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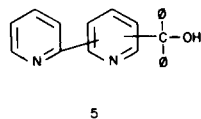
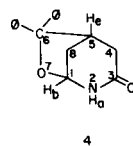
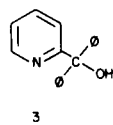
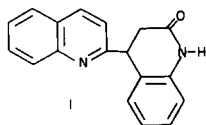
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The photoinitiated reaction of 2-pyridinecarbonitrile and benzophenone in acidic 4:1 2-propanol-water yields substitution product **3** and bicyclic product **4**. In nonacidic solution **3** is the principal product in addition to small amounts of a bipyridyl compound **5**.

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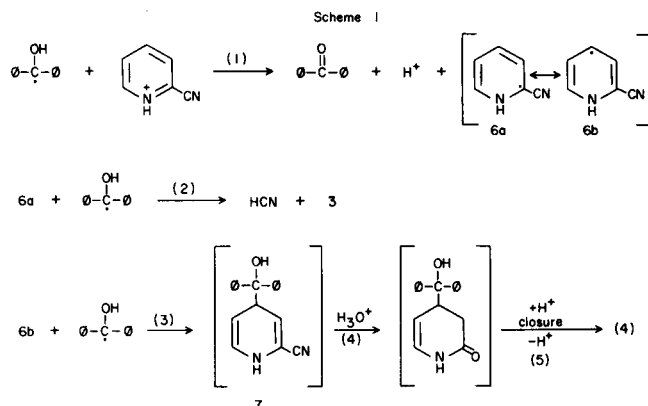
6-Membered monoazaaromatic compounds have been shown to undergo a number of interesting photochemical reactions. For example, irradiation of a mixture of 2-quinolinecarbonitrile and benzophenone in acidic aqueous-2-propanol results in triplet-triplet energy transfer and through a series of steps leads to the lactam **1** (1).

Furihata and Sugimori have reported that direct irradiation of 2-pyridinecarbonitrile (**2**) in acidic ethanolic solution, using a low pressure Mercury lamp, yields 6-ethoxypyridine-2-carbonitrile and 2-(1-hydroxyethyl)pyridine (**2**). We have now examined the reaction of **2** with benzophenone under conditions in which most of the incident light is absorbed by benzophenone.



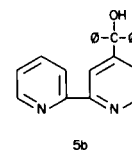
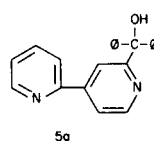
When the reaction was carried out at 350 nm in acidic medium (4:1 2-propanol/water acidified with hydrochloric acid) the principal products isolated were diphenyl(2-pyridyl)carbinol **3** (56% yield) and 7-oxa-2-azabicyclo[3,2,1]-6-diphenyloctan-3-one (**4**) (8.5% yield). Relatively large amounts of benzopinacol were also formed. Since benzopinacol was a product of this reaction, it is logical to assume that the mechanism involves diphenyl ketyl radicals produced by the known process of hydrogen atom abstraction by the T ($n\pi^*$) state of benzophenone. An electron transfer could then readily occur from diphenyl ketyl to a protonated 2-pyridinecarbonitrile forming radical **6** (3). Cross coupling of diphenyl ketyl radical and **6** at the 2

position results in **3** while coupling at the 4 position yields **7**. Hydrolysis of **7** and ring closure at position 6 yields **4** (Scheme 1) (4). The hydrolysis shown in step (4) is similar to that observed in the formation of **1** from 2-quinolinecarbonitrile (1).



When the reaction of **2** with benzophenone was repeated in neutral medium, **3** formed in 64% yield in addition to a 2% yield of dipyridyl compound **5**. Benzopinacol also forms while **4** was absent. Under these conditions, electron transfer would be much less favorable and **6a** most likely forms in a hydrogen atom abstraction reaction by an excited 2-pyridinecarbonitrile (5).

The analytical data obtained for the dipyridyl compound **5** does not allow us to distinguish between structures **5a** and **5b**. The fact, however, that no 4-(hydroxydiphenylmethyl)pyridine-2-carbonitrile was isolated points



to **5a** as the more probable structure. It is not clear, at this time, why **4** forms only in acid solution. It is possible,

however, that the first step in its formation may be an attack of diphenyl ketyl on the 4 position of protonated **2** followed by electron transfer to form **7**, hydrolysis and ring closure.

EXPERIMENTAL

Nuclear magnetic resonance spectra (nmr) were recorded with a Varian XL-100-15 spectrometer using tetramethylsilane as an internal reference. Infrared spectra were determined on a Perkin-Elmer 177 spectrophotometer. Mass spectra were recorded with a Hitachi-Perkin-Elmer RMU 6D single focusing spectrometer. Melting points were not corrected. The yields were calculated on converted base.

Photoinitiated Reaction of 2-Pyridinecarbonitrile in Acidic Medium.

A solution of 3 g. (0.028 mole) of 2-pyridinecarbonitrile and 6 g. (0.03 mole) of benzophenone in 80 ml. of 2-propanol and 20 ml. of water acidified with 2.48 ml. of hydrochloric acid (36%, 0.028 mole) was placed in a quartz tube and subjected to three freeze-vacuum-thaw cycles and then irradiated at 350 nm in a Rayonet RPR 100 photochemical reactor for 17 hours. After irradiation, the mixture had a strong odor of hydrogen cyanide and contained white crystals which were collected by filtration (2.5 g.) and shown to be benzopinacol by melting point determination and infrared analysis. The filtrate was made basic with 10% sodium hydroxide and extracted several times with chloroform. The combined extracts were dried over anhydrous sodium sulfate and the solvent removed under vacuum. From the residual oil, a white product (**4**) crystallized which was collected on a filter and washed with chloroform (0.350 g., 8.6% yield). The filtrate was evaporated down and the residue subjected to chromatography on a silica gel column. Elution with hexane-ethyl acetate 90:10 gave 0.3 g. of benzophenone, 0.6 g. benzopinacol, and 2.1 g. of **3** (56% yield). When the column was eluted with hexane-ethyl acetate 70:30, 1.5 g. of 2-pyridinecarbonitrile was recovered (50% recovery).

Diphenyl(2-pyridyl)carbinol (**3**) was recrystallized from hexane, m.p. 104-104.5° (Lit. (6) 105°). Identification of this compound was made by ir, nmr, and elemental analysis, and mass spectroscopy.

7-Oxa-2-azabicyclo[3,2,1]-6-diphenyloctan-3-one (**4**).

This compound was purified by recrystallization from either benzene or chloroform, m.p. 258-260°; ir (nujol): 3210 (NH) and 1685 (C=O) cm^{-1} ; nmr (DMSO): δ 8.48 (d, H_a , 1, $J_{ab} = 2.5$ Hz), 7.6-7.0 (m, aryl, 10), 5.22

(dd, H_b , 1, $J_{ab} = 2.5$ Hz, $J_{bc} = J_{bd} = 2$ Hz), 3.55 (m, H_e , 1), and 2.6-1.75 (an ABX and an ABX₂ unresolved system, 4H); ¹³C-nmr (25.18 MHz, DMSO): δ 169.7 (s, C₃), 146.6, 144.3 (s, aryl, -C=), 128-124.5 (aryl, -CH=), 90.0 (s, C₆), 81.2 (d, C₁), 39.5 (d, C₅), 36.2, 35.1 (t, C₄ and C₈); ms: M⁺ 279.

Anal. Calcd. for C₁₈H₁₇NO₂: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.28; H, 6.24; N, 4.86.

Photoinitiated Reaction of 2-Pyridinecarbonitrile in Neutral Medium.

The reaction mixture was prepared in the same way as described above except for the absence of hydrochloric acid. After 17 hours of irradiation at 350 nm a large amount of benzopinacol (2.7 g.) was formed and collected on a filter. The remaining solution was extracted with chloroform, dried over anhydrous sodium sulfate, and the solvent removed by evaporation. The residual oil was chromatographed on a silica gel column. Elution with hexane-ethyl acetate 90:10 yielded 0.4 g. of benzophenone, 0.6 g. of benzopinacol and 2.9 g. of **3** (64% yield). Elution with hexane-ethyl acetate 70:30 yielded first 1.2 g. of unreacted 2-pyridinecarbonitrile (40% recovery) and then, 0.1 g. of **5** (2% yield). Highly polar products were also eluted with methanol as before. The dipyriddy compound **5** was recrystallized from ethanol, m.p. 165-167°; ir (potassium bromide): 3445 (OH) cm^{-1} , no cyanide band was present; nmr (deuteriochloroform): δ 8.73 (dd, α to nitrogen, 2, $J_{33} = 5$ Hz, $J_{24} = 1$ Hz), 7.5-7.92 (m, 4), 7.1-7.5 (m, 11), 6.37 (broad s, OH, 1); ms: m⁺ 338.

Anal. Calcd. for C₂₃H₁₈N₂O: C, 81.63; H, 5.36; N, 8.28. Found: C, 81.66; H, 5.32; N, 8.34.

REFERENCES AND NOTES

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