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CIDNP Studies of the Photoreduction of Aromatic Ketones by Aromatic Amines. Singlet vs. Triplet Radical Ion Pair Formation by Selective Excitation

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Abstract: Photoreduction of acetonitrile solutions of 4-substituted acetophenones by *N,N*-dimethylanilines has been investigated by observing the CIDNP signals of regenerated ketone and amine. Irradiation in the wavelength range absorbed by the ketone gives CIDNP signals of opposite polarity to those produced by excitation of the amine. Addition of biphenyl as triplet quencher enhances the CIDNP signals produced by amine excitation, but effectively annihilates those produced by ketone absorption. These results are interpreted in terms of two pathways for radical ion pair formation. Ketone excitation results principally in electron transfer from ground-state amine to triplet-state ketone, with formation of triplet radical ion pairs. Singlet ion pairs are formed by electron transfer from singlet excited amine to ground-state ketone. This is the dominant process subsequent to amine excitation, but it is accompanied by energy transfer to ketone and triplet ion pair formation. This model is consistent with the known energies of the species involved and the rate constants for their interconversion. Similar results are obtained for benzophenone–aromatic amine systems. An example of reverse electron transfer which yields triplet-state products is also reported.

Introduction

The photoreduction of benzo- and acetophenones by amines has been studied extensively[2] during the past 10 years, and several primary reactions have been clearly established. For instance, selective excitation of benzophenone (K) in solutions containing a tertiary aromatic amine (A:) such as *N,N*-diethylaniline or *N,N*-dimethyl-*p*-toluidine leads to an encounter complex between triplet ketone and ground-state amine with high charge transfer character.[3] This decays subsequently to radical ions by electron transfer, or to neutral free radicals by hydrogen abstraction. In polar solvents electron transfer dominates, and this process (1) is observed exclusively in acetonitrile:[3]

$$\mathrm{A{:}^0 + K^0 \xrightarrow{h\nu} A{:}^0 + {}^1K^* \xrightarrow{isc} A{:}^0 + {}^3K^*}$$
$$\mathrm{\rightarrow (A^{+}\cdot K^{-}\cdot)^3 \rightarrow A^{+}\cdot + K^{-}\cdot} \quad (1)$$

Less is known about primary reactions under conditions of selective excitation of the amine. The fluorescence of *N,N*-diethylaniline is effectively quenched by ground-state electron acceptors.[4] More recently, it has been shown[5] that the efficient quenching of the fluorescence of *N*-methylpiperidine by 2-adamantanone in *n*-hexane is accompanied by partial appearance of ketone fluorescence. This indicates singlet energy transfer from excited amine to ketone:

$$\mathrm{A{:}^0 + K^0 \xrightarrow{h\nu} {}^1A{:}^* + K^0 \rightarrow A{:}^0 + {}^1K^*} \quad (2)$$

If this mechanism is dominant also in aromatic ketone–aromatic amine systems, the fast intersystem crossing of the ketone[6] would lead to radical ion formation via (1) in polar solvents. On the other hand, energetics also allow radical ion formation on selective excitation of aromatic amines in polar media via the process

$$\mathrm{A{:}^0 + K^0 \xrightarrow{h\nu} {}^1A{:}^* + K^0 \rightarrow (A^{+}\cdot\, K^{-}\cdot)^1 \rightarrow A^{+}\cdot + K^{-}\cdot} \quad (3)$$

This time, the excited singlet amine acts as the electron *donor* to the ground-state ketone, whereas in (1) the excited triplet ketone acts as an efficient electron *acceptor* from the ground-state amine. The two processes differ in the initial spin states of the radical ion precursors and may occur simultaneously.

Chemically induced dynamic nuclear polarization (CIDNP)[7] is an excellent tool by which to distinguish between reactions like (1) and (3). One observes the nuclear polarization of that fraction of the educts A: and K which is re-formed by reverse electron transfer in reencounters of geminate pairs of radical ions produced by dissociation of the encounter complexes in (1) and (3). The multiplicity of the precursor can be deduced from the phases of the effects since singlet and triplet precursors lead to inverse polarizations. This concept has been applied by Roth and co-workers[7,8] to benzophenone–aliphatic amine systems and to solutions of benzophenone and *N,N*-diethyl-*p*-toluidine (ketone excitation) and his results confirm a triplet precursor, i.e., reaction 1, as expected. Chemically induced electron polarization measurements[9] have led to the same result.

In this paper we present a CIDNP study of the photoreduction of substituted acetophenones and of benzophenone by *N,N*-dimethylanilines in acetonitrile. The effects are compatible with reaction 1 for conditions selected to favor ketone excitation, but demonstrate the occurrence of reaction 3 in addition to (1) for conditions favoring amine excitation. Further, we report some results on amine–biphenyl solutions.

Experimental Section

Instrumentation. The CIDNP experiments were carried out at ambient temperature (~30 °C) on a Varian HA-100 NMR spectrometer modified to permit illumination of the sample.[10] The light source was a water-cooled high-pressure mercury lamp, Philips Model SP 1000W. Gas chromatographic (GC) analyses were carried out on a Carlo Erba Fractovap 2101 with flame ionization detector. The 30-m column (0.35 mm diameter) contained a surface coating of UCON 50-HB-5100. After injection and passage of the solvent peak at 100 °C, temperature was programmed to rise 50 °C/min on each sample to 200 °C maximum. GC–mass spectrometer runs were carried out on the Perkin-Elmer Model 270 instrument. In this case, the column was 46 m long and 0.5 mm diameter, with a surface coating of OS-138. The temperature program was the same as that used on the other instrument. Optical spectra were run on a Pye Unicam spectrophotometer.

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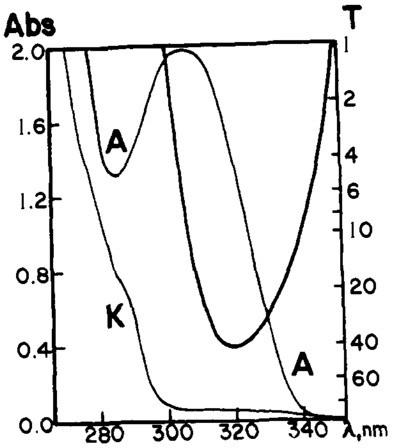

Figure 1. Transmittance curve (heavy line) for a filter system made up of 3-cm aqueous nickel(II) sulfate–cobalt(II) sulfate solution (after Kasha), followed by a WG 320 glass filter, filter system II. Note that this transmittance curve must be corrected for the large variation with wavelength of the light emission of the Philips lamp to give the actual distribution of light incident upon the sample. Absorption curves for 0.0010 M solutions of *N,N*-dimethyl-p-toluidine (A:) and 4-methylacetophenone (K) also are shown.

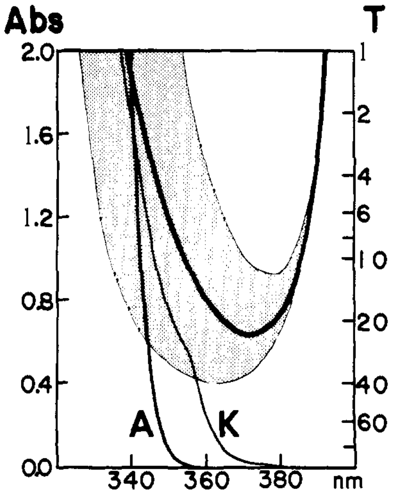

Figure 2. Change of transmittance with age (zero, outside curve, to 8 days, inside curve) of a filter system made up of 3-cm aqueous copper(II) sulfate solution followed by UG 11 and WG 345 glass filters (hatched area). The heavy line gives the transmittance curve for solution aged 3 days. All curves must be corrected for the large variation with wavelength of the light emitted by the Philips lamp to give the actual distribution of light incident upon the sample. Absorption curves for 0.05 M *N,N*-dimethyl-*p*-toluidine (A:) and 4-methylacetophenone (K) solutions also are shown.

Samples and Solvent. *N,N*-Dimethylaniline and *N,N*-dimethyl-*p*-toluidine were purchased from Fluka AG (Buchs, CH), and contained significant amounts of impurities which were identified by GC as the mono-*N*-methyl compounds. In addition, these samples were more or less brown. They were treated with tin(II) chloride to remove sulfur compounds (alleged to produce the brown color on standing in air), using the procedure of Weissberger and Strasser.[11] The amines recovered from this step as solutions in methylene chloride were then treated with *p*-toluenesulfonyl chloride by the Hinsberg procedure[12] to remove the monomethyl impurity, dried over solid potassium hydroxide, and vacuum distilled. These purified samples were initially relatively free of the monomethyl compound, but the amount of an impurity with the same GC retention time and mass spectrum appeared to increase when the liquid amines were stored for several weeks in the refrigerator.

Commercial 4-methylacetophenone (initially ca. 95% pure) was converted to the semicarbazone; this derivative was recrystallized by extraction into ethanol and then hydrolyzed with hydrochloric acid in acetic acid solution. The product boiled at 95.5–96.6 °C (11 mm) and was 97% pure by GC. The remaining impurity appeared to be another carbonyl compound, since it accompanied the sample through the semicarbazone recrystallization. From the mass spectrum (nearly identical with that of 4-methylacetophenone) we infer that it is a ring isomer of this substance. The other ketones for which results are mentioned in this study were better than 99% pure in their commercial form, and were used without further purification. Biphenyl (purum, Fluka AG) and biphenyl-d_{10} (Merck Sharp and Dohme) were used as purchased.

The acetonitrile solvent was Merck UVASOL grade. Newly opened bottles of this solvent were stored over freshly activated 3 Å molecular sieve. No special precautions were taken during transfers of solvent while samples were made up; no doubt the dry solvent absorbed some water during these manipulations. Acetonitrile-d_3 from CEA-France, to which was added 17% acetonitrile to provide the lock signal, was used for many of the runs in which signals from the aliphatic protons were recorded, to minimize problems arising from the nearby solvent line. Solutions for the CIDNP experiments were made up with 0.10 M ketone and 0.10 M amine in these solvents. Biphenyl was used at 0.50 M concentration as the triplet quencher. The solutions were deaerated for at least 15 min with a sweep of argon or prepurified nitrogen. Oxygen present in these samples affects the CIDNP signals in the same way as does added biphenyl.

Filter Systems. The output of the Philips lamp was filtered to select wavelength ranges appropriate for selective excitation of either the ketones or the amines. The filter system used must include a filter solution capable of absorbing infrared radiation to protect glass filters and the probe from overheating. For aromatic amine–biphenyl solutions we used the nickel(II) sulfate–cobalt(II) sulfate solution suggested by Kasha,[13] with a Schott WG 295 glass filter (filter system I); excitation of the amine then dominates. For aromatic amine–aromatic ketone solutions the nickel sulfate–cobalt sulfate filter was combined with a Schott WG 320 glass filter. This gives the transmission window illustrated in Figure 1. This figure also shows the absorption curves in that wavelength range for 4-methylacetophenone and *N,N*-dimethyl-*p*-toluidine. We estimate that for this filter system (II) over 90% of the radiation is absorbed by the amine.

Absorbance of the aromatic ketones exceeds that of the aromatic amines for wavelengths greater than about 345 nm. The nickel–cobalt filter solution already mentioned is unsuitable in this region because it cuts off most of the incident radiation. It was replaced with a copper sulfate solution (125 g of copper(II) sulfate pentahydrate + 2 mL of sulfuric acid per liter), together with the Schott WG 335 and UG 11 glass filters. This filter combination gave unreproducible results until we recognized that the solution undergoes an aging process (independent of exposure to radiation) which involves a shift of the long-wavelength edge of the UV absorption band to still longer wavelengths.[14] The effect of this is to cut off just that radiation region in which ketone absorbance exceeds that of the amine. Figure 2 shows the variation of the radiation window as the filter solution ages over a period of 8 days, together with the absorption curves of the aromatic ketone and amine. Solution which is about 3 days old gives the optimum radiation window for ketone absorption. However, this filter combination was not completely satisfactory because the solution transmits enough infrared radiation to overheat the UG 11 glass filter which subsequently absorbs it. We lost six of these filters by thermal cracking during these experiments. The ketone is estimated to absorb over 90% of the radiation transmitted by this filter system (III), even in the presence of equal concentrations of aromatic amine.

Acetonitrile solutions of acetophenone, *N,N*-dimethylaniline, and of both together were checked carefully for spectrophotometric evidence of a charge-transfer band. None was observed, although the same amine in solution with phthalonitrile gave an easily detected charge-transfer absorption.

Results

The general features of the CIDNP are the same for the reactions of acetophenone or of its 4-methyl or 4-methoxy derivatives with either *N,N*-dimethylaniline or its *p*-methyl derivative. The effects observed appear to be somewhat stronger with the substituted ketones than with acetophenone. Both for this reason and because the aromatic proton NMR lines are easier to disentangle for the para-disubstituted compounds, our most extensively studied system involves 4-

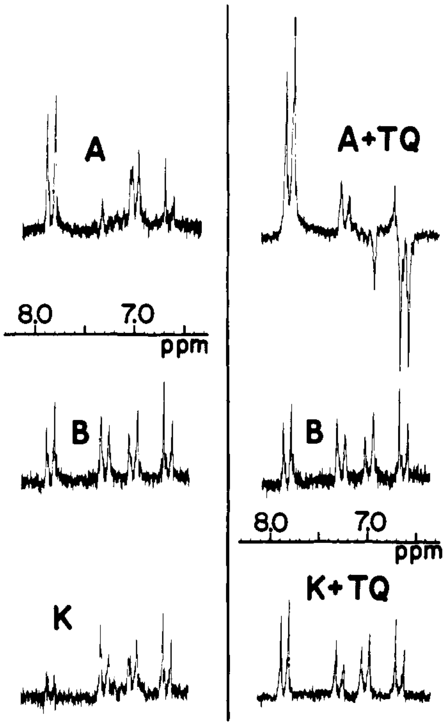

Figure 3. CIDNP signals of aromatic protons during photoreaction of 4-methylacetophenone with *N*,*N*-dimethyl-*p*-toluidine in acetonitrile. The middle spectra (B) are taken before illumination of the samples. Top spectra: amine absorbs the light in the absence (left) and in the presence (right) of biphenyl. Bottom spectra: ketone absorbs the light in the absence (left) and in the presence (right) of biphenyl. For assignments of lines see Table I.

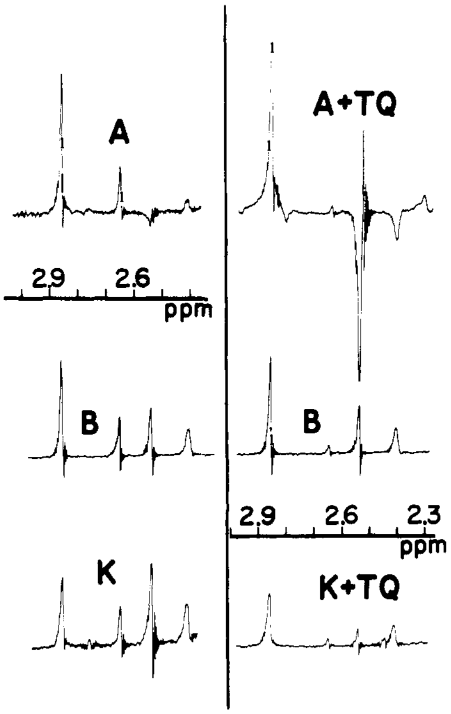

Figure 4. CIDNP signals of aliphatic protons during photoreaction of 4-methylacetophenone with *N*,*N*-dimethyl-*p*-toluidine. The middle spectra (B) were taken prior to illumination of the samples. Top spectra: amine absorbs light in the absence (left) and in the presence (right) of triplet quencher, biphenyl. Bottom spectra: ketone absorbs light in the absence (left) and in the presence (right) of triplet quencher. (For assignments of lines see Table I.) Spectra in the left column were run on samples dissolved in acetonitrile, while those in the right column were dissolved in acetonitrile-d_3 containing 17% acetonitrile.

methylacetophenone reacting with *N*,*N*-dimethyl-*p*-toluidine, and the following description of results applies to this system.

Figure 3 shows the aromatic proton signals, and Figure 4 the signals from the aliphatic protons observed under the conditions we have investigated. It is more difficult to record good spectra in the aliphatic region because these lines are within 30-95 Hz of the intense proton line of the acetonitrile solvent, which was used as a lock signal. The downfield signal of the pair of proton NMR lines produced by coupling with ^{13}C in the solvent (δ 2.65 ppm) affords a useful calibration point 65 Hz downfield from the lock signal, and within the pattern of aliphatic proton lines of the educts.

In both figures, the center rows of spectra were obtained on the reaction system prior to irradiation. The top row contains the CIDNP signals when the samples are irradiated in the region where the amine absorbs most of the light (filter system II), and the bottom row gives the signals when the ketone absorbs the light (filter system III). Some broadening of the amine *N*-methyl line is observed in most spectra;[15-17] the effects of amine concentration upon line width were not investigated. The ring methyl-group protons of the amine only occasionally show significant CIDNP effects. The net effects seen in Figures 3 and 4 are summarized in Table I, where possible multiplet effects (never very clearly displayed) are also given. Within the limits of our detection capabilities, there is no significant change in these CIDNP effects produced by sample impurities at the levels present in our commercial chemicals before purification: we saw the same effects for the unpurified samples and for those subjected to the purification procedures already described.

As is evident from the figures and Table I, control of the incident radiation to produce selective excitation of amine or of ketone in the absence of biphenyl leads to inversion of the CIDNP effects. Addition of biphenyl increases the CIDNP effects dramatically with amine excitation, while it diminishes and in part inverts the CIDNP effects for ketone excitation. These effects produced by ketone excitation clearly are weaker than those produced by excitation of the amine. We attribute the difference to the much lower extinction coefficient (only a few percent of that for the amine) of the ketone in the region irradiated; see Figures 1 and 2. Our confidence that the effects in the bottom spectra of Figures 3 and 4 are real is enhanced by the observation that they appear in all of the ketone-amine combinations studied.

After prolonged irradiation product NMR signals appear in the spectra. They do not exhibit CIDNP, and in most cases were not assigned. However, GC-MS analysis of reaction mixtures identified *N*-methyl-*p*-toluidine as a product formed during irradiation of all samples. The amount formed as a result of amine excitation is larger than that formed by excitation of the ketone.

In general the CIDNP effects observed during reaction of benzophenone with the anilines resemble those observed with acetophenones, with some differences in details. The CIDNP signal of the amine *N*-methyl group is much stronger, and product signals appear after shorter irradiation times. Furthermore, addition of biphenyl reduces but does not eliminate the *N*-methyl emission observed when the ketone absorbs the radiation.

Several blank experiments were carried out to assure that these effects are due solely to photoreactions of the ketones with the amines. Solutions of ketones without amines showed no polarization, with or without the presence of added triplet quencher. Solutions of the amines alone gave a weak emission signal for the α protons of the *N*,*N*-dialkylanilines. For solutions of the amines containing biphenyl (with filter system I),

Table I. Summary of CIDNP Signals Observed with 4-Methylacetophenone and *N,N*-Dimethyl-*p*-toluidine[a]

	aromatic proton CIDNP signals				aliphatic proton CIDNP signals		
	of the ketone		of the amine		of amine	of the ketone	
radiation absorbed by	ortho[b] δ 7.85	meta[b] 7.30	ortho[b] 6.68	meta[b] 7.03	NCH_3[c,d] 2.86	acetyl 2.54	methyl 2.41
amine	A	E	E?	E? br	A	E	E
amine + TQ	A	E br	E + A/E	E + A/E	A	E	E
ketone	E	A?	?	?	E? br	A	A
ketone + TQ	A wk	E wk	?	?	A? br	E wk	E wk

[a] A means net enhanced absorption, E means net emission, A/E means multiplet type polarization, wk means a weak effect, and br means the line is broadened. [b] The terms ortho and meta are used to give positions relative to the acetyl group in the ketone and relative to the dimethylamino group in the amine. [c] The signal of the ring *p*-methyl protons of the amine appears at δ 2.28 ppm, or only 32 Hz downfield from the lock signal. Consequently, observation of its CIDNP effects is difficult, but in several runs enhanced absorption was observed with amine excitation; this increased in the presence of biphenyl. [d] A signal due to solvent protons coupled with ^{13}C appears at δ 2.65 ppm.

Table II. Singlet and Triplet Energies and Oxidation and Reduction Potentials

compd	E_S, eV	E_T, eV	$E(C/C^{+}\cdot)$, V	$E(C^{-}\cdot/C)$, V
acetophenone	3.47[a]	3.21[a]		−2.12[b]
p-methylacetophenone	3.52[c]	3.16[c]		−2.20[d]
benzophenone	3.24[b,c]	2.99[b]		−1.81[b]
N,N-dimethylaniline	≃3.85[c]	≃3.35[e]	0.78[f]	
N,N-diethylaniline	3.90[g]	3.33[g]	0.76[h]	
N,N-dimethyl-*p*-toluidine			0.75[i]	
biphenyl	4.28[f]	3.01[f]	1.48[j]	≃ −2.70[j]

[a] Reference 6. [b] Reference 27a. [c] Reference 22. [d] Reference 40. [e] Reference 41. [f] Reference 29. [g] Reference 42. [h] Reference 33. [i] Reference 43. [j] Reference 44.

a small enhanced absorption of the α-proton signals was observed. These signals also broadened increasingly with decreasing amine concentration.[15] These results are noteworthy and will be considered in the Discussion section. The effects are, however, too small to interfere with the larger polarizations observed for solutions which contained both amine and ketone.

Discussion

With the aid of Kaptein's rules[18] and the Closs amendment[16]

$$\Gamma_n = \mu\epsilon\Delta g a \gamma \tag{4}$$

$$\Gamma_{m,ij} = \mu\epsilon a_i J_{ij}\sigma_{ij}\gamma \tag{5}$$

the directions of CIDNP effects of all ketone-amine systems can be explained by nuclear spin-dependent intersystem crossing in geminate pairs of the radical ions $A^{+}\cdot$ and $K^{-}\cdot$. Furthermore, the line-broadening phenomena point to the occurrence of ionic (as opposed to neutral) radical pairs by the argument given by Roth and Lamola.[8a] Since the general features of the CIDNP effects are the same for all of these systems, we will discuss in detail only the effects observed during the photoreaction of 4-methylacetophenone and *N,N*-dimethyl-*p*-toluidine presented in Figures 3 and 4 and in Table I. For the application of eq 4 to the observed net effects, knowledge of the difference in *g* factors of the acetophenone anion radical ($K^{-}\cdot$) and the toluidine cation radical ($A^{+}\cdot$) is of crucial importance. Available data[19,20] permit a reasonable estimate for the *g* factor for acetophenone radical anion: $g(K^{-}\cdot) \approx 2.0035$. Para-methyl substitution is not expected to change this value by more than +0.0002.

The *g* value for the *N,N*-dimethyl-*p*-toluidine radical cation ($A^{+}\cdot$) is not known. However, Neugebauer has recently determined $g = 2.0029$ for the cation radical of *m,m′*-di-*tert*-butyl-*N,N*-dimethylaniline, and the same author has also measured $g = 2.0028$ for the *p*-toluidine radical cation.[21] Therefore we take $g(A^{+}\cdot) < g(K^{-}\cdot)$, in contrast to the aromatic ketone-aliphatic amine systems where $g(A^{+}\cdot) > g(K^{-}\cdot)$. With the known sign of the *g*-factor difference the net CIDNP effects of *p*-methylacetophenone are easily explained via eq 4. For amine excitation we set $\mu < 0$ (singlet precursor), $\epsilon > 0$ (reverse transfer), and $\gamma > 0$ (singlet exit channel). We then obtain the observed CIDNP phases for the various groups of protons in the ketone by inserting the usual signs of the coupling constants $a_{H(COCH_3)} > 0$, $a_{H(ortho)} < 0$, $a_{H(meta)} > 0$, $a_{H(p\text{-}CH_3)} > 0$. For ketone excitation without added biphenyl the observed inverse phases are explained if a triplet precursor is assumed ($\mu > 0$). If biphenyl is present, a singlet precursor ($\mu < 0$) is again required. The polarizations of the NCH_3 and ortho protons of the amine also follow for all types of excitation with the usual assumption that $a_{H(NCH_3)} > 0$ and $a_{H(ortho)} < 0$. With $a_{H(meta)} > 0$, however, enhanced absorption of the meta protons is predicted for the case of amine excitation, whereas, at least in the presence of biphenyl, clear emission is observed (Figure 3). This could mean that $a_{H(meta)} < 0$ for the toluidine cation, and this conclusion would be supported by the multiplet effect of the ortho and meta proton transitions (A/E for amine excitation); the explanation via eq 5 requires like signs of $a_{H(ortho)}$ and $a_{H(meta)}$, with $\mu < 0$, $\epsilon > 0$, $\gamma > 0$, $J_{ij} > 0$, and $\sigma_{ij} > 0$. However, these effects are more likely due to $a_{H(meta)} > 0$ with polarization transfer from the ortho-proton transitions as recently described by Closs and Czeropski.[17]

From the analysis of CIDNP phases the triplet pathway (1) is clearly dominant for ketone excitation in the absence of biphenyl, whereas a singlet pathway like (2) dominates for amine excitation. These findings do not rule out minor contributions of pathways with the opposite multiplicity, and the effects of biphenyl addition strongly point to such contributions. Table II shows the singlet and triplet energies of the species involved. Obviously, biphenyl will act as a triplet quencher.[22,23] The enhancement of the CIDNP effects for amine excitation and the inversion of CIDNP effects with ketone excitation are then readily understood by quenching of triplet pathways which are of minor importance for amine but dominant for ketone excitation.

Figure 5 shows energies of states and transition rate constants (s^{-1}) of processes which we think important for the system 4-methylacetophenone-*N,N*-dimethyl-*p*-toluidine. We estimate the energy of the contact ion pair ($A^{+}\cdot\,K^{-}\cdot$) relative to that of the ground state from

$$E(A^{+}\cdot K^{-}\cdot) = E(A/A^{+}\cdot) - E(K^{-}\cdot/K) - \frac{e^2}{\epsilon a} \tag{6}$$

and take $a = 7.0$ Å;[24] this gives 0.056 eV for the coulomb term.

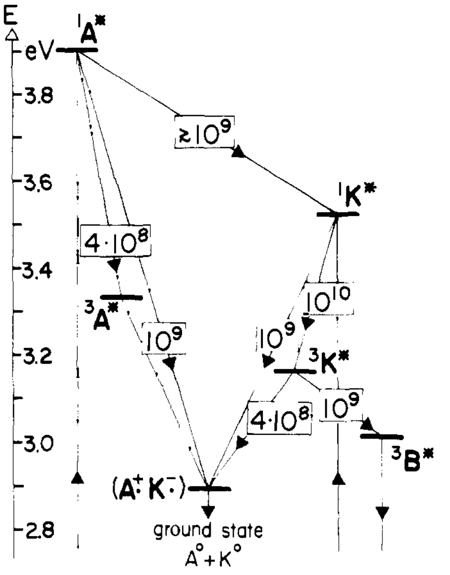

Figure 5. Low-lying excited electronic energy states, radical ion pair state, and approximate transition rate constants (s^{-1}) for the system 4-methylacetophenone-*N*,*N*-dimethyl-*p*-toluidine-biphenyl in acetonitrile solution.

The oxidation potential for the amine and the reduction potential for the ketone (Table II) then lead to $E(A^{+}\cdot K^{-}\cdot) = 2.89$ eV. The rate constants are estimated from the literature.[25-31] One should bear in mind the fact that CIDNP arises only from that fraction of ion pairs which diffuses apart for about 10^{-10}–10^{-8} s and subsequently returns to permit back transfer of the electron.[7] This fraction is not known, and will generally be different for singlet and triplet pairs.[7] Consequently the rates given in Figure 5 may only roughly reflect those pertinent to the development of CIDNP. Nevertheless, they support the conclusions drawn above.

After amine excitation, direct electron transfer to the ketone to yield singlet ion pairs (reaction 3) is energetically favorable. It should be accompanied by singlet energy transfer to the ketone (2) with partial subsequent rapid electron transfer from the neighboring amine. This also leads to singlet ion pairs, and it would be difficult to distinguish between the two mechanisms. Ion-pair formation by reaction of triplet amine and/or of triplet ketone after intersystem crossing will compete with the singlet pathways but not dominate. Addition of biphenyl quenches the latter processes. After ketone excitation triplet ion pair formation is dominant because of the fast intersystem crossing. The weak effects remaining on addition of biphenyl require a singlet precursor, in agreement either with some quenching of acetophenone excited singlet by the amine or with residual direct amine excitation. Our results obtained for benzophenone–aromatic amine systems agree with this general scheme. The weaker effect of biphenyl addition in this case is a consequence of the inefficient triplet quenching.[23]

In this study we have not observed CIDNP effects which could be attributed to intermediate pairs of neutral radicals, i.e., $\mathrm{ArN(CH_3)\dot{C}H_2}$ and $\mathrm{CH_3\dot{C}(OH)Ar}$. Roth and Manion[8b] have shown that both ionic and neutral radical pairs occur during UV irradiation of *N*,*N*-diethyl-*p*-toluidine and decadeuteriobenzophenone in acetone-d_6. For the reaction of the toluidine with decafluorobenzophenone in acetonitrile (ketone excitation), they find evidence only for pairs of ionic radicals, in agreement with our result and with expectation.[3]

The enhanced absorption for the α protons of *N*,*N*-dialkylanilines observed during irradiation of amine solutions (without ketone) in acetonitrile containing biphenyl is accompanied by selective line broadening which indicates the intermediacy of radical ions. This and the quenching of diethylaniline fluorescence by biphenyl[4] lead us to assume singlet radical ion pair formation by electron transfer from the excited amine to biphenyl. From the data of Table II and eq 6, this ion pair lies 3.4 eV above the ground state and 0.4 eV above the triplet state of biphenyl. Reverse electron transfer during reencounters of the geminate radical ion pairs may now lead to re-formation of ground-state amine and ground-state biphenyl, or to the formation of ground-state amine and triplet biphenyl. The triplet exit channel should be favored,[32,33] and is in fact required for the interpretation of the observed CIDNP effect via eq 4 ($\mu < 0$, $\epsilon > 0$, $g(A^{+}\cdot) > g(B^{-}\cdot)$,[34] $a_{H(CH_3)} > 0$, $\gamma < 0$). Several CIDNP observations leading to the same conclusion have been reported previously.[16,17,35-37]

Finally, the weak emission of the α protons of *N*,*N*-dialkylanilines in acetonitrile solutions containing neither ketone nor biphenyl may be explained by photodealkylation:[38,39]

$$\mathrm{Ar\text{-}NR_2} \xrightarrow{h\nu} \mathrm{Ar(R)N\cdot} + \mathrm{R\cdot} \qquad (7)$$

On the other hand, photoreactions of ground-state electron donor–acceptor complexes between amine and acetonitrile may be involved as for tertiary aliphatic amines,[36] though we have searched for but not found evidence for such species (see Experimental Section). Anyway, their reactions must be of minor importance and cannot interfere effectively with those occurring in our ketone–amine systems since the CIDNP effects observed in the absence of ketone are much smaller than those observed with ketone present.

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(15) Broadening of NMR lines due to aliphatic protons α to amine nitrogen, >N-CH<, was observed for most of the systems studied, and generally increased with decreasing amine concentration. In some cases broadening precluded observation of the CIDNP effect during irradiation. If this occurred, the CIDNP could usually be observed by the technique first described by Closs and Czeropski.[16,17] The broadening is due to degenerate electron transfer between escaping amine cation radicals and amine:[8a]

$$A^{+}\cdot + A{:} = A{:} + A^{+}\cdot$$

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(27) For quenching of triplet ketone by amine, $k \simeq 4 \times 10^9\ M^{-1}\ s^{-1}[A\!:^0] = 4 \times 10^8\ s^{-1}$. For related systems, see (a) R. O. Loutfy and R. O. Loutfy, *Can. J. Chem.*, **50**, 4050–4052 (1972); (b) S. G. Cohen and A. D. Litt, *Tetrahedron Lett.*, 837–840 (1970).

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(29) Quenching of excited singlet amine by ketone to give the ion pair is assumed to be near the diffusion limit: $k \simeq 10^{10}\ M^{-1}\ s^{-1}[A\!:^0] = 10^9\ s^{-1}$. See D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259–271 (1970).

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Cyclopropylcarbinyl Radicals in the Photochemistry of β,γ-Cyclopropyl Ketones

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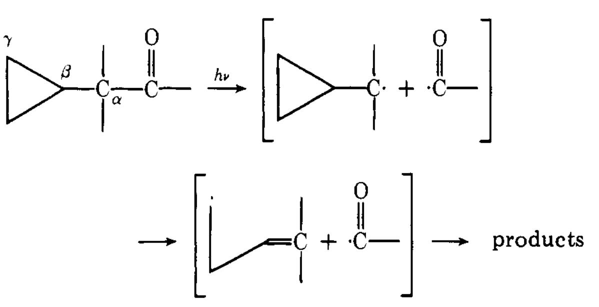
Abstract: Photolysis of tricyclic ketones **8b–d**, **9b**, and **10** leads to the products collected in Table I. These results, along with earlier findings with related ketones **6** and **7**, are interpreted as strong evidence for the stepwise mechanism of eq 1, in which opening of the three-membered ring occurs by way of α-cleavage, rearrangement of the initial cyclopropylcarbinyl radical to a homoallyl radical under stereoelectronic control, and then product formation.

One of the principal modes of photochemical reaction of β,γ-cyclopropyl ketones can be explained as an α-cleavage, rearrangement of the cyclopropylcarbinyl radical to a homoallyl radical, and then product formation through disproportionation, coupling, or some more complex transformation of the resulting radical pair or biradical (eq 1). This intuitively reasonable, stepwise mechanism, first advanced over a decade ago,[1] satisfactorily accounts for a variety of rearrangements,[2,3] although there is at least one observation suggesting that some refinement of it may be necessary. This is the report[3] that photolysis of both *cis*- and *trans*-4-caranone (**1**) leads selectively to products explainable by way of eq 1, as particularized in eq 2. There is no concomitant epimerization of the methyl group, and less than 1% of product attributable to α-cleavage toward the methyl group (as **3**) is found. This result contrasts with the behavior of typical 2-alkylcyclohexanones, which undergo α-cleavage predominantly or solely on the more substituted side; the products from 2-methylcyclohexanone (**4**), for example, arise only from biradical **5**.[4] Thus, if the photochemistry of the 4-caranones (**1**) follows eq 1, it is necessary to specify that the β,γ-cyclopropane ring controls the site of α-cleavage. As originally suggested,[3] the cyclopropane ring appears to weaken the appropriate bond α to the carbonyl group by conjugative or inductive effects. Although the authors did not carry the argument so far, at the extreme this observation might mean that no discrete cyclopropylcarbinyl intermediate is involved and that α-cleavage and fragmentation



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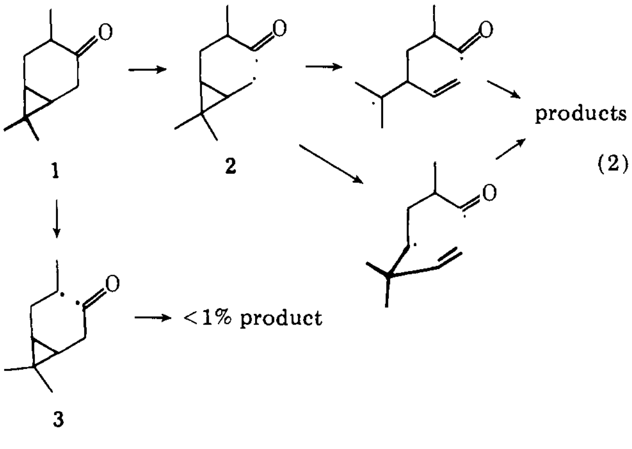

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