these compounds.[8,9] Further work on the eremantholides is in progress.

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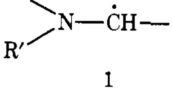
Photoreactions of Ketones with Amines. CIDNP Criteria for the Intermediacy of Aminoalkyl Radicals and Aminium Radical Ions

Sir:

Many intermolecular reactions of photoexcited species involve hydrogen abstraction (a) whereas others proceed via electron transfer (b). Since many substrates are potential electron donors as well as hydrogen atom sources, it is not always trivial to distinguish between these mechanisms. We have applied the CIDNP technique[1,2] to this problem and have suggested two methods[3,4] to distinguish between CIDNP effects originating in pairs of neutral radicals, which would result from reaction (a), and in pairs of radical ions produced via route (b). In photoreactions of aromatic ketones with anilines we favored reaction (a), because *N,N*-dialkylanilines, which may form anilinium radical ions but not neutral anilinyl radicals, did not show CIDNP effects similar to those found for anilines.[3] In other ketone-amine systems an assignment was based on the relatively large difference in the electron *g* factors of aminoalkyl radicals (**1**; $g \sim 2.0032$) and aminium radical ions (**2**; $g \sim 2.0040$).[4] In this paper, we introduce a third criterion which is based on the difference in the hyperfine coupling patterns of the neutral radicals (**1**)[5] and the radical cations (**2**).[6]

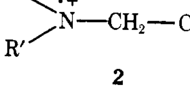
We illustrate the CIDNP patterns induced in these species with spectra observed during the photoreactions of benzophenones (**3**) with tertiary amines (**4**). In these systems, the effect of solvent polarity on the quantum yields suggests that charge transfer is involved in the initial stages of the reaction.[7] If this interaction results in hydrogen abstraction and thus in the formation of **1**, nuclear spin polarization of comparable magnitude is expected for the protons in α- and β-position. In contrast, only the α-protons are expected to show polarization, if the charge transfer interaction leads to electron transfer and thus to the formation of **2** as an intermediate.



$$\mathrm{RR'N{-}\dot{C}H{-}CH_3}$$

1

$g = 2.0030$
$a_{CH} = -13.6\,G$
$a_{CH_3} = +19.6\,G$



$$\mathrm{RR'\overset{\cdot +}{N}{-}CH_2{-}CH_3}$$

2

$g = 2.0040$
$a_{CH_2} = +37\,G$
$a_{CH_3} < 1\,G$

The irradiation of *p,p'*-dichlorobenzophenone (**3a**) in the presence of triethylamine (**4a**) in acetonitrile-d_3 produced an enhanced spectrum (Figure 1) which we ascribe to the olefinic protons of diethylvinylamine (**5a**). The signals of the terminal (β-) protons, two overlapping doublets near 3.5 ppm (A), were of comparable magnitude but of opposite sign to the doublet of doublets at 6.1 ppm representing the internal (α-) proton. This result reflects the hyperfine coupling pattern of the neutral radical, **1a**, and thus established this species as an intermediate in the formation of **5a**. When

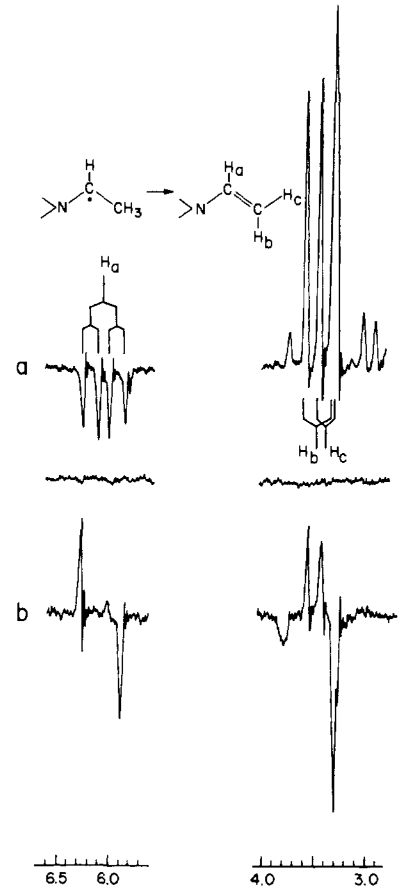


Figure 1. ^{1}H NMR spectra (60 MHz) of the internal (left) and terminal olefinic protons (right) of polarized diethylvinylamine observed during uv irradiation of solutions of 0.05 *M* triethylamine and 0.01 *M* *p,p'*-dichlorobenzophenone (a) or *p,p'*-dimethylbenzophenone (b), respectively in acetonitrile-d_3. The center trace shows the spectrum of the same region in the absence of uv irradiation.

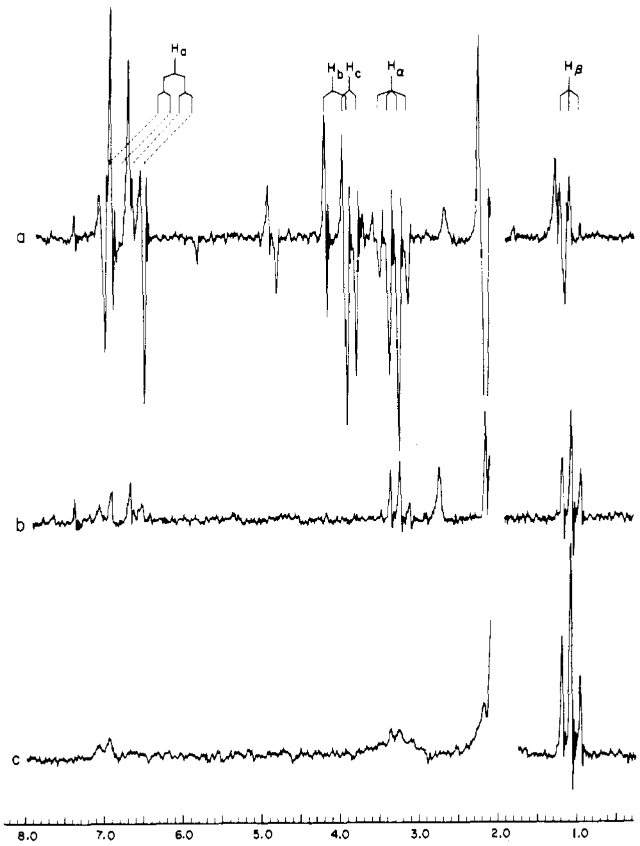


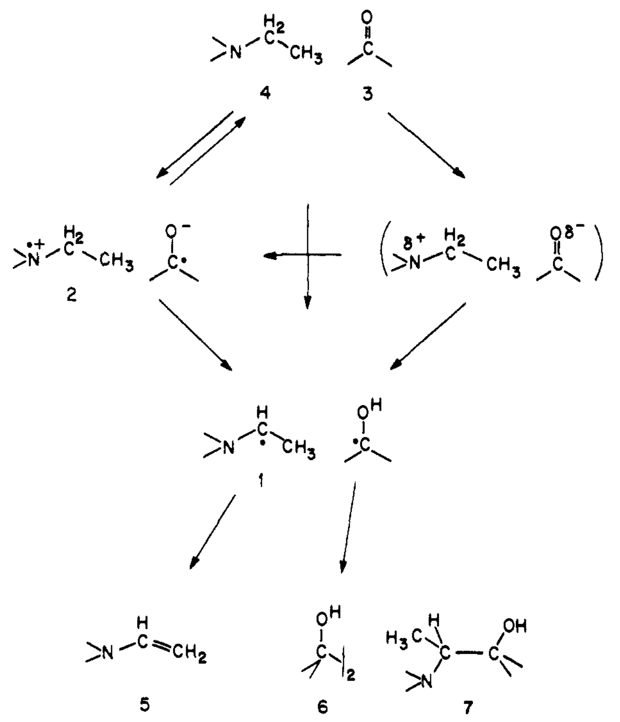
Figure 2. ^1H NMR spectra (60 MHz) of a solution of 0.02 *M* *N,N*-diethyl-*p*-toluidine and 0.02 *M* decadeuteriobenzophenone in acetone-d_6 in the dark (b) and during uv irradiation (a), and of a solution of 0.02 *M* *N,N*-diethyl-*p*-toluidine and 0.02 *M* decafluorobenzophenone in acetonitrile during uv irradiation (c).

p,p'-dimethylbenzophenone (**3b**), *p,p'*-dimethoxybenzophenone (**3c**), or acetone-d_6 were irradiated in the presence of **4a**, the vinylamine, **5a**, showed multiplet polarization[8,9] (Figure 1b). Again, the α- and β-protons were of comparable intensity suggesting the neutral radical, **1a**, as intermediate. The starting materials and products, such as pinacols, **6**, or cross-coupling products, **7**, showed little, if any, polarization.[10]

The spectra observed during the photoreactions of aromatic ketones with *N,N*-diethyl-*p*-toluidine (**4b**) are considerably more complex than those observed with **4a**. During the irradiation of decafluorobenzophenone (**3d**) the signals of **4b** showed selective line broadening (Figure 2c). We have reported several cases where line broadening limits the observation of CIDNP effects and ascribed this phenomenon to rapid, degenerate electron exchange between radical ions and their diamagnetic precursors.[4,12] In the "fast exchange limit"[13,14] the degree of line broadening reflects the electron spin density distribution of the radical ion, $\Delta T_2^{-1} \propto a^2$. In the case of **4b**, the α-methylene quartet ($a_{2b} \sim 12$ G)[15] was substantially broadened, whereas the β-methyl triplet ($a_{2b} < 1$ G)[16] remained essentially unchanged; the aromatic region showed pronounced broadening of the ortho protons ($a_o = 5.3$ G)[15] and somewhat weaker broadening of the meta protons ($a_m = 1.35$ G).[15] This broadening pattern indicates an intermediate of structure **2** (Scheme I).

During the reactions of **4b** with several other aromatic ketones a variety of nuclear spin polarization effects were observed. A typical spectrum, recorded during the illumination of decadeuteriobenzophenone (**3e**), is shown in Figure 2a. The A/E multiplet effects for the signals at 3.8, 4.0 and 6.7 ppm resemble those observed in the system **3b**–**4a**. We ascribe these signals to the vinyl group of ethyl-*p*-tolylvinylamine (**5b**). Since the internal and terminal protons showed comparable intensities, an aminoalkyl radical, **1b**, must be an intermediate, thus indicating net hydrogen abstraction.

Scheme I



However, the starting amine also showed CIDNP signals and its polarization pattern was unlike that of **5b**, therefore suggesting an additional intermediate of different structure. The methylene group (3.3 ppm; Hα;E) and the ortho protons (6.6 ppm; A) showed strong net polarization, whereas the β-methyl triplet showed only small changes. This polarization pattern reflects a spin density distribution typical for an aminium radical ion (**2b**). Thus, we find evidence for both, a net hydrogen abstraction and an electron transfer process. The neutral radical, **1b**, is an intermediate in the formation of product **5b** whereas the radical ion, **2b**, regenerates the starting amine by reverse electron transfer.

The results presented here demonstrate that the CIDNP method can distinguish between aminoalkyl radicals and aminium radical ions and that, in favorable cases, these species may be identified in the presence of each other. Similar CIDNP effects demonstrating the formation of radical ions and of neutral radicals from the same precursor were observed during the photoreductions of benzoquinones and of aromatic hydrocarbons by amines. A priori, we cannot distinguish whether these intermediates are formed independently from a common precursor or whether the radical ion, **2**, is a precursor of the neutral radical, **1**. Further experiments in related systems are being carried out in order to elucidate the mechanistic details of these reactions. The results will be discussed in a full paper.

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(10) A detailed discussion of the reaction mechanisms involved and of the parameters determining the signal direction[11] or the multiplet phase[11] of the vinylamine goes beyond the scope of this communication. We note, however, that the results indicate two different pathways. The signal directions observed in the reaction of **3a** with **4a** suggest an escape mechanism ($\mu > 0$; $\Delta g < 0$; $a_{CH} < 0 < a_{CH_3}$; $\Gamma_{CH} < 0 < \Gamma_{CH_2}$ $\therefore$ $\epsilon < 0$) whereas the multiplet effect observed during the reaction of **3b**, **c** with **4a** indicates an in-cage mechanism ($\mu > 0$; $a_{CH} < 0 < a_{CH_3}$; $\sigma > 0$; $J > 0$; $\Gamma < 0$ $\therefore$ $\epsilon > 0$).
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Bonding Interactions in Anhydrous and Hydrated Chlorophyll a

Sir:

The currently accepted models[1-3] for anhydrous and hydrated Chl a aggregates are respectively given by (a) unsymmetrical Chl a-Chl a interactions involving the intermolecular C-9 keto C=O···Mg linkage[1,2] and (b) unsymmetrical Chl a-H_2O-Chl a interactions, C-10 ester C=O···HO(Mg)H···O=C keto C-9, involving the ring V cyclopentanone ester and keto carbonyls.[1,3]

A survey of the literature reveals that there are difficulties with both suggestions. Trifunac and Katz found[4] that lanthanide-induced-shift NMR observations demand an equivalence of the two Chl a molecules in the anhydrous dimer. They alluded to the difficulties of reconciling the unsymmetrical interaction (a) with the observed symmetry, and concluded that "a final detailed dimer structure still eludes" them.

The hydrated Chl a model (b) leads to the stoichiometry[1,3] (Chl a·H_2O)$_n$, and appears to be in conflict with the conclusions derived from the elemental analysis by Holt and Jacobs[5] and the x-ray study by Strouse[6] that the hydrated Chl a crystalline precipitate is the polymeric dihydrate (Chl a·$2H_2O$)$_n$.

In this communication, we propose that the probable molecular configuration for the anhydrous dimer is given by the symmetrical adduct shown in Figure 1, and offer experimental evidence that the long-wavelength (743 nm) absorbing Chl a-H_2O adduct is in fact most probably (Chl a·$2H_2O$)$_n$, in agreement with earlier analyses.[5,6]

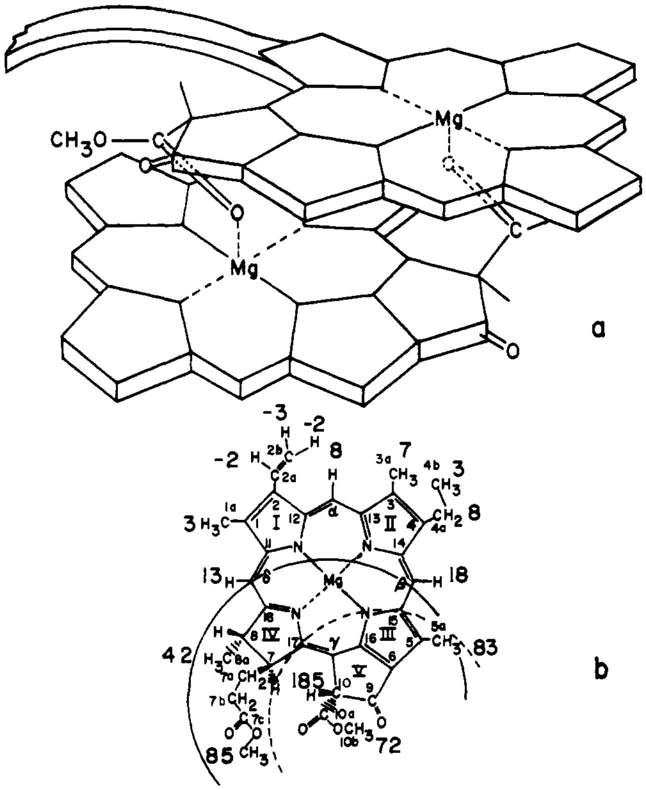

Figure 1. The C_2 symmetrical Chl a-Chl a adduct: (a) scaled model representation displaying the self-aggregating C-10 ester C=O···Mg linkages; (b) aggregation map of methyl chlorophyllide a from ref 1. The boldface numbers indicate the change in parts per million in the indicated resonance between dimer and monomer chlorophyll a. The solid semicircle centered on the ester carbonyl represents the circle of influence of the upfield ring current in the symmetrical structure shown in (a). The dashed semicircle which gives a poor fit of the upfield shifts at the protons of C-8a and the methoxy group at C-7c corresponds to the Katz model invoking the C-9 keto C=O···Mg linkage.

Chlorophyll a was extracted from spinach and purified using standard procedures.[7] Absorption spectra of the purified Chl a in anhydrous ether (AR grade) solutions had absorption maxima at 4286 ± 1 and 6604 ± 1 Å with blue/red absorbancy ratios of 1.29 ± 0.01. These data have been consistently reproduced and they agree with established criteria for Chl a purity.[7] Solid Chl a, which under reduced pressure deposited from CCl_4 solution on the walls of a vessel, was heated under vacuum (~1 μ) at 75°C for time periods up to 24 hr. From room-temperature fluorescence intensity measurements, using the procedure after Livingston et al.,[8] it was found that hydrocarbon solutions prepared from samples heated for periods longer than 30 min at this temperature do not show any appreciable changes in the amounts of adventitious water. The two component solvents used in this study, methyl cyclohexane and *n*-pentane, were rigorously dried by distillation over $LiAlH_4$ in a dry nitrogen atmosphere. The solvent, a 1:1 mixture of rigorously dried methylcyclohexane and *n*-pentane, was transferred into sample tubes through vacuum-tight septa using syringes. A stock solution (suspension) of high purity water in methylcyclohexane was prepared by sonication. Aliquots of this solution were added along with the solvents to obtain solutions of known added water and Chl a concentrations. The solution employed in the present study contained 2×10^{-5} *M* Chl a.

In agreement with Livingston et al.,[8] we find that the addition of water to hydrocarbon Chl a solutions activated the fluorescence intensity I_f of the chlorophyll. This intensity increases monotonically with increasing water concentration C_w. At $C_w = 3 \times 10^{-3}$ *M*, the value I_f for the 2×10^{-5} *M* Chl a solution is approximately half that of $I_{f,max}$ for the fully activated ($C_w = 1.5 \times 10^{-2}$ *M*) sample. The ratio $\eta = I_f/I_{f,max}$ (representing the fraction of Chl a in the form of the monohydrate[8]) is found to be 0.18 for the "dry" preparation. This result is in excellent agreement with the corresponding values obtained by Livingston et al.[8] who found that η ($\simeq$0.18) remains practically invariant in "dry" benzene solutions of Chl a ranging in concentration from 4.8×10^{-5} to 2.3×10^{-4} *M*. From water titration experiments using dilute ($C_0 \sim 10^{-6}$ *M*) Chl a solutions, in which apparently only the monomeric anhydrous and hydrated species, Chl a and Chl a·H_2O, are important, it was established[8] that the driest Chl a sample contained 0.5-1.0 molar equivalent of water.