Rearrangement Reactions of Allylic Anilinium Ylides Derived from *o*- and *p*-Dimethylaminophenol

By Sivapathasuntharam Mageswaran, W. David Ollis,* Ian O. Sutherland, and Yodhathai Thebtaranonth
(*Department of Chemistry, The University, Sheffield* S3 7HF)

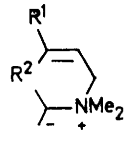
Summary The *ortho*-ylides (**4**) are isolable compounds which on heating give a variety of products, including the ethers (**5**) formed by a [1,4] sigmatropic rearrangement; the *para*-ylides (**11**) are less stable, and above 0° the ylides (**11a** and **b**) undergo consecutive [2,3] and [3,3] sigmatropic rearrangements whereas the ylides (**11c**—**e**) apparently react by homolytic fission and recombination.

Carbonyl-stabilised ammonium ylides with *N*-allyl substituents [*cf.* (**1**)] are usually not isolable[1] because of the ease with which they undergo the [2,3] sigmatropic rearrangement (**1**) → (**2**). We have previously demonstrated that this rearrangement may be inhibited by geometrical restraints[2] and we now report that incorporation of the ylide residue in a phenolate system [*e.g.* (**4**) or (**11**)] also slows down the rearrangement reaction and in some cases leads to reaction pathways other than the [2,3] sigmatropic rearrangement.

The quaternary ammonium salts (**3**; X = Cl or Br) gave the crystalline ylides (**4a**, m.p. 64°), (**4b**, m.p. 106—107°), and (**4c**, m.p. 95—97°) on treatment with aqueous sodium hydroxide, and the ammonium salts (**3**) could be regenerated from the ylides with halogen acids. The ylide (**4a**) gave the ether (**5a**, 79%) on heating (80°) together with the phenol (**6**, 11%): the ylide (**4b**) in boiling benzene gave the ether (**5b**, 55%) as the only isolated reaction product. The base-catalysed thermal transformation of the salt (**3c**) to the ether (**5c**) has been reported previously[3] and we have now shown that heating the ylide (**4c**) at 110° gives a very complex mixture of products from which the compounds (**5c**, 32%), (**7**, 12%), (**8**, 2·4%), and (**9**, 5·3%) were isolated. The ethers (**5**) are the major products from the thermal rearrangements of the ylides (**4**) and it is shown in the accompanying communication[4] that this is an intramolecular process which therefore probably involves an endocyclic[5] symmetry-allowed suprafacial [1,4] sigmatropic rearrangement.[6] The phenol (**6**) cannot be formed by a sequence of symmetry-allowed rearrangements and the products (**7**) and (**8**) clearly result from intermolecular processes.

Although the *ortho*-ylides (**4**) are stable isolable compounds, treatment of the quaternary salts (**10**)† with methanolic sodium methoxide at temperatures lower than 0° yielded unstable ylides (**11**), whose presence in solution could be demonstrated by their n.m.r. spectra. At temperatures above 0° these ylides rearranged to give the products described below. This difference in stability between the *ortho*-ylides (**4**) and the *para*-ylides (**11**) is presumably a consequence of the stabilising coulombic interaction which is present only in the *ortho*-ylides.[7] The *para*-ylides (**11**) rearranged thermally in two different ways depending upon the nature of the substituent R.

The ylides (**11a**) and (**11b**) each gave a single product, identified as the corresponding enamine (**12**) by its spectroscopic properties: treatment of the enamines (**12**) with silica gel gave the more stable ene-diones (**13**). These rearrangements, (**11a**) → (**12a**) and (**11b**) → (**12b**), each give a single product and are regarded as involving consecutive [2,3] and [3,3] sigmatropic rearrangements (Scheme). The quaternary salt (**10c**) gave two products in approximately equal amounts: one of these was identified as the enamine (**12c**) and the other as the dienone (**14c**) on the basis of their spectroscopic properties, and treatment of the product mixture with silica gel which gave the enedione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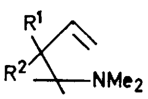
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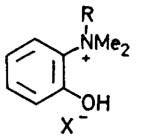
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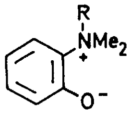
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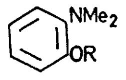
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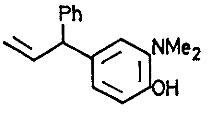
trans

In (4)—(5) (a) R = PhCH=CHCH$_2$ (b) R = Me$_2$C=CHCH$_2$

(c) R = PhCH$_2$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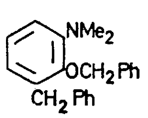
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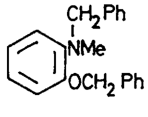
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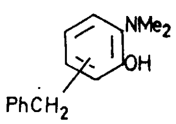
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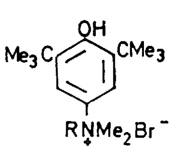
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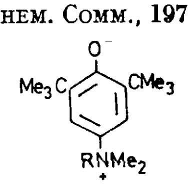
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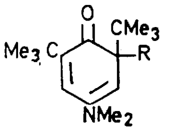
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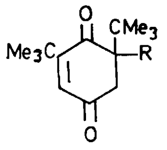
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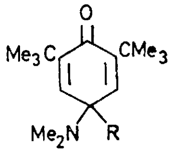
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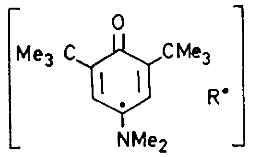
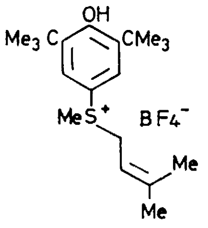

(15)

trans

In (10) — (15) (a) R = PhCH=CHCH$_2$ (b) R = CH$_2$=CHCH$_2$

(c) R = Me$_2$C=CH·CH$_2$ (d) R = PhC≡CCH$_2$

(e) R = PhCH$_2$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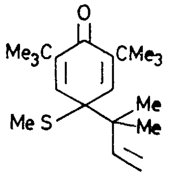
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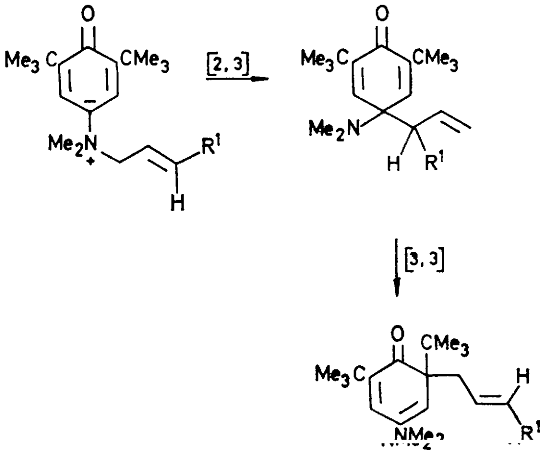

Scheme. *Concerted rearrangements of N-allyl-4-oxyanilinium ylides* (R^1 = H or Ph)

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† The t-butyl substituents are required in this series to prevent intermolecular side-reactions that occur with the unsubstituted compounds.

(**13c**) and unchanged dienone (**14c**). The formation of these two products is best accounted for in terms of homolysis of the ylide (**11c**) to give the radical pair (**15c**) followed by recombination to give the observed products. In support of this mechanism the ylides derived from the salts (**10d**) and (**10e**) behaved in a similar fashion and gave in each case a mixture of the enamine (**12**) and dienone (**14**).

Thus the *p*-oxyanilinium ylides (**11**) rearrange by concerted or apparent radical pair processes, and it is evident from the dependence of the reaction pathway upon the group R that these pathways, although geometrically distinct, do not differ a great deal energetically. It is of interest that the [2,3] sigmatropic rearrangement[8] of the ylide derived from the sulphonium salt (**16**) takes place even at −40°; in this case the [3,3] rearrangement of the product (**17**) did not occur and the reaction followed a concerted pathway, in contrast with the behaviour of the corresponding anilinium ylide (**11c**).

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[3] J. L. Dunn and T. S. Stevens, *J. Chem. Soc.*, 1934, 279.

[4] W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, following communication.

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[7] This interaction may be of importance in the structures of carbonyl-stabilised ammonium ylides, N. A. Bailey, S. E. Hull, G. F. Kersting, and J. Morrison, *Chem. Comm.*, 1971, 1429.

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