

Perkin Communications

4-(1,2,4-Triazolyl) Cation: Possible Generation and Reactions

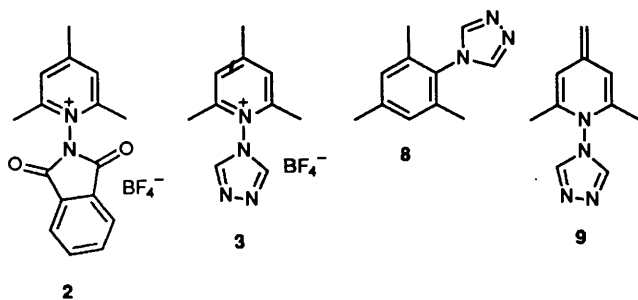
Rudolph A. Abramovitch,* Joseph M. Beckert and William T. Pennington
Department of Chemistry, Clemson University, Clemson, SC 29634-1905, USA

Thermolysis of *N*-(1,2,4-triazol-4-yl)-2,4,6-trimethylpyridinium tetrafluoroborate **3** in mesitylene-hexafluoroisopropyl solution gives a variety of products, but none derived from attack of the free nitrenium ion upon mesitylene; a possible explanation is a SET from trimethylpyridine to the nitrenium ion within the solvent cage.

Nitrenium ions have received much attention in recent years:¹ synthetic applications,² and their implication as 'ultimate carcinogens' from aromatic amines.³ Alkyl-,⁴ aryl-,^{2a} acyl-,^{2d,e} and methoxynitrenium⁵ ions have all been generated but there is no reference to the production of 5-membered heteroaromatic σ -nitrenium ions. The only papers on 5-membered heteroaromatic cations deal with calculations of the orbital energy levels of the π -cations of 1*H*-imidazol-1-ylum, -pyrazolylium and -pyrrolylium,⁶ and the generation of such π -cations stabilised by two or more electron-donor dimethylamino groups.⁷

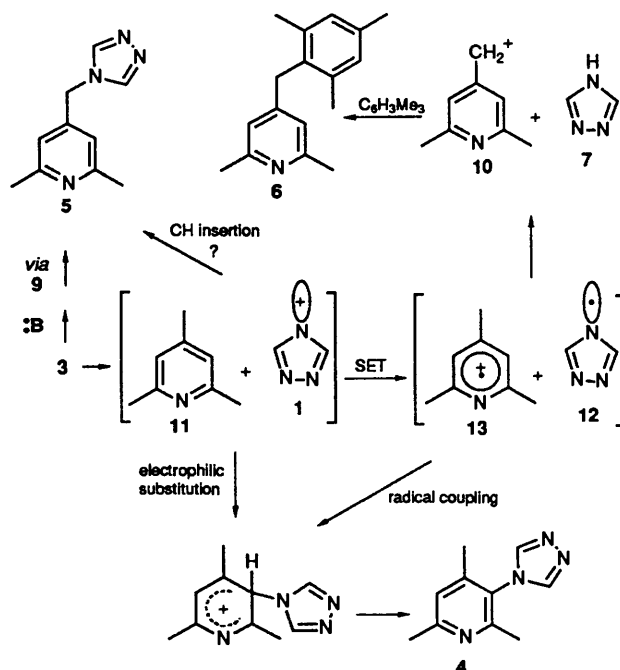
We now report some experiments on the generation and reactions of 4-(1,2,4-triazolyl) cation **1** from readily available, cheap 4-amino-1,2,4-triazole. Thermolysis of *N*-aminopyridinium salts yields nitrenium ions. Thus, 1-phthalimido-2,4,6-triphenylpyridinium tetrafluoroborate when heated in mesitylene-(CF₃)₂CHOH at 180 °C gave *N*-mesitylphthalimide (42.8%), while thermolysis or photolysis with CF₃CO₂H gave the same product together with significant amounts of amidation of the 2-phenyl group. Anisole gave the phthalimidoanisoles in 71.6% yield.^{2e}

To avoid the amidation of the 2-phenyl group we now photolysed 1-(*N*-phthalimido)-2,4,6-trimethylpyridinium **2** (m.p. 228–230 °C)⁸ in anisole [(CF₃)₂CHOH–CF₃CO₂H]. Anisidines (94.5%) (*o*–*m*–*p*–::66.4:8.3:20.3) resulted following hydrazinolysis.



The (*N*-1,2,4-triazolyl-4-yl) salt **3** (m.p. 220–221 °C)⁸ was decomposed in degassed mesitylene and (CF₃)₂CHOH at 208 °C to give a mixture of at least 8 compounds from which the following were isolated: 3-(1,2,4-triazol-4-yl)-2,4,6-trimethylpyridine **4** (3.9%), 4-(1,2,4-triazol-4-yl)-2,6-dimethylpyridine **5** (4.7%), 4-(2,4,6-trimethylbenzyl)-2,6-dimethylpyridine **6** (20.4%) and 1,2,4-triazole **7** (60.5%). No 2-(1,2,4-triazol-4-yl)mesitylene **8**, m.p. 226–227 °C,⁸ was detected.

Clearly, the reactive intermediate does not diffuse away from the pyridine into the bulk of the medium to react with the mesitylene. Instead, it reacts with collidine, probably within the solvent cage (the solution was homogeneous before thermolysis so that no reaction is occurring in the solid phase). Homolysis



Scheme 1

of the N–N bond is conceivable but cannot account for the formation of **4** since the single electron of the *N*-pyridyl radical cation formed (initially a σ -radical) cannot be delocalised to C-3. More likely, the nitrenium **1** attacks collidine within the solvent cage.⁹ Compound **5** could be formed from the anhydrobase **9** which could either undergo a concerted 1,5-shift of triazolyl to give **5** directly, or homolysis followed by radical recombination.¹⁰ Direct insertion of **1** into the 4-methyl (but not the 2-methyl?) group is also possible. Nucleophilic addition of **7** to **9** should be ruled out (as would reaction of **7** with a 4-picolyl cation **10**) since 1,2,4-triazoles are alkylated at N-1 almost invariably.¹¹

Formation of **6** as a 'major' product cannot involve a 4-picolyl radical which would dimerise rather than attack mesitylene.¹² Electrophilic attack of mesitylene by **10** (Scheme 1) could best account for **6**, involving a SET from collidine **11** to **1** to give the radical **12** and π -radical cation **13**, thence to **6** or **4**. Anodic oxidation of methylbenzenes give benzyl cations that react with an excess of hydrocarbon to form diphenylmethanes.¹³ This could also explain the formation of 2,3',4,5',6-pentamethyldiphenylmethane^{2d} and 2- and 4-benzyltoluene⁴ in related nitrenium ion reactions (*cf.* bibenzyl formed from sulphonylnitrenes in toluene¹²).

Experimental

Thermolysis of 3.—A solution of **3** (0.45 g) in degassed mesitylene (10 ml) and just sufficient hexafluoroisopropyl alcohol to dissolve the solid was heated at 208 °C (external bath temp.) under dry N₂ for 7 h. The solution was extracted with water and the products in the organic layer were separated by prep. TLC [silica gel, ether–THF (1:1 v/v)] to give **4**, m.p. 233–235 °C (structure confirmed by X-ray analysis¹⁴); **5** m.p. 149–150 °C (ethanol); δ_H(CDCl₃) 6.71 (s, 2 H), 6.21 (s, 2 H), 5.15 (s, 2 H) and 2.51 (s, 6 H) (Found: M⁺, 188.1064. C₁₀H₁₂N₄ requires M, 188.1062); **6**, m.p. 51–52 °C (Et₂O); δ_H(CDCl₃) 6.69 (s, 2 H), 6.61 (s, 2 H), 3.91 (s, 2 H), 2.43 (s, 6 H), 2.29 (s, 3 H) and 2.17 (s, 6 H) (Found: C, 85.0; H, 8.9; C₁₇H₂₁N requires C, 85.3; H, 8.8). The aqueous layer was extracted with CH₂Cl₂ to give **7**, m.p. 118–120 °C (confirmed by determination of the unit cell parameters¹⁵).

Acknowledgements

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