More [4,5] Sigmatropic Rearrangements

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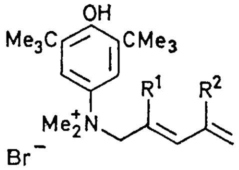
Summary The *N*-pentadienyl-2-oxyanilinium ylides derived from the salts (**2**) rearrange at 0° by competing [1,4] and [4,5] sigmatropic processes to give the ethers (**6**) and the phenols (**7**).

The sigmatropic rearrangement reactions of 2- and 4-oxyanilinium ylides give products that, for the most part, result from allowed concerted processes.[1] In view of these results and the observation[2] of the symmetry-allowed [4,5] sigmatropic rearrangements of a number of acyclic ammonium ylides, it was of interest to examine the rearrangement reactions of the *N*-pentadienyloxyanilinium ylides derivable from the salts (**1**) and (**2**). These salts were in all cases prepared by alkylation of the dimethylaniline derivative with the appropriate pentadienyl bromide in acetonitrile. The assigned configurations of the double bonds in these salts and their rearrangement products are based upon n.m.r. coupling constant data (4′- and 5′-methylpentadienyl systems) and comparison with compounds of known configuration[2] (2′-methylpentadienyl systems).

The reactions of the salts (**1a**) and (**1b**) with methanolic sodium methoxide at 0° both gave the same enamine (**3**), identified on the basis of spectroscopic properties and hydrolysis with hydrated silica gel, which gave the enedione (**4**). Although in the case of the salt (**1a**) this product (**3**) could be the result of a [4,5] rearrangement of the corresponding ylide, it is more likely in both cases (**1a**) and (**1b**) that the ylide initially undergoes a [2,3] rearrangement giving the dienone (**5**), and that this is followed by a [3,3] rearrangement to give the enamine (**3**) (*cf.* ref. 1).

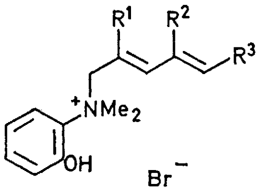
The 2-oxyanilinium ylide derived from the *trans,trans*-5-methylpentadienyl salt (**2a**) rearranges at 0° to give a mixture of the ether (**6a**; 53%) and the phenol (**7a**; 13%). The structural relationship between these two products was clearly established by heating the ether (**6a**) (boiling benzene solution, 7 days) which gave a quantitative yield of the phenol (**7a**) by a [5,5] sigmatropic rearrangement.[3] The indicated stereochemistry of the ether (**6a**) and the phenol (**7a**) is consistent with this observation as are the observable n.m.r. coupling constants. The salts (**2b**) and (**2c**) also rearranged on treatment with aqueous base at 0° to give mixtures of the corresponding ethers, (**6b**; 14%) and (**6c**; 22%) and the pentadienyl phenols, (**7b**; 57%) and (**7c**; 20%) respectively. The ether (**6b**) could be converted into the phenol (**7b**) by heating it (boiling xylene solution, 24 h). The specificity of the rearrangements, (**2a**) → (**6a**) + (**7a**), (**2b**) → (**6b**) + (**7b**), and (**2c**) → (**6c**) + (**7c**), establishes that the ethers are produced by a [1,4] rearrangement[1,4] and the phenols by a [4,5] rearrangement. Products resulting from consecutive [2,3] and [3,3] rearrangements could not be detected. The established configurational relationships between the phenols (**7**) and the salts (**2**) indicate that the configuration of the [4,5] rearrangement is that shown diagramatically in (**8**) (*cf.* type [B], ref. 2).



(1)

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

b; R^1 = H, R^2 = Me

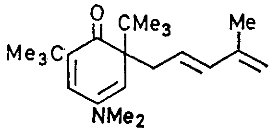


(2)

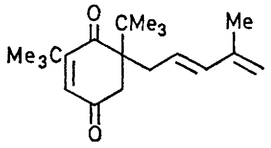
a; R^1 = R^2 = H, R^3 = Me

b; R^1 = Me, R^2 = R^3 = H

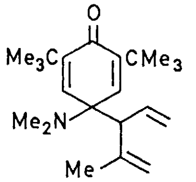
c; R^1 = R^3 = H, R^2 = Me



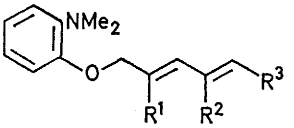
(3)



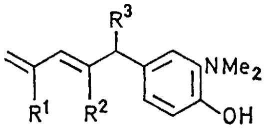
(4)



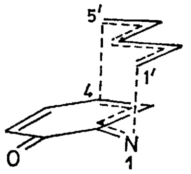
(5)



(6)



(7)



(8)

In (6) and (7) a; R^1 = R^2 = H, R^3 = Me

b; R^1 = Me, R^2 = R^3 = H

c; R^1 = R^3 = H, R^2 = Me

In anionic [4,5] sigmatropic rearrangements eight stereochemical possibilities can be associated with suprafacially participating 4-atom and 5-atom units. Examples having transition state geometries [A] and [B] (see ref. 2) have been recognised and the search for alternative transition state geometries continues.

(*Received*, 16*th April* 1973; *Com.* 540.)

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