

Tullio Caronna, Angelo Clerici, Dianella Coggiola and Sergio Morrocchi\*

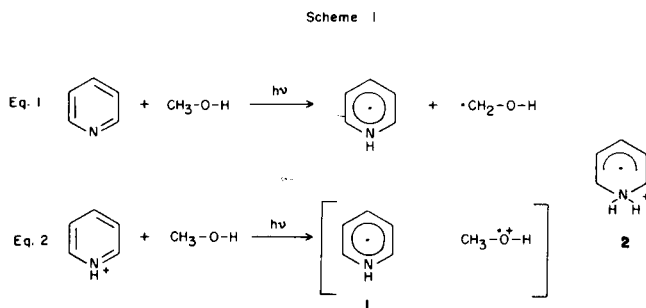
Istituto di Chimica del Politecnico di Milano, Via Golgi 39, 20133 Milano, Italy

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Chemical evidence is given that the title photo-reactions proceed *via* hydrogen abstraction by the photo-excited base from the alcohol in neutral medium and *via* electron-transfer process between the photo-excited base and the alcohol in hydrochloric acid acidified medium.

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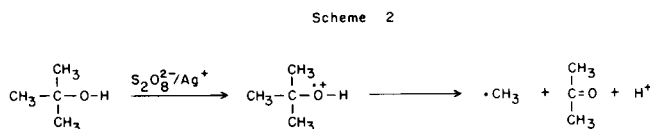
The photochemical reaction of six-membered ring monoazaaromatic compounds with alcohols is a process widely studied in the last decade and takes place both in neutral and acidified medium (1-5). These photo-reactions have been postulated to proceed *via* a radical mechanism but, while an esr study of the structure of the radicals involved and a discussion of the mechanism of their formation has been made by Lablache-Combiere and co-workers (6), no chemical evidence has been so far given to support such a mechanism. The conclusion Lablache-Combiere arrived at regarding the photoreaction of six-membered ring monoazaaromatic compounds with neutral (Equation 1) and acidified methanol (Equation 2) was that identical semiquinone radicals were formed in both cases but by two different mechanisms (Scheme 1).



Since identical semiquinone radicals **1** were detected in esr experiments, their structure is in contrast with the radical cation **2** proposed by Stermitz (7) and Stenberg (1) in the photo-reaction of quinoline with ethanol and pyridine with methanol in acidic medium.

Our purpose in this paper is to show adequate evidence supporting the two different mechanisms in neutral and acidified medium.

We have approached the problem by exploiting the experimental observation that the oxidation of saturated aliphatic alcohols by the redox system dipersulphate/silver salt leads to formation of alkoxy radicals (8) which, depending on their chain structure, undergo  $\beta$ -scission to give the corresponding alkyl radicals. The case of *t*-butyl alcohol is shown in Scheme 2.

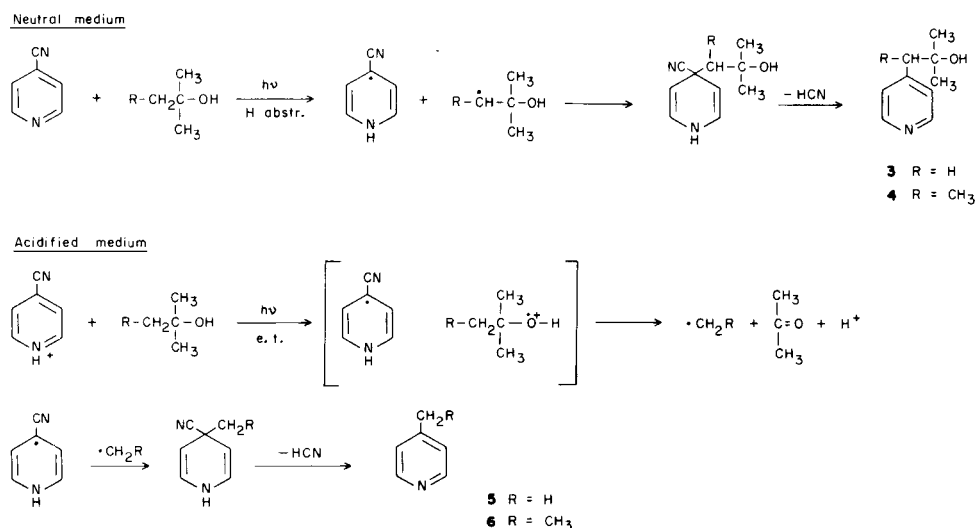


When the oxidation is carried out in the presence of a protonated heteroaromatic base, selective alkylation is observed owing to the very high rate constant of addition of alkyl radicals to these bases (9). Now, if it is true that heteroaromatic photo-excited bases can oxidize aliphatic alcohols by electron-transfer to give alkoxy radicals, as the redox system does, the photo-reaction between an heteroaromatic protonated base and aliphatic alcohols suitable to undergo  $\beta$ -scission would give the corresponding alkylation products. In order to verify this hypothesis we have carried out the photolysis at 254 nm of 4-pyridinecarbonitrile with *t*-butyl alcohol and 2-methylbutan-2-ol both in neutral and hydrochloric acid medium (10). In all cases substitution occurs at the 4 position of the pyridine ring with displacement of the cyano group (11). In neutral medium the sole products of photo-substitution deriving from hydrogen abstraction were isolated and respectively identified as 3-(4-pyridyl)-2-methylpropan-2-ol (**3**) and 3-(4-pyridyl)-2-methylbutan-2-ol (**4**). In acidified medium the products of alkylation, 4-methylpyridine (**5**) and 4-ethylpyridine (**6**), originated by  $\beta$ -scission of the intermediate alkoxy radicals, were obtained along with small amounts of hydroxyalkyl products.

Based on this chemical evidence, we proposed the following mechanisms (Scheme 3) which clearly show that hydrogen abstraction by the excited base, followed by coupling and HCN elimination, account for the hydroxyalkylation products in neutral medium, while the formation of an alkoxy radical *via* an electron-transfer process between the protonated base and the alcohol, followed by  $\beta$ -scission, coupling and HCN elimination, is responsible for the alkylation products in acidified medium.

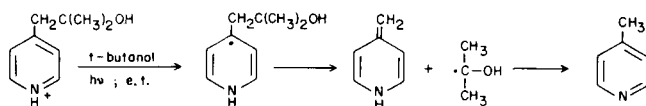
It is worth noting that when compound **3** is photolyzed at 254 nm in the presence of acidified *t*-butyl alcohol, formation of 4-methylpyridine is observed. To ascertain

Scheme 3



whether **3** might be a precursor in the formation of 4-methylpyridine in acidified medium, we have carried out the competitive photo-reaction between **3** and 4-pyridinecarbonitrile in hydrochloric acid in the presence of *t*-butyl alcohol. Glc analysis of the reaction mixture unequivocally revealed formation of 4-methylpyridine from 4-pyridinecarbonitrile together with compound **3** unchanged. This observation allows us to exclude that **3** is a precursor of 4-methylpyridine but it suggests that an electron transfer probably occurs when **3** itself is photolyzed in acidified medium (Scheme 4).

Scheme 4



Studies are currently in progress with the aim of testing the generality of these findings to other six-membered heteroaromatic compounds bearing different substituents.

## EXPERIMENTAL

Nuclear magnetic resonance spectra (nmr) were recorded with a Varian XL-100-15 spectrometer using tetramethylsilane as an internal reference. Mass spectra were recorded with a Hitachi-Perkin-Elmer RMU 6D single focusing spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard 5750 gas chromatograph using a 2 m glass column (internal diameter 2 mm) packed with 10% Carbowax 20 M.

**Photo-reaction of 4-Pyridinecarbonitrile with *t*-Butyl Alcohol in Neutral Medium. 3-(4-Pyridyl)-2-methylpropan-2-ol (**3**).**

A solution of 90 mg (0.86 mole) of 4-pyridinecarbonitrile, 5.5 ml of 1 ml of water and 0.5 ml of acetonitrile was placed in a quartz tube and then irradiated (under nitrogen) at 254 nm in a Rayonet RPR 100 photochemical reactor for 7 hours. After irradiation, the crude mixture was ex-

tracted several times with methylene chloride. The combined extracts were dried over anhydrous sodium sulphate and after removing the solvent, chromatographed by tlc (2 mm Merck Kieselgel GF 254, eluent ethyl acetate). Product **3** along with unreacted 4-pyridinecarbonitrile was isolated as an oil and identified by conventional spectroscopic techniques; <sup>1</sup>H-nmr (deuteriochloroform): δ 1.22 (s, 6H, 2CH<sub>3</sub>), 2.74 (s, 2H, CH<sub>2</sub>), 3.53 (s, broad, 1H, OH), 7.20 (d, 2H, Ar-H, β to N), 8.43 (d, 2H, Ar-H, α to N); ms: 151 (M<sup>+</sup>), 136, 93, 59.

*Anal.* Calcd. for C<sub>9</sub>H<sub>13</sub>NO: C, 71.49; H, 8.77; N, 9.26. Found: C, 71.60; H, 8.53; N, 9.12.

Yields of product **3** based on starting 4-pyridinecarbonitrile determined by glc analysis with the internal standard method for comparison with authentic sample were 60%. No 4-methylpyridine was detected.

**Photo-reaction of 4-Pyridinecarbonitrile with *t*-Butyl Alcohol in Acidic Medium 4-Methylpyridine (**5**).**

The solution was prepared in the same way as described above except for the presence of 0.16 ml of hydrochloric acid (36%, 1.76 mmoles). After 7 hours of irradiation at 254 nm in a quartz vessel under nitrogen, the solution was basified with dilute ammonia and extracted with methylene chloride. 4-Methylpyridine (30% yield) **5**, 4-pyridinecarbonitrile unreacted (66%), and **3** (4%), were identified by glc analysis for comparison with authentic samples.

**Photo-reaction of 4-Pyridinecarbonitrile with 2-Methylbutan-2-ol in Neutral Medium. 3-(4-Pyridyl)-2-methylbutan-2-ol (**4**).**

A solution of 90 mg (0.86 mmole) of 4-pyridinecarbonitrile, 5.5 ml of 2-methylbutan-2-ol, 1 ml of water, 0.5 ml of acetonitrile was irradiated at 254 nm in a quartz vessel (under nitrogen) for 7 hours. The reaction mixture was extracted with methylene chloride and after removing the solvent chromatographed by tlc (eluent ethyl acetate). Product **4** as oil, along with unreacted 4-pyridinecarbonitrile was isolated and identified; <sup>1</sup>H-nmr (deuteriochloroform): δ 1.1-1.4 (m, 9H, 3CH<sub>3</sub>), 2.67 (s, broad, 1H, OH), 2.74 (m, 1H, CH), 7.18 (d, 2H, Ar-H, β to N), 8.43 (d, 2H, Ar-H, α to N); ms: 165 (M<sup>+</sup>), 150, 107, 93, 73, 59.

*Anal.* Calcd. for C<sub>10</sub>H<sub>15</sub>NO: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.47; H, 9.21; N, 8.32.

Yields of product **4** based on starting 4-pyridinecarbonitrile determined by glc were 50%. No 4-ethylpyridine was detected.

**Photo-reaction of 4-Pyridinecarbonitrile with 2-Methylbutan-2-ol in Acidic Medium. 4-Ethylpyridine (**6**).**

A solution was prepared in the same way as described above except for

the presence of 0.16 ml of hydrochloric acid (36%, 1.76 mmoles). After irradiation (7 hours at 254 nm, quartz vessel, under nitrogen) the reaction mixture was basified and extracted with methylene chloride. 4-Ethylpyridine (25%) **6**, and 4-pyridinecarbonitrile (75%) were identified by glc analysis for comparison with authentic samples.

Photo-reaction of 3-(4-Pyridyl), 2-Methylpropan-2-ol in Acidic Medium.

A solution of 30 mg (0.18 mmole) of **3**, 2 ml *t*-butyl alcohol, 0.5 ml of water and 0.02 ml of hydrochloric acid (36%, 0.44 mmole) was irradiated at 254 nm for 3 hours. After irradiation, the solution was basified with dilute ammonia and extracted with methylene chloride. Glc analysis revealed 4-methylpyridine (7% yield) and **3** unreacted (92% yield).

Photo-reaction of 3-(4-pyridyl), 2-Methylpropan-2-ol and 4-Pyridinecarbonitrile in Acidic Medium.

A solution of 15 mg (0.09 mole) of **3** with 90 mg of 4-pyridinecarbonitrile (14% of **3** and 86% of 4-pyridinecarbonitrile by glc), 5 ml of *t*-butyl alcohol 0.5 ml of water 1 ml of acetonitrile and 0.18 ml of hydrochloric acid (36%, 2 mmoles) was irradiated for 3 hours at 254 nm under nitrogen. After irradiation the solution was basified with dilute ammonia and extracted with methylene chloride. Glc analysis (using 2-pyridinecarbonitrile as the internal standard) revealed 15% of **3** 13% of 4-methylpyridine and 72% of 4-pyridinecarbonitrile.

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