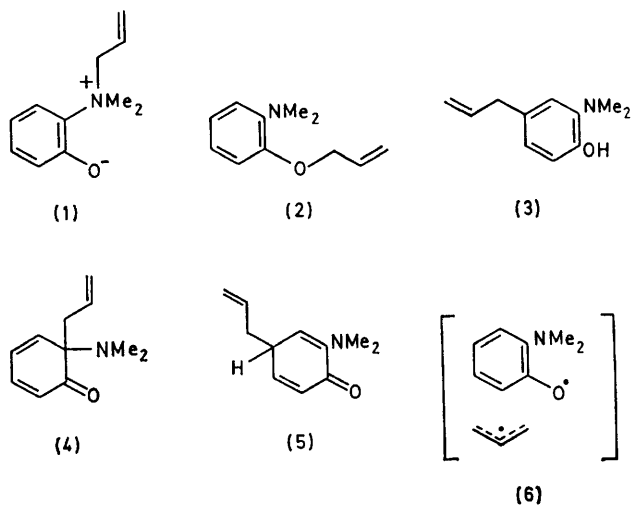


Base Catalysed Rearrangements Involving Ylide Intermediates. Part 13.¹ Further Rearrangements of 2-Oxidoanilinium Ylides

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The 2-oxidoanilinium ylides (7) rearrange on heating to give the ethers (10) together with the dienones (8) and the phenols (11) for cases where the aromatic ring has a 5-alkyl substituent or a mixture of the dienones (8) and (12) for cases where the aromatic ring is 3,5-disubstituted. A study of the deuteriated ylides (25) shows that these reactions involve competing concerted and radical-pair processes. The base-catalysed rearrangements of the 2-hydroxy-*N*-pentadienylanilinium salts (33) give the ethers (34) and the phenols (35): these products result from competing concerted [1,4] and [5,4] rearrangements of the ylides (36) corresponding to the salts (33).

In the preceding paper¹ it was shown that the *N*-allyl-2-oxidoanilinium ylide (1) rearranges on heating to give a mixture of the ether (2) and the phenol (3). These products are formed largely by concerted^{2,3} orbital-symmetry-allowed² sigmatropic rearrangements; in particular the ether (2) is formed by a [1,4] rearrangement, (1) \rightarrow (2), and the phenol (3) by a sequence of [3,2] and [3,3] rearrangements, (1) \rightarrow (4) \rightarrow (5), followed by aromatisation of the dienone (5). Detailed studies of deuterium-labelled compounds and of CIDNP during the rearrangement showed that the products (2) and (3) are formed simultaneously, but to a lesser extent, by a radical-pair mechanism involving homolysis of the ylide (1) to give the radical pair (6) and subsequent recombination to give the ether (2) and the dienone (5).



It was of interest to examine the rearrangement reactions of analogous ylides (7; $R^2 \neq H$) which would lead to dienones (8; $R^2 \neq H$) in which aromatisation [cf. (5) \rightarrow (3)] is prevented by the presence of an alkyl substituent R^2 in position 5. Accordingly the 5-methyl- and 5-*t*-butyl-2-hydroxyanilinium salts (9a–e) were synthesised by reaction of the appropriate 2-dimethylaminophenol with an alkyl halide. Reaction of the salts (9a–e) with cold methanolic sodium methoxide gave the ylides (7) in good yields as either gums (7a–c and 7f–h) or crystalline solids (7d and e).

The ylides (7a–e) rearranged at 40 °C to give in each case three reaction products that depended upon the nature of the substituents R^1 and R^2 in the ylide (7). These products were the ethers (10a–e), the dienones (8a–e), and the phenols (11a–e) which were identified on the basis of molecular formulae (high resolution mass spectrum or analysis of the methiodide derivatives) and spectroscopic properties. The identification of the rearrangement products from the ylide (7a) is typical. The single phenolic product (isolated by its solubility in Claisen alkali) had an n.m.r. spectrum that indicated a 1,2,3,5-tetrasubstituted aromatic ring having methyl, allyl, dimethylamino-, and hydroxy-substituents. Its derivation from the ylide (7a) indicated that this phenolic compound was the aminophenol derivative (11a). The first non-phenolic product was readily identified as the ether (10a) from its n.m.r. spectrum which indicated the presence of a 1,2,4-trisubstituted aromatic ring having methyl, dimethylamino-, and allyloxy-substituents: this identification was confirmed by its characterisation as the crystalline methiodide derivative. The second non-phenolic product had an infrared spectrum consistent with a 2,5-dienone structure (ν_{\max} 1 660, 1 630, and 1 600 cm^{-1}); the n.m.r. spectrum indicated the presence of three hydrogen substituents on the dienone ring at positions 3, 5, and 6 (ABX system, τ_A 3.29, τ_B 3.79, τ_X 4.27, J_{AB} 10 Hz, J_{AX} 3 Hz), a dimethyl-

TABLE 1

Rearrangement reaction of the ylides (7). Yields^a of the products (8), (10), (11), (12), and (13)

Ylide	R^1	R^2	R^3	Yields of products (%)		
				(8)/(13) ^b	(10)	(11)/(12) ^c
(7a)	H	Me	H	29	22	12
(7b)	Me	Me	H	11	10	55
(7c)	CMe ₃	Me	H	41	<i>d</i>	<i>d</i>
(7d)	H	CMe ₃	H	2	45	13
(7e)	Me	CMe ₃	H	<i>e</i>	36	33
(7f)	Me	H	H	39	27	
(7g)	H	Me	Me	62		15
(7h)	Me	Me	Me	34	10	12

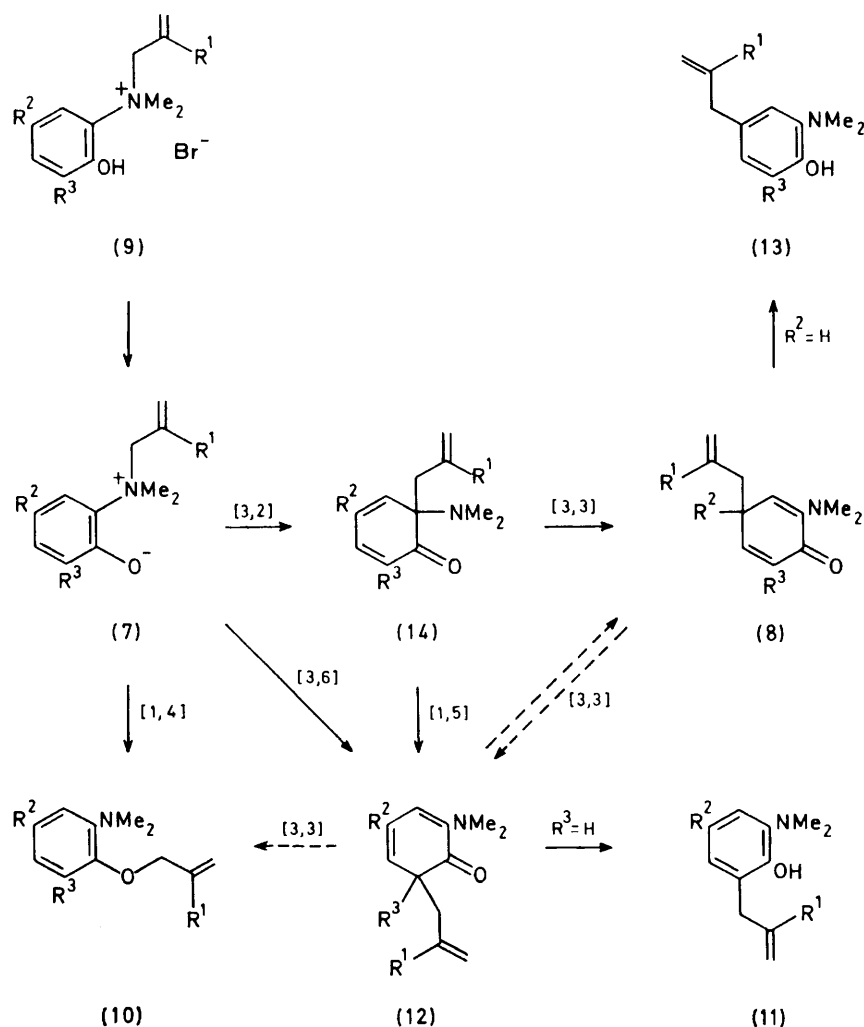
^a Yields are based upon isolated products. ^b In cases where $R^2 = H$, the dienone (8) aromatises to give the phenol (13).

^c In cases where $R^3 = H$, the dienone (12) aromatises to give the phenol (11). ^d The n.m.r. spectrum of the total rearrangement product indicated that these products had been formed but they were not isolated. ^e This product was detectable in low yield from the n.m.r. spectrum of the total rearrangement product.

amino-substituent, and methyl and allyl substituents at position-4. These spectral data, and the formation of this compound from the ylide (7a), showed clearly that this third product was the 2,5-dienone (8a).

The ylides (7b–e) gave analogous products in the yields indicated in Table 1. The 5-*t*-butyl ylides (7d and e) give, not unexpectedly, rather low yields of the dienones [(8d) 2% isolated yield and (8e) only detectable in low yield from the n.m.r. spectrum of the total rearrangement products]. The formation of the ethers (10) and the dienones (8) from the ylides (7) may

obviously be rationalised on the basis of the same sequence of allowed sigmatropic rearrangements that give rise to the ether (2) and the phenol (3) from the ylide (1), with presumably similar competition¹ from a minor radical-pair pathway. The formation of the phenols (11) is without analogy in our earlier work and their derivation can be considered in terms of a number of sequences of allowed rearrangements (see Scheme 1). The Claisen [3,3] rearrangement (10) \rightarrow (11) can be excluded because the ethers (10a) and (10d) fail to rearrange, even at 80 °C. The Cope [3,3] rearrangement

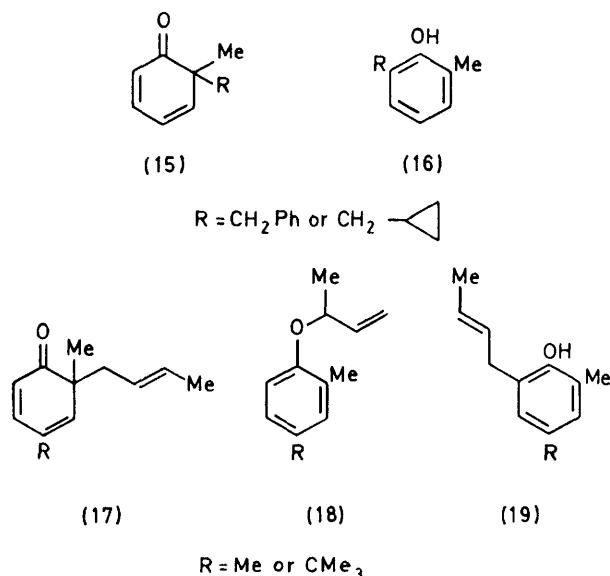


	R ¹	R ²	R ³
a;	H	Me	H
b;	Me	Me	H
c;	CMe ₃	Me	H
d;	H	CMe ₃	H
e;	Me	CMe ₃	H
f;	Me	H	H
g;	H	Me	Me
h;	Me	Me	Me

SCHEME 1 Sigmatropic rearrangements of ylides (7) at 40 °C (full arrows) and further reactions of dienones (8) and (12) at 80 °C (broken arrows)

of the allyl dienone (8) to give the dienone (12) has ample analogy, both in the reactions of allyl dienones⁴ and the rearrangement sequence involved in the *para*-Claisen rearrangement,⁵ but when the dienone (8b) was heated at 40 °C, under the conditions used for the rearrangement (7b) \rightarrow (8b) + (10b) + (11b), it remained unchanged over a period of 48 h. It therefore seems improbable that the aminophenols (11) are formed solely by the route (8) \rightarrow (12) \rightarrow (11) and alternative modes of formation by the [1,5] rearrangement of the dienones (14) or by the [3,6] rearrangement of the ylides (7) remain possibilities.

[1,5] Rearrangements involving the migration of sp^2 - and sp^3 -hybridised carbon are well known,⁶ particularly for 5-membered cyclic diene systems.⁷ Furthermore a number of relevant examples have been reported for 6-membered rings. Thus the benzyl- and cyclopropylcyclohexa-2,4-dienones (15) undergo [1,5] rearrangement⁸ to give the phenols (16) but the corresponding allyldienones (17) undergo a reverse Claisen [3,3] rearrangement to give the ethers (18), and the product (19) of a [1,5] rearrangement is only obtained in extremely low yield. The [1,5] rearrangement has also been reported for cyclohexadiene derivatives⁹ although some apparent [1,5] rearrangements of this type may involve¹⁰ electrocyclic ring opening and ring closure rather than a direct [1,5] rearrangement. The [1,5] migration of the group $-COX$ in 6-membered cyclic dienyl systems has, however, been rather more commonly observed.¹¹



The [3,6] rearrangement (7) \rightarrow (12) is, as far as we are aware, without analogy and we were unable to detect the [3,6] rearrangement as a competing reaction in our work on [5,4] sigmatropic rearrangements.¹² Furthermore this type of reaction was not detected for the ylide (1) in our earlier work and the ylide (7f) behaves in a similar manner; thus when the ylide (7f) was heated only the ether (10f) (27%) and the phenol (13f) (39%) could be identified as rearrangement products. The

reaction sequence leading to the phenols (11) cannot therefore be totally defined on the basis of these results although the [1,5] rearrangement (14) \rightarrow (12) may be regarded as their most likely origin.

The intermediate dienones (14) could not be detected amongst the rearrangement products of the ylides (7a–e) and further experiments were therefore carried out, using the 3,5-disubstituted ylides (7g and h), to determine whether the dienone (14) could be detected in these cases in equilibrium with the dienones (8) and (12), since the aromatisation pathways (8) \rightarrow (13) and (12) \rightarrow (11) would both be blocked by the substituents. The quaternary salts (9g) and (9h) each reacted with methanolic sodium methoxide to give the corresponding ylides (7g) and (7h) as oils. Both ylides rearranged on heating at 40 °C in benzene to give the corresponding ethers (10g or h) in low yield together with a mixture of two dienones that could be separated by chromatography. In the case of the ylide (7g) the major dienone (62% yield) was identified as the cyclohexa-2,5-dienone (8g) by its n.m.r. spectrum [ABX₃ system τ_A 3.48, τ_B 4.22, τ_X 8.12, J_{AB} 3 Hz, J_{AX} 1.5 Hz assignable to the $CH_B-C-CH_A=C-C(H_X)_3$ system of the 6-methylcyclohexa-2,5-dienone]; the minor dienone (15% yield) was similarly identified as the cyclohexa-2,4-dienone (12g) (AB system, τ_A 4.25, τ_B 4.45, J_{AB} 2 Hz, assignable to the $CH_A=CMe-CH_B$ system of the 4-methylcyclohexa-2,4-dienone). The distinction between the structural possibilities (12g) and (14g) for this second dienone was made on the basis of further infrared and n.m.r. data;¹³ thus the minor dienone had infrared absorption (ν_{max} , 1645 cm⁻¹) consistent with an enamine structure and the chemical shift of the NMe₂ group in the n.m.r. spectrum (τ 7.35) was consistent with the location of this group in the enamine system of (12g) ($C=C-NMe_2$) rather than in the unconjugated position characteristic of the alternative structure (14g).

The third dienone (14g) could not be detected in the rearrangement products of the ylide (7g). The ylide (7h) rearranged in a similar fashion at 40 °C to give the cyclohexa-2,5-dienone (8h) as the major product (34% yield) and the cyclohexa-2,4-dienone (12h) as the minor product (12% yield). The dienone (8g) did not rearrange on heating in benzene at 40 °C but at 80 °C it gave a mixture of the three reaction products (8g), (10g), and (12g). The interconversion of the dienones (8) and (12) presumably involves the [3,3] rearrangement indicated by broken arrows in Scheme 1. The formation of the ether (10) could involve the reversal of any of the processes indicated by full arrows in Scheme 1 or even the direct [3,3] rearrangement (12) \rightarrow (10) [*cf.* refs. 4 and 8 and the rearrangement (17) \rightarrow (18)]. As in our earlier work,¹ thermal rearrangement of each of the *N*-cinnamyl-2-oxyanilinium ylides (20) gave the corresponding cinnamyl ether (21) as the only identified reaction product in good yield. In these cases, however, the ylide (20) was not isolated and the rearrangement occurred when the quaternary salt (22) was treated with methanolic sodium methoxide at room temperature.

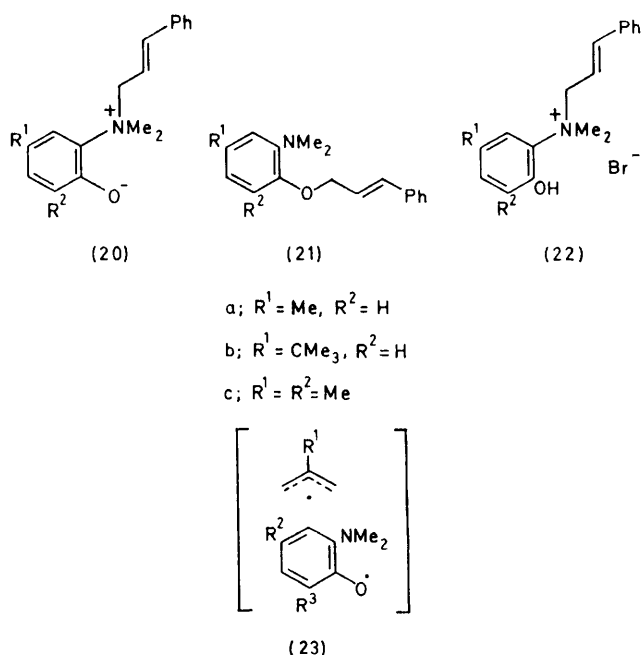
TABLE 2

Deuterium distribution in the ylides (25a and b)^a and in the rearrangement products (26a and b), (27a and b), and (28a and b).

Starting ylide	Reaction ^b		Deuterium distribution							% Radical-pair mechanism ^c		
			Ether		Phenol		Dienone		Ether	Phenol	Dienone	
	C-1'	C-3'	°C	C-1'	C-3'	C-1'	C-3'					
(25a)	1.82	0	40	1.71	0.11	0.31	1.51	1.64	0.18	12 (3)	34 (1)	20 (4)
			80	1.69	0.13	0.36	1.46	1.55	0.27	14 (3)	41 (3)	30 (3)
(25b)	1.86	0	40	1.71 ^d	0.15 ^d	0.46	1.40	1.60	0.26	16 (9)	49 (3)	28 (1)
			80	1.70	0.16	0.51	1.35	1.67	0.19	17 (4)	55 (4)	20 (1)

^a Total deuterium content based upon mass spectra of (25a) and (25b). Deuterium distribution based upon the n.m.r. spectra of the ylides (25a) and (25b), the ethers (26a) and (26b), the dienones (27a) and (27b), and the phenols (28a) and (28b). The numbers refer to the average number of deuterium atoms (± 0.03) at positions 1' and 3' of the allyl side-chain. ^b In benzene. ^c Based upon the assumption that 2x% of deuterium scrambling due to the radical-pair mechanism leads to x% of the [1,1-²H₂]allyl product and x% of the [3,3-²H₂]allyl product. The numbers in parentheses refer to the relative yields of products for each rearrangement. Since these estimates are based upon the integration of n.m.r. spectra, errors may be as great as $\pm 5\%$. ^d These figures are calculated so that the total deuterium content corresponds to that found in the starting ylide.

The sigmatropic rearrangements^{2,3,14} summarised in Scheme 1 all involve transition states derived from appropriate pericyclic bonding interactions between the two components of the radical pair (23). Our



previous experience of the rearrangements of 2-oxyanilinium ylides¹ suggested that the radical pair (23) would provide a competing pathway for at least some of the rearrangements summarised in Scheme 1 and this possibility was investigated using appropriately deuterated ylides. The salts (24a and b) were prepared by the reaction of [1,1-²H₂]allyl toluene-*p*-sulphonate with the appropriate dimethylaminophenol; reaction of each of the salts (24) with sodium hydroxide gave the corresponding deuterated ylide (25). The ylides (25) were each heated at 40 and 80 °C and the products were separated to give the deuterated allyl ether (26), allyl dienone (27), and allylphenol (28). The total deuterium content of the ylides (25a and b) was estimated by mass spectrometry and the deuterium content of each of the

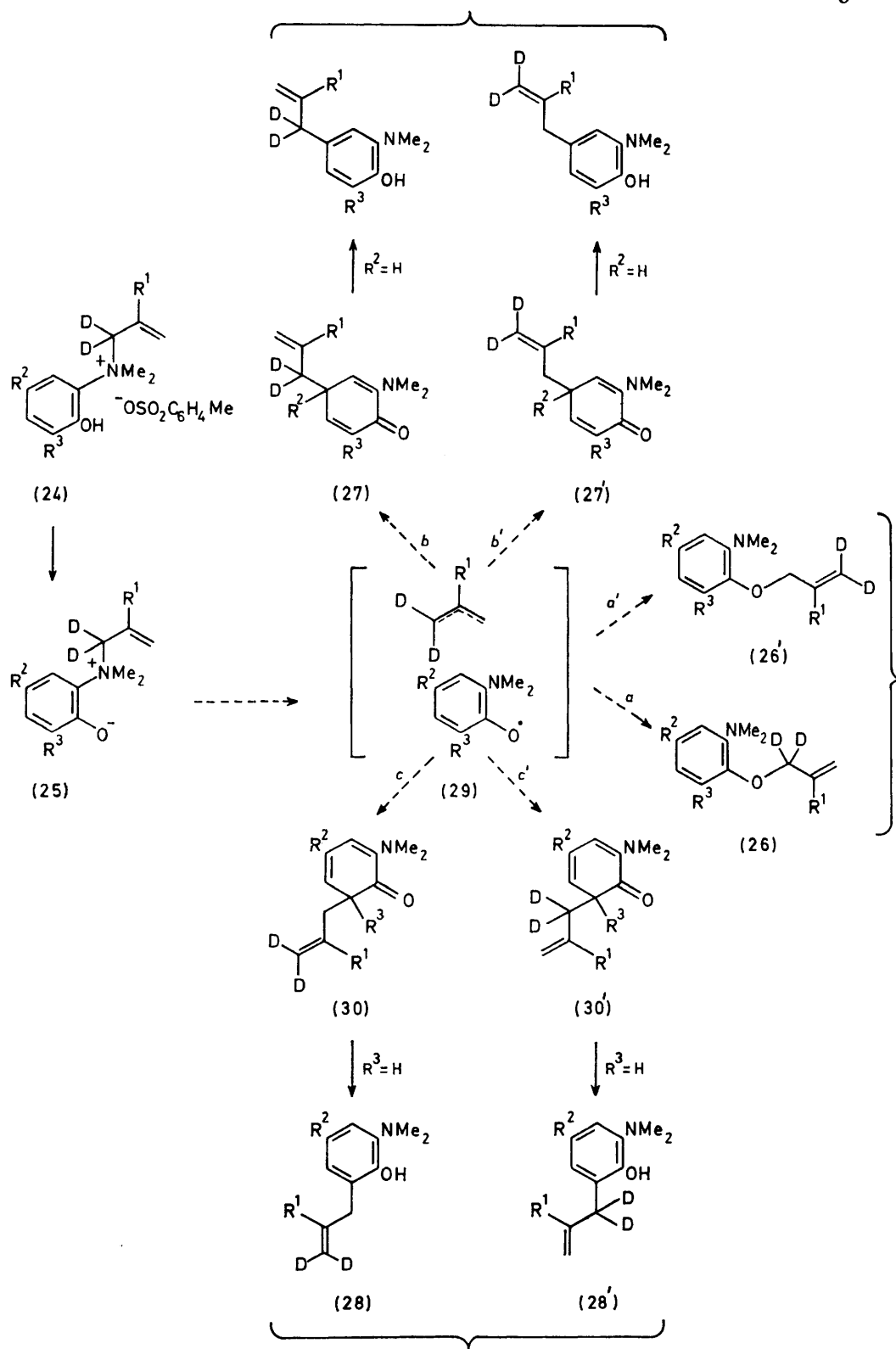
* The fourth possible coupling mode to give a dienone analogous to (14) is excluded on the basis of evidence presented in our previous paper¹ for the ylide (25; R¹ = R² = R³ = H).

rearrangement products was found to be within experimental error of this value, with the exception of the ether (26b) for which the estimated deuterium content was anomalously low. The distribution of deuterium between positions 1' and 3' of the allyl side-chains of the compounds (25), (26), (27), and (28) was estimated by integration of the appropriate regions of their ¹H n.m.r. spectra. The results of this investigation are summarised in Table 2.

The 1',3'-allylic scrambling of deuterium in the products (26), (27), and (28) may be equated with product formation that involves coupling of the radical pair (29) in the three * possible modes (a, b, and c) indicated in Scheme 2 and at position 1' or 3' of the allyl radical. These radical coupling processes, which lead to 1:1 mixtures of the pairs of products (26) and (26'), (27) and (27'), and (28) and (28'), are followed by aromatisation of the dienones (27) and (30) in cases where the substituents R² and R³ are hydrogen, but for the examples examined (25a and b) the ring methyl substituent prevents the aromatisation of the dienones (27). The radical-coupling processes summarised in Scheme 2 compete with the concerted processes outlined in Scheme 1 and Table 2 summarises the extent to which the rearrangement reactions follow the pathways shown in these two Schemes. The significant contribution to these rearrangement reactions from radical-pair processes is consistent with the conclusions drawn from our earlier work¹ and is a feature that causes complexity in many other ylide rearrangements.¹⁵

There are relatively few reports^{4,16} of [*m,n*]sigmatropic rearrangements in which more than six centres are involved in the pericyclic transition state although a number of high order [1,*n*] rearrangements have been reported.⁶ In a previous paper¹² we reported the observation of [5,4] rearrangements of ylides derived from allyl(pentadienyl)ammonium cations, (31) → (32), and the analogous [5,4] sigmatropic rearrangement of an *N*-pentadienyl-2-oxidoanilinium ylide appeared to be a further possible example of this reaction.¹⁷ The required quaternary salts (33) were readily prepared by the reaction of 2-dimethylaminophenol with the appropriate pentadienyl bromide.[†] The reaction of the salt (33a)

† The configuration of the double bonds in each of the pentadienyl bromides had been established in our earlier work.¹⁷

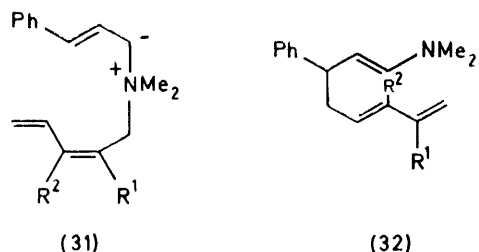


a; $R^1 = R^3 = H$, $R^2 = Me$

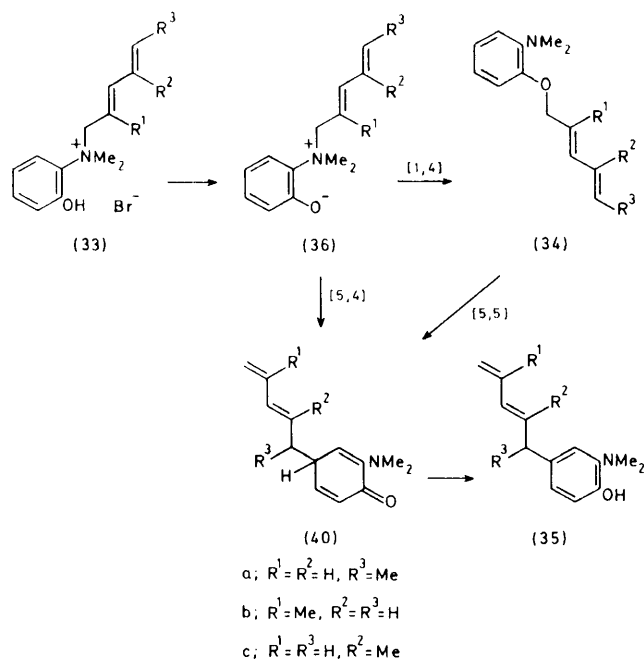
b; $R^1 = R^3 = H$, $R^2 = CMe_3$

SCHEME 2 Rearrangements involving the radical-pair mechanism. The pairs of products (26) and (26') etc. are obtained in equal amounts by this mechanism but only the product (26) etc. is obtained by the concerted processes outlined in Scheme 1

with aqueous sodium hydroxide at 0 °C gave two products identified as the ether (34a) and the phenol (35a). The nature of the pentadienyl side-chain in each of these products was clearly established by its n.m.r. spectrum



and the 1,2,4-substitution pattern of the aromatic ring in the phenol (35a) was proved by the n.m.r. spectrum of the aryl hydrogens (ABC system, J_{AB} 2 Hz, J_{BC} 8 Hz). Similar results were obtained using the 2- and 4-methyl-pentadienyl salts (33b) and (33c); thus (33b) gave a



SCHEME 3 Rearrangements of *N*-pentadienyl-2-oxidoanilinium ylides (36)

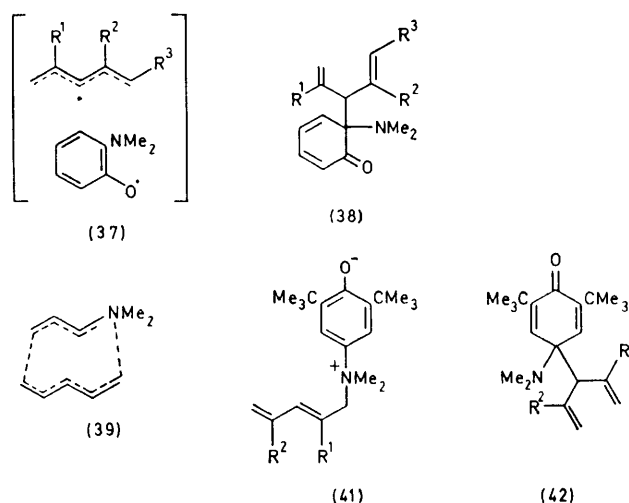
mixture of (34b) and (35b), with no trace of (34c) and (35c), and (33c) gave only (34c) and (35c). The reaction products (34) and (35) were fully characterised by their spectroscopic properties and by the properties of their methiodide derivatives.

These results establish that the ethers (34) are formed by a clean [1,4] sigmatropic rearrangement of the ylides (36) with no detectable competition from either a [5,4] rearrangement or radical-coupling processes involving the radical pair (37) (*cf.* Scheme 2 and ref. 1). Similarly the phenols (35) are formed by a clean [5,4] sigmatropic rearrangement of the ylides (36) with no trace of either a competing [1,4] rearrangement or a sequence of [3,2] and [3,3] rearrangements (*cf.* Scheme 1) involving the intermediate (38) which would necessarily give identical

mixtures of the phenols (35b) and (35c) from both the salts (33b and c). The radical pair (37) may also be eliminated as a possible precursor of the phenol (35) since it would also give rise to identical products from both (33b and c), as found in our work on hydrazinium ylide systems.¹⁸

Thus the rearrangements of *N*-pentadienyl-2-oxidoanilinium ylides (36) differ from those¹ of *N*-allyl-2-oxidoanilinium ylides (7) in that the reaction proceeds at a lower temperature (<0 °C), there is no evidence for products resulting from the radical pair (37), and the two competing modes of rearrangement are the [1,4] and the [5,4] rearrangement. The four possible allowed transition states for a [5,4] rearrangement of an ammonium ylide were discussed in our earlier paper;¹² the stereochemical relationships between reactants (33) and products (35) leave no doubt that these reactions involve a transition state of type B (39),* and no products were detected from [5,4] rearrangements involving other stereochemical arrangements of the migrating pentadienyl group. Thus, for example, the large spin-spin coupling between 2'-H and 3'-H observed in the n.m.r. spectra of the products (35a) and (35b) (J 16 Hz and 15 Hz respectively) establishes the (2*E*)-configuration for the pentadienyl side-chain in both cases and it is assumed, by analogy, that (35c) also has the (2*E*)-configuration.

It is of interest that the high-order [5,4] rearrangement (36) \rightarrow (40) competes successfully with the lower-order [3,2] rearrangement (36) \rightarrow (38). Similar discrimination in favour of higher-order rearrangements is shown by the ethers (34a) and (34b) which rearrange on heating, in benzene and xylene respectively, to give only the phenols (35a) and (35b), presumably by the [5,5] rearrangement¹⁶ (34) \rightarrow (40) followed by aromatisation, the products that would result from the



lower order Claisen [3,3] rearrangement were not detectable in either case. This tendency towards higher order rearrangements is not, however, shown in all cases

* The formula (39) shows the stereochemical relationships in the 5-centre and 4-centre components of the pericyclic suprafacial-suprafacial transition state of the [5,4] rearrangement.

where such competition is possible and even in the closely related case¹⁷ of the *N*-pentadienyl-4-oxidoanilinium ylides (41) the [3,2] rearrangement (41) \rightarrow (42) is the preferred process.

EXPERIMENTAL

For general directions see Part 1.^{3c}

Preparation of *N*-Allyl-*NN*-dimethylanilinium Salts (9).—2-Dimethylaminophenols were prepared¹⁹ by heating a methanolic solution of the 2-hydroxyaniline hydrochloride in an autoclave at 180 °C for 6 h. Equimolar amounts of the 2-dimethylaminophenol and the alkyl halide dissolved in acetonitrile were stirred at room temperature for 14 h. The solvent was evaporated and the residual crude anilinium salt recrystallised from ethanol-ether. The following salts were prepared using this method. *N*-Allyl-2-hydroxy-5,5,NN-trimethylanilinium bromide (9a) was obtained as a crystalline solid (90%), m.p. 150–152 °C (Found: C, 52.8; H, 6.7; Br, 29.3; N, 4.9. $C_{12}H_{18}BrNO$ requires C, 52.9; H, 6.6; Br, 29.4; N, 5.1%); ν_{max} , 3 100 cm^{-1} ; $\tau(CF_3CO_2H)$ 2.66–2.92 (m, 3 aryl H), 4.38 (m, $CH=CH_2$), 5.30 (m, $\dot{N}CH_2$), 6.32 (s, $\dot{N}Me_2$), and 7.62 (s, CH_3). 2-Hydroxy-5,5,NN-trimethyl-*N*-(2-methylallyl)anilinium bromide (9b) was obtained as a crystalline solid (90%), m.p. 152–153 °C (Found: C, 54.3; H, 6.4; Br, 27.9; N, 4.7. $C_{13}H_{20}BrNO$ requires C, 54.5; H, 7.0; Br, 28.0; N, 4.9%); ν_{max} , 3 200 cm^{-1} ; $\tau(CF_3CO_2H)$ 2.66–2.98 (m, 3 aryl H), 4.56 (s, $C=CH$), 4.93 (s, $C=CH$), 5.29 (s, $\dot{N}CH_2$), 6.30 (s, $\dot{N}Me_2$), 7.62 (s, $ArCH_3$), and 8.52 (s, $C=CCH_3$). 2-Hydroxy-5,5,NN-trimethyl-*N*-(2-*t*-butylallyl)anilinium bromide (9c) was obtained as a crystalline solid (83%), m.p. 154–155 °C (Found: C, 58.4; H, 7.8; Br, 24.1; N, 4.3. $C_{16}H_{26}BrNO$ requires C, 58.5; H, 7.9; Br, 24.4; N, 4.3%); ν_{max} , 3 200 cm^{-1} ; τ , ABX system, τ_A 2.20, τ_B 2.88, τ_X 2.91 (J_{AB} 8, J_{BX} 2 Hz, 3-H, 4-H, and 6-H), 4.89 (s, $C=CH$), 4.95 (s, $C=CH$), 5.27 (s, $\dot{N}CH_2$), 6.14 (s, $\dot{N}Me_2$), 7.74 (s, $ArCH_3$), and 8.95 (s, CMe_3). *N*-Allyl-2-hydroxy-*NN*-dimethyl-5-*t*-butylanilinium bromide (9d) was obtained as a crystalline solid (95%), m.p. 160–163 °C (Found: C, 57.5; H, 7.5; Br, 25.4; N, 4.5. $C_{15}H_{24}BrNO$ requires C, 57.3; H, 7.6; Br, 25.45; N, 4.45%); ν_{max} , 3 200 cm^{-1} ; $\tau(CF_3CO_2H)$, ABX system, τ_A 2.79, τ_B 2.46, τ_X 2.61 (J_{AB} 8, J_{BX} 2 Hz, 3-H, 4-H, and 6-H), 4.40 (m, $CH=CH_2$), 5.28 (m, $\dot{N}CH_2$), 6.30 (s, $\dot{N}Me_2$), and 8.64 (s, CMe_3). 2-Hydroxy-*NN*-dimethyl-*N*-(2-methylallyl)-5-*t*-butylanilinium bromide (9e) was obtained as a crystalline solid (85%), m.p. 131–132 °C (Found: C, 58.5; H, 7.9; Br, 24.4; N, 4.2. $C_{16}H_{26}BrNO$ requires C, 58.4; H, 8.1; Br, 24.45; N, 4.5%); ν_{max} , 2 980 cm^{-1} ; $\tau(CF_3CO_2H)$, ABX system, τ_A 2.82, τ_B 2.44, τ_X 2.57 (J_{AB} 8, J_{BX} 2 Hz, 3-H, 4-H, and 6-H), 4.56 (s, $C=CH$), 4.73 (s, $C=CH$), 5.29 (s, $\dot{N}CH_2$), 6.28 (s, $\dot{N}Me_2$), 8.56 (s, $C=CCH_3$), and 8.66 (s, CMe_3). 2-Hydroxy-*NN*-dimethyl-*N*-(2-methylallyl)anilinium bromide (9f) was obtained (90%) as crystals, m.p. 137 °C (Found: C, 52.6; H, 6.7; Br, 29.7; N, 5.1. $C_{12}H_{18}BrNO$ requires C, 53.0; H, 6.6; Br, 29.7; N, 5.1%); ν_{max} , 3 250 cm^{-1} ; $\tau(CF_3CO_2H)$, 2.44–2.98 (m, 4 aryl H), 4.57 (s, $C=CH$), 4.72 (s, $C=CH$), 5.26 (s, $\dot{N}CH_2$), 6.26 (s, $\dot{N}Me_2$), and 8.52 (s, $C=CCH_3$).

N-Allyl-2-hydroxy-3,5,NN-tetramethylanilinium bromide (9g) was obtained as a crystalline solid (82%), m.p. 105–

107 °C (Found: C, 54.45; H, 7.0; Br, 27.8; N, 4.8. $C_{13}H_{20}BrNO$ requires C, 54.5; H, 7.0; Br, 28.0; N, 4.9%); ν_{max} , 3 400 cm^{-1} ; $\tau(CF_3CO_2H)$ 2.75 (s, 4-H or 6-H), 2.88 (s, 6-H or 4-H), 4.39 (m, $CH=CH_2$), 5.27 (m, $\dot{N}CH_2$), 6.33 (s, $\dot{N}Me_2$), 7.62 (s, $ArCH_3$), and 7.66 (s, $ArCH_3$). 2-Hydroxy-3,5,NN-tetramethyl-*N*-(2-methylallyl)anilinium bromide (9h) was obtained as a crystalline solid (70%), m.p. 128–132 °C (Found: C, 55.1; H, 7.3; Br, 26.55; N, 4.65. $C_{14}H_{22}BrNO$ requires C, 56.0; H, 7.3; Br, 26.7; N, 4.7%); ν_{max} , 3 100 cm^{-1} ; $\tau(CF_3CO_2H)$ 2.76 (s, 4-H or 6-H), 2.88 (s, 6-H or 4-H), 4.59 (s, $C=CH$), 4.75 (s, $C=CH$), 5.29 (s, $\dot{N}CH_2$), 6.30 (s, $\dot{N}Me_2$), 7.62 (s, $ArCH_3$), 7.66 (s, $ArCH_3$), and 8.56 (s, $C=CCH_3$). *N*-Cinnamyl-2-hydroxy-5,5,NN-trimethylanilinium bromide (22a) was obtained as a crystalline solid (86%), m.p. 151–152 °C (Found: C, 61.4; H, 6.2; Br, 24.0; N, 4.3. $C_{18}H_{22}BrNO$ requires C, 61.1; H, 6.0; Br, 23.95; N, 4.2%); ν_{max} , 3 400 cm^{-1} ; $\tau(CF_3CO_2H)$ 2.72–2.92 (m, 8 aryl H), ABX₂ system, τ_A 3.15, τ_B 4.07, τ_X 5.17 [J_{AB} 16, J_{BX} 8 Hz, $CH_A=CH_B-C(H_X)_2$], 6.33 (s, $\dot{N}Me_2$), and 7.71 (s, $ArCH_3$). *N*-Cinnamyl-2-hydroxy-*NN*-dimethyl-5-*t*-butylanilinium bromide (22b) was obtained as a crystalline solid (92%), m.p. 153–154 °C (Found: C, 64.4; H, 7.4; Br, 20.5; N, 3.45. $C_{21}H_{28}BrNO$ requires C, 64.6; H, 7.2; Br, 20.5; N, 3.6%); ν_{max} , 3 200 cm^{-1} ; $\tau(CF_3CO_2H)$, ABX system, τ_A 2.77, τ_B 2.44, τ_X 2.60 (J_{AB} 8, J_{AX} 2 Hz, 3-H, 4-H, and 6-H), 2.73 (m, 5 aryl H), ABX₂ system, τ_A 3.18, τ_B 4.08, τ_X 5.17 [J_{AB} 16, J_{BX} 8 Hz, $CH_A=CH_B-C(H_X)_2$], 6.27 (s, $\dot{N}Me_2$), and 8.70 (s, CMe_3). *N*-Cinnamyl-2-hydroxy-3,5,NN-tetramethylanilinium bromide (22c) was obtained as a crystalline solid (79%), m.p. 139–140 °C (Found: C, 62.9; H, 6.55; Br, 22.25; N, 3.8. $C_{19}H_{24}BrNO$ requires C, 62.9; H, 6.6; Br, 22.1; N, 3.9%); $\tau(CD_3OD)$ 2.72 (m, 7 aryl H), ABX₂ system, τ_A 3.15, τ_B 4.02, τ_X 5.08 [J_{AB} 16, J_{BX} 8 Hz, $CH_A=CH_B-C(H_X)_2$], 6.30 (s, $\dot{N}Me_2$), 7.68 (s, $ArCH_3$), and 7.74 (s, $ArCH_3$).

***N*-Alkyl-*NN*-dimethylanilinium-2-olates (7).**—The following general procedure was used unless otherwise stated. Sodium hydride (5 mol equiv.) was added to a solution of the anilinium bromide (1 g) in methanol (10 ml) at 0 °C. The mixture was left at 0 °C for 14–16 h, the solvent was evaporated off under reduced pressure at room temperature, and the residue was extracted into dichloromethane. The extract was evaporated to give the ylide, usually as a gum, identified by its spectroscopic properties. *N*-Allyl-5,5,NN-trimethylanilinium-2-olate (7a) was obtained as a pale yellow gum (64%) (Found: M^+ , 191.1307. $C_{12}H_{17}NO$ requires M , 191.1310); τ 3.07–3.36 (m, 3 aryl H), 4.44–4.71 (m, $CH=CH_2$), 5.10 (d, $\dot{N}CH_2$), 6.49 (s, $\dot{N}Me_2$), and 7.83 (s, $ArCH_3$). 5,5,NN-Trimethyl-*N*-(2-methylallyl)anilinium-2-olate (7b) was obtained as a pale yellow gum (83%) (Found: M^+ , 205.1464. $C_{13}H_{19}NO$ requires M , 205.1469); τ 3.01–3.40 (m, 3 aryl H), 4.78 (s, $C=CH$), 4.91 (s, $C=CH$), 5.04 (s, $\dot{N}CH_2$), 6.45 (s, $\dot{N}Me_2$), 7.87 (s, $ArCH_3$), and 8.50 (s, $C=CCH_3$). *N*-(2-*t*-Butylallyl)-5,5,NN-trimethylanilinium-2-olate (7c) was obtained as a pale yellow semi-solid (85%) (Found: M^+ , 247.1934. $C_{16}H_{23}NO$ requires M , 247.1936); τ 3.30–3.34 (m, 3 aryl H), 4.82 (s, $C=CH$), 4.88 (s, $C=CH$), 5.32 (s, $\dot{N}CH_2$), 6.44 (s, $\dot{N}Me_2$), 7.95 (s, $ArCH_3$), and 8.93 (s, CMe_3). *N*-Allyl-*NN*-dimethyl-5-*t*-butylanilinium-2-olate (7d) was obtained as crystals (64%), m.p. 122 °C (Found: M^+ , 233.1786. $C_{15}H_{23}NO$ requires M ,

233.1780); τ , ABX system, τ_A 3.30, τ_B 2.88, τ_X 3.13 (J_{AB} 8, J_{BX} 2 Hz, 3-H, 4-H, and 6-H), 4.12–4.80 (m, $\text{CH}=\text{CH}_2$), 5.03 (d, J 6 Hz, NCH_2), 6.48 (s, NMe_2), and 8.79 (s, CMe_3). NN-Dimethyl-N-(2-methylallyl)-5-*t*-butylanilinium-2-olate (7e) was obtained as crystals (77%), m.p. 137–138 °C (Found: M^+ , 247.1928. $\text{C}_{16}\text{H}_{25}\text{NO}$ requires M , 247.1936); τ , ABX system, τ_A 3.32, τ_B 2.80, τ_X 3.10 (J_{AB} 8, J_{BX} 2 Hz, 3-H, 4-H, and 6-H), 4.78 (s, $\text{C}=\text{CH}$), 4.90 (s, $\text{C}=\text{CH}$), 5.05 (s, NCH_2), 6.42 (s, NMe_2), 8.56 (s, $\text{C}=\text{CCH}_3$), and 8.73 (s, CMe_3). NN-Dimethyl-N-(2-methylallyl)anilinium-2-olate (7f) was obtained as a pale yellow gum (99%) (Found: M^+ , 191.1311. $\text{C}_{12}\text{H}_{17}\text{NO}$ requires M , 191.1310); τ 2.88–3.29 (m, 3 aryl H), 3.81 (m, 1 aryl H), 4.80 (s, $\text{C}=\text{CH}$), 4.87 (s, $\text{C}=\text{CH}$), 5.03 (s, NCH_2), 6.41 (s, NMe_2), and 8.57 (s, $\text{C}=\text{CCH}_3$). N-Allyl-3,5,NN-tetramethylanilinium-2-olate (7g) was obtained as a pale yellow oil (80%) (Found: M^+ , 205.1470. $\text{C}_{13}\text{H}_{19}\text{NO}$ requires M , 205.1467); τ 3.07 (s, 4-H or 6-H), 3.34 (s, 6-H or 4-H), 4.37–4.69 (m, $\text{CH}=\text{CH}_2$), 4.94 (d, J 6 Hz, NCH_2), 6.48 (s, NMe_2), 7.80 (s, ArCH_3), and 7.96 (s, ArCH_3). 3,5,NN-Tetramethyl-N-(2-methylallyl)anilinium-2-olate (7h) was obtained as a pale yellow oil (Found: M^+ , 219.1621. $\text{C}_{14}\text{H}_{21}\text{NO}$ requires M , 219.1623); τ 3.10 (s, 4-H or 6-H), 3.37 (s, 6-H or 4-H), 4.78 (s, $\text{C}=\text{CH}$), 4.92 (s, $\text{C}=\text{CH}$), 5.02 (s, NCH_2), 6.46 (s, NMe_2), 7.80 (s, ArCH_3), 7.86 (s, ArCH_3), and 8.48 (s, $\text{C}=\text{CCH}_3$).

Thermal Rearrangement of N-Allyl-5,NN-trimethylanilinium-2-olate (7a). Formation of 2-Allyloxy-5,NN-trimethylaniline (10a), 2-Allyl-6-dimethylamino-4-methylphenol (11a), and 4-Allyl-2-dimethylamino-4-methylcyclohexa-2,5-dienone (8a).—The ylide (7a) (500 mg) in benzene (5 ml) was heated at 40 °C for 6 h. The reaction product was washed with sodium hydroxide (5% aqueous) and Claisen alkali* to separate it into non-phenolic and phenolic (soluble in Claisen alkali) fractions. The phenolic fraction was acidified (2M-HCl), neutralised (aqueous NaHCO_3), and extracted with ether.

The ethereal extract was dried and evaporated and the residual oil purified by preparative t.l.c. (chloroform–ethyl acetate; 10:1 v/v) to give 2-allyl-6-dimethylamino-4-methylphenol (11a) (60 mg, 12%) as a reddish brown oil (Found: M^+ , 191.1307. $\text{C}_{12}\text{H}_{17}\text{NO}$ requires M , 191.1310); ν_{max} 3 400 cm^{-1} ; τ 3.20 (s, 3-H or 5-H), 3.30 (s, 5-H or 3-H), AMNX₂ system, τ_A 4.01, τ_M 4.96, τ_N 4.97, τ_X 6.65 [J_{AM} 17, J_{AN} 10, J_{AX} 6 Hz, $\text{CH}_M\text{H}_N=\text{CH}_A-\text{C}(\text{H}_X)_2$], 7.41 (s, NMe_2), and 7.79 (s, ArCH_3). The methiodide had m.p. 135–140 °C (Found: C, 47.0; H, 6.25; I, 38.2; N, 4.1. $\text{C}_{13}\text{H}_{20}\text{INO}$ requires C, 46.8; H, 6.0; I, 38.1; N, 4.2%); ν_{max} 3 100 cm^{-1} ; τ (CD_3OD) 2.58 (s, 3-H or 5-H), 2.86 (s, 5-H or 3-H), AMNX₂ system, τ_A 4.09, τ_M 4.92, τ_N 4.96, τ_X 6.58 [J_{AM} 8, J_{AN} 16, J_{AX} 6 Hz, $\text{CH}_M\text{H}_N=\text{CH}_A-\text{C}(\text{H}_X)_2$], 6.22 (s, NMe_2), and 7.68 (s, ArCH_3).

The non-phenolic fraction was dried and evaporated and the residual oil separated into two components by preparative t.l.c. (chloroform–ethyl acetate; 10:1 v/v). (i) 2-Allyloxy-5,NN-trimethylaniline (10a) (112 mg, 22%) was obtained as a yellow oil (Found: M^+ , 191.1296. $\text{C}_{12}\text{H}_{17}\text{NO}$ requires M , 191.1310); τ 3.29 (s, 3 aryl H), AMNX₂ system, τ_A 3.92, τ_M 4.63, τ_N 4.77, τ_X 5.45 [J_{AM} 17, J_{AN} 12, J_{AX} 5 Hz, $\text{CH}_M\text{H}_N=\text{CH}_A-\text{C}(\text{H}_X)_2\text{O}$], 7.21 (s, NMe_2), and 7.74 (s, ArCH_3). The methiodide had m.p. 148–150 °C (Found: C,

46.5; H, 6.0; I, 38.3; N, 4.1. $\text{C}_{13}\text{H}_{20}\text{INO}$ requires C, 46.8; H, 6.0; I, 38.1; N, 4.2%); τ (CD_3OD) 2.63–2.83 (m, 3 aryl H), AMNX₂ system, τ_A 3.83, τ_M 4.53, τ_N 4.64; τ_X 5.19 [J_{AM} 15, J_{AN} 10, J_{AX} 6 Hz, $\text{CH}_M\text{H}_N=\text{CH}_A-\text{C}(\text{H}_X)_2\text{O}$], 6.25 (s, NMe_2), and 7.63 (s, ArCH_3). (ii) 4-Allyl-4-methyl-2-dimethylaminocyclohexa-2,5-dienone (8a) (145 mg, 29%) was obtained as a yellow oil (Found: M^+ , 191.1311. $\text{C}_{12}\text{H}_{17}\text{NO}$ requires M , 191.1310); ν_{max} 1 660, 1 630, 1 600 cm^{-1} ; τ , ABX system, τ_A 3.29, τ_B 3.79, τ_X 4.27 (J_{AB} 10, J_{AX} 3 Hz, 5-H_A, 6-H_B, and 3-H_X), AMNX₂ system, τ_A 4.39, τ_M 4.97, τ_N 5.01, τ_X 7.68 [J_{AN} 16, J_{AM} 11, J_{AX} 7 Hz, $\text{CH}_M\text{H}_N=\text{CH}_A-\text{C}(\text{H}_X)_2$], 7.36 (s, NMe_2), and 8.68 (s, $\text{C}=\text{CH}_3$).

The products of the thermal rearrangements of the ylides (7b–h) were separated using similar procedures.

Thermal Rearrangement of 5,NN-trimethyl-N-(2-methylallyl)anilinium-2-olate (7b). Formation of 6-Dimethylamino-4-methyl-2-(2-methylallyl)phenol (11b), 5,NN-Trimethyl-2-(2-methylallyloxy)aniline (10b), and 2-Dimethylamino-4-methyl-4-(2-methylallyl)cyclohexa-2,5-dienone (8b).—A solution of the ylide (7b) (1.56 g) in benzene (5 ml) was heated at 40 °C for 12 h. The product was separated to give the following compounds. (i) 6-Dimethylamino-4-methyl-2-(2-methylallyl)phenol (11b) was obtained as a brown oil (852 mg, 55%) (Found: M^+ , 205.1464. $\text{C}_{13}\text{H}_{19}\text{NO}$ requires M , 205.1467); ν_{max} 3 400 cm^{-1} ; τ 3.19 (s, 3-H or 5-H), 3.31 (s, 5-H or 3-H), 5.22 (s, $\text{C}=\text{CH}$), 5.33 (s, $\text{C}=\text{CH}$), 6.69 (s, NCH_2), 7.38 (s, NMe_2), 7.78 (s, ArCH_3), and 8.26 (s, $\text{C}=\text{CCH}_3$). The methiodide had m.p. 150–152 °C (Found: C, 48.1; H, 6.6; I, 36.4; N, 3.8. $\text{C}_{14}\text{H}_{22}\text{INO}$ requires C, 48.4; H, 6.3; I, 36.5; N, 4.0%); ν_{max} 3 200 cm^{-1} ; τ (CD_3OD) 2.59 (s, 3-H or 5-H), 2.90 (s, 5-H or 3-H), 5.18 (s, $\text{C}=\text{CH}$), 5.46 (s, $\text{C}=\text{CH}$), 6.24 (s, NMe_2), 6.63 (s, NCH_2), 7.68 (s, ArCH_3), and 8.27 (s, $\text{C}=\text{CCH}_3$). (ii) 5,NN-Trimethyl-2-(2-methylallyloxy)aniline (10b) was obtained as a yellow oil (148 mg, 10%) (Found: M^+ , 205.1464. $\text{C}_{13}\text{H}_{19}\text{NO}$ requires M , 205.1467); τ 3.32 (m, 3 aryl H), 4.92 (s, $\text{C}=\text{CH}$), 5.07 (s, $\text{C}=\text{CH}$), 5.77 (s, OCH_2), 7.32 (s, NMe_2), 7.96 (s, ArCH_3), and 8.18 (s, $\text{C}=\text{CCH}_3$). The methiodide had m.p. 142–145 °C (Found: C, 48.0; H, 6.5; I, 36.4; N, 3.8. $\text{C}_{14}\text{H}_{22}\text{INO}$ requires C, 48.4; H, 6.3; I, 36.5; N, 4.0%); τ (CD_3OD), ABX system, τ_A 2.84, τ_B 2.96, τ_X 2.32 (J_{AB} 8, J_{AX} 2 Hz, 3-H_B, 4-H_A, and 6-H_X), 4.91 (s, $\text{C}=\text{CH}_2$), 5.36 (s, OCH_2), 5.98 (s, NMe_2), 7.59 (s, ArCH_3), and 8.13 (s, $\text{C}=\text{CCH}_3$). (iii) 2-Dimethylamino-4-methyl-4-(2-methylallyl)cyclohexa-2,5-dienone (8b) was obtained as a yellow oil (172 mg, 11%) (Found: M^+ , 205.1464. $\text{C}_{13}\text{H}_{19}\text{NO}$ requires M , 205.1467); ν_{max} 1 650 cm^{-1} ; τ , ABX system, τ_A 3.37, τ_B 3.84, τ_X 4.23 (J_{AB} 10, J_{BX} 2 Hz, 6-H_A, 5-H_B, and 3-H_X), 5.25 (s, $\text{C}=\text{CH}$), 5.40 (s, $\text{C}=\text{CH}$), 7.37 (s, NMe_2), 7.67 (s, CH_2), 8.37 (s, $\text{C}=\text{CCH}_3$), and 8.85 (s, 4- CH_3).

Thermal Rearrangement of N(3,3-Dimethyl-2-methylenebutyl)-5,NN-trimethylanilinium-2-olate (7c). Formation of 2-Dimethylamino-4-(3,3-dimethyl-2-methylenebutyl)-4-methylcyclohexa-2,5-dienone (8c).—A solution of the ylide (7c) (600 mg) in benzene (5 ml) was heated at 40 °C for 12 h. The non-phenolic fraction of the product was purified by preparative t.l.c. (chloroform–ethyl acetate; 85:15 v/v) to give 2-dimethylamino-4-(3,3-dimethyl-2-methylenebutyl)-4-methylcyclohexa-2,5-dienone (8c) as a yellow oil (248 mg, 41%) (Found: M^+ , 247.1928. $\text{C}_{16}\text{H}_{25}\text{NO}$ requires M , 247.1926); ν_{max} 1 650 and 1 630 cm^{-1} ; τ , ABX system, τ_A 3.25, τ_B 3.80, τ_X 4.20 (J_{AB} 10, J_{AX} 3 Hz, 3-H_X, 5-H_A, and 6-H_B), 5.21 (s, $\text{C}=\text{CH}$), 5.27 (s, $\text{C}=\text{CH}$), 7.35 (s, NMe_2), 7.57 (s, CH_2), 8.71 (s, $\text{C}=\text{CH}_3$), and 9.10 (s, CMe_3). The n.m.r. spectrum of the total rearrangement product indicated that

* Prepared by adding methanol (100 ml) to an ice-cold solution of potassium hydroxide (35 g) in water (25 ml).

the ether (10c) and the phenol (11c) had been formed but these products were not isolated.

Thermal Rearrangement of N-Allyl-NN-dimethyl-5-t-butylanilinium-2-olate (7d). Formation of 2-Allyl-6-dimethylamino-4-t-butylphenol (11d), 2-Allyloxy-NN-dimethyl-5-t-butylaniline (10d), and 4-Allyl-2-dimethylamino-4-t-butylcyclohexa-2,5-dienone (8d).—A solution of the ylide (7d) (770 mg) in benzene (5 ml) was heated at 40 °C for 12 h. The product was separated to give the following compounds.

(i) *2-Allyl-6-dimethylamino-4-t-butylphenol (11d)* was obtained as a brown oil (100 mg, 13%) (Found: M^+ , 233.1781. $C_{15}H_{23}NO$ requires M , 233.1780); ν_{\max} 3 300 cm^{-1} ; τ , AB system, τ_A 2.99, τ_B 3.11 (J_{AB} 2 Hz, 4-H and 6-H), AMNX₂ system, τ_A 3.99, τ_M 4.94, τ_N 4.99, τ_X 6.63 [J_{AM} 18, J_{AN} 10, J_{AX} 6 Hz, $CH_MH_N=CH_A-C(H_X)_2$], 7.38 (s, NMe₂), and 8.74 (s, CMe₃). The methiodide had m.p. 134–135 °C (Found: C, 50.7; H, 7.35; I, 33.8; N, 3.5. $C_{16}H_{26}INO$ requires C, 51.2; H, 6.9; I, 33.9; N, 3.7%); τ (CD₃OD), AB system, τ_A 2.57, τ_B 2.64 (J_{AB} 2 Hz, 4-H and 6-H), AMNX₂ system, τ_A 4.16, τ_M 4.89, τ_N 5.03, τ_X 6.53 [J_{AM} 10, J_{AN} 17, J_{AX} 6 Hz,

$CH_MH_N=CH_A-C(H_X)_2$], 6.23 (s, NMe₃), and 8.67 (s, CMe₃). (ii) *2-Allyloxy-NN-dimethyl-5-t-butylaniline (10d)* was obtained as a yellow oil (348 mg, 45%) (Found: M^+ , 233.1781. $C_{15}H_{23}NO$ requires M , 233.1780); τ 3.05–3.29 (m, 3 aryl H), AMNX₂ system, τ_A 3.94, τ_M 4.61, τ_N 4.76, τ_X 5.43 [J_{AM} 15, J_{AN} 10, J_{AX} 5 Hz, $CH_MH_N=CH_A-C(H_X)_2$], 7.19 (s, NMe₂), and 8.70 (s, CMe₃). The methiodide had m.p. 129–130 °C (Found: C, 51.1; H, 6.9; I, 34.0; N, 3.8. $C_{16}H_{26}INO$ requires C, 51.2; H, 6.9; I, 33.9; N, 3.7%); τ (CD₃OD), ABX system, τ_A 2.91, τ_B 2.61, τ_X 2.56 (J_{AB} 8, J_{BX} 2 Hz, 3-H, 4-H, and 6-H), AMNX₂ system, τ_A 3.98, τ_M 4.69, τ_N 4.86, τ_X 5.35 [J_{AM} 15, J_{AN} 10, J_{AX} 5 Hz, $CH_MH_N=CH_A-C(H_X)_2$], 6.42 (s, NMe₃), and 8.86 (s, CMe₃). (iii) *4-Allyl-2-dimethylamino-4-t-butylcyclohexa-2,5-dienone (8d)* was obtained as a yellow oil (15 mg, 2%) (Found: M^+ , 233.1788. $C_{15}H_{13}NO$ requires M , 233.1780); ν_{\max} 1 660, 1 630, and 1 600 cm^{-1} ; τ , ABX system, τ_A 3.18, τ_B 3.70, τ_X 4.19 (J_{AB} 11, J_{AX} 3 Hz, 3-H_X, 5-H_A, and 6-H_B), AMNX₂ system, τ_A 4.66, τ_M 5.11, τ_N 5.13, τ_X 7.56 [J_{AM} 16, J_{AN} 12, J_{AX} 6 Hz, $CH_MH_N=CH_A-C(H_X)_2$].

Thermal Rearrangement of NN-Dimethyl-N-(2-methylallyl)-5-t-butylanilinium-2-olate (7e). Formation of 6-Dimethylamino-2-(2-methylallyl)-4-t-butylphenol (11e) and NN-Dimethyl-2-(2-methylallyloxy)-5-t-butylaniline (10e).—A solution of the ylide (7e) (600 mg) in benzene (5 ml) was heated at 40 °C for 14 h. The product was separated to give the following compounds. (i) *6-Dimethylamino-2-(2-methylallyl)-4-t-butylphenol (11e)* was obtained as a brown oil (200 mg, 33%) (Found: M^+ , 247.1937. $C_{16}H_{25}NO$ requires M , 247.1936); ν_{\max} 3 300 cm^{-1} ; τ , AB system, τ_A 2.97, τ_B 3.10 (J_{AB} 2 Hz, 3-H and 5-H), 5.22 (s, C=CH), 5.32 (s, C=CH), 6.66 (s, ArCH₂), 7.37 (s, NMe₂), 8.26 (s, C=CCH₃), and 8.73 (s, CMe₃). The methiodide had m.p. 152–154 °C (Found: C, 52.5; H, 7.0; I, 32.85; N, 3.4. $C_{17}H_{28}INO$ requires C, 52.4; H, 7.2; I, 32.6; N, 3.6%); τ (CD₃OD), AB system, τ_A 2.51, τ_B 2.64 (J_{AB} 2 Hz, 3-H and 5-H), 5.16 (s, C=CH), 5.44 (s, C=CH), 6.23 (s, NMe₃), 6.57 (s, ArCH₂), 8.25 (s, C=CCH₃), and 8.68 (s, CMe₃). (ii) *NN-Dimethyl-2-(2-methylallyloxy)-5-t-butylaniline (10e)* was obtained as a yellow oil (215 mg, 36%) (Found: M^+ , 247.1937. $C_{16}H_{25}NO$ requires M , 247.1936); τ , ABX system, τ_A 3.26, τ_B 3.10, τ_X 3.15 (J_{AB} 8, J_{BX} 2 Hz, 3-H, 4-H, and 6-H), 4.89 (s, C=CH), 5.04 (s, C=CH), 5.54 (s, OCH₂), 7.29 (s, NMe₂), 8.16 (s, C=CCH₃), and 8.71 (s, CMe₃). The methiodide had m.p.

114–115 °C (Found: C, 52.2; H, 7.1; I, 32.65; N, 3.6. $C_{17}H_{28}INO$ requires C, 52.4; H, 7.2; I, 32.6; N, 3.6%); τ (CD₃OD) ABX system, τ_A 2.71, τ_B 2.41, τ_X 2.35 (J_{AB} 8, J_{BX} 2 Hz, 3-H, 4-H, and 6-H), 4.85 (s, C=CH), 4.90 (s, C=CH), 5.23 (s, OCH₂), 6.21 (s, NMe₃), 8.09 (s, C=CCH₃), and 8.70 (s, CMe₃).

Thermal Rearrangement of NN-Dimethyl-N-(2-methylallyl)-anilinium-2-olate (7f). Formation of NN-Dimethyl-2-(2-methylallyloxy)aniline (10f) and 2-Dimethylamino-4-(2-methylallyl)phenol (13f).—A solution of the ylide (7f) (695 mg) in benzene was heated at 80 °C for 14 h. The product was separated into non-phenolic and phenolic fractions and each fraction was purified by preparative t.l.c. (chloroform-ethyl acetate; 10 : 1 v/v) to give two products. (i) *NN-Dimethyl-2-(2-methylallyloxy)aniline (10f)* was obtained as a yellow oil (191 mg, 27%) (Found: M^+ , 191.1311. $C_{13}H_{17}NO$ requires M , 191.1310); τ 3.22–3.30 (m, 4 aryl H), 4.90 (s, C=CH), 5.04 (s, C=CH), 5.53 (s, OCH₂), 7.20 (s, NMe₂), and 8.16 (s, C=CCH₃). The methiodide had m.p. 132–133 °C (Found: C, 46.75; H, 6.05; I, 38.25; N, 4.2. $C_{13}H_{20}INO$ requires C, 46.8; H, 6.0; I, 38.1; N, 4.2%); τ (CD₃OD), ABCD system, τ_A 2.18, τ_B 2.43, τ_C 2.64, τ_D 2.83 ($J_{AB} = J_{CD} = ca. 1.5$, $J_{AD} = J_{BC} = 8$, J_{BD} 7 Hz, 3-H_C, 4-H_B, 5-H_D, and 6-H_A), 4.84 (s, C=CH), 4.89 (s, C=CH), 5.19 (s, OCH₂), 6.20 (s, NMe₃), and 8.08 (s, C=CCH₃). (ii) *2-Dimethylamino-4-(2-methylallyl)phenol (13f)* was obtained as a brown oil (271 mg, 39%) (Found: M^+ , 191.1311. $C_{12}H_{17}NO$ requires M , 191.1310); ν_{\max} 3 300 cm^{-1} ; τ 3.09 (m, 3-H), 3.20 (m, 5-H and 6-H), 5.28 (s, C=CH), 5.34 (s, C=CH), 6.82 (s, ArCH₂), 7.40 (s, NMe₂), and 8.37 (s, C=CCH₃). The methiodide had m.p. 133–134 °C (Found: C, 47.1; H, 6.3; I, 38.0; N, 4.1. $C_{12}H_{20}INO$ requires C, 46.8; H, 6.0; I, 38.1; N, 4.2%); ν_{\max} 3 200 cm^{-1} ; τ , ABC system, τ_A 2.50, τ_B 2.87, τ_C 2.98 (J_{BC} 8 Hz, 6-H_C, 5-H_B, and 3-H_A), 5.21 (s, C=CH), 5.25 (s, C=CH), 6.24 (s, NMe₃), 6.55 (s, ArCH₂), and 8.33 (s, C=CCH₃).

Thermal Rearrangement of N-Allyl-3,5,NN-tetramethyl-anilinium-2-olate (7g). Formation of 4-Allyl-4,6-dimethyl-2-dimethylaminocyclohexa-2,5-dienone (8g) and 6-Allyl-4,6-dimethyl-2-dimethylaminocyclohexa-2,4-dienone (12g).—A solution of the ylide (7g) (560 mg) in benzene (5 ml) was heated at 40 °C for 14 h. The crude product was separated by preparative t.l.c. (chloroform-ethyl acetate; 85 : 15 v/v) to give two products, identified as below. The n.m.r. spectrum of the product indicated that some ether (10g) was present, but this was not isolated. (i) *4-Allyl-4,6-dimethyl-2-dimethylaminocyclohexa-2,5-dienone (8g)* was obtained as a yellow oil (345 mg, 62%) (Found: M^+ , 205.1464. $C_{13}H_{19}NO$ requires M , 205.1467); λ_{\max} 317 nm (ϵ 2 000); ν_{\max} 1 600, 1 640, and 1 610 cm^{-1} ; τ , ABX₃ system, τ_A 3.48, τ_B 4.22, τ_X 8.12 [J_{AB} 3, J_{AX} 1.5 Hz, $[CH_B-C-CH_A=C-C(H_X)_2]$], AMNX₂ system, τ_A 4.46, τ_M 5.08, τ_N 5.12, τ_X 7.73 [J_{AM} 12, J_{AN} 16, J_{AX} 7 Hz, $CH_MH_N=CH_A-C(H_X)_2$], 7.38 (s, NMe₂), and 8.80 (s, C-CH₃).

(ii) *6-Allyl-4,6-dimethyl-2-dimethylaminocyclohexa-2,4-dienone (12g)* was obtained as a yellow oil (85 mg, 15%) (Found: M^+ , 205.1464. $C_{13}H_{19}NO$ requires M , 205.1467); λ_{\max} 375 nm (ϵ 2 170); ν_{\max} 1 670 and 1 645 cm^{-1} ; τ , AB system, τ_A 4.25, τ_B 4.45 (J_{AB} 2 Hz, 3-H and 5-H), AMNX_Y system, τ_A 4.39, τ_M 5.04, τ_N 5.08, τ_X , τ_Y 7.5–7.92 [J_{AM} 16, J_{AN} 10, $J_{AX} = J_{AY} = 7$ Hz, $CH_MH_N=CH_A-CH_X-CH_Y$], 7.35 (s, NMe₂), 8.13 (s, 4-CH₃), and 8.87 (s, 6-CH₃).

Thermal Rearrangement of 3,5,NN-Tetramethyl-N-(2-methylallyl)anilinium-2-olate (7h). Formation of 3,5,NN-Tetramethyl-2-(2-methylallyloxy)aniline (10h), 4,6-Dimethyl-

4-(2-methylallyl)-2-dimethylaminocyclohexa-2,5-dienone (8h), and 4,6-Dimethyl-6-(2-methylallyl)-2-dimethylaminocyclohexa-2,4-dienone (12h).—A solution of the ylide (7h) (693 mg) in benzene (5 ml) was heated at 40 °C for 14 h. The product was separated by preparative t.l.c. (chloroform–ethyl acetate; 9:1 v/v) to give three products. (i) 3,5,NN-Tetramethyl-2-(2-methylallyloxy)aniline (10h) was obtained as a yellow oil (70 mg, 10%) (Found: M^+ , 219.1619. $C_{14}H_{21}NO$ requires M , 219.1623); τ 3.46 (s, 4-H and 6-H), 4.80 (s, C=CH), 5.08 (s, C=CH), 5.92 (s, OCH₃), 7.23 (s, NMe₂), 7.78 (s, 3-CH₃ and 5-CH₃), and 8.12 (s, C=CCH₃). (ii) 4,6-Dimethyl-4-(2-methylallyl)-2-dimethylaminocyclohexa-2,5-dienone (8h) was obtained as a yellow oil (238 mg, 34%) (Found: M^+ , 219.1619. $C_{14}H_{21}NO$ requires M^+ , 219.1623), ν_{\max} 1 655, 1 640, and 1 600 cm⁻¹; τ , ABX₃ system, τ_A 3.46, τ_B 4.21, τ_X 8.12 [J_{AB} 3, J_{AX} 1.5 Hz, $CH_B-C-CH_A=C(H_X)_2$], 5.25 (s, C=CH), 5.41 (s, C=CH), 7.37 (s, NMe₂), 7.70 (s, CH₂), 8.39 (s, C=CCH₃), and 8.77 (s, 4-CH₃). (iii) 4,6-Dimethyl-6-(2-methylallyl)-2-dimethylaminocyclohexa-2,4-dienone (12h) was obtained as a yellow oil (84 mg, 12%) (Found: M^+ , 219.1615. $C_{14}H_{21}NO$ requires M , 219.1623); ν_{\max} 1 660 and 1 640 cm⁻¹; τ , ABX₃ system, τ_A 4.19, τ_B 4.40, τ_X 8.10 [J_{AB} 2, J_{BX} 2 Hz, $C=CH_A-CC(H_X)_2=CH_B$], 5.38 (s, C=CH), 5.51 (s, C=CH), 7.30 (s, NMe₂), 7.82 (s, CH₂), 8.43 (s, C=CCH₃), and 8.84 (s, 4-CH₃).

Thermal Rearrangements of Dienones (8b), (8g), and (8h). The dienones (8b), (8g), and (8h) remained unchanged when heated in benzene at 40 °C for up to 48 h. A solution of the dienone in benzene was heated at 80 °C for 12 h [(8b) and (8h)] or 18 h (8g). The n.m.r. spectrum of the total reaction product showed that rearrangements had occurred. The *para*-dienone (8b) gave a mixture of the phenol (11b) and the unchanged *para*-dienone (8b). The *para*-dienone (8g) gave a mixture of the ether (10g), the *ortho*-dienone (12g), and the unchanged *para*-dienone (8g). The *para*-dienone (8h) gave a mixture of the ether (10h), the *ortho*-dienone (12h), and the unchanged *para*-dienone (8h).

Base-catalysed Rearrangements of N-Cinnamyl-2-hydroxy-NN-dimethylanilinium salts (22a), (22b), and (22c). **Formation of 2-Cinnamyloxy-NN-dimethylanilines (21a), (21b), and (21c).**—The N-cinnamyl salts (22a), (22b), and (22c) rearranged in methanolic sodium methoxide at room temperature to give, as the major reaction product, the corresponding 2-cinnamyloxy-NN-dimethylanilines (21a), (21b), and (21c), respectively. 2-Cinnamyloxy-5,NN-trimethylaniline (21a) was obtained as a yellow crystalline solid, m.p. 70–72 °C (73%) (Found: C, 80.5; H, 8.5; N, 5.1. $C_{18}H_{21}NO$ requires C, 80.9; H, 7.9; N, 5.2%). τ 2.60–2.86 (m, 5 aryl H), 3.29 (m, 3-H, 4-H, and 6-H), ABX₂ system, τ_A 3.46, τ_B 3.58, τ_X 5.33 [J_{AB} 16, J_{BX} 5 Hz, $C(H_X)_2CH_B=CH_A$], 7.18 (s, NMe₂), and 7.85 (s, ArCH₃). 2-Cinnamyloxy-NN-dimethyl-5-*t*-butylaniline (21b) was obtained as a yellowish brown solid, m.p. 55–58 °C (71%) (Found: M^+ , 309.2085. $C_{21}H_{27}NO$ requires M , 309.2093); τ 2.56–3.28 (m, 8 aryl H), ABX₂ system, τ_A 3.43, τ_B 3.58, τ_X 5.29 [J_{AB} 15, J_{BX} 6 Hz, $C(H_X)_2CH_B=CH_A$], 7.20 (s, NMe₂), and 8.72 (s, CMe₃). The *methiodide* had m.p. 85–87 °C (Found: C, 58.4; H, 6.8; I, 28.1; N, 2.9. $C_{22}H_{30}INO$ requires C, 58.5; H, 6.65; I, 28.5; N, 3.1%); τ (CD₃OD) 2.34–2.78 (m, 8 aryl H), ABX₂ system, τ_A 3.12, τ_B 3.44, τ_X 5.01 [J_{AB} 16, J_{BX} 6 Hz, $C(H_X)_2CH_B=CH_A$], 6.22 (s, NMe₃), and 8.66 (s, CMe₃). 2-Cinnamyloxy-3,5,NN-tetramethylaniline (21c) was obtained as a yellow semi-solid (87%) (Found: M^+ , 281.1787. $C_{19}H_{23}NO$ requires M , 281.1780); τ 2.60–2.93 (m, 5 aryl H), 3.48 (s, 4-H and 6-H), ABX₂ system, τ_A 3.35, τ_B 3.59, τ_X 5.50

[J_{AB} 16, J_{BX} 6 Hz, $C(H_X)_2CH_B=CH_A$], 7.22 (s, NMe₂), and 7.79 (s, 3-CH₃ and 5-CH₃). The *methiodide* had m.p. 135–137 °C (Found: C, 56.4; H, 6.3; I, 29.8; N, 3.5. $C_{20}H_{26}INO$ requires C, 56.7; H, 6.1; I, 30.0; N, 3.3%); τ (CD₃OD), 2.43–2.78 (m, 7 aryl H), ABX₂ system, τ_A 3.08, τ_B 3.33, τ_X 5.20 [J_{AB} 16, J_{BX} 6 Hz, $C(H_X)_2CH_B=CH_A$], 6.26 (s, NMe₃), 7.56 (s, ArCH₃), and 7.62 (s, ArCH₃).

N-[1,1-²H₂]Allyl-2-hydroxy-5,NN-trimethylanilinium Toluene-*p*-sulphonate (24a).—A solution of [1,1-²H₂]allyl toluene-*p*-sulphonate¹ (3.4 g) was added to a stirred solution of 2-dimethylamino-4-methylphenol (2.7 g) in methyl cyanide (5 ml) and the mixture was stirred at room temperature for 14 h. The solvent was evaporated off and the residual solid was recrystallised from ethanol–ether to give the salt (24a) as crystals, m.p. 125–128 °C, (4.4 g, 72%) (Found: C, 62.2; H, 7.1; N, 3.7; S, 8.7. $C_{19}H_{23}D_2NO_4S$ requires C, 62.5; H, 7.4; N, 3.8; S, 8.9%); τ (CF₃CO₂H), AA'BB' system, τ_A 2.14, τ_B 2.94 ($J_{AB} = J_{A'B'} = 8$ Hz, 4 aryl H), 2.44–2.79 (m, 3 aryl H), 4.41 (s, CH=CH₂), 6.38 (s, NMe₂), 7.58 (s, ArCH₃), and 7.65 (s, ArCH₃).

N-[1,1-²H₂]Allyl-5,NN-trimethylanilinium-2-olate (25a) was obtained as a pale yellow oil (64%) with an average deuterium content of 1.82 atoms per molecule (Found: M , 193.1431. $C_{12}H_{10}D_2NO$ requires M , 193.1436); τ , ABX system, τ_A 3.32, τ_B 3.10, τ_X 3.28 (J_{AB} 8 Hz, J_{BX} 2 Hz, 3-H, 4-H and 6-H), 4.40–4.62 (m, CH=CH₂), 6.51 (s, NMe₂), and 7.86 (s, ArCH₃).

Thermal Rearrangement of N-[1,1-²H₂]Allyl-5,NN-trimethylanilinium-2-olate (25a). **Formation of 2-[²H₂]Allyloxy-5,NN-trimethylaniline (26a), 2-[²H₂]Allyl-6-dimethylamino-4-methylphenol (28a), and 4-[²H₂]Allyl-2-dimethylamino-4-methylcyclohexa-2,5-dienone (27a).**—A solution of the ylide (25a) (500 mg) in benzene (5 ml) was heated at 40 °C for 6 h. The solution was evaporated to dryness and the product was extracted into ether. The ether-soluble material was separated into non-phenolic and phenolic fractions. The non-phenolic fraction was separated by t.l.c. to give the ether (26a) and the dienone (27a). The phenolic fraction gave the phenol (28a). (i) 2-[²H₂]Allyloxy-5,NN-trimethylaniline (36 mg) was shown by mass spectrometry to have an average deuterium content of 1.88 atoms per molecule (Found: M^+ , 193.1431. $C_{12}H_{10}D_2NO$ requires M , 193.1436). The n.m.r. spectrum showed that this product consisted of 2-[1,1-²H₂]allyloxy-5,NN-trimethylaniline (26a) (94%) and 2-[3,3-²H₂]allyloxy-5,NN-trimethylaniline (26'a) (6%). (ii) 2-[²H₂]Allyl-6-dimethylamino-4-methylphenol (13 mg) was shown by mass spectrometry to have an average deuterium content of 1.82 atoms per molecule (Found: M^+ , 193.1431. $C_{12}H_{10}D_2NO$ requires M , 193.1436). The n.m.r. spectrum showed that this product consisted of 2-[3,3-²H₂]allyl-6-dimethylamino-4-methylphenol (28a) (83%) and 3-[1,1-²H₂]allyl-6-dimethylamino-4-methylphenol (28'a) (17%). (iii) 4-[²H₂]Allyl-2-dimethylamino-4-methylcyclohexa-2,5-dienone (50 mg) was shown by mass spectrometry to have an average deuterium content of 1.82 atoms per molecule (Found: M^+ , 193.1431. $C_{12}H_{10}D_2NO$ requires M , 193.1436). The n.m.r. spectrum showed that this product consisted of 4-[1,1-²H₂]allyl-2-dimethylamino-4-methylcyclohexa-2,5-dienone (27a) (90%) and 4-[3,3-²H₂]allyl-2-dimethylamino-4-methylcyclohexa-2,5-dienone (27'a) (10%). The n.m.r. spectrum of the

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

unchanged ylide (25a) showed that no 1,3-deuterium scrambling had occurred.

The same three products were isolated from the rearrangement of the ylide (25a) at 80 °C. The ether (26a) was shown to consist of the [1,1-²H₂]allyl isomer (26a) (93%) and the [3,3-²H₂]allyl isomer (26'a) (7%), the phenol (28a) was shown to consist of the [3,3-²H₂]allyl isomer (28a) (80%) and the [1,1-²H₂]allyl isomer (28'a) (20%), and the dienone (27a) was shown to consist of the [1,1-²H₂]allyl isomer (27a) (85%) and the [3,3-²H₂]allyl isomer (27'a) (15%).

N-[1,1-²H₂]Allyl-2-hydroxy-NN-dimethyl-5-t-butylanilinium Toluene-*p*-sulphonate (24b), obtained (94%) from the reaction of 2-dimethylamino-4-t-butylphenol with [1,1-²H₂]allyl toluene-*p*-sulphonate, had m.p. 150–153 °C (Found: C, 65.3; H, 7.8; N, 3.3; S, 8.1. C₂₂H₂₉D₂NO₄S requires C, 65.2; H, 8.1; N, 3.4; S, 7.9%). τ (CF₃CO₂H), AA',BB' system, τ_A 2.16, τ_B 2.91 (J_{AB} = J_{A'B'} = 8 Hz, 4 aryl H), ABX system, τ_A 2.70, τ_B 2.49, τ_X 2.64 (J_{AB} 8, J_{BX} 2 Hz, 3-H, 4-H, and 6-H), 4.44 (s, CH=CH₂), 6.38 (s, NMe₂), 7.61 (s, ArCH₃), and 8.68 (s, CMe₃). N-[1,1-²H₂]Allyl-NN-dimethyl-5-t-butylanilinium-2-olate (25b) was obtained (83%) as a crystalline solid, m.p. 122–124 °C, shown by mass spectrometry to have an average deuterium content of 1.86 atoms per molecule (Found: M⁺, 235.1912. C₁₅H₂₁D₂NO requires M, 235.1905); τ, ABX system, τ_A 3.30, τ_B 2.78, τ_X 3.14 (J_{AB} 9, J_{BX} 2 Hz, 3-H, 4-H, and 6-H), 4.20–4.74 (m, CH=CH₂), 6.48 (s, NMe₂), and 8.79 (s, CMe₃).

Thermal Rearrangement of N-[1,1'-²H₂]Allyl-NN-dimethyl-5-t-butylanilinium-2-olate (25b). Formation of 2-[²H₂]Allyloxy-5-t-butyl-N,N-dimethylaniline (26b), 2-[²H₂]Allyl-6-dimethylamino-4-t-butylphenol (28b), and 4-[²H₂]Allyl-4-t-butyl-2-dimethylaminocyclohexa-2,5-dienone (27b).—A solution of the ylide (25b) (770 mg) in benzene was heated at 40 °C for 6 h. The crude product was separated into non-phenolic and phenolic fractions followed by preparative t.l.c. to give three products. (i) 2-[²H₂]Allyloxy-NN-dimethyl-5-t-butylaniline (26b) was obtained as a yellow oil (348 mg) and was shown by mass spectrometry to have an average deuterium content of 1.70 atoms per molecule (Found: M⁺, 235.1912. C₁₅H₂₁D₂NO requires M, 235.1905). The n.m.r. spectrum showed that this product consisted of 2-[1,1-²H₂]allyloxy-NN-dimethyl-5-t-butylaniline (26b) (92%) and 2-[3,3-²H₂]allyloxy-NN-dimethyl-5-t-butylaniline (26'b) (8%). (ii) 2-[²H₂]Allyl-6-dimethylamino-4-t-butylphenol (28b) (100 mg) was shown by mass spectrometry to have an average deuterium content of 1.86 atoms per molecule (Found: M⁺, 235.1912. C₁₅H₂₁D₂NO requires M, 235.1905). The n.m.r. spectrum showed that this product consisted of the 3-[3,3-²H₂]allyl isomer (28b) (75%) and the 3-[1,1-²H₂]allyl isomer (28'b) (25%). (iii) 4-[²H₂]Allyl-2-dimethylamino-4-t-butylcyclohexa-2,5-dienone (27b) (15 mg) was shown by mass spectrometry to have an average deuterium content of 1.84 atoms per molecule (Found: M⁺, 235.1912. C₁₅H₂₁D₂NO requires M, 235.1905). The n.m.r. spectrum showed that this product consisted of the 4-[1,1-²H₂]allyl isomer (27b) (86%) and the 4-[3,3-²H₂]allyl isomer (27'b) (14%).

The same three products were isolated from the rearrangement of the ylide (25b) at 80 °C. The ether (26b) was shown to consist of the [1,1-²H₂]allyl isomer (26b) (91.5%) and the [3,3-²H₂]allyl isomer (26'b) (8.5%), the phenol (28b) was shown to consist of the [3,3-²H₂]allyl isomer (28b) (72.5%) and the [1,1-²H₂]allyl isomer (28'b) (27.5%), and the dienone (27b) was shown to consist of the [1,1-²H₂]allyl

isomer (27b) (90%) and the [3,3-²H₂]allyl isomer (27'b) (10%).

N-[(2E,4E)-Hexa-2,4-dienyl]-2-hydroxy-NN-dimethylanilinium bromide (33a) was obtained (86%) from the reaction of 2-dimethylaminophenol with (2E,4E)-hexa-2,4-dienyl bromide²⁰ as a crystalline solid, m.p. 98–99 °C (Found: C, 56.3; H, 6.7; Br, 26.7; N, 4.55. C₁₄H₂₀BrNO requires C, 56.45; H, 6.7; Br, 26.75; N, 4.7%). τ (CD₃OD) 2.53–3.20 (m, 4 aryl H), 3.68 (dd, J 16 and 10 Hz, CH=CHCH₃), 4.15–4.43 (m, CH=CH=CHCH₃), 4.82 (dt, J 16 and 8 Hz, CH₂-CH=CH), 5.36 (d, J 8 Hz, NCH₂CH), 6.43 (s, NMe₂), and 8.40 (d, J 5 Hz, CHCH₃). 2-Hydroxy-NN-dimethyl-N-[(2E)-2-methylpenta-2,4-dienyl]anilinium bromide (33b) was obtained (74%) from the reaction of 2-dimethylaminophenol with (2E)-2-methylpenta-2,4-dienyl bromide¹² as crystals, m.p. 104–105 °C; τ (CF₃CO₂H) 2.47–3.02 (m, 4 aryl H), ABXY system, τ_A 3.81, τ_B 3.52, τ_X 4.65, τ_Y 4.67 (J_{AB} 11, J_{BX} 15, J_{BY} 10 Hz, CH_A-CH_B=CH_XH_Y), 5.30 (s, NCH₂), 6.34 (s, NMe₂), and 8.63 (s, C=CCH₃).

2-Hydroxy-NN-dimethyl-N-[(2E)-4-methylpenta-2,4-dienyl]anilinium bromide (33c) was obtained (84%) from the reaction of 2-dimethylaminophenol with (2E)-4-methylpenta-2,4-dienyl bromide¹² as crystals, m.p. 135–137 °C; τ (CD₃OD) 2.42–3.14 (m, 4 aryl H), ABX₂ system, τ_A 3.46, τ_B 4.63, τ_X 5.20 (J_{AB} 16, J_{BX} 8 Hz, CH_A=CH_B-C(H_X)₂), 4.94 (s, C=CH₂), 6.31 (s, NMe₂), and 8.33 (s, C=CCH₃).

Base Catalysed Rearrangement of N-[(2E,4E)-Hexa-2,4-dienyl]-2-hydroxy-NN-dimethylanilinium bromide (33a). Formation of 2-[2E,4E]-Hexa-2,4-dienyloxy-NN-dimethylaniline (34a) and 2-Dimethylamino-4-[(2E)-1-methylpenta-2,4-dienyl]phenol (35a).—A solution of the salt (33a) (1.00 g) in water (15 ml) containing sodium hydroxide (1 mol equiv.) was left at 0 °C for 4 h. The reaction mixture was diluted with water and the products were extracted into dichloromethane. The extract was dried and evaporated and the residual brown oil was separated into non-phenolic and phenolic fractions. Preparative t.l.c. gave two products. (i) 2-[(2E,4E)-Hexa-2,4-dienyloxy]-NN-dimethylaniline (34a) was obtained as a brown oil (383 mg, 53%) (Found: M⁺, 217.1473. C₁₄H₁₉NO requires M, 217.1467); τ 3.14 (m, 4 aryl H), 3.68 (dd, J 16 and 10 Hz, CH=CH-CH), 3.97–4.49 (m, CH=CH-CH=CH), 5.42 (d, J 5 Hz, OCH₂), 6.23 (s, NMe₂), and 8.28 (d, J 6 Hz, C=CCH₃). The methiodide had m.p. 145–147 °C (Found: C, 49.95; H, 6.1; I, 35.5; N, 4.0. C₁₅H₂₂INO requires C, 50.1; H, 6.2; I, 35.3; N, 3.9%); τ [(CD₃)₂CO + 2 drops D₂O], ABCD system, τ_A 2.04, τ_B 2.40, τ_C 2.54, τ_D 2.81 (J_{AD} 8, J_{AB} 1.5, J_{BC} 8, J_{BD} 7, J_{CD} 2 Hz, 3-H_C, 4-H_B, 5-H_D, and 6-H_A), 3.42 (dd, J 10 and 16 Hz), CH=CH-CH), 3.72–4.36 (m, CH=CH-CH=CH), 5.06 (d, J 6 Hz, OCH₂), 6.06 (s, NMe₂), and 8.26 (d, J 6 Hz, C=CCH₃). (ii) 2-Dimethylamino-4-[(2E)-1-methylpenta-2,4-dienyl]phenol (35a) was obtained as a brown oil (93 mg, 13%) (Found: M⁺, 217.1473. C₁₄H₁₉NO requires M, 217.1467); ν_{max} 3 300 cm⁻¹; τ 3.04 (m, 3-H), 3.35 (m, 5-H and 6-H), 3.50–4.31 (m, CH=CH=CH), 4.88 (dd, J 2 and 16 Hz, C=CH), 5.02 (dd, J 2 and 10 Hz, C=CH), 6.59 (quintet, J 7 Hz, CH-CH-CH₃), 7.39 (s, NMe₂), and 8.86 (d, J 7 Hz, CHCH₃); τ (C₆F₆-CDCl₃; 3:1 v/v), ABC system, τ_A 2.97, τ_B 3.20, τ_C 3.41 (J_{AB} 2, J_{BC} 8 Hz, 3-H_C, 4-H_B, and 6-H_A). The methiodide had m.p. 136–137 °C (Found: C, 50.4; H, 6.5; I, 35.4; N, 3.7. C₁₅H₂₂INO requires C, 50.1; H, 6.2; I, 35.3; N, 3.9%); ν_{max} 3 100

cm^{-1} ; τ [(CD₃)₂CO + 2 drops D₂O] 2.34 (s, 3-H), 2.70 (s, 5-H and 6-H), 3.44–4.18 (m, CH=CH-CH), 4.88 (dd, J 2 and 16 Hz, C=CH), 5.02 (dd, J 2 and 10 Hz, C=CH), 6.10 (s, NMe₃), 6.37 (quintet, J 7 Hz, CH-CH-CH₃), and 8.64 (d, J 7 Hz, CH-CH₃).

Base-catalysed Rearrangement of 2-Hydroxy-NN-dimethyl-N-[(2E)-2-methylpenta-2,4-dienyl]anilinium Bromide (33b). Formation of NN-Dimethyl-2-[(2E)-2-Methylpenta-2,4-dienyloxy]aniline (34b) and 2-Dimethylamino-4-[(2E)-4-methylpenta-2,4-dienyl]phenol (35b).—A solution of the salt (33b) (1.00 g) in water (15 ml) containing sodium hydroxide (1 mol equiv.) was left at 0 °C for 4 h. The reaction mixture was diluted with water and the product was extracted with dichloromethane. The extract was dried and evaporated and the residual brown oil was separated into non-phenolic and phenolic fractions. Preparative t.l.c. gave two products. (i) NN-Dimethyl-2-[(2E)-2-methylpenta-2,4-dienyloxy]aniline (34b) was obtained as a yellow oil (101 mg, 14%) (Found: M^+ , 217.1459. C₁₄H₁₉NO requires M , 217.1467); τ 3.12 (m, 4 aryl H), ABXY system, τ_A 3.38, τ_B 3.82, τ_X 4.81, τ_Y 4.88 (J_{AB} 11, J_{AX} 17, J_{AY} 10 Hz, CH_B-CH_A=CH_XH_Y), 5.50 (s, OCH₂), 7.20 (s, NMe₂), and 8.12 (s, C=CCH₃). The methiodide had m.p. 139–141 °C (Found: C, 50.2; H, 6.45; I, 35.0; N, 3.9. C₁₅H₂₂INO requires C, 50.1; H, 6.2; I, 35.3; N, 3.9%); τ (CD₃OD), ABCD system, τ_A 2.20, τ_B 2.45, τ_C 2.65, τ_D 2.86 (J_{AB} 1.5, J_{AD} 8, J_{BC} 8, J_{BD} 7, J_{CD} 2 Hz, 3-H_C, 4-H_B, 5-H_D, and 6-H_A), ABXY system, τ_A 3.32, τ_B 3.53, τ_X 4.70, τ_Y 4.79 (J_{AB} 10, J_{AX} 16, J_{AY} 10 Hz, CH_B-CH_A=CH_XH_Y), 5.30 (s, OCH₂), 6.21 (s, NMe₃), and 8.06 (s, C=CCH₃). (ii) 2-Dimethylamino-4-[(2E)-4-methylpenta-2,4-dienyl]phenol (35b) was obtained as a brown oil (392 mg, 57%) (Found: M^+ , 217.1473. C₁₄H₁₉NO requires M , 217.1467); ν_{max} 3350 cm^{-1} ; τ (C₆F₆), ABC system, τ_A 3.02, τ_B 3.35, τ_C 3.66 (J_{AB} 2, J_{BC} 8 Hz, 6-H_C, 5-H_B, and 3-H_A), ABX₂ system, τ_A 3.90, τ_B 4.76, τ_X 6.71 [J_{AB} 15, J_{BX} 6 Hz, CH_A=CH_B-C(H_X)₂], 5.29 (s, C=CH₂), 7.28 (s, NMe₂), and 8.21 (s, C=CCH₃). The methiodide had m.p. 140–143 °C (Found: C, 50.1; H, 6.4; I, 35.4; N, 3.9. C₁₅H₂₂INO requires C, 50.1; H, 6.2; I, 35.3; N, 3.9%); τ (CD₃OD), ABC system, τ_A 2.51, τ_B 2.76, τ_C 2.96 (J_{AB} 2, J_{BC} 8 Hz, 6-H_C, 5-H_B, and 3-H_A), ABX₂ system, τ_A 3.76, τ_B 4.27, τ_X 6.51 [J_{AB} 15, J_{BX} 6 Hz, CH_A=CH_B-C(H_X)₂], 5.24 (s, C=CH₂), 6.26 (s, NMe₃), and 8.20 (s, C=CCH₃).

Base-catalysed Rearrangement of 2-Hydroxy-NN-dimethyl-N-[(2E)-4-methylpenta-2,4-dienyl]anilinium Bromide (33c). Formation of NN-Dimethyl-2-[(2E)-4-methylpenta-2,4-dienyloxy]aniline (34c) and 2-Dimethylamino-4-[(2E)-2-methylpenta-2,4-dienyl]phenol (35c).—A solution of the salt (33c) (1.00 g) in water (15 ml) containing sodium hydroxide (1 mol equiv.) was left at 0 °C for 4 h. The product was separated into non-phenolic and phenolic fractions which were purified by preparative t.l.c. to give two compounds. (i) NN-Dimethyl-2-[(2E)-4-methylpenta-2,4-dienyloxy]aniline (34c) was obtained as an oil (156 mg, 22%) (Found: M^+ , 217.1461. C₁₄H₁₉NO requires M , 217.1467); τ 3.12 (m, 4 aryl H), ABX₂ system, τ_A 3.41, τ_B 4.06, τ_X 5.07 [J_{AB} 16, J_{BX} 6 Hz, CH_A=CH_B-C(H_X)₂], 4.93 (s, C=CH₂), 6.23 (s, NMe₂), and 8.11 (s, C=CCH₃). The methiodide had m.p. 117–120 °C (Found: C, 50.0; H, 6.3; I, 35.55; N, 3.7. C₁₅H₂₂INO requires C, 50.1; H, 6.2; I, 35.3; N, 3.9%); τ (CD₃OD), ABCD system, τ_A 2.21, τ_B 2.45, τ_C 2.62, τ_D 2.86 (J_{AD} 8, J_{BC} 8, J_{BD} 7 Hz, 3-H_C, 4-H_B, 5-H_D, 6-H_A), ABX₂ system, τ_A 3.41, τ_B 4.06, τ_X 5.07 [J_{AB} 16, J_{BX} 6 Hz, CH_A=

CH_B-C(H_X)₂], 4.93 (s, OCH₂), 6.23 (s, NMe₃), and 8.11 (s, C=CCH₃). (ii) 2-Dimethylamino-4-[(2E)-2-methylpenta-2,4-dienyl]phenol (35c) was obtained as a brown oil (143 mg, 20%) (Found: M^+ , 217.1466. C₁₄H₁₉NO requires M , 217.1467); ν_{max} 3350 cm^{-1} ; τ 3.10–3.19 (m, 3 aryl H), ABXY system, τ_A 3.49, τ_B 4.13, τ_X 4.89, τ_Y 5.01 (J_{AB} 12, J_{AX} 16, J_{AY} 8 Hz, CH_B-CH_A=CH_XH_Y), 6.75 (s, ArCH₂), 7.37 (s, NMe₂), and 8.31 (s, C=CCH₃). The methiodide had m.p. 150–152 °C (Found: C, 50.0; H, 6.2; I, 35.3; N, 3.9. C₁₅H₂₂INO requires C, 50.1; H, 6.2; I, 35.3; N, 3.9%); ν_{max} 3200 cm^{-1} ; τ (CD₃OD) 3.50–3.82 (m, 3 aryl H), ABXY system, τ_A 3.73, τ_B 4.17, τ_X 4.93, τ_Y 5.06 (J_{AB} 12, J_{AX} 16, J_{AY} 10 Hz, CH_B-CH_A=CH_XH_Y), 6.62 (s, ArCH₂), 6.24 (s, NMe₃), and 8.31 (s, C=CCH₃).

Thermal Rearrangement of 2-[(2E,4E)-Hexa-2,4-dienyloxy]-NN-dimethylaniline (34a).—The ether (34a) was heated under reflux in benzene for 7 days. The solvent was evaporated off to give a residual oil which had an n.m.r. spectrum identical with that of 2-dimethylamino-4-[(2E,4E)-1-methylpenta-2,4-dienyl]phenol (35a).

Thermal Rearrangement of NN-Dimethyl-2-[(2E)-2-methylpenta-2,4-dienyloxy]aniline (34b).—The ether (34b) was heated under reflux in xylene for 24 h. The solvent was evaporated off to give a residual oil which had an n.m.r. spectrum identical with that of 2-dimethylamino-4-[(2E)-4-methylpenta-2,4-dienyl]-NN-dimethylaniline (35b).

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