The Electron Transfer Reactions of Cyano Substituted Pyridines and Quinolines with Thermally Generated Diphenyl Ketyl

Patricia McDevitt and Bruno M. Vittimberga*

Chemistry Department, University of Rhode Island,
Kingston, RI 02881

Received April 25, 1990

Electron transfer reactions of cyano substituted pyridines and quinolines with thermally generated diphenyl ketyl are reported. When E½(-) for the heterocycle is less negative than -2V, electron transfer occurs from the ketyl to the heterocyclic base. In some cases the products obtained from the thermal reaction are the same as those obtained from the photochemical reaction with benzophenone and alcohols. In other cases different products are formed. Two bases, 2-pyridinecarbonitrile and 2,4-pyridinedicarbonitrile, undergo regiospecific reactions in which the course of the reaction is determined by the acidity of the medium. A mechanism in which the heterocyclic nitrogen is involved in the substitution process at the 2 position is proposed.

J. Heterocyclic Chem., **27**, 1903 (1990).

The photochemistry of 6-membered monoazaaromatic compounds has been studied extensively over the last ten years [1]. When alcohol is the solvent, radical formation occurs either by electron transfer or by hydrogen atom abstraction from the alcohol through the triplet state of the nitrogen base. The former generally results when the reactive state is π, π^* and the latter when this state is n, π^* [2].

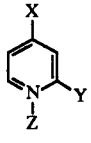
Because of the poor intersystem crossing efficiency of these nitrogen heterocycles, benzophenone is often used as an energy transfer agent to populate the triplet state. In solvents of moderate polarity, such as 2-propanol, if efficient quenching of benzophenone triplets does not occur, electron transfer from diphenyl ketyl formed by the photoreaction of these triplets with alcohol could become a major pathway for radical formation.

In order to examine the feasibility of electron transfer from diphenyl ketyl to nitrogen heterocycles while avoiding the possibility of triplet state involvement in either hydrogen atom abstraction or energy transfer, we examined the reactions of a number of 6-membered monoazaaromatic compounds with diphenyl ketyl generated by the thermal homolysis of benzopinacol [3].

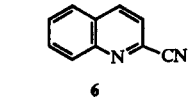
All reactions were run in 5:1 2-propanol-water containing the heterocycle and benzopinacol. Solutions were deaerated by nitrogen bubbling and then heated at reflux under nitrogen (82°). Preliminary tests conducted with 4,4′-bipyridyl dihydrochloride, which forms a blue radical ion on electron transfer, indicate that homolysis of benzopinacol begins at approximately 68° and increases with increasing temperature. The heterocycles that were studied by this procedure include pyridine, 2-pyridinecarbonitrile (**1**), 4-pyridinecarbonitrile (**2**), 2-chloropyridine (**3**), 4-chloropyridine (**4**), 2,4-pyridinedicarbonitrile (**5**), 2-quinolinecarbonitrile (**6**), and 1-methyl-4-cyanopyridinium iodide (**7**) (Table 1). Most reactions were run for 48 hours, though reaction times varied from 10 to 72 hours and included both neutral and acidic conditions. Reaction mixtures were usually separated by column chromatography on silica gel using combinations of hexane and chloroform as eluents.

Table 1

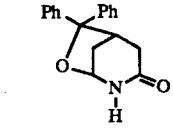
Heterocycles Studied and Products Obtained in the Reaction with Thermally Generated Diphenyl Ketyl



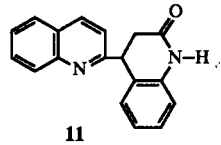
Compound	X	Y	Z
1	H	CN	–
2	CN	H	–
3	H	Cl	–
4	Cl	H	–
5	CN	CN	–
7	CN	H	CH_3
8		H	–
9	H		–
12		H	–
13	CN		–
14			–



6



10



11

The results show that in some cases removal of the $E_{o,o}$ component from the electron transfer process resulted in substantially the same products with thermally generated diphenyl ketyl as was obtained in the photochemical reactions with benzophenone but with different yields. In other cases different products were formed as can be seen in Table 2.

Table 2
Product Percentages for the Reaction of Heterocyclic Bases with Thermally Generated Diphenyl Ketyl

Nitrogen Base	Acidic (A) Neutral (N)	Product	% Yield [a]	References
1	A	8	16.5 (0)	[4]
		9	0 (54)	
		10	23 (8.5)	
	N	9	32 (65)	[4]
2	A	8	52 (7.2)	[5]
		12	0 (18.7)	
	N	8	38 (100)	[5]
5	A	13	38 (21)	[6]
		14	2.7 (16)	
	N	13	22.4 (35)	[6]
		14	7.1 (0)	
		1	0 (31)	
6	A	11	44 (41)	[7]

[a] The numbers in parentheses refers to yields in the corresponding photochemical reactions.

The free energy, ΔG_{et}, for the electron transfer from ketyl to base was calculated using equation 1:

$$\Delta G_{et} = -nF[(E_{1/2}(+) + E_{1/2}(-)] \qquad (1)$$

and was found to be negative for all compounds studied except for pyridine and 2- and 4-chloropyridines. An accurate value of $E_{1/2}(+)$ for the ketyl was not available. Since, however, electron transfer from diphenyl ketyl does not occur with bases which have $E_{1/2}(-)$ values more negative than -2.0V, we assumed a value of $E_{1/2}(+) = +2.0$V for this ketyl in determining the ΔG_{et} values found in Table 3. Pyridine and the chloropyridines which have $E_{1/2}(-)$ values less than -2.0V do not undergo electron transfer reactions with diphenyl ketyl (Table 3).

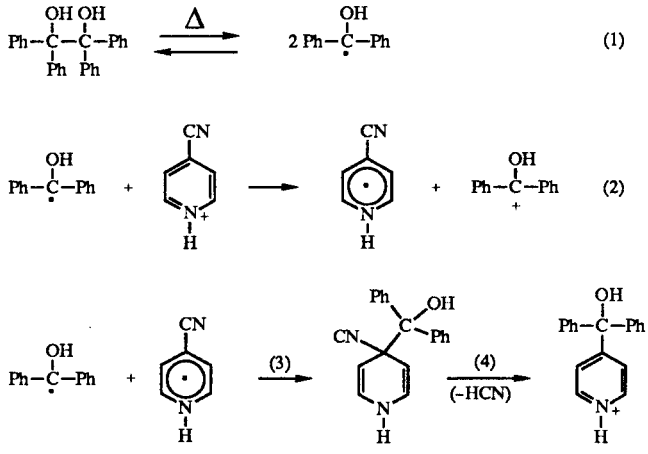
Table 3
Reduction Potentials and Approximate ΔG_{et}

Compound	$E_{1/2}$ (-) (V) [a]	Approximate ΔG_{et} (kcal/mole) [b]
Pyridine	> 2.0	> 0
2-Chloropyridine	> 2.0	> 0
4-Chloropyridine	> 2.0	> 0
4-Chloropyridine•HCl	- 1.79	- 4.84
2-Pyridinecarbonitrile	- 1.70	- 6.92
4-Pyridinecarbonitrile	- 1.87	- 2.99
1-methyl-4-cyanopyridinium iodide	- 0.66	- 30.8
2-quinolinecarbonitrile	- 1.65	- 8.05
2,4-pyridinedicarbonitrile	- 1.38	- 14.3

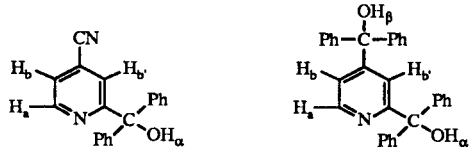
[a] $E_{1/2}$ (-) were measured against SCE in acetonitrile. [b] ΔG_{et} was calculated from the eqation, $\Delta G_{et} = -nF[E_{1/2}(+) + E_{1/2}(-)]$, with $E_{1/2}$ (+) for diphenyl ketyl taken as + 2.00 volts.

The mechanism that explains these results involves the homolysis of benzopinacol to diphenyl ketyl and the electron transfer from the ketyl to the receptor heterocycle as shown in Scheme 1 for 4-pyridinecarbonitrile in acidic solution.

Scheme 1
Mechanism for the Reaction of Thermally Gencrated Diphenyl Ketyl with 4-Pyridinecarbonitrile



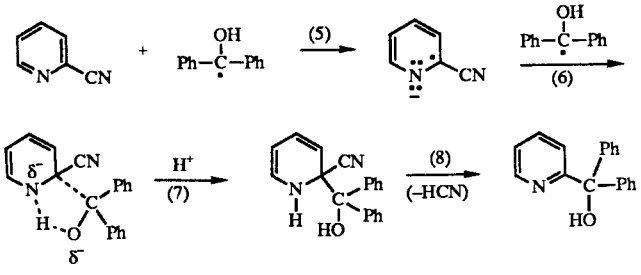
Particularly interesting results were obtained with two of the heterocycles studied, 2-pyridinecarbonitrile (**1**) and 2,4-pyridinedicarbonitrile (**5**) which undergo regiospecific reactions with diphenyl ketyl. Spin density calculations show that the highest spin population in the ring resides at position 2 in **15** [8] and 4 in **16** [6]. However, in acidic medium attack occurs at position 4 of **15**, while in neutral medium the only product isolated, **9**, is the result of radical coupling at the 2 position of **15**.



For both **1** and **5**, the degree of protonation in neutral medium should be essentially zero, while in acid solution in which the molarity of the base considerably exceeds that of the acid, one would expect little salt formation with **1** and very little or none with **5** [9]. After an electron is transferred from ketyl to heterocycle, the radical anion from **1** should be more basic and more easily protonated than **1** while the radical anion from **5** would still be of lower basicity than that of **1** and slow to protonate.

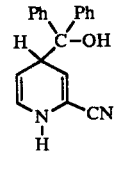
With **5** the monosubstitution product **13** is formed in substantially higher yield than the disubstitution product **14** under all reaction conditions. This implies that preferred coupling occurs at position 2 of radical **16** even though the highest spin density is found at position 4. With both **1** and **5** preference for attack at the 2 position in unacidified

solution can be explained by assuming that first pyridinyl radical anion is formed by electron transfer from a ketyl radical to the heterocyclic base. This increases the electron density on the ring and promotes hydrogen bonding between the ketyl-OH and the nitrogen atom of the ring leading to substitution at the 2 position through a 5-membered transition state as shown in equations (5) through (8) for **1**.

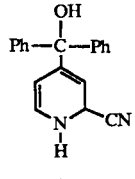


This mechanism explains the sensitivity of the reactions of **1** to acidic conditions. The reactions at the 2 and 4 positions of **1** reflect the competition between protonation of the radical anion and hydrogen bonding with the ketyl radical. The results with **1** indicate that coupling at the 2 position and attack at the 4 position are mutually exclusive processes, with reaction occurring at the 2 position under neutral conditions and at the 4 position in acidic medium. The manifestation of this regioselective reaction is the fact that **8** and **10**, which both involve attack at the 4 position, form only in acidic medium.

The decyanation of the molecules that have undergone attack at the 4 position to yield **8** requires an explanation. It is reasonable to assume that the attack by ketyl on **1** at the four position would yield the dihydro intermediate **17**.



17



18

We have previously reported that a step in the formation of **10** involves the hydrolysis of the bond bearing the cyano group [4]. It would, however, seem equally possible that a proton could catalyze an allylic shift that would place the double bonds in conjugation as shown by **18**. Elimination of HCN would then follow yielding **8**. The product in which the cyano group remains on the ring was not observed.

The reaction pattern observed with **5** clearly shows that substitution in the 2 position is the preferred reaction. However, the effect of acidity on mono and disubstitution is difficult to explain at this time. The ratio of **13**:**14** is 3.2 under neutral conditions and 14 under acidic conditions. The formation of pyridinyl radical with **5** is expected. However, since exclusive substitution at the 4 position is not observed, it may be concluded that cross-coupling at this position with diphenyl ketyl, if it occurs, is reversible. Reaction at the 2 position most likely involves the nitrogen atom in a manner similar to that described for **1**, and this may prevent what would most likely also be a reversible reaction from occuring. It seems reasonable to assume that with the decrease in basicity anticipated for the radical anion corresponding to **16** over that of **15**, that hydrogen bonding of the ketyl with the ring nitrogen resulting in 2 substitution should compete reasonably well with protonation of the nitrogen atom to form the pyridinyl radical. In the photochemical work done with **5** it was determined that decyanation in the 4 position involves the corresponding radical anion [10]. We must assume that in the thermal reaction, since we do not isolate any products in which decyanation has occurred, either the intermediate radical anion does not have a lifetime long enough to effect this reaction or the mechanism leading from the radical anion to the decyanation product is not possible under the conditions of the thermal reaction. Once the cyano group is gone from the 2 position, the spin density at the 4 position should increase to a level similar to that of **2** and coupling at this position should no longer be reversible.

EXPERIMENTAL

All melting points were determined on either a Thomas-Hoover or a Mel-Temp capillary melting point apparatus. Infrared Spectra were determined using a Beckmann Acculab IV or a Perkin Elmer Model 821 infrared spectrophotometer. Wherever possible, spectra were taken with neat samples using sodium chloride cells, or in pellet form using spectrograde potassium bromide. Ultraviolet and visible spectra were recorded on the Cary 15 or 210 Model Recording ultraviolet spectrophotometer using known concentrations in quartz cells. The nuclear magnetic resonance spectra were recorded on a Varian EM 360 A or a EM 390 A NMR spectrophotometer and the chemical shifts are reported in parts per million (ppm) from tetramethylsilane (internal standard for pmr). The coupling constants, J, are reported in cycles per sec (cps). Deuterated solvents were obtained from the Aldrich Chemical Company.

Column chromatography on silica gel (Woelm, mesh 60) was used to separate components of complex chemical reaction mixtures with combinations of hexane, benzene, chloroform, and methanol as eluents. The number of components in the reaction mixtures was first determined by tlc using plastic sheets that were precoated with silica gel impregnated with fluorescent indicator (Polygram Sil UV_{254}) (Macherey-Nagel and Co.). Elemental analyses were performed by Micro Analysis, Inc., Wilmington, Delaware. Product yields are based on the limiting reagent present in the reaction.

Materials.

The compounds 2- and 4-pyridinecarbonitrile, 2-chloropyridine, and 4-chloropyridine hydrochloride were available from the Aldrich Chemical Company, 2,4-Pyridinedicarbonitrile was

obtained from ICN Pharmaceutical, Inc., *N*-Methyl-4-cyanopyridinium iodide was synthesized in this laboratory by a direct displacement reaction on methyl iodide. All solid compounds were recrystallized once before use. 2-Quinolinecarbonitrile was synthesized by a procedure previously published [11]. The liquid compounds were distilled under vacuum and used the same day. All reagents were A.C.S. reagent grade solvents. All reaction mixtures were deaerated with nitrogen gas which was first bubbled through pyrogallol and then passed through a drying tube containing drierite.

Preparation of Benzopinacol.

Benzopinacol was prepared by the photochemical reaction of benzophenone with 2-propanol according to the method of Ciamician and Silber [12] and was recrystallized twice from ethanol and dried under vacuum. The melting point of the dried crystals was 179-180° [13].

Thermal Decomposition of Benzopinacol in the Presence of 4,4'-Bipyridyl Dihydrochloride.

The double salt analog of Paraquat, 4,4'-bipyridyl dihydrochloride, was used in this model experiment to monitor the formation of diphenyl ketyl. In a reaction vessel was placed 4,4'-bipyridyl dihydrochloride (0.12 g, 5 x 10^{-4} mole) dissolved in 51 ml of 2-propanol and water (5:1). The solution was deaerated with nitrogen for one-half hour and then heated to 82°. No color change was observed. The mixture was then cooled and benzopinacol (0.35 g, 9 x 10^{-4} mole) added, deaerated again, and heated. At 68° a slight color change was observed. When the temperature reached 78° a deep blue color formed which persisted as the solution was heated to reflux at 82°. Heating was stopped after ten minutes and the mixture cooled to room temperature. When air was introduced into the reaction vessel, the color disappeared.

Thermal Reaction of Benzopinacol and 2-Pyridinecarbonitrile Under Acidic Conditions.

Benzopinacol (1.03 g, 0.003 mole) and 2-pyridinecarbonitrile (1.0 ml, 0.010 mole) were placed in an acidic solution of 2-propanol and water (0.50 ml of 1*M* sulfuric acid in 31 ml of 5:1 2-propanol and water). The solution was deaerated for one hour and then heated at reflux for forty-eight hours. During that time all the cyrstals dissolved and the solution had acquired a yellow tint. When the mixture was cooled, crystals formed. The crystals were collected and the filtrate neutralized with a 10 percent sodium hydroxide solution and then extracted three times with chloroform. The extracts were combined and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent by evaporation under reduced pressure leaving an oil as residue which was subjected to column chromatography on silica gel. Three compounds were eluted from the column. These were shown by infrared and nmr spectroscopy to be benzophenone (1.0 g, 50% yield), diphenyl-(4-pyridyl)methanol (**8**) (0.12 g, 17% yield, mp 234-235.5°, lit 235° [14]) and 7-oxa-2-azabicyclo[3.2.1]-6-diphenyloctan-3-one (0.18 g, 23% yield, mp 254-256°, lit 254° [4]).

Thermal Reaction of Benzopinacol and 2-Pyridinecarbonitrile Under Neutral Conditions.

Benzopinacol (5.12 g, 0.014 mole) and 2-pyridinecarbonitrile (2.00 ml, 0.021 mole) were dissolved in 170 ml of 2-propanol and water (5:1) and the mixture treated in the same manner as described above. Four compounds were isolated by column chromatography. These included benzophenone (1.56 g, 36% yield), benzopinacol (0.74 g, 14% recovery), 2-pyridinecarbonitrile (0.77 g, 36% recovery), and diphenyl(2-pyridyl)methanol (**9**) (1.11 g, 32%, mp 104-105° (hexane), lit 105° [4]). The yield of product is based on the amount of pyridinecarbonitrile used. Infrared and nmr analyses are consistent with the assigned structure.

The Reaction of Thermally Generated Diphenyl Ketyl with 4-Pyridinecarbonitrile in Acidic Medium.

Benzopinacol (7.6 g, 0.02 mole) and 4-pyridinecarbonitrile (2.0 g, 0.02 mole) were placed in an acidified solution of 2-propanol and water (10 ml of 1M sulfuric acid in 250 ml of 2-propanol and water (5:1)). The mixture was deaerated and then heated at reflux (81°) for 48 hours. When the reaction mixture was cooled, crystals separated and were collected on a filter. This was shown to be diphenyl(4-pyridyl)methanol (**8**) by infrared analysis and mixture melting point determination. The reaction mixture was then neutralized and extracted with chloroform and the combined extracts dried and the solvent removed as usual. The residual oil contained some crystalline matter which was isolated by filtration and recrystallized twice from acetone yielding 2.6 g (52%) of diphenyl(4-pyridyl)methanol mp 235-236 [14]. The infrared spectrum was superimposable on that of a known sample and the nmr spectrum was consistent with the assigned structure.

The Reaction of Thermally Generated Diphenyl Ketyl with 4-Pyridinecarbonitrile Under Neutral Conditions.

Benzopinacol (2.0 g, 5.5 x 10^{-3} mole) and 4-pyridinecarbonitrile (0.58 g, 5.5 x 10^{-3} mole) were dissolved in a solution of 2-propanol and water (5:1). The mixture was deaerated and the reaction run in the same way as described above for the acidified solution. The residual oil that was obtained was subjected to column chromatography, as usual, yielding four compounds. These included benzophenone (0.45 g, 40% yield), benzopinacol (0.87 g, 44% recovery), and diphenyl(4-pyridyl)methanol (0.43 g, 38% yield).

When this reaction was repeated using 2-propanol as the only solvent, diphenyl(4-pyridyl)methanol was isolated in 5.6% yield.

The Reaction of Thermally Generated Diphenyl Ketyl with 2,4-Pyridinedicarbonitrile in an Acidic Medium.

Benzopinacol (1.63 g, 4.5 x 10^{-3} mole) and 2,4-pyridinedicarbonitrile (0.40 g, 3.1 x 10^{-3} mole) were placed in a round bottomed flask containing an acidic solution of 2-propanol and water (1 ml of solution of 1*M* sulfuric acid in 70 ml of 5:1 2-propanol-water). The solution was deaerated for one hour with nitrogen and then heated at reflux at 81° for forty-eight hours. Work up and column chromatography were performed as usual. Five compounds were eluted from the column. These included benzophenone (0.59 g, 37% yield), recovered benzopinacol (0.01 g, 0.7%), unreacted 2,4-pyridinedicarbonitrile (**5**) (0.01 g, 2.4% recovery), and 2-(α-hydroxydiphenylmethyl)pyridine-4-carbonitrile (**13**), mp 82-83° (0.36 g, 38% yield); ir (potassium bromide): 3420 (sharp) (OH), and 2240 cm^{-1} (C≡N); ^1H nmr (acetone-d_6): δ 5.91 (s, 1, H_α), 7.31 (s, 10, Ar), 7.58 (dd, 1, H_b), 7.89 (s, 1, $H_{b'}$) 8.75 (dd, 1, H_a), J_{ab} = 5 Hz, $J_{b'b}$ = 0.5-1 Hz); ms: m/e (M^+) = 286 (Calcd. 286) [15].

Anal. Calcd. for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.93. Found: C, 79.91; H, 5.18.

2,4-*bis*(α-Hydroxydiphenylmethyl)pyridine (**14**) was also obtain-

ed in 2.7% yield (0.37 g) mp 148-148.5; ir (potassium bromide): 3540 (sharp) (OH) and 1600 cm^{-1} (sharp) (-C=C-); ^1H nmr (acetone-d_6): δ 5.50 (s, 1, H_β), 6.05 (s, 1, H_α), 7.20-7.39 (s, 22, Aryl-H), 7.35 (1, H_b) 7.35 (1, $H_{b'}$), 8.40 (dd, 1, H_a) ($J_{a,b}$ = 5 Hz); ms: m/e (M^+) = 443 (Calcd. 443).

Compound **14** was purified by recrystallization from ethanol.

Anal. Calcd. for $C_{31}H_{25}NO_2$: C, 83.95; H, 5.68; N, 3.16. Found: C, 84.02; H, 5.90; N, 3.23.

Reaction of Thermally Generated Diphenyl Ketyl with 2,4-Pyridinedicarbonitrile Under Neutral Conditions.

Benzopinacol (1.78 g, 4.8 x 10^{-3} mole) and 2,4-pyridinedicarbonitrile (0.43 g, 3.3 x 10^{-3} mole) were dissolved in 70 ml of 2-propanol water (5:1). This mixture was deaerated for 20 minutes with nitrogen bubbling and the reaction conducted in the same manner as described above for **1**. Column chromatography of the residual oil isolated from the reaction mixture gave four compounds which included benzophenone (0.78 g, 51% yield), recovered benzopinacol (0.20 g, 11%), **13** (0.21 g, 22% yield), and **14** (0.01 g, 7.1% yield). All structures were confirmed by mixture melting point determination and infrared and nmr analysis.

Reaction of Thermally Generated Diphenyl Ketyl with *N*-Methyl-4-Cyanopyridinium Iodide.

N-Methyl-4-cyanopyridinium iodide (**7**) (2.1 g, 8.4 x 10^{-3} mole), benzopinacol (5.57 g, 0.015 mole) and 170 ml of 2-propanol-water (5:1) were placed in a 500 ml three necked round-bottomed flask equipped with reflux condenser and bubbling tube. The mixture was deaerated with nitrogen and heated to reflux for forty-two hours with nitrogen bubbling. During this time the solution exhibited several visible color changes which included from the original orange to blue in twenty-four hours, then to green followed by amber twenty hours later. When the solution was cooled and air introduced, the amber color changed to orange and quickly disappeared. The mixture was reduced to a dark orange oil under vacuum on a rotary evaporator. Water was added (50 ml) and this mixture was extracted with chloroform several times. The combined extracts were dried and the solvent and drying agent removed as usual. Chromatography on silica gel yielded benzophenone as the only identifiable compound. When the column was washed with 6*N* hydrochloric acid, the residue obtained was shown by infrared analysis to contain both cyano and aromatic absorption and to be, most likely, a 2-substituted pyridine compound. The aqueous layer was concentrated *in vacuo* and the residue chromatographed on silica gel using mixtures of tetrahydrofuran and methanol as eluents. Three compounds were eluted in salt form from the column. One of these was identified as a 1,1'-dimethyl-4,4'-bipyridinium salt (0.044 g) mp 258-259°; ir (potassium bromide): 3000 (ArC-H), 2850 (-CH_3), 1640 cm^{-1} (-C=C-); ^1H nmr (methanol-d_4): δ 4.28 (s, CH_3, 6), 7.8 (d, Ar, 4), 8.6 (d, Ar, 4). The other two compounds crystallized under vacuum, but upon exposure to the atmosphere, they absorbed moisture and dissolved. The infrared spectra of these compounds showed absorption at 2250 cm^{-1} for a cyano group, broad absorption between 2600-3000 cm^{-1} for a pyridine salt and sharp absorption at 2800 cm^{-1} for a methyl group. Both ir and ^1H nmr analysis indicated that the compounds were most likely 2,2- and 2.4-coupled bipyridyls. Due to the small quantities isolated (9.0 x 10^{-3} g and 9.6 x 10^{-3} g) no further work was done on either of these compounds.

Attempted Reaction of Pyridine and 2- and 4-Chloropyridine With Thermally Generated Diphenyl Ketyl in Acidic Aqueous 2-Propanol.

Pyridine and 2-chloropyridine were subjected to the thermal reaction with benzopinacol in acidified aqueous 2-propanol for seventy-two hours and 4-chloropyridine for forty-eight hours. The reaction mixtures were treated in the usual manner and the residue chromatographed on silica gel. No products were isolated that contained the pyridine ring.

The Reaction of Diphenyl Ketyl with 2-Quinolinecarbonitrile in Acidic Aqueous 2-Propanol.

2-Quinolinecarbonitrile (0.100 g, 6.5 x 10^{-4} mole), benzopinacol (0.22 g, 6.0 x 10^{-4} mole), and acidic aqueous 2-propanol (10 ml of a solution composed of 200 ml of 2-propanol, 40 ml of water, and 1.28 g of 37% hydrochloric acid) were placed in a three-necked flask fitted with a nitrogen inlet tube, a condenser with cotton plug, and a thermometer. Nitrogen was bubbled into the solution for 15 minutes and then heating was begun using a mantle. The temperature reached 80° in 35 minutes. Heating was continued maintaining the temperature at 78-80° with nitrogen bubbling for twenty-two hours. At the end of this time the reaction mixture was yellow. Two drops of water and one of 37% hydrochloric acid were added and the solution cooled to room temperature. A white solid crystallized which was isolated by filtration and shown by infrared analysis to be benzopinacol (0.094 g). Four milliliters of water was added to the filtrate and the filtrate made strongly basic with 10% sodium hydroxide. The basic solution was extracted with four 20 ml portions of chloroform and the combined extracts dried over anhydrous magnesium sulfate. The solvent and drying agent were removed as usual leaving a yellow oil as residue which was subjected to column chromatography on silica gel. The products included the dimer **11** (0.019 g, 44% yield, mp 247-248.5° dec, lit 249° dec [7]) and 0.05 g (43% yield) of benzophenone. In addition, 0.10 g of benzopinacol and 0.053 g of **6** were recovered. The products were identified by comparison of melting points and infrared spectra with those of known samples.

Acknowledgement.

We would like to thank Ruo Xu for his technical assistance in the latter stages of this work.

REFERENCES AND NOTES

[1] For a review of the photochemical reactions of six-membered-ring aromatic monoazaheterocycles with hydrogen containing solvents, see A. Lablache-Combier, Elements de Photochemie Avanceé, P. Courtot, ed, Hermann, Paris , 1972, p 289; see also the references therein.

[2] N. J. Turro, Modern Molecular Photochemistry, Benjamin Cummings Publishing Co, Menlo Park, CA, 1978, p 368; D. G. Whitten and Y. J. Lee, *J. Am. Chem. Soc.*, **93**, 961 (1971).

[3] D. C. Neckers and D. P. Colenbrander, *Tetrahedron Letters*, 5048 (1968).

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

[5] B. M. Vittimberga, F. Minisci and S. Morrocchi, *J. Am. Chem. Soc.*, **97**, 4377 (1975).

[6] T. Caronna, S. Morrocchi and B. M. Vittimberga, *J. Am. Chem. Soc.*, **108**, 2205 (1986).

[7] T. Caronna, S. Morrocchi and B. M. Vittimberga, *J. Org. Chem.*, **46**, 34 (1981).

[8] J. K. Dohrmann and R. Becker, *J. Magn. Reson.*, **27**, 371 (1977).

[9] J. L. M. Abboud, J. Catalan, J. Elguero, and R. W. Taft, *J. Org. Chem.*, **53**, 1137 (1988) and references therein.

[10] T. Caronna, S. Morrocchi and B. M. Vittimberga, unpublished data.

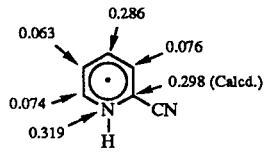
[11] A. Reissert, *Chem. Ber.*, **38**, 1610 (1905); A. Kaufmann and P. Dändliker, *ibid.*, **46**, 2927 (1913).

[12] G. Ciamician and P. Silber, *ibid.*, **33**, 2911 (1900).

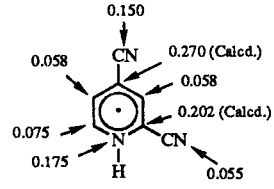
[13] M. Gomberg and N. E. Bachman, *J. Am. Chem. Soc.*, **49**, 236 (1927).

[14] A. E. Tschitschibabin and S. W. Benewolenskaja, *Chem. Ber.*, **61B**, 547 (1928).

[15] Subscript refer to hydrogens in the structures:



15



16