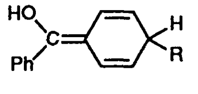
The Photoreduction of 3-Benzoylpyridine: An Experimental and Theoretical Study of the Formation of the Intermediate LAT†

Angelo Albini,[a] Pietro Bortolus,*[,b] Elisa Fasani,*[,a] Sandra Monti,[b] Fabrizia Negri*[,c] and Giorgio Orlandi[c]
[a] *Dipartimento di Chimica Organica, Università di Pavia, Viale Taramelli 10, 27100 Pavia, Italy*
[b] *Istituto di Fotochimica e Radiazioni d'Alta Energia-C.N.R., Via de' Castagnoli 1, 40126 Bologna, Italy*
[c] *Dipartimento di Chimica 'G. Ciamician', Via Selmi 2, 40126 Bologna, Italy*

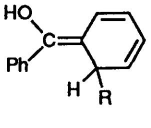
3-Benzoylpyridine (3-BPy) triplet abstracts hydrogen from alcohols to give a ketyl radical similar in its properties to that of benzophenone. In neat isopropanol, the main product of the ketyl radical reactions is the pinacol while in water–isopropanol mixed solvent a 'light absorbing transient' (LAT) accumulates. This is much more stable than the LAT formed by photolysis of benzophenone and results from the coupling of two 3-BPy ketyl radicals, with attack of one of them on the 6 position of the pyridine ring of the other. Chemical evolution of this intermediate leads in part to an oxidized product conserving the same skeleton. Theoretical calculations and transient absorption spectroscopy support the structure of the intermediate and the proposed mechanism of reaction.

The photochemical properties of benzoylpyridines (BPy) have been the object of a relatively small number of papers.[1–6] The lowest excited state of these compounds is an n,π^* triplet localized on the carbonyl group,[3] just as in benzophenone (BP). The photophysical properties[4–6] and the photoreactivity[1,2] of this state are influenced by the position of the aza-substituent. As might be expected, 3-BPy is the isomer most similar to BP. Thus, in benzene solutions, the triplet lifetime and quantum yield of 3-BPy are very similar to those of BP while appreciable differences have been found for 2- and 4-benzoylpyridine.[4]

The triplet state of 3-BPy, like BP, gives a ketyl radical by H-abstraction from H-donor species. However, in the course of an investigation on 3-BPy in aqueous solutions we noticed that UV irradiation in the presence of β-cyclodextrin leads to relatively stable products absorbing at λ > 300 nm, while this phenomenon was not observed for irradiation of similar BP solutions.[7,9] For the sake of comparison, we checked the photochemistry of 3-BPy in alcohols. Preliminary experiments showed that irradiation in water–isopropanol causes the appearance of a new long-wavelength absorption for both 3-BPy and BP. For the latter molecule, such spectral changes are already known and have been attributed to the formation of 'light absorbing transients' (LAT) for which the structures **1** and **2** [R = $(CH_3)_2COH^\cdot$ or $Ph_2COH^\cdot$] have been proposed.[10–13] However, despite intensive investigations in several laboratories, no unambiguous proof of the LATs structure has been obtained. Since in the case of 3-BPy the long-wavelength absorption is much more persistent and, in particular, it is rather stable also in the presence of oxygen, it appeared worthwhile to study in detail the photochemistry of 3-BPy in the hope that this would give more substantial evidence about the LAT structure. We supplemented the experimental investigations with a theoretical study aimed at understanding the LATs structure and the mechanism of their formation.



para-LAT
1



ortho-LAT
2

Experimental

3-Benzoylpyridine (Aldrich) was recrystallized from light petroleum (b.p. 30–40 °C). Isopropanol (Carlo Erba, RP grade) was used as received; water was distilled twice.

UV absorption spectra were measured on a Perkin-Elmer 320 spectrophotometer. NMR spectra were obtained on a Bruker 300 MHz instrument. IR spectra were measured on a Perkin-Elmer 190 spectrophotometer.

Preparative Irradiations.—Several irradiation procedures were adopted, in which both the solvent and the concentration of BP and 3-BPy were changed. A solution (1.9×10^{-3} mol dm^{-3}) of 3-BPy (117 mg) in water–isopropanol (9 : 1, 330 cm^3) was deaerated by flushing with purified nitrogen and irradiated by means of a 15 W low pressure mercury arc in an immersion well apparatus at 17 °C. After 1 h some precipitate had formed and TLC showed almost total consumption of 3-BPy. Three such solutions were reunited and extracted with CH_2Cl_2 (100 cm^3). The extract was dried, evaporated and examined by NMR and UV spectroscopy, and then submitted to chromatography on a silica gel column (50 g, eluent cyclohexane–ethyl acetate 1 : 1, ethyl acetate, and ethyl acetate–methanol 9 : 1). The following products were obtained. 3-BPy, 140 mg (40%). 6-[1-Hydroxy-1-phenyl-1-(3-pyridyl)methyl]-3-benzoylpyridine (**5**, 56 mg, 16%), colourless crystals m.p. 70–72 °C (ethanol) (Calc. for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.3; H, 5.2; N, 7.5%); *m*/*z* 366; ν_{max}/cm^{-1} 3500–2800br, 1600, 1585; δ_H(CDCl$_3$) 8.97 (d, *J* 2, 1 H), 8.5 (br, 2 H), 8.05 (dd, *J* 2, 8, 1 H), 7.8 (d, *J* 8, 1 H), 7.5–7.9 (m, 4 H) and 7.2–7.3 (m, 8 H); λ_{max}(ethanol)/nm 257 (log ε = 4.23). 1-(3-Pyridyl)phenylmethanol (**4**, 10 mg, 3%) identical to a sample prepared according to published procedures.[14] 1,2-Diphenyl-1,2-bis(3-pyridyl)ethanediol (**3**, 28 mg, 8%), colourless crystals, m.p. 172–173 °C (chromatographic fraction washed with ethanol; the product is highly insoluble) (Calc. for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60. Found: C, 78.3; H, 5.7; N, 7.3%). *m*/*z* 368; ν_{max}/cm^{-1} 3300–2800br, 1595, 1585, 1060, 1030, 760, 700; δ_H(DMSO) 8.3 (d, *J* 2, 1 H), 8.28 (d, *J* 7, 1 H), 7.2–7.6 (m, 4 H), 7.0–7.2 (m, 3 H) and 6.3 (s, 1 H, exch).

More dilute solutions (5×10^{-4} mol dm^{-3}) in mixed solvents were also irradiated. In a beaker (15 cm diameter) 250 cm^3 of a water–isopropanol (50/50 v/v) solution vigorously stirred with

---

† Paper presented in part at the XIIIth IUPAC Symposium on Photochemistry, Warwick, Coventry (U.K.), July 22–28, 1990.

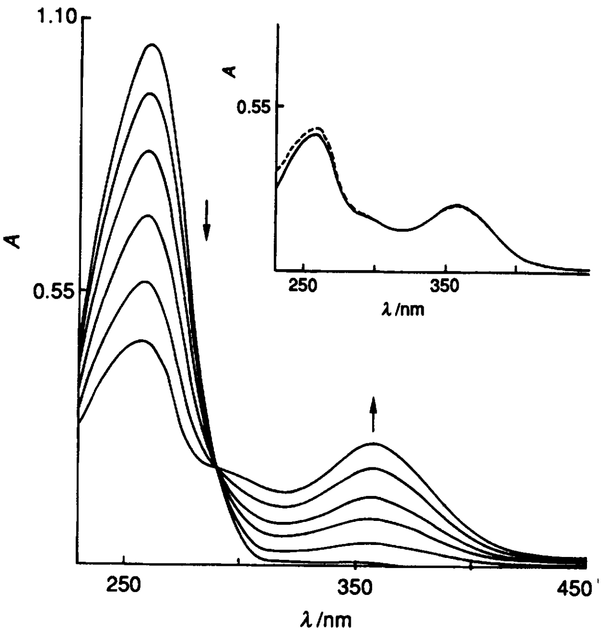


Fig. 1 Time course of irradiation at 254 nm of 3-BPy 8.5 × 10^{-5} mol dm^{-3} in deaerated water–isopropanol (50/50 v/v) mixture. Cell path 10 mm. Irradiation times: 0, 5, 10, 20, 35, 60 s; incident photons 4 × 10^{15} photons s^{-1}. Inset: effect of 5 min O_2 bubbling (– – – –).

a magnetic stirrer and bubbled with pure nitrogen were irradiated with a low pressure mercury arc (Mineral Light): the intensity of the incident light was 5 × 10^{14} photons cm^{-2} s^{-1}. The irradiation was stopped when the value of the absorbance $A_{259}/A_{360} = 2$. The solution was then extracted with dichloromethane (three times) and the combined extracts reduced to a small volume by distillation under reduced pressure. The combined small volumes (rich in isopropanol) were stored at low temperature until the manipulation for the identification. 600 mg of 3-BPy were transformed in the crude photoproducts by following the described procedure. The solution was evaporated and chromatographed as above. The products obtained were: 3-BPy (170 mg, 28.3%), **5** (59 mg, 9.8%), **4** (32 mg, 5.3%) and **3** (5 mg, 0.8%).

An isopropanol solution of 3-BPy (c = 1.1 × 10^{-1} mol dm^{-3}, 100 mg in 5 cm^3) in a quartz tube was deaerated and irradiated for 3 h by means of an external 15 W low pressure mercury arc. The precipitate was filtered and identified as product **3**. The solution was evaporated and chromatographed as above and gave the following products: 3-BPy (30 mg, 30%), **3** (62 mg, 62%), traces of products **4** and **5**.

Irradiation of 2 × 10^{-4} mol dm^{-3} isopropanol solution gives 3-BPy (35%), **3** (45%) and traces of products **4** and **5** (HPLC evaluation). Lastly a 0.5 cm^3 sample of 1.1 × 10^{-1} mol dm^{-3} in octadeuterio isopropanol was similarly irradiated and the NMR spectrum showed a clean conversion into product **3** (a part precipitated out).

Laser Photolysis.—Experiments were carried out with equipment described elsewhere.[7] The laser light (266 nm or 355 nm, 15 ns pulse duration) was focussed on a rectangular area, 3 mm high and 10 mm wide, of the cell containing the sample. The first two millimetres were analysed for transmitted light in a right angled geometry. The solutions were deoxygenated by bubbling N_2 during the measurements. 3-BPy ground state absorbance was *ca.* 0.8 at the excitation wavelength. Care was taken in changing the solution after a few laser shots to avoid troubles from photoproducts accumulation. Temperature was 22 ± 2 °C.

Theoretical Section.—Potential energy curves for the coupling reaction between the ketyl radical $(CH_3)_2COH^•$ and the radicals 3-BPyH$^•$ or BPH$^•$ to form a closed shell adduct have been computed by the AM1 hamiltonian.[15] We have used the unrestricted Hartree–Fock (UHF) procedure which is more suitable than the closed shell HF to describe the breaking or formation of a bond.[16]

The potential energy curves were computed with respect to the distance between the two interacting carbon atoms, chosen as the reaction coordinate; all the remaining internal coordinates were optimized separately for each value of the reaction coordinate.

We have checked the values of S^2, indicating the total spin, which should be zero in the case of a singlet state. The values of S^2 for all intermolecular distances are found to be > 1. These values are uncomfortably high and indicate that triplet, quintet *etc.*, multiplicity components are present to a substantial degree in the UHF function. Even after annihilation of the first two spurious components did the S^2 values remain too high (about 0.5). Thus we present the results obtained for the unprojected calculations. Given the high value of S^2, the energy results obtained should be considered as qualitative and should be used only to establish trends and preference for the attack on different positions.

Excitation energies and oscillator strengths for the $S_0 \longrightarrow S_1$ transition of the adducts have been calculated by the CNDO/S[17] hamiltonian at the geometry obtained by the AM1 calculation. The CI treatment comprises the electronic configurations in the 3 × 3 and 4 × 4 MO space.

Results and Discussion

Steady State Irradiations.—In the absence of oxygen, the irradiation of 3-BPy, both in alcohols and in water–alcohol mixtures, leads to the growth of a long-wavelength absorption: the phenomenon is more remarkable in water-rich solutions. In Fig. 1 are reported the spectral variations following the irradiation of 3-BPy 8.5 × 10^{-5} mol dm^{-3} in water–isopropanol (50/50 v/v). The decrease of the intense $\pi\pi^*$ band of the ketone peaking at 259 nm, is accompanied by the increase of the absorption in the region 300–450 nm with a maximum at 360 nm and a shoulder around 315 nm. An isosbestic point is observed at 290 nm and could indicate that the primary products are accumulated without significant further transformation. This is confirmed by TLC analysis during the time course of irradiation.

Photolysis of BP under the same conditions is shown in Fig. 2. In this case the decrease of the band peaking at 254 nm corresponds to the growth of an absorption with maximum at 320 nm, extending toward 400 nm, with isosbestic point at 288 nm. These spectral changes have been attributed to the formation of a mixture of unstable intermediates, the so-called LATs (**1** and **2**) An *ortho* adduct with absorption maximum at 358 nm and a *para* adduct, more stable and predominant, with maximum at 317 nm have been proposed.[13] These products undergo a slow thermal decomposition[13] and are known to be rapidly removed by O_2 as we confirmed (see the inset of Fig. 2).

The products of the photolysis of 3-BPy are less sensitive to the O_2 attack (see inset of Fig. 1) and are stable in diluted solutions for days. In neat isopropanol the spectral changes following irradiation are qualitatively similar, but the long-wavelength maximum grows less than in water–isopropanol, and less at higher 3-BPy concentrations.

Preparative Irradiations.—The distribution of the isolated products depends considerably on solvent and BPy concentration. Irradiation of 10^{-1} mol dm^{-3} 3-BPy in neat isopropanol up to *ca.* 80% conversion (the long wavelength absorption is

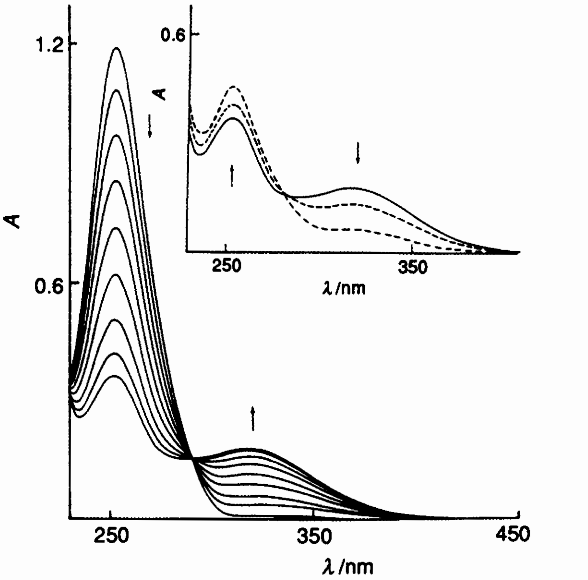


Fig. 2 Time course of irradiation at 254 nm of BP in water–isopropanol (50/50 v/v) mixture under the same experimental conditions as in Fig. 1. Inset: effect of 2 and 5 min O_2 bubbling (– – – –).

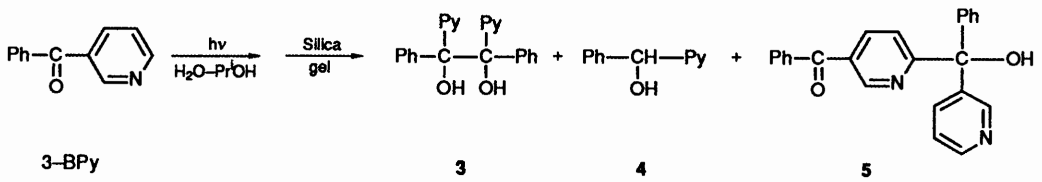
very little developed under these conditions) leads essentially to a single photoproduct in high yield. In part, this precipitates out if the starting 3-BPy concentration is $> 10^{-2}$ mol dm^{-3} and is easily recognized as the pinacol **3** from its analytical and spectral properties. A low amount of the alcohol **4** and other products in traces are also present. In more dilute solutions ([3-BPy] = 2×10^{-4} mol dm^{-3}), pinacol **3** remains the main product, but the quantity of the minor products is somewhat higher than in 10^{-1} mol dm^{-3} solution.

The irradiation in water–isopropanol leads to different results. A 1.9×10^{-3} mol dm^{-3} solution was irradiated up to *ca.* 95% conversion (TLC, UV); under this condition the long-wavelength absorption is quite important. Extraction with dichloromethane gave a solution conserving the same spectrum. Evaporation gave a yellow oil which shows, when redissolved in CH_2Cl_2, the same spectrum as the original extract. Some diminution in intensity (*ca.* 8%), was observed. At this stage TLC showed proportions of 3-BPy larger than in the raw photolysate. Examination of this oil by NMR showed some olefinic signals (6.9 d, 5.45 dd, 5.0 dd, 3.9 d), but no aliphatic signals; this system could be accounted for by formula **6** (see Scheme 2). From the integral ratio this is > 50% of the mixture, with 3-BPy 10–15% and other products not detected (see below). Chromatography on silica gel afforded a large amount of 3-BPy (40% of the starting material), alcohol **4** (3%), 8% of pinacol **3** and a new product. Elemental analysis and mass spectrum show that it has formula $C_{24}H_{18}N_2O_2$; it contains a carbonyl and a hydroxy function and one of the pyridine rings is substituted at position 6. The protons at position 2, 4 and 5 are clearly identified at δ 8.97, 8.05 and 7.8 respectively. The substituted benzoylpyridine **5** (16% yield) accounts well for these analytical data (Scheme 1). Irradiation of more dilute (5×10^{-4} mol dm^{-3}) solutions leads to the same photoproducts, but with a higher proportion of the alcohol **4** (5.3%) and a lower one of products **3** (0.8%) and **5** (9.8%).

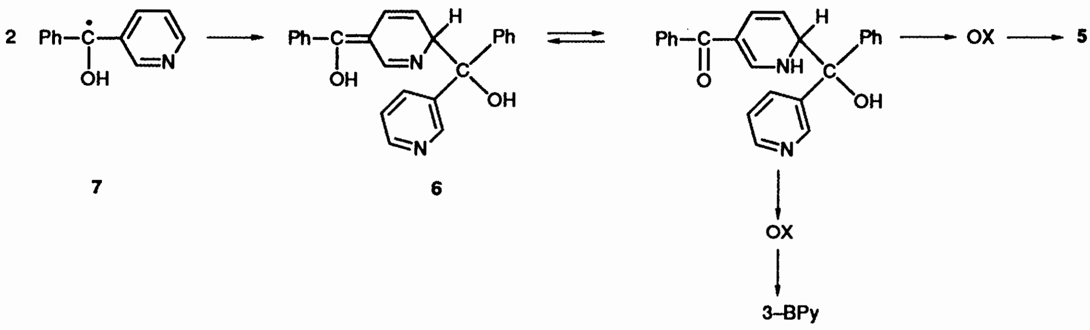
Laser Flash Photolysis.—Excitation at 266 nm of 3-BPy 7.1×10^{-5} mol dm^{-3} in water–isopropanol (50/50 v/v) leads to the formation of ketyl radicals upon H-abstraction from an alcohol molecule by the triplet state of the ketone. Such a species is easily recognized on the basis of its absorption properties, known by pulse radiolysis,[8] in the difference spectrum 400 ns after the laser pulse [Fig. 3, curve (*a*)]. The decay of this radical does not depend on 3-BPy concentration up to 5×10^{-3} mol dm^{-3} and closely follows second-order kinetics. From the disappearance of the absorbance at $\lambda_{max} = 560$ nm, and assuming[8] $\varepsilon_{max} = 3400$ dm^3 mol^{-1} cm^{-1}, a value of $2k = 5.7 \times 10^8$ dm^3 mol^{-1} s^{-1} is calculated, very close to that obtained in pulse radiolysis experiments in water–isopropanol (85/15 v/v) or in water–*tert*-butyl alcohol (90/10 v/v), where the self-coupling reaction is the only path for radical decay.[*,8] The time evolution of the difference spectrum shows in the region 340–450 nm the build up of an absorption, which parallels the decay of the radical and that can be attributed to a LAT-like product [Fig. 3 curves (*b*), (*c*)]. The kinetic analysis in this wavelength range has been performed after subtraction of the contribution due to the 3-BPyH$^\bullet$ radical, whose initial concentration is known from the absorbance at 560 nm.[11] A plot of $Y = [A(t) - A_{3\text{-BPyH}^\bullet}(t)]^{-1}$ *vs.* $1/t$ for $\lambda = 360$ nm is reported in Fig. 3 inset. The value of $2k$ extracted is 5.8×10^8 dm^3 mol^{-1} s^{-1} in excellent agreement with the value obtained

---

[*] In neat isopropanol the disappearance of the radical is characterized by $2k = 6.1 \times 10^8$ dm^3 mol^{-1} s^{-1} (value determined at $\lambda_{max} = 560$ nm by assuming $\varepsilon_{max} = 3400$ dm^3 mol^{-1} cm^{-1}).



Scheme 1



Scheme 2

Table 1 Electronic energies (kcal mol^{-1}) computed by AM1 for increasing values of the C–C bond distance for the reaction between the 3-BPy and BP ketyl radicals with the dimethyl ketyl radical

3-BPy						BP	
Position 2		Position 4		Position 6		Position 4	
R/Å	*E*	*R*/Å	*E*	*R*/Å	*E*	*R*/Å	*E*
1.57	−17.76	1.56	−24.12	1.56	−26.42	1.56	−38.47
1.67	−15.46	1.66	−21.62	1.66	−23.21	1.66	−35.17
1.77	−9.98	1.76	−15.78	1.76	−17.85	1.76	−29.39
1.87	−4.36	1.86	−9.78	1.86	−11.52	1.86	−22.50
1.97	−0.28	1.96	−5.14	1.96	−6.48	1.96	−16.70
2.07	−0.63	2.06	−3.39	2.06	−5.26	2.06	−14.69
2.27	−2.89	2.26	−6.81	2.26	−8.86	2.26	−17.31
2.47	−9.82	2.46	−10.99	2.46	−12.99	2.46	−21.2
2.77	−11.05	2.76	−14.75	2.76	−16.13	2.76	−24.8
∞	−19.20	∞	−19.20	∞	−19.20	∞	−28.9
$E_{barrier}$	18.92		15.81		13.94		14.21

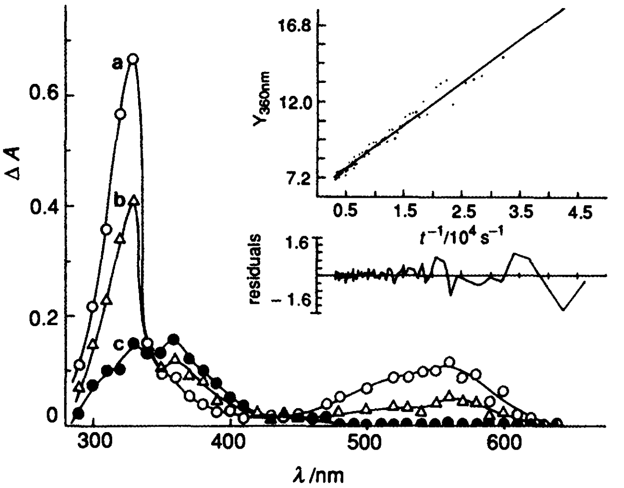


Fig. 3 Difference spectra obtained after 266 nm excitation of a 7.1×10^{-5} mol dm^{-3} deaerated solution of 3-BPy in water–isopropanol (50/50 v/v): (*a*) 400 ns; (*b*) 50 μs; (*c*) 800 μs after a 8 mJ laser pulse. Inset: kinetic analysis of Δ*A* at 360 nm using the treatment described in the text.

from the analysis at 560 nm. So the formation of the LAT appears to be the main path for radical decay.

Theoretical Calculations.—The main aim of our effort in this section is to evaluate the possibility of LAT-like product formation through the calculation of the potential energy curves for the addition of $(CH_3)_2COH^•$ radical to 3-BPyH• and BPH• radicals. We found that the presence of components of multiplicity higher than singlet in the UHF functions (see Experimental section) is greater when the interaction of two aromatic ketyl radicals is taken into consideration. Therefore we limited the discussion to a simplified model system, the addition of $(CH_3)_2COH^•$ to 3-BPyH• and BPH•.

Different attack sites have been considered on the ring and the results are shown in Table 1 and, for illustrative purposes, in Fig. 4. The results for the attack of the $(CH_3)_2COH^•$ on the phenyl ring of 3-BPyH• have not been reported because they are indistinguishable from those involving the BPH• radical. The electronic energies for increasing values of the C–C bond distances show relatively high barriers, of the order of 15 kcal mol^{-1}.* However, it should be remembered that, since the barrier corresponds to the region intermediate between the separated radicals and the formed C–C bond, its height is overestimated by a UHF calculation. In the pyridyl ring positions 2, 4 and 6 are the most reactive. The adduct in position 6 seems to be the most stable and positon 4 is clearly favoured with respect to position 2. A comparison of the height of the barriers, shows that reaction rates are in the order 6 > 4 > 2. No appreciable difference was found in reactivity at position 4 for BPH• and 6 for 3-BPyH• (both *para* with respect to the radical carbon).

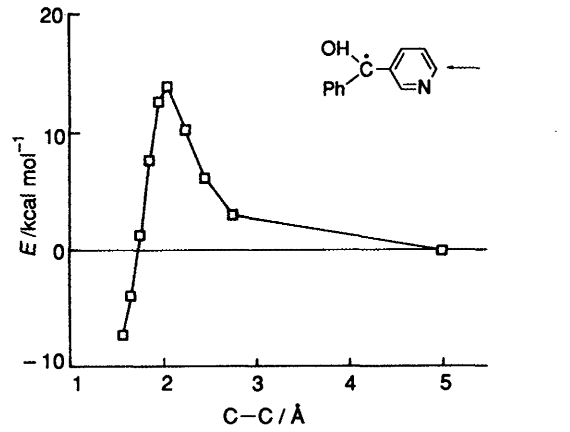


Fig. 4 Potential energy curves for the addition of the isopropyl alcohol radical in position 6 of the pyridyl ring of the 3-BPy ketyl radical

In Table 2 are reported the transition energies and the oscillator strengths for the lowest singlet state S_1 of the various adducts. It appears that S_1 energies depend on the reaction site. The values computed are in good agreement with the absorption changes reported in Figs. 1 and 2 and this is a good indication that a mixture of products with similar structure may be present in the irradiated solutions.

Finally it should be noted that the C–C equilibrium distances are 1.56–1.57 Å, *i.e.* larger than a C–C single bond. Thus the low stability of these intermediates, which prevents their separation and characterization, could be explained by the presence of a weaker bond (the ease of oxidation also makes an important contribution, see later). On the basis of this calculation, no differences in the stability of the 3-BPy and BP adducts are evidenced.

Mechanism of Reaction.—The previous experiments show that the fate of the 3-BPyH• radical formed by H-abstraction from isopropanol strongly depends on the medium and, to some degree, on the 3-BPy concentration.

---

* 1 cal = 4.184 J.

Table 2 $S_0 \longrightarrow S_1$ transition energies (eV) and oscillator strengths of 3-BPy and BP adducts calculated by the CNDO/S hamiltonian[a]

	3-BPy adduct			BP adduct
	Position 2	Position 4	Position 6	Position 4
ΔE	4.34 (3.87)	3.65 (3.54)	4.33 (4.04)	4.14 (3.92)
f	0.52 (0.32)	0.52 (0.54)	0.87 (0.71)	0.76 (0.76)

[a] CI in the 3 × 3 MO space; in brackets CI in the 4 × 4 MO space.

In neat isopropanol the reaction course is very similar to that of BP. The formation of some LAT is spectroscopically observed, but by far the main product is the pinacol. The reaction reasonably follows the mechanism proposed for benzophenone, where the $(CH_3)_2COH^{\bullet}$ radical reduces a second molecule of the ketone and the two radicals couple to give pinacol.[18-22]

In aqueous mixtures, in contrast, the LAT is accumulated to a much larger extent. NMR and UV measurements indicate that its concentration grows to more than 50% of the starting material. There is no doubt about the structure of this species since its electronic spectrum corresponds to the calculated one, the NMR spectrum in the mixture is compatible, and, what is more compelling, a stable end product conserving the same skeleton has been isolated. Flash photolysis measurements are also consistent with the formation of LAT-like products as the main channel for the self-coupling reaction of the radical 3-BPyH$^{\bullet}$ (**7**, Scheme 2).

Thus, while in isopropanol the radical **7** couples through the hydroxylated carbon to give pinacol **3**, in water–isopropanol the coupling involves position 6 of one pyridine ring. A rationale would be that a more polar and more strongly H-bonding medium alters the electronic distribution in the radical and/or favours an intermediate complex with some charge separation leading to the compound **6**. In agreement with theoretical predictions, the attack at position 6 is favoured. This compound is an aza-analogue of the 'isobenzopinacol', first proposed[10,12] for the BP-derived LAT. With respect to this latter, the 3-BPy-derived LAT is more stable in solution even in the presence of oxygen since aza-substitution makes its oxidation less easy. Compound **6** does not survive chromatography. Apparently, a main path of decomposition is a reverse cleavage to the ketyl radicals, in agreement with calculations which show that the C–C bond is weak. The radicals are then dehydrogenated to 3-BPy, as can be inferred from the fact that the amount of starting material obtained from chromatography is larger than that present in the raw photolysate. However, there is another important path for **6**: the dehydrogenation without C–C bond cleavage to give the product **5**.

The photolysis of benzophenone in alcohols leads, in addition to the main products benzopinacol and benzhydrol, to the isolation of a small amount (1%) of 4-(α-hydroxyalkyl)-benzophenone.[19] The presence of this product and the lack of LAT formation in the photolysis of the benzophenone–benzydrol system have suggested[13] that the benzophenone LAT arises from the coupling of the benzophenone ketyl (BPH$^{\bullet}$) with the $(CH_3)_2COH^{\bullet}$ radical. However, in the photolysis of 3-BPy, we have found no indication for the occurrence of such a process which would give the intermediate **8**. We hypothesize that the reaction of the dimethylketyl radical with the 3-BPyH$^{\bullet}$ radical (**7**) occurs by H transfer rather than by attack at the ring as in the BP case. The formation of the carbinol **4**, whose yield is larger at lower starting 3-BPy concentration, where the alcohol radical is not trapped by 3-BPy itself,[9] is in agreement with this mechanism.

The failed isolation of a product analogous to **5** in the photolysis of BP could indicate a different reactivity of BPH$^{\bullet}$ and 3-BPyH$^{\bullet}$, but it could be also explained by a high instability of the hypothetical BP-isobenzopinacol: this question cannot be settled by us at the moment. However the present results give firm support (through the isolation of a stable photoproduct and theoretical calculation of the spectrum and reaction path) to the long time formulated hypothesis that coupling of aryl ketones' ketyl radicals can involve the aromatic ring.

Acknowledgements

We thank Dr. Nadia Camaioni for the computerization of the data acquisition in the flash photolysis apparatus.

References

1 J. P. Blanchi, *J. Chim. Phys.*, 1972, **69**, 1171.
2 C. R. Hurt and N. Filipescu, *J. Am. Chem. Soc.*, 1972, **94**, 3649.
3 J. Blanchi and A. R. Watkins, *Mol. Photochem.*, 1974, **6**, 133.
4 G. Favaro, *J. Chem. Soc., Perkin Trans. 2*, 1976, 869.
5 G. Favaro, *J. Photochem.*, 1981, **15**, 89.
6 G. Favaro and F. Masetti, *J. Phys. Chem.*, 1978, **82**, 1213.
7 S. Monti, N. Camaioni and P. Bortolus, *Photochem. Photobiol.*, 1991, **54**, 577.
8 D. A. Nelson and E. Hayon, *J. Phys. Chem.*, 1972, **76**, 3200.
9 S. Monti, L. Flamigni, A. Martelli and P. Bortolus, *J. Phys. Chem.*, 1988, **92**, 4447.
10 G. O. Schenck, M. Cziesla, K. Eppinger, G. Matthias and M. Pape, *Tetrahedron Lett.*, 1967, 193.
11 P. Colman, A. Dunn and M. F. Quinn, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 2605.
12 N. Filipescu and F. L. Minn, *J. Am. Chem. Soc.*, 1968, **90**, 1544.
13 A. Demeter and T. Berces, *J. Photochem. Photobiol.*, 1989, **46**, 27.
14 J. P. Wibaut, H. P. Wallingford, H. J. Rany and D. K. Kettes, *Rec. Trav. Chim. Pays-Bas*, 1955, **74**, 1049.
15 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
16 H. B. Schlegel, *J. Chem. Phys.*, 1986, **84**, 4530.
17 Del Bene and H. H. Jaffè, *J. Chem. Phys.*, 1968, **48**, 1807.
18 J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, *J. Am. Chem. Soc.*, 1952, **81**, 1068.
19 M. B. Rubin, *Tetrahedron Lett.*, 1982, **23**, 4615.
20 Y. M. A. Naguib, C. Steel and S. G. Cohen, *J. Phys. Chem.*, 1988, **92**, 6574.
21 A. Demeter, B. Lazlo and T. Berces, *Ber. Bunsenges Phys. Chem.*, 1988, **92**, 1478.
22 A. Demeter and T. Berces, *J. Phys. Chem.*, 1991, **95**, 1228.

Paper 2/06135J
Received 18*th November* 1992
Accepted 11*th January* 1993