Reaction of 2,4-Dinitrobenzenediazonium ions with Thiophens. An Acidic Gomberg Reaction

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Summary 2,4-Dinitrobenzenediazonium ions react with thiophen and both methylthiophens in acidic media to yield the corresponding dinitrophenylthiophens; under similar reaction conditions benzene was recovered unchanged, while anisole and the diazonium salt couple to give the corresponding azo-dye; thianaphthen also arylates but 2- and 3-methylthianaphthen couple to give azo-dyes.

3-HYDROXYTHIOPHEN[1] and 2-acetoaminothiophen[2] couple with diazonium salts to yield the expected azo-dyes. The only reported reactions of thiophen itself with diazonium salts are arylation reactions carried out specifically under conditions in which arylation occurs with benzene and would be expected with thiophen also.[3] Treatment of thiophen with 2,4-dinitrobenzenediazonium ions in acetic acid–aqueous sulphuric acid medium yielded 2-(2,4-dinitrophenyl)thiophen, m.p. 60° (25%) and 2,5-bis(2,4-dinitrophenyl)thiophen, m.p. 172° (12%). The reaction time was 24 h during which period 75% of the theoretical nitrogen was evolved. Benzene treated under similar conditions did not react, no nitrogen was evolved, and diazonium salt was still present at the end of the reaction. Anisole coupled with the diazonium salt to yield 2,4-dinitro-4′-methoxy-azobenzene[4] (26%). With 2-methyl- and 3-methyl-thiophen arylation was the only observed reaction. Likewise thianaphthen underwent arylation to yield 2-(2,4-dinitrophenyl)thianaphthen, m.p. 104° (49%) and 2,3-bis(2,4-dinitrophenyl)thianaphthen, m.p. 120° (13%). In contrast to these arylation reactions, 2-methyl- and 3-methyl-thianaphthen coupled with the diazonium salt to yield the azo-dye 3-(2,4-dinitrophenyl)azo-2-methylthianaphthen m.p. 182° and 2-(2,4-dinitrophenyl)azo-3-methylthianaphthens m.p. 190° respectively. These reactions and the coupling of t-butylthiophen and polymethylthiophens (see following communication) are the first reports of hydrocarbon thiophens undergoing coupling reactions.

An analogous case where the aromatic species appears to initiate arylation, is in the reaction of ferrocene with diazonium salts.[5] Ferrocene is arylated rapidly by benzene diazonium chloride, but thiophen is unaffected by benzene diazonium ions, although arylation occurs with 4-nitrobenzenediazonium ions. There seems little reason to doubt that the reaction involves a one-electron transfer from the thiophen nucleus to the diazonium salt. The reaction must occur within the solvent cage since no tetranitrobiphenyl or bithiophen is formed, and indeed the reactions are clean and free from any of the polymeric products usually associated with the Gomberg reaction. The methyl thianaphthens and polymethylthiophens (see following communication) couple. The factors which govern the choice of reaction path remain obscure. As far as we are aware no similar acidic Gomberg reaction initiated by an heterocyclic aromatic nucleus has been reported.

The arylated thiophens and azo-thianaphthens are new compounds; analysis figures and relevant spectral data *etc.* are consistent with the proposed structures.

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