Thermolysis of 1-(*N*-Acetyl-*N*-aryl)amino-2,4,6-triphenylpyridinium Tetrafluoroborates: A New Source of Arylnitrenium Ions

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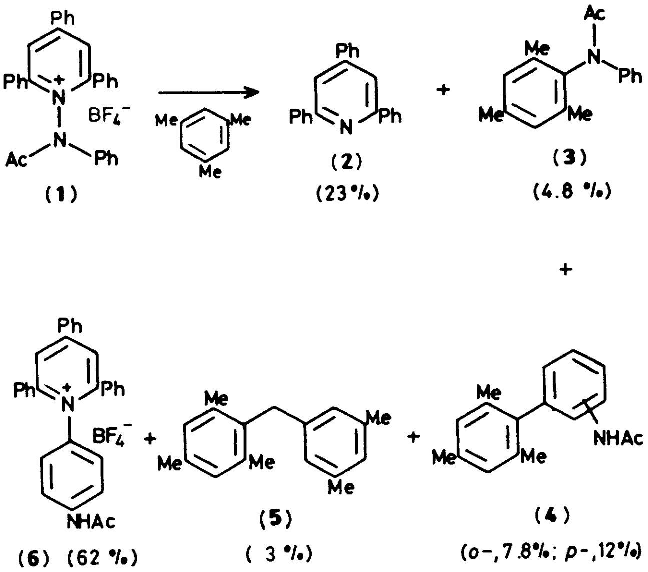
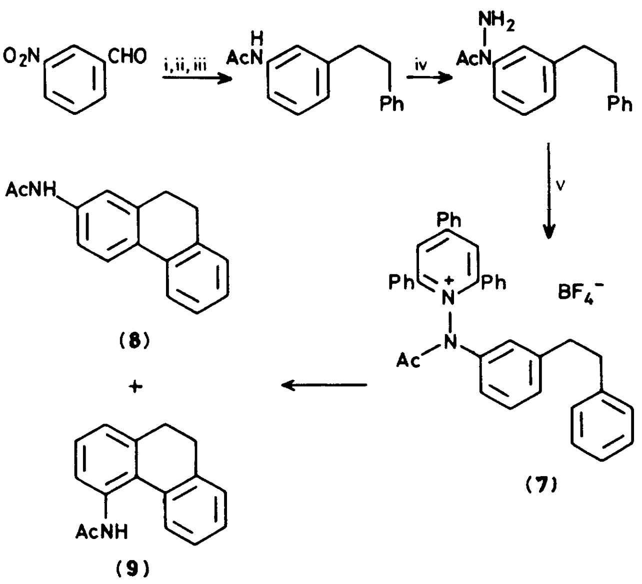
Thermolysis of 1-(*N*-acetyl-*N*-aryl)amino-2,4,6-triphenylpyridinium tetrafluoroborates provides a new and synthetically useful source of arylnitrenium ions under non-acidic conditions; a *p*-semidine-type byproduct is obtained from the phenylamino compound.

The chemistry of of nitrenium ions has received considerable attention in the past twenty years.[1] Work has focused on the structure, mode of formation, and synthetic utility of these charged reactive intermediates. Certainly one reason for the increased interest in arylnitrenium ions has been their implication as 'ultimate carcinogens' from aromatic amines and amides.[2] *N*-Chloroaniline derivatives,[3] *N*-arylhydroxylamines,[1] *O*-(arylsulphonoxy)arylhydroxylamines,[4] *O*-(acyl)-arylhydroxylamines,[2] and aryl azides in strong acids[1,5] serve as sources of arylnitrenium ions.





Scheme 1. *Reagents*: i, $PhCH_2PP^+Ph_3Cl^-$, LiOEt; ii, H_2/Pd–C; iii, Ac_2O; iv, Bu^tOK, $Ph_2P(O)ONH_2$; v, 2,4,6-triphenylpyrylium tetrafluoroborate.

Useful synthetic transformations have resulted from the intramolecular remote trapping of arylnitrenium ions produced from the acid-catalysed decomposition of aryl azides.[1,5] Unfortunately, the utility of this method is limited to the synthesis of compounds containing no strong-acid-sensitive group other than the azido group. We have developed a potentially general method of generating such ions under neutral conditions by the thermolysis of 1-(*N*-acetyl-*N*-aryl)-amino-2,4,6-triphenylpyridinium tetrafluoroborates,[6] patterned after our earlier work on the generation of aryloxenium ions from *N*-aryloxypyridiniums.[7] The publication of a photochemical generation of nitrenium ions from *N*-aminopyridiniums[8] prompts us to report our work now.

The reaction of 1-acetyl-1-phenylhydrazine with 2,4,6-triphenylpyrylium tetrafluoroborate under the usual conditions[9] produced the pyridinium tetrafluoroborate (**1**).† The geometry of (**1**) in the solid state was established by *X*-ray crystallographic analysis.‡ The steric effect upon the phenyl groups at C-2 and C-6 is also clearly visible and its elimination by N–N bond cleavage should provide an appropriate driving force for the desired reaction.

Salt (**1**) (0.05 M) in a degassed solution of 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) and mesitylene (0.14 M) undergoes 100% decomposition in 43 h at 180 °C, generating (**2**)—(**6**).[10]†§

The production of 2,4,6-triphenylpyridine (TPP) (**2**), to the exclusion of the salt from a radical cation of TPP, argues against initial homolysis of (**1**).[8] Preliminary kinetic studies have shown that the rate of decomposition of (**1**) is independent of the initial concentration of mesitylene, unlike the situation found with 1-diphenylamino- and 1-carbazol-9-yl-pyridinium cations reacting with pyridines by an S_N2' process at 120 °C, in which the nucleophile attacks only the position *para* to the amino group.[11] Thus, mesitylene-derived products (**3**) and (**4**) arise here from attack of mesitylene by some electrophilic intermediate. The formation of the non-symmetrical mesitylene dimer (**5**) may be explained by invoking a mesitylene radical cation intermediate.[12] The absence of 3,3′,5,5′-tetramethylbibenzyl makes a radical process unlikely.¶ It seems probable that compound (**6**) is formed either by trapping of a free *N*-acylarylnitrenium ion by (**2**), or by a *p*-semidine-type rearrangement.[14] Attack by (**2**) initially formed on (**1**) is also a possibility. Further studies will elucidate the inter- or intra-molecular nature of the formation of (**6**), and ways to minimize it so as to lead to better yields of (**3**) and (**4**).

Products (**2**), (**3**), and (**4**) and the kinetic data are consistent with the production of *N*-acetyl-*N*-phenylnitrenium ion (at least to some extent) under these reaction conditions. This led us to explore the use of pyridinium ion as the leaving group in a remote intramolecular functionalisation. The tetrafluoroborate (**7**), m.p. 183—184 °C, prepared as in Scheme 1, was decomposed thermally in degassed HFP, for 42 h at 180 °C to give (**2**) (36%), (**8**) (40%), and (**9**) (10.3%), identical with authentic samples prepared by acetylation of the corresponding amines.[5a,10] No semidine-type product was detected.

Thus, this methodology will allow one to effect intramolecular cyclisations like those using acid-catalysed decomposition of aryl azides, but under initially non-acidic conditions. Work is now in progress on the study of the mechanistic details of this thermal decomposition and of improving the nature of the leaving group so as to eliminate byproduct formation.

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† All new compounds gave the expected microanalytical and spectral data.

‡ The data will be given in the full paper.

§ Yields were determined by u.v. or g.l.c. analysis and are based on (**1**) for compounds (**2**)—(**6**) and on decomposed (**7**) for (**8**) and (**9**).

¶ See, however, ref. 8; in the example given therein, one would have expected bibenzyl formation rather than *o*- and *p*-benzyltoluenes if a triplet nitrene were indeed generated in toluene,[13] but none was reported.[8]

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