“Ionic liquids”, i.e., organic salts with melting points below room temperature, have been known for many years. A major advance in this area in the last few years has been the discovery of a new class of ionic liquids, the 1-alkyl-3-methylimidazolium tetrafluoroborates and hexafluorophosphates (1).\(^1\)\(^2\) These substances, particularly the 1-butyl tetrafluoroborate, have attracted widespread attention as polar, non-volatile, recyclable solvents for organic synthesis. Ionic liquids, being electrolytes as well as solvents, would appear to be attractive media for organic electrochemistry. Although a few applications to the electrochemical behavior of inorganic and organometallic substances have been reported,\(^3\)\(^4\) to our knowledge no organic systems have been studied in these media. We have examined, \textit{inter alia}, the cyclic voltammetric behavior of nitrobenzene and the 1,2, 1,3-, and 1,4-dinitrobenzenes in a series of 1-alkyl-3-methylimidazolium tetrafluoroborates (R = ethyl, n-butyl, sec-butyl, hexyl, and octyl) without added supporting electrolyte Significant ion-pairing effects are observed, particularly between the medium and the dianions of the dinitro compounds. On the other hand, charging currents are relatively high in these media, and diffusion coefficients are 50-100 times smaller than in conventional organic solvents; voltammetry is therefore of necessity carried out at relatively high concentrations of electroactive substance, typically \textit{ca}. 10 mM. Addition of acetic anhydride to the voltammetric solutions produces major changes in the voltammetry. The controlled-potential reduction of the nitro compounds was therefore carried out in 1-n-butyl-3-methylimidazolium tetrafluoroborate in the presence of acetic anhydride. The major products are 1-N,O-diacetylhydroxylamino-X-nitrobenzenes (2), presumably formed via the corresponding nitroso compounds. Products can be extracted from the ionic liquid with toluene, hence it is possible to use the same batch of ionic liquid for several successive electrolyses.

\(\text{R}^{+}\text{N}=\text{N}-\text{Me}^-\text{X}^-\) \(\text{1}\)

\(\text{2a} \quad \text{X} = \text{H}\)

\(\text{2b} \quad \text{X} = \text{OAc}\)


