Table III. Oxidation Potentials and Fluorescence Quantum Yields of the Activators of Figure 8

activator	fluorescence yield[a]		oxidation potential, V vs. SCE
	24-28 °C	94-100 °C	
DMAC	0.04	0.04	0.14
DMP	0.40	0.18	0.14
DMB1	0.88	0.88	0.46
rubrene	1.00	0.56	0.82
DPAP	1.00	1.00	0.90
perylene	0.84	0.84	1.00
DPEA	0.96	0.96	1.16
DPA	0.85	0.85	1.22
DBA	0.10	0.017	1.45

[a] Determined in argon-purged benzene solution. The previously unknown fluorescence quantum yields were determined relative to DPA (DMP, DMB1), perylene (DPAP), or DPEA (DMAC).

Thermolysis of 1 at 100 °C. The direct chemiluminescence from 1 was too weak to permit determination of the yield of excited states. In the presence of perylene, a double-reciprocal plot of perylene concentration against the integrated intensity was done for dioxetane 3 and 1, both at 1×10^{-3} M in benzene. Comparison of the total intensities at infinite perylene concentration gives a singlet yield from 1 and perylene by activated chemiluminescence of 0.02%. This assumes a singlet yield from 3 of 0.02%.[41,42] A similar comparison, with use of biacetyl indirect chemiluminescence, to obtain the yield of triplet, was not possible due to the very low indirect chemiluminescence intensities observed for 1 and biacetyl. However, an upper limit of 0.02% was established by comparison of the total intensities of TMD and 1 (2.3×10^{-5} M) in the presence of biacetyl (4.5×10^{-2} M) in benzene by assuming a triplet yield of 30% for TMD.

Determination of the Yield of Singlet and Triplet *p*-(Dimethylamino)benzoic Acid from the Thermolysis of 2c at 92.2 °C. The yield of singlet acid from 2c was determined by comparing the total intensity of 2c (1×10^{-4} M) with the extrapolated intensity obtained from a double-reciprocal plot of DBA concentration against intensity with TMD (1×10^{-4} M). The intensities are corrected for photomultiplier tube response, DBA fluorescence yield at 95 °C (0.017), TMD yield of triplet acetone (30%), efficiency of energy transfer from acetone to DBA (0.2), and the fluorescence yield of 4-(dimethylamino)benzoic acid at 94 °C (see above).

The yield of triplet acid from 2c was determined by comparing the extrapolated intensity values of double-reciprocal plots of DBA concentration vs. total intensity for 2c and TMD. The appropriate corrections, as described above, were made. The assumption is made that the energy-transfer efficiencies of acetone and *p*-(dimethylamino)benzoic acid to DBA are the same.

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[41] N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **94**, 2886 (1972); W. Adam, N. Duran, and G. A. Simpson, *ibid.*, **97**, 5464 (1975).

[42] W. Adam, C.-C. Cheng, O. Cueto, K. Sakaniski, and K. Zinner, *J. Am. Chem. Soc.*, **101**, 1324 (1979); K. R. Kopecky and J. E. Filby, *Can. J. Chem.*, **57**, 283 (1979).

Reactions of Phenols with Photoexcited Benzophenones. A CIDNP Study

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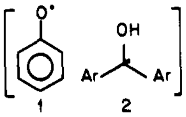
Abstract: The photoreactions of benzophenones with phenols have been studied by using CIDNP techniques. The results suggest that in most solvents triplet benzophenone abstracts a hydrogen atom from phenol to generate phenoxyl radicals. In benzene-d_6, a complex is formed between the reactants resulting in a predominantly singlet-state reaction. During the reaction of tetrafluorophenol, multiplet effects are superimposed on dominant net effects due to the interaction of the strongly coupled fluorine nuclei with the more weakly coupled proton. One system provides evidence for a cross-polarization mechanism.

Introduction

Aroxyl radicals have been identified as intermediates in several important processes such as polymer stabilization.[1] These radicals are often stable and can be studied by spectroscopic techniques.[2] In addition, aroxyl radicals have been postulated as intermediates in many photoreactions including the photo-Fries[3] and the photo-Claisen rearrangements.[4] Phenoxyl radicals have also been suggested as intermeidates in the quenching of photoexcited ketones by phenols.[5] All products formed in this reaction, including fuchsones (4) and oxetanes (5) appear to be derived from a common intermediate, the photoadduct (3).



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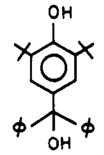

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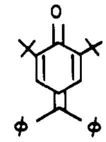

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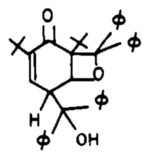

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The formation of this adduct can be explained by the coupling of phenoxyl (1) and hydroxymethyl radicals (2) which, in turn, are generated by abstraction of a phenolic hydrogen atom by triplet-state benzophenone.

We have studied the photoreaction between benzophenones and phenols using chemically induced dynamic nuclear polarization

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[1] Loan, L. D.; Winslow, F. H. "Polymer Stabilization"; Hawkins, W. L., Ed.; Wiley: Interscience, New York, 1972.

[2] (a) Lloyd, R. V.; Wood, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 659. (b) Kreilick, R. W. *Mol. Phys.* **1968**, *14*, 495. (c) Kreilick, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 2711.

[3] Kobsa, H. *J. Org. Chem.* **1962**, *27*, 2293.

[4] (a) Carroll F. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 7151. (b) Adam, W.; Fischer, H.; Hansen H.-J.; Heimgartner, H.; Schmid, H.; Waespe, H.-R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 662.

[5] (a) Bäckström, H. L. J.; Sandros, K. *Acta Chem. Scand.* **1958**, *12*, 823. (b) Becker, H. D. *J. Org. Chem.* **1967**, *32*, 2115, 2124, 2140.

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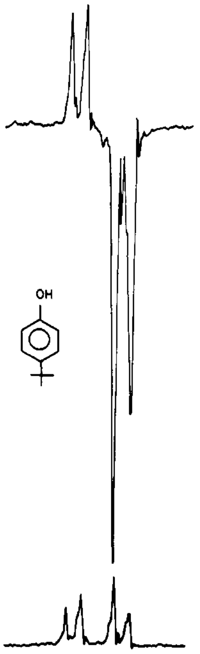

Figure 1. ^1H NMR spectra (60 MHz) of a solution of 0.1 M 4-*tert*-butylphenol and 0.1 M decadeuteriobenzophenone in ethanol-d_6 in the dark (bottom) and during UV irradiation (top).

(CIDNP) techniques[6] to elucidate its mechanism. The diamagnetic products of a radical pair reaction may exhibit greatly enhanced NMR spectra in either absorption or emission immediately after their formation. The direction and magnitude of the CIDNP signals provide information about the nature of the radical intermediates and about the mechanisms of product formation.

Experimental Section

All materials were commerically available and were used without further purification.

The CIDNP experiments were carried out on a JEOL JNM-C-60-HL continuous-wave spectrometer or on a Bruker WH-90 Fourier transform spectrometer. Both instruments were modified to permit UV irradiation of the samples in the area of the receiver coil. An Osram 200-W high-pressure mercury lamp was used for irradiation at 60 MHz, and a 1000-W high-pressure mercury lamp was used at 90 MHz. The duration of the irradiation was controlled by a pressure-activated shutter. All samples were deaerated with argon immediately before irradiation.

Results

In our studies of the photoreactions of benzophenones with phenols, we have observed strong CIDNP effects in a variety of solvents. Polarization effects can be observed for the ketones as well as for the phenols. In most cases, however, decadeuterio- or decafluorobenzophenone (DDBP and DFBP, respectively) were used so that the phenol polarization could be observed without being obscured by benzophenone polarization. For phenol itself, the ring protons are strongly coupled, and the signals for the meta protons are only slightly downfield from the overlapping ortho and para resonances. During irradiation, the overall spectrum appeared in strong emission. Those signals of the meta protons which could be observed separately remained essentially unchanged. For many substituted phenols, the signals for the individual ring positions are better resolved. Therefore, the CIDNP effects for ortho, meta, and para protons may be observed and analyzed individually. For example, the ortho and meta protons can be assessed in the reaction of 4-*tert*-butylphenol with DDBP in ethanol-d_6: the ortho protons appeared in strong emission whereas the meta protons appeared in weakly enhanced absorption (Figure 1).

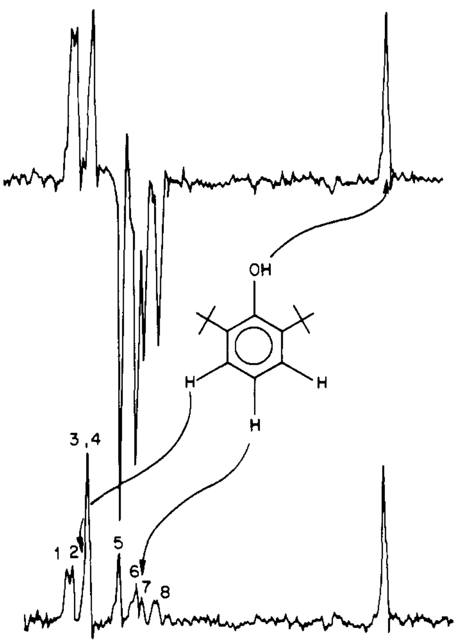

Figure 2. ^1H NMR spectra (60 MHz) of a solution of 0.1 M 2,6-di-*tert*-butylphenol and 0.1 M decafluorobenzophenone in carbon tetrachloride in the dark (bottom) and during UV irradiation (top).

Table I. CIDNP Effects for Reactions of Substituted Phenols with Photoexcited Benzophenones

			CIDNP signal directions		
substituted phenol	solvent	ketone[a]	ortho	meta	para
4-methyl	C_6D_6	DDBP	A	E	
4-*tert*-butyl	C_6D_6	DFBP	A	E	
	C_6D_6	DDBP	A	E	
	CD_3CN	DFBP	E	A	
	CD_3CN	DDBP	E	E	
	CD_3CN	DiMeBP	E		
	C_5D_5N	DDBP	E	A	
	CD_3OD	DDBP	E	A	
	CD_3CD_2OD	DDBP	E	A	
	CD_3COCD_3	DDBP	E	A	
3,5-di-*tert*-butyl	C_6D_6	DDBP	A		A
	CD_3CN	DDBP	E		E
	CD_3CN	DiMeBP	E		E
	C_5D_5N	DDBP	E		E
	CD_3OD	DDBP	E		E
	CD_3COCD_3	DDBP	E		E
3,5-dimethyl	C_6D_6	DiMeBP	A		A
	CD_3CN	DiMeBP	E		E
3,5-dimethoxy	CD_3CN	DiMeBP	E		E
2,6-di-*tert*-butyl	C_6D_6	DDBP		A	E
	CD_3CN	DDBP		A	E
	C_5D_5N	DDBP		A	E
	CD_3OD	DDBP		A	E
	CD_3COCD_3	DDBP		A	E
	CCl_4	DDBP		A	E
	CCl_4	DFBP		A	E

[a] DDBP = decadeuteriobenzophenone; DFBP = decafluorobenzophenone; DiMeBP = dimethylbenzophenone.

In the CIDNP spectrum of 2,6-di-*tert*-butylphenol obtained during irradiation of DFBP, the meta signals were again seen in weak absorption, and the para signals were seen in strongly enhanced emission (Figure 2). The ortho and para protons can be observed during the reaction of 3,5-di-*tert*-butylphenol with photoexcited 4,4′-dimethylbenzophenone: very strongly enhanced emission was observed for both (Figure 3). The CIDNP results for these and for several other substituted phenols in a variety of solvents are summarized in Table I. With few exceptions, the polarization pattern is similar regardless of substituents or solvent; i.e., the ortho and para signals appear in strongly enhanced emission, and the meta signals appear in weakly enhanced absorption.

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(6) (a) Roth, H. D. *Mol. Photochem.* **1973**, *5*, 91. (b) Roth, H. D. "Chemically Induced Magnetic Polarization"; Muus, L. T., et al., Eds.; Reidel: Dordrecht, Holland, 1977; p 39.

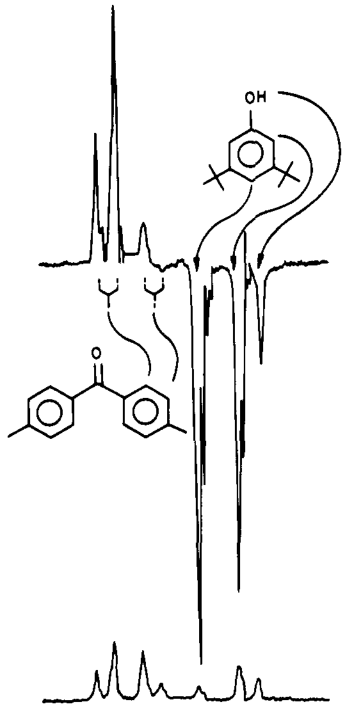

Figure 3. ^{1}H NMR spectra (60 MHz) of a solution of 0.1 M 3,5-di-*tert*-butylphenol and 0.1 M 4,4′-dimethylbenzophenone in acetonitrile-d_3 in the dark (bottom) and during UV irradiation (top).

Figure 4. ^{1}H NMR spectra (60 MHz) of a solution of 0.1 M 4-*tert*-butylphenol and 0.1 M decadeuteriobenzophenone in benzene-d_6 in the dark (bottom) and during UV irradiation (top).

The choice of solvent, in most cases, influences only the magnitude of the CIDNP signals but does not affect the signal direction. For example, methanol-d_4 and pyridine-d_5 give rise to stronger but otherwise similar CIDNP effects than do acetone-d_6 and acetonitrile-d_3. However, principally different effects were observed for several phenols in benzene-d_6. In this solvent, the signal directions were opposite those observed in other solvents as seen in a comparison of Figures 1 and 4.

In general, the CIDNP effects observed in the reactions between phenols and ketones are net effects (i.e., emission or absorption). Occasionally, however, weak multiplet effects are superimposed on these net effects. The single aromatic proton of 2,3,5,6-tetrafluorophenol appears as a triplet of triplets. During irradiation of DFBP, weak multiplet effects are superimposed on the overall emission spectrum as well as on each individual triplet (Figure 5).

Discussion

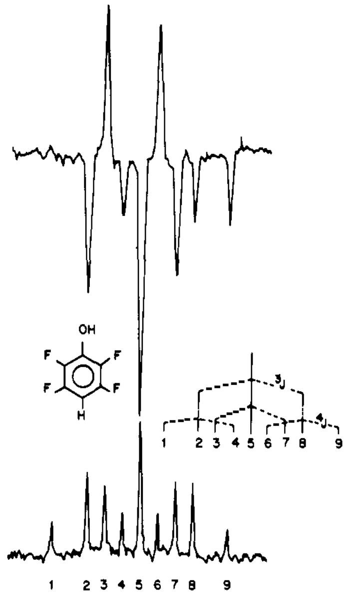

Figure 5. ^{1}H NMR spectra (90 MHz) of a solution of 0.1 M 2,3,5,6-tetrafluorophenol and 0.1 M decafluorobenzophenone in acetone-d_6 in the dark (bottom) and during UV irradiation (top).

The observation of CIDNP effects is generally interpreted on the basis of spin selection in competing radical pair reactions, e.g., the competition between recombination (an electron-spin-dependent reaction) and diffusional separation (an electron-spin-independent reaction). Combined with the nuclear-spin dependence of intersystem crossing, this competition results in characteristic nonequilibrium populations in the nuclear spin levels of in-cage reaction products and in complementary nonequilibrium populations in the spin levels of free radical products. In view of these considerations, the CIDNP effects observed during the photoreactions of benzophenones with phenols indicate a radical pair pathway.

An analysis of the CIDNP signal directions provides further insight into the reaction mechanism. The directions of the enhanced signals are determined by four parameters: the initial spin multiplicity of the radical pair (μ), the mode of product formation (ϵ), the difference in the isotropic g factors of the individual radicals (Δg), and the signs of the hyperfine coupling constants, hfc's (a). The relation between the observed effects, Γ_{NE}, and these four parameters has been formulated by Kaptein in a qualitative rule[7] (eq 1). If three of these parameters can be assigned, the fourth one can be derived from the observed signal directions.

$$\Gamma_{\mathrm{NE}} = \mu \epsilon a \Delta g \tag{1}$$

The polarization patterns for the phenol-derived radicals reveal some information about the nature of the intermediate. The signals of the ortho and para protons have stronger intensities and are opposite in direction to those of the meta protons. This pattern is consistent with the hfc's of a π radical ($a_{\mathrm{H}}{}^{\mathrm{o,p}} < 0 < a_{\mathrm{H}}{}^{\mathrm{m}}$)[8] such as the phenoxyl radical. The isotropic g factor of this phenol-derived radical ($g = 2.0052$)[9] is larger than the g factor of the diphenylhydroxymethyl radical ($g = 2.0032$).[10] Therefore, the g factor difference is positive for the phenoxyl radical ($\Delta g > 0$). The initial spin multiplicity of the radical pair is determined by the precursor spin multiplicity. Aromatic ketones react mainly in the triplet state because intersystem crossing from the initially excited singlet state to the lower lying triplet states is very rapid. Therefore, it is not unreasonable to assume that the radical pair involved is generated predominantly in the triplet state ($\mu > 0$). Given these parameters, the observed signal directions suggest that phenol is regenerated by hydrogen return from hydroxymethyl radicals to phenoxyl radicals in a geminate pair (i.e., $\epsilon > 0$). This reaction mechanism is not the rule for hydroxymethyl radicals. For example, Closs and Paulson[11] concluded that the radical pair

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[7] Kaptein, R. *Chem. Commun.* **1971**, 732.

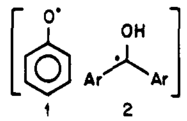
[8] Carrington, A.; McLachlan, A. D. "Introduction to Magnetic Resonance"; Harper and Row: New York, 1967.

[9] Wertz, J.; Koelsch, C. F.; Vino, J. C. *J. Chem. Phys.* **1955**, *23*, 2194.

[10] (a) Wilson, R. *J. Chem. Soc. B* **1968**, *84*. (b) Eiben, K.; Fessenden, R. W. *J. Phys. Chem.* **1971**, *75*, 1186.

hydroxybenzyl–benzoyl does not react by hydrogen transfer to form benzaldehyde. The different results observed in these systems reflects the different reactivity of the phenoxyl and benzoyl radicals.

For a complete understanding of the mechanism, it is important to determine the exact nature of the radical pair. Mechanisms involving either the neutral radicals **1** and **2**, formed by net hydrogen abstraction, or the radical ions **6** and **7**, formed by electron transfer, could be consistent with the experimental results. In the case of hydrogen abstraction, coupling of the resulting neutral radicals produces the adduct **3**, and hydrogen return regenerates the reactants and, therefore, could account for the low quantum yield of product formation. However, an electron-transfer mechanism proceeding via the radical ions **6** and **7** can account for the observed effects equally well. Reverse electron transfer regenerates the reactants, and a subsequent proton transfer would produce the neutral radicals, **1** and **2**, that are responsible for product formation. Both pathways may give similar CIDNP spectra since both phenol-derived radicals could be π radicals. The g-factor difference is the key to the identification of the intermediates. As discussed above, radical **1** has a substantially larger g factor than radical **2**, so net CIDNP effects would be expected for the hydrogen abstraction reaction. On the other hand, radicals **6** ($g = 2.0031$)[12] and **7** ($g = 2.0032$)[10] have similar g factors, and their interaction would give rise to strong multiplet effects. Therefore, the almost exclusive observation of net effects is consistent with a hydrogen abstraction mechanism involving neutral radicals **1** and **2**.



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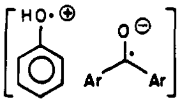

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This assignment is supported by two additional observations. We have studied the solvent dependence of the CIDNP effects, and have used aryl methyl ethers as potential quenchers. The CIDNP effects observed for the phenols are somewhat solvent dependent (Table I). However, there is no direct correlation between signal intensity and solvent polarity as would be expected for a mechanism involving radical ions. Another argument against the electron-transfer mechanism is the lack of CIDNP effects in simple aryl methyl ethers during the irradiation of benzophenones. The (gas phase) ionization potentials of the phenol ethers are comparable or slightly lower than those for the corresponding phenols.[13] Correlating the gas-phase ionization potentials with the solution oxidation potentials, one would expect similar CIDNP spectra for phenols and for their methyl ethers if both reactions proceeded via an electron-transfer mechanism. Since no CIDNP effects are observed in the reaction of the aryl methyl ethers, we conclude that the CIDNP effects resulting from the interaction of photoexcited benzophenones with phenols are generated predominantly in pairs of neutral radicals formed by net hydrogen abstraction and that electron transfer in itself does not contribute significantly to the observed CIDNP effects. These results are in accord with the work of Porter[14] showing that the phenol cation is a strong acid.

In a few reactions such as that of tetrafluorophenol with DFBP, we observed multiplet effects superimposed on dominant net effects. These are not sufficiently pronounced to suggest the intermediacy of an ion pair such as **6**–**7**; however, these effects can be used to derive information about the sign of the ^1H–^{19}F couplings in the intermediates. There are two factors contributing to CIDNP: one dependent mainly on the magnitude of Δg and the other dependent mainly on the hfc's of the radicals. In systems where the g-factor difference dominates, pure net CIDNP effects are produced, as observed for most of the phenols. If Δg is close to zero as in the case of pair **6**–**7**, pure multiplet effects would be expected. For cases where the Δg term and hfc's are of comparable magnitude, a superposition of net and multiplet effects may be observed. The ortho fluorine nuclei of the tetrafluorophenoxyl radical have very strong hfc's (17 G). Their interaction with the more weakly coupled proton can explain multiplet effects such as those in Figure 5 despite the large g-factor difference of the radical pair.

Table II. ^1H and ^{13}C Chemical Shift Changes[a] for Phenols and Benzophenone in Benzene-d_6

substituted phenol	shift difference, ppm		
	OH	ipso C	BP C=O
4-*tert*-butyl	−0.8	−0.7	−1.5
3,5-di-*tert*-butyl	−0.7	−0.7	−1.3
2,6-di-*tert*-butyl	0.0	+0.1	−0.1

[a] The chemical shift changes reported are the differences between the shifts of each component alone in benzene-d_6 solution and the corresponding shifts of mixtures of the two components. Negative shifts are downfield; positive shifts are upfield.

The phase of a multiplet effect (Γ_{ME}) can be analyzed in terms of Kaptein's second rule[7] (eq 2), where a_i and a_j are the signs of

$$\Gamma_{ME} = \mu\epsilon a_i a_j J_{ij} \sigma_{ij} \tag{2}$$

the hfc's for the nuclei i and j, which are coupled to each other, J_{ij} is the absolute sign of the nuclear spin–spin coupling constant, and σ_{ij} is a parameter describing the position of these nuclei relative to each other. σ_{ij} is positive for nuclei on the same radical and negative for nuclei on different radicals. In this formalism, Γ_{ME} is defined as positive for a multiplet with low-field lines in emission and high-field lines in absorption and as negative for the opposite polarization pattern.

The proton of tetrafluorophenol is strongly coupled to two different pairs of equivalent fluorine nuclei, either through three or through four bonds. The observed spectrum is a triplet of triplets with coupling constants as shown in Figure 5. Signals separated by the larger coupling (e.g., between lines 2, 5, and 8, $^3J_{HF}$) show an E/A multiplet effect. In contrast, signals separated by the smaller coupling constant (e.g., between lines 3, 5, and 7, $^4J_{HF}$) show an A/E multiplet effect. Since all nuclei discussed here are on the same radical, σ_{ij} is positive; as derived above, μ and ϵ are both positive for this reaction; and $a_H{}^p$ is negative. The ^{19}F nuclei in the ortho (meta) position of tetrafluorophenoxyl [i.e., four (three) bonds separated from the hydrogen in the para position] have a positive (negative) hfc. Since the hfc's are opposite in sign, the phase difference between the multiplets coupled through three or four bonds is accounted for, and both $^3J_{HF}$ and $^4J_{HF}$ are positive. CIDNP multiplets can provide information about the absolute signs of the spin–spin coupling constants which are otherwise very difficult to determine.

The above considerations are valid for a wide range of solvents; however, for the reactions carried out in benzene-d_6, some of the observed CIDNP effects are dramtically different. The CIDNP effects observed for 4-*tert*-butyl, 4-methyl, and 3,5-dimethylphenol are opposite in direction, though similar in magnitude, to those observed in all other solvents studied; i.e., the ortho and para nuclei appear in enhanced absorption and the meta protons in emission. This result indicates that one of the four polarization determining parameters must be different for the reaction in benzene-d_6.

The magnetic parameters, Δg and the hfc's, are properties of the radicals involved; their signs cannot be expected to be solvent dependent. Likewise, the mode of product formation is usually unaffected by solvent. Therefore, a change in the predominant spin multiplicity of the precursor is suggested unless the reaction proceeds via a different intermediate. A possible explanation involves association of the phenol with benzophenone in benzene-d_6. This assumption is supported by the observation of changed ^1H and ^{13}C NMR chemical shifts for mixed solutions relative to the

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[11] Closs, G. L.; Paulson, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 7229.

[12] Dixon, W. T.; Kok, P. M.; Murphy, D. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1528.

[13] Pignataro, S.; Foffani, A.; Innorta, G.; Distefano, G. *Z. Phys. Chem.* (*Wiesbaden*) **1966**, *49*, 291.

[14] (a) Land, E. J.; Porter, G.; Strachan, E. *Trans. Faraday Soc.* **1961**, *57*, 1885. (b) Bridge, N. K.; Porter, G. *Proc. R. Soc. London, Ser. A* **1958**, *244*, 259.

spectra of the individual components. In the ^{1}H NMR spectrum, all signals of the phenol are shifted downfield, most significantly the hydroxyl proton (Table II). In the ^{13}C spectrum, the principal changes are observed for the ipso carbon. For benzophenone we observed no change in the ^{1}H NMR spectrum but a downfield shift of the carbonyl carbon resonance. These shifts suggest a weak interaction between the hydroxyl proton and the carbonyl group in benzene-d_6 solutions.

Due to the close proximity of the carbonyl moiety and the phenolic hydrogen in the aggregate, it is not impossible that the photoexcited benzophenone molecules react with the phenol predominantly in the singlet state before intersystem crossing to the triplet state can occur. The resulting change in spin multiplicity ($\mu > 0 \rightarrow \mu < 0$) would explain the observed change in signal directions [ortho, para (meta): E(A) → A(E)].

The concept of singlet quenching in a complex suggests several control experiments. For example, complex formation should be sensitive to steric hinderance. This is confirmed by the system 2,6-di-*tert*-butylphenol–benzophenone–benzene-d_6. Neither the ^{1}H NMR nor the ^{13}C NMR spectrum of 2,6-di-*tert*-butylphenol is affected by admixture of benzophenone (Table II), and the observed polarization is that expected for triplet quenching. However, other attempts to support this concept did not produce unambigous results. Since the observed effects represent a competition between singlet and triplet state reactions, the addition of a triplet quencher such as biphenyl should enhance the effects due to the singlet reaction.[15] Also the relative intensity of the CIDNP effects as a function of phenol concentration should provide information about the relative amounts of singlet and triplet reaction. The results in both experiments are ambiguous, perhaps suggesting additional interactions.

All of the CIDNP results discussed thus far reflect the hyperfine coupling pattern of the phenoxyl radical. In certain experiments, however, the polarization observed for the phenol does not reflect the spin densities of this intermediate. For example, the irradiation of DDBP in a CD_3CN solution containing 4-*tert*-butylphenol led to a CIDNP spectrum which showed both ortho and meta protons in emission (Table I). The polarization of the ortho protons is that expected for a phenoxy radical, but the polarization of the meta protons appears to be inconsistent with that intermediate. In order to explain this effect, we invoke the cross-polarization mechanism previously delineated for anilinium radical cations[16] and for phenoxyl radicals.[17] This mechanism involves transfer of polarization from a strongly polarized nucleus to a nucleus having weak or negligible hyperfine interaction. In order for the polarization transfer to occur these nuclei must be coupled indirectly and must experience a periodic exchange between paramagnetic and diamagnetic states. In the case of 4-*tert*-butylphenol, the polarization of the ortho protons (strong hfc) is transferred to the meta protons (weak hfc) so that both are observed in emission. The occurrence of polarization transfer will depend critically on factors which influence the rate of exchange such as solution acidity. Accordingly, the cross-polarization mechanism cannot be expected to be generally operative.

By applying CIDNP techniques we have been able to identify phenoxyl radicals as intermediates in the quenching of photoexcited ketones by simple phenols and have elucidated several facets of the reaction as well as the polarization mechanism. We are extending the application of these techniques to phenolic resin systems in order to determine the composition of mixed resins.

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[15] (a) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820. (b) Hammond, G. S.; Caldwell, R. A.; King, J. M.; Kristinsson, H.; Whitten, D. G. *Photochem. Photobiol.* **1968**, *7*, 695.

[16] (a) Closs, G. L.; Czeropski, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 6127. (b) Closs, G. L.; Czeropski, M. S. *Chem. Phys. Lett.*, **1978**, *53*, 321. (c) Hendricks, B. M. P.; Walter, R. I.; Fischer, H. *J. Am. Chem. Soc.* **1979**, *101*, 2378.

[17] (a) Kaptein, R., *Nature (London)* **1978**, *274*, 293. (b) Garssen, G. J.; Kaptein, R.; Schoenmakers, J. G. G.; Hilbers, C. W. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 5281.

Enantioselective Alkylation of Ketones via Chiral, Nonracemic Lithioenamines. An Asymmetric Synthesis of α-Alkyl and α,α′-Dialkyl Cyclic Ketones

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Abstract: Chiral imines (*S*)-**2** are readily prepared from cyclic ketones and the chiral methoxyamine, (*S*)-**1**. Metalation and alkylation followed by imine hydrolysis lead to 2-alkylcycloalkanones **5** in 87–100% enantiomeric purity. A method to determine % ee of 2-alkylcyclohexanones via their diastereomeric acetals by ^{13}C NMR is also described. Dialkylation of the chiral imines (*S*)-**2** has produced 2,6-dialkylcyclohexanones, which for the dimethyl case were formed in 85% ee.

The alkylation of ketone enolates is among the most fundamental and widely used methods for carbon–carbon bond formation. Unfortunately, this process does not lend itself to enantioselective control due to the symmetric nature of the enolate π-system, and, thus, asymmetric C–C bond-forming reactions in simple, flexible, structures is not feasible. From Scheme I nucleophilic attack by the enolate would generally be expected to introduce an electrophile above and below the π-system with equal facility and thus provide equal amounts of the enantiomeric ketones ($k_1 \simeq k_2$; $\Delta\Delta G^{\ddagger} \simeq 0$). With the advent of metalloenamines[2] as enolate equivalents came the opportunity to introduce a chiral environment which could influence the direction and the rate of

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[2] (a) Stork, G.; Dowd, S. *J. Am. Chem. Soc.* **1963**, *85*, 2178. (b) Wittig, G.; Frommeld, H. D.; Suchanek, P. *Angew. Chem.* **1963**, *75*, 978.

0002-7863/81/1503-3081$01.25/0