Duality of Mechanism in Reactions of *o*-Halogenobenzenediazonium Ions with Sodium Methoxide in Methanol

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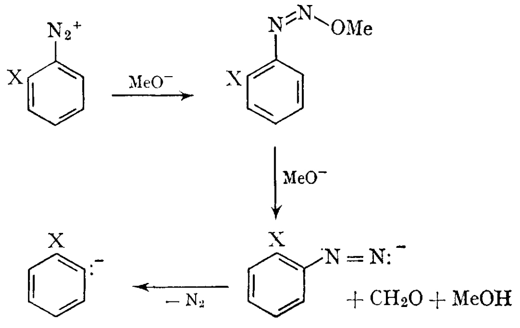
THE reactions of *o*-chloro- and *o*-bromo-benzenediazonium fluoroborates with NaOMe in methanol afford chlorobenzene in 70—93% yields and bromobenzene in 67—86% yields, depending somewhat on the NaOMe concentration. The corresponding *o*-halogenophenylazo phenyl sulphones, $o\text{-}XC_6H_4N{=}NSO_2{\cdot}Ph$, are similarly converted into halogenobenzenes.

The reaction of *o*-chlorobenzenediazonium fluoroborate with NaOMe was run in *O*-deuteromethanol (MeOD) solution in order to ascertain the origin of the hydrogen atom which takes the place of the diazonium group. The outcome was discovered to be remarkably dependent on the NaOMe concentration. The chlorobenzene from reaction with one mole of NaOMe per mole of diazonium salt had an infrared spectrum indistinguishable from that of ordinary chlorobenzene, and by mass-spectrometric analysis was 97% C_6H_5Cl and 3% C_6H_4DCl. The chlorobenzene from reaction of the diazonium salt with 2M-NaOMe in MeOD (40-fold excess of base) matched in its infrared spectrum the best sample of 1-chloro-2-deuterobenzene prepared by Zoltewicz and Bunnett,[1] and by mass spectrometer comprised 10% C_6H_5Cl and 90% C_6H_4DCl. Nearly identical observations were made in respect to reactions of *o*-chlorophenylazo phenyl sulphone with NaOMe in MeOD.

The reactions of the analogous bromo-compounds were investigated only in ordinary methanol, but again a sharp difference in behaviour was noted, now in regard to the amount of bromide ion liberated. Reactions of either *o*-bromobenzenediazonium fluoroborate or *o*-bromophenylazo phenyl sulphone with 2M-NaOMe in MeOH afforded 8% of bromide ion and 7—8% of anisole, plus bromobenzene. Reactions with one molar equivalent of NaOMe gave, besides bromobenzene, only 1% of bromide ion and about the same percentage of anisole.

The formation of 1-chloro-2-deuterobenzene in MeOD and liberation of 8% of bromide ion in MeOH testify that the reactions with 2M-NaOMe proceed for the most part *via* *o*-halogenophenyl anion intermediates. *o*-Chlorophenyl anion, as a carbanion, captures a deuteron from MeOD. The partitioning of *o*-bromophenyl anion in methanol between proton capture and bromide ion loss (forming benzyne and thence anisole) is known to give bromide ion in about 11% yield.[2,3]

A possible mechanism for generation of *o*-halogenophenyl anions involves initial co-ordination of diazonium ion with methoxide ion to form a covalent diazo-ether, and then attack of methoxide ion on methyl hydrogen initiating an *E*2 fragmentation:



(Arylazo phenyl sulphones are known to dissociate reversibly to diazonium and benzenesulphinate ions,[4] and we have spectral evidence for benzenesulphinate ion as a by-product.) Another possibility, suggested by Dr. Christoph Rüchardt, is that the diazonium ion captures a hydride ion from methoxide ion. The resulting aryldi-imide then decomposes under strongly alkaline conditions to aryl anion and nitrogen.

The formation of mainly chlorobenzene in MeOD and liberation of only 1% of bromide ion in MeOH indicate that the reactions with an equimolar amount of NaOMe occur only to a slight extent *via* *o*-halogenophenyl anion intermediates. Such behaviour is, however, consistent with the intermediacy of *o*-halogenophenyl radicals. Evidence that the decomposition of diazonium ions in mildly alkaline methanol occurs *via* radical intermediates has been presented by DeTar and Turetzky,[5] and further evidence will be described in a subsequent publication from this laboratory.

Details of the radical mechanism are uncertain. A mechanism has been proposed by DeTar and Turetzky.[5] Alternatively, an adaptation of the mechanism of Rüchardt and Merz[6] for the Bachmann–Gomberg reaction is conceivable, provided that aryldiazotate ions can be formed in the system.

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[1] J. A. Zoltewicz and J. F. Bunnett, *J. Amer. Chem. Soc.*, 1965, **87**, 2640.

[2] J. F. Bunnett and D. A. R. Happer, *J. Org. Chem.*, in the press.

[3] *Cf.* R. W. Hoffmann, *Chem. Ber.*, 1965, **98**, 222.

[4] C. D. Ritchie, J. D. Saltiel, and E. S. Lewis, *J. Amer. Chem. Soc.*, 1961, **83**, 4601.

[5] D. F. DeTar and M. N. Turetzky, *J. Amer. Chem. Soc.*, 1955, **77**, 1745; 1956, **78**, 3925, 3928.

[6] C. Rüchardt and E. Merz, *Tetrahedron Letters*, 1964, 2431.