Base Catalysed Rearrangements involving Ylide Intermediates. Part 14.[1] Rearrangements of 4-Oxidoanilinium Ylides and 3-Oxidoanilinium Betaines

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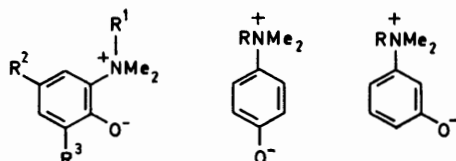
The N-allyl-4-oxidoanilinium ylides (11a—c) undergo a [3,2] sigmatropic rearrangement at 0 °C to give initially the products (9a—c), which undergo a further [3,3] rearrangement to give the isolated reaction products (8a—c). The N-(3,3-dimethylallyl)-4-oxidoanilinium ylide (11d) reacts at 0 °C by the alternative pathway involving homolysis and radical pair recombination to give a mixture of the products (8d) and (13d). The ylides (15a—c) rearrange by a similar radical pair mechanism. The N-pentadienyl-4-oxidoanilinium ylides derived from the salts (24a and b) also rearrange at 0 °C by a sequence of [3,2] and [3,3] sigmatropic rearrangements to give in each case the product (26b). The N-allyl-3-oxidoanilinium betaines (29a and b) undergo [3,3] rearrangements on heating at 40 °C to give mixtures of the products (32) and (33) whereas the N-pentadienyl-3-oxidoanilinium ylide (30) gives only the product (35) of a [5,5] rearrangement followed by aromatisation.

IN the previous two parts [1,2] of this series the preparation and the rearrangement reactions of a variety of 2-oxido-anilinium ylides (1) have been described. These reactions involved competition between concerted sigmatropic processes and radical pair processes and it was therefore of interest to examine the reactions of the analogous 4-oxidoanilinium ylides (2) and the 3-oxido-anilinium betaines (3).† Preliminary experiments in-

R¹ = alkyl, allyl, or pentadienyl
R², R³ = H or alkyl
(1)   (2)   (3)

(4)   (5)   (6)

dicated that the rearrangement reactions of 4-oxido-anilinium ylides (2) with further substituents in the aromatic ring gave complex mixtures of products, and the 3,5-di-t-butyl derivatives (4) were therefore investigated.

The choice of the t-butyl substituents was based upon

† These compounds (3) are described as betaines because there is no formal relationship with the carbonyl-stabilised ammonium ylides containing the Me₂N–C=C–O⁻ structural unit, in contrast with the 4-oxidoanilinium ylides (2) which may be regarded formally as vinylogues of the carbonyl-stabilised ammonium ylides.

the expected steric hindrance to intermolecular reactions involving the phenolic oxygen atom in such systems. During the course of the work the rearrangement (5) ⟶ (6) of the corresponding sulphonium ylide was reported;[3] the ylide (5) was generated by the reaction of the corresponding sulphonium fluoroborate with butyl-lithium at −40 °C and, even under these mild conditions, the rearrangement (5) ⟶ (6) occurred spontaneously.

The salts (7) were prepared in high yields by reaction of 2,6-di-t-butyl-4-dimethylaminophenol [4,5] with the appropriate bromo-compound in methyl cyanide. Treatment of the salt (7a) with methanolic sodium methoxide at 0 °C gave a single product which was identified as the 4-dimethylaminocyclohexa-2,4-dienone (8a) from its spectroscopic properties ($\nu_{max.}$ 1 650 and 1 630 cm⁻¹; n.m.r. AB system assignable to 3-H and 5-H, ABCXY system assignable to $CH_XH_YCH_A=CH_BH_C$, and singlet signals assignable to NMe_2, 2-CMe_3, and 6-CMe_3). These properties, particularly the n.m.r. spectrum, were quite different from those expected for the symmetrical 4-dimethylaminocyclohexa-2,5-dienone (9a) [see below and Experimental section for spectral details of products of structural type (9)] which might have been expected as the product by analogy with the reaction (5) ⟶ (6). The dienone (8a) was hydrolysed during chromatography on silica gel to give the corresponding cyclohexenedione (10a), which was identified on the basis of molecular formula and spectroscopic properties ($\nu_{max.}$ 1 670 cm⁻¹; n.m.r. ABCXY system assignable to $CH_XH_YCH_A=CH_BH_C$, and singlet signals assignable to 5-H, C(3)H₂, 2-CMe_3, and 6-CMe_3). The base catalysed rearrangement of the salt (7b) gave similar results; the initial product was identified as the cyclohexa-2,4-dienone (8b) and hydrolysis by silica gel gave the cyclohexenedione (10b). In both cases, (7a) and (7b), the n.m.r. spectrum of the initial product provided no evidence for the presence of unchanged ylide (11) or of the alternative rearrangement product (9).
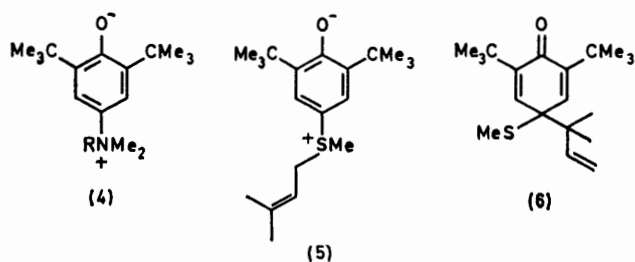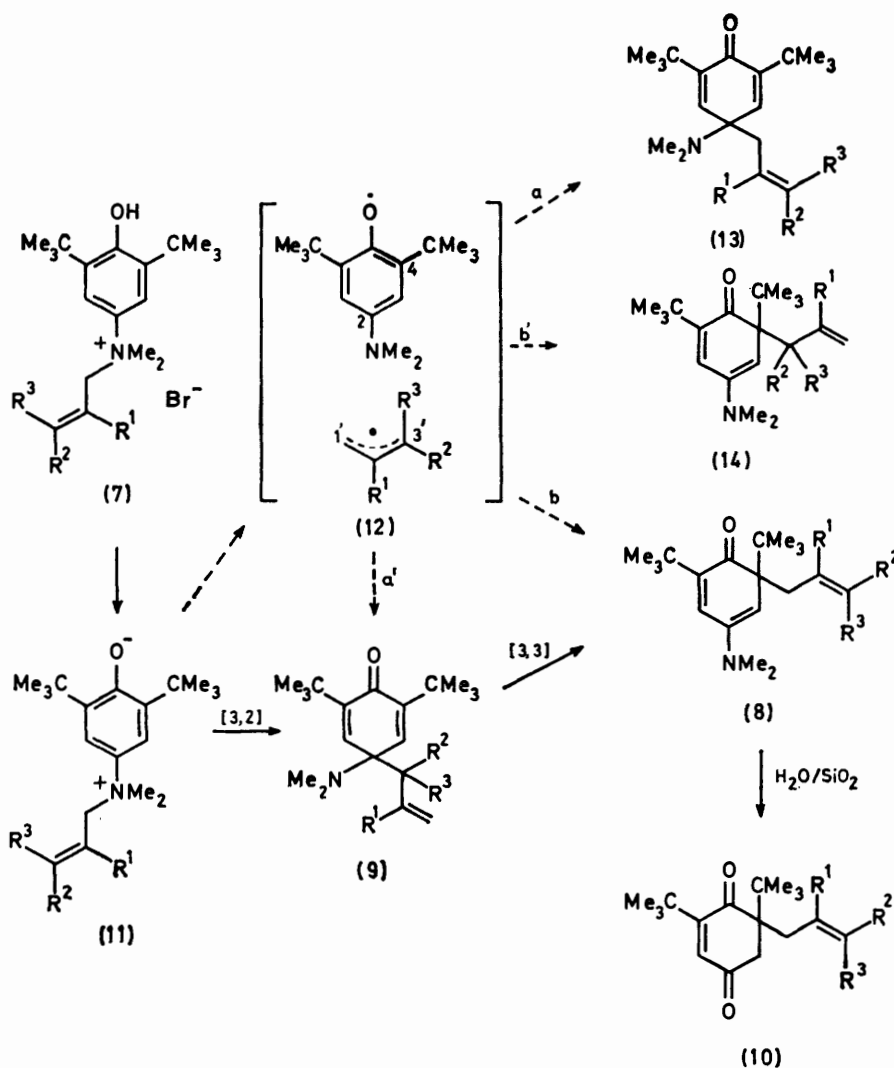
The origin of the cyclohexa-2,4-dienones (8a and b) is readily explained by the sequence of ylide formation and

In formulae (7)—(14): a, $R^1 = R^2 = R^3 = H$; b, $R^1 = R^3 = H$, $R^2 = Ph$; c, $R^1 = Me$, $R^2 = R^3 = H$; d, $R^1 = H$, $R^2 = R^3 = Me$

SCHEME 1 Rearrangement reactions of 4-oxidoanilinium ylides (11); the broken arrows refer to radical pair processes

concerted [3,2][6] and [3,3] rearrangements outlined in Scheme 1 [(7) ⟶ (11) ⟶ (9) ⟶ (8)]. This reaction sequence has a close analogy [1,2] in the reactions of N-allyl-2-oxidoanilinium ylides (1), although in the cases of the N-allyl-4-oxidoanilinium ylides (11a and b) the [3,2] rearrangement proceeds at a lower temperature (<0 °C * as compared with >40 °C). The proposed intermediacy of the cyclohexa-2,5-dienones (9) was supported by an examination of the rearrangement of the N-(2-methylallyl)-2-oxidoanilinium ylide (11c). In this case the salt (7c) reacted with aqueous sodium hydroxide at 0 °C to give a product identified as the symmetrical cyclohexa-2,5-dienone (9) on the basis of its spectroscopic properties ($v_{max.}$ 1 660 and 1 640 cm^{-1}; n.m.r. singlets assignable to the pairs of equivalent groups 3-H

+ 5-H and 2-CMe$_3$ + 6-CMe$_3$, and further singlet signals assignable to NMe$_2$, C=CMe, and C=CH$_2$). The initial product (9c) rearranged on heating in benzene at 40 °C to give the asymmetrical cyclohexa-2,4-dienone (8c), having spectroscopic properties analogous to those of (8a) and (8b). This result provides a close parallel to the rearrangement [3] of the sulphonium ylide (5) and indicates that the cyclohexa-2,4-dienones (8) are more stable than the corresponding cyclohexa-2,5-dienones (9).

The concerted sigmatropic rearrangements of 2-oxidoanilinium ylides (1) are accompanied [1,2] by processes that involve homolysis to give a radical pair followed by radical pair recombination. These processes have been studied in some detail [1,2] using deuterium-labelled ylides to detect the 1,3-allylic scrambling that results from processes involving an intermediate allyl radical. The 4-oxidoanilinium ylides present a different probe for the detection of radical pair processes in that homolysis to

* The n.m.r. spectrum of the salt (7b) in CD$_3$OD containing CD$_3$ONa suggests that the ylide (11b) may be stable up to −10 °C.

give the radical pair (12) would be followed by four modes of radical pair recombination [7] (denoted by a and a' and b and b' in Scheme 1) to give a mixture of cyclohexa-2,5-dienones [(9) and (13) by recombinations a' and a respectively] and cyclohexa-2,4-dienones [(8) and (14) by recombinations b and b' respectively] in yields dependent upon steric and electronic factors. This type of process is exemplified by the base catalysed rearrangement of the anilinium salt (7d). Thus treatment of the salt (7d) with methanolic sodium methoxide at 0 °C gave a 1 : 1 mixture of two products identified (i.r. and n.m.r. spectra) as a mixture of the dienones (8d) and (13d). In this case steric effects associated with the 3,3-dimethyl-allyl group in the ylide (11d) apparently inhibit the [3,2] rearrangement (11d) —→ (9d) and homolysis to give the radical pair (12d) is the preferred reaction mode; the recombination of the radical pair (12d) to give the two products (8d) and (13d) only is expected on obvious steric grounds. Hydrolysis of the total product gave the cyclohexenedione (10d) as the only isolated product, in a yield consistent with its origin from the dienone (8d) only. This result is in interesting contrast with the reported rearrangement [3] of the sulphonium ylide (5) and provides a further demonstration of the similarity of the activation energies for concerted and radical pair processes originating from allylic ammonium ylides.[1,2,8]

The occurrence of similar radical coupling processes has been demonstrated for the rearrangement reactions of a number of other 4-oxidoanilinium ylides (15). Thus rearrangement of the salt (16a), using methanolic sodium methoxide at 0 °C, gave a mixture of the cyclohexa-2,4-dienone (17a) and the cyclohexa-2,5-dienone (18a). Hydrolysis of this mixture gave a mixture of the cyclohexenedione (19a) and unchanged cyclohexa-2,5-dienone (18a) that could be separated by chromatography. In a number of previous examples of the rearrangement reactions of N-(3-phenylprop-2-ynyl)ylide systems [6,9,10] the triple bond has participated in an apparent [3,2] rearrangement that probably proceeds by a two-step [10] mechanism. In this case, however, the formation of the two products, (17a) and (18a), provides strong evidence that the radical pair mechanism predominates. A similar mixture of the products (17b) and (18b) was also obtained from the base catalysed rearrangement of the salt (16b). In these two cases that involve apparent participation by phenyl-propynyl radicals we note that radical coupling is selective, involving only the methylene centre of the propynyl radical. The phenylpropynyl radical is also probably involved [10] in the [1,2] rearrangement of the ylide (20), but in this case the product (21) is accompanied by the product (22) of an apparent [3,2] rearrangement.[10]

The N-benzyl-4-oxidoanilinium ylide (15c) also rearranges by the radical pair pathway. Thus treatment of the salt (16c) with methanolic sodium methoxide at 0 °C gave a mixture of the products (17c) and (18c) in a 1 : 2 ratio; hydrolysis with silica gel gave a mixture of the cyclohexa-2,5-dienone (18c) and the cyclohexenedione (19c) which was readily separated by chromato-

graphy. The intervention of a radical pair process in this case has ample analogy in the [1,2] Stevens rearrangement [11] and other reactions of N-benzyl-ammonium ylides.[12]
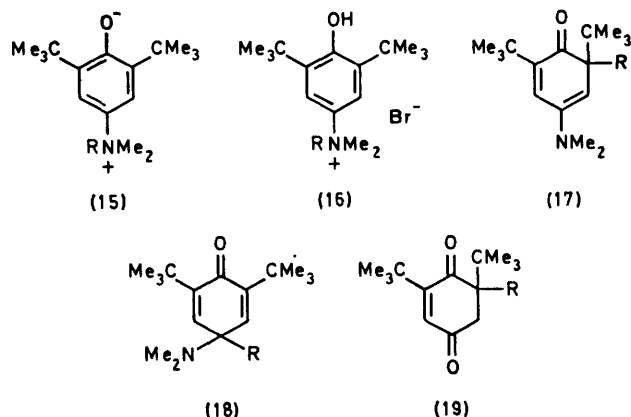

In (15)—(19): a, R = CH$_2$C≡CPh;
b, R = CH$_2$C≡C–C(Me)=CH$_2$; c, R = CH$_2$Ph
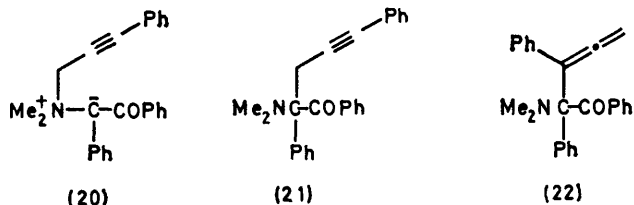
The participation of pentadienyl groups in the rearrangements of ammonium ylides [9] and 2-oxidoanilinium ylides [1] has been described in previous papers of this series. In particular the N-pentadienyl-4-oxidoanilin-ium ylides (23) could potentially undergo [5,4] sigmatropic rearrangements analogous to those of the N-pentadienyl-2-oxidoanilinium ylides. The 4-hydroxyanilinium salts (24a) and (24b) were prepared by reaction of 3,5-di-t-butyl-4-hydroxy-N,N-dimethylaniline with (2E)-2-methylpenta-2,4-dienyl bromide and (2E)-4-methyl-penta-2,4-dienyl bromide, respectively. The salt (24a) reacted with methanolic sodium methoxide at 0 °C to give an initial product that was hydrolysed by silica gel to give 2-(4-methylpenta-2,4-dienyl)cyclohex-5-ene-1,4-dione (25b) (n.m.r. spectrum, ABXY system assignable to CH$_A$CH$_B$CH$_X$H$_Y$, singlet assignable to C=CH$_2$ and singlet assignable to C=CMe). This indicates that the initial product was the cyclohexa-2,4-dienone (26b) formed by a [5,4] sigmatropic rearrangement of the ylide corresponding to (24a) or a sequence of a [3,2] rearrangement to give (27) followed by a selective [3,3] rearrangement of (17) to give (26b). The latter route is probably correct since the salt (24b) undergoes similar base catalysed rearrangement, followed by hydrolysis of the initial product with silica gel, to give the cyclohexene-dione (25b), identical with a sample obtained from the salt (24a). We conclude therefore that the ylides derived from the salts (24a and b) undergo [3,2] rather than [5,4] rearrangement to give in both cases the inter-

mediate (27) which rearranges selectively to give (25b). The selectivity of the [3,3] rearrangement (27) —► (25b) is presumably a consequence of the steric effect of the methyl substituent. The slower [3,3] rearrangement of the cyclohexa-2,5-dienone (9c) as compared with that of the analogous dienone (9a) is a further example of this steric effect. The preference for the [3,2] rather than the [5,4] rearrangement of the ylides derived from (24a


(24)

(25)

(26)   (27)
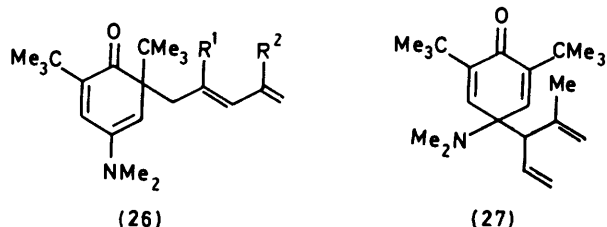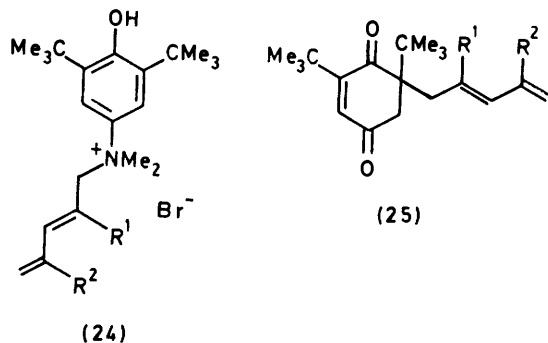
In (24)—(26): a, R^1 = Me, R^2 = H; b, R^1 = H, R^2 = Me

and b) contrasts with the preferred [5,4] rearrangements [1] of the corresponding 2-oxidoanilinium ylides (1), and is presumably a consequence of the inhibition of the [5,4] rearrangement by the bulky t-butyl substituent at the migration terminus.

Although the mechanisms of the rearrangements of the 4-oxidoanilinium ylides have not been subject to rigorous examination, as in some of our earlier work [1,2] on 2-oxidoanilinium ylides, we believe that the conclusions that we have reached regarding them are reasonable. In particular, radical coupling processes involving the radical pair (12) result in coupling at positions 2 and 4 of the aromatic component of the radical pair and at the less sterically hindered position 1' of the allyl radical. In contrast, a concerted reaction mode results exclusively in a [3,2] rearrangement followed by a [3,3] rearrangement, other allowed reaction modes such as [1,4] and [5,4] rearrangements being excluded by steric restraints that are not present in the 2-oxidoanilinium ylides (1).

For obvious structural reasons the 3-oxidoanilinium betaines (3) can only rearrange to give neutral products by [1,3], [3,3], and analogous [m,n] rearrangements where (m + n) is even. However, because of the charge dissipation that results from such a reaction we expected the betaines (3) to react more readily than analogous neutral systems, as for example the Claisen [3,3] rearrangement [13] of aryl allyl ethers. The salts (28a and b) were readily

prepared by the reaction of 3-dimethylaminophenol with the appropriate halide and reacted with methanolic sodium methoxide to give the corresponding betaines (29a and b), (30), and (31) as yellow gums. The betaine structures were in accord with their molecular formulae and spectroscopic properties (n.m.r. signals assignable to a 1,3-disubstituted aromatic ring and the $\overset{+}{N}Me_2R$ substituent). The N-allyl-3-oxidoanilinium betaines (29a and b) rearranged on heating in benzene at 40 °C to give in each case two products. The minor product was identified as the appropriate 2-allyl-3-hydroxy-N,N-dimethylaniline (32a or b) on the basis of its molecular formula and n.m.r. spectrum (ABC system, $J_{AB} = J_{AC} = 8$, J_{BC} 2 Hz, consistent with a 1,2,3-trisubstituted aromatic ring). The major product had a molecular formula and n.m.r. spectrum consistent with the structure of either the appropriate 6-allyl-3-hydroxy-N,N-dimethylaniline (33a or b) or 4-allyl-3-hydroxy-N,N-dimethylaniline (34a or b). A distinction between these two possibilities was made when it was observed that (i) this product did not undergo the acid catalysed cyclisation characteristic of o-allylphenols such as (34), and (ii) the n.m.r. spectrum of the methiodide derivative of the product from (29b) was consistent with the methiodide of (33b) rather than that of (34b) [see Experimental section for details and compare with the n.m.r. spectrum of the methiodide of (35)]. The formation of these two products (32) and (33) can readily be rationalised by the reactions summarised in Scheme 2. Evidently the

(28)   (37)   (38)
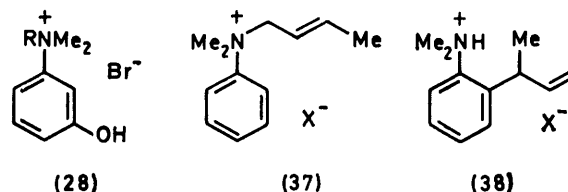
a; R = $CH_2CH=CH_2$
b; R = $CH_2CMe=CH_2$
c; R = $(E)-CH_2CH=CH-CMe=CH_2$
d; R = CH_2Ph

aromatisation that leads to (32) and (33) is fast compared with further [3,3] rearrangements of the intermediate dienones and the product (34) is not detectable.

The N-pentadienyl-3-oxidoanilinium betaine (30) rearranged at 40 °C to give the phenol (35), identified by its molecular formula and n.m.r. spectrum (ABC system J_{AB} 8, J_{BC} 2 Hz, assignable to the protons of a 1,2,4-trisubstituted aromatic ring, ABXY system assignable to $CH_B-CH_A=CH_XH_Y$, singlet assignable to CH_2, and singlet assignable to C=CMe); no other products could be isolated. The substitution pattern in the aromatic ring of this product was determined unambiguously by the comparison of the n.m.r. spectra of (35) and its methiodide derivative with those of (33b) and its methiodide derivative. Thus the betaine (30) rearranges largely to give a single product (35), and it is difficult to account for the formation of this product other than in the terms of [5,5]

(29)

(32)

(33)

(34)
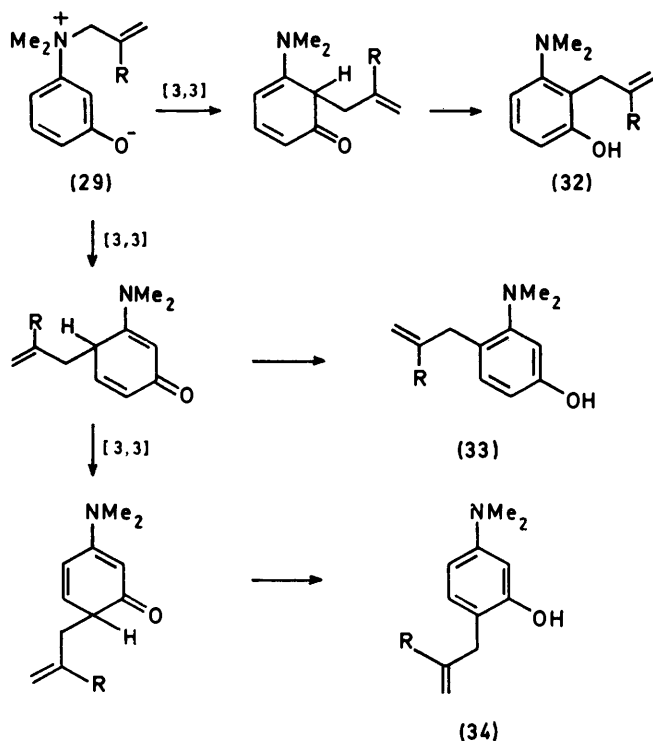
In (29) and (32)—(34): a, R = H; b, R = Me

(30)

(35)

(31)

(36)
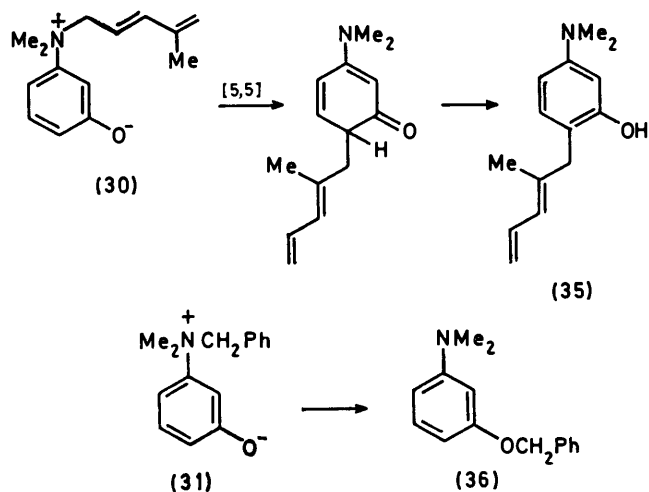
Scheme 2 Rearrangement reactions of 3-oxidoanilinium betaines

sigmatropic rearrangement (Scheme 2). This reaction has a close parallel in the known sigmatropic rearrangements of pentadienyl phenyl ethers [14] and the same preference for a high-order rearrangement is exemplified by the [5,4] sigmatropic rearrangements [1] of N-pentadienyl-2-oxidoanilinium ylides (2).

The N-benzyl-3-oxidoanilinium betaine (31) was less reactive than the N-allyl (29) and N-pentadienyl (30) betaines, but in refluxing methanol it rearranged to give

a moderate yield of the ether (36). This is the only example of ether formation from a 3-oxidoanilinium betaine that we have observed and, in view of the stereochemical improbability of a concerted [1,5] rearrangement [15] with the unfavourable geometry presented by the betaine system, we conclude that the rearrangement (31) ⟶ (36) is probably an intermolecular process, although this has not been proved. Thus this brief examination of the rearrangement reactions of 3-oxidoanilinium betaines, summarised in Scheme 2, has revealed reactions similar to those of the corresponding allyl and pentadienyl phenyl ether and consistent with the HOMO symmetries [16] of the allyl, pentadienyl, and 1,3-disubstituted benzene systems. The accelerations of the [3,3] and [5,5] sigmatropic rearrangements of the oxidoanilinium betaines are presumably attributable to charge dispersal during the reaction so that reaction rates are rather similar to those of the [3,2] and [5,4] rearrangements observed for oxidoanilinium ylides. It should however be noted that these sigmatropic processes do not occur significantly more rapidly than the radical pair processes observable for the oxidoanilinium ylides and for the, probably, intermolecular benzyl transfer noted for the oxidoanilinium betaine (31). Analogous rearrangements of N-allyl anilinium salts, for example (37), have been reported [17] but the reactions require rather more vigorous conditions, presumably because the formation of rearrangement products, such as (38), is not accompanied by as much charge dispersal.

EXPERIMENTAL

Preparation of 3,5-Di-t-butyl-4-hydroxy-N,N-dimethylanilinium Bromides (7), (16), *and* (24).—The salts were prepared by the reaction of 2,6-di-t-butyl-4-dimethylaminophenol [4] with the appropriate alkyl bromide in methyl cyanide. Unless stated otherwise the salts crystallised from methanol–ether.

N-*Allyl*-3,5-*di-t-butyl*-4-*hydroxy*-N,N-*dimethylanilinium bromide* (7a) was obtained as plates, m.p. 184 °C (86% yield) (Found: C, 61.4; H, 8.4; Br, 21.2; N, 4.0. $C_{19}H_{32}BrNO$ requires C, 61.6; H, 8.7; Br, 21.6; N, 3.8%); $\nu_{max.}$ 3 600 cm^{-1}; τ (CF$_3$CO$_2$H) 2.61 (s, 2-H and 6-H), 4.35—4.44 (m, CH=CH$_2$), 5.60 (m, NCH$_2$), 6.42 (s, NMe$_2$), and 8.50 (s, 3-CMe$_3$ and 5-CMe$_3$).

3,5-*Di-t-butyl*-N-(E)-*cinnamyl*-4-*hydroxy*-N,N-*dimethylanilinium bromide* (7b) was obtained as prisms, m.p. 159—160 °C (94% yield) (Found: C, 67.2; H, 8.2; Br, 18.05; N, 3.1. $C_{25}H_{36}BrNO$ requires C, 67.4; H, 8.1; Br, 17.9; N, 3.1%); $\nu_{max.}$ 3 510 cm^{-1}; τ 2.54 (s, 2-H and 6-H), 2.76 (s, C$_6$H$_5$), ABX$_2$ system, τ_A 2.97, τ_B 4.20, τ_X 4.71 [J_{AB} 17, J_{BX} 7.5 Hz, CH$_A$=CH$_B$C(H$_X$)$_2$], 4.38 (s, OH), 6.00 (s, NMe$_2$), and 8.53 (s, 3-CMe$_3$ and 5-CMe$_3$).

3,5-*Di-t-butyl*-4-*hydroxy*-N,N-*dimethyl*-N-(2-*methylallyl*)-*anilinium bromide* (7c) was obtained as a crystalline solid, m.p. 141—143 °C (45% yield) (Found: C, 62.8; H, 8.6; Br, 20.9; N, 3.9. $C_{20}H_{34}BrNO$ requires C, 62.5; H, 8.9; Br, 20.8; N, 3.6%); $\nu_{max.}$ 3 615 cm^{-1}; τ (CF$_3$CO$_2$H) 2.54 (s, 2-H and 6-H), 4.50 (s, =CH), 4.62 (s, =CH), 5.62 (s, NCH$_2$),

6.35 (s, $\overset{+}{N}Me_2$), 8.48 (s, 3-CMe$_3$ and 5-CMe$_3$), and 8.78 (s, C=CMe).

3,5-*Di-t-butyl*-N-(3,3-*dimethylallyl*)-4-*hydroxy*-N,N-*dimethylanilinium bromide* (7d) was obtained as plates, m.p. 135—136 °C (75% yield) (Found: C, 63.1; H, 9.4; Br, 20.1; N, 3.5. $C_{21}H_{36}BrNO$ requires C, 63.3; H, 9.1; Br, 20.1; N, 3.5%); $v_{max.}$ 3 600 cm^{-1}; τ 2.69 (s, 2-H and 6-H), 4.40 (s, OH), 5.15 (s, $\overset{+}{N}CH_2CH=$), 6.11 (s, $\overset{+}{N}Me_2$), 8.34 (s, C=CMe), 8.37 (s, C=CMe), and 8.56 (s, 3-CMe$_3$ and 5-CMe$_3$).

3,5-*Di-t-butyl*-4-*hydroxy*-N,N-*dimethyl*-N-(3-*phenylprop-2-ynyl*)*anilinium bromide* (16a) was obtained as needles, m.p. 180 °C (91% yield) (Found: C, 67.2; H, 7.6; Br, 17.9; N, 3.4. $C_{25}H_{34}BrNO$ requires C, 67.6; H, 7.7; Br, 18.0; N, 3.15%); $v_{max.}$ 3 600 and 2 220 cm^{-1}; τ (CDCl$_3$–CF$_3$CO$_2$H) 2.55 (s, 2-H and 6-H), 2.73 (s, C$_6$H$_5$), 4.84 (s, $\overset{+}{N}CH_2$), 6.12 (s, $\overset{+}{N}Me_2$), and 8.55 (s, 3-CMe$_3$ and 5-CMe$_3$).

N-*Benzyl*-3,5-*di-t-butyl*-4-*hydroxy*-N,N-*dimethylanilinium bromide* (16c) was obtained as prisms, m.p. 172—173 °C (95% yield) (Found: C, 65.6; H, 8.3; Br, 19.05; N, 3.45. $C_{23}H_{34}BrNO$ requires C, 65.7; H, 8.15; Br, 19.0; N, 3.35%); $v_{max.}$ 3 600 cm^{-1}; τ 2.65 (s, 2-H and 6-H), 2.65—3.01 (m, C$_6$H$_5$), 4.33 (s, OH and $\overset{+}{N}CH_2$), 5.93 (s, $\overset{+}{N}Me_2$), and 8.56 (s, 3-CMe$_3$ and 5-CMe$_3$).

3,5-*Di-t-butyl*-4-*hydroxy*-N,N-*dimethyl*-N-(4-*methylpent-4-en-2-ynyl*)*anilinium bromide* (16b) was obtained as a crystalline solid, m.p. 149—151 °C (93% yield) (Found: C, 64.4; H, 8.4; Br, 19.7; N, 3.4. $C_{22}H_{34}BrNO$ requires C, 64.7; H, 8.3; Br, 19.6; N, 3.4%); $v_{max.}$ 3 600 and 2 275 cm^{-1}; τ 2.57 (s, 2-H and 6-H), 4.40 (s, $\overset{+}{N}CH_2$), 4.81 (m, C=CH$_2$), 5.92 (s, $\overset{+}{N}Me_2$), 8.30 (s, C=CMe), and 8.52 (s, 3-CMe$_3$ and 5-CMe$_3$).

3,5-*Di-t-butyl*-4-*hydroxy*-N,N-*dimethyl*-N-[(2E)-2-*methylpenta*-2,4-*dienyl*]*anilinium bromide* (24a) was obtained as a crystalline solid, m.p. 110—115 °C (50% yield) (Found: C, 64.3; H, 8.6; Br, 19.5; N, 3.2. $C_{22}H_{36}BrNO$ requires C, 64.4; H, 8.8; Br, 19.5; N, 3.4%); $v_{max.}$ 3 400 cm^{-1}; τ 2.73 (s, 2-H and 6-H), ABXY system τ_A 3.41—3.79, τ_B 4.05, τ_X 4.71, τ_Y 4.74 (J_{AB} 10, J_{AX} 10, J_{AY} 16 Hz, CH$_B$=CH$_A$–CH$_X$=H$_Y$), 5.80 (s, $\overset{+}{N}CH_2$), 6.53 (s, $\overset{+}{N}Me_2$), 8.61 (s, 3-CMe$_3$ and 5-CMe$_3$), and 8.71 (s, C=CMe).

3,5-*Di-t-butyl*-4-*hydroxy*-N,N-*dimethyl*-N-[(2E)-4-*methylpenta*-2,4-*dienyl*]*anilinium bromide* (24b) was obtained as a crystalline solid, m.p. 145—150 °C (58% yield) (Found: C, 62.2; H, 8.7; Br, 19.3; N, 3.4. $C_{22}H_{36}BrNO,H_2O$ requires C, 61.7; H, 8.9; Br, 18.7; N, 3.3%); $v_{max.}$ 3 600 cm^{-1}; τ (CD$_3$OD) 2.62 (s, 2-H and 6-H), ABX$_2$ system, τ_A 3.54, τ_B 4.59, τ_X 5.53 [J_{AB} 16, J_{BX} 7 Hz, CH$_A$=CH$_B$C(H$_X$)$_2\overset{+}{N}$].

Base Catalysed Rearrangement of N-*Allyl*-3,5-*di-t-butyl*-4-*hydroxy*-N,N-*dimethylanilinium Bromide* (7a); *Formation of* 2-*Allyl*-2,6-*di-t-butyl*-4-*dimethylaminocyclohexa*-3,5-*dienone* (8a).—Cold (0 °C) methanolic sodium methoxide (3.5%; 20 ml) was added to a solution of the salt (7a) (2.0 g) in methanol (20 ml) at 0 °C. The resulting solution was kept at 0 °C for 20 h, poured into ice–water and extracted with dichloromethane. The extract was dried and evaporated to give the *enamine* (8a) (1.25 g, 81%) as a brown, viscous oil (Found: M^+, 289.2391. $C_{19}H_{31}NO$ requires M, 289.2405); $v_{max.}$ 1 650 and 1 630 cm^{-1}; τ, AB system τ_A 3.26, τ_B 4.95 (J 3 Hz, 3-H$_B$ and 5-H$_A$), ABCXY system, τ_A 4.63, τ_B 5.13, τ_C 5.22, τ_X 7.07, τ_Y 8.81 (J_{AB} 16, J_{AC} 10, J_{AX} 6, J_{AY} 6, J_{XY} 13.5 Hz, CH$_X$H$_Y$CH$_A$=CH$_B$H$_C$), 7.38 (s, NMe$_2$), 8.79 (s, 6-CMe$_3$), and 9.11 (s, 2-CMe$_3$). Additional signals at τ 3.49

and τ 8.73 indicated that the product was contaminated by a small amount of 2,6-di-t-butyl-*p*-quinone. The enamine (8a) (1.25 g) was adsorbed on silica gel and left for 65 h. Elution with chloroform gave 2-*allyl*-2,6-*di-t-butylcyclohex-5-ene*-1,4-*dione* (10a) (935 mg, 83%) as a reddish-brown oil (Found: M^+, 262.1926. $C_{17}H_{26}O_2$ requires M, 262.1933); $\lambda_{max.}$ 240 nm (ε 11 500); $v_{max.}$ 1 670 cm^{-1}; τ 3.43 (s, 5-H), ABCXY system, τ_A 4.50, τ_B 4.96, τ_C 5.00, τ_X 7.06, τ_Y 8.16 (J_{AC} 18, J_{AB} 11, J_{AX} 5, J_{AY} 8.5, J_{XY} 13 Hz, CH$_X$H$_Y$CH$_A$= CH$_B$H$_C$), 7.20 [s, C(3)H$_2$], 8.74 (s, 6-CMe$_3$), and 9.06 (s, 2-CMe$_3$).

Base Catalysed Rearrangement of 3,5-*Di-t-butyl*-N-(E)-*cinnamyl*-4-*hydroxy*-N,N-*dimethylanilinium Bromide* (7b); *Formation of* 2,6-*Di-t-butyl*-2-(E)-*cinnamyl*-4-*dimethylaminocyclohexa*-3,5-*dienone* (8b).—The salt (7b) (300 mg) in methanol (10 ml), after reaction with methanolic sodium methoxide (2.5%; 10 ml) at 0 °C for 14 h, gave the *enamine* (8b) (220 mg, 90%) as a brown oil (Found: M^+, 365. $C_{25}H_{35}NO$ requires M, 365); $v_{max.}$ 1 630 cm^{-1}; τ 2.81 (s, C$_6$H$_5$), AB system, τ_A 3.28, τ_B 4.88 (J_{AB} 3 Hz, 3-H$_B$ and 5-H$_A$), ABXY system, τ_A 3.73, τ_B 4.26, τ_X 6.94, τ_Y 7.74 (J_{AB} 16, J_{BX} 7, J_{BY} 6, J_{XY} 12.5 Hz, CH$_A$=CH$_B$CH$_X$H$_Y$), 7.45 (s, NMe$_2$), 8.81 (s, 6-CMe$_3$), and 9.07 (s, 2-CMe$_3$). The enamine (8b) (1.65 g) was adsorbed on silica gel from chloroform solution. After 18 h, elution with chloroform gave 2,6-*di-t-butyl*-2-(E)-*cinnamylcyclohex-5-ene*-1,4-*dione* (10b) (1.2 g, 79%) as an oil which crystallised from light petroleum (b.p. 40—60 °C) as needles, m.p. 108—109 °C (Found: C, 81.4; H, 8.7%; M^+, 338. $C_{23}H_{30}O_2$ requires C, 81.6; H, 8.9%; M, 338); $\lambda_{max.}$ 215 (ε 15 800), 247 (ε 27 500), 285 (ε 2 350), and 293 nm (ε 1 950); $v_{max.}$ 1 670 cm^{-1}; τ 2.79 (s, C$_6$H$_5$), 3.45 (s, 5-H), ABXY system, τ_A 3.65, τ_B 4.08, τ_X 6.94, τ_Y 7.97 (J_{AB} 16, J_{AX} 1.5, J_{BX} 5.5, J_{BY} 9, J_{XY} 13 Hz, CH$_A$=CH$_B$CH$_X$H$_Y$), 7.14 [s, C(3)H$_2$], 8.76 (s, 6-CMe$_3$), and 9.03 (s, 2-CMe$_3$).

Base Catalysed Rearrangement of 3,5-*Di-t-butyl*-4-*hydroxy*-N,N-*dimethyl*-N-(2-*methylallyl*)*anilinium Bromide* (7c); *Formation of* 2,6-*Di-t-butyl*-4-*dimethylamino*-4-(2-*methylallyl*)*cyclohexa*-2,5-*dienone* (9c) *and* 2,6-*Di-t-butyl*-4-*dimethylamino*-2-(2-*methylallyl*)*cyclohexa*-3,5-*dienone* (8c).—A solution of the salt (7c) (1.0 g) in water (10 ml) containing sodium hydroxide (1 mol. equiv.) was left at 0 °C for 12 h. The solution was extracted with dichloromethane and the extract dried and evaporated to give the cyclohexa-2,5-dienone (9c) (600 mg, 77%) as a reddish, crystalline solid; $v_{max.}$ 1 660 and 1 640 cm^{-1}; τ 3.51 (s, 3-H and 5-H), 5.25 (s, C=CH), 5.44 (s, C=CH), 7.72 (s, NMe$_2$), 8.42 (s, CH$_2$), 8.57 (s, C=CMe), and 8.79 (s, 2-CMe$_3$ and 6-CMe$_3$). A solution of the cyclohexa-2,5-dienone (9c) (600 mg) in benzene was heated at 40 °C for 12 h to give the *cyclohexa-3,5-dienone* (8c) as a reddish brown oil (Found: M^+, 303.2553. $C_{20}H_{33}NO$ requires M, 303.2562); $v_{max.}$ 1 640 cm^{-1}; τ, AB system, τ_A 3.27, τ_B 4.93 (J_{AB} 3 Hz, 3-H$_B$ and 5-H$_A$), 5.49 (br s, C=CH$_2$), 7.40 (s, NMe$_2$), 8.64 (s, C=CMe), 8.74 (s, CH$_2$), 8.79 (s, 6-CMe$_3$), and 9.12 (s, 2-CMe$_3$).

Base Catalysed Rearrangement of 3,5-*Di-t-butyl*-4-*hydroxy*-N,N-*dimethyl*-N-(3-*phenylprop-2-ynyl*)*anilinium Bromide* (16a); *Formation of* 2,6-*Di-t-butyl*-4-*dimethylamino*-2-(3-*phenylprop-2-ynyl*)*cyclohexa*-3,5-*dienone* (17a) *and* 2,6-*Di-t-butyl*-4-*dimethylamino*-4-(3-*phenylprop-2-ynyl*)*cyclohexa*-2,5-*dienone* (18a).—A solution of the salt (16a) (800 mg) in methanol was treated with methanolic sodium methoxide (2%; 10 ml) at 0 °C. After 20 h at 0 °C extraction gave a 1 : 1 mixture of two products identified as the cyclohexa-3,5-dienone (17a) and the cyclohexa-2,5-dienone (18a)

(Found: M^+, 363. $C_{25}H_{33}NO$ requires M, 363); $\nu_{max.}$ 1 650 and 1 630 cm^{-1}; the n.m.r. spectrum showed signals assignable to the cyclohexa-3,5-dienone (17a) (see below) and the cyclohexa-2,5-dienone (18a), τ 2.79 (m, C_6H_5), AB system, τ_A 3.22, τ_B 4.78 (J_{AB} 3 Hz, 3-H$_B$ and 5-H$_A$), AB system, τ_A 6.88, τ_B 7.52 (J_{AB} 16 Hz, CH$_A$H$_B$C≡C), 7.36 (s, NMe$_2$), 8.75 (s, 6-CMe$_3$), and 9.06 (s, 2-CMe$_3$). The mixture was adsorbed on silica from chloroform solution and left for 15 h; elution with chloroform gave two fractions: (i) 2,6-*di-t-butyl*-2-(3-*phenylprop-2-ynyl*)*cyclohex*-5-*ene*-1,4-*dione* (19a) (295 mg, 50%) as an oil (Found: M^+, 336.2081. $C_{23}H_{28}O$ requires M, 336.2089); $\lambda_{max.}$ 239 (ε 22 100), 250 (19 500), 272 (1 800), and 278 nm (1 300); $\nu_{max.}$ 1 670 cm^{-1}; τ 2.78 (s, C_6H_5) 3.38 (s, 5-H), AB system, τ_A 6.76, τ_B 7.04 [J_{AB} 17 Hz, C(3)H$_A$H$_B$], AB system, τ_A 6.83, τ_B 7.70 (J_{AB} 16.5 Hz, CH$_A$H$_B$C≡C), 8.74 (s, 6-CMe$_3$), and 9.04 (s, 2-CMe$_3$); (ii) 2,6-*di-t-butyl*-4-*dimethylamino*-4-(3-*phenylprop-2-ynyl*)*cyclohexa*-2,5-*dienone* (18a) (325 mg, 50%) as an oil (Found: M^+, 363.2561. $C_{25}H_{33}NO$ requires M, 363.2562); $\lambda_{max.}$ 239 (ε 20 000), 251 (17 000), 272 (3 600), and 278 nm (2 900); $\nu_{max.}$ 1 655 and 1 635 cm^{-1}; τ 2.77—2.85 (m, C_6H_5), 3.44 (s, 3-H and 5-H), 7.17 (s, CH$_2$C≡C), 7.65 (s, NMe$_2$), and 8.75 (s, 3-CMe$_3$ and 5-CMe$_3$).

*Base Catalysed Rearrangement of 3,5-Di-t-butyl-4-hydroxy-*N,N-*dimethyl*-N-(3,3-*dimethylallyl*)*anilinium Bromide* (7d); *Formation of 2,6-Di-t-butyl-4-dimethylamino-2-(3,3-dimethylallyl*)*cyclohexa-3,5-dienone* (8d) *and 2,6-Di-t-butyl-4-dimethylamino-4-(3,3-dimethylallyl*)*cyclohexa-2,5-dienone* (13d).—A solution of the salt (7d) (1.0 g) in methanol (10 ml) was treated with methanolic sodium methoxide (2.5%; 10 ml) and left at 0 °C for 15 h. Extraction gave a mixture of two components in a 1 : 1 ratio, identified as the cyclohexa-3,5-dienone (8d) and the cyclohexa-2,5-dienone (13d); $\nu_{max.}$ 1 650 and 1 635 cm^{-1}; the n.m.r. spectrum showed signals assignable to the cyclohexa-2,5-dienone (13d), τ 3.50 (s, 3-H and 5-H), 5.31 (br t, J 8 Hz, =CHCH$_2$), 7.68 (s, NMe$_2$), and 8.75 (s, 2-CMe$_3$ and 6-CMe$_3$), and the cyclohexa-3,5-dienone (8d), AB system, τ_A 3.28, τ_B 4.91 (J_{AB} 3 Hz, 3-H$_B$ and 5-H$_A$), 5.11 (br t, J ca. 8 Hz, =CHCH$_2$), 7.48 (s, NMe$_2$), 8.75 (s, 6-CMe$_3$), and 9.07 (s, 2-CMe$_3$). The mixture was adsorbed on silica gel and left for 15 h; elution with chloroform gave 2,6-*di-t-butyl*-2-(3,3-*dimethylallyl*)*cyclohex-4-ene*-1,4-*dione* (10d) (355 mg, 49%) as an oil (Found: M^+, 290.2235. $C_{19}H_{30}O_2$ requires M, 290.2246); $\lambda_{max.}$ 243 nm (ε 9 900); $\nu_{max.}$ 1 665 cm^{-1}; τ 3.44 (s, 5-H), AXY system, τ_A 5.16, τ_X 7.30, τ_Y 8.01 (J_{AX} 6.5, J_{AY} 9, J_{XY} 13 Hz, C=CH$_A$CH$_X$H$_Y$), 7.26 [s, C(5)H$_2$], 8.40 (s, C=CMe), 8.44 (s, C=CMe), 8.73 (s, 6-CMe$_3$), and 9.04 (s, 2-CMe$_3$).

Base Catalysed Rearrangement of N-*Benzyl-3,5-di-t-butyl-4-hydroxy*-N,N-*dimethylanilinium Bromide* (16c); *Formation of 2-Benzyl-2,6-di-t-butyl-4-dimethylaminocyclohexa-3,5-dienone* (17c) *and 4-Benzyl-2,6-di-t-butyl-4-dimethylaminocyclohexa-2,5-dienone* (18c).—A solution of the salt (16c) (1 g) in methanol (10 ml) was treated with methanolic sodium methoxide (3%; 10 ml) and left at 0 °C for 12 h. Extraction gave a mixture (823 mg) of two components in 1 : 2 ratio identified as the cyclohexa-3,5-dienone (17c) and the cyclohexa-2,5-dienone (18c); $\nu_{max.}$ 1 655 and 1 635 cm^{-1}; the n.m.r. spectrum included signals assignable to the 2,5-dienone (18c) (see below) and the 3,5-dienone (17c) τ, AB system, τ_A 3.52, τ_B 4.84 (J_{AB} 3 Hz, 3-H$_B$ and 5-H$_A$), AB system, τ_A 6.46, τ_B 7.42 (J_{AB} 12 Hz, CH$_A$H$_B$Ph), and 7.58 (s, NMe$_2$). The mixture was adsorbed on silica gel and left for 15 h; elution with chloroform gave two compounds (i) 2-*benzyl-2,6-di-t-butylcyclohex-5-ene*-1,4-*dione* (19c) (180

mg, 24%) as an oil (Found: M^+, 312.2080. $C_{21}H_{28}O_2$ requires M, 312.2089); $\lambda_{max.}$ 238 nm (ε 9 200); $\nu_{max.}$ 1 665 cm^{-1}; τ 2.73—3.14 (m, C_6H_5), 3.67 (s, 5-H), AB system, τ_A 6.34, τ_B 7.61 (J_{AB} 13 Hz, CH$_A$H$_B$Ph), AB system, τ_A 7.17, τ_B 7.38 [J_{AB} 17.5 Hz, C(3)H$_A$H$_B$], 8.78 (s, 6-CMe$_3$), and 8.97 (s, 2-CMe$_3$); (ii) 4-*benzyl-2,6-di-t-butyl-4-dimethylaminocyclohexa-2,5-dienone* (18c) (500 mg, 63%) as an oil; $\lambda_{max.}$ 238 nm (ε 8 900); $\nu_{max.}$ 1 655 and 1 635 cm^{-1}; τ 2.90—3.18 (m, C_6H_5), 3.48 (s, 3-H and 5-H), 6.96 (s, CH$_2$Ph), 7.62 (s, NMe$_2$), and 8.90 (s, 2-CMe$_3$ and 6-CMe$_3$).

*Base Catalysed Rearrangement of 3,5-Di-t-butyl-4-hydroxy-*N,N-*dimethyl*-N-(4-*methylpent-4-en-2-ynyl*)*anilinium Bromide* (16b); *Formation of 2,6-Di-t-butyl-4-dimethylamino-4-(4-methylpent-4-en-2-ynyl*)*cyclohexa-2,5-dienone* (18b) *and 2,6-Di-t-butyl-4-dimethylamino-2-(4-methylpent-4-en-2-ynyl*)-*cyclohexa-3,5-dienone* (17b).—The salt (16b) (1.0 g) in methanol (10 ml) was left with sodium methoxide (1 equiv.) at room temperature for 4 h. Extraction gave a product (700 mg, 89%) consisting largely of a 1 : 1 mixture of the cyclohexa-2,5-dienone (18b) and the cyclohexa-3,5-dienone (17b) (Found: M^+, 327.2557. $C_{22}H_{33}NO$ requires M, 327.2562); $\nu_{max.}$ 1 650 cm^{-1}; signals assignable to the cyclohexa-2,5-dienone (18b) τ 3.44 (s, 3-H and 5-H), 4.95 (q, J 1.2 Hz, C=CH), 5.03 (q, J 1.2 Hz, C=CH), 7.32 (s, CH$_2$), 7.73 (s, NMe$_2$), 8.31 (t, J 1.2 Hz, CH$_2$C=CH$_3$), and 8.81 (s, 2-CMe$_3$ and 6-CMe$_3$), and to the cyclohexa-3,5-dienone (17b) τ, AB system, τ_A 3.27, τ_B 4.87 (J_{AB} 3 Hz, 3-H$_B$ and 5-H$_A$), 4.95 (q, J 1.2 Hz, C=CH), 5.03 (q, J 1.2 Hz, C=CH), 7.39 (s, NMe$_2$), 8.81 (s, 6-CMe$_3$), and 9.13 (s, 2-CMe$_3$). Further (unassigned) signals indicated the presence of impurities but chromatography on silica gel failed to purify the products or to give the cyclohex-5-ene-1,4-dione obtainable by hydrolysis of the enamine (17b).

*Base Catalysed Rearrangement of 3,5-Di-t-butyl-4-hydroxy-*N,N-*dimethyl*-N-[(2E)-2-*methylpenta-2,4-dienyl*]*anilinium Bromide* (24a); *Formation of 2,6-Di-t-butyl-4-dimethylamino-2-[(2E)-4-methylpenta-2,4-dienyl*]*cyclohexa-3,5-dienone* (26b).—The salt (24a) (1.0 g) in methanol (10 ml) was left with sodium methoxide (1 equiv.) at 0 °C for 4 h. Extraction gave the *cyclohexa-3,5-dienone* (26b) (700 mg, 88%) as a yellow oil (Found: M^+, 329.2711. $C_{22}H_{35}NO$ requires M, 329.2718); $\nu_{max.}$ 1 650 cm^{-1}; τ, AB system, τ_A 3.27, τ_B 4.88 (J_{AB} 3 Hz, 3-H$_B$ and 5-H$_A$), ABXY system, τ_A 3.98, τ_B 4.80, τ_X 7.05, τ_Y 7.76 (J_{AB} 16, J_{BX} 6, J_{BY} 6, J_{XY} 14 Hz, CH$_A$= CH$_B$–CH$_X$H$_Y$), 5.25 (s, C=CH$_2$), 7.40 (s, NMe$_2$), 8.38 (s, C=CMe), 8.80 (s, 6-CMe$_3$), and 9.08 (s, 2-CMe$_3$). The enamine (26b) (700 mg) was adsorbed on silica gel and left for 12 h; elution with benzene gave 2,6-*di-t-butyl*-2-[(2E)-4-*methylpenta-2,4-dienyl*]*cyclohex-5-ene*-1,4-*dione* (25b) (150 mg, 20%) as an orange oil (Found: M^+, 302.2255. $C_{20}H_{30}O_2$ requires M, 302.2246); $\nu_{max.}$ 1 650 cm^{-1}; τ 3.44 (s, 5-H), ABXY system, τ_A 3.92, τ_B 4.66, τ_X 7.05, τ_Y 8.08 (J_{AB} 16, J_{BX} 6, J_{BY} 9, J_{XY} 13 Hz, CH$_A$=CH$_B$–CH$_X$H$_Y$), 5.16 (s, C=CH$_2$), 7.22 [s, C(3)H$_2$], 8.31 (s, C=CMe), 8.77 (s, 6-CMe$_3$), and 9.05 (s, 2-CMe$_3$).

*Base Catalysed Rearrangement of 3,5-Di-t-butyl-4-hydroxy-*N-[(2E)-4-*methylpenta-2,4-dienyl*]*anilinium Bromide* (24b); *Formation of 2,6-Di-t-butyl-4-dimethylamino-2-[(2E)-4-methylpenta-2,4-dienyl*]*cyclohexa-3,5-dienone* (26b).—The salt (24b) (1.0 g) was treated with methanolic sodium methoxide as in the previous experiment. The n.m.r. spectrum of the total crude product was identical with that of the enamine (26b), and hydrolysis gave the enedione (25b) with n.m.r., i.r., and mass spectra identical with those of the sample obtained from the salt (24a).

3-Hydroxy-N,N-*dimethylanilinium Salts* (28).—3-Hydroxyanilinium chloride (100 g) was converted into 3-hydroxy-N,N-dimethylaniline by the general method used [1,2] for the preparation of 2-hydroxy-N,N-dimethylanilines; the product had b.p. 148 °C at 1 mmHg (lit.,[18] 182 °C at 30 mmHg). Reaction with the appropriate alkyl halide in methyl cyanide gave the corresponding anilinium salt.

N-*Allyl*-3-*hydroxy*-N,N-*dimethylanilinium bromide* (28a) was obtained as a reddish brown gum (58% yield) (Found: C, 51.9; H, 6.4; Br, 31.1; N, 5.0. $C_{11}H_{10}BrNO$ requires C, 51.2; H, 6.25; Br, 30.95; N, 5.4%); $\nu_{max.}$ 3 200 cm^{-1}; τ (CF$_3$CO$_2$H) 2.36—2.95 (m, 4 aryl H), 4.32 (m, CH=CH$_2$), 5.56 (m, $\overset{+}{N}$CH$_2$), and 6.37 (s, $\overset{+}{N}$Me$_2$).

3-*Hydroxy*-N,N-*dimethyl*-N-(2-*methylallyl*)*anilinium bromide* (28b) was obtained as crystals, m.p. 112—115 °C (92% yield) (Found: C, 52.6; H, 6.75; Br, 29.45; N, 4.9. $C_{12}H_{18}BrNO$ requires C, 53.0; H, 6.6; Br, 29.7; N, 5.1%); $\nu_{max.}$ (KBr) 3 400 cm^{-1}; τ (CD$_3$OD) 2.56—3.08 (m, 4 aryl H), 4.63 (s, C=CH), 4.69 (s, C=CH), 5.45 (s, $\overset{+}{N}$CH$_2$), and 6.36 (s, $\overset{+}{N}$Me$_2$), and 8.63 (s, C=CMe).

N-*Benzyl*-3-*hydroxy*-N,N-*dimethylanilinium bromide* (28d) was obtained as a reddish brown gum (98%) (Found: C, 58.8; H, 6.3; Br, 25.9; N, 4.7. $C_{15}H_{18}BrNO$ requires C, 58.4; H, 5.9; Br, 25.9; N, 4.5%); $\nu_{max.}$ 3 300 cm^{-1}; τ (CF$_3$CO$_2$H) 2.44—2.98 (m, 9 aryl H), 5.11 (s, $\overset{+}{N}$CH$_2$), and 6.41 (s, $\overset{+}{N}$Me$_2$).

3-*Hydroxy*-N,N-*dimethyl*-N-[(2E)-4-*methylpenta*-2,4-*dienyl*]*anilinium bromide* (28c) was obtained as a reddish brown gum (89% yield) (Found: C, 53.6; H, 6.8; Br, 25.4; N, 4.6. $C_{14}H_{20}BrNO,H_2O$ requires C, 53.2; H, 7.0; Br, 25.3; N, 4.4%); τ [(CD$_3$)$_2$CO–D$_2$O] 2.48—3.10 (m, 4 aryl H), ABX$_2$ system, τ_A 3.35, τ_B 4.57, τ_X 5.26 [J_{AB} 16, J_{BX} 8 Hz, CH$_A$=CH$_B$C(H$_X$)$_2$], 4.96 (s, C=CH$_2$), 6.30 (s, $\overset{+}{N}$Me$_2$), and 8.35 (s, C=CMe).

N,N-*Dimethylanilinium*-3-*olates* (29), (30) and (31) were obtained from the corresponding salts (28) by reaction with methanolic sodium methoxide as for the preparation of the analogous N,N-dimethylanilinium-2-olates.[1,2]

N-*Allyl*-N,N-*dimethylanilinium*-3-*olate* (29a) was obtained as a yellow gum (81% yield) (Found: M^+, 177.1158. $C_{11}H_{15}NO$ requires M, 177.1154); τ 3.12 (t, J 9 Hz, 5-H), 3.34—3.60 (m, 3 aryl H), 4.62 (m, CH=CH$_2$), 5.84 (m, $\overset{+}{N}$CH$_2$), and 6.49 (s, $\overset{+}{N}$Me$_2$).

N,N-*Dimethyl*-N-(2-*methylallyl*)*anilinium*-3-*olate* (29b) was obtained as a yellow gum (74% yield) (Found: M^+, 191.1309. $C_{12}H_{17}NO$ requires M, 191.1310); τ 3.06—3.54 (m, 3 aryl H), 3.94 (d, J 8 Hz, 4-H), 4.85 (s, C=CH), 4.90 (s, C=CH), 5.86 (s, $\overset{+}{N}$CH$_2$), 6.69 (s, $\overset{+}{N}$Me$_2$), and 8.76 (s, C=CMe).

N-*Benzyl*-N,N-*dimethylanilinium*-3-*olate* (31) was obtained as a yellow gum (74% yield) (Found: M^+, 227.1313. $C_{15}H_{17}NO$ requires M, 227.1310); τ (CD$_3$OD) 2.66—3.00 (m, 8 aryl H), 3.32 (d, J 8 Hz, 4-H), 5.02 (s, $\overset{+}{N}$CH$_2$), and 6.61 (s, $\overset{+}{N}$Me$_2$).

N,N-*Dimethyl*-N-[(2E)-4-*methylpenta*-2,4-*dienyl*]*anilinium*-3-*olate* (30) was obtained as a yellow gum (80% yield) (Found: M^+, 217.1471. $C_{14}H_{19}NO$ requires M, 217.1467); τ 2.75—3.24 (m, 4 aryl H), ABX$_2$ system, τ_A 3.83, τ_B 4.24, τ_X 5.16 [J_{AB} 16, J_{BX} 6 Hz, CH$_A$=CH$_B$–C(H$_X$)$_2$], 5.16 (s, C=CH$_2$), 6.74 (s, $\overset{+}{N}$Me$_2$), and 8.22 (s, C=CMe).

Rearrangement of N-*Allyl*-N,N-*dimethylanilinium*-3-*olate* (29a); *Formation of* 2-*Allyl*-3-*hydroxy*-N,N-*dimethylaniline* (32a) *and* 6-*Allyl*-3-*hydroxy*-N,N-*dimethylaniline* (33a).—A solution of the betaine (29a) (580 mg) in benzene was heated at 40 °C for 12 h. The products were separated by preparative t.l.c. (chloroform–ethyl acetate) to give two products: (i) 2-*allyl*-3-*hydroxy*-N,N-*dimethylaniline* (32a) as a yellow oil (60 mg, 10%) (Found: M^+, 177.1154. $C_{11}H_{15}NO$ requires M, 177.1154); $\nu_{max.}$ 3 600 cm^{-1}; τ, ABC system, τ_A 2.98, τ_B 3.34, τ_C 3.42 (J_{AB} 8, J_{AC} 8, J_{BC} 2, Hz, 4-H, 5-H, and 6-H), AMNX$_2$ system, τ_A 3.67—4.33, τ_M 4.84, τ_N 4.93, τ_X 6.46 [J_{AM} 16, J_{AN} 10, J_{AX} 6 Hz, CH$_M$H$_N$=CH$_A$–C(H$_X$)$_2$], and 7.35 (s, NMe$_2$); (ii) 6-*allyl*-3-*hydroxy*-N,N-*dimethylaniline* (33a) as a yellow oil (247 mg, 43%) (Found: M^+, 177.1153. $C_{11}H_{15}NO$ requires M, 177.1154); $\nu_{max.}$ 3 600 cm^{-1}, τ, ABC system, τ_A 3.05, τ_B 3.58, τ_C 3.53 (J_{AB} 7, J_{BC} 2 Hz, 2-H$_C$, 4-H$_B$, and 5-H$_A$), AMNX$_2$ system, τ_A 3.90—4.30, τ_M 4.98, τ_N 4.99, τ_X 6.65 [J_{AM} 16, J_{AN} 10, J_{AX} 6 Hz, CH$_M$H$_N$=CH$_A$–C(H$_X$)$_2$], and 7.47 (s, NMe$_2$).

Rearrangement of N,N-*Dimethyl*-N-(2-*methylallyl*)*anilinium*-3-*olate* (29b); *Formation of* 3-*Hydroxy*-N,N-*dimethyl*-2-(2-*methylallyl*)*aniline* (32b) *and* 3-*Hydroxy*-N,N-*dimethyl*-6-(2-*methylallyl*)*aniline* (33b).—A solution of the betaine (29b) (1.50 g) in benzene was heated at 40 °C for 12 h. The products were separated by preparative t.l.c. to give (i) 3-*hydroxy*-N,N-*dimethyl*-2-(2-*methylallyl*)*aniline* (32b) (108 mg, 15%) as an oil (Found: M^+, 191.1309. $C_{12}H_{17}NO$ requires M, 191.1310); $\nu_{max.}$ 3 600 cm^{-1}; τ, ABC system, τ_A 2.94, τ_B 3.36, τ_C 3.43 (J_{AB} 8, J_{AC} 8, J_{BC} 2 Hz, 4-H, 5-H, and 6-H), 4.75 (br s, OH), 5.15 (s, C=CH), 5.29 (s, C=CH), 6.52 (s, CH$_2$), 7.39 (s, NMe$_2$), and 8.19 (s, C=CMe) {*methiodide*, m.p. 152—155° (Found: C, 46.5; H, 6.1; I, 38.2; N, 3.9. $C_{13}H_{20}$INO requires C, 46.8; H, 6.0; I, 38.1; N, 4.2%); $\nu_{max.}$ 3 500 cm^{-1}; τ [(CD$_3$)$_2$CO + D$_2$O] ABC system, τ_A 2.58, τ_B 2.68, τ_C 2.82, (J_{AB} 9, J_{BC} 9, J_{AC} 2 Hz, 4-H, 5-H, and 6-H), 5.25 (m, C=CH), 5.85 (s, C=CH), 6.18 (s, $\overset{+}{N}$Me$_3$), 6.42 (s, CH$_2$), and 8.09 (s, C=CMe)} and (ii) 3-*hydroxy*-N,N-*dimethyl*-6-(2-*methylallyl*)*aniline* (33b) (208 mg, 41%) as an oil (Found: M^+, 191.1309. $C_{12}H_{17}NO$ requires, M, 191.1310); τ, ABC system, τ_A 3.03, τ_B 3.45, τ_C 3.55 (J_{AC} 8, J_{BC} 2 Hz, 5-H$_A$, 4-H$_B$, and 2-H$_C$), 4.39 (br s, OH), 5.22 (s, C=CH), 5.38 (s, C=CH), 6.72 (s, CH$_2$), 7.45 (s, NMe$_2$), and 8.36 (s, C=CMe) {*methiodide*, m.p. 160—162 °C (Found: C, 46.7; H, 6.2; I, 38.2; N, 3.95. $C_{13}H_{20}$INO requires C, 46.8; H, 6.0; I, 38.1; N, 4.2%); $\nu_{max.}$ 3 500 cm^{-1}; τ [(CD$_3$)$_2$CO–D$_2$O] ABC system, τ_A 2.64, τ_B 2.76, τ_C 3.00 (J_{AC} 2, J_{BC} 8 Hz, 2-H$_A$, 4-H$_C$, and 5-H$_B$), 5.09 (s, C=CH), 5.65 (s, C=CH), 6.11 (s, $\overset{+}{N}$Me$_3$), 6.19 (s, CH$_2$), and 8.05 (s, C=CMe)}.

Rearrangement of N-*Benzyl*-N,N-*dimethylanilinium*-3-*olate* (31); *Formation of* 3-*Benzyloxy*-N,N-*dimethylaniline* (36).—The betaine (31) (762 mg) in methanol was heated under reflux for 14 h. The product was purified by preparative t.l.c. (chloroform) to give the *ether* (36) (500 mg, 66%) as an oil (Found: M^+, 227.1311. $C_{15}H_{17}NO$ requires M, 227.1310); τ 2.59—3.03 (m, 8 aryl H), 3.71 (d, J 8 Hz, 4-H or 6-H), 5.05 (s, OCH$_2$), and 7.19 (s, NMe$_2$).

Rearrangement of N,N-*Dimethyl*-N-[(2E)-4-*methylpenta*-2,4-*dienyl*]*anilinium*-3-*olate* (30); *Formation of* 3-*Hydroxy*-N,N-*dimethyl*-4-[(2E)-2-*methylpenta*-2,4-*dienyl*]*aniline* (35).—The betaine (30) (560 mg) was heated in benzene at 40 °C for 14 h. The product was separated into neutral and phenolic fractions and the phenolic fraction gave 3-*hydroxy*-N,N-*dimethyl*-4-[(2E)-2-*methylpenta*-2,4-*dienyl*]*aniline* (35) (280 mg, 50%) as a yellow oil (Found: M^+, 217.1471. $C_{14}H_{19}NO$ requires M, 217.1467); $\nu_{max.}$ 3 600 cm^{-1}; τ,

ABC system, τ_A 3.09, τ_B 3.71, τ_C 3.79 (J_{AB} 8, J_{BC} 2 Hz, 2-H_C, 5-H_A, and 6-H_B), ABXY system, τ_A 3.41, τ_B 4.11, τ_X 4.95, τ_Y 5.02 (J_{AY} 16, J_{AX} 11, J_{AB} 11 Hz, =CH_B–CH_A= CH_XH_Y), 6.69 (s, CH_2), 7.14 (s, NMe_2), and 8.26 (s, C=CMe). The *methiodide* had m.p. 139—144 °C (Found: C, 49.9; H, 6.3; I, 35.2; N, 3.6. $C_{15}H_{22}INO$ requires C, 50.1; H, 6.2; I, 35.3; N, 3.9%); $\nu_{max.}$ 3 250 cm^{-1}; τ [$(CD_3)_2CO$–D_2O] ABC system, τ_A 2.38, τ_B 2.59, τ_C 2.76 (J_{AB} 2, J_{BC} 9 Hz, 2-H_A, 5-H_C, and 6-H_B), ABXY system, τ_A 3.41, τ_B 4.11, τ_X 4.95, τ_Y 5.02 (J_{AB} 11, J_{AX} 16, J_{AY} 11 Hz, CH_B–CH_A=CH_XH_Y), 6.19 (s, $\overset{+}{N}Me_3$), 6.63 (s, CH_2), and 8.27 (s, C=CMe).

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