 2.30—

3.40 (m, 8 aryl H), 4.85br (s, $CD_2{-}CH{=}CHD$), 6.60 (s, $\overset{+}{N}Me_2$), and 7.92 (s, ArMe).

Thermal Rearrangement of N-{(*Z*)-[1,1,3-$^2H_3$]*Allyl*}-NN-*dimethylanilinium-2-olate* (41i). *Formation of* 4-[$^2H_3$]*Allyl-2-dimethylaminophenol* (42i—k) *and* 2-[$^2H_3$]*Allyloxy*-NN-*dimethylaniline* (45i and k).—The [$^2H_3$]allyl salt (40i; X = *p*-$MeC_6H_4SO_3$) reacted with sodium hydroxide to give the [$^2H_3$]allyl ylide (41i) (75%); τ 2.92—3.21 (m, 3 aryl H), 3.88 (ddd, *J* 7, 8, and 1.5 Hz, 5-H), AB system, τ_A 4.27, τ_B 4.52 (J_{AB} 11 Hz, (*Z*)-$CD_2CH_A{=}CH_BD$, H_A broadened by H–D coupling), and 6.45 (s, $\overset{+}{N}Me_2$). The mass spectrum of the ylide indicated an average deuterium content of 2.85 atoms per molecule. The ylide was rearranged using two methods.

(*a*) The rearrangement was carried out at 60 °C in chloroform and two major products were isolated by t.l.c. (i) 2-[$^2H_3$]Allyloxy-*NN*-dimethylaniline (45i and k) (18%) was shown by mass spectrometry to have an average deuterium content of 2.85 atoms per molecule. The *methiodide* (43i and k) had m.p. 178 °C (decomp.) (Found: C, 44.75; H, 5.65; N, 4.6; I, 39.65. $C_{12}H_{15}D_3INO$ requires C, 44.7; H, 5.6; N, 4.35; I, 39.4%). The n.m.r. spectrum showed that this product consisted of 2-{(*Z*)-[1,1,3-$^2H_3$]allyloxy}-*NNN*-trimethylanilinium iodide (43i) (94%) and 2-([1,3,3-$^2H_3$]-allyloxy)-*NNN*-trimethylanilinium iodide (43k) (6%). (ii) 4-[$^2H_3$]Allyl-2-dimethylaminophenol (42i—k) (46%) was shown by mass spectrometry to have an average deuterium content of 2.85 atoms per molecule. The *methiodide* (44i—k) had m.p. 187 °C (decomp.) (Found: C, 44.6; H, 5.8; N, 4.5; I, 39.2. $C_{12}H_{15}D_3INO$ requires C, 44.7; H, 5.6; N, 4.35; I, 39.4%). The n.m.r. spectrum showed that this product consisted of 5-([1,1,3-$^2H_3$]allyl)-2-hydroxy-*NNN*-trimethylanilinium iodide (44i and j) (91%) and 5-([1,3,3-$^2H_3$]allyl)-2-hydroxy-*NNN*-trimethylanilinium iodide (44k) (9%).

(*b*) The ylide (41i) was heated in nitrobenzene at 115 °C in an n.m.r. tube and the resulting CIDNP studied. The crude product was purified by t.l.c. to give 4-[$^2H_3$]allyl-2-dimethylaminophenol. Mass spectrometry indicated an average deuterium content of 2.85 atoms per molecule. The n.m.r. spectrum of the methiodide, m.p. 184—186 °C, indicated that it was a mixture of 5-([1,1,3-$^2H_3$]allyl)-2-hydroxy-*NNN*-trimethylanilinium iodide (44i andj) (80.5%) and 5-([1,3,3-$^2H_3$]allyl)-2-hydroxy-*NNN*-trimethylanilinium iodide (44k) (19.5%).

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