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INTRAMOLECULAR CYCLISATION REACTIONS OF 2-ALKYLBIPHENYL-2'-YLDIAZONIUM SALTS

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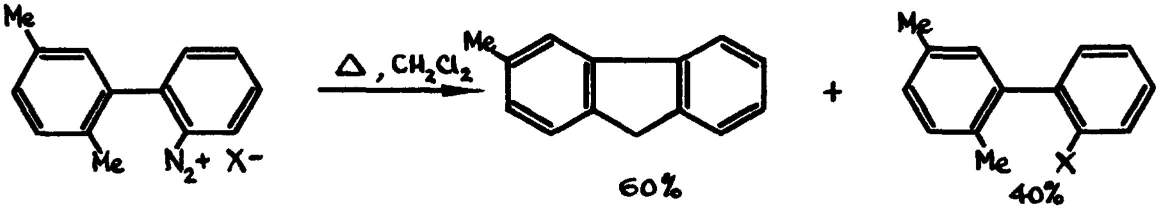
Our interest in nucleophilic cyclisation reactions of 2-alkoxybiphenyl-2'-yldiazonium salts[1] prompted us to re-investigate certain aspects of the Mascarelli reaction. We were particularly interested to obtain evidence concerning the possible steps involved in these interesting reactions. At the time we commenced our study there was no general agreement as to whether aryl cations were really involved in the heterolytic dediazoniation reactions.[2] Good evidence for the involvement of aryl cations is now available.[3]

It was shown at an early stage[4] that although 2-methyl- and 2-ethyl-biphenyl-2'-yldiazonium salts gave, in aqueous solution, fluorene and 9-methylfluorene respectively, in aqueous acidic media 2-methyl-6,6'-disubstituted-biphenyl-2'-yldiazonium salts do not afford 4,5-disubstituted-fluorenes.[4a] This latter result is evidently related to the inability of the two aryl residues to achieve co-planarity in a key intermediate. Thus 5-amino-4-methylphenanthrene does give 4,5-methanophenanthrene in 50% yield after diazotisation.[5] A number of other examples of the Mascarelli reaction involving polymethylbiphenyls has been reported.[6] Included in these is the report that whereas 2,4,4',5,5'-pentamethylbiphenyl-2'-yldiazonium salts afford 2,3,6,7-tetramethylfluorene in almost constant yield (47% ± 5%) in aqueous solution at a range of acidities, the corresponding diazonium fluoroborate gave the fluorene derivative in only 25% yield. Our experiments with the alkoxyarenediazonium salts have been carried out using dry diazonium salts in non-aqueous solvents and hence in the present study we used similar conditions.

A number of possible mechanisms can be envisaged. These include the involvement of hydride ion abstraction by an initial aryl cation, a [1,5] shift in the examples quoted, to give a benzyl cation,[7] and proton loss from the alkyl group to give a dipolar ion which could react as a cyclohexadienyl carbene.[6] We should in addition not discount radical mechanisms or a mechanism involving a penta-co-ordinate carbo-cation.

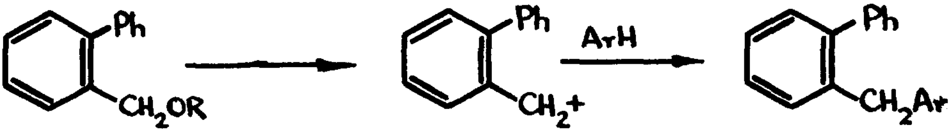
In our experiments we observed that the biarenediazonium chlorides and bromides gave fluorenes and 2-halobiaryls in methylene chloride in ratios which were unaffected either by the addition of bromotrichloromethane or by carrying out the reactions by passing either oxygen or nitrogen through the solutions. (Equation 1)



(1)

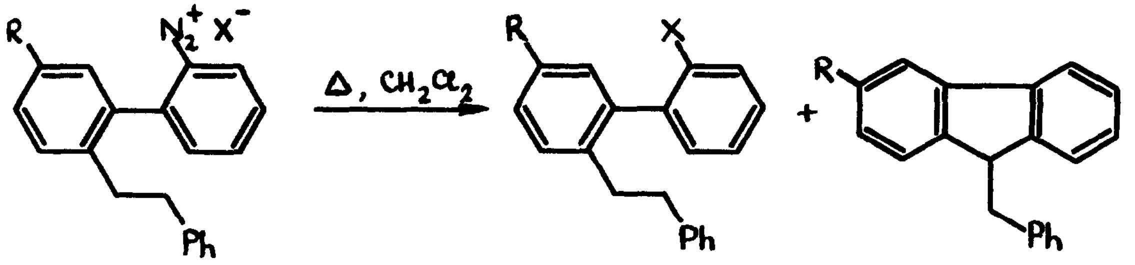
In particular we did not detect the presence of the bromobiaryls using an arenediazonium chloride in the reactions carried out in the presence of bromotrichloromethane. Similarly the reactions of the arenediazonium bromides in dichloromethane did not give chlorobiaryls. It is therefore unlikely that radical reactions are involved. The cyclisation of the arenediazonium salts to fluorene derivatives also proceed in benzene.

The possible intermediacy of 2-phenylbenzyl cations may be checked by generating such species by alternative routes. When 2-phenylbenzyl alcohol was heated in benzene solution with Amberlist-15 no fluorene was detected by gas chromatography and 2-phenyldiphenylmethane was isolated in 90% yield. The high reactivity of the 2-phenylbenzyl cation is indicated by the fact that a repeat reaction carried out in nitrobenzene gave 3-nitro-2'-phenyldiphenylmethane, which was isolated in 30% yield. The intermediacy of the 2-phenylbenzyl cation, in these reactions, was shown by obtaining the same products when 2-phenylbenzylchloroformate was treated, in benzene (98% yield) or nitrobenzene (30% yield), with silver(I) hexafluoroantimonate (Equation 2). The reactions of alkylchloroformates with silver(I) salts are knwon to involve 'hot' alkyl cations.[8] A reaction of 2-phenylbenzyl alcohol with Amberlist-15 in cyclohexane proceeded slowly and gave fluorene in 60% yield.



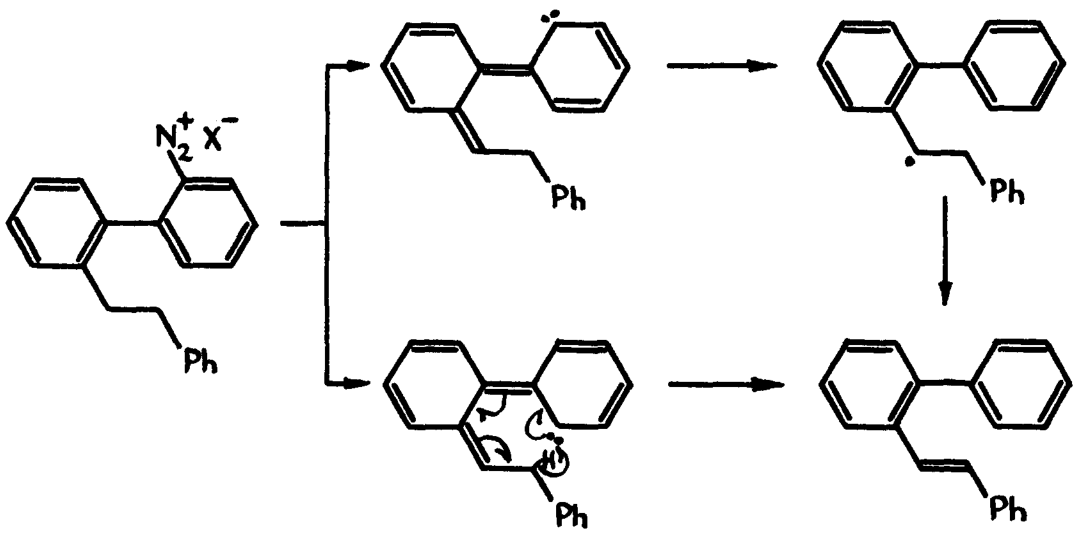
(2)

The possible involvement of benzyl cations was also checked by carrying out the dediazoniation reactions of diazonium salts derived from 2-amino-2'-(β-phenylethyl)biphenyl and 2-amino 2'-(β-phenylethyl)-5'-methylbiphenyl. Abstraction of hydride ion by an aryl cation might have been expected to proceed to give two different benzylic cations. No 9-phenyl-9,10-dihydrophenanthrene or 2-phenylstilbene was detected in these reactions: we only isolated 9-benzylfluorenes (Equation 3), together with 2-halo-2'-(β-phenylethyl)biphenyls.



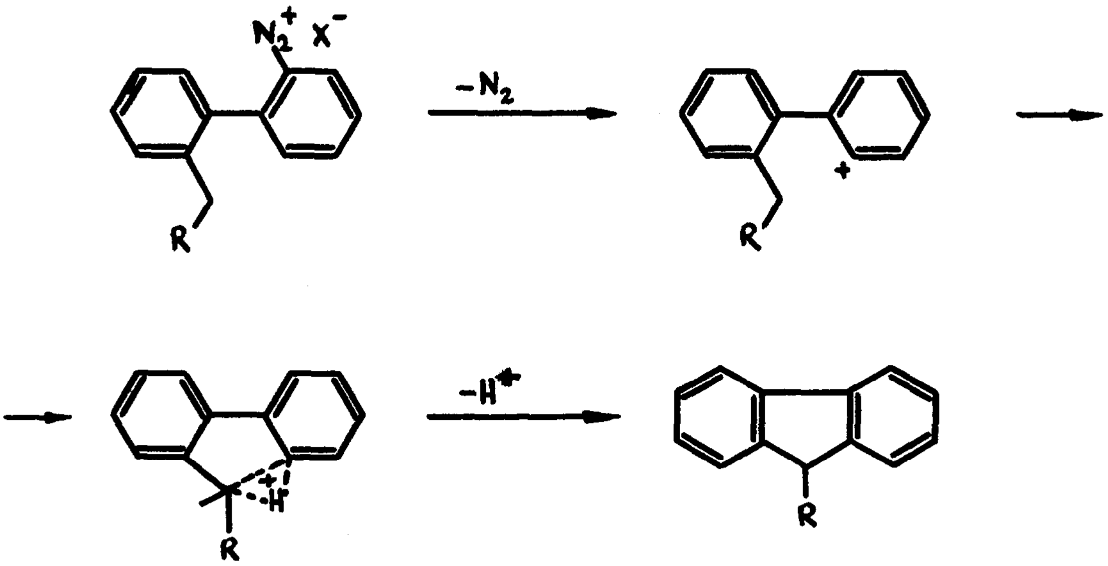
(3

The possible involvement of cyclohexadienyl carbenes is more difficult to exclude. The generation of carbenes by the loss of nitrogen from 3,5-dibromo- and 3,6-dichloro-benzene-1,4-diazo-oxide in arenes such as benzene gave biaryls.[9] However, although in our reactions we did not observe attack on benzene, such reactions may be precluded for steric reasons. On the other hand certain carbene insertion reactions are known to proceed by hydrogen abstraction[10] and, as shown in Equation 4, a carbene generated from 2-(β-phenylethyl)-biphenyl-2'-yldiazonium salts might have been expected to afford 2-phenylstilbenes. None was detected.



(4)

In our view, the most satisfactory explanation of the mechanism of the Mascarelli reaction (shown in Equation 5) involves the loss of a proton from a pentaco-ordinate carbon species.[11]



(5)

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