PHOTOLYTIC GENERATION OF N-ACYLNITRENIUM IONS UNDER NEUTRAL CONDITIONS: SYNTHESIS OF POLYCYCLIC LACTAMS*

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Abstract-Intramolecular electrophilic aromatic acylamination has been achieved by the photolysis of N-aroylaminopyridinium tetrafluoroborates under neutral conditions. Acylnitrenium ions were most likely generated which substituted the adjacent ring without undergoing Curtius-type rearrangement.

Nitrenium ions have received much attention in the past twenty years,[1] mainly owing to their postulated role in carcinogenesis,[2] but also owing to their potential synthetic utility.[3] They have been generated in many ways.[1] Recently, Falvey and his coworkers[4] stated that few methods exist[5-7] for the photogeneration of nitrenium ions, and reported the photochemical behavior of the N-tert-butyl-3-methylanthranilium ion. Earlier, we had reported the photogeneration of the corresponding diacylnitrenium from 1-phthalimido-2,4,6-triphenylpyridinium tetrafluoroborate and its trapping by aromatic solvents.[8] In still earlier work, we extended our thermal generation of aryloxenium ions from N-aryloxypyridiniums[9] (developed in 1973) to the formation of arylnitreniums using 1-(N-acetyl-N-aryl)amino-2,4,6-triphenylpyridinium tetrafluoroborates.[10] Thermolysis products and preliminary kinetic data were consistent with the production of some N-acetyl-N-arylnitrenium ions under both acidic and non-acidic conditions.[10] We had also shown[11] that suitable aryloxypyridiniums produced the corresponding aryloxenium ions on photolysis. This has been extended to the photogeneration of acylnitrenium ions (including an N-arylnitrenium) under neutral conditions and their intramolecular cyclization, and this is reported now in view of Falvey's comment.[4]

1-(N-Phenyl-N-2-biphenyloyl)aminopyridinium tetrafluoroborate (1), mp 208-208.5 °C, prepared from N-phenylaminopyridinium tetrafluoroborate (2)[12] (Scheme 1), was photolyzed (l = 2537 Å) in hexafluoroisopropanol (HFP) for 72 h under dry, deoxygenated N_2 to give N-phenylphenanthridone (3) (65%), mp 226-226.5 °C (lit.,[13] mp 226-227 °C) indicating that the desired product had formed. Its ir, mass

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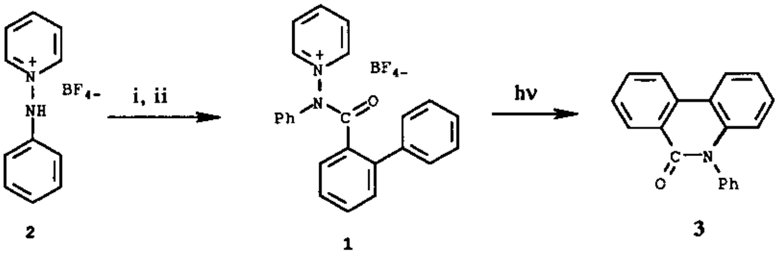
and ^{1}H nmr spectra were as expected. Photolysis (λ = 2537 Å) of pyridinium salt (**1**) in trifluoroacetic acid in the presence of catalytic amounts of trifluoromethanesulfonic acid for 56 h under N_2 gave **2** (62%), and two additional products: 9-fluorenone (8%), and biphenyl-2-carboxanilide (4%), identical with available authentic samples. No rearrangement products were observed in either case. The fluorenone probably arises from the corresponding 2-biphenyloyl cation, while the biphenyl-2-carboxanilide is the product of hydrogen-abstraction.

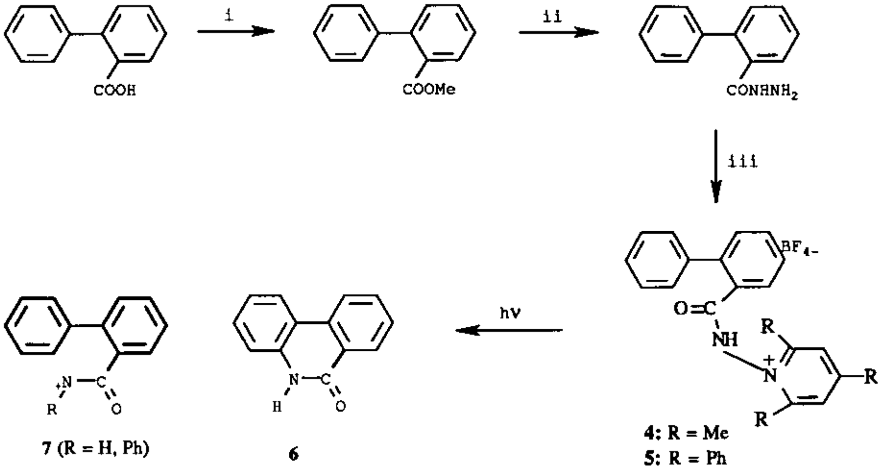
In order to compare the effect of different substituted pyridine leaving groups, 1-(2-biphenyloylamino)-2,4,6-trimethylpyridinium tetrafluoroborate (**4**), mp 200-202 °C and 1-(2-biphenyloylamino)-2,4,6-triphenylpyridinium tetrafluoroborate (**5**), mp 239-240 °C, were prepared (Scheme 2). Pyridinium (**4**), in HFP, was photolyzed (λ = 2537 Å) for 72 h under dry, deoxygenated N_2.



Scheme 1. Reagents: i, 2-biphenylcarbonyl chloride, K_2CO_3; ii $NaBF_4$.

Alumina column chromatography gave 6(5H)-phenanthridone (**6**) (52%), identical (ir, ^{1}H nmr, GC ms) with an authentic sample,[14] and recovered starting material (**4**) (11%). The corresponding photolysis of **5** gave **6** (85%). In neither case was any Curtius-type rearrangement product observed (GC ms). All the above yields are isolated yields. In all cases, the parent trisubstituted pyridine was formed and isolated in good yield.

The simplest way to account for these results is to assume the formation of the acylnitrenium (**7**) by the photoheterolysis of the N-N bond. When **5** was the precursor, it appears that, as expected from the steric point of view, the 2,4,6-triphenylpyridine was the better leaving group, leading as it did to a higher yield of lactam. Unlike the situation with the corresponding thermolysis, no p-semidine-type rearrangement product,[10] nor products formed from trapping of the acylnitrenium by a 2-phenyl group in the pyridine ring[9] were observed. The photochemical reactions are very clean and easy to work up, and show promise as a general method for a variety of other intramolecular lactamizations.



Scheme 2. Reagents: i, MeOH, $BF_3 \cdot Et_2O$; ii, NH_2NH_2; iii, 2,4,6-tri-R-pyrylium tetrafluoroborate (R = Me, Ph).

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