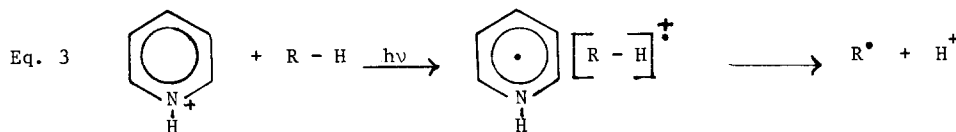
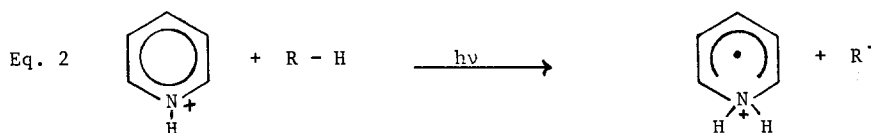
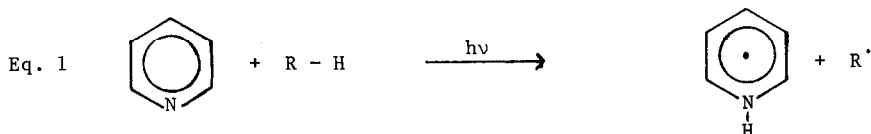


PHOTOREACTIONS OF 4-CYANOPYRIDINE WITH ALKENOLS
 INFLUENCE OF THE MEDIUM ON THE REACTION MECHANISM AND PHOTOPRODUCTS FORMATION

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Summary: Irradiation of 4-cyanopyridine in the presence of 4-penten-1-ol and 5-hexen-1-ol is reported. Hydrogen abstraction from the methylene α to the hydroxyl group in neutral medium and an electron transfer from the double bond in acidified medium account for the photo-products obtained.

The photochemical behaviour of heteroaromatic bases is now a well established process in neutral medium. There is a general agreement that the first step involves an hydrogen abstraction from a suitable donor by the $n \rightarrow \pi^*$ excited base¹ (Eq. 1).

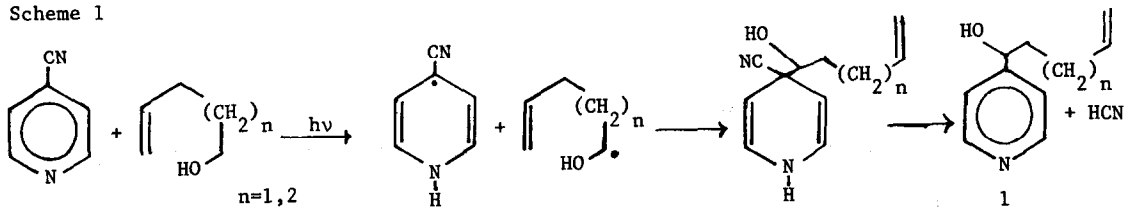


On the contrary the matter seems to be rather unclear in acidified medium. Some authors claim an hydrogen abstraction by the $\pi \rightarrow \pi^*$ excited protonated base¹ (Eq. 2) to be the first step in the mechanism, while others agree that an electron transfer occurs between an upper excited state of the protonated base and the R-H molecule² (Eq. 3).

In order to clarify which mechanisms are really involved we report here the photoreactions of 4-cyanopyridine with 4-penten-1-ol and 5-hexen-1-ol in neutral and hydrochloric acid acidified medium.

When a solution of 4-cyanopyridine (0.125 g, $1.2 \cdot 10^{-3}$ mole) and the alkenol ($6 \cdot 10^{-3}$ mole) in 20 ml of $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (9:1) sol. was irradiated for 50 hrs at 254 nm, product 1 was isolated after work up³. Undoubtedly this product arises from direct hydrogen abstraction at the α -position of the hydroxyl group followed by radical cross coupling and HCN elimination according to scheme 1 and Eq. 1.

Scheme 1

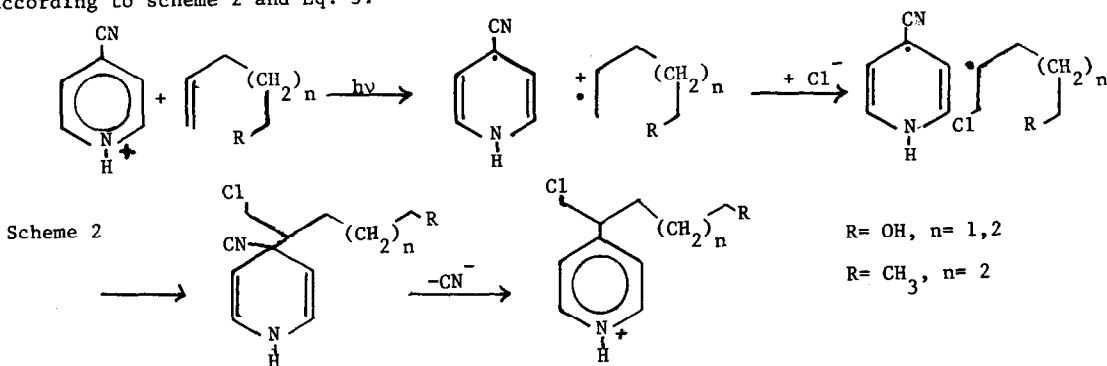


On the contrary, when the same solution of 4-cyanopyridine was acidified with 10 M HCl (0.12 ml $1.2 \cdot 10^{-3}$ mole) and photolyzed at the same wavelength, product 2 was isolated instead.



To determine whether or not the -OH group is involved in the primary step of the reaction, the same HCl acidified solution of 4-cyanopyridine was irradiated in the presence of 1-hexene. In this reaction product 3 was isolated. No reaction took place in neutral medium.

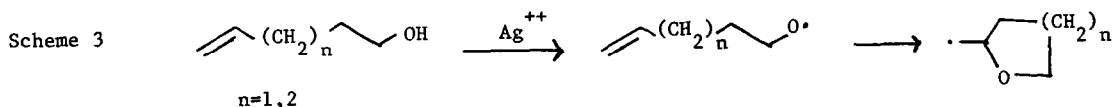
In our opinion, the formation of 2 and 3 is consistent with the fact that an electron-transfer takes place between an excited state of the protonated base and the double bond of the substrate according to scheme 2 and Eq. 3.



Formation of a termolecular excited state complex (exterplex)⁽⁴⁾ among the excited base, Cl^- and double bond, might explain the exclusive trapping of radical cation (I) by Cl^- .

Work is in progress to evidentiare the exterplex formation.

At a first sight, these results seem somewhat in contrast with those reported in the oxidation of 4-penten-1-ol and 5-hexen-1-ol with the redox system $\text{S}_2\text{O}_8^{2-}/\text{Ag}^+$ where an alkoxy radical is formed in the first step of the reaction⁽⁵⁾. (Scheme 3).



In our point of view, the different behaviour may be adequately explained by the fact that in the photoreaction, the excited protonated base promotes an electron-transfer from the double bond which is the electron richer part of the alkenol, while in the redox reaction, Ag^{++} specie promotes oxidation of the hydroxyl group rather than that of the double bond because of the larger equilibrium constant for the complex formation with 5-hexen-1-ol (29 l/m) compared with the one of 1-hexene (0.095 l/m)⁽⁶⁾.

Spectral data of the products[†]

- 1 (n=1): mass (m/e): 163, 145, 135, 132, 120. H^1 NMR: 8.52 δ (d 2H H_A and H_B , $J_{AC}=J_{BD}=4.5$ Hz) 7.30 δ (d 2H H_C and H_D , $J_{CA}=J_{DB}=4.5$ Hz), 5.75 and 5.10 δ (b ss 3H $\text{CH}_2=\text{CH}-$), 3.67 δ (b s 1H $\text{Py}-\text{CHOH}-$), 2.70 δ (s 1H $-\text{OH}$), 2.2 δ (b s 2H $-\text{CH}_2-\text{CH}=\text{}$), 1.84 δ (b s 2H $-\text{CH}_2-\text{CHOH}-$)
Yield 33%
- 1 (n=2): mass (m/e): 177, 159, 149, 144, 134, 121. H^1 NMR: 8.52 δ (d 2H H_A and H_B , $J_{AC}=J_{BD}=4.5$ Hz) 7.30 δ (d 2H H_C and H_D , $J_{CA}=J_{DB}=4.5$ Hz), 5.65 and 5.0 δ (b ss 3H $\text{CH}_2=\text{CH}-$), 3.67 δ (b s 1H $\text{Py}-\text{CHOH}-$), 2.98 δ (s 1H $-\text{OH}$), 2.16 δ (b s 2H $-\text{CH}_2-\text{CH}=\text{}$), 1.65 δ (b s $-\text{CH}_2-\text{CH}_2-\text{CHOH}-$)
Yield 31%
- 2 (n=1): mass (m/e): 198 (M^+-H), 163, 144, 130, 120. H^1 NMR: 8.53 δ (d 2H H_A and H_B , $J_{AC}=J_{BD}=4.7$ Hz), 7.18 δ (d 2H H_C and H_D , $J_{CA}=J_{DB}=4.7$ Hz), 3.65 δ (b s 5H $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{OH}$, $-\text{OH}$), 3.0 δ (b s 1H $-\text{CHPy}-$), 1.82 and 1.50 δ (b ss 4H $-\text{CH}_2-\text{CH}_2-$). C^{13} NMR: 151.3 δ (s C_3), 149.5 δ (d C_1 and C_5), 123.4 δ (d C_2 and C_4), 61.8 δ (t CH_2OH), 48.2 δ (d CHPy), 30.2 δ and 29.3 δ (t $-\text{CH}_2-\text{CH}_2-$).
Yield 25%
- 2 (n=2): mass (m/e): 212 (M^+-H), 178, 158, 144, 130, 118, 105. H^1 NMR: 8.52 δ (d 2H H_A and H_B , $J_{AC}=J_{BD}=4.7$ Hz), 7.18 δ (d 2H H_C and H_D , $J_{CA}=J_{DB}=4.7$ Hz), 4.08 δ (s 1H $-\text{OH}$), 3.60 δ (b s 4H $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{OH}$), 2.95 δ (b s 1H $-\text{CHPy}-$), 1.6 δ (b s 6H $-(\text{CH}_2)_3-$). C^{13} NMR: 151.3 δ (s C_3), 149.5 δ (d C_1 and C_5), 123.3 δ (d C_2 and C_4), 62.0 δ (t $-\text{CH}_2\text{OH}$), 48.2 δ (t $-\text{CH}_2\text{Cl}$), 47.6 δ (d $-\text{CHPy}-$), 32.6, 32.4, 23.5 δ (t $-(\text{CH}_2)_3-$).
Yield 30%
- 3 : mass (m/e): 197, 149, 118, 104. H^1 NMR: 8.50 δ (d 2H H_A and H_B , $J_{AC}=J_{BD}=4.7$ Hz), 7.12 δ (d 2H H_C and H_D , $J_{CA}=J_{DB}=4.7$ Hz), 3.62 δ (d 2H 6 Hz $-\text{CHPy}-\text{CH}_2\text{Cl}$), 2.92 δ (b s 1H $-\text{CHPy}-$), 1.72 and 1.25 δ (b ss 6H $-(\text{CH}_2)_3-$), 0.90 δ (t 3H $-\text{CH}_3$, $J_{\text{CH}_2-\text{CH}_3}=4.2$ Hz).
Yield 30%

† All products are oils.

NMR spectra were recorded on a Varian XL-100-15 spectrometer using TMS and CDCl_3 as internal standards for H^1 and C^{13} respectively. As $\text{H}_A, \text{H}_B, \text{H}_C, \text{H}_D$ are reported the hydrogen atoms respectively in position 2 and 6 and 3 and 5 in pyridine ring.

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