Rearrangement Reactions of 1-*NN*-Dimethylaminobenzobarrelene Derivatives (Benzobarrelene = 1,4-Dihydro-1,4-ethenonaphthalene)

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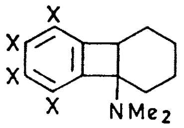
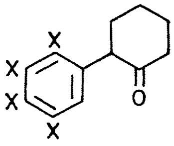
Summary The title compounds are rearranged to 4-*NN*-dimethylaminobiaryl derivatives on being heated in protic media; however, that the driving force for the rearrangement does not involve the aromatisation step has been shown by the isolation of a 4,4-disubstituted cyclohexadienone in one example.

WE have found that compounds of the type (**1**; $X = F$ or Cl) are much less stable than the analogous non-halogenated compounds, *e.g.* (**1**; $X = H$).† The compounds (**1**; $X = F$ or Cl) undergo rapid ring opening and hydrolysis in protic media to form 2-arylcyclohexanones (**2**; $X = F$ or Cl). These results prompted similar investigations of the title compounds.



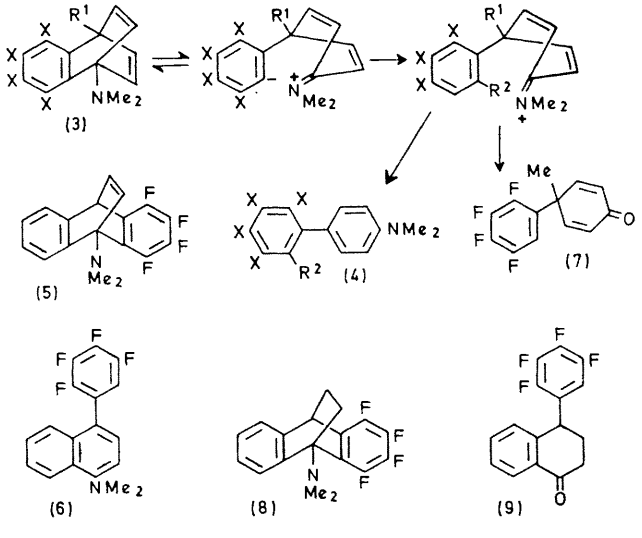
(1)



(2)

When the compound (**3**; $X = F$, $R^1 = H$)‡ was heated under reflux in aqueous ethanol it was converted slowly into the biphenyl (**4**; $X = F$, $R^2 = H$) in almost quantitative yield. That the isomerisation does not occur by an intramolecular mechanism was shown by carrying out a reaction in 1,2-dimethoxyethane in the presence of deuterium oxide, when (**4**; $X = F$, $R^2 = D$) was isolated. No deuteriation of (**4**; $X = F$, $R^2 = H$) occurs under the same conditions. The compound (**3**; $X = Cl$, $R^1 = H$) similarly gave (**4**; $X = Cl$, $R^2 = H$) quantitatively.

In order to distinguish between a number of different mechanistic pathways, we have studied similar reactions with the compounds (**5**) and (**3**; $X = F$, $R^1 = Me$). The compound (**5**) was rearranged in aqueous diglyme to form only one naphthalene derivative (**6**). The isolation of the dienone (**7**) from the hydrolysis of (**3**; $X = F$, $R^1 = Me$) shows that the driving force for the rearrangement does not involve the aromatisation step. Similarly, the compound (**8**) gave the α-tetralone (**9**). Satisfactory analytical and spectroscopic data were obtained for all of the compounds described.



SCHEME

These results suggest the mechanism shown in the Scheme.

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† The compounds (**1**) were prepared by treatment of the appropriate aryne with 1-*NN*-dimethylaminocyclohexene. Similar reactions of benzyne with enamines have been reported previously (D. J. Keyton, G. W. Griffin, M. E. Kuehne, and C. E. Bayha, *Tetrahedron Letters*, 1969, 4163).

‡ The compounds (**3**) and (**5**) were prepared by treatment of the appropriate aryne with the appropriate *NN*-dimethylaminoarene as outlined previously (H. Heaney and T. J. Ward, *Chem. Comm.*, 1969, 810).