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Photosensitized Decomposition of Methyl Diazoacetate. Triplet Carbomethoxycarbene *via* Energy Transfer

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Abstract: The mechanisms involved in the photosensitized decomposition of methyl diazoacetate (**1**) were studied by examining the effect of **1** on the CIDNP phenomena observed during the ultraviolet irradiation of benzaldehyde (**2**) and benzoin (**3**) in cyclohexane-benzene solutions. The CIDNP spectra generated by photolysis of **3** were not changed significantly by the addition of **1**. In contrast, the spectra observed during irradiation of **2** were suppressed by the addition of **1** and replaced by CIDNP signals of products formed by reaction of **1** with **2** or with cyclohexane. These results exclude a chemical sensitization mechanism and therefore support an alternative mechanism, energy transfer from triplet **2** to **1** leading to triplet carbomethoxycarbene.

The photolysis of diazo compounds and diazirines is generally assumed to produce divalent-carbon intermediates in the singlet state. If the reaction rates of these intermediates are faster than the rates of intersystem crossing (3), as for example in the case of methylene or carbomethoxycarbene, the characteristic reactions of singlet carbenes are observed: insertion into carbon–hydrogen bonds and stereospecific addition to olefins. For other carbenes such as diphenylmethylene, the rate of intersystem crossing is faster than the singlet reaction rates so that reactions typical for triplets are observed: abstraction of hydrogen atoms and nonstereospecific addition to olefins.[1]

$$\text{RR}'\text{C}{=}\text{N}_2\ (\text{S}_0) \xrightarrow{h\nu} \text{RR}'\text{C}{=}\text{N}_2\ (\text{S}_1) \tag{1}$$

$$\text{RR}'\text{C}{=}\text{N}_2\ (\text{S}_1) \longrightarrow \text{RR}'\text{C};\ (\text{S}_1) + \text{N}_2 \tag{2}$$

$$\text{RR}'\text{C}:\ (\text{S}_1) \xrightarrow{\text{isc}} \text{RR}'\text{C}:\ (\text{T}) \tag{3}$$

In cases where the singlet carbenes react sufficiently fast to prevent intersystem crossing, two techniques have been developed to observe the reactions of the corresponding triplet states. One method is based on the use of inert diluents such as hexafluorobenzene in order to statistically delay the encounter of the reactive intermediate with the substrate.[2] The second technique circumvents the formation of the singlet carbene by photosensitized decomposition[3] of the precursors, *i.e.*, by exciting the triplet state of the diazo compound *via* energy transfer (eq 6). Both methods have been employed with apparent success in studying addition reactions of various methylenes.

Mechanisms involving energy transfer and triplet carbenes have also been invoked to explain the abstraction–recombination products (eq 8 and 9) observed during the photosensitized decomposition of diazo compounds in the presence of hydrogen donors.[4] However, this assignment has not been generally accepted because an alternative

$$\text{sens}\ (\text{S}_0) \xrightarrow{h\nu} \text{sens}\ (\text{S}_1) \tag{4}$$

$$\text{sens}\ (\text{S}_1) \xrightarrow{\text{isc}} \text{sens}\ (\text{T}_1) \tag{5}$$

$$\text{sens}\ (\text{T}_1) + \text{RR}'\text{C}{=}\text{N}_2\ (\text{S}_0) \longrightarrow \text{sens}\ (\text{S}_0) + \text{RR}'\text{C}{=}\text{N}_2\ (\text{T}_1) \tag{6}$$

$$\text{RR}'\text{C}{=}\text{N}_2\ (\text{T}_1) \longrightarrow \text{RR}'\text{C}:(\text{T}) + \text{N}_2 \tag{7}$$

$$\text{SH} + \text{RR}'\text{C}:\ (\text{T}) \longrightarrow \text{RR}'\dot{\text{C}}\text{H} + \dot{\text{S}} \tag{8}$$

$$\text{RR}'\dot{\text{C}}\text{H} + \dot{\text{S}} \longrightarrow \text{RR}'\text{CHS} \tag{9}$$

reaction sequence amounting to chemical sensitization[5] was not excluded. In this sequence, the sensitizer initiates the formation of products by hydrogen abstraction from the substrate (eq 10); the resulting radicals induce the decomposition of the diazo compound by transfer of a hydrogen atom (eq 11) or by radical addition followed by loss of N_2 (eq 12). Products are formed by disproportionation (eq 13) or by chain transfer steps (eq 14).

$$\text{sens}\ (\text{T}_1) + \text{SH} \longrightarrow \dot{\text{s}}\text{ens H} + \dot{\text{S}} \tag{10}$$

$$\text{sens H} + \text{RR}'\text{C}{=}\text{N}_2\ (\text{S}_0) \longrightarrow \text{sens} + \text{RR}'\dot{\text{C}}\text{H} + \text{N}_2 \tag{11}$$

$$\dot{\text{S}} + \text{RR}'\text{C}{=}\text{N}_2\ (\text{S}_0) \longrightarrow \text{RR}'\dot{\text{C}}\text{S} + \text{N}_2 \tag{12}$$

$$\text{RR}'\dot{\text{C}}\text{S} + \dot{\text{s}}\text{ens H} \longrightarrow \text{RR}'\text{CHS} + \text{sens} \tag{13}$$

$$\text{RR}'\dot{\text{C}}\text{S} + \text{SH} \longrightarrow \text{RR}'\text{CHS} + \text{S}\cdot \tag{14}$$

In an attempt to differentiate between the energy-transfer mechanism and the radical-induced decomposition route, we have studied the effect of methyl diazoacetate (**1**) on the photoreactions of benzaldehyde (**2**) and benzoin (**3**). These reactions were studied by applying the chemically in-

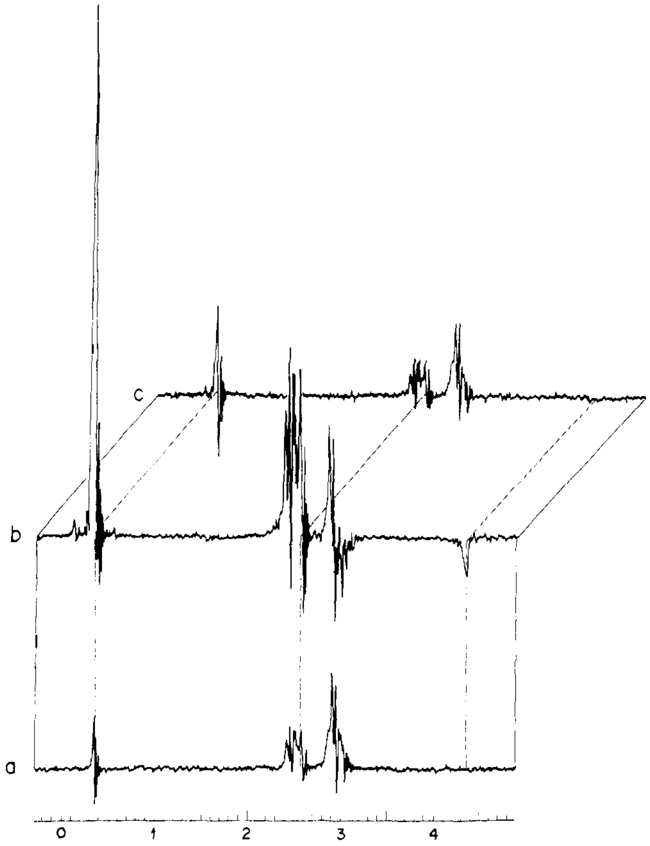


Figure 1. (a) Nmr spectrum (60 MHz) of a 0.1 *M* solution of benzaldehyde in cyclohexane-d_{12}-benzene-d_6 (1:1). (b) Spectrum of the same sample during uv irradiation. (c) Spectrum of the same solution with added methyl diazoacetate (0.1 *M*) during uv irradiation.

duced dynamic nuclear polarization (CIDNP) technique, a new nmr method which utilizes the observation of strongly enhanced signals for the diamagnetic products of radical pair reactions. The theory underlying this effect is sufficiently well understood that the directions and/or intensity patterns of CIDNP signals can be derived from the magnetic properties (g, a) of the individual radicals and from the initial spin multiplicity (μ) and the chemical fate (ϵ) of the pair.[6]

CIDNP effects have been applied to elucidate subtle mechanistic details in a wide range of reaction types. In the area of carbene chemistry, the CIDNP technique provides the opportunity to determine the spin multiplicity of divalent-carbon species involved in radical pair reactions and to study the reactivity patterns of triplet carbenes, even in the presence of considerable amounts of the corresponding singlet carbenes.

Experimental Section

Materials. Benzaldehyde (Eastman Kodak) was distilled prior to use. Benzoin (Aldrich) was recrystallized twice from methanol. Methyl diazoacetate was prepared according to Searle,[7] vacuum distilled below room temperature, and stored at −30°. The solvents, cyclohexane-d_{12} (99% D, Aldrich) and benzene-d_6 (100% D, Aldrich, Gold Label), were stored over molecular sieves and used without further purification.

α-Phenylcyclohexanemethanol (4). Cyclohexyl phenyl ketone (**8**) (3 g, 0.016 mol; Aldrich) in 10 ml of anhydrous diethyl ether was reduced with a solution of lithium aluminum hydride (0.3 g, 0.008 mol) in 10 m*l* of anhydrous ether. The reaction mixture was hydrolyzed with saturated sodium sulfate solution, the organic phase dried over sodium sulfate, and the solvent removed *in vacuo*. Distillation of the remaining oil [95° (0.1 mm)] yielded a mixture of **8** and **4**. The carbinol **4** was isolated by liquid chromatography (Waters Associates high speed liquid chromatograph) using a Porasil (75–125 mesh) column: nmr ($CDCl_3$) τ 8.17–9.35 (broad, 11 H, cyclohexyl H), 8.07 (s, 1 H, OH), 5.90 (d, 1 H, benzyl H), 3.0 (s, 5 H, phenyl H).

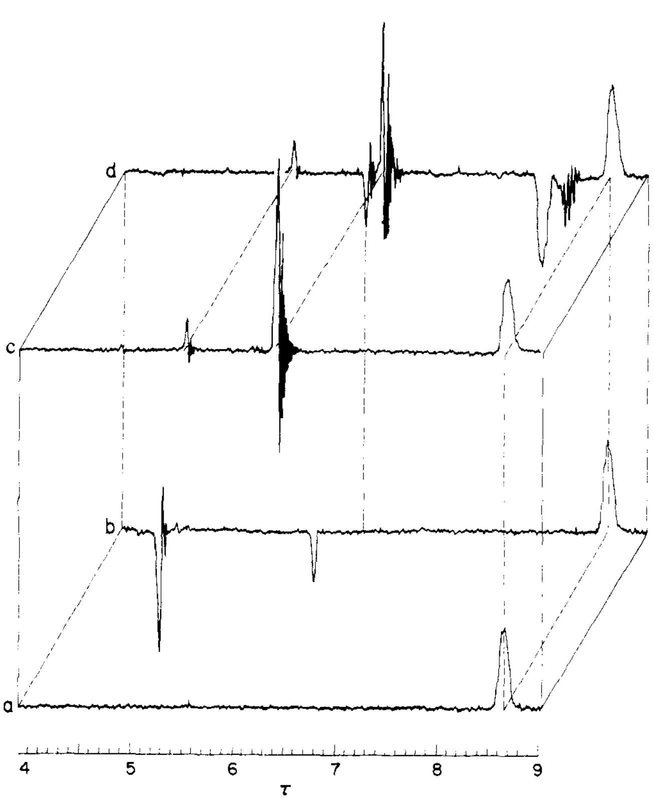


Figure 2. Nmr spectra (τ 4.0–9.0 section) of 0.1 *M* solutions of benzaldehyde in cyclohexane-d_{12} without (a,b) or with (c,d) added methyl diazoacetate, in the dark (a,c) or during uv irradiation (b,d).

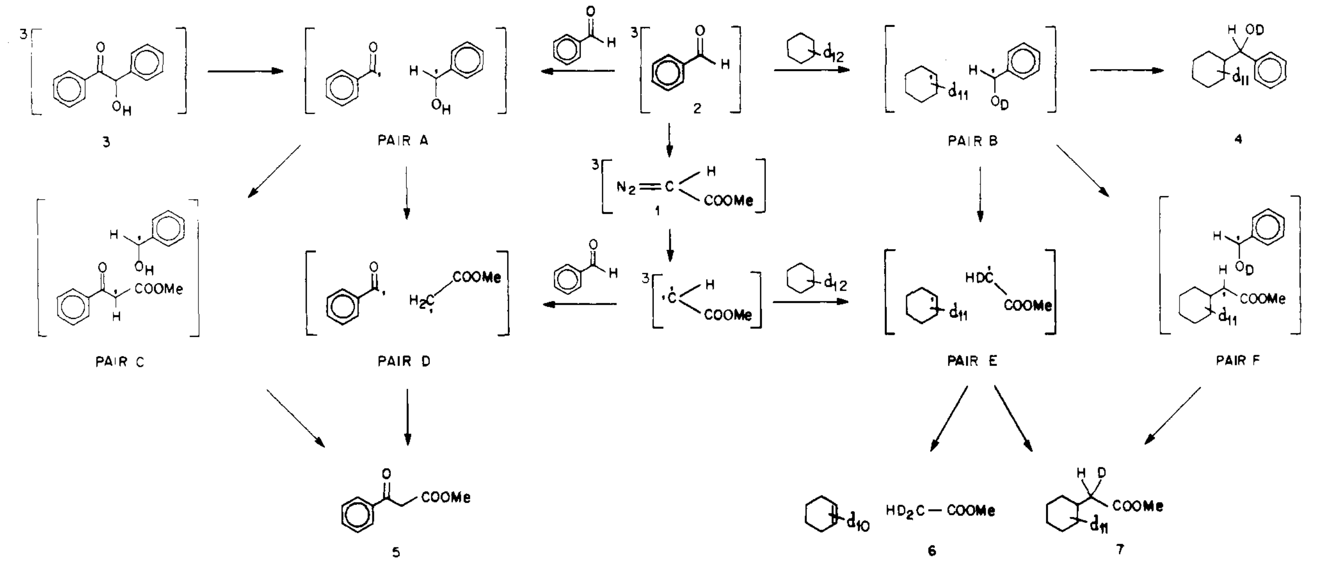
Apparatus. The nmr spectra were recorded on a Jeolco JNM-C-60HL spectrometer; the probe of this instrument was modified by the manufacturer to permit uv irradiation of the samples in the area of the receiver coil. The collimated light of an Osram 200-W high-pressure mercury lamp enters the probe in a direction parallel to the sample tube and is reflected onto the receiver coil by a front-side 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 was monitored by a photodiode inserted into an nmr tube.

Results and Discussion

Cocivera and Trozzolo and Closs and Paulson reported the observation of polarized benzaldehyde (**2**) and benzoin (**3**) during the irradiation of **2** (*cf.* Figure 1b) in benzene-d_6.[8] These CIDNP effects were interpreted in support of the following mechanism. Photo-excited benzaldehyde, in its lowest triplet state, abstracts a hydrogen atom from gound-state benzaldehyde to generate a pair of radicals, hydroxybenzyl and benzoyl (pair A), initially of triplet multiplicity. Individual pairs that undergo intersystem crossing may couple to form polarized benzoin (**3**, $\epsilon > 0$). Pairs that maintain triplet multiplicity can only diffuse apart; polarized free hydroxybenzyl radicals may form polarized benzaldehyde ($\epsilon < 0$) by transfer of a hydrogen atom to a suitable acceptor.

Since the reaction of triplet **2** to form pair A is intermolecular, it is not unreasonable that alternative bimolecular reactions can compete with it. In cyclohexane-d_{12} solutions, for example, we observe an additional emission signal which we assign to the benzylic protons of α-phenylcyclohexanemethanol (**4**; τ 5.9; Figure 2b). This product can be explained by invoking radical pair B, cyclohexyl-d_{11}-hydroxybenzyl-d_1, produced in competition with pair A. Intersys-

Scheme I



tem crossing and subsequent coupling of pair B would produce polarized **4**. However, even in pure cyclohexane (~9.3 *M*), the signal of **3** is stronger than that of **4** (Figure 2b) indicating that triplet **2** preferentially reacts with **2** despite its comparatively low concentration (0.1 *M*).

When methyl diazoacetate (0.1 *M*) was added to solutions of benzaldehyde (0.1 *M*), the CIDNP effects of **2**, **3**, and **4** were efficiently suppressed (Figures 1c and 2d), most notably the strong absorption singlet of polarized benzaldehyde. Instead, three new emission signals were observed (Figure 2d) which we assign to the α-methylene groups of methyl benzoylacetate (**5**; sharp singlet, τ 6.3) and methyl cyclohexylacetate (**7**; broad signal, τ 8.0) and the acetyl group of methyl acetate (**6**; quintet, τ 8.2).

Several mechanisms may be invoked to explain the changes occurring with the addition of the diazo compound. However, most of them are readily eliminated. For example, one might consider a shortened spin-lattice relaxation time (T_1); however, T_1 is not noticeably affected by the presence of **1**. Optical screening of **2** cannot be important since at 313 nm, the wavelength most important for our experiments, **1** has an absorption minimum, its extinction coefficient being one-third of the extinction coefficient of **2**. Finally, any major contribution from processes involving physical quenching of triplet **2** by **1** can be excluded because the polarization of **2**, **3**, and **4** is not merely suppressed but is replaced by polarization in products derived by reaction of **1** with the sensitizer (→ **5**) or the solvent (→ **6**,**7**; Scheme I). The choice of decomposition mechanism is further restricted by the apparent specific deuterium distribution in the acetyl groups of product **6**, as suggested by the shape of its CIDNP signal.

The multiplet representing **6** has a coupling constant (~2 Hz) which is typical for geminal H-D coupling, and its intensity pattern resembles the 1:2:3:2:1 ratio which would be characteristic for methyl dideuterioacetate (**6**-d_2). The shape of this quintet should be a sensitive test for the isotopic composition of **6** since the 1:1:1 triplet of **6**-d_1 and the singlet of **6**-d_0 should have slightly different chemical shifts. In addition, the signals of **6**-d_1 and **6**-d_0 should be sharper than the spectrum of **6**-d_2 since they experience less or no quadrupole broadening. Clearly, the multiplet representing **6** should loose its quintet character if an appreciable percentage of **6**-d_1 or **6**-d_0 were formed by radical-pair processes.

In contrast, the signals representing the acetyl protons of **5** and **7** are not very sensitive to changes in their deuterium content. The sharp singlet due to **5**-d_0 should not be changed significantly by superposition of a quadrupole-broadened 1:1:1 triplet due to **5**-d_1 unless a substantial percentage of this species is produced. Similarly, the acetyl signal of **7**, considerably broadened by the presence of 12 deuterium nuclei, should not be affected noticeably, even if a substantial percentage of **7**-*acetyl*-h_2 were formed. Nevertheless, since the signal of **6** indicates a specific deuterium distribution, we eliminate from consideration all pathways involving free-radical decomposition of **1** and product formation *via* random encounter of free radicals. This limits our discussion to two mechanistic pathways.

One of these mechanisms involves triplet energy transfer from photoexcited benzaldehyde to the diazo compound followed by loss of nitrogen. The resulting triplet carbomethoxycarbene would generate benzoyl-carbomethoxymethyl radical pairs (pair D) by hydrogen abstraction from the sensitizer and cyclohexyl-d_{11}-carbomethoxymethyl-d_1 radical pairs (pair E) by deuterium abstraction from the solvent. Coupling (D → **5**; E → **7**) or disproportionation (E → **6**) of these radical pairs would account for the polarized products. The polarization-determining parameters listed in Table I predict the observed signal directions correctly.[6]

As an alternative to this energy-transfer mechanism, we consider a chemical sensitization sequence initiated *via* the previously discussed hydrogen or deuterium abstraction by triplet **2** from sensitizer (→ pair A) or solvent (→ pair B), respectively. Each of the resulting radical intermediates might induce the decomposition of **1**, either by hydrogen (or deuterium) atom transfer[5] (hydroxybenzyl radicals) or by addition[9] (benzoyl or cyclohexyl radicals). An encounter of the resulting radicals with an appropriate partner radical (→ pairs C-F) could account for the CIDNP signal direction of **5**, **6**, and **7**. However, the previously discussed specific deuterium distribution would require a specific pathway allowing for the decomposition of the diazo compound before an appreciable fraction of the primary radical pairs have separated or lost their spin correlation. This provision would ensure that each type of secondary radical could be formed in the propinquity of a specific counter radical with correlated spin. Mechanisms involving the rapid production

$$\mathrm{A} + \mathbf{1} \begin{array}{l} \nearrow \mathrm{C} \\ \searrow \mathrm{D} + \mathbf{2} \end{array} \qquad\qquad \mathrm{B} + \mathbf{1} \begin{array}{l} \nearrow \mathrm{E} + \mathbf{2} \\ \searrow \mathrm{F} \end{array}$$

Table I. CIDNP Effects in the System Benzaldehyde (Benzoin)–Methyl Diazoacetate–Cyclohexane-d_{12}

Pair	Radical	g factor	a, G[a]	Product	Kaptein parameters[b]			
					ϵ	Δg	Γ_{theor}	Γ_{exptl}
A	$C_6H_5\dot{C}{=}O$	2.0014[c]		**2**	−	+	+	A
	$C_6H_5\dot{C}H^*OH$	2.0031[d]	15[d]	**3**	+	+	−	E
B	$\cdot C_6D_{11}$	2.0025[e]		**4**	+	+	−	E
	$C_6H_5CH^*OD$	2.0031[d]	15[d]					
C	$C_6H_5CO\dot{C}H^*COOMe$	>2.0045[f]	~20[f]	**2**	+	−	+	[i]
	$C_6H_5\dot{C}H^*OH$	2.0031[d]	15[d]	**5**	+	+	−	E
D	$C_6H_5\dot{C}{=}O$	2.0014[c]		**5**	+	+	−	E
	$\cdot CH_2^*COOMe$	2.0033[g]	21[g]					
E	$\cdot C_6D_{11}$	2.0025[e]		**6**	+	+	−	E
	$\cdot CH^*DCOOMe$	2.0033[g]	21[g]	**7**	+	+	−	E
F	$C_6D_{11}\dot{C}H^*COOMe$	2.0033[h]	~25[h]	**2**	+	−	+[j]	[i]
	$C_6H_5\dot{C}H^*OD$	2.0031[d]	15[d]	**6**	+	+	−[j]	E

[a] Hyperfine coupling constant of starred hydrogen atom. [b] The initial spin multiplicity, μ, was assumed to be >0 for all pairs; all a's were assumed to be <0, as typical for α protons in π radicals. [c] P. J. Krusic and T. A. Rettig, *J. Amer. Chem. Soc.*, **92**, 722 (1970). [d] R. Wilson, *J. Chem. Soc. B*, 84 (1968). [e] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963). [f] By analogy to alkanonyl radicals, $R\dot{C}HCOR'$: D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *J. Amer. Chem. Soc.*, **95**, 7978 (1973). [g] K. Möbius, K. Hoffmann, and M. Plato, *Z. Naturforsch. A*, **23**, 1209 (1968). [h] By analogy to $R\dot{C}HCOOH$.[g] [i] Not observed. [j] Only weak effects expected because of small Δg.

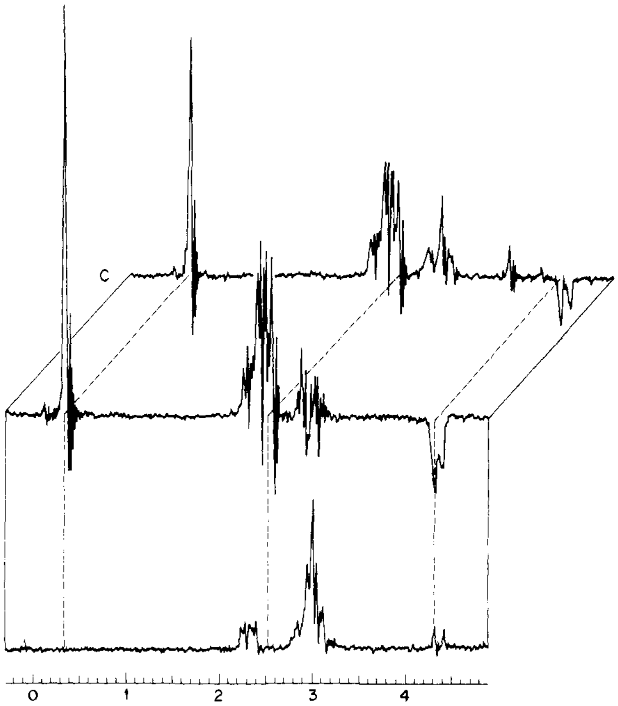


Figure 3. (a) Nmr spectrum of a 0.075 *M* solution of benzoin in cyclohexane-d_{12}-benzene-d_6. The benzoin concentration of this solution was adjusted so that the CIDNP intensity of the aldehydic proton was comparable to that of the 0.1 *M* benzaldehyde solution. (b) Spectrum of the same sample during uv irradiation. (c) Spectrum of the same solution during uv irradiation in the presence of methyl diazoacetate (0.1 *M*).

of a secondary radical pair with conservation of spin correlation are not without precedence. Similar pathways have been postulated in several decomposition reactions of alkyl or aryl peroxides in order to explain the apparent singlet character of secondary radical pairs.[10]

The feasibility of the specific chemical sensitization mechanism outlined above can be tested unambiguously, because pair A can be generated independently by Norrish type I cleavage of photoexcited benzoin. Accordingly, the photolysis of benzoin or some of its derivatives produced CIDNP spectra very similar to those observed during illumination of the corresponding benzaldehydes (*cf. e.g.*, Figure 3b).[8] However, in contrast to benzaldehyde, benzoin produces pair A in an efficient unimolecular reaction and is therefore not likely to be involved in bimolecular processes such as hydrogen abstraction or energy transfer.

If pair A were indeed involved in the benzaldehyde-photosensitized decomposition of **1**, the addition of **1** to the benzoin solution should have a similar effect on the CIDNP spectrum as its addition to the benzaldehyde solution. Our experiments showed that the addition of methyl diazoacetate to a benzoin solution had only a relatively small effect on the polarization of **2** and **3** (Figure 3c) and produced at best a very weak signal representing product **5**. This result cannot be construed as an argument against the radical-induced decomposition of diazo compounds in general. In fact, hydrogen transfer from hydroxybenzyl radicals to **1** yielding **2** and carbomethoxymethyl radicals might be an efficient step in preserving the polarization of **2**. However, our findings document unambiguously that **1** does not scavenge pair A with a reasonable degree of efficiency.

In the light of these facts, the lack of pair A derived polarization during the irradiation of **2** in the presence of **1** precludes any significant involvement of pair A and suggests that methyl diazoacetate deactivates triplet benzaldehyde directly. Since the reaction partners **1** and **2** are present in comparable concentrations, the reaction of triplet **2** with **1** must be at least one order of magnitude more efficient than the hydrogen abstraction leading to pair A. We consider these results a strong argument in favor of an energy-transfer mechanism and, consequently, of triplet carbomethoxycarbene as intermediate.

The experiments described in this paper indicate that triplet carbomethoxycarbene readily abstracts hydrogen atoms from hydrocarbons and from substrates such as benzaldehyde. In contrast, singlet carbomethoxycarbene, which may be generated by direct photolysis or by pyrolysis of **1**, did not show any evidence for hydrogen abstraction[11] but was found to readily abstract chlorine atoms from substrates such as tetra- and trichloromethane or hexachloroacetone.[12] Thus, the reactivity patterns of singlet and triplet carbomethoxycarbene, respectively, are similar to those established for the corresponding spin states of methylene.

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Evidence for Phenyl Cation as an Intermediate in Reactions of Benzenediazonium Salts in Solution[1,2]

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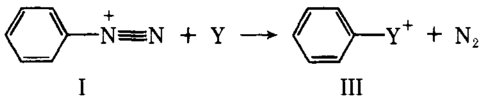
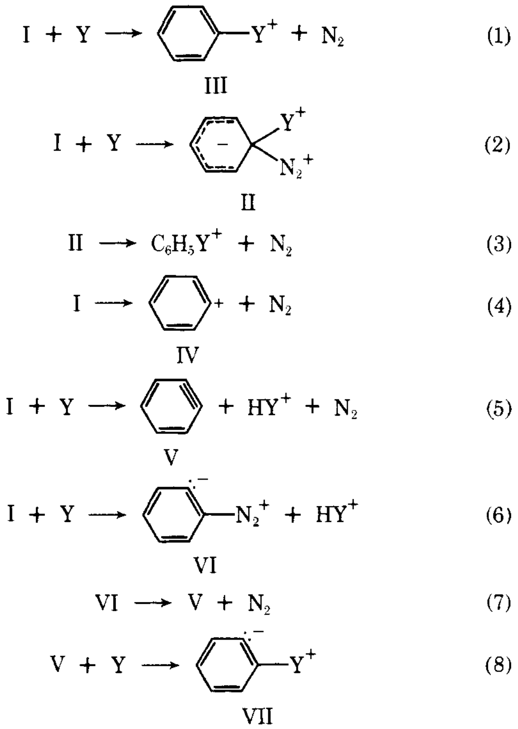
Abstract: Displacements on benzenediazonium cation, $C_6H_5N_2^+$, in solution in the absence of strong bases, reducing agents, or light proceed by rate-determining cleavage to a singlet phenyl cation intermediate, $C_6H_5^+$, rather than by the bimolecular mechanism proposed in 1969. In aqueous solution at 25°, only unrearranged products are obtained, and negligible incorporation of deuterium from solvent D_2O occurs, showing that aryne processes do not occur to a significant extent. The low selectivity between nucleophiles nevertheless requires a highly reactive intermediate. In the hydrolysis of $C_6H_5N_2^+$, the high entropy of activation (+10.5 cal mol^{-1} deg^{-1}) and the constancy of k_1 (within 4%) from H_2O to D_2O demonstrate that water is not involved as a nucleophile in the rate-determining step. The constancy of k_1 (within 10%) in solutions as diverse as 14–21 *M* H_2SO_4 and 100% CH_3CO_2H and CH_2Cl_2 is in accord with a common rate-determining step over this whole range of solvents. Para-substituent effects can be dissected into nearly equal field (predominantly transition state) and resonance (predominantly reactant) contributions by an analysis using dual substituent constants (previously published), with a correlation coefficient of 0.992, although analysis using the Hammett $\rho\sigma$ equation, *i.e.*, with only a single set of substituent constants, yields a correlation coefficient worse than zero.

The purpose of this work was to determine whether a weakly basic nucleophile Y (*e.g.*, H_2O, Br^-, Cl^-, or F^-) replacing the N_2^+ group in an ordinary substitution reaction ("dediazoniation") of benzenediazonium cation (I) in solution is in the transition state or not.[6] The observed kinetics



with benzenediazonium bromide, chloride, bisulfate, or fluoborate in water at 5–64° is first order in diazonium salt.[7] However, when Y is a solvent molecule (H_2O), the kinetics must be first order even with a bimolecular rate-determining step. When Y is a solute anion (Br^- or Cl^-), a bimolecular mechanism involving Y could still give deceptive first-order kinetics because of compensating salt effects, as shown by excellent first-order kinetics for bimolecular reactions of trimethyl- or tribenzylsulfonium ion with chloride ion in 90% acetone–10% water and 16 other solvents and solvent mixtures at 18–100°.[8] Analogous bimolecular possibilities for reactions of *I* with anions have not been eliminated in any previously published work by recourse to kinetic studies at constant ionic strength.

Possible Mechanisms. At the outset of this work, there appeared to be eight possibilities for the rate-determining step, where Y may be H_2O, Br^-, Cl^-, or F^-. Mechanism 1 is a one-step bimolecular displacement. This simplest mechanism was rejected for a long time, because it appeared difficult to reconcile with the kinetics, *e.g.*, with first-order



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