The Trapping of 1,X-Biradicals, Photochemically Produced, with 4-Cyanopyridine in Neutral and Acidic Medium

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4-Cyanopyridine is able to trap 1,x-biradicals produced by direct photochemical excitation of some ketones, showing in some cases that unaspected species are formed and pyridine producs which are not explainable on the basis of actual knowledge.

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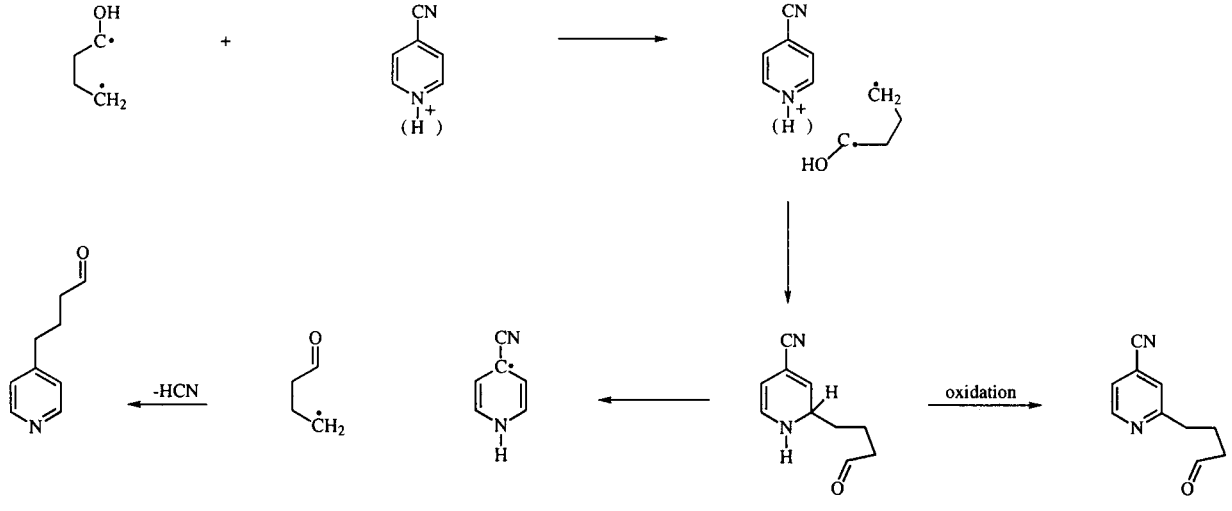
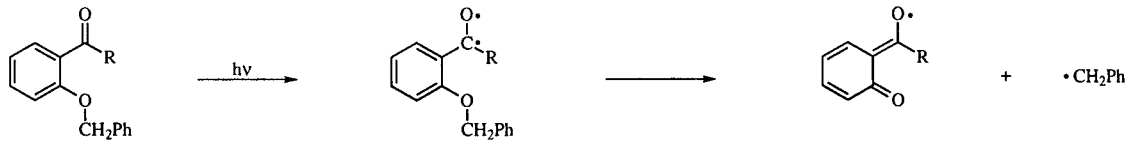
In a previous paper [1], we showed the usefulness of the presence of 4-cyanopyridine, either in neutral or in acidic medium, in the trapping of 1,4-biradicals, formed during the photolysis of a series of ketones ranging from valerophenone to *o*-methylacetophenone and others with related structures. In pursuing our studies, we decided to increase the scope of our research to other ketones able to form 1,x-biradicals under excitation. Studies were reported for some of the ketones used regarding either the spectroscopic properties of the corresponding biradicals as well the products that are formed during the photolysis [2a-e]. Our results are intended to show that most of the biradicals formed during the photolysis of the ketones under study may be trapped either confirming some of the proposed mechanism or showing unexpected pathways. For a better comprehension of the results, in Scheme 1 is reported the mechanism that we believe is operating [3]: once the biradical is formed the first step is, in any case, the transfer of a hydrogen in neutral medium or an electron in acidic medium forming a pyridinyl radical and restoring the ketone; in the meanwhile the other radical is driven in position 2 to form a dihydro derivative. If the reoxidation occurs at this stage the product attacked is obtained. If instead the intermediate may break back, cross-coupling may occur at position 4 of the pyridinyl radical and rearomatization occurs *via* HCN elimination forming substitution products. We need also to emphasize that some of the reported biradicals possess very short lifetimes. For this and on the basis of the mechanism in Scheme 1, it is possible to suggest that the quenching of the biradicals is more efficient in acidic medium and that the yields of the pyridine products should be generally low. The normal photochemical reactivity is to a large extent the preferred process.

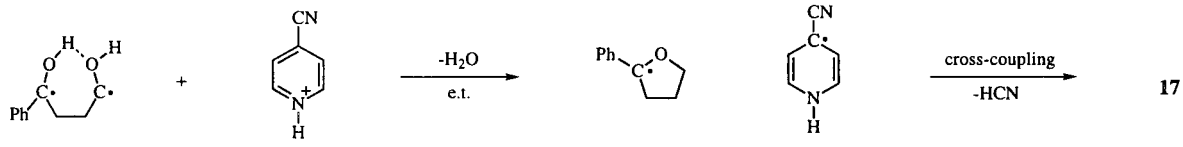
Scheme 1



Scheme 2

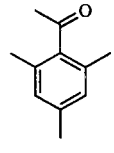


Scheme 3



Results and Discussion.

The ketones we used in this study are reported in Figure 1. The pyridine derivatives formed are indicated in Figures 2 to 6.



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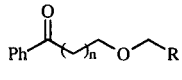
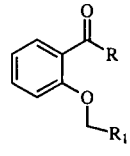
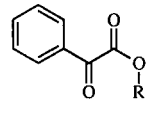


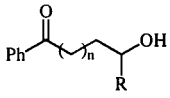
2a n = 1, R = CH_3
2b n = 2, R = H



3a R = CH_3, R_1 = C_2H_5
3b R = CH_3, R_1 = Ph
3c R = Ph, R_1 = C_2H_5
3d R = Ph, R_1 = Ph



4 R = *n*-C_3H_7, *i*-C_3H_7, CH_2-Ph



5a n = 2, R = H
5b n = 2, R = CH_3
5c n = 3, R = H

Figure 1.

In neutral medium ketone **1** behaves as noted for *o*-methylacetophenone or 2(4)(di)methylbenzophenone forming CN-substitution and attack at position 2, products **6** and **7** (ratio **6**:**7** = 5:1) (Figure 2). A striking difference was found in acidic medium, where not only product **6** is formed but also products **8** and **9** (ratio **6**:**8**:**9** = 2.5:1:2.5).

In an attempt to understand if these products arise from the trapping of radicals formed from an intermolecular or an intramolecular hydrogen abstraction by the excited ketone, a series of reactions were run at different concentrations over a 20 fold range (0.004 *M* to 0.09 *M*). No difference was found in the products distribution. As far as we know, the photochemistry of this ketone was not studied, but, for the corresponding aldehyde the presence of the biradical was hypothesized [4] and considering that generally excited aldehydes and ketones behave in the same way (see for example *o*-methylbenzaldehyde and *o*-methylacetophenone [4]), we think that an explanation may be attributed to the fact that **1** in the excited state gives rise, in one of its resonance forms, to a radical at position 4 and eventually an intramolecular hydrogen shift may occur. A similar resonance form was already taken into account [5], but as far we know, no other reports were given. As further consideration, **8** and **9** are formed in acidic medium, it is possible that the resonance form is more stabilized at lower *p*H.

In Figure 3 are reported the products obtained with compound **2a** and **2b**. For ketone **2a** no trapping was possible in neutral medium, while in acidic medium **10a** and **11a** were isolated. These findings seem to be in contrast with earlier studies that were carried out to determine the selectivity of the 1-4 hydrogen transfer compared with the 1-6 transfer [6]. The conclusion was that the 1-6 transfer is by far the most prevalent. From our experiments, however, it seems that abstraction occurs, to the same extent, from both positions considering that a 1:1 ratio of pyridine compounds **10a** and **11a** were obtained. If the 1-5 hydrogen transfer is possible, ketone **2b**, only this kind of hydrogen transfer occurs and only the pyridine product corresponding to this abstraction is obtained. In Figure 4 are reported the products from irradiating *o*-alkoxyphenylketones. In this case only 1-6 hydrogen transfer

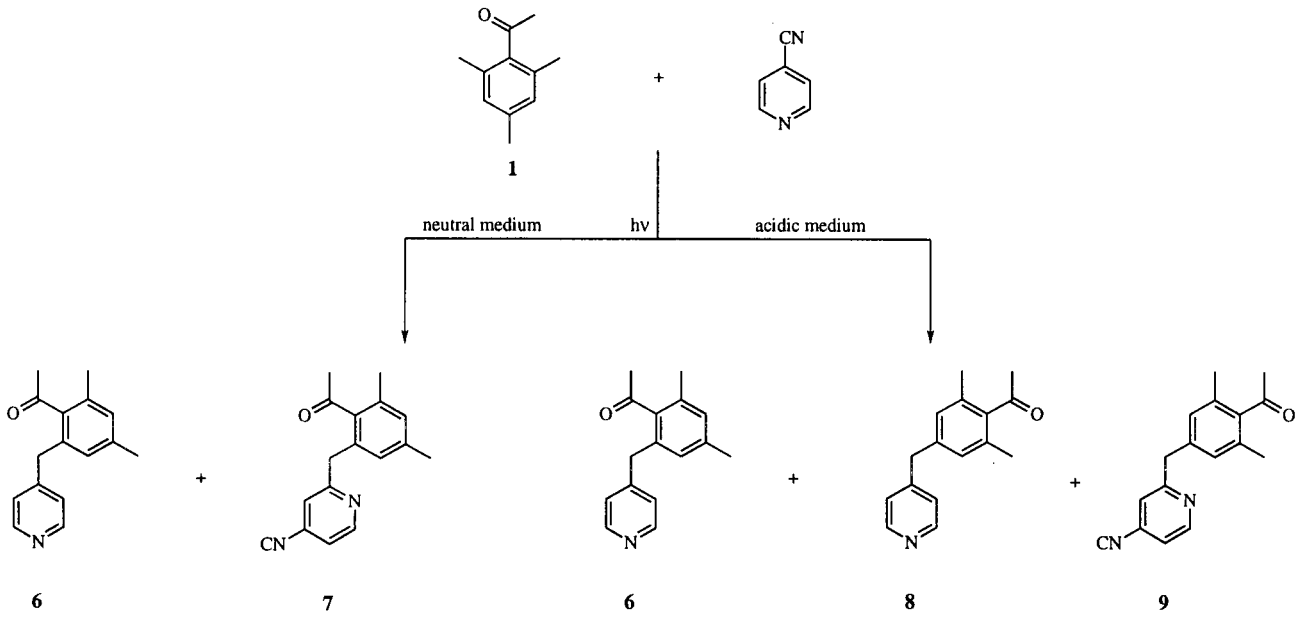


Figure 2.

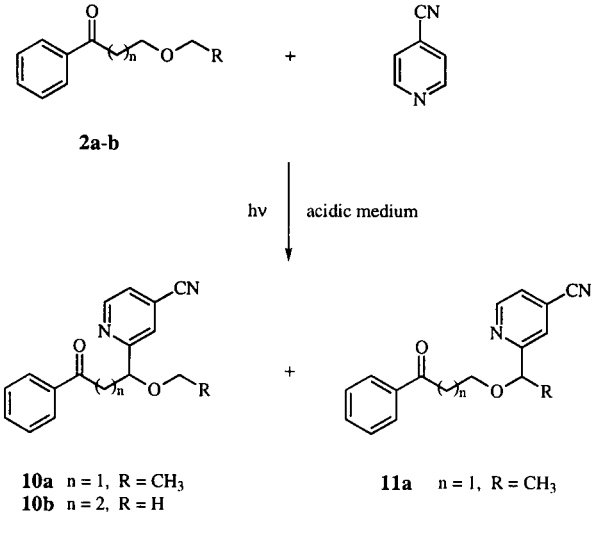


Figure 3.

may occur. The pyridine products, formed only in acidic medium, depend on the group attacked by the ethereal oxygen. For all these derivatives, the formation of a 1,5-biradical is reported to depend on the kind of alkoxy moiety as well as from the ketone (acetophenone or benzophenone) [7-8]. Indeed, in the case of the propyloxy derivatives, the formation of the pyridine products shows that the biradical is formed upon excitation of the ketone. Slightly more complex is the behavior of the benzyloxy derivatives. The obtaining of compounds **13** and **14** shows that a certain degree of reversibility of the intermediate may occur, but the obtaining of 4-benzylpyridine **15** demonstrates that scission of the *O*-benzyl bond may occur before H-abstraction. In Figure 5 is reported the product formed in the photolysis of the benzoylformate esters. In all the cases the same product **16** is formed. A pathway reported for their photolysis is the 1-4 biradical formation that decomposes, before being trapped by the base, to the analgous ketene, this is, in turn, trapped by water to form mandelic acid [9]. The photolysis of this acid in the presence of the protonated 4-cyanopyridine produces **16**. Confirmation of this pathway was achieved by irradiating mandelic acid under the same conditions again obtaining **16**. The yield of **16** is dependent upon the possibility to abstract the hydrogen of the ester group. The benzyl group gives a higher yield compared with the *n*-propyl or the isopropyl group for irradiation carried out under the same conditions.

Finally in Figure 6, the products arising from the photolysis of ketones **5a-c** are reported. The construction of the tetrahydrofuran ring **17** is obviously not easy to explain. As far we know, the only paper dealing with these kinds of derivatives described the photolysis of γ-hydroxy-γ-phenylbutyrophenone, concluding that intramolecular hydrogen bonding is operating in the 1,4-biradical [10]. This hypothesis give us the possibility

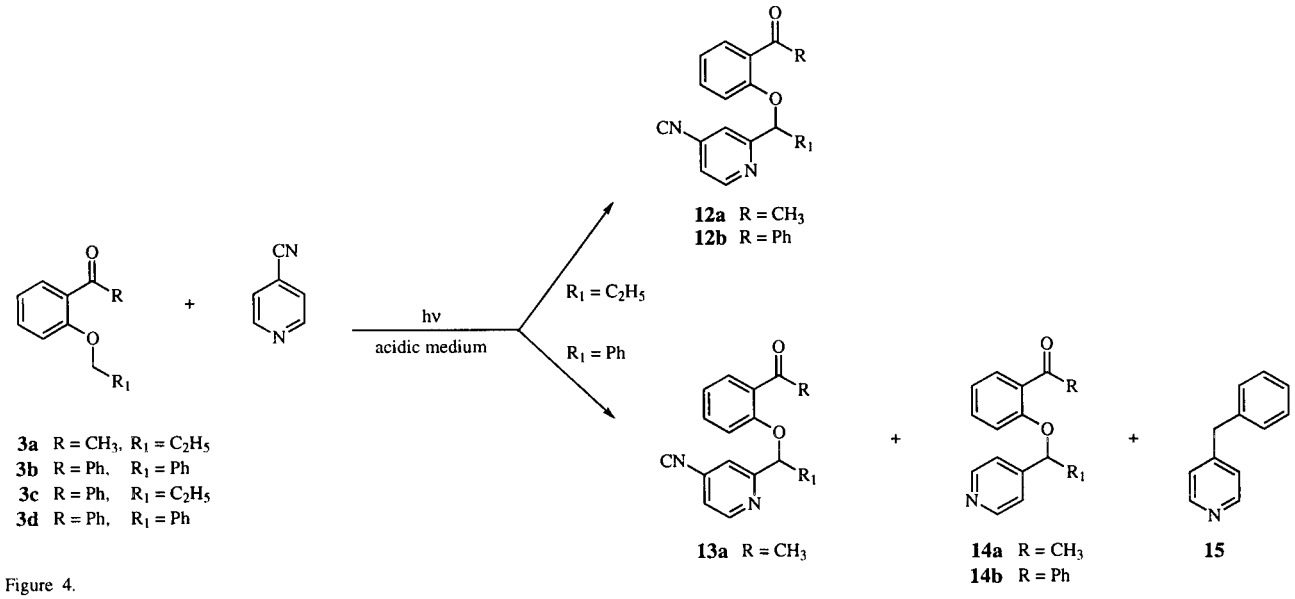


Figure 4.

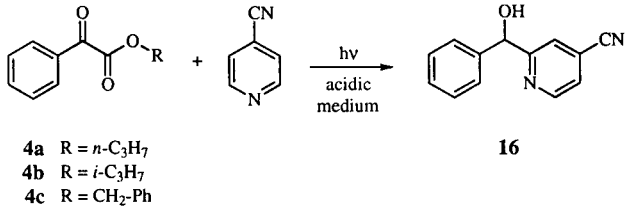


Figure 5.

to advance a mechanism in which the key step lay in the fact that this hydrogen bonding stabilized intermediate may eliminate a water molecule, close the tetrahydrofuran ring, eventually favored by the acidic medium and transfer an electron to the pyridine ring.

This behavior occurs only if the OH is on the carbon atom prone to be attacked by the excited ketone. Moving the alcohol far from the radical center reverts back to the normal behavior: ketone **5c** forms product **18**.

In conclusion, the presence of 4-cyanopyridine, both in neutral or acidic medium, was diagnostic in determining the kind of radicals formed during the photolysis of the ketones examined. In turn the reactivity of the biradicals formed displayed unexpected behavior in some instances.

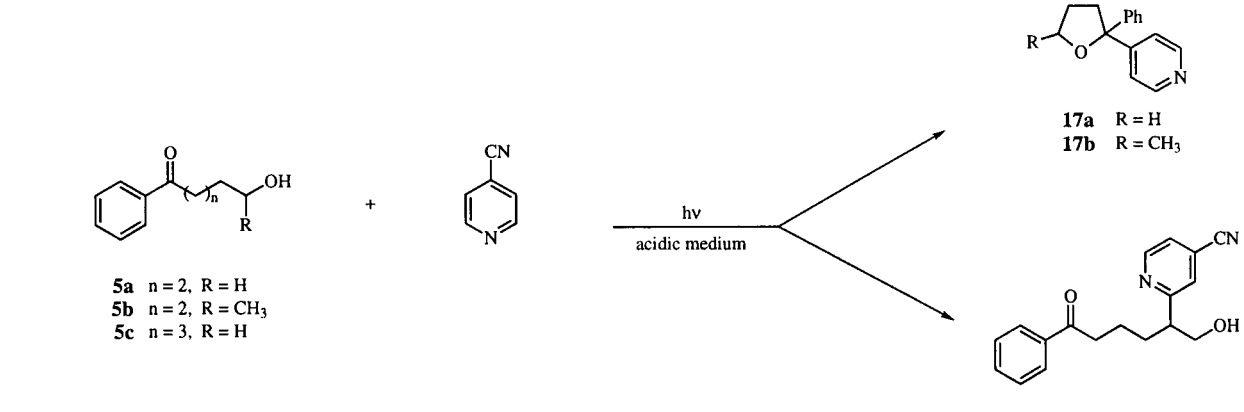


Figure 6.

EXPERIMENTAL

4-Cyanopyridine and 2,4,6-trimethylacetophenone are commercial products. Propyl or benzyl ether, *o*-hydroxyacetophenone or *o*-hydroxybenzophenone were synthesized by treating the sodium salt of the hydroxyketone with propyl or benzyl chloride. β-ethoxypropiophenone was prepared *via* Friedel-Craft acylation of benzene with β-ethoxypropionyl chloride. γ-Methoxybutyrophenone was prepared treating γ-butyrolactone with sodium methylate; the resulting methoxyacid was transformed with thionyl chloride in the corresponding acyl chloride, so that with a Friedel-Craft acylation on benzene gave the final product. γ-Hydroxybutyrophenone, γ-hydroxyvalerophenone and 1-phenyl-6-hydroxyhexan-1-one were synthesized by treating with phenyl lithium in anhydrous ether, respectively, butyrolactone, γ-valerolactone, or ε-caprolactone. Benzoylformate esthers were obtained by boiling benzoylformic acid with the appropriate alcohol with a catalytic amount of *p*-toluensulphonic acid.

The nmr spectra were measured in deuteriochloroform using tetramethylsilane as internal standard at a 250 MHz. The ^1H operating frequency. H_A, H_B, H_C, H_D and H_E refers respectively to the hydrogen atom in position 2, 3, 4, 5 and 6 of the pyridine ring. Mass spectra were recorded on a triple quadrupole spectrometer. Melting points are uncorrected. Standard flash chromatography refers to the procedure reported by Still [11]. Gas chromatographic analyses were performed on a 2 m glass column (i.d. 2 mm) packed with 5% SP-1000 at 220° or a 2 m glass column (i.d. 2 mm) packed with 10% UCC-W 982 and temperature programmed from 120 to 235° (8°/minute after the first 4 minutes) or an OV-1 fused silica capillary column 25 m x 0.25 μm (i.d.) d_f 0.25 mm, carrier gas hydrogen, linear velocity *ca.* 50 cm sec^{-1}; temperature program: 1' at 40°, 20° min^{-1} to 150°, 2' at 150°, 3° min^{-1} to 180°, 1' at 180°, 10° min^{-1} to 260°. A mixture of weighed compounds and the standard was used to calibrate the detector response and peak areas were used to determine the product ratios. Fluorescence and phosphorescence spectra were run on frozen glass using acetonitrile or cyclohexane. All the photochemical reaction were run in Pyrex vessels in a RPR-100 Rayonet reactor equipped with 16 lamps irradiating at 313 or 366 nm.

Reaction in Neutral Medium.

The ketone (3 mmoles) and 4-cyanopyridine (1 mmole) were dissolved in acetonitrile (10 ml) and 0.75 ml of water. The solution was irradiated for 15 hours. At the end of the irradiation, the solvent was evacuated and the residue was chromatographed using mixtures of hexane and ethyl acetate. For these reactions and those reported in acidic medium, the total yields and the ratios between the two products may vary with the ratio of pyridine to ketone and with the concentration. The reported values refer to the conditions given here.

Reaction in Acidic Medium.

The ketone (3 mmoles) and 4-cyanopyridine (1 mmole) were dissolved in acetonitrile (10 ml), 0.75 ml of water, and 0.1 ml of 10 *M* hydrochloric acid. The solution was irradiated for 15 hours. At the end of the irradiation, the solvent was evacuated, the residue was diluted with water and extracted with dichloromethane. The organic solvent was dried with sodium sulfate, the solvent was evacuated, and the residue was chromatographed using mixtures of hexane-ethyl acetate.

4-(2-Acetyl-3,5-dimethylbenzyl)pyridine (**6**).

This compound was obtained in 5% yield in neutral medium and 10% yield in acidic medium as an oil; ms: m/z 239 (M^+), 224 (M^+-CH_3), 209, 181, 147, 84; ^1H nmr: 8.47 (d, 2H, H_A and H_E, J = 5 Hz), 6.92 (d, 2H, H_B and H_D, J = 5 Hz), 6.92 (s, 1H aromatic), 6.80 (s, 1H aromatic), 3.86 (s, 2H, CH_2), 2.29, 2.27, 2.25 (ss, 9H, 3 CH_3).

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.22; H, 7.14; N, 5.83.

2-(2-Acetyl-3,5-dimethylbenzyl)-4-cyanopyridine (**7**).

This compound was obtained in 1% yield as an oil; ms: m/z 264 (M^+), 263, 249 (M^+-CH_3), 221 (M^+-$COCH_3$), 203; ^1H nmr: 8.69 (d, 1H, H_E, J = 5 Hz), 7.34 (d, 1H, H_D, J = 5 Hz), 7.32 (s, 1H, H_B), 6.95 (s, 1H, aromatic), 6.87 (s, 1H, aromatic), 4.08 (s, 2H, CH_2), 2.41 (s, 3H, CH_3-CO), 2.30 and 2.28 (ss, 6H, 2 CH_3).

Anal. Calcd. for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.44; H, 6.09; N, 10.63.

4-(4-Acetyl-3,5-dimethylbenzyl)pyridine (**8**).

This compound was obtained in 4% yield as an oil; ms: m/z 239 (M^+), 224 (M^+-CH_3), 209, 181, 175, 147; ^1H nmr: 8.60 (d, 2H, H_A and H_E, J = 5 Hz), 7.19 (d, 2H, H_B and H_C, J = 5 Hz), 6.83 (s, 2H aromatics), 3.89 (s, 2H, CH_2), 2.47 (s, 3H, CH_3-CO), 2.21 (s, 6H, 2 CH_3).

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.44; H, 7.15; N, 5.86.

2-(4-Acetyl-3,5-dimethylbenzyl)-4-cyanopyridine (**9**).

This compound was obtained in 10% yield as an oil; ms: m/z 264 (M^+), 249 (M^+-CH_3), 221 (M^+-$COCH_3$), 206; ^1H nmr: 8.82 (d, 1H, H_E, J = 5 Hz), 7.37 (dd, 1H, H_D, J = 5 Hz, J = 1 Hz), 7.32 (s, 1H, H_B, J = 1 Hz), 6.90 (s, 2H, aromatics), 4.12 (s, 2H, CH_2), 2.45 (s, 3H, CH_3-CO), 2.22 (s, 6H, 2 CH_3).

Anal. Calcd. for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.40; H, 6.10; N, 10.57.

1-Phenyl-3-ethoxy-3-(4-cyanopyridin-2-yl)propan-1-one (**10a**).

This compound was obtained in 12% yield as an oil; ms: m/z 280 (M^+), 251, 235, 175, 131 (4CNPy-CH-CH_3^+), 105 (PO-CO^+), 77 (Ph^+); ^1H nmr: 8.74 (d, 1H, H_E, J = 5 Hz), 7.96 (m, 2H, aromatics), 7.79 (s, 1H, H_B), 7.65-7.40 (m, 4H, H_D and 3H aromatics), 5.15 (t, 1H, CHPy, J = 6 Hz), 3.70-3.40 (m, 4H, -CH_2-O- and CH_2-CO), 1.26 (t, 3H, 7 Hz); ^{13}C nmr: 15.3 (CH_3), 45.0 (CH_2-CO), 66.0 (CH_2-O), 78.1 (CHPy), 116.7 (CN), 121.1, 122.8, 123.9, 150.3, 163.8 (Pyridine), 128.2, 128.6, 133.3 (Phenyl), 197.0 (C=O). The multiplicity of ^{13}C signals was determined by DEPT experiment.

Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.92; H, 5.75; N, 10.02.

1-Phenyl-3-[1-(4-cyanopyridin-2-yl)ethoxy]propan-1-one (**11a**).

This compound was obtained in 12% yield as an oil; ms: m/z 280 (M^+), 235, 175, 131 (4CNPy-CH-CH_3), 105 (PO-CO^+), 77 (Ph^+); ^1H nmr: 8.70 (d, 1H, H_E, J = 5 Hz), 8.00 (m, 2H, aromatics), 7.66 (s, 1H, H_B), 7.60-7.40 (m, 4H, H_D and 3H aromatics), 4.63 (q, 1H, CHPy, J = 7 Hz), 3.89 (m, 2H, -CH_2-O-), 3.30 (m, 2H, CH_2-CO), 1.48 (d, 3H, 7 Hz).

Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.77; H, 5.77; N, 9.98.

1-Phenyl-4-methoxy-4-(4-cyanopyridin-2-yl)butan-1-one (**10b**).

This compound was obtained in 25% yield as an oil; ms: m/z 280 (M^+), 251, 207, 175, 105 (Ph-CO^+), 77 (Ph^+); ^1H nmr: 8.75 (d, 1H, H_E, J = 5 Hz), 7.95 (m, 2H, aromatics), 7.69 (s, 1H, H_B), 7.60-7.40 (m, 4H, H_D and 3H aromatics), 4.47 (dd, 1H, CHPy, J = 7 Hz, J = 5 Hz), 3.35 (s, 3H, -OCH_3), 3.12 (t, 2H, -$COCH_2$-, J = 7 Hz), 2.24 (m, 2H, CH_2-CH).

Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.87; H, 5.77; N, 9.99.

2-[1-(4-Cyanopyrid-2-yl)propyloxy]acetophenone (**12a**).

This compound was obtained in 5% yield as an oil; ms: 280 (M^+), 250, 236, 144, 130, 117; ^1H nmr: 8.78 (d, 1H, H_E, J = 5 Hz), 7.75 (dd, 1H, aromatic), 7.55 (s, 1H, H_B), 7.46 (d, 1H, H_D, J = 5 Hz), 7.28 (m, 1H, aromatic), 6. 99 (m, 1H, aromatic), 6.67 (m, 1H, aromatic), 5.36 (t, 1H, O-CHPy, J = 6.0 Hz), 2.80 (s, 3H, CH_3-CO), 2.09 (q, 2H, CH_2, J = 7.2 Hz), 1.08 (t, 3H, CH_3-CH_2, J = 7.2 Hz).

Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.80; H, 5.76; N, 9.96.

2-[1-(4-Cyanopyrid-2-yl)propyloxy]benzophenone (**12b**).

This compound was obtained in 2% yield as an oil; ms: 342 (M^+), 313 (M^+-C_2H_5), 237 (M^+-PhCO), 197 (M^+-4CNPy-C_3H_6), 145 (M^+-PhCOPhO); ^1H nmr: 8.70 (d, 1H, H_E, J = 5 Hz), 7.85-6.75 (m, 11H, 9 aromatics, H_B and H_D), 5.28 (t, 1H, -O-CH, J = 4 Hz), 1.90 (dd, 2H, CH_2, J = 4 Hz, J = 7 Hz) 1.00 (t, 3H, CH_3, J = 7 Hz).

Anal. Calcd. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.98; H, 5.28; N, 8.20.

2-[1-(4-Cyanopyrid-2-yl)benzyloxy]acetophenone (**13a**).

This compound was obtained in 7% yield as an oil; ms: 328 (M^+), 209, 193, 121, 105, 91, 77; ^1H nmr: 8.75 (d, 1H, H_E, J = 5 Hz), 7.83 (s, 1H, H_B), 7.71 (dd, 1H, aromatic, J = 7 Hz, J = 1 Hz), 7.54-7.23 (m, 7H, 6 aromatics and H_D), 7.01 (t, 1H, aromatic, J = 7 Hz), 6.84 (d, 1H, aromatic, J = 8 Hz), 6.46 (s, 1H, -O-CH), 2.67 (s, 3H, CH_3-CO).

Anal. Calcd. for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found: C, 76.71; H, 4.93; N, 8.53.

2-[1-(Pyrid-4-yl)benzyloxy]acetophenone (**14a**).

This compound was obtained in 2% yield as an oil; ms: 303 (M^+), 285, 207, 168, 136, 121, 105; ^1H nmr: 8.58 (d, 2H, H_A and H_E, J = 5 Hz), 7.70 (dd, 1H, aromatic, J = 7 Hz), 7.46-7.23 (m, 8H, 6 aromatics and H_B and H_D), 6.96 (t, 1H, aromatic, J = 7 Hz), 6.83 (d, 1H, aromatic, J = 8 Hz), 6.29 (s, 1H, CHPy), 2.67 (s, 3H, CH_3-CO).

Anal. Calcd. for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62. Found: C, 79.38; H, 5.67; N, 4.63.

2-[1-(Pyrid-4-yl)benzyloxy]benzophenone (**14b**).

This compound was obtained in 14% yield as an oil; ms: 365 (M^+), 307, 197, 168, 149, 121, 105, 77; ^1H nmr: 8.37 (d, 2H, H_A and H_E, J = 5 Hz), 7.86 (m, 2H, aromatics), 7.7-6.8 (mms, 14H, H_B, H_D and 12 aromatics), 6.11 (s, 1H, O-CH-Py).

Anal. Calcd. for $C_{25}H_{19}NO_2$: C, 82.17; H, 5.24; N, 3.83. Found: C, 82.28; H, 5.23; N, 3.82.

4-Benzylpyridine (**15**).

This compound was obtained in 3-5% yield as an oil. The structure was assigned on the basis of the spectroscopic properties as well by comparison with an authentical sample.

α-(5-Cyanopyridin-2-yl)benzyl Alcohol (**16**).

This compound was obtained in 13% yield as an oil; ms: 210 (M^+), 133, 105, 77; ^1H nmr: 8.74 (d, 1H, H_E, J = 5 Hz), 7.50 (s, 1H, H_B). 7.44 (d, 1H, H_D), 7.35 (m, 5H, aromatics), 5.84 (s, 1H, CH-OH), 4.56 (bs, 1H exchangeable with deuterium oxide-OH).

Anal. Calcd. for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.47; H, 4.80; N, 13.32.

2-Phenyl-2-(4-pyridyl)tetrahydrofuran (**17a**).

This compound was obtained in 23% yield as an oil; ms: 225 (M^+), 147, 105, 77; ^1H nmr: 8.51 (d, 2H, H_A and H_E, J = 5 Hz), 7.50-7.10 (m, 7H, H_B, H_D and 5 aromatics), 4.08 (t, 2H, CH_2-O, J = 6 Hz)), 2.70-2.40 (m, 2H, PyPhC-CH_2), 2.00 (m, 2H, CH_2-CH_2).

Anal. Calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.74; H, 6.71; N, 6.21.

2-Phenyl-2-(4-pyridyl)-5-methyltetrahydrofuran (**17b**).

This compound was obtained in 15% yield as an oil; ms: 239 (M^+), 161, 105, 77; ^1H nmr: 8.51 (d, 2H, H_A and H_E, J = 5 Hz), 7.50-7.14 (m, 7H, H_B, H_D and 5 aromatics), 4.28 (s, 1H, CH_3-C*H*-O, J = 6 Hz)), 2.60 (m, 2H, PyPhC-CH_2), 2.20 and 1.64 (m, 2H, CH-CH_2), 1.35 (d, 3H, CH_3, J = 6 Hz); ^{13}C nmr: 21.7 (CH_3), 32.9 (CH_2-CH), 38.7 (CH_2-CPyPh), 75.7 (O-*C*H-CH_3), 87.3 (O-CPyPh), 121.0, 149.8, 155.9 (Pyridine), 125.8, 127.1, 128.4, 145.8 (Phenyl).

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.46; H, 7.16; N, 5.84.

5-(4'-Cyanopyrid-2'-yl)-6-hydroxy-1-phenyl-1-hexanone (**18**).

This compound was obtained in 10% yield as an oil; ms: 294 (M^+), 277, 157, 131, 105, 77; ^1H nmr: 8.74 (d, 1H, H_E, J = 5 Hz), 7.88 (m, 2H, 2 aromatics), 7.70-7.30 (m, 5H, H_B, H_D and 3 aromatics), 3.64 and 3.48 (2ms, 2H, CH_2-OH, J = 6 Hz), 3.18 (q, 1H, CH-Py, J = 7 Hz), 2.87 (m, 2H, CH_2-CO), 2.40 (bs exchangeable with deuterium oxide, 1H, -OH), 2.21 and 2.03 (m, 4H, C*H*-CHPy-C*H*, J = 6 Hz).

Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.62; H, 6.15; N, 9.53.

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