# Chemically Induced Dynamic Nuclear Polarization and Exchange Broadening in an Electron-Transfer Reaction

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**Abstract:** The solution photolysis of para,para'-disubstituted benzophenones (1) in the presence of Dabco (2) has been investigated with the help of nmr techniques. During the irradiation, the ketones showed nuclear spin polarization (CIDNP) effects for the ortho (enhanced absorption) and meta protons (net emission). These results are interpreted as evidence for electron transfer from the amine to the excited triplet ketones. Simultaneously, nmr line broadening was observed for 2 and for $p,p'$-dichlorobenzophenone (1e). These phenomena were ascribed to degenerate electron transfer between 2 and its radical cation (4) and between the ketyl radical (3e) and its parent ketone.

Aryl ketones in their triplet states undergo fast reactions with alkylamines, resulting in ketone reduction or quenching of the triplet ketone without net chemical change. The efficiency of photoreduction varies greatly depending upon the ketone–amine pair and upon the solvent. Much of the experimental data indicate that charge transfer from the amine to the excited ketone must be considered in any mechanistic formulation.[1]

A generalized scheme which includes the several pathways which have been suggested for the interactions of amines with triplet aryl ketones is given below. Before discussing the scheme, it is worth pointing out that electronic energy transfer from the triplet-state ketone to the amine is precluded as a quenching mechanism because the energy required to excite the alkylamine triplet state ($\geq 4$ eV)[2] is much greater than the triplet energy of the aryl ketone ($\sim 3$ eV).[3]

**Scheme I**
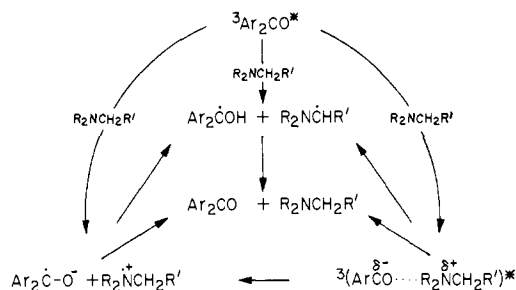


Formation of the neutral radicals, $Ar_2\dot{C}OH$ and $R_2\bar{N}\dot{C}HR'$, required as intermediates to explain the products, may occur *via* hydrogen abstraction from the amine ($R_2\bar{N}CH_2R'$) by the triplet-state ketone ($^3Ar_2CO^*$). Reverse hydrogen atom transfer[4] giving the original ketone and amine is a possible degenerate pathway (apparent quenching).

For many amine–ketone combinations energy con-

siderations (*vide infra*) allow the primary photochemical step to be formulated as an electron transfer producing the pair of radical ions, $Ar_2\dot{C}O^-$ and $R_2\dot{N}^+CH_2R$. Reverse electron transfer to give the original reactants provides another degenerate pathway or quenching mechanism. Proton transfer from $R_2\dot{N}^+CH_2R'$ to $Ar_2\dot{C}O^-$ could produce the same neutral radical pair ($Ar_2\dot{C}OH$ and $R_2\bar{N}\dot{C}HR'$) in a two-step sequence rather than by direct hydrogen abstraction.[5,6]

An alternative formulation involves the intermediacy of a ketone–amine exciplex, $^3(Ar_2CO^{\delta-}\cdots R_2N^{\delta+}-CH_2R')^*$, whose relaxation could be proportioned among three paths: decay to the ground-state species (quenching), hydrogen atom transfer to form the neutral radical pair, and electron transfer to form the discrete radical ions. Since the excitation energies of the aryl ketone and alkylamine are poorly matched, the binding energy of the exciplex would necessarily be chiefly provided by charge-transfer interactions. Arguments for charge-transfer mechanisms are generally based on experimental evidence such as the dependence of yield, reaction rate, or lifetime of the reactant excited state upon the polarity of the solvent and the redox potentials of the reactants.[1] More directly, electron transfer is indicated by the observation of photoconductivity[7] and unambiguously by the spectroscopic identification of the transient radical ions.[8,9]

We have attempted to elucidate mechanistic details of reactions between photoexcited benzophenones and tertiary amines with the help of a new nmr technique, chemically induced dynamic nuclear polarization (CIDNP). This method is based on the observation of strongly enhanced nmr signals, in emission or absorption, for the diamagnetic products of radical pair or radical ion pair reactions. The theory underlying this effect is well understood; therefore, the directions and the intensity patterns of CIDNP signals can be predicted if certain experimental parameters are known; alternatively, one of these parameters can be derived

(1) S. G. Cohen, A. Parola, and G. H. Parsons, *Chem. Rev.*, **73**, 141 (1973).

(2) Y. Muto, Y. Nakato, and H. Tsubomura, *Chem. Phys. Lett.*, **9**, 597 (1971).

(3) See N. J. Turro in "Energy Transfer and Organic Photochemistry," P. A. Leermakers, Jr., and A. Weissberger, Ed., Interscience, New York, N. Y., 1969, p 199.

(4) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967).

(5) A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, **93**, 6998 (1971).

(6) P. J. Wagner and T. Jellinek, *J. Amer. Chem. Soc.*, **93**, 7330 (1971).

(7) *Cf.*, *e.g.*, Y. Taniguchi, Y. Nishina, and N. Mataga, *Bull. Chem. Soc. Jap.*, **45**, 764 (1972).

(8) K. H. Grellmann, A. R. Watkins, and A. Weller, *J. Lumin.*, **1**, **2**, 678 (1970).

(9) R. S. Davidson and S. Santhanam, *J. Chem. Soc., Perkin Trans. 2*, 2351, 2355 (1972).

from the observed signal directions if the other parameters are known.

The CIDNP method has been applied to a wide range of problems;[10] in the area of photochemistry, a particularly attractive application lies in the opportunity to study degenerate reactions that may contribute to the nonradiative decay of photoexcited species.[11] In general, CIDNP effects cannot be expected if exciplexes are the only intermediates which lead back to the starting materials. In contrast, degenerate reactions involving either radical ion pairs (3, 4) or pairs of neutral radicals (5, 6) could give rise to CIDNP effects if competing reactions occur simultaneously. In favorable cases, the CIDNP method might differentiate between the possibilities of radical ions or neutral radicals as intermediates.

In this paper we report the changes of the nmr spectra observed during the solution photolysis of several 4,4'-symmetrically disubstituted benzophenones (1) in the presence of 1,4-diazabicyclo[2.2.2]octane (Dabco, 2). The use of these derivatives appeared advantageous since the substituents simplify the nmr patterns so that the ortho and meta protons are observed in clearly separated multiplets; at the same time the para substituents allow for the modification of the electron affinity of the ketones. The solvents employed ranged from highly polar ones to nonpolar ones.

**Scheme II**



a, X=OCH₃    b, X=CH₃    c, X=H    d, X=F    e, X=Cl
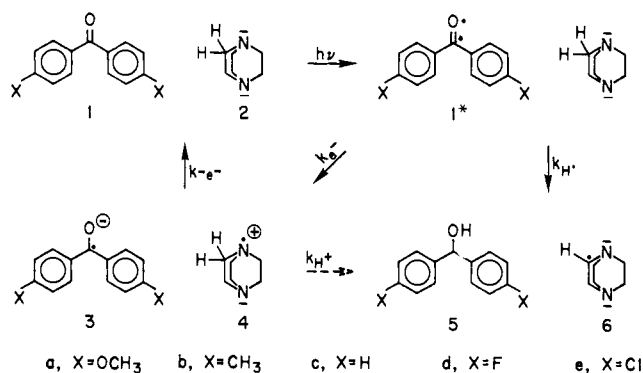
## Experimental Section

**Materials.** Benzophenone (J. T. Baker, "for photochemical use") was used as supplied; dimethylbenzophenone (Eastman Kodak) and dimethoxy-, difluoro-, and dichlorobenzophenone (Aldrich) were recrystallized from methanol. Diazabicyclo[2.2.2]octane (Aldrich) was sublimed prior to use. The solvents, acetonitrile-$d_3$ (Diaprep, 99% D), pyridine-$d_5$ (Merck, 99% D), methanol-$d_4$ (Merck, 99.5% D) and benzene-$d_6$ (Aldrich, Gold Label, 99.5% D), were stored over molecular sieves and used without further purification. Hexafluorobenzene was purified by stirring with three successive portions of oleum, washing with water, drying over phosphorus pentoxide, and vacuum distilling.

**Sample Preparation.** The samples containing one of the ketones (0.01 $M$) and Dabco (up to 0.05 $M$) were deaerated in 5-mm nmr tubes by purging with argon for periods of 150–180 sec. Purging proved to be essential for the observation of CIDNP signals, since photolysis of samples that had not been purged produced considerably weaker effects or no effects at all.

**Apparatus.** The nmr spectra were recorded on a Jeolco JNM-C-60HL spectrometer; the probe of this instrument was modified by the manufacturer to permit uv irradiation of the samples in the area of the receiver coil. The collimated light of an Osram 200-W

(10) "Chemically Induced Magnetic Polarization," A. R. Lepley and G. L. Closs, Ed., Wiley, New York, N. Y., 1973.
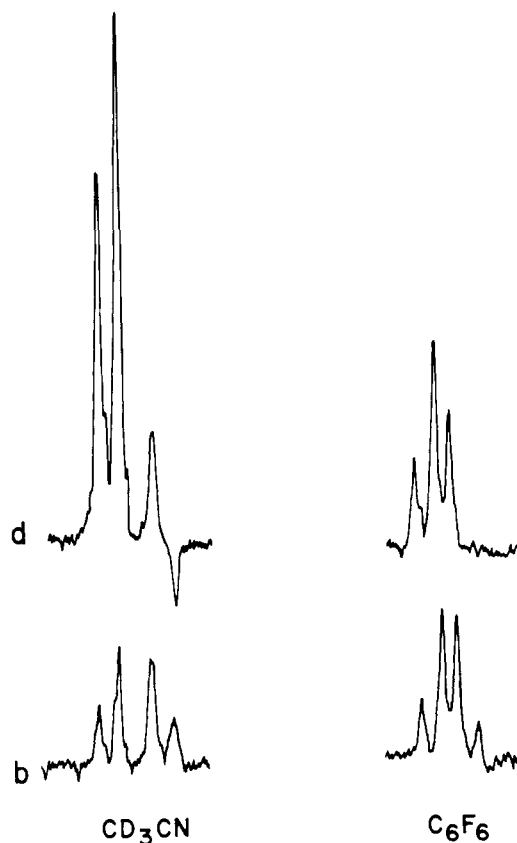(11) H. D. Roth, *Mol. Photochem.*, **5**, 91 (1973).

**Figure 1.** Pmr spectra (60 MHz) of argon-deaerated 4,4'-dimethylbenzophenone solutions ($10^{-2}$ $M$) in acetonitrile-$d_3$ (left) and hexafluororobenzene (right), containing 5 × $10^{-2}$ $M$ Dabco in the dark (b) and during uv irradiation (d).

high-pressure mercury lamp enters the probe in a direction parallel to the sample tube and is reflected on to the receiver coil by a frontside aluminum mirror mounted in front of it at an angle of 45°. The rear wall of the all-quartz insert is covered with aluminum. The light intensity in the probe can be monitored by a photodiode inserted into an nmr tube.

## Results

Illumination of benzophenone–Dabco systems in the probe of an nmr spectrometer produced a variety of changes in the nmr spectra. In polar solvents such as acetonitrile-$d_3$, the spectrum of 4,4'-dimethylbenzophenone (1b; Figure 1, left) showed enhanced absorption for the ortho protons (downfield signals), an A/E multiplet superimposed on net emission for the protons in meta position, and emission for the methyl group (Figure 2). The spectrum of 4,4'-dimethoxybenzophenone (1a) showed similar CIDNP effects in the aromatic region; however the methoxy signal was unchanged during irradiation. Photolysis of 4,4'-difluorobenzophenone (1d) produced a strong emission effect for the triplet of triplets in the fluorine nmr spectrum.[12] In contrast, 4,4'-dichlorobenzophenone (1e) did not show a CIDNP spectrum when irradiated in acetonitrile-$d_3$ solution in the presence of Dabco; instead, pronounced line broadening was observed (Figure 3, left). This line broadening was observed only during irradiation; the sharper spectrum shown on the bottom left of Figure 3 reappeared within seconds after the irradiation was discontinued.

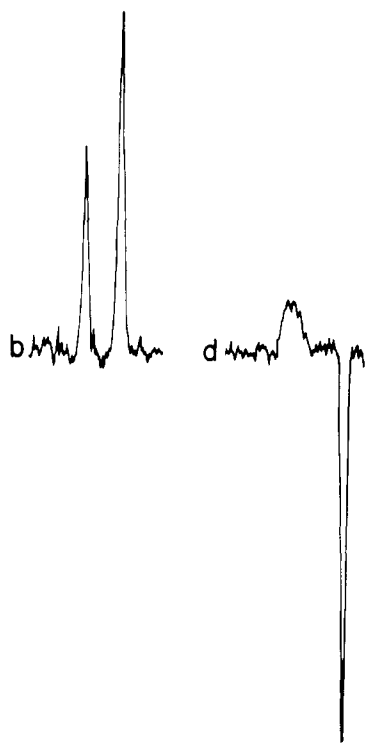(12) H. D. Roth, M. L. Manion, and M. L. Kaplan, unpublished results.

Figure 2. Pmr spectra (60 MHz) of an argon-deaerated 4,4'-dimethylbenzophenone solution ($10^{-2}$ $M$) in acetonitrile-$d_3$ containing 5 × $10^{-3}$ $M$ Dabco in the dark (b) and during uv irradiation (d).

In solvents less polar than acetonitrile ($\epsilon = 39$), for example, hexafluorobenzene or benzene-$d_6$ ($\epsilon = 2.3$), the CIDNP effects of 1a–c were considerably weaker (cf., e.g., Figure 1, right); but for 1e a CIDNP spectrum (Figure 3, right) similar to that of 1b in acetonitrile was observed.

In all solvents used the nmr signal of Dabco was broadened, regardless of the effect observed for the reaction partners, 1a–c (Figure 2). We did not observe any polarization documenting net chemical reaction, even in solvents (e.g., benzene), from which the coupling product (7) of radicals 5c (X = H) and 6 has been isolated.[13]

## Discussion

**Nuclear Spin Polarization Phenomena.** The observation of nuclear spin polarization in the starting ketones indicates that they are regenerated from radical intermediates, whose nature will be derived by an analysis of the polarization-determining parameters.[10] The direction of a CIDNP net effect depends on four parameters: the initial spin multiplicity of the radical pair ($\mu$), the mode of product formation ($\epsilon$), the difference in the isotropic $g$ factors of the individual radicals ($\Delta g$) and the signs of their electron–nuclear hyperfine coupling constants ($a$). If three of these parameters are known, the fourth one can be derived from the observed CIDNP signal direction. For example, we inferred the intermediacy of radical ions in the photochemical system anthraquinone–1,3-dimethylthymine, because the observed polarization pattern indicated hyperfine coupling constants of signs and relative magnitudes matching those expected for the dimethylthymine

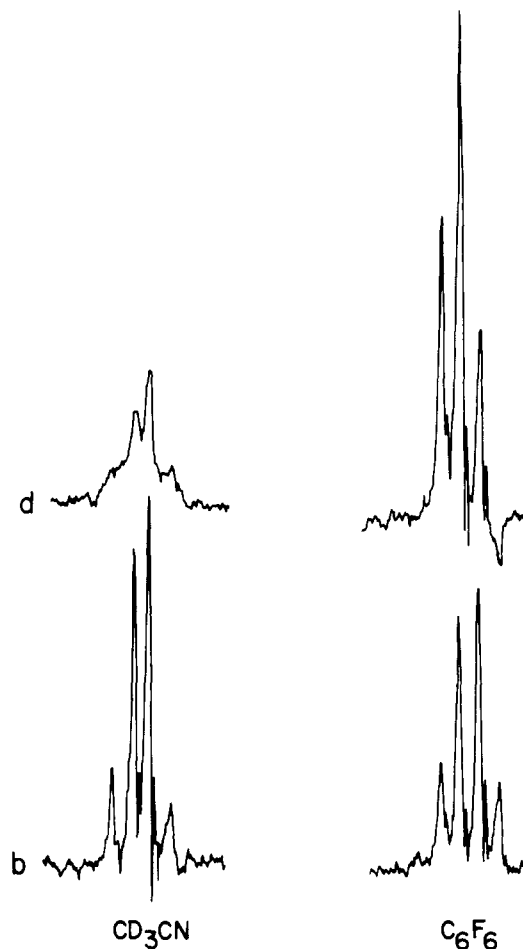(13) R. F. Bartholomew and R. S. Davidson, J. Chem. Soc. C, 2342 (1971).



Figure 3. Pmr spectra (60 KHz) of argon-deaerated 4,4'-dichlorobenzophenone solutions ($10^{-2}$ $M$) in acetonitrile-$d_3$ (left) and hexafluororobenzene (right), containing 5 × $10^{-2}$ $M$ Dabco in the dark (b) and during uv irradiation (d).

radical cation.[14] For the system discussed here the polarization-determining parameters of the potential intermediates, pair 3–4 or pair 5–6, are assigned as follows. All of the benzophenones we employed undergo extremely fast intersystem crossings from the lowest excited singlet to the lowest triplet state ($k_{isc} \sim 10^{11}$ sec$^{-1}$)[3,15] but also in the reverse direction,[16] so that an equilibrium ratio of the two states could be maintained even under conditions where photochemical reactions take place. The relative populations of singlet and triplet states at equilibrium are approximately $\exp(-\Delta E_{S-T}/kT)$, where $\Delta E_{S-T}$ is the difference between the electronic energies of singlet and triplet states.[16] For benzophenone, $\Delta E_{S-T}$ is $\sim$0.3 eV; thus, at room temperature the singlet:triplet ratio should be near $1:10^4$. For reactions which are slow compared to the intersystem crossing rates the ratio of participation of the singlet and triplet states would depend upon their relative reaction rates multiplied by the population ratio. Thus, the singlet state would have to react $10^2$ times faster than the triplet state to achieve even 1% participation. In cases where the triplet reaction rate is diffusion

(14) H. D. Roth and A. A. Lamola J. Amer. Chem. Soc., 94, 1013 (1972).
(15) A. Nitzan, J. Jortner, and P. M. Rentzepis, Chem. Phys. Lett., 8, 445 (1971).
(16) J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, J. Amer. Chem. Soc., 92, 410 (1970).

controlled, singlet participation cannot exceed $\sim 10\%$, since the lifetime of the encounter complex, certainly shorter than $10^{-8}$ sec in the cases discussed here,[17] is at least 10 times shorter than the triplet lifetime with respect to back intersystem crossing $(\sim 10^{-11} \times 10^4 \simeq 10^{-7}$ sec). In view of these considerations we deem it unlikely that singlet-state participation is important for any of the primary ketone–amine interactions which we have considered. Therefore, we assume that the radical pairs, 5–6 or 3–4, are generated in the triplet state $(\mu > 0)$.

The benzophenone-derived radicals, 3 and 5, are $\pi$ radicals with alternating spin density; in radicals of this type the hyperfine coupling constants of ortho hydrogen nuclei are usually negative $(a_H^o < 0)$, whereas those of the protons in the meta position and in the methyl group are positive $(a_H^m, a_H^{Me} > 0)$.[18] As for the mechanism of regenerating 1 and 2, two principally different pathways can account for the observed ketone polarization: in-cage return $(\epsilon > 0)$ of the hydrogen atom or the electron, respectively, or a degenerate exchange of, respectively, a hydrogen atom (a) or an electron (b) between polarized, paramagnetic radical (5 or 3) and ground-state ketone $(\epsilon < 0$; the asterisks denote nuclear spin polarization).

$$5^* + 1 \longrightarrow 1^* + 5 \qquad \text{(a)}$$

$$3^* + 1 \longrightarrow 1^* + 3 \qquad \text{(b)}$$
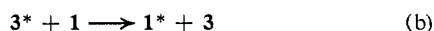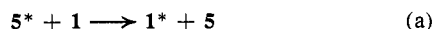
Reactions a and b are not without precedent. Several substituted hydroxymethyl radicals are well known to transfer hydrogen atoms to carbonyl compounds,[19,20] and degenerate electron transfer has been observed, for example, between amines[21,22] or aromatic hydrocarbons[23] and their radical ions. We base our choice of $\epsilon$ on the fundamental prerequisite for CIDNP, that the radical pair must undergo two competing reactions, whose rates must be electron spin dependent.[10] Pairs possessing singlet spin multiplicity usually undergo in-cage reactions such as coupling, disproportionation, or electron return, whereas pairs of triplet spin multiplicity can only diffuse apart and undergo free radical reactions such as (a) or (b). In most of the reactions discussed here coupling products are either not formed at all or formed in very low quantum yields. Therefore, only a return process can provide the in-cage reaction required for the observation of CIDNP effects, and polarized ketone must be produced by one of these reactions $(\epsilon > 0)$. Simultaneously, of course, polarized ketone will also be produced by degenerate hydrogen or electron exchange $(\epsilon < 0)$. According to all CIDNP theories[10] the polarization of an escaping radical is initially exactly equal in magnitude but opposite in sign to the polarization of the corresponding in-cage product. The enhancement of the in-cage products decays at

rates dictated by the spin-lattice relaxation times $(T_{1D})$ of the diamagnetic products (typically 1–100 sec). The polarization of the escaped radicals decays at considerably faster rates dictated by the spin-lattice relaxation times of the radicals $(T_{1P} \sim 10^{-5}-10^{-4}$ sec).[24] In view of the dramatic difference between $T_{1D}$ and $T_{1P}$ the contribution of the ketone fraction produced by free radicals $(\epsilon < 0)$ can at most weaken, but not cancel or override, the ketone polarization due to in-cage return $(\epsilon > 0)$.

The relative assignment of $\mu$ and $\epsilon$ is in keeping with the multiplet effect of the meta protons $(A/E; \Gamma < 0)$. The phase of a CIDNP multiplet is determined by six parameters; in addition to $\mu$ and $\epsilon$ and the hyperfine coupling constants of the two nuclei coupled to each other, one needs to know the sign of their spin–spin coupling constant $(J)$ and their position relative to each other in the radical pair $(\sigma)$.[10] For both 3 and 5 four of these parameters are unambiguously established: $a_H^o$ $(<0)$ and $a_H^m$ $(>0)$ have been discussed; the coupling of aromatic protons through three bonds is generally positive $(^3J_{o,m} > 0)$,[25] and the parameter $\sigma$ is defined as positive for nuclei residing in the same radical.[10] Since the product of these four parameters is identical with the sign of $\Gamma$ the parameters $\mu$ and $\epsilon$ must have identical signs. Consequently, one cannot ascribe the observed ketone polarization to an escape mechanism without simultaneously postulating that the singlet state of benzophenone is predominantly involved in the reaction with Dabco. Since any significant involvement of the singlet state is highly unlikely in view of our earlier discussion, the assumed sign of $\epsilon$ $(>0)$ appears to be beyond doubt.

The key to the nature of the intermediates involved in the degenerate quenching reactions lies in their $g$ factors. Not all the potential intermediates have been studied by esr spectroscopy or other techniques. However, for species whose $g$ factors have not been reported, reliable $g$ factors of close analogs are available. The neutral diphenylhydroxymethyl radical (5c) generated by photolysis of benzophenone (1c) in alcohol solutions has a $g$ factor of 2.0030;[26] its derivatives 5a, 5b, 5d, 5e have not been studied. We assume that the methyl groups (5b) will not affect the $g$ factor appreciably, that methoxy and fluoro substituents (5a, 5d) will increase the $g$ factor slightly, and that the para chlorine atoms (5e) will increase the $g$ factor noticeably because of their appreciably higher spin–orbit coupling.[24,27]

The esr spectra of the diphenylketyl radical (3c) have been studied, but its $g$ factor was not reported. Based on the finding of Eiben and Fessenden that the $g$ factor of dimethylketyl (2.00335) is slightly higher than that of dimethylhydroxymethyl (2.00315)[28] we assume that the radical ions 3a–e have slightly higher $g$ factors than the radicals 5a–e.

The radicals derived from the quencher by electron transfer (4) and hydrogen abstraction (6), respectively, have considerably different $g$ factors, because the spin-orbit coupling in the nitrogen radical (4) and the carbon

(17) S. W. Benson, "The Foundation of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 495.

(18) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, J. Amer. Chem. Soc., 90, 4201 (1968).

(19) G. O. Schenck, G. Koltzenburg, and E. Roselius, Z. Naturforsch. B, 24, 222 (1968).

(20) G. L. Closs and D. R. Paulson, Z. Naturforsch. B, 92, 7229 (1970).

(21) C. R. Bruce, R. E. Norberg, and S. I. Weissman, J. Chem. Phys., 24, 473 (1956).

(22) C. S. Johnson, J. Chem. Phys., 39, 2111 (1963).

(23) Cf., e.g., M. Szwarc, "Carbanions, Living Polymers, and Electron-Transfer Processes," Interscience, New York, N. Y., 1968, Chapter VI.

(24) G. L. Closs and A. D. Trifunac, J. Amer. Chem. Soc., 92, 2186 (1970).

(25) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 368.

(26) R. Wilson, J. Chem. Soc., B, 84 (1968).

(27) J. Sinclair and D. Kivelson, J. Amer. Chem. Soc., 90, 5074 (1968).

(28) K. Eiben and R. W. Fessenden, J. Phys., Chem., 75, 1186 (1971).

radical (6) are quite different. The radical ion 4 can be generated by electrolysis, and its magnetic properties are known.[29] The magnitude of its $g$ factor $(2.0040)$[30] agrees well with those of other nitrogen-centered radicals such as the trimethylamine radical cation ($g = 2.0044$)[31] or the dimethylaminyl radical $(2.0044)$.[32] The $g$ factor of the carbon-centered radical, 6, can be estimated in analogy to radicals such as aminomethyl, methylaminomethyl, or dimethylaminomethyl $(2.0028)$.[33]

A comparison of these $g$ factors shows that, in the case of net electron transfer ($\rightarrow$ 3–4), the ketyl radical ions have smaller $g$ factors than the counter radical ion ($\Delta g < 0$), whereas in the case of net hydrogen abstraction ($\rightarrow$ 5–6), the ketone-derived radicals have larger $g$ factors than the neutral radical derived from Dabco.

If the parameters $\mu$, $\epsilon$, and $a$ have the signs as discussed above, the CIDNP signal directions of the ketones, 1, indicate that $\Delta g < 0$, and thus identify the intermediates as the radical ions 3 and 4. The simplest mechanism leading from 1-$T_1$ and 2 to the radical ions and back to 1 and 2 in their ground states is direct electron transfer. This mechanism appears energetically feasible on the basis of the following considerations.

The change in free energy ($\Delta G$) for the reaction

$$^3 1^* + 2 \longrightarrow 3 + 4 \qquad (c)$$
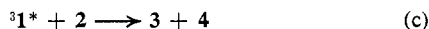
can be calculated from the equation[34]

$$\Delta G = E(2/4) - E(3/1) - E_T(1) - e^2/\epsilon a \qquad (1)$$

where $E(2/4)$ is the one-electron oxidation potential of the amine, $E(3/1)$ is the one-electron reduction potential of the ketone, $E_t(1)$ is the triplet excitation energy (0–0 transition) of the ketone, and $e^2/\epsilon a$ is the coulomb term, which accounts for ion pairing. The reduction potentials (vs. sce) of 1a–e in acetonitrile lie between $-1.81$ (1a) and $-1.54$ V (1e).[35,36] The oxidation potential (vs. sce) of 2 in acetonitrile is $+0.68$ V.[29] The energies of the lowest triplet states of 1a–e are all very close to 3.0 eV.[3] Since the coulomb term is positive, the reactions (c) in acetonitrile are at least 0.5 V (12 kcal/mol) exothermic (Table I)[37] and should occur at nearly the diffusion-

controlled rate.[39] The reverse reaction, at least 12 kcal/mol endothermic, is not likely to compete with other processes such as proton transfer, ion separation by diffusion, and spin inversion. Neglecting the small contributions from entropy and solvation factors, the change in free energy of the reactions in which the radical ion pairs in a singlet state undergo electron re-

$$3 + 4 \longrightarrow 1 + 2 \qquad (d)$$

turn to regenerate 1 and 2 in their electronic ground states, can be approximated by the expression

$$\Delta G = E(2/4) - E(3/1) - e^2/\epsilon a \qquad (2)$$

and, depending on the coulomb term, can be up to 2.5 eV exothermic.

The data summarized in Table I also account for qualitative differences of the CIDNP intensities. In solvents less polar than acetonitrile the oxidation potentials $E(2/4)$ and $E(3/1)$ should be somewhat higher; therefore, the formation of the radical ion pair should be less favorable and the CIDNP intensity should be lower. A comparison of CIDNP spectra of 1b obtained in acetonitrile and hexafluorobenzene, respectively, shows that, indeed, intensities are considerably higher in acetonitrile (Figure 1). Similarly, these data lead one to expect that reaction c is more favorable for ketones with electron-withdrawing substituents (1e, X = Cl) than for ketones with electron-donating substituents (1b, X = CH₃). At the same time, reaction d should be somewhat less favorable for the pair 3e–4 than for the pair 3b–4. The resulting higher steady-state concentrations of radical ion pairs, 3e–4, and their longer lifetimes should give rise to stronger enhancements for 1e than for 1b. This prediction is confirmed by the signal intensities of 1e and 1b, respectively, in hexafluorobenzone (Figures 1 and 3).

In summary, we derive from CIDNP signal directions that radical ion pairs, 3–4, and not the neutral radicals, 5–6, are intermediates in the degenerate quenching reaction of photoexcited benzophenones with Dabco. A mechanism involving electron transfer from Dabco to 1-$T_1$, electron spin inversion of the intermediate ion pair, and electron return can account for the experimental observations. In view of current reports discussing the intermediacy of exciplexes in similar systems[1] we emphasize that our results neither support nor eliminate the possibility of an additional energy minimum (corresponding to an exciplex) on the surface defined by 1-$T_1$ and 2 and the two radical ions, 3 and 4, derived from them.

The application of the CIDNP technique to distinguish between hydrogen abstraction and electron transfer, aside from requiring an exact knowledge of the parameters $\mu$, $\epsilon$, and $a$, depends critically on the condition that the radical pair derived by hydrogen abstraction and the radical ion pair have sufficiently different $\Delta g$ values. It appears that the use of CIDNP for this purpose is not restricted to cases where the two pairs have $\Delta g$'s of different signs and, correspondingly, the expected CIDNP signals have opposite directions. In cases where the $\Delta g$ value is small for one pair but considerably larger ($\Delta g > 1 \times 10^{-3}$) for the alternate pair, the nature of the observed polarization, multiplet or net effect, respectively, could be used to distinguish between the two potentially competing mechanisms.

**Table I**

| Ketone | Substituents | $E(3/1)$, V | $E(2/4) - E(3/1)$, V | $E_T(1)$, eV |
|--------|--------------|-------------|----------------------|--------------|
| 1a | OCH₃ | $-1.81$ | $+2.49$ | 3.01 |
| 1b | CH₃ | $-1.72$ | $+2.40$ | 2.99 |
| 1c | H | $-1.68$ | $+2.36$ | 2.97 |
| 1d | F | | | |
| 1e | Cl | $-1.54$ | $+2.22$ | 2.95 |

(29) T. M. McKinney and D. H. Geske, *J. Amer. Chem. Soc.*, **87**, 3013 (1965).

(30) J. H. Marshall, personal communication.

(31) A. J. Tench, *J. Chem. Phys.*, **38**, 593 (1963).

(32) W. C. Danen, C. T. West, and T. T. Kensler, *J. Amer. Chem. Soc.*, **95**, 5716 (1973).

(33) P. Neta and R. W. Fessenden, *J. Phys. Chem.*, **75**, 738 (1971).

(34) H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 257 (1968).

(35) L. Nadjo and J. M. Savean, *J. Electroanal. Chem.*, **30**, 41 (1971).

(36) *Cf.* P. Zuman, "Organic Polarographic Analysis," Macmillan, New York, N. Y., 1964, p 247.

(37) In this estimate we have neglected the entropy term. If we assume the entropy of formation of an exciplex (−18 eu)[38] as the upper limit for this term, then the estimated $\Delta G$ values are at most 0.2 eV too exothermic.

(38) H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 839 (1969).

(39) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969).

**Line-Broadening Phenomena.** Two of the observations reported here cannot be explained as a direct result of the postulated in-cage electron return: the pronounced line broadening observed for the Dabco resonances in nearly all experiments and for the 4,4'-dichlorobenzophenone resonances (**1e**) in acetonitrile (Figure 3, left). In most cases, the broadening of the Dabco signal appears to be selective; *i.e.*, the signal width of reaction partners or solvent is not affected. For example, **1b** displays a CIDNP spectrum (*cf.*, *e.g.*, Figure 2) whose lines remain narrow throughout the experiment. Consequently, a general line broadening mechanism such as thermal paramagnetic relaxation is ruled out and a more selective mechanism is indicated.

Selective line broadening phenomena have been observed in several reacting systems and have been explained by various chemical exchange mechanisms.[40] For example, the broadening of phenol spectra in the presence of phenoxyl radicals[41] and the broadening of the allyl iodide spectrum by transient allyl radicals[42] were explained by degenerate transfer of hydrogen and iodine atoms, respectively. In solutions containing $N,N,N',N'$-tetramethylphenylenediamine (**8**) and its radical cation, Wurster's Blue (**9**), the observed line broadening was explained by rapid exchange of an electron between **8** and **9**.[21,22] One case of photoinduced line broadening, in the system pyrene–benzene-$d_6$, was explained by degenerate triplet energy transfer.[43]

For the case discussed here, fast degenerate electron exchange between **2** and its paramagnetic ion, **4**, can account for the observed broadening. For the exchange contribution to the nmr line width, $\Delta T_2^{-1}$, two limiting cases have been formulated, the strong-pulse (slow-exchange) case[21,44]

$$\Delta T_2^{-1} = k_e[P] \qquad (3)$$

and the weak-pulse (rapid-exchange) case[45]

$$\Delta T_2^{-1} = [P]a_N{}^2/([D]^2 4k_e) \qquad (4)$$

where [D] and [P] are the concentrations of the diamagnetic species (*e.g.*, **2**) and its radical ion (*e.g.*, **4**), respectively, $k_e$ is the rate constant of electron transfer, and $a_N$ is the hyperfine coupling constant (in radians per second) of the nucleus whose spectrum is being observed.

We found that the excess line width of Dabco decreased with increasing concentration of **2** and showed a negative temperature coefficient, as expected for the weak-pulse (rapid-exchange) limit. In the strong-pulse limit (eq 3) the line broadening should be independent of the concentration of **2** and should have a positive temperature coefficient. A $5 \times 10^{-2}$ M solution of **2** in acetonitrile (containing $1 \times 10^{-2}$ M **1e**) showed a line-width increase of 6 Hz. Given the hyperfine coupling constant of **4** ($a_H = 7.34$ G; $1.32 \times 10^8$ radians $\sec^{-1}$)[29] and assuming a rate constant of electron exchange similar to that for transfer between **8** and **9** ($k_e \sim 2 \times 10^8$ l. $\mathrm{mol}^{-1}$ $\sec^{-1}$; in acetonitrile)[22,46] we derive a steady-state radical ion concentration of $\sim 7 \times 10^{-10}$ mol l.$^{-1}$.

The lifetime of the free-radical intermediates follows from

$$\tau = [P]\left(\frac{d[P]}{dt}\right)_{\mathrm{decay}}^{-1} \qquad (5)$$

Under steady-state condition the decay rate equals the rate of radical formation which can be derived from the rate of photons absorbed, $5 \times 10^{16}$ photons $\mathrm{cm}^{-3}$ $\sec^{-1}$, and an estimated quantum yield of electron transfer from amine to photoexcited ketone. Assuming $\varphi_e = 1$, a radical concentration of $\sim 9 \times 10^{-5}$ mol l.$^{-1}$ $\sec^{-1}$ would be generated indicating a radical lifetime of $\sim 6 \times \times 10^{-6}$ sec.

The lifetime and steady-state concentration of the radical intermediates should depend on the relative rates of radical-pair formation and radical-pair decay. Therefore, the nature of para substituents and of the solvents could have a marked influence on the broadening phenomena. This view was confirmed by the observation that photolysis of **1b** (electron-donating substitutents) caused weaker effects than irradiation of **1e** (electron-widthdrawing substituents) and that the effects of nonpolar solvents ($C_6F_6$) were weaker than those in polar solvents ($CD_3CN$). Since radicals **3** and **4** are generated in pairs and since electron return after re-encounter is the only apparent radical termination reaction, the steady-state concentration of ketyl radicals, **3**, should be equal to that of **4**. The rate constant of electron exchange between diphenylketyl and benzophenone is close to $10^8$ $\mathrm{mol}^{-1}$ $\sec^{-1}$.[47] Consequently, one might also expect to observe broadening of the ketone signals. We found an example of such an effect during the irradiation of dichlorobenzophenone (**1e**) in the presence of **2** in acetonitrile. The downfield signals representing the ortho protons are broadened somewhat more than the upfield ones (meta nuclei). Qualitatively, this reflects the relative magnitude of the proton hyperfine coupling constants of **3c** ($a_0 \sim 2.71$ G; $a_m \sim 0.94$ G).[48] A quantitative evaluation of these spectra is difficult because the ortho and meta protons are strongly coupled and do not show a first-order spectrum. It appears that ketyls derived from substituted acetophenones lend themselves more readily to the investigation of line-broadening effects. The CIDNP spectra observed during the photolysis of acetophenones in the presence of Dabco are very similar to the effects described in this paper and we are presently involved in studying the line broadening effects induced in acetophenones during their photolysis in the presence of several electron donors.

In conclusion, we have ascribed photoinduced nmr line broadening phenomena to degenerate electron transfer between Dabco (**2**) and its radical cation (**4**) and between a ketyl radical (**3e**) and its parent ketone (**1e**). We are actively involved in delineating the conditions limiting the observation of CIDNP in favor of line broadening.

(40) E. de Boer and H. van Willigen, *Progr. Nucl. Magn. Resonance Spectrosc.*, 2, 111 (1967).
(41) R. W. Kreilick and S. I. Weissman, *J. Amer. Chem. Soc.*, 88, 2645 (1966).
(42) R. G. Lawler, H. R. Ward, R. B. Allen, and P. E. Ellenbogen, *J. Amer. Chem. Soc.*, 93, 791 (1971).
(43) M. Cocivera, *Chem. Phys. Lett.*, 2, 529 (1968).
(44) H. M. McConnell and S. B. Berger, *J. Chem. Phys.*, 27, 230 (1957).
(45) I. Solomon and N. Bloembergen, *J. Chem. Phys.*, 25, 261 (1957).
(46) *Cf.*, *e.g.*, L. M. Dorfman, *Accounts Chem. Res.*, 3, 224 (1970).
(47) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, 86, 2537 (1964).
(48) A. H. Reddoch, *J. Chem. Phys.*, 43, 3411 (1965).