chloride salt of **7** with methyl vinyl ketone, ferric chloride, and zinc chloride in ethanol, followed by polyphosphoric acid at 110°, gave the strongly fluorescent pyridoquinolone **8** ($C_{15}H_{12}N_2O_2$, mp 235–238°)[6,7,12] in 34% yield. Methylation of **8** with dimethyl sulfate in refluxing benzene gave its methosulfate which was not purified but treated directly with potassium hydroxide and potassium ferricyanide at 3° for 7 hr[13] to give **1** ($C_{16}H_{14}N_2O_3$)[6] in 21% yield (from **8**).

The synthetic sample of **1**, prepared by the route described, was identical with authentic deoxynybomycin, prepared from nybomycin, in the following characteristics: melting point behavior, thin layer chromatographic behavior, infrared spectrum (Nujol and KBr), nmr spectrum (trifluoroacetic acid), mass spectrum. As seen in Table I, both the ring protons and those of the methyl substituent appear at about 0.1-ppm higher field in the methylene-bridged quinolones, a correlation of use in assigning the structure of nybomycin.[1]

Table I. Chemical Shifts (δ) of Quinolone Ring Substituents[a]

Compd	5-H	6-CH_3	2-CH_2	3-H	4-CH_3
2				7.26	2.89
3				7.30	2.90
4				7.40	2.91
6	7.26	2.82	6.83		
7	7.21	2.81	6.72		
8	7.16	2.89	6.90		
1	7.18	2.90	6.85	7.38[b,c]	2.98[b,d]

[a] Spectra obtained on trifluoroacetic acid solutions at 100 MHz. [b] Corresponding protons, but numbering system changed; see formulas in text. [c] 9-H. [d] 8-CH_3.

Acknowledgment. This work was supported in part by Public Health Service Grants No. AI 01278 and AI 04769 from the National Institute of Allergy and Infectious Diseases.

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(12) High-resolution mass spectral data agree with the molecular formula shown.

(13) E. A. Prill and S. M. McElvain in "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 419.

(14) National Science Foundation Predoctoral Fellow.

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Photochemical Reaction of Bis(1,3-diketonato)nickel(II) Chelates

Sir:

As a part of our general investigation of the photochemical reactions of transition metal chelates,[1,2] we have studied the photoreduction of a series of bis(1,3-diketonato)nickel(II) complexes in ethanol. To our knowledge there are no reports in the literature of photochemical reactions of nickel(II) complexes. Previous studies of divalent nickel complexes have reported no photosensitivity[3] in the ultraviolet region. However, exposure of degassed ethanol solutions of these neutral 1,3-diketonato chelates to 254-nm radiation does result in a photochemical reaction. The reaction is accompanied by a change from the initial light green solution to a colorless or brownish solution containing a dispersed black solid. In addition, a greyish-white metallic nickel film is formed on the irradiated cell face. The other major product is the protonated ligand which has been isolated and identified spectrally. The amount of metallic nickel formed as well as the amount of nickel(II) remaining in solution was determined by atomic absorption spectroscopy for a series of bis(acetylacetonato)nickel(II), $Ni(AA)_2$, solutions. These determinations resulted in a molar ratio of 0.8 ± 0.3 for the moles of metallic nickel produced to the moles of chelated nickel consumed. Thus the overall reaction may be written as

$$Ni(AA)_2 \xrightarrow[EtOH]{h\nu} Ni + 2HAA + \text{oxidized solvent} \qquad (I)$$

Quantitative measurement of the protonated ligand produced during the photolysis has been hindered by the heterogeneous nature of the solution.

The rate of the photoreduction was studied as a function of the initial concentration of chelate in a series of optically dense solutions, *ca.* 10^{-3}–10^{-2} *M*. The rate of formation of metallic nickel was found to be independent of the chelate concentration.

The light intensity dependence was determined by irradiating 5×10^{-3} *M* solutions of the various chelates. The reduction has a first-order dependence on the incident light intensity as evidenced by an average slope of 0.8 ± 0.2 for plots of the log of the initial rate *vs.* the log of the average intensity. The range of light intensity studied was from 5×10^{15} quanta/sec to 2.4×10^{16} quanta/sec. Thus the rate equation for optically dense solutions can be written as

$$d(Ni^0)/dt = \phi I_a^{0.8\pm0.2} \qquad (II)$$

A resonable mechanism involves a one-electron reduction to a Ni(I) intermediate followed by a second one-electron reduction to Ni^0. In this mechanism, the first step is a primary photochemical reaction, while the second step is a thermal reaction. This tentative mechanism is supported by the appearance of a black solid dispersed in the solution. The black substance is believed to be the Ni(I) intermediate. It is extremely reactive and disappears immediately when exposed to the atmosphere.

The results of quantum yield determinations for the chelates studied are summarized in Table I. Each average quantum yield was calculated from at least four independent determinations. The rate of the photoreduction is relatively independent of the presence of water, as evidenced by the similar quantum yields in ethanol and ethanol–water.

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(1) H. D. Gafney, R. L. Lintvedt, and I. S. Jaworiwsky, *Inorg. Chem.*, **9**, 1728 (1970).

(2) H. D. Gafney and R. L. Lintvedt, submitted for publication.

(3) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968), and references therein.

Table I. Quantum Yield of Photoreduction for Irradiation at 254 nm[a]

Compound	Solvent	Initial concn, *M*	Intensity, quanta/sec	Rate, *R*, molecules/sec	ϕ_{av}[b]
$Ni(AA)_2$	Ethanol	5.20×10^{-3}	1.98×10^{16}	5.64×10^{13}	1.8×10^{-2}
$Ni(AA)_2$	95% ethanol–water	5.20×10^{-3}	2.37×10^{16}	2.35×10^{14}	2.3×10^{-2}
$Ni(TFA)_2$[c]	Ethanol	5×10^{-3}	2.35×10^{16}	5.64×10^{13}	4.6×10^{-3}

[a] Results obtained at 23 ± 1° in ethanol. The ethanol was degassed by freeze–thaw techniques. [b] The quantum yields shown are calculated from $R/\{(I_i^Q)(I_i^f)\}^{1/2}$, where I_i^Q is the incident light intensity and I_i^f is the final incident corrected for the absorbance of the deposited nickel film as described in ref 2. [c] TFA is 1,1,1-trifluoro-2,4-pentanedionato anion.

The wavelength dependence of the quantum yield was determined by irradiating ethanolic solutions of $Ni(AA)_2$ at 312 nm. This mercury line was isolated by filtering with Corex glass which has 0% *T* at wavelengths shorter than 260 nm. The degassed solutions showed no detectable photochemical reaction after irradiating for 17.5 hr at 312 nm. The ultraviolet spectrum of $Ni(AA)_2$ in dry ethanol consists of a complex, strong absorption whose maximum is at 295–300 nm [$\epsilon \sim 3 \times 10^4$ l./(mol cm)]. The band has a low-energy shoulder at about 312 nm and a high-energy shoulder at about 250–260 nm. The high-energy shoulder is quite weak [$\epsilon \sim 100$ l./(mol cm)]. The intense absorption at *ca.* 300 nm is undoubtedly due to a $\pi \rightarrow \pi^*$ transition primarily localized on the ligands. Since the photoreduction takes place from the high-energy side of the intense band (254 nm) but not from the low-energy side (312 nm), the reaction must occur from a specific high-energy state. The exact nature of this state is not known as yet. However, the reaction does not take place from the ligand π^* vibrational ground state which is on the low-energy side of the 300-nm band. The photoreduction of tris(hexafluoroacetylacetonato)iron(III), on the other hand, does occur by such a mechanism.[1] Since there are no readily observable charge-transfer bands for the Ni(II) chelates in this spectral region, the reduction may take place from vibrationally excited ligand π^* states or from ligand states resulting from loss of π-level degeneracy due to chelation.[4] It is also possible that the broad band has considerable ligand-to-metal charge-transfer character.

Cotton and Fackler[5] have assigned an absorption at 260 nm to the trimer $Ni_3(AA)_6$ which is stable in noncoordinating solvents. This band decreases in intensity in coordinating solvents in which the solvated monomer has been shown to be present. The appearance of this band in ethanol may be due to low concentrations of the timer. Therefore, the possibility exists that only the trimer is photoactive. To investigate this possibility, we have photolyzed ethanolic solutions of bis(dipivaloylmethane)nickel(II), $Ni(DPM)_2$, which is known to be monomeric both in the solid and in solution.[5,6] Preliminary results show that $Ni(DPM)_2$ undergoes the same photoreduction as $Ni(AA)_2$ at 254 nm with similar efficiency.

The effect of oxygen on these photoreductions is pronounced. Ethanolic solutions of $Ni(AA)_2$ where no effort had been made to remove dissolved air showed no photochemical activity.

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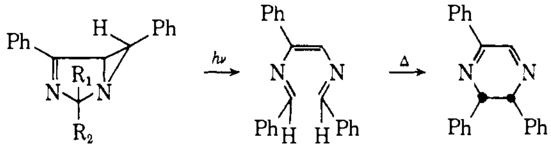
The Mechanism of Photoisomerization in a 1,3-Diazabicyclo[3.1.0]hex-3-ene[1a]

Sir:

In a recent communication, Padwa, Clough, and Glazer[1b] reported that 2,4,6-triphenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene (**1** and **2**) photoisomerized to enediimine **3** which thermally cyclized to dihydropyrazine **4**. The reactions were discussed in terms of possible applicability of the Woodward–Hoffman orbital symmetry rules. We have independently found a similar photoisomerization with 2,2-dimethyl-4-phenyl-6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-ene, but now have trapped a 1,3-dipolar intermediate by cycloaddition with a dipolarophile and by matrix isolation. This new evidence demonstrates that the reaction occurs stepwise *via* the formation of an azomethine ylide which subsequently opens to the enediimine.



1, $R_1 = Ph; R_2 = H$
2, $R_2 = H; R_1 = Ph$

3

4

Aziridine **5** was prepared according to the procedure of Heine, *et al.*[2] (λ_{max}^{EtOH} 283 nm, ϵ 23,000). Irradiation of an argon-purged solution of **5** in benzene (150 mg in 30 ml, 450-W Hanovia lamp, Pyrex filter) at room temperature for 10 sec produced a bright red color (λ_{max} 565 nm) which faded after several minutes to yellow. Continued irradiation regenerated the red-colored species, but after 3 hr, the reaction mixture became quite yellow and most of the aziridine had reacted to give enediimine **7** in 40% yield. The

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(1) (a) A portion of this work was presented at the CIC–ACS Joint Conference, Toronto, Ontario, Canada, May 1970; (b) A. Padwa, S. Clough, and E. Glazer, *J. Amer. Chem. Soc.*, **92**, 1778 (1970).

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