Table I. Isomeric Product Distributions Obtained from Brominations of Butyl Bromide with Molecular Bromine

Time, min	% conversion	Rel amounts of isomeric dibromobutanes[a] 1,1	1,2	1,3	Av dev, %
		25 ± 1°; $BuBr:Br_2$ = 6.8:1[c]			
2	1.37		7.3	1.0	1.1
4	2.95		7.3	1.0	2.1
8	6.41	0.1	7.6	1.0	1.5
16	10.5	0.1	7.5	1.0	1.4
32	22.1	0.1	7.3	1.0	1.3
64	43.5	0.1	7.3	1.0	0.98
128	75.4	0.1	8.9	1.0	1.2
		60.7 ± 1.5°; $BuBr:Br_2$ = 7.5:1[c]			
1	1.74	0.1	4.5	1.0	2.0
3	22.5	0.09	4.5	1.0	2.4
10	71.5	0.10	5.2	1.0	0.65
25	89.8	0.11	5.7	1.0	0.94
40	99.8	0.11	6.1	1.0[b]	1.1
		4 ± 1°; $BuBr:Br_2$ = 5.9:1[c]			
4	1.01	0.1	11	1.0	0.39
10	2.12	0.1	11	1.0	0.52
25	3.42	0.1	11	1.0	1.5
63	13.05	0.1	11	1.0	1.6

[a] Each line of data is the average from two to three gc injections; the average deviations are given in the last column. [b] The distribution in this line, equivalent to the ratios 1,1:1,2:1,3 = 1.4:84.7:13.9, is nearly identical, within the deviation limits specified, to that reported by Thaler.[3] [c] Mol ratio of reactants.

Table II. Isomeric Product Distributions Obtained from Photoinitiated NBS Bromination of Butyl Bromide in Acetonitrile at 60 ± 1° (Mol ratio $NBS:BuBr:CH_3CN = 1:5.9:27$)

Time, min	% NBS consumed	—Rel amounts of isomeric dibromides— 1,1	1,2	1,3	1,4
4	5.4	0.29	0.30	1.0	0.17
30	35.7	0.27	0.53	1.0	0.12
62	58.1	0.24	0.89	1.0	0.08
105	80.5	0.20	1.16	1.0	0.06
165	93.5	0.20	1.10	1.0	0.06
230	95.9	0.23	1.13	1.0	0.06

sumed to be the same (Br·) in both the molecular Br_2 and the NBS reactions, and the NBS was presumed to consume HBr rapidly as it was generated.[2] These two brominating reagents do show the same selectivities toward different benzylic hydrogens,[4c] but few data comparing their selectivities toward alkanic hydrogens are available. Their relative reactivities toward benzylic and alkanic hydrogens may be different;[11] that is, the hydrogen-abstracting species may be different. In fact, the relative reactivities of the various hydrogens in cyclohexyl bromide with Cl_2, with Br_2, and with NBS[2b] strongly imply that the hydrogen-abstracting radical in the NBS reaction is much closer to Cl· than to Br· in selectivity.[12] High selectivity by the attacking radical (substantial bond breaking and radical character development in the transition state) is essential for neighboring bromine participation.[4a] If the attacking radical in NBS brominations of alkanes is not Br· and is lower in selectivity than is Br·,[10,11] the difference in product distributions for NBS and Br_2 brominations of alkyl bromides[2] is comprehendible, and the apparent relevance of the NBS reactions to the actual mechanism of molecular bromine bromination is lost. We are currently investigating the relative reactivities of a series of alkanes toward Br_2 and NBS to help clarify this point.

In summary, we believe that the interpretation[2] of the butyl bromide–bromine reaction which places paramount importance on polar deactivation and HBr reversal of the initial alkyl radical formation is erroneous and that the earlier interpretation[3] in terms of kinetic assistance by neighboring bromine is supported by the present data.

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(11) In ref 2b, a sentence, rationalizing the different product distributions obtained from cyclohexyl bromide and NBS with photoinitiation and with AIBN initiation, reports that a bromine color developed during the more rapid photoinitiated reaction, and a portion of the bromination was attributed to utilization of the molecular bromine. Since the color developed early when plenty of NBS was available for reaction with HBr, this sentence seems tantamount to acknowledging different selectivities and different attacking radicals for the NBS and Br_2 reactions.

(12) The single publication that attacks the mechanism of *alkanic* bromination by NBS seems to be that by P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Amer. Chem. Soc.*, **85**, 2850 (1963). The stereochemical data therein led to the conclusion that "the alkyl radical intermediate is not brominated by NBS, but presumably by molecular Br_2 present in steady low concentration." It seems likely at this time that NBS competes poorly with Br_2 as a chain-transfer reagent when some bromine (even at low concentration) is available for reaction. One should expect a mechanism (and selectivity) different from that with molecular Br_2 only early in the photoinitiated NBS reaction or in a radical (*e.g.*, AIBN) initiated NBS reaction, when Br_2 (and HBr) are essentially excluded. These are precisely the reaction conditions that give different product mixtures from those obtained with molecular Br_2.[2b]

(13) (a) The original version of this manuscript was prepared while JGT was a NATO Senior Fellow in Science at the Institut für organische Chemie, Universität des Saarlandes, Saarbrücken, Germany; JGT acknowledges with appreciation the courtesies extended to him by Professor M. Hanack and the Institut. (b) JGT gratefully acknowledges the exchange of correspondence and manuscripts about this work with Professor P. S. Skell prior to publication.

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Photo-CIDNP Arising from a Minor Reaction Pathway during the Cleavage of α-Aryl Aldehydes

Sir:

The solution phase photolysis of a variety of β,γ-unsaturated aldehydes[1] leads, *via* the excited singlet state, to decarbonylation.[2] A cleavage of the α carbon–carbon bond, to form a closely associated allyl–formyl radical pair, is fully consistent with the experimental data, although a major contribution by concerted decarbonylation has not been excluded. The available data on the photolysis of α-aryl aldehydes suggest that decarbonylation proceeds from an excited singlet state in this system as well.[3] Thus, excitation (3130 Å) of the n → π* transition of 2-methyl-2-phenylpropanal (I) leads to cumene (Φ = 0.76) in a reaction shown by deuterium labeling to be predominantly intramolecular. The amount of bicumyl formed (18% of the cumene formed at 0.01 *M* I) decreases with decreasing concentration of I. This reaction is not quenched by *cis*-

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(1) Photo-CIDNP has been observed for aromatic aldehydes by Cocivera and Trozzolo and by Closs and Paulson. Polarization in these cases, however, results from the intermolecular reaction of triplet excited state aldehydes leading, in the case of benzaldehyde, to a benzoyl–hydroxybenzyl radical pair: (a) M. Cocivera and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **92**, 1772 (1970); (b) G. L. Closs and D. R. Paulson, *ibid.*, **92**, 7227 (1970).

(2) E. Baggiolini, H. P. Hamlow, and K. Schaffner, *ibid.*, **92**, 4906 (1970).

(3) H. Küntzel, H. Wolf, and K. Schaffner, *Helv. Chim. Acta*, **54**, 868 (1971).

Figure 1. (A) Photo-CIDNP spectrum recorded during the irradiation of 2-methyl-2-phenylpropanal (I). (B) Normal absorption spectrum of cumene.

piperylene or naphthalene, nor can it be sensitized by acetone. We initiated a photo-CIDNP (photochemically induced dynamic nuclear polarization) study of this reaction in an attempt to assess the importance of the intermediacy of singlet radical pairs.

When a benzene solution of I was photolyzed in the modified probe of an HA-60 spectrometer, with the unfiltered beam of a high-pressure mercury arc lamp, the spectrum in Figure 1a was recorded. Comparison with Figure 1b allows the assignment of the enhanced signals at δ 2.8 and 1.1 as the methyne and methyl protons of cumene. The low-field line of the methyl doublet is superimposed on the methyl absorption of I. The aldehyde proton of I shows emission at δ 9.2. Similar spectra were obtained with either methanol or *p*-dioxane as solvent. The same photo-CIDNP signals were obtained whether or not samples were degassed.

Application of the modified[4] radical pair model[5] to Scheme I, with the use of literature values for the g factors and hyperfine coupling constants for the cumyl (g = 2.0025, $a_{\mathrm{CH_3}} = +18$ G, estimated from benzyl[6] and isopropyl[7] radicals) and formyl[8] (g = 2.0008,

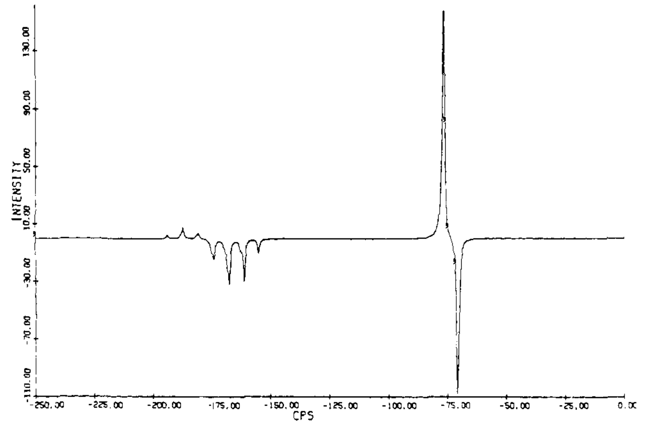
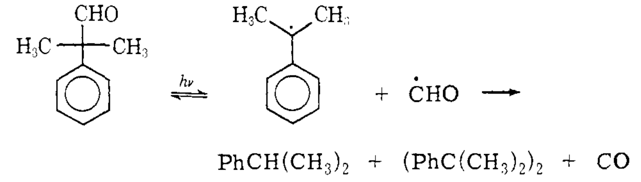


Figure 2. Computer simulation of the photo-CIDNP spectrum of cumene formed from a triplet (or a diffusive encounter) pair composed of a cumyl and a formyl radical.

Scheme I



$a_{\mathrm{H}} = +137$ G) radicals allows the simulation shown in Figure 2, only if the multiplicity of the radical pair precursor is *triplet* or if the pair is formed by *diffusive encounters* of cumyl and formyl radicals. The unusual appearance of both substantial net enhancement (cumene methyne) and multiplet effect (cumene methyls) in the same product results from the unusually large hyperfine splitting of the proton in formyl radical. The apparent discrepancy between simulated and observed multiplet patterns for the methyne proton is readily explained by recognizing that the relaxation times of the methyl and methyne protons are different.[9] Under these conditions anomalously large net enhancement is to be expected.[10] The enhancement of the aldehyde proton of I with the same sign as that of the methyne proton in cumene indicates that coupling as well as disproportionation of the cumyl–formyl radical pair takes place. Analogous spectra are obtained during photolysis of phenylacetaldehyde (II) in the same solvents and have also been shown by computer simulation to be consistent with a benzyl-formyl radical pair.

The observations of photo-CIDNP and the formation of dimeric products (bicumyl and bibenzyl from I and II, respectively) require the presence of both radical pairs and free radicals. Therefore, *the photodecarbonylation reaction cannot be entirely concerted.* Likewise, reaction proceeding predominantly *via* a singlet-born radical pair is not consistent with the observed CIDNP and a purely triplet pair is contradicted by photochemical studies.[3] Thus, any single reaction path seems inadequate to explain both the CIDNP and chemical data. *We are consequently forced to consider mechanisms in which the principal pathways for induction of CIDNP and for formation of products are different.*

Two such mechanisms are: (a) the products are formed mainly by a concerted reaction[11] and the

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[4] F. J. Adrian, *J. Chem. Phys.*, 54, 3912 (1971).

[5] R. G. Lawler, *Accounts Chem. Res.*, 5, 25 (1972); R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, 4, 214 (1969); G. L. Closs, *J. Amer. Chem. Soc.*, 91, 4552 (1969).

[6] A. Carrington and I. C. P. Smith, *Mol. Phys.*, 9, 137 (1965).

[7] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 39, 2147 (1963).

[8] J. A. Brivati, N. Keen, and M. C. R. Symons, *J. Chem. Soc.*, 237 (1962); F. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, 36, 1661 (1962).

[9] T. L. Penred, A. M. Pritchard, and R. E. Richards, *J. Chem. Soc. A*, 1009 (1966).

[10] K. Müller and G. L. Closs, *J. Amer. Chem. Soc.*, 94, 1002 (1972).

CIDNP arises from a smaller triplet-born radical pair component which is undetected in scavenging and quenching attempts; (b) the reaction is mainly concerted,[11] with a smaller singlet radical pair component giving rise to free radicals in which CIDNP is produced during diffusive encounters.

Attempts to distinguish a and b by adding known triplet quenchers such as *cis*-piperylene have so far proven ambiguous because such additives also either absorb light or act as free-radical scavengers. It is observed, however, that photolysis of I produces enhancement of the aldehyde proton which is twice as large (and lasts ~15% longer) in benzene as in pentane. This suggests that benzene acts as a triplet sensitizer which increases the production of triplet-born radical pairs.[12] Further, the enhancement of the aldehyde proton of I is larger during photolysis in acetone despite the fact that the rate of disappearance of I is half that in pentane.

2-Methyl-2-(1-naphthyl)propanal and 1-naphthylacetaldehyde photolyze in benzene at a rate comparable to I and II but give no CIDNP in either the decarbonylation products or the aldehydes themselves. Although both the carbonyl and naphthalene groups in these compounds absorb light (to give excited singlet states), the naphthalene triplet state is of sufficiently low energy to accept energy from the carbonyl triplet. Consequently the lowest, preferentially populated triplet state probably is predominantly naphthalene-like and therefore unlikely to react to form triplet radical pairs by cleavage of the C–C bond of the carbonyl group.

Finally, if mechanism b were responsible for the observations, the cage effect for geminate recombination of cumyl and formyl radicals would have to be lower than that for recombination of the free radicals diffusively encountering each other. In the present case this might be expected if the fragments formed in the initial photodissociation possessed excess kinetic energy. However, this would be at least partially compensated by the fact that a significant portion of the cumyl radicals escaping from a geminate cage recombine with each other and therefore decrease the number of cumyl–formyl diffusive encounters.

For the above reasons we presently consider mechanism a to be the most likely explanation for all of the experimental results.

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(11) A singlet radical pair which reacts with a cage effect of unity would not be distinguished from a concerted reaction by our techniques.

(12) Low concentrations of *cis*-piperylene substantially quench both toluene formation and the disappearance of II when the photolysis is conducted in benzene solution.

(13) Alfred P. Sloan Foundation Research Fellow.

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Interactions between Closed- and Open-Shell Molecules.[1] ^{13}C Contact Shift Studies on the Interaction between Aromatic Hydrocarbons and Nitroxide Radical

Sir:

Recently we have been studying the nmr contact shifts for diamagnetic solvent molecules induced by weak interactions with stable organic free radicals.[1-4] Quite-sensitive induced contact shifts were proved to be a potential probe for studies of the hydrogen bond[2] and charge-transfer interactions[1,3] involving free radicals. In the X–H···DTBN (di-*tert*-butyl nitroxide radical) hydrogen bond, the proton and X (carbon, for example) nuclei of the proton donor molecules sense negative and positive electron spin densities, respectively, which have been interpreted in terms of a spin polarization mechanism.[2,4] On the other hand, in the charge-transfer interaction between halogenated molecules and DTBN, positive spin densities are induced on both the halogen atom and on the carbon atom which is bonded directly to the halogen atom through a spin delocalization mechanism.[1,3] These studies were associated with saturated molecules. In the present study we are concerned with ^{13}C contact shift studies of weak interactions between aromatic hydrocarbons and nitroxide radical where a π-type interaction as well as σ-type one is expected to be involved.[5] The evidence for ground-state complexing between DTBN and aromatic hydrocarbons could be also of value in understanding recent studies on the DTBN-induced quenching of the photoexcited state of aromatic hydrocarbons.[6]

Addition of DTBN radical to benzene in cyclohexane solution caused substantial downfield shift of the ring carbon resonances.[7] For naphthalene, however, the junction carbon (C_9) exhibited an upfield contact shift while the ternary carbons (C_1 and C_2) experienced downfield contact shifts.[8] In substituted benzenes, such as nitro- and fluorobenzene, the ring carbons showed sizable downfield DTBN-induced contact shifts while the substituted one (junction carbon) exhibited an upfield contact shift. From these results it is likely that the aromatic C–H proton can serve as a weak proton donor

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(1) Part VIII in this series. Part VII: I. Morishima, T. Inubushi, K. Endo, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, **94**, 4812 (1972).

(2) I. Morishima, K. Endo, and T. Yonezawa, *ibid.*, **93**, 2048 (1971); *Chem. Phys. Lett.*, **9**, 143, 203 (1971); *J. Chem. Phys.*, in press.

(3) I. Morishima, T. Inubushi, K. Endo, and T. Yonezawa, *Chem. Phys. Lett.*, **14** 372 (1972).

(4) I. Morishima, T. Matsui, T. Yonezawa, and K. Goto, *J. Chem. Soc., Perkin Trans. II*, 633 (1972).

(5) Here the π-stacking interaction between aromatic hydrocarbon and nitroxide radical is referred to as a π-type interaction and the C–H···DTBN hydrogen bond as a σ-type interaction.

(6) R. A. Caldwell and R. E. Schwerzel, *J. Amer. Chem. Soc.*, **94**, 1035 (1972), and references cited therein.

(7) Proton-decoupled ^{13}C nmr spectra were obtained at 15.1 MHz on a JEOL-C-60HL spectrometer. The spectra were measured in 15 mol % solutions in cyclohexane or CS_2 containing varying amounts of DTBN radical ranging from 0 to 7.0×10^{-4} *M*. The DTBN-induced ^{13}C contact shifts, the shift from the diamagnetic solution to the paramagnetic one, were proportional to the concentration of DTBN. Cyclohexane was most insensitive to DTBN and was used as an internal reference for ^{13}C chemical shift measurements, the precision being ± 0.05 ppm. Addition of DTBN (4.0×10^{-4} *M*) to a C_6H_{12} solution (15 mol %) of benzene caused a -0.45 ppm downfield shift for the benzene carbons but had no effect on the ^{13}C shift of C_6H_{12} within an experimental error.

(8) We used CS_2 as the solvent for polycyclic aromatic hydrocarbons. Actual contact shifts were -0.25, -0.26, and $+0.20$ ppm for C_1, C_2, and C_9, respectively, in the presence of 3.0×10^{-4} *M* DTBN.