Photochemically Induced Reactions of Selected Ketones with 4-Cyanopyridine in Neutral and Acidic Medium

Rosanna Bernardi [a], Tullio Caronna [b]*, Sergio Morrocchi [b], and Maurizio Ursini [b]

[a] Centro per lo Studio delle Sostanze Organiche Naturali, c/o
[b] Dipartimento di Chimica del Politecnico, Via Mancinelli 7, I-20131 Milano Italy

Received April 6, 1995
Revised March 14, 1996

The presence of the 4-cyanopyridine, in neutral or acidic medium, interferes with the normal behavior of the biradicals obtained by direct excitation of selected ketones, and results in formation of pyridinic derivatives.

J. Heterocyclic Chem., **33**, 1137 (1996).

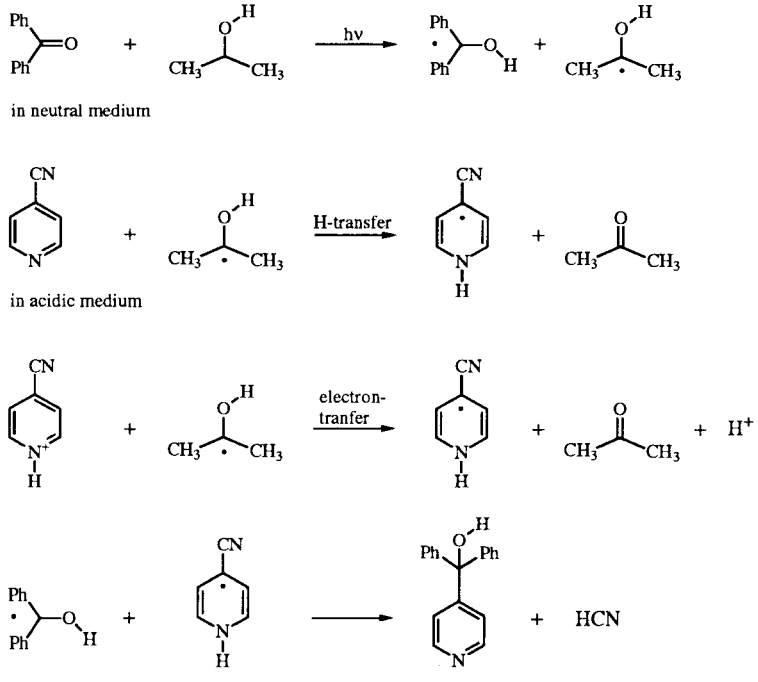
Hydrogen abstraction by photochemically excited ketones is a well documented reaction. This reaction may occur intermolecularly forming two different radicals or intramolecularly forming a biradical (Norrish type II reaction). The fate of this biradical is different depending upon the starting ketone. Valerophenone and *o*-methylacetophenone are representative of ketone photobehaviors. Generally speaking, biradicals arising from excitation of valerophenone and ketones with similar structure have a shorter lifetime (*ca.* 100 ns), while the ones derived by *o*-methylacetophenone and ketones with related structure have a longer lifetime (*ca.* 1500 ns) [1]. Both types of ketones have been studied [2] but their reactivity with other molecules is a function of the biradical lifetime; very little is reported about the reactivity of the short-lived biradicals [3], whereas a great deal of work is reported on the long-lived species [4].

Heterocyclic bases may work as (a) a radical trap in neutral or acidic medium [5], or, (b) in the presence of a reducing species, they may act as an acceptor of hydrogen atoms as well as an acceptor of electrons, forming a heterocyclic radical [6]. In case (a) attack on a free position on the heterocyclic ring occurs, in case (b), if a suitable substituent is present, ipso substitution occurs [7]. A typical reaction for this last case is depicted in Scheme 1.

This study describes the reactions carried out irradiating ketones 1-10 (Table 1) in the presence of 4-cyanopyridine.

4-Cyanopyridine does not absorb at wavelength higher than 300 nm while aromatic ketones absorb near 350 nm; furthermore the triplet energies of the starting aromatic ketones (*ca.* 74 Kcal/ mol) are lower than that of the base (*ca.* 81 Kcal/mol). Thus, it is possible to selectively excite

Scheme 1

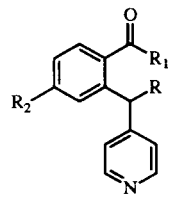


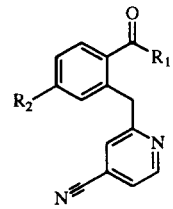
the ketone without energy transfer to the base, which should result in intramolecular hydrogen abstraction. Once the biradicals are formed, they own a ketyl system that may reduce the cyanopyridine. Rate constants for the reduction of pyridine derivatives by ketyl radicals were already reported [8]. In our particular case, the ΔG° for the electron transfer from a dimethyl ketyl radical (halfwave potential for the oxidation:-0.28 V *vs.* SCE [9]) to 4-cyanopyridine (halfwave potential for the reduction: -0.67 V *vs.* SCE in acidic medium [10]), was estimated to be exoergonic (*ca.* -24 Kcal/mol). For this reason, we decided to study the effect of the presence of the 4-cyanopyridine in neutral or acidic medium on the photochemical behavior of some aryl alkyl or diaryl ketones.

In Figure 1 are reported the pyridinic products obtained from irradiation of the ketones and 4-cyanopyridine in neutral condition.

For these experiments, two different behaviors are clearly depicted despite the presence of the base, ketones 1-6 (valerophenone types) show only the typical reactions of intramolecular hydrogen abstraction followed by fragmentation, cyclization, *etc.* We can presume that the lifetime of these biradicals is too short to allow any kind of reaction with the pyridine in non acidic environment. Irradiation of the ketones **7-9** with 4-cyanopyridine gave two different pyridinic products. One arising from the ipso substitution and the other from the attack in position 2. A possible explanation is that the ipso substitution arises from a hydrogen atom transfer from the ketyl moiety to the pyridine as shown in Scheme 1, while the substitution in position 2 may be due to the benzyl radicals that escape from the solvent cage and attack on the pyridine. It is obvious that the pyridine interferes with the normal behavior of the biradical for ketone **7-9**.

Figure 2 lists the pyridinic products obtained from irradiation of the ketones in acidic conditions. In this medium, all the studied ketones gave rise to pyridinic products. Ketones **1-5** and **7** give only attack in position 2, ketone **6** yields only ipso substitution, ketones **8** and **9** produce both





11, R = H R_1 = Me R_2 = H **12**, R_1 = Me R_2 = H **11:12** = 2:1
13, R = Me R_1 = Me R_2 = H
14, R = H R_1 = Ph R_2 = H **15**, R_1 = Ph R_2 = H **14:15** = 1:2
16, R = H R_1 = Ph R_2 = Me **17**, R_1 = Ph R_2 = Me **16:17** = 1:1,3

Figure 1.

kinds of products. The fact that only one product is obtained with ketone **3**, rules out the direct participation of the pyridine in the formation of the final product.

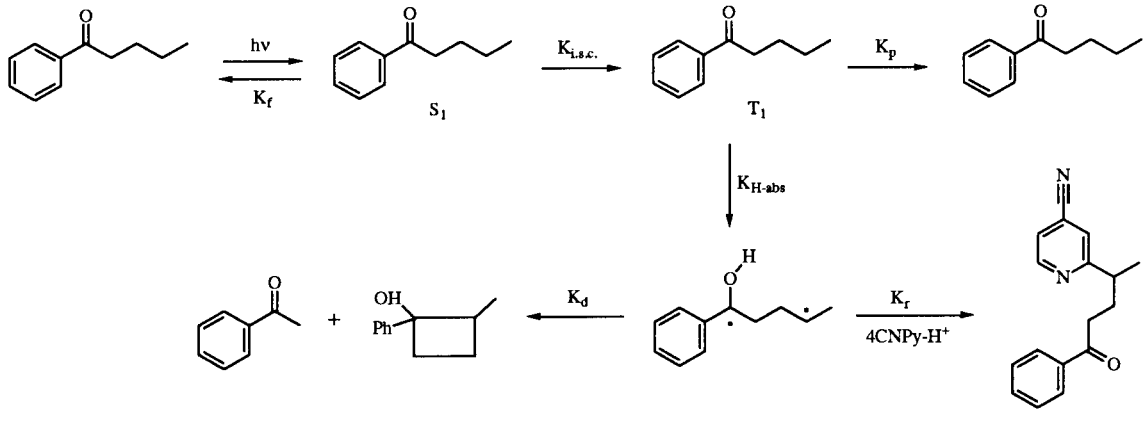
In acidic medium, we demonstrated that the mechanism operating is an electron transfer from a donor [7], and this is not possible from an alkyl chain; moreover, if it is the pyridine to abstract the hydrogen, almost all the methylenes of the chain are equivalent, and this means that we should obtain a mixture of products. A further demonstration that the intramolecular hydrogen abstraction is still operating, is shown by the fact that it is also possible to isolate the products coming from the Norrish type II reaction: for example, ketone **3** gave rise to acetophenone and dec-1-ene; ketone **6** gave rise also to the formation of acetophenone and styrene. In the case of valerophenone, it was possible to determine the efficiency of the quenching of the biradical by the salified 4-cyanopyridine, and from the kinetic scheme, it is possible to derive the following equation (Scheme 2 and Equation 1).

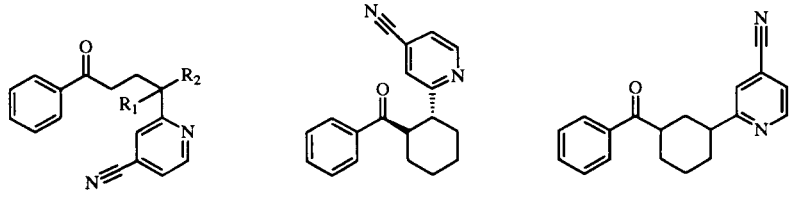
Where $Prod_o$ and $Prod_{Py}$ are respectively the amount of decomposition and cyclization products in absence and in the presence of different amount of salified 4-cyanopyridine and τ is the lifetime of the biradical: namely $1/k_d$. A linear Stern-Volmer plot (Figure 3) with a slope of 11 ± 1 was obtained.

$$Prod_o/Prod_{Py} = 1 + k_a \tau [4CNPy\text{-}H^+]$$

Equation 1.

Scheme 2

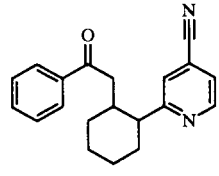




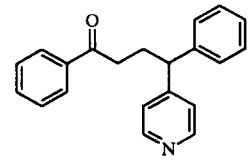
18, $R_1 = H$ $R_2 = CH_3$
19, $R_1 = R_2 = CH_3$
20, $R_1 = H$ $R_2 = C_8H_{17}$

21

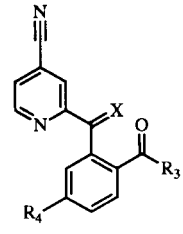
22 + **23**
22 + **23**:**21** = 2.0

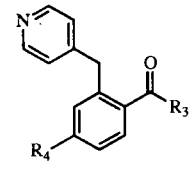


24



25

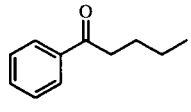




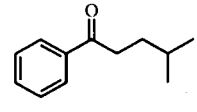
12, $X = H_2$ $R_3 = CH_3$ $R_4 = H$ or **26**, $X = O$ $R_3 = CH_3$ $R_4 = H$
15, $X = H_2$ $R_3 = Ph$ $R_4 = H$ or **27**, $X = O$ $R_3 = Ph$ $R_4 = H$ **14**, $R_3 = Ph$ $R_4 = H$ **15** or **27**:**14** = 10:1
17, $X = H_2$ $R_3 = CH_3$ $R_4 = CH_3$ or **28**, $X = O$ $R_3 = Ph$ $R_4 = CH_3$ **16**, $R_3 = Ph$ $R_4 = CH_3$ **17** or **28**:**16** = 16:1

Figure 2.

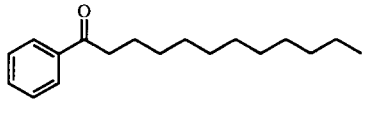
Table 1



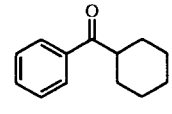
1



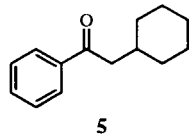
2



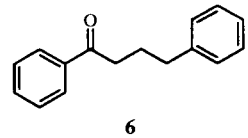
3



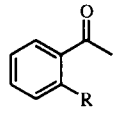
4



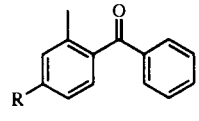
5



6



7, $R = CH_3$
8, $R = CH_2\text{-}CH_3$



9, $R = H$
10, $R = CH_3$

Assuming a value of *ca.* 100 ns as lifetime of the biradical, it is possible to determine k_q as $(1.1 \pm 0.1) \cdot 10^8$, that is a reasonable value compared with that reported for the quenching of the same biradical with paraquat ($4.6 \cdot 10^9$) [2c].

The products arising from ketone **4** show that either the β or the γ hydrogen abstraction is operating probably a result of equatorial *vs.* axial orientation of the phenyl group. In the case of the β abstraction, only the *trans* isomer **21** is obtained, in the case of the γ abstraction two products, **22** and **23**, ratio 8:2 respectively, are obtained. While no attempt was made to assign the *cis* and *trans* structures, the fact that product (**22**) is present in higher amount, leads us to prefer **22** as the *trans* isomer.

For ketones **7-9** care must be taken in the work-up: if the solution is made basic, the benzylic methylene is oxidized to the corresponding ketone, **26**, **27**, **28**, during the work-up, simple dilution with water followed by extraction allow the isolation of the derivative **12**, **15** and **17**.

Despite the fact that in acidic medium the explanation of the products obtained is not straightforward, the first step is clearly an intramolecular hydrogen abstraction by the excited ketone. Several mechanisms are possible. The formation of the pyridinyl radical *via* the oxidation of the ketyl part of the molecule could explain the ipso substitu-

tion products. Attack of the alkyl radical on a protonated pyridine may occur directly by the alkyl part of the biradical or once the oxidation of the ketyl moiety is already occurred. A third hypotheses involves the formation of a cyclic intermediate with the ketyl part of the biradical approaching the pyridine nitrogen to transfer the electron, while the alkyl part bonds at position 2; a similar intermediate has been proposed in the trapping of the photoenol from 2-methylbenzophenone with benzoquinone [11]. At this stage, the product distribution does not allow to choose between the mechanisms, even if we think that this third mechanism may explain in a better way the products formed. In any case, we think we demonstrated that the presence of the 4-cyanopyridine in both neutral and acidic medium may be a useful trap for the radicals that are

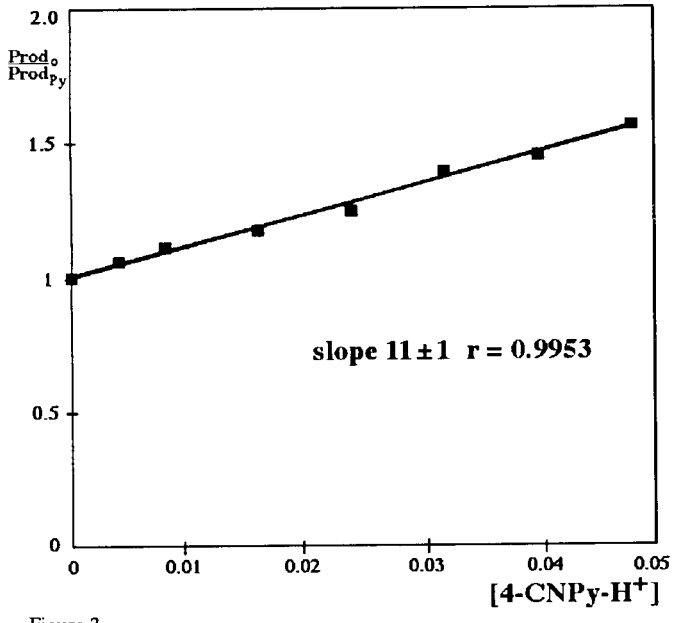


Figure 3.

formed during the irradiation of ketones. Work is in progress to extend the study.

EXPERIMENTAL

4-Cyanopyridine, 2-methyl acetophenone, 2-methyl benzophenone, 2,4-dimethylbenzophenone, valerophenone and cyclohexyl phenyl ketone are commercial products. 3-Methylvalerophenone, undecyl phenyl ketone, and α-cyclohexyl acetophenone were prepared *via* Friedel-Craft acylation on benzene from the corresponding acyl chloride and aluminum chloride. Phenyl 3-phenylpropyl ketone was prepared in the same way from 3-chloropropanoyl chloride

The nmr spectra were measured in deuteriochloroform using TMS as internal standard on a 250 MHZ spectrometer. H_A, H_B, H_C, H_D, and H_E refer respectively to the hydrogen atom in position 2, 3, 4, 5 and 6 in the pyridine ring. Mass spectra were recorded on a single focusing spectrometer. Melting points are uncorrected. Standard flash chromatography refers to the procedure reported by Still [12]. Solid products obtained from chromatography were sufficiently pure to the gas-chromatographic analysis and were not purified further. 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°/minutes after the first 4 minutes) or an OV-1 fused silica capillary column 25 m x 0.25 mm (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°C, 1' at 180°, 10° min^{-1} to 260°. A mixture of weighted compounds and 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 quartz vessels in a RPR-100 Rayonet reactor equipped with 16 lamps irradiating at 366 nm.

Reaction in Neutral Medium.

The ketone (3 mmoles) and 4-cyanopyridine (1 mmole) were dissolved in acetonitrile (10 ml) and 0.25 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 varied with the ratio of pyridine to ketone and with the concentration. The reported ones 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), 0.25 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 to yield **12**, **15**, **17**. If the solution is basified instead of diluted, then a deep blue color develops. Extraction with dichloromethane dissolves the blue color in the organic phase. When the organic solvent is dried with sodium sulfate, the color fades. The solvent was evacuated and the residue was chromatographed using mixtures of hexane-ethyl acetate. The oxidation products **26**, **27**, **28**, were obtained. The yields reported are relative to reacted pyridine, the unreacted pyridine is recovered quantitatively.

Reactions of Valerophenone with Different Amounts of 4-Cyanopyridine.

Two different mother solutions were used: solution **A** was prepared dissolving 0.048 mole of valerophenone, 4.8 ml of 10 *M* hydrochloric acid (0.048 mole), 1.7 ml of water and bringing the volume to 100 ml with acetonitrile; solution **B** was 0.1 *M* 4-cyanopyridine in acetonitrile. To same volumes of solution **A** (6.25 ml) different volumes of solution **B** were added (6, 5, 4, 3, 2, 1, 0.5, 0 ml) and the total volumes were adjusted to 12.5 ml with acetonitrile; the resulting mixtures were irradiated for 10 minutes all together on a Merry-go-round. At the end of the irradiation each solution was concentrated, made basic with aqueous ammonia, extracted with dichloromethane, added with a weighted amount of benzophenone as internal standard, and the amount

of acetophenone and cyclobutane derivative determined by gc.

4-(2-Acetylbenzyl)pyridine (**11**).

This compound was obtained in 27% yield as an oil; ms: m/z 211 (M^+), 196 (M^+-CH_3), 167, 139; ^1H nmr: 8.34 (d, 2H, H_A and H_E, J = 5 Hz), 7.79-7.10 (m, 4H, H arom), 6.95 (d, 2H, H_B and H_D, J = 5 Hz), 4.24 (s, 2H, Py-CH_2), 2.48 (s, 3H, $COCH_3$).

Anal. Calcd. for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.85; H, 6.03; N, 6.41.

2-(2-Acetylbenzyl)-4-cyanopyridine (**12**).

This compound was obtained in 21% yield as an oil; ms: m/z 236 (M^+), 221 (M^+-CH3), 193 (M^+-$COCH_3$); ^1H nmr: 8.66 (d, 1H, H_A, J = 5 Hz), 7.82 (d, 1H, H arom, J = 7 Hz), 7.54-7.28 (m, 5H, H_B, H_D, and 3H arom), 4.50 (s, 2H, Py-CH_2), 2.58 (s, 3H, CO-CH_3).

Anal. Calcd. for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 75.94; H, 5.14; N, 11.90.

4-[1-(2-Acetylphenyl)ethyl]pyridine (**13**).

This compound was obtained in 12% yield as an oil; ms: m/z 225 (M^+), 210 (M^+-CH_3), 195 (M^+-$2CH_3$), 182 (M^+-$COCH_3$), 167, 133; ^1H nmr: 8.47 (d, 2H, H_A, and H_E, J = 5 Hz), 7.61, 7.43, 7.32, 7.29 (m, 4H, H arom), 7.11 (d, 2H, H_B and H_D, J = 5 Hz), 4.94 (d, 1H, Py-C*H*-CH_3, J = 7.5 Hz), 2.44 (s, 3H, CO-CH_3), 1.60 (d, 3H, C*H*$_3$-CH, J = 7.5 Hz).

Anal. Calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.32; H, 6.92; N, 6.11.

4-(2-Benzoylbenzyl)pyridine (**14**).

This compound was obtained in 7% yield as an oil; ms: m/z 273 (M^+), 195 (M^+-Py), 167, 105 (Ph-CO^+); ^1H nmr: 8.36 (d, 2H, H_A and H_E, J = 5 Hz), 7.70 (d, 3H, H arom, J = 7 Hz), 7.61-7.24 (m, 6H, H arom), 7.10 (d, 2H, H_B and H_D, J = 5 Hz), 4.07 (s, 2H, Py-CH_2).

Anal. Calcd. for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.27; H, 5.72; N, 4.94.

2-(2-Benzoylbenzyl)-4-cyanopyridine (**15**).

This compound was obtained in 4% yield as an oil; ms: m/z 298 (M^+), 221 (M^+-Ph), 193 (M^+-Ph-CO), 165; ^1H nmr: 8.56 (d, 1H, H_A, J = 5 Hz), 7.74 (d, 2H, H arom, J = 7 Hz), 7.60-7.20 (m, 9H, H_B, H_D, and 7H arom), 4.33 (s, 2H, Py-CH_2).

Anal. Calcd. for $C_{20}H_{14}N_2O$: C, 80.52; H, 4.73; N, 9.39. Found: C, 80.72; H, 4.78; N, 9.18.

4-(2-Benzoyl-4-methylbenzyl)pyridine (**16**).

This compound was obtained in 12% yield as an oil; ms: m/z 287 (M^+), 272 (M^+-CH_3), 209 (M^+-Py),195 (M^+-CH_2Py); ^1H nmr: 8.41 (d, 2H, H_A and H_E, J = 5 Hz), 7.70 (d, 3H, H arom, J = 7 Hz), 7.60-7.20 (m, 5H, H arom), 7.12 (d, 2H, H_B and H_D, J = 5 Hz), 4.13 (s, 2H, Py-CH_2), 2.40 (s, 3H, CH_3).

Anal. Calcd. for $C_{20}H_{17}NO$: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.29; H, 6.18; N, 4.95.

2-(2-Benzoyl-4-methylbenzyl)-4-cyanopyridine (**17**).

This compound was obtained in 16% yield as an oil; ms: m/z 312 (M^+), 235 (M^+-Ph), 207 (M^+-Ph-CO),105 (Ph-CO^+); ^1H nmr: 8.54 (d, 1H, H_A, J = 5 Hz), 7.72 (d, 2H, H arom, J = 7 Hz), 7.60-7.10 (m, 8H, H_B, H_D, and 6H arom), 4.34 (s, 2H, Py-CH_2), 2.40 (s, 3H, CH_3).

Anal. Calcd. for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 81.07; H, 5.14; N, 8.93.

1-Phenyl-4-(4-cyanopyrid-2-yl)pentan-1-one (**18**).

This compound was obtained in 30% yield as an oil; ms: m/z 264 (M^+), 159 (M^+-Ph-CO),145 (M^+-Ph-CO-CH_2), 132, 105 (Ph-CO^+) ;^1H nmr: 8.69 (d, 1H, H_A, J = 5 Hz), 7.92 (d, 2H, H arom, J = 7 Hz), 7.64-7.25 (m, 5H, H_B, H_D, and 3H arom), 3.20-2.72 (m, 3H, Py-CH- and CH_2-CO), 2.28-1.96 (m, 2H, C*H*$_2$-CH), 1.36 (d, 3H, CH_3, J = 7.5 Hz).

Anal. Calcd. for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.05; H, 6.12; N, 10.62.

1-Phenyl-4-(4-cyanopyrid-2-yl)-4-methylpentan-1-one (**19**).

This compound was obtained in 27% yield as an oil; ms: m/z 278 (M^+), 173 (M^+-Ph-CO), 159 (M^+-Ph-C-CH_2), 146, 105 (Ph-CO^+); ^1H nmr: 8.79 (d, 1H, H_A, J = 5 Hz), 8.05 (d, 2H, H arom, J =7 Hz), 7.94-7.30 (m, 5H, H_B, H_D, and 3H arom), 2.92-2.59 (m, 2H, CH_2-CO), 2.35-2.12 (m, 2H, CH_2-C), 1.45 (s, 6H, $2CH_3$).

Anal. Calcd. for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.36; H, 6.48; N, 10.09.

1-Phenyl-4-(4-cyanopyrid-2-yl)dodecan-1-one (**20**).

This compound was obtained in 32% yield as a white solid mp 57-59°; ms: m/z 362 (M^+), 243 (M^+-Ph-CO-CH_2), 230, 131, 120, 105 (Ph-CO^+); ^1H nmr: 8.72 (d, 1 H, H_A, J = 5 Hz), 7.86 (d, 2H, H arom, J = 7 Hz), 7.60-7.20 (m, 5H, H_B, H_D, and 3H arom), 3.00-2.70 (m, 3H, Py-CH- and CH_2-CO), 2.18-1.74 (m, 4H, C*H*$_2$-CHPy-C*H*$_2$), 1.20 (m, 12H, -$(CH_2)_6$-), 0.85 (t, 3H, CH_3, J = 6 Hz).

Anal. Calcd. for $C_{24}H_{30}N_2O$: C, 79.52; H, 8.34; N, 7.73. Found: C, 79.78; H, 8.31; N, 7.69.

[Trans-2-(4-cyanopyrid-2-yl)cyclohexyl] Phenyl Ketone (**21**).

This compound was obtained in 12% yield as an oil; ms: m/z 290 (M^+), 185 (M^+-Ph-CO), 131, 118, 105 (Ph-CO^+); ^1H nmr: 8.50 (d, 1H, H_A, J = 5 Hz), 7.90 (d, 2H, H arom, J = 7 Hz), 7.49-7.38 (m, 4H, H_D, and 3H arom), 7.20 (dd, 1H, H_B, J = 5 Hz, J = 2 Hz), 4.04 (m, 1H, CH-Py), 3.35 (m, 1H, CH-CO), 2.20-1.20 (m, 8H, $(CH_2)_4$).

Anal. Calcd. for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.42; H, 6.24; N, 9.68.

[3-(4-cyanopyrid-2-yl)cyclohexyl] Phenyl Ketone (*cis* and *trans*) (**22** and (**23**)).

These compounds were obtained in 25% yield as oils; ratio 22:23 = 1.8; ms: m/z 290 (M^+), 185 (M^+-Ph-CO), 105 (Ph-CO^+), 77; ^1H nmr: 8.74 (8.70) (d, 1H, H_A, J = 5 Hz), 7.98 (7.97) (d, 2H, H arom, J = 7 Hz), 7.66-7.30 (m, 5H, H_B and H_D and 3H arom), 3.40 (3.50) (m, 1H, CHPy), 3.86 (3.00) (m, 1H, CH-CO), 2.10-1.50 (2.20-1.50) (m, 8H, CH_2 and $(CH_2)_3$).

Anal. Calcd. for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.90; H, 6.23; N, 9.63; C, 78.25; H, 6.29; N, 9.69).

1-Phenyl-2-[4-cyanopyrid-2-yl)cyclohexyl]ethanone (**24**).

This compound was obtained in 38% yield a white solid mp 105-107°; ms: m/z 304 (M^+), 199 (M^+-Ph-CO), 185 (M^+-Ph-CO-CH_2), 131, 120, 105 (Ph-CO^+); ^1H nmr: 8.63 (d, 1H, H_A, J = 5 Hz), 7.75 (d, 2H, H arom, J = 7 Hz), 7.56-7.28 (m, 5H, H_B and H_D and 3H arom), 3.30-2.50 and 2.10-1.30 (ms, 12H, CHPy, C*H*-CHPy, CH_2-CO, and $(CH_2)_4$).

Anal. Calcd. for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20. Found: C, 78.55; H, 6.58; N, 9.16.

1-Phenyl-4-(4-cyanopyrid-2-yl)-4-phenylbutan-1-one (**25**).

This compound was obtained in 12% yield as a white solid, mp 89-92°; ms: m/z 301 (M^+), 182 (M^+- Ph-CO-CH_2), 167, 149, 120, 105 (Ph-CO^+); ^1H nmr: 8.50 (d, 2H, H_A and H_E, J = 5 Hz), 7.86 (d, 2H, H arom, J = 7 Hz), 7.50-7.15 (m, 10H, H_B, H_D, and 8H arom), 4.20 (t, 1 H, Ph-CH-Py, J = 8 Hz), 2.93 (m, 2H, CH_2-CO, J = 7.5 Hz), 2.50 (m, 2H, CH_2-CH_2-CH).

Anal. Calcd. for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.96; H, 6.35; N, 4.58.

2-(2-Acetylbenzoyl)-4-cyanopyridine (**26**).

This compound was obtained in 39% yield as a white solid mp 183-185°; ms: m/z 250 (M^+), 235 (M^+-CH_3), 221, 207 (M^+-CO-CH_3); ^1H nmr: 8.63 (d, 1H, H_A, J = 5 Hz), 8.46 (d, 1H, H_D, J = 1 Hz), 7.93 (dd, 1H, H arom, J = 7 Hz, J = 2 Hz), 7.75-7.43 (m, 4H, H_C and 3H arom), 2.52 (s, 3H, CO-CH_3).

Anal. Calcd. for $C_{15}H_{10}N_2O_2$: C, 71.99; H, 4.03; N, 11.19. Found: C, 71.70; H, 4.07; N, 11.23.

2-(2-Benzoylbenzoyl)-4-cyanopyridine (**27**).

This compound was obtained in 6% yield as an oil; ms: m/z 312 (M^+), 235 (M^+-Ph), 207 (M^+-Ph-CO), 193, 105 (Ph-CO^+); ^1H nmr : 8.42 (d, 1H, H_A, J = 5 Hz), 8.30 (d, 1H, H_D, J = 1 Hz), 7.82-7.30 (m, 10H, H_B and 9 H arom).

Anal. Calcd. for $C_{20}H_{12}N_2O_2$: C, 76.91; H, 3.87; N, 8.97. Found: C, 76.50; H, 3.80; N, 9.03.

2-(2-Benzoyl-5-methylbenzoyl)-4-cyanopyridine (**28**).

This compound was obtained in 9% yield as an oil; ms: m/z 326 (M^+), 249 (M^+-Ph), 221 (M^+-Ph-CO), 119, 105 (Ph-CO^+); ^1H nmr: 8.43 (d, 1H, H_A, J = 5 Hz), 8.31 (d, 1H, H_D, J = 1 Hz), 7.73 (d, 3H, H arom, J = 7 Hz), 7.65-7.35 (m, 6H, H_B and 5H arom), 2.50 (s, 3H, CH_3).

Anal. Calcd. for $C_{21}H_{14}N_2O_2$: C, 77.29; H, 4.32; N, 8.58. Found: C, 77.61; H, 4.17; N, 8.54.

Acknowledgment.

We gratefully acknowledge Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial support and Ms. Daniela dal Pio Luogo for technical assistance.

REFERENCES AND NOTES

[1] See for example J. C. Scaiano, *Acc. Chem. Res.*, **15**, 252 (1982) and references cited herein.

[2a] L. J. Johnston and J. C. Scaiano, *Chem. Rev.* **89**, 521 (1989); [b] R. Marshall Wilson and K. A. Schnapp, *Chem. Rev.*, **93**, 223 (1993); [c] L. J. Johnston, *Chem. Rev.*, **93**, 251 (1993).

[3a] P. J. Wagner and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 288 (1972); [b] J. C. Scaiano, *J. Am. Chem. Soc.*, **99**, 1494 (1976); [c] R. D. Small and J. C. Scaiano, *J. Phys. Chem.*, **81**, 828, (1977); [d] M.V. Encinas, P.J. Wagner and J.C. Scaiano; *Am. Chem. Soc.*, **102**, 1357 (1980); [e] P. K. Das, *Tetrahedron Letters*, **22**, 1307 (1981).

[4a] J. Kapecky, Organic Photochemistry: A Visual Approach, VCH Publisher, New York, U.S.A. 1992; [b] W. Horspool and D. Armesto, Organic Photochemistry: A Comprehensive Treatment, Ellis Horwood Limited, Chichester, England, 1992.

[5] See for example F. Minisci, A. Citterio and C. Giordano, *Acc. Chem. Res.*, **16**, 27 (1983) and references cited herein.

[6] T. Caronna, S. Morrocchi and B. M. Vittimberga, *J. Heterocyclic Chem.*, **17**, 399 (1980).

[7] For the mechanism operating in neutral or acidic medium, see: [a] T. Caronna, A. Clerici, D. Coggiola and S. Morrocchi; *Tetrahedron Letters*, **22**, 2115 (1981); [b] T. Caronna, A. Clerici, D. Coggiola and S. Morrocchi, *J. Heterocyclic Chem.*, **18**, 1421 (1981).

[8] P. Neta and L. K. Patterson; *J. Phys. Chem.*, **78**, 2211 (1974).

[9] U. Brühlmann and E. Hayon, *J. Am. Chem. Soc.*, **96**, 6169, (1974).

[10] J. Volke and A. M. Kardos, *Collect. Czech. Chem. Commun.*, **33**, 2560 (1968).

[11] R. M. Wilson, K. Hannemann, W. R. Heineman and J. R. Kirchhoff; *J. Am. Chem. Soc.*, **109**, 4743 (1987).

[12] W. C. Still, M. Kahan and A. Mitra, *J. Org. Chem.*, **43**, 2923 (1978).