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STEVENS REARRANGEMENTS IN DIHYDROPHENANTHRIDINIUM COMPOUNDS

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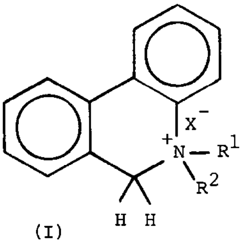
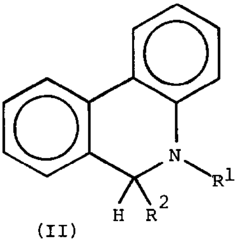
The dihydrophenanthridinium salts (I) undergo the Stevens rearrangement selectively on treatment with n-butyl-lithium, forming the 5,6-disubstituted-5,6-dihydrophenanthridines (II) and allowing migratory aptitudes to be assessed.

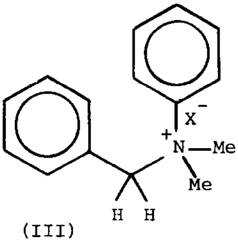
We have examined the base-catalysed rearrangements of some 5,5-disubstituted-5,6-dihydrophenanthridinium salts. The required compounds, I(a-d)*, were obtained from phenanthridine or an N-alkylphenanthridinone by established methods[1], although 5-benzyl-5,6-dihydrophenanthridine proved resistant to alkylation, presumably for steric reasons. The tetrafluoroborate I(d) was obtained eventually (in moderate yield) by the prolonged action of $[\mathrm{Me_3O^+}][\mathrm{BF_4^-}]$ in dichloromethane at room temperature: higher temperatures led to aromatisation to N-benzylphenanthridinium tetrafluoroborate.



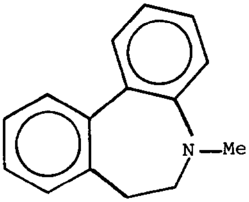
(I)



(II)



(III)



(IV)

a: $R^1=R^2=\mathrm{Me}$, X=Cl; b: $R^1=R^2=\mathrm{Et}$, X=Cl; c: $R^1=\mathrm{Me}$, $R^2=\mathrm{Et}$, X=Cl; d: $R^1=\mathrm{CH_2Ph}$, $R^2=\mathrm{Me}$, $X=\mathrm{BF_4}$.

In the presence of butyl-lithium, N-benzyl-N,N-dimethylanilinium salts (III) form, in rather low overall yields, mixtures of rearranged products from both possible ylide intermediates;[2,3] additionally, deprotonation at an N-methyl group opens both Stevens and Sommelet-Hauser pathways[4] so that direct comparisons of migratory aptitude are difficult. In the dialkyldihydrophenanthridinium salts I(a-d), molecular geometry precludes Sommelet-Hauser rearrangements involving the nucleus and when I(a) was treated with n-butyl-lithium in ether/hexane at room temperature rearrangement took place smoothly and in excellent yield, but

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*Satisfactory analytical and spectroscopic data have been obtained for novel compounds.

to II(a) alone; no evidence was found for a competing benzyl migration, which would have produced the dihydrodibenzazepine (IV). (This behaviour contrasts sharply with that of 6,7-dihydro-1,6,6,11-tetramethyl-5H-dibenz [c,e] azepinium bromide, which undergoes exclusive benzyl migration despite the introduction of considerable overcrowding consequent upon ring contraction)[5]. On treatment with butyl-lithium I(b) gave II(b) as the sole rearrangement product, with only traces of 5-ethyl-5,6-dihydrophenanthridine produced by the competing Hofmann elimination. More significantly, when I(c) was allowed to rearrange under the same conditions only II(c) was formed, in excellent yield; the marked preference for ethyl migration, relative to methyl, is striking and parallels a similar, recent observation.[6] As predicted by analogy with the behaviour of 2-benzyl-2-methyl-1,2,3,4-tetrahydroisoquinolinium salts,[7] I(d) rearranged smoothly to 6-benzyl-5-methyl-5,6-dihydrophenanthridine, II(d); qualitatively, the rate of rearrangement was considerably higher than that of any of the dialkyl analogues, the insoluble quaternary salt passing rapidly into solution upon addition of the base. The order of migratory aptitude observed in the present instance ($PhCH_2$>Et>Me) is consistent with the radical-pair mechanism[9,10] which has gained acceptance over the alternative, concerted process proposed for alkyl migration under Stevens conditions. Other, related salts are under investigation.[11]

1 B. R. T. Keene and P. Tissington, *Adv. Heterocyclic Chem.*, 1971, **13**, 315.

2 S. H. Pine, *Org. Reactions*, 1970, **18**, 403.

3 A. R. Lepley and A. G. Giumanini, reported in ref. 2.

4 C. L. Bumgardner, H. Hsu, F. Afghahi, W. L. Roberts and S. T. Purrington, *J. Org. Chem.*, 1979, **44**, 2348.

5 G. Wittig and H. Zimmermann, *Chem. Ber.* 1953, **86**, 629; H. Joshua, R. Gans and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4884.

6 K. Akiba, Y. Ohara and N. Inamoto, *Heterocycles*, 1978, **11**, 231.

7 G. Grethe, H. L. Lee and M. R. Uskokovic, *Tetrahedron Lett.*, 1969, 1937.

8 J. E. Baldwin, J. E. Brown and R. W. Cordell, *J. Chem. Soc. Chem. Commun.*, 1970, 31.

9 W. D. Ollis, M. Rey, I. O. Sutherland and G. L. Closs, *J. Chem. Soc. Chem. Commun.*, 1975, 543.

10 For a definitive account of the pathways involved see R. W. Jemison, T. Laird, W. D. Ollis and I. O. Sutherland, *J. Chem. Soc. Perkin I*, 1980, 1436.

11 M. J. S. Dewar and C. A. Ramsden, *J. Chem. Soc. Perkin I*, 1974, 1839.

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