The Role of Hydrogen Iodide in Free-radical Reactions: the Reaction with *N*-Methylbenzanilide-2-diazonium Fluoroborate

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Summary The title reaction proceeds smoothly in methylene chloride to give *N*-methylphenanthridone (V) and 2-methyl-3-oxoisoindoline-1-spiro-1′-cyclohexa-2′,5′-diene (VI).

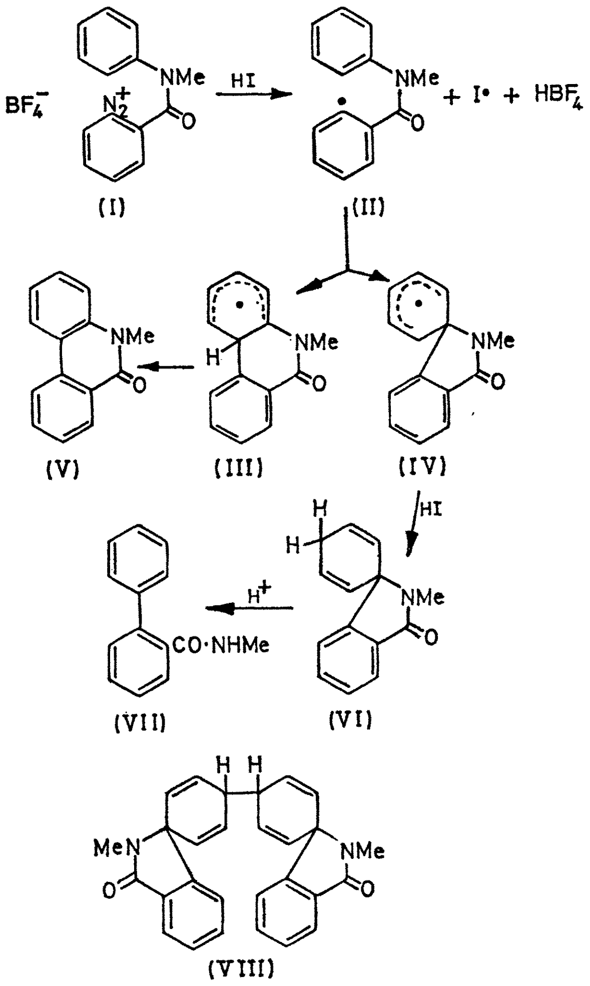
THE formation of phenanthridone by photolysis of 2-iodobenzanilide was described recently.[1] In an extension[2] of this reaction to *N*-alkyl-2-iodobenzanilides (designed to probe the relationship between the photochemical reaction and the radical decomposition of the corresponding *N*-alkylbenzanilide-2-diazonium salts), traces of by-products were identified which appeared to require the intervention of hydrogen iodide or iodine produced in the photolysis system. We were therefore prompted to investigate the genesis and fate of *N*-methyl-2-kenobenzanilide (II)† in the presence of an excess of iodine and/or hydrogen iodide.

When hydrogen iodide is bubbled through a well-stirred suspension of *N*-methylbenzanilide-2-diazonium fluoroborate (I) in dry oxygen-free methylene chloride at room temperature, rapid dissolution of the salt occurs. After *ca.* 5 min., the homogeneous reaction mixture contains two major products which together account for 80% of the diazonium salt. These have been identified as *N*-methylphenanthridone (V) (35%) and a new spiro-diene (VI) (45%). The latter product (m.p. 63—65°) was identified by analytical and spectroscopic data, together with the fact that prolonged exposure to hydrogen iodide caused isomerisation to *N*-methyl-2-phenylbenzamide (VII).‡ The same isomerisation is also catalysed by base.

In other reaction systems in which the radical (II) is produced in the absence of iodine or hydrogen iodide,[2,4] the major products from the isomeric spiro-dienyl radical (IV) are dimers, though some interception by oxygen has also been inferred.[4] In the present instance the very high reactivity of hydrogen iodide as a homolytic hydrogen donor is manifesting itself. The radical (IV) is in fact efficiently intercepted by hydrogen iodide before dimerisation can occur. This type of reactivity of hydrogen iodide does not appear to have been widely recognised,[5] despite the low dissociation energy (71 kcal. mole^{-1}) of the molecule.§

The second significant feature of the reaction described here is the molecule-induced homolysis of the diazonium salt. The formation of aryl iodides by reactions between diazonium salts and iodide ion is, of course, well known. However, reactions between hydrogen iodide and diazonium salts in nonpolar media do not appear to have been reported. We consider an electron-transfer process to be the most plausible mechanism,[6,7] analogous to that discussed for the reaction between iodide ion and peroxides.[8] The reaction between hydrogen iodide and di-t-butyl peroxide in dry carbon tetrachloride has been noted,[9] and seems to fit into a similar general pattern.

Unsuccessful attempts to synthesise the spirodiene (VI) were described by Collington, Hey, and Rees,[10] who regarded it as a suitable precursor from which to obtain the dimer (VIII) of radical (IV). As predicted by these workers, it is now found that reaction of (VI) with butoxy-radicals (from di-t-butyl peroxyoxalate) does in fact lead to the required dimer which is isolated as a mixture of three stereoisomeric forms.[2]



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† The use of "keno" as a prefix to signify a radical site has been advocated recently.[3] It implies the removal of a hydrogen atom from the position indicated.

‡ The diene and its rearrangement product are not readily separated, either preparatively or by analytical g.l.c., and the interesting possibility that a small quantity of amide may be formed directly in a homolytic reaction has not been ruled out.

§ It is possible that the isomeric intermediate (III) may also be intercepted by hydrogen iodide. However, in this case the resulting diene could be oxidised irreversibly to (V) by the iodine which accumulates during the reaction.

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