Tetrahedron Letters No.20, pp. 1503-1507, 1965. Pergamon Press Ltd.
Printed in Great Britain.

REACTION OF ARYLDIAZONIUM SALTS WITH DIMETHYLFORMAMIDE

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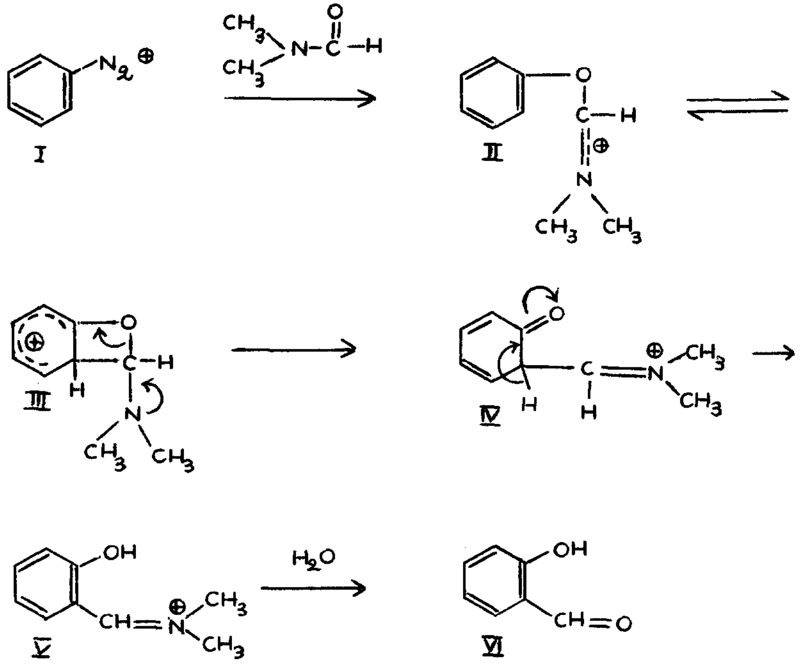
(Received 23 February 1965; in revised form 30 March 1965)

Addition of *solid* benzenediazonium chloride into a I:I mixture of benzene-dimethylformamide at 60-70°C and subsequent addition of water results in the formation of salicylaldehyde (I7% yield)(I). It was identified as the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 248°C (lit.(2) 248°C). The same product is obtained from benzenediazonium sulphate or fluoroborate, though in a somewhat lower yield. From the reactions of substituted aryl diazonium chlorides with dimethylformamide it became obvious that the hydroxy group of the derived salicylaldehyde occupied the place of the nitrogen and the aldehyde was *ortho* to this position.

Thus p-tolyldiazonium chloride afforded 2-hydroxy-5-methyl-benzaldehyde, o-tolyldiazonium chloride afforded 2-hydroxy-3-methyl-benzaldehyde (5-I0% yield) and β-naphthyldiazonium chloride produced 2-hydroxy-I-naphthaldehyde (I0-20% yield).

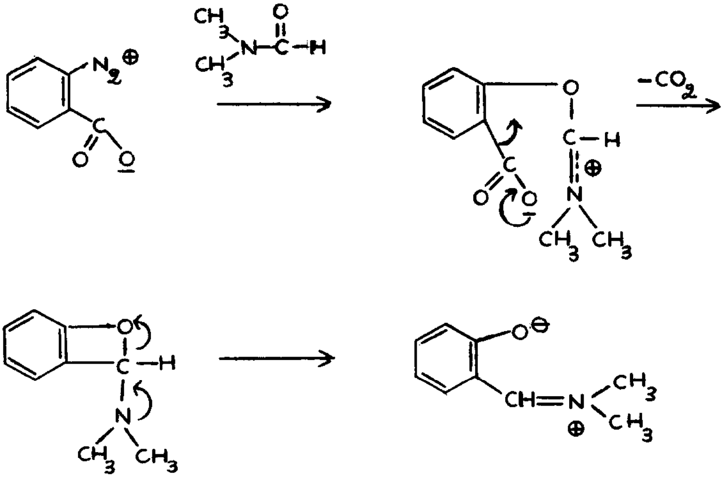
The substitution of the nitrogen by the hydroxy group and formation of ortho-aldehydes can be rationalized by the following mechanism(3) :



The tendency of a formamide's carbonyl-oxygen to be attached to an electron-poor center (step I) is well exemplified in the Vilsmeier reaction(4) and the reaction.

of formamides with acid chlorides(5). Intermediates such as (II) ensue(4,5). Their positive charge explains a subsequent intermolecular attack on an electron-rich site (step III) such as in the Vilsmeier reaction. A case of an intramolecular electrophilic attack by a similar intermediate, which had been isolated, has recently been clarified(6,7). Step IV is a ring-chain tautomerism. Finally hydrolysis of imine (V) furnishes the salicylaldehyde.

With benzenediazonium-2-carboxylate(8,9) 32% of salicylaldehyde is formed under the same conditions. In this case the intramolecular electrophilic substitution is preferential to the site of the carboxylate anion and is therefore accompanied



by evolution of carbon dioxide. With 4-chloro-benzenediazonium-2-carboxylate, 2-hydroxy-5-chlorobenzaldehyde, m.p. 52.5°C (lit.(10) 52.5°C), was isolated in 30-40% yield after base extraction. The predominance of this isomer also supports the former mechanism, though some benzyne contributions remain as a possibility.

Acknowledgement. The author gratefully acknowledges the assistance and advice of Professor R. Breslow during the performance of this work.

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