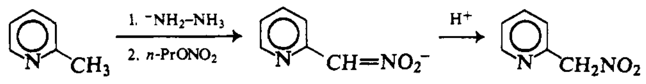
Table I

Reactant[a]	Product	Mp or bp, °C (mm)	Yield, %
2-Picoline	2-Nitromethylpyridine	70 (0.2)	58
4-Picoline	4-Nitromethylpyridine	97 dec	66
2,4-Lutidine	2-Methyl-4-nitromethylpyridine	120 dec	69
2,6-Lutidine	6-Methyl-2-nitromethylpyridine	62–70 (0.04)	46
s-Collidine	2,6-Dimethyl-4-nitromethylpyridine	129 dec	76
2-Methyl-5-ethylpyridine[b]	5-Ethyl-2-nitromethylpyridine	[c]	42
1-(4-Pyridyl)-3-phenylpropane	3-Phenyl-1-(4-pyridyl)-nitropropane	58	90
Lepidine[b]	4-Nitromethylquinoline	136 dec	93
2-Methylquinoxaline[b]	2-Nitromethylquinoxaline	121[d]	58
2-Methylbenzothiazole	2-Nitromethylbenzothiazole	141 dec	66
2-Methylbenzoxazole	2-Nitromethylbenzoxazole	76[e]	62
2-Picoline N-oxide[b]	[f]		

[a] Unless noted otherwise sodium amide was the base employed. [b] The base used was potassium amide. [c] Purified by chromatography over neutral alumina (benzene). [d] Lit.[7] mp 122–123°. [e] Lit.[6] mp 78° dec. [f] The product was isolated in 71% yield as the dibromo derivative, 2-(dibromonitromethyl)pyridine N-oxide, mp 181–183° dec.

propionate with *o*-phenylenediamine to obtain 2-nitromethylquinoxaline.

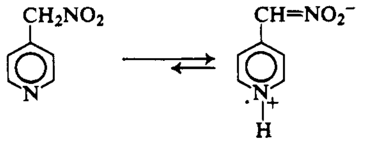
Our new synthesis involves the alkyl nitration of alkyl-substituted heteroaromatic compounds, in which activation of the α-hydrogen atoms is provided by the heterocyclic ring. Both sodium and potassium amides were found to be effective as bases in the nitration reaction.



The following procedure is typical. To a freshly prepared solution of sodium amide (0.21 mol) in 300 ml of liquid ammonia is added rapidly 7.6 g (0.08 mol) of 4-picoline at −35°. After stirring for 10 min, 26.9 g (0.26 mol) of *n*-propyl nitrate is added as rapidly as possible (5 min) while maintaining the temperature below −33°. Replacing the ammonia with absolute ether and recrystallizing the solid from 95% ethanol affords 12.1 g (92%) of sodium 4-picolylnitronate (**1**), mp 255–257°. Infrared and nmr spectra and an elemental analysis were in agreement with the proposed structure.

Acidifying a solution of 5.0 g (0.03 mol) of **1** in 25 ml of water with 3.8 g (0.06 mol) of glacial acetic acid at room temperature and recrystallizing from 95% ethanol affords 3.1 g (72%) of 4-nitromethylpyridine (**2**), mp 97° dec. Some pertinent examples are listed in Table I. The elemental analyses of the new compounds were satisfactory, and infrared and nmr spectra were consistent with the proposed structures. In addition, the nitroalkyl compounds were converted to bromonitro derivatives which, in turn, analyzed correctly.

Preliminary data obtained from infrared and nmr spectra indicate that the 4-nitromethyl compounds such as **2** exist largely as dipolar ions whereas no evidence of this type of behavior has been obtained with the 2-nitromethyl compounds.



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Extension of this reaction to the synthesis of other α-nitroalkyl heterocyclics, which are at present unknown, or which are accessible only with difficulty, is in progress.

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Evidence for Electron Transfer in the Photochemistry of π–π* Triplet States

Sir:

The correlation of photochemical reactions of aryl ketones with the nature of their excited states is a subject of current interest.[1-6] The photoreactivity of these systems depends on the nature of the lowest triplet, with $^3(n-\pi^*)$ states being generally reactive and $^3(\pi-\pi^*)$ states nonreactive. An illustration of this concept is that butyrophenone, with a low-lying $^3(n-\pi^*)$ state, undergoes the Norrish type II reaction with ease, while *p*-phenylbutyrophenone, with a low-lying $^3(\pi-\pi^*)$ state, is unreactive.[7] Yang, Pitts, and Wagner have recently made some observations[8-10] which question the generality of these correlations and suggest that in some cases excited

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(3) L. H. Piette, J. H. Sharp, T. Kuwana, and J. N. Pitts, Jr., *J. Chem. Phys.*, **36**, 3094 (1962).

(4) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).

(5) G. Porter and P. Suppan, *ibid.*, **61**, 1664 (1965).

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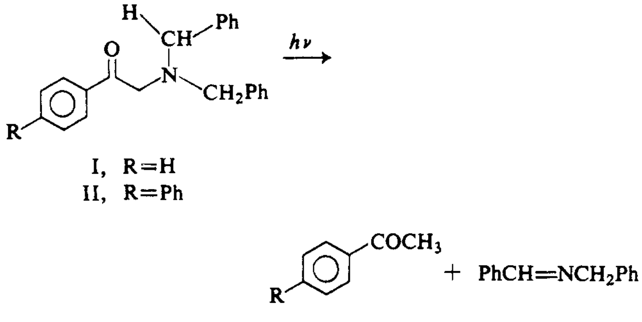
(8) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *ibid.*, **89**, 5466 (1967); N. C. Yang and R. Dusenberg, *ibid.*, **90**, 5899 (1968).

(9) J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *ibid.*, **90**, 5902 (1968).

(10) P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5898 (1968).

ketones may be reactive in hydrogen abstraction even when the lowest triplet state has a π-π^* configuration. In this communication we report on the ease of photoreduction and photocycloelimination of certain substituted aryl ketones that possess low-lying π-π^* triplet states.

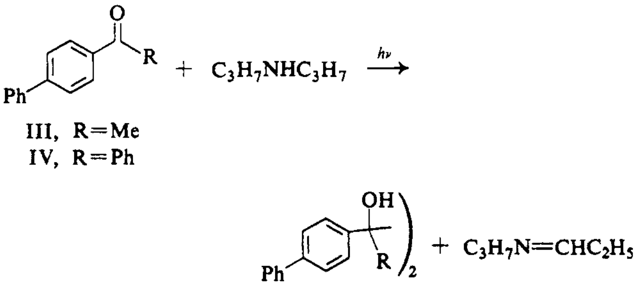
The major products of the solution-phase photolysis of N,N-dibenzylphenacylamine (I) in benzene or ethanol are those resulting from the photocycloelimination reaction. The quantum yield at 3130 Å for the production of acetophenone in ethanol is 0.14. Irradiation of N,N-dibenzyl-4-phenylphenacylamine[11] (II) gave comparable results, with the quantum yield for ketone formation being 0.12.



I, R=H
II, R=Ph

The lowest lying triplet state of I was demonstrated to be n-π^* as evidenced from its phosphorescence emission spectrum in a methanol–ethanol glass (4:1) at 77°K. The 0–0 band of I corresponds to a triplet energy of 73 kcal and the vibrational spacing between the 0–0 and 0–1 band is 1870 cm^{-1}. The 77°K lifetime was determined as *ca.* 20 msec, also consonant with an n-π^* assignment. In sharp contrast, the triplet energy of II was determined to be 61 kcal and the radiative lifetime was 1.4 sec. These observations verify that the low-lying triplet state of II is π-π^* in nature.[12]

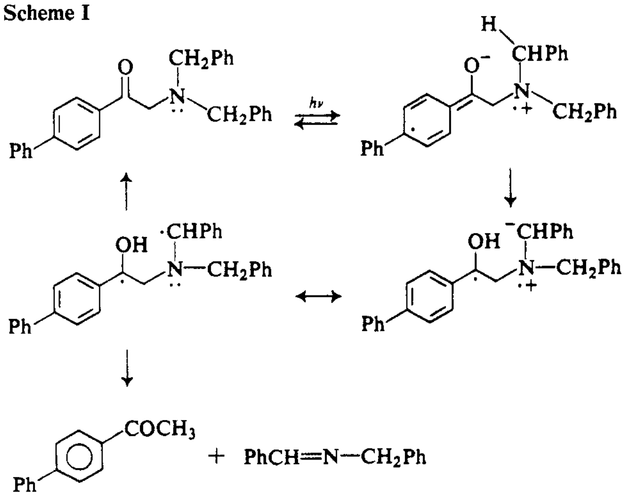
Although the *p*-phenyl-substituted phenacylamine II has a low lying $^3(\pi$-$\pi^*)$ state,[13] it still exhibits photoreactivity comparable to that of I. A related situation was encountered during the photolysis of biphenyl-substituted ketones with secondary amines. Irradiation of 0.02 *M* 4-acetylbiphenyl (III) and 0.1 *M* di-*n*-propylamine in benzene led to a high yield of pinacol and the corresponding imine. Photoreduction of 4-phenylbenzophenone (IV) in di-*n*-propylamine was quite similar, and afforded good yields of the pinacol.[14] Both ketones possess low-lying $^3(\pi$-$\pi^*)$ states[13] that photoreduce with essentially the same quantum efficiency ($\Phi = 0.20 \pm 0.02$). The photoreduction could be quenched with 1,3-cyclohexadiene (E_t = 54 kcal),[16] indicating that the reaction proceeds through a quenchable excited triplet. While both ketones undergo appreciable photoreduction with alkylamines, they are not photoreduced by alcohols or hydrocarbons.



III, R=Me
IV, R=Ph

In an attempt to determine the rate constants for photocycloelimination of the excited states of I and II, we have studied the variation of quantum yield *vs.* quencher concentration. Surprisingly, the elimination of both ketones could not be quenched by moderate concentrations (0.05 mol) of 1,3-cyclohexadiene or high concentrations of piperylene. The failure to quench implies that the reaction of both ketones is too rapid for diffusion of the excited state to quencher molecule. The low quantum efficiency of the photoreduction coupled with the failure to quench either triplet suggests that the excited state interacts with an electron on nitrogen to form an ion pair or a charge-transfer complex. The lack of quenching implies that this process proceeds at a rate exceeding diffusional control. Back transfer of an electron in the complex would regenerate the starting ketone and account for the less than maximum quantum yield.[17] Transfer of a proton from the benzylic carbon to the ketyl radical and electron reorganization will produce the same 1,4 biradical as would be obtained by simple hydrogen abstraction. The sequence of steps in Scheme I is not without precedent and is closely related to the scheme proposed by Cohen to account for the results obtained in the benzophenone- and *p*-aminobenzophenone–alkylamine systems.[20,21] Further analogy is provided by the work of Weller[22] and Ware[23]

Scheme I



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(11) All new compounds were properly characterized, and acceptable chemical analyses were obtained.

(12) 4-Acetylbiphenyl has been reported to have a low-lying π-π^* configuration and a triplet energy of 61 kcal.[13]

(13) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 5.

(14) 2-Acetonaphtone was also observed to undergo photoreduction in the presence of alkylamines, in agreement with Cohen's results.[15]

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(16) D. F. Evans, *J. Chem. Soc.*, 1735 (1960); R. E. Kellogg and W. T. Simpson, *J. Am. Chem. Soc.*, **87**, 4230 (1965).

(17) Reverse γ-hydrogen transfer of the biradical intermediate[18,19] does not satisfactorily explain the low quantum yield in ethanol unless this species has an unusual partitioning pattern.

(18) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5898 (1967).

(19) A. Padwa and E. Alexander, *ibid.*, **90**, 6871 (1968).

(20) S. G. Cohen and R. J. Baumgarten, *ibid.*, **89**, 3471 (1967); S. G. Cohen and H. M. Chao, *ibid.*, **90**, 165 (1968); S. G. Cohen, N. Stein, and H. M. Chao, *ibid.*, **90**, 521 (1968).

(21) S. G. Cohen and J. L. Cohen, *J. Phys. Chem.*, **72**, 3782 (1968).

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wherein aromatic amines are thought to quench π–π* singlets by charge-transfer interactions. It appears that attack at an electron of nitrogen occurs for π–π* triplet states and perhaps for n–π* triplet states as well, although rapid γ-hydrogen abstraction by the n–π* state is not necessarily eliminated from the available data. The above scheme would predict a decrease in the quantum efficiency of reaction as the pair of electrons on nitrogen become less available. Preliminary experiments have shown that the quantum yield of the photoreaction decreases substantially when the substituted phenacylamine (I and/or II) is converted to its "onium" derivative by protonation.

Electron-transfer processes also seem to be important in the photochemistry of aroylaziridines and -azetidines[24] and in fact may be a general phenomenon in the photochemistry of many nitrogen-containing compounds. Further work both on the mechanism of the rearrangement and on the scope and application to other heteroatoms is currently under way and will be the subject of future reports.

Acknowledgment. The authors are indebted to the National Science Foundation (Grant GP-9385) for generous support of this research.

[24] R. Gruber and W. Eisenhardt unpublished results. See A. Padwa and R. Gruber, *J. Am. Chem. Soc.*, **90**, 4456 (1968); A. Padwa and W. Eisenhardt, *ibid.*, **90**, 2442 (1968).

[25] Alfred P. Sloan Fellow, 1968–1970.

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Jahn–Teller Distortions in Octahedral Copper(II) Complexes

Sir:

Recently, there has been an interest in the existence (or nonexistence) of Jahn–Teller distortions in the tris chelates of copper(II)[1] and manganese(III).[2] We wish to report our X-ray diffraction and electron spin resonance studies of the novel bipyridine (bipy) adduct of bis(hexafluoroacetylacetonato)copper(II), Cu(hfacac)$_2$. This unusual molecule distorts two of the three symmetrical chelating ligands to remove the orbital degeneracy present in an octahedral d^9 configuration. Therefore, the present study provides the first example of a symmetrical ligand undergoing distortion because of the Jahn–Teller effect in the copper(II) ion.

A series of similar complexes is easily prepared by treating either bis(hexafluoroacetylacetonato)copper(II) or bis(theonyltrifluoroacetonato)copper(II) with either bipyridine or 1,10-phenanthroline. For example, if solutions of Cu(hfacac)$_2$ and bipy in a minimum amount of chloroform are mixed, a green precipitate is formed.

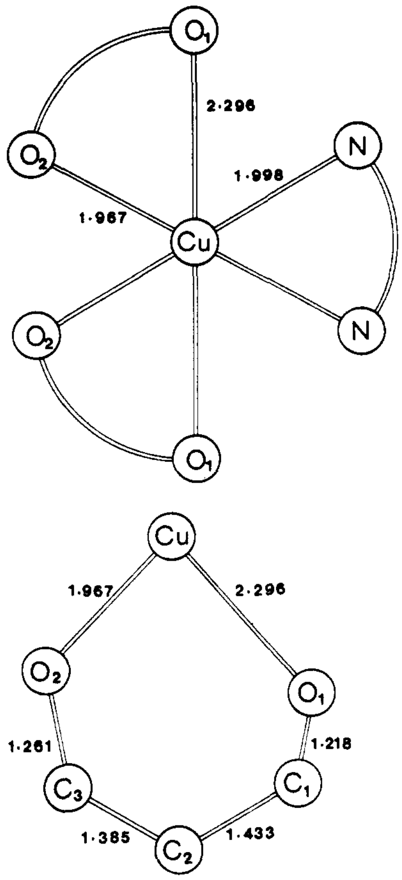

Figure 1. The upper figure gives the over-all geometry of the Cu(hfacac)$_2\cdot$bipy adduct together with the Cu–O and Cu–N bond lengths. The twofold axis bisects the bipy ligand represented by N–N. The hfacac ligand is represented by O–O. The lower figure gives the bond distances in the β-diketone–Cu ring system and shows the alternation of bond lengths resulting from the Jahn–Teller distortion.

The complex can be recrystallized from benzene in the form of long, bright green needles. The analysis corresponds to the 1:1 complex. *Anal.* Calcd for $F_{12}C_{10}O_4H_2Cu\cdot C_{10}N_2H_8$: C, 37.88, H, 1.88; N, 4.42. Found: C, 37.69; H, 1.44; N, 4.44.

Single-crystal X-ray studies revealed that the crystals are monoclinic with a = 16.55, b = 16.62, c = 8.80 Å and β = 100.7°. The space group is either Cc or C2/c, with the latter preferred on the basis of intensity statistics. With four molecules per unit cell (the densities are 1.740 g/cm^3 observed and 1.755 g/cm^3 calculated), the molecule is required to have a twofold symmetry axis. The intensity data were measured by the stationary crystal–stationary counter method using an automatic diffractometer. A total of 6688 measurements were made and reduced to a unique set of 2036 reflections of which 1768 were considered observed and used in the analysis. The structure was solved by locating the copper atom in the Patterson function and locating the light atoms by using a minimum function and Fourier syntheses. The trial structure was refined by isotropic least squares to an R (the usual residual) of 18.7% and by anisotropic least squares to an R of 8.0%. The location of the hydrogen atoms and further refinement are continuing.

The molecule is illustrated in Figure 1 together with some pertinent bond distances. The twofold axis passes through the bipy ligand and requires the two Cu–N bonds

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