σ- and π-Aryl Nitrenium Ions

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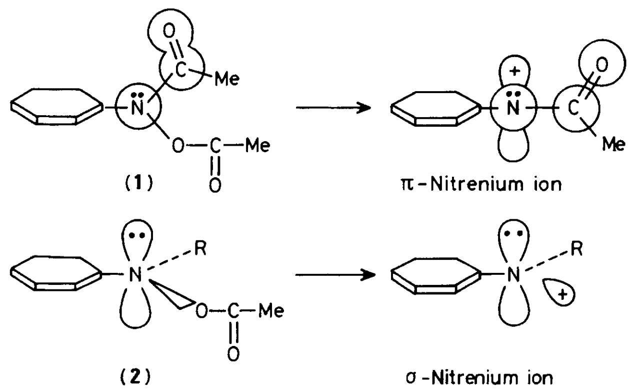
It is suggested that *N*-acyl-*N*-acetoxyarylamines solvolyse readily *via* a π-nitrenium ion, whereas *N*-alkyl-*N*-acetoxyarylamines, which would have to react *via* a σ-nitrenium ion, are stable to solvolysis.

Aryl nitrenium ions[1] have continued to be of interest for, among other things, their possible intermediacy in the solvolysis of *N*-acyl-*N*-acetoxyarylamines, (**1**), and *N*-alkyl-*N*-acetoxyarylamines, (**2**). We suggest that solvolysis of compounds of the type (**1**) and (**2**) would lead to different kinds of nitrenium ions, a π-nitrenium ion in the former case and a σ-nitrenium ion in the latter case. (This distinction is analogous to the one developed for the succinimidyl radical by Hedaya[2] and by Skell.[3])

The lowest energy conformation of an *N*-acetyl-*N*-acetoxyarylamine, (**1**), is the one in which the nitrogen n electrons are conjugated with the amide carbonyl group.



Solvolysis from this conformation can lead directly to a π-nitrenium ion in which the positive charge is delocalized into the aromatic system. This delocalization should be partially present in the transitition state leading to the nitrenium ion, thus facilitating the solvolysis.

The lowest energy conformation present in an *N*-alkyl-*N*-acetoxyarylamine, (**2**), is the one in which the nitrogen n electrons are conjugated with the aromatic ring. Ionization from this conformation would lead to a high energy σ-nitrenium ion in which the orbital developing the positive charge is not conjugated with the aromatic ring. [Alternately, a π-nitrenium ion could be generated from a conformation 90° away along the aromatic-*N* axis, however, this would require the energy of uncoupling the nitrogen n electrons in (**2**) from ring conjugation.] This stereoelectronic effect should retard the solvolysis of compounds of type (**2**).

There is evidence in the literature for the facile solvolysis of compounds of type (**1**).[4] We now present evidence for the lack of reactivity of compounds of type (**2**).

N-Acetoxy-*N*-t-butylaniline[5] (**2**, R = Bu^t) [m.p. 35—37 °C, i.r. (neat) 2960, 1790, 800, 695 cm^{-1}; n.m.r. ($CDCl_3$), δ 1.23 (s, 9), 2.10 (s, 3), 7.32 (br. s, 5)] (3.6×10^{-2} M), lithium acetate (2.8 M), and acetic acid (2.4×10^{-1} M) in methanol solvent was deaerated and then heated at 50 °C for 20 h. On work-up a 97% yield of starting material was obtained, having i.r. and n.m.r. spectra identical with those of (**2**). This experiment was repeated in benzene solvent yielding a 96% recovery of starting material.

By contrast, solvolysis of compounds of type (**1**)[4a,b] yielded complete conversion into products under similar conditions, probably[6] *via* a nitrenium ion intermediate.

The greater reactivity in a nitrenium ion forming reaction of a compound having an electron withdrawing acyl group [*i.e.*, (**1**)] strikes us as sufficiently odd to require explanation. We suggest that the σ- *vs.* π-nitrenium ion hypothesis advanced above fills this need.

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