Genesis and Reactions of Some Spirocyclohexadienyl Radicals

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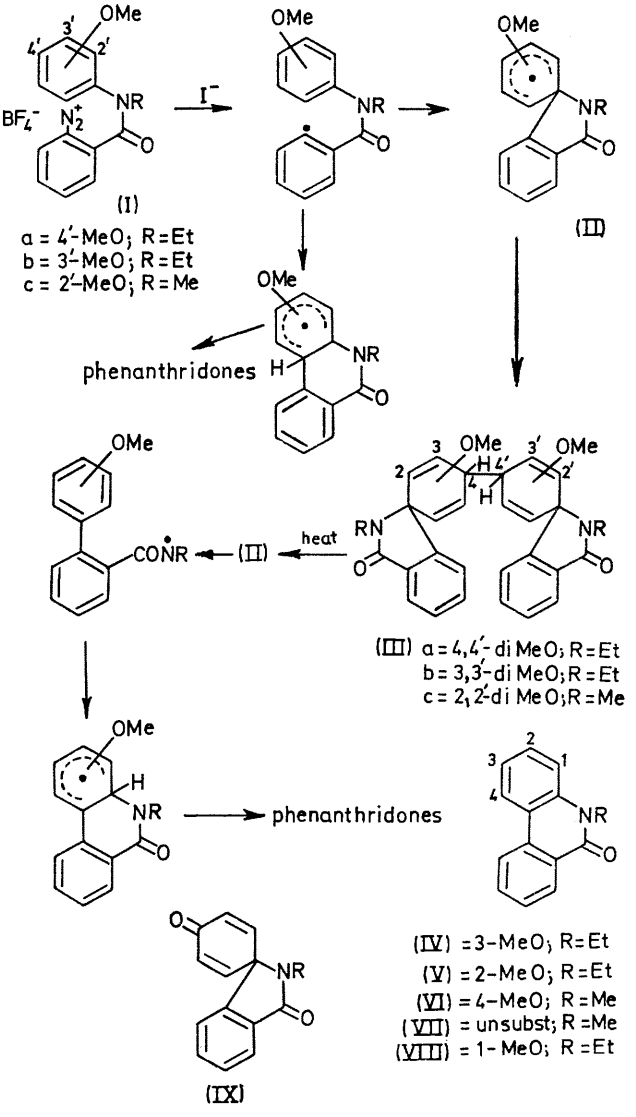
Summary Formation of the spirocyclohexadienyl dimers (III) from diazonium salts (I) by reaction with sodium iodide in acetone supports a radical mechanism for the interaction of iodide ions with diazonium compounds; pyrolysis of (III) give *N*-alkyl-phenanthridones by migration of nitrogen and not of aryl in the spirodienyl radicals (II), but pyrolytic decomposition of (IIIa) in the presence of iodine gives the dienone (IX) in high yield.



(I) a = 4'-MeO; R=Et
b = 3'-MeO; R=Et
c = 2'-MeO; R=Me

(II)

(III) a = 4,4'-di MeO; R=Et
b = 3,3'-di MeO; R=Et
c = 2,2'-di MeO; R=Me

(IV) = 3-MeO; R=Et
(V) = 2-MeO; R=Et
(VI) = 4-MeO; R=Me
(VII) = unsubst; R=Me
(VIII) = 1-MeO; R=Et

(IX)

It was shown recently that phenanthrenes could be synthesised by the reaction between stilbene-2-diazonium fluoroborates and sodium iodide in acetone.[1] When the diazonium salt (Ia) was subjected to these reaction conditions, *N*-ethyl-3-methoxyphenanthridone (IV) was formed, together with other products characteristic of the homolytic decomposition of (Ia) (*e.g.* promoted by copper[2]). In addition, a new product, isolated from the iodide-catalysed decomposition in modest yield and now also believed to be formed in the copper-promoted reaction, was the spiro-dimer (IIIa) which results from the dimerisation of the intermediate (IIa) at the methoxy-substituted carbon atom. One geometrical isomer of (IIIa), m.p. 209—210° dec., was isolated, analytically pure, by a combination of chromatography and crystallization. Coupling of cyclohexadienyl radicals at carbon bearing a substituent other than hydrogen is unusual but has been inferred previously to explain the formation of *p*-quaterphenyl from the decomposition of benzoyl peroxide in chlorobenzene.[3]

The iodide-promoted decompositions of (Ib) and (Ic) similarly gave the spiro-dimers (IIIb) and (IIIc), respectively, the latter being isolated (as a mixture of stereoisomers) in *ca.* 70% yield. The formation of products which are characteristic of free-radical processes supports the view that reaction between iodide ions and diazonium salts may quite generally involve free-radical intermediates;[4] presumably the first step is electron-transfer reduction by iodide ion.[5] In neutral (unbuffered) aqueous solution, reaction between diazonium fluoroborates and sodium iodide is negligibly slow, whilst the reaction in acetone is complete in a matter of seconds at the same temperature. The pronounced solvent-dependence probably reflects a change

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† The remarkable selectivity found in this rearrangement [compound (VIII) was absent (not more than 1%) from the products] is currently under investigation.

in the balance between the ionisation potential of the iodide ion and the electron affinity of the diazonium compound.

When compound (IIIa) was heated in boiling 1,2,4-trichlorobenzene, in the absence of oxygen, it decomposed to give *N*-ethyl-2-methoxyphenanthridone (V) in *ca.* 55% yield (assuming 2 moles/mole dimer = 100%). Formation of this product is most readily explained by rupture of the inter-cyclohexadienyl bond, followed by fission of the relatively weak C–N bond in (IIa) and subsequent recyclisation of the resulting amido-radical,[6] as shown. From earlier experiments on the pyrolysis of compounds related to (III) it had been concluded that it was the aryl group, and not nitrogen, which migrated.[7] However, pyrolyses of both (IIIb) and (IIIc) again give phenanthridones with substitution patterns consistent with their formation by 1,2-shifts of the amide nitrogen; from (IIIb), (IV) was obtained in *ca.* 80% yield,† and (IIIc) gave (VI) (23%) and unsubstituted *N*-methylphenanthridone (VII) (19%). Displacement of a methoxy-group finds analogy in the cyclisation reactions of *o*-(2-methoxyphenyl)-benzoyloxy radicals.[8] Furthermore, preliminary re-investigation of the systems studied previously[7] leads us to believe that here again nitrogen migration occurs; this aspect of the work will be elaborated in the full paper.

It was observed that the dienone (IX), a major product of decomposition of (Ia) promoted both by copper[2] and by sodium iodide, is absent from the products of pyrolysis of (IIIa), though it is found to be stable to the pyrolysis conditions. This suggests that the demethylation which leads to (IX) in the diazonium decompositions is in fact the result of an ionic reaction in which electron-transfer oxidation of (IIa) (*e.g.* by cupric ions, or by iodine) gives the corresponding carbonium ion, and the methyl group is then removed by a nucleophile. In support of this, pyrolysis of dimer (IIIa) in the presence of iodine gives a 70% yield of dienone (IX).

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[1] B. Chauncey and E. Gellert, *Austral. J. Chem.*, 1969, **22**, 993.

[2] D. H. Hey, C. W. Rees, and A. R. Todd, *J. Chem. Soc.* (*C*), 1967, 1518.

[3] D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, 1963, 5604.

[4] *E.g.*, J. D. Roberts and M. C. Caserio in "Basic Principles of Organic Chemistry," Benjamin, New York, 1964, p. 841.

[5] *Cf.* D. H. Hey, G. H. Jones, and M. J. Perkins, *Chem. Comm.*, 1969, 1375; Dr. Chauncy has informed us that a similar mechanism has been inferred for the phenanthrene synthesis.[1]

[6] Formation of phenanthridones by cyclisation of biphenyl-2-carboxamido-radicals has been observed in these laboratories [D. H. Hey, G. H. Jones, and M. J. Perkins, *J. Chem. Soc.* (*C*), in the press] and by P. M. Brown, P. S. Dewar, A. R. Forrester, A. S. Ingram, and R. H. Thomson, *Chem. Comm.*, 1970, 849. We are grateful to Professor Thomson and Dr. Forrester for valuable exchange of information prior to publication.

[7] D. M. Collington, D. H. Hey, and C. W. Rees, *J. Chem. Soc.* (*C*), 1968, 1026.

[8] D. I. Davies and C. Waring, *J. Chem. Soc.* (*C*), 1967, 1639; P. M. Brown, J. Russell, R. H. Thomson, and A. G. Wylie, *ibid.*, 1968, 842.