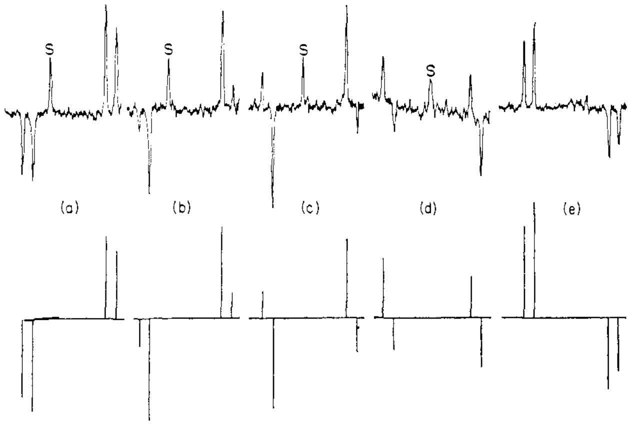

Figure 2. Experimental and calculated spectra of the benzylic protons in reactions IIa–e. Field increases from left to right. The low-field doublet originates from the proton on the hydroxybenzyl carbon atom. S denotes the low-field ^{13}C satellite of the methylene protons of the solvent $[CH_2(C_6H_4\text{-}p\text{-}Y)_2]$.

0.47×10^{-3}, -0.33×10^{-3}, and -2.7×10^{-3}, respectively. The calculated spectra should be taken as demonstrative rather than as a best fit to the experimental data because the assumed invariance of the hyperfine coupling constants with introduction of substituents cannot be expected to hold strictly.[6] Nevertheless, the calculated g shifts are within expectations, and the general reproduction of the experimental results constitutes a strong support for the theory.

(6) For an exact solution, the phenyl protons would have to be included in the model. The relative intensities do not vary very much with J and w_{er}, which affect mostly the absolute intensities.

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Theory of Chemically Induced Nuclear Spin Polarization. V. Comparison of Coupling Reactions in Singlet and Triplet Derived Radical Pairs and of Radicals Not Generated in Pairs[1]

Sir:

In a series of recent communications we have shown that singlet–triplet mixing *via* hyperfine interaction and g shifts in radical pairs provides a suitable model for explaining chemically induced nuclear spin polarizations.[2–4] The theory has been tested with several photochemical coupling reactions in which the coupling radicals were generated in pairs and had triplet precursors. In this communication, we wish to show that the theory is equally capable of accounting for spectra of products obtained from radical pairs (RP) with singlet precursors, as well as coupling products of radicals not generated in pairs. As examples we have studied the formation of 1,1,2-triarylethanes (E) from benzhydryl and benzyl radicals *via* three different reaction paths: the photochemical formation of triplet diphenylmethylenes followed by hydrogen abstraction from toluenes (I),[5] the thermolyses of the corresponding azo compounds (II),[2b] and the formation of benzyl and benzhydryl radicals from mixtures of diphenylmethanes and toluenes *via* hydrogen abstraction with benzoyl peroxide (III).

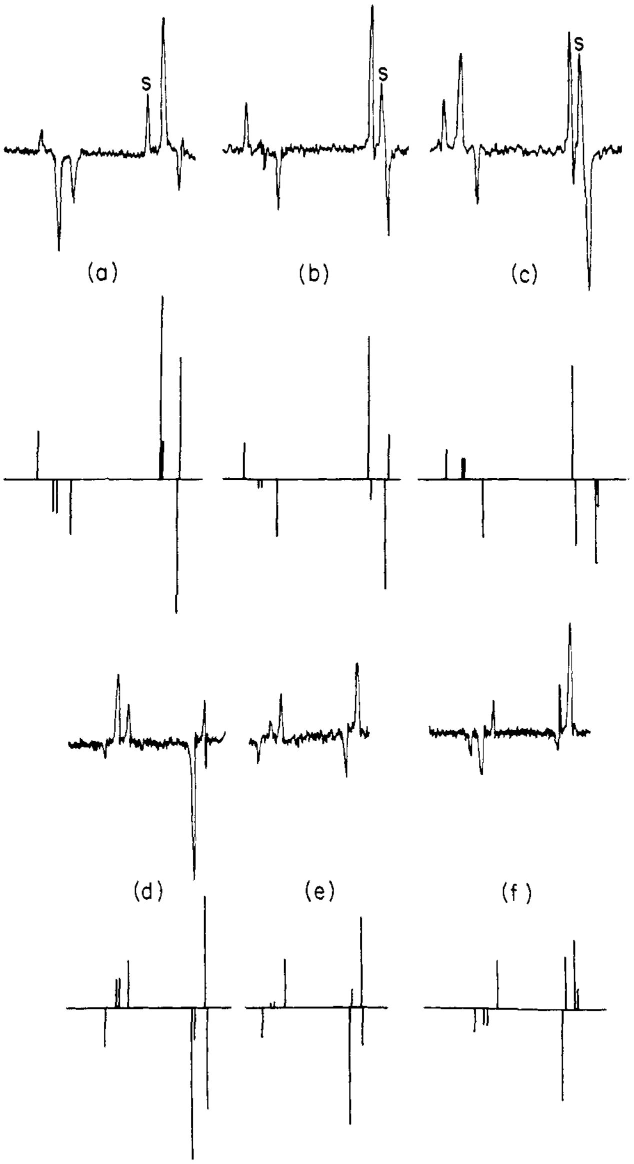

Figure 1. Experimental and calculated spectra of the benzylic protons in E formed in reactions Ia–c and IId–f. Field increases from left to right with the low-field multiplets originating from the methine protons. S denotes ^{13}C satellites of CH_3 groups in $CH_3C_6H_4\text{-}p\text{-}Y$ solvents.

The singlet–triplet mixing coefficients in RP for the eight nuclear spin states of the benzylic protons (AB_2 system) are listed in Table I. From these and eq 1 and 2 of ref 4, the polarizations of the individual transitions in E derived by reactions Ia–c can be calculated with the spin Hamiltonian and kinetic parameters. Figure 1 (spectra a–c) shows the experimental results with the calculated relative intensities of the transitions based on the following parameters: $A_1 = -2.1 \times 10^8$, $A_2 = -2.9 \times 10^8$,[6] $J = 10^8$ radians/sec, $\tau = 10^{-9}$ sec, and

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(1) Supported in part by the National Science Foundation (Grant GP-7043X) and the Petroleum Research Fund, administered by the American Chemical Society (Grant 3965-C4).

(2) (a) G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969); (b) G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554 (1969).

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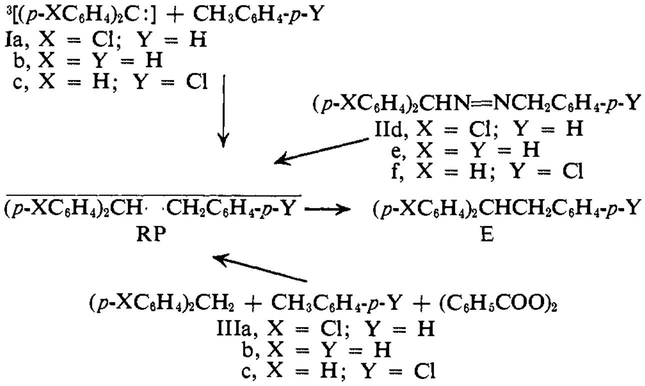
Table I. Mixing Coefficients, M_j, for AB_2 Systems[a]

j	M_j
$\beta\beta\beta$	$\beta H_0\Delta g/2 - A_1/4 + A_2/2$
$\alpha\beta\beta$	$\beta H_0\Delta g/2 + A_1/4 + A_2/2$
$2^{-1/2}\beta(\alpha\beta + \beta\alpha)$	$\beta H_0\Delta g/2 - A_1/4$
$2^{-1/2}\beta(\alpha\beta - \beta\alpha)$	$\beta H_0\Delta g/2 - A_1/4$
$2^{-1/2}\alpha(\alpha\beta + \beta\alpha)$	$\beta H_0\Delta g/2 + A_1/4$
$2^{-1/2}\alpha(\alpha\beta - \beta\alpha)$	$\beta H_0\Delta g/2 + A_1/4$
$\beta\alpha\alpha$	$\beta H_0\Delta g/2 - A_1/4 - A_2/2$
$\alpha\alpha\alpha$	$\beta H_0\Delta g/2 + A_1/4 - A_2/2$

[a] Nuclear spin characterized by hyperfine constant A_1 is on component 1. The two identical spins characterized by A_2 are on component 2; $\Delta g = g_1 - g_2$.

$w_{er} > 50w_j$; Δg was adjusted to fit the experimental results, giving the values 8×10^{-4}, 1.6×10^{-4}, and -5×10^{-4} for spectra a–c, respectively. There is good semiquantitative agreement, and the g-shift differences are within expectations.[7]



The theory predicts (eq 9 of ref 3) that singlet-derived E from reaction II should show spectra with opposite polarizations. Figure 1 (spectra d–f) shows the experimental results from reactions IId–f and the calculated relative intensities of the transitions using the same parameters used for reaction I. Again agreement is acceptable. Variation of Δg from positive to negative values shifts the signals of the methine protons from net emission to net absorption, and those of the methylene protons go from absorption to emission. The trend is reversed in the singlet reaction. With $\Delta g = 0$, each group of proton signals shows a multiplet with no net polarization.

The spectra arising from reaction III can be understood if one assumes the following model. The individually generated benzhydryl and benzyl radicals form on collision new radical pairs with spins in random phase. This corresponds to half-singlet and half-triplet character (not including $|1,1\rangle$ and $|1,\bar{1}\rangle$ states). The time development of this state results from the loss of RP to coupling product which in turn leads to an increase in the triplet character in the remainder. This provides the basis for triplet–singlet mixing *via* the hyperfine and g-shift mechanism. Therefore the type of polarization expected is that observed in the triplet reaction I, only of smaller magnitude. In agreement with this prediction all spectra derived from reactions IIIa–c had identical relative intensities as those obtained from reactions Ia–c which are shown in Figure 1a–c.

Finally, it is worth noting that the model assumes a lifetime of the free radicals longer than T_1 of the nuclei in free radicals (10^{-4}–10^{-5} sec). This assumption is most probably correct for cases where radical coupling and disproportionation reactions are the only pathways available. If, however, the radicals are more reactive than benzylic radicals, other reactions, such as transfer reactions to the solvent or other substrates, are possible, and the final diamagnetic compound may show nuclear spin polarizations originating from free radicals which escaped the cage by diffusion. We will discuss these cases in future publications.

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(7) The calculated relative intensities should be regarded as demonstrative rather than as best fits, because A_1 and A_2 cannot be expected to be constant in all three reactions. Also, for an exact fit the phenyl protons would have to be included.

Vapor-Phase Photolysis of Phenyl Acetate

Sir:

The photo-Fries rearrangement, the photochemical conversion of phenyl esters to *o*- and *p*-hydroxyphenones, has been investigated extensively in solution and shown to give varying amounts of phenol in addition to the two major photoproducts.[1-12] As an example, phenyl acetate rearranges in cyclohexane to give *o*-hydroxyacetophenone $\phi = 0.17$, *p*-hydroxyacetophenone $\phi = 0.15$, and phenol $\phi = 0.06$.[7] Mechanistic studies of this rearrangement in solution do not distinguish clearly between two pathways to the hydroxyacetophenones. In one mechanism, a solvent cage recombination of the acyl and phenoxy radicals gives the observed photoproducts,[3,7] and in the other the *o*- and *p*-hydroxyphenones are formed *via* a concerted mechanism in which the phenoxy and acyl portions of the molecule remain bonded throughout the rearrangement.[2,5,6,8] While the first mechanism neatly accounts for the formation of phenol by simple escape of the phenoxy radical from the solvent cage followed by hydrogen abstraction from the solvent, the concerted mechanism requires that the phenol be produced by a separate, competing photoreaction of the phenyl acetate. Although we have no deep-seated prejudice against dual pathways in the chemical decay of excited states, there is a real problem in that approach in this case. If radical pairs are produced, common experience indicates that some should undergo geminate recombination including coupling at the *ortho* and *para* positions of the aromatic ring. While most of the attempts to reach mechanistic conclusions have been obtained from sol-

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