

Studies of the Spin Correlation Effect in Acyclic Azo Compounds

Paul S. Engel,* David J. Bishop, and Matthew A. Page

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. Received May 1, 1978

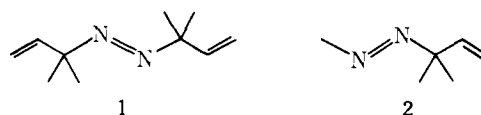
Abstract: The direct and triplet-sensitized photolysis of two acyclic azoalkanes **1** and **2** has been examined in some detail. Whereas triplet sensitization usually leads to no reaction for acyclic azoalkanes, the triplet state of compounds **1** and **2** decomposes moderately efficiently without the intermediacy of the *cis* isomers. It was found that the cage effect for direct irradiation is much greater than that for sensitized decomposition. Although this result would normally be interpreted as a spin correlation effect (SCE), the difference is better explained as arising from stepwise decomposition of the azoalkane triplet state. The product distribution from **1** and **2** and the mechanism of azoalkane photolysis are discussed.

A radical pair which gives different products depending upon its multiplicity is said to exhibit a spin correlation effect (SCE).¹⁻³ Because loss of nitrogen provides an appealing method of producing radical pairs, azo compounds have found considerable use in studying SCEs. The difference in product composition from many cyclic azo compounds on direct irradiation vs. triplet sensitization has been neatly explained as a SCE;⁴⁻¹² an alternate rationalization¹³ of these results involving "hot" diradicals has not fared as well.¹⁴⁻¹⁷ In the acyclic azoalkanes, however, all attempts to observe a SCE have been unsuccessful.^{18,19} The reason for this failure in at least one case¹⁹ is that the supposed triplet photosensitizer (triphenylene) was transferring singlet energy to the azo compound.¹ Thus both direct and sensitized photolysis produced singlet radical pairs, which gave the same cage effect.

A solution to the problem of singlet sensitization might be to employ an aromatic ketone sensitizer, which would inter-system cross so rapidly as to preclude the transfer of singlet energy. Although Fox and Hammond¹⁸ measured nitrogen quantum yields (Φ_{N_2}) for decomposition of azo-1-cyanocyclohexane sensitized by several aromatic ketones, none of these sensitizers were used in the cage effect work, presumably because they decomposed the azo compound much less efficiently than did triphenylene. Similarly, Nelsen and Bartlett¹⁹ decided upon triphenylene and pyrene as sensitizers for azocumene photolysis because "use of acetophenone and benzophenone in this system led to new products, probably by photoreduction of the sensitizer."¹⁹ In later studies^{1,20} it was shown that azo-*tert*-butane (ATB) was an efficient quencher of triplet states but that aromatic ketone sensitizers gave such low quantum yields that the evolved nitrogen could be attributed entirely to stray light absorbed directly by ATB. Thus the situation in 1968 was that Fox and Hammond's ketenimine¹⁸ was the only acyclic compound of any type which showed a SCE while azo compounds appeared to be useless as precursors to a triplet radical pair. Several other SCEs have been reported since that time.²¹⁻²⁴

A further complication in the photochemistry of acyclic azo compounds was discovered in 1969, namely, that irradiation of *trans*-ATB at low temperatures caused only isomerization to *cis*.²⁵ Since *cis*-ATB produced almost no nitrogen until the solution was warmed, it became apparent that the "photolysis" of tertiary azoalkanes was really photoisomerization followed by thermolysis of the labile *cis* isomer.^{25,26}

Our interest in allylic radicals led us to prepare azo compounds **1** and **2** and to study their thermolysis.^{26,27} Despite the



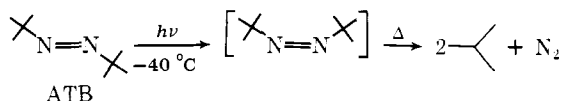
lack of any encouraging precedent, the availability of **1** provided an irresistible temptation to try triplet-sensitized photolysis. To our amazement, the nitrogen quantum yield appeared to be rather substantial. This observation encouraged us to look further into the mechanism of triplet-sensitized photolysis of acyclic azoalkanes and to search for a spin correlation effect. The results of this quest are reported herein.

Results

Quantum Yields of Azoalkane Photolysis. Nitrogen quantum yields for five azo compounds are reported in Table I. Contrary to the results with ATB, triplet sensitization proceeds with moderate efficiency for **1**, **2**, and AIBN (azoisobutyronitrile).²⁸

On the Intermediacy of *Cis* Azoalkanes. With the realization that triplet-sensitized decomposition occurs in **1** and **2**, we were encouraged about the prospects of observing a spin correlation effect. One remaining doubt, however, was the possibility that the nonzero quantum yields were due to triplet-sensitized isomerization of **1** and **2** to their *cis* isomers, which then decomposed thermally. (Cf. Scheme I, path b.) In this case, both direct and sensitized photolysis would proceed via the *cis* azoalkane and no SCE could possibly be observed. It was therefore important to establish that A^{*3} decomposed directly to nitrogen (Scheme I, path a).

Two ideas were conceived to establish which of the paths (a or b) was correct, but the extreme lability of *cis*-**1** (half-life = 10 min at -120°C)²⁶ made it necessary to execute the work with **2** (*cis* half-life = 10 min at 7°C).²⁶ The first experiment was to irradiate *trans*-**2** at a sufficiently low temperature that the *cis* isomer would be indefinitely stable. Direct irradiation was expected to produce no nitrogen until the solution was warmed since all decomposition should be due to thermolysis of *cis*. On the other hand, we hoped that triplet sensitization would give all the nitrogen while the solution remained cold. As seen in Table II, direct irradiation did produce most of the nitrogen after the solution was warmed to decompose *cis*-**2**; however, some nitrogen must have come from direct photolysis of *trans*-**2**. Triplet-sensitized photolysis was not very efficient



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Scheme I

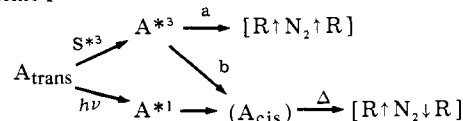


Table I. Nitrogen Quantum Yields for Azoalkane Photolysis^a

sensitizer	E_T^b	1 ^c	2 ^d	EAB ^e	AIBN ^f	ATB ^g
none ^h		0.57	0.47 ⁱ	0.42	0.44	0.46
acetophenone	73.6	0.14	0.12		0.14	0.018
<i>p</i> -MAP ^j	71.5	0.13	0.12		0.14	0.021
benzophenone	68.5	0.11	0.10	0.06	0.10	0.02
thioxanthone	65.5	0.12	0.10		0.07	0.017
anthraquinone	62.8	0.11			0.05	0.017
Michler's ketone	61.0	0.086			0.06	0.018
β -acetonephthone	59.3	0.068		0.10	0.04	0.017
1-naphthyl phenyl ketone	57.5			0.06		
9-fluorenone	53.3	0.049			0.05	0.015

^a In benzene by nitrogen evolution with 313-nm irradiation. Corrected for direct photolysis. ^b Triplet energy, kcal mol⁻¹. ^c At 10 °C. ^d At 23 °C. ^e Ethyl azoisobutyrate; quantum yield for disappearance of starting material at 25 °C; ref 18. ^f Azoisobutyronitrile at 13.5 °C. ^g Azotert-butane. ^h At 366 nm. ⁱ In toluene at 313 nm. ^j *p*-Methoxyacetophenone.

Table II. Irradiation of **2** in Toluene at -80 °C with 313-nm Light

mode	$\Phi_{N_2}(-80\text{ °C})$	Φ_{N_2} (after warming)	CH ₄ /N ₂ ^a
direct irradiation	0.08	0.40	0.12
triplet sensitization ^b	0.034	<0.007 ^c	0.28

^a Methane/nitrogen ratio in the gas obtained while the irradiated solution was kept at -80 °C. ^b With *p*-methoxyacetophenone. ^c Reference 30.

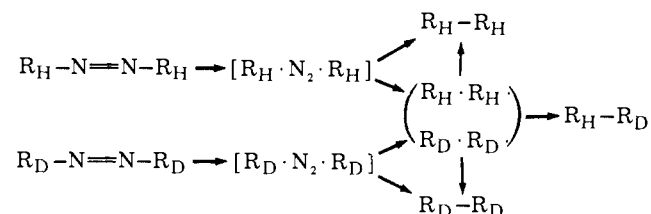
at -80 °C, but all of the nitrogen was evolved before warming.³⁰ It follows that triplet-sensitized formation of *cis*-**2** is not an important process, suggesting that path a in Scheme I is the correct one for both **1** and **2**. An unexpected bonus from these experiments was the considerably higher ratio of methane to nitrogen in the sensitized runs. The significance of this observation will be explained in the Discussion.

A second method of disproving path b in Scheme I is to demonstrate by low-temperature NMR that *cis*-**2** is formed under direct irradiation but not by triplet sensitization. A solution of **2** in toluene-*d*₈ was irradiated at -70 °C until its NMR spectrum at -55 °C showed the presence of new peaks corresponding to 18.8% *cis*-**2** plus some hydrocarbons from decomposition of **2**. After warming, the new peaks were gone and 22.6% of *trans*-**2** had disappeared, exactly the figure expected from the data in Table II. Both the presence of decomposition hydrocarbons before warming and the extra 3.8% decomposition are accounted for by the direct photolysis of **2**. The triplet sensitization experiment was carried out with 0.054 M **2** and 0.2 M *p*-MAP in toluene-*d*₈, using Fourier transform (FT) ¹H NMR spectroscopy to monitor the low concentration of **2**. Irradiation at 313 nm led to the expected hydrocarbon products while the solution was kept at -78 °C, but no *cis*-**2** could be detected.³⁰

The conclusion from these experiments is that triplet-sensitized photolysis of **2** and, by analogy, of **1** proceeds directly from the *trans* isomer and not by thermolysis of photochemically produced *cis* isomers. Thus the stage was set for an attempt to observe a SCE in photolysis of **1** and **2**.

Determination of the Cage Effect for 1. The most straightforward methods of measuring cage effects are to determine how much of an added free-radical scavenger disappears as a given amount of initiator decomposes (excess scavenger technique) or to observe the zero-order disappearance of scavenger when the initiator is in large excess (excess initiator technique).^{2,19} Because scavengers reactive enough to capture dimethylallyl radicals are also likely to interfere with the photochemistry, we determined cage effects by the considerably more laborious technique of isotope labeling. This method

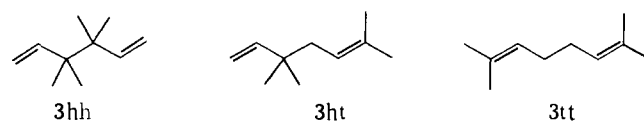
has been used on three previous occasions to measure cage effects in azoalkane decomposition.³²⁻³⁴ A mixture of deuterio and protio azoalkane was decomposed and the products were analyzed by mass spectrometry for deuterium content. As shown below, a cage effect of 100% predicts the exclusive formation of R_H-R_H and R_D-R_D whereas a cage effect of 0%



would lead to free R_H· and R_D· which recombine to a 1:2:1 statistical mixture of R_H-R_H, R_H-R_D, and R_D-R_D. The cage effect (α) for any ratio of R_H-R_D to the symmetrical dimers can be calculated from the equation

$$\alpha = \frac{2n}{2n+m} - \frac{m}{2h+m} \quad (1)$$

where *n*, *m*, and *h* are the mass spectral molecular ion intensities corresponding to R_H-R_H, R_H-R_D, and R_D-R_D, respectively. The present study is somewhat more complex in that all three possible hydrocarbon dimers (**3**) were formed. These



are designated according to whether recombination occurred at the head (h) or tail (t) end of the allylic radicals. A further difficulty is that none of the dimers gives a very strong molecular ion; in fact, the low chemical yield of 3hh coupled with its vanishingly small molecular ion prevented its use in measuring cage effects.³⁵

The value of α for direct and sensitized irradiation of **1** was determined by mass spectral analysis of the hydrocarbons from decomposition in benzene of an equimolar solution of **1** and **1-d**₆ (prepared according to Scheme II).³⁷ The raw data (Table III)³⁸ were corrected for incomplete deuteration³⁹ of **1-d**₆ and for unavoidable direct photolysis occurring during triplet sensitization, giving the cage effects shown in Table IV.

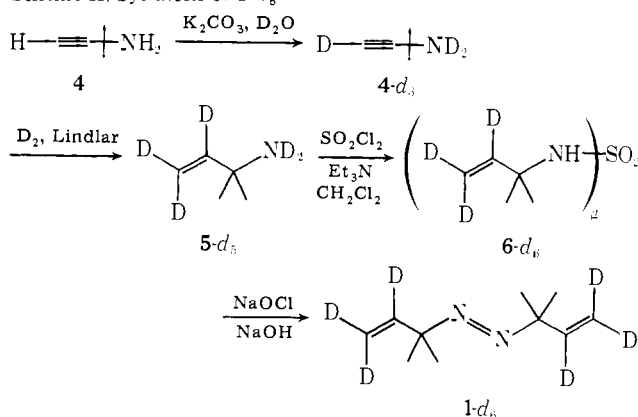
In order to check our analytical method, α was determined for thermolysis of **1** by the excess scavenger technique. With Koelsch radical, α was 0.50 whereas 2,2,6,6-tetramethylpiperidine-1-oxyl gave a value of 0.45 for thermolysis at 53 °C. As seen in Table IV, these numbers agree rather well with the 0.44 (average of three runs) determined mass spectrometrically. A control experiment demonstrated the absence of label scrambling during irradiation of the product hydrocarbons **3**

Table III. Mass Spectral Peak Intensities and Uncorrected^a Cage Effects (α_{obsd}) from Decomposition of an Equimolar Solution of **1** and **1-d₆** in Benzene at 12 °C

run no.	mode of decompn	hydrocarbon 3 monitored	intensity at <i>m/e</i>			α_{obsd}
			138	141	144	
1	thermolysis at 51 °C	ht	148.5	100.0	95.6	0.40
		tt	159.0	100.0	99.6	0.42
2	direct photolysis	ht	235.3	100.0	160.4	0.59
		tt	214.1	100.0	143.5	0.55
3	acetophenone sensitized	ht	58.6	100.0	55.2	0.06
		tt	58.9	100.0	43.9	0.00
4	<i>p</i> -MAP sensitized	tt	74.3	100.0	47.7	0.08
		ht	1280	736	768	0.45
5	thermolysis at 45 °C	tt	6816	3776	4096	0.47
		ht	1243	672	736	0.47
6	thermolysis at 65 °C	tt	6880	4448	4288	0.41
		ht	1344	416	736	0.65
7	direct photolysis	tt	6976	2784	4416	0.59
		tt ^b	960	320	704	0.67
		ht	800	704	416	0.23
8	acetophenone sensitized	tt	3040	3200	1856	0.19
		tt ^b	416	480	256	0.15
		ht	1120	1216	726	0.19
9	<i>p</i> -MAP sensitized	tt	7168	7648	4384	0.18
		tt ^b	832	896	480	0.17
		ht	1120	1216	576	0.13
10	thioxanthone sensitized	tt	5792	7328	3744	0.11
		tt	672	832	480	0.15
		ht	1120	1216	576	0.13

^a Calculated from eq 1. ^b Run 1 month after photolysis on the same solutions.

Scheme II. Synthesis of **1-d₆**



with triplet sensitizers (cf. Experimental Section). *Despite the variation in the results,*^{35,38} *it is apparent that the cage effect for **1** is much lower under triplet sensitization than by direct photolysis.*

Products from **1 and **2**.** The ratio of recombination hydrocarbons **3** from thermolysis of **1** has been rationalized on the basis of steric hindrance to radical recombination at the tertiary end.²⁷ It is shown in Table V that the percentage of **3**tt decreases while the amount of **3**hh increases at lower temperatures. Thermolysis at 50 °C gave 0.02% 3-methyl-1-butene and 0.26% 2-methyl-2-butene, but in view of possible contamination of **1** by traces of half-saturated azoalkane, these figures should be taken as maxima. The upper limit previously set²⁷ on the amount of disproportionation products was 2%, but more recent work has revealed no disproportionation in other allylic radicals.⁴⁰

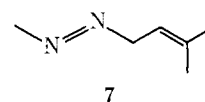
Thermolysis of **2** in the presence of benzoquinone, a good free-radical scavenger,⁴¹ gave the products listed in Table VI. The radicals which escape the solvent cage do not show up as any of these products; so the apparent hydrocarbon yield is substantially less than 100%. A possible product from **2** is the turnaround azoalkane **7**; however, this material was synthe-

Table IV. Average Cage Effects for Decomposition of **1**

decompn	runs ^a	α_{cor}
thermolysis at 54 °C	1, 5, 6	0.44
direct photolysis	2, 7	0.61
acetophenone sensitized	3, 8	0.09
<i>p</i> -MAP sensitized	4, 9	0.13
thioxanthone sensitized	10	0.07
direct photolysis	1-d₂	0.60
<i>p</i> -MAP sensitized	1-d₂	0.12
thioxanthone sensitized	1-d₂	0.10
thermolysis at 53 °C	scavenging	0.48

^a See Table III for the numbered runs. Those marked **1-d₂** were carried out with equimolar **1** and **1-d₂**.³⁷ The last entry is the average cage effect determined by the excess scavenger technique.

sized independently⁴² and demonstrated to be absent in both thermal and photochemical decomposition of **2**.



The hydrocarbon products from direct and *p*-MAP sensitized photolysis of **2** to completion in toluene at -78 °C were analyzed by GC. In addition to the products listed in Table VII, direct irradiation at 25 °C formed *o*-, *m*-, and *p*-xylene (relative molar amounts 0.0330, 0.0102, and 0.0105, respectively), 1-phenyl-2,2-dimethyl-3-butene (0.0475), and 1-phenyl-4-methyl-3-pentene (0.147). The structure of the two products from dimethylallyl-benzyl recombination was deduced from their mass spectrum (larger molecular ion for tail recombination products), from their relative retention times (tail longer than head), and from their relative amounts (tail larger than head). The most significant observation to be made about Table VII is that the ratio of dimethylallyl dimers **3** to recombination products (3,3-dimethyl-1-butene and 2-methyl-2-pentene) was nearly 14 times greater in the triplet-sensitized reaction than under direct irradiation at -80 °C. It is of in-

Table V. Hydrocarbon Products^a from **1**

temp, °C	3hh	3ht	3tt
50 ^b	16	29	55
0 ^c	20	28	52
-78 ^c	26	28	46
-196 ^{c,d}	30	39	31

^a Expressed as percent of total hydrocarbons; determined by GC; solvent was ethanol-ether (2:1 by volume). ^b Thermolysis. ^c Direct photolysis. ^d *cis*-**1** is stable at -196 °C; thermolysis occurs at about -120 °C.²⁶

Table VI. Cage Products from Thermolysis of **2**

product ^a	% yield
nitrogen	85
methane	2.8
3,3-dimethyl-1-butene	5.6
2-methyl-2-pentene	29.3

^a In diphenyl ether containing 0.1 M benzoquinone at 138 °C.

terest that fewer products are formed in the low-temperature experiments than at 25 °C.

CIDNP Studies of 1. In view of its potential benefit in this study, the powerful technique of chemically induced dynamic nuclear polarization (CIDNP)⁴³ was applied to the decomposition of **1**. Our own experiments were hampered by the lack of suitable equipment; so a sample of **1** was sent to Professor G. L. Closs⁴⁴ (University of Chicago), who kindly agreed to examine its decomposition. Whereas thermolysis at 108 °C in Me₂SO produced only a steady increase in the NMR peaks due to **3**, and direct photolysis gave only some minor CIDNP signals, thioxanthone-sensitized photolysis in CDCl₃ or in benzene-*d*₆ produced greatly enhanced absorption for the methyl protons of the hydrocarbon recombination products. As expected, the methylene groups were seen in emission.

Discussion

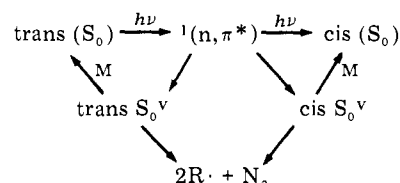
Mechanism of Photolysis of Acyclic Azoalkanes. An appealing mechanism was set forth recently by Fogel and Steel³¹ for the direct photolysis of azoisopropane (AIP). In order to rationalize the effect of pressure, temperature, and wavelength on *cis*- and *trans*-AIP, these workers postulated that excitation of either isomer produces a common ¹(n,π*) state, which populates vibrationally excited *cis* and *trans* ground states (*trans* S₀^v and *cis* S₀^v) with nearly equal probability. Deactivation of these vibrationally excited species (leading to isomerization) is favored over decomposition by higher pressure (addition of M) and lower temperature (cf. Scheme III).

The solution phase direct photolysis of all compounds listed in Table I proceeds with an efficiency of approximately 0.5. In terms of the above mechanism, the ¹(n,π*) state produces a thermally labile *cis* isomer with the same probability that it decays to the stable *trans* starting material. If this mechanism were complete, irradiation in solution of azoalkanes whose *cis* isomers are stable under the reaction conditions should lead only to isomerization and not to decomposition, since the solution phase corresponds to a very high pressure. However, compound **2** exhibits a quantum yield of direct photolysis of 0.08 at -80 °C, where the half-life of its *cis* isomer is over 3000 years. The inefficient but nevertheless important⁴⁵ photolysis of acyclic azoalkanes in solution which does not proceed via thermolysis of the *cis* isomer will be referred to as residual direct photolysis.⁴⁶ The question is, from what state does residual direct photolysis originate? The direct photolysis of azomethane has been attributed²⁹ to decomposition of S₀^v (a vibrationally excited ground state) in solution. Whereas a molecule as simple as azomethane may indeed have so few

Table VII. Products of Photolysis of **2** in Toluene^a

product	direct at -80 °C	sensitized at -80 °C	direct at 25 °C
isoprene	0.086	0.0194	0.0131
3,3-dimethyl-1-butene	0.216	0.159	0.0736
2-methyl-2-pentene	0.682	0.630	0.505
3hh	0.001	0.0196	0.0202
3ht	0.003	0.0447	0.0424
3tt	0.012	0.127	0.0975

^a Relative molar amounts listed in order of increasing GC retention times; corrected for GC detector response.

Scheme III

vibrational degrees of freedom that unimolecular homolysis can compete with vibrational quenching, S₀^v of the large azoalkanes is not expected to decompose in solution. Hence one must postulate that decomposition originates from a state which is either thermally equilibrated or whose lifetime is exceedingly short.

Some authors⁵⁰⁻⁵² have suggested that the ¹(n,π*) state intersystem crosses to a decomposing triplet state. Indeed, the ³(n,π*) state of acyclic azoalkanes is known to exist at about 53 kcal mol⁻¹⁵³ and triplet-sensitized dissociation of azoalkanes in the gas phase has been reported in several cases.^{31,50,52,54,55} Of course these studies do not demand that *direct* photolysis need involve the triplet state; in fact, both the present work and an apparently unnoticed communication by den Hollander⁵⁶ argue against the intermediacy of triplets. Residual direct photolysis of azomethane was shown by low-field CIDNP to occur "predominantly from the singlet state".⁵⁶ In our work, the cage effect for triplet-sensitized decomposition of **2** is lower than that for direct photolysis at the same temperature (see below), again implying that the major part of direct photolysis does not proceed via the triplet. Sensitized photolysis of **1** produces strong CIDNP in the hydrocarbon recombination products but direct irradiation gives hardly any polarization. In view of the moderate quantum yield for residual direct photolysis of **2** (Table II) room temperature photolysis of **1** is likely to proceed in part by the same mechanism.

With the weight of chemical evidence against residual direct photolysis proceeding via a triplet state and the argument given above opposing decomposition from S₀^v, we are left with either an energy-randomized ¹(n,π*) state or an energy-localized ¹(n,π*) state⁵¹ as the species involved. The latter is an appealing suggestion of Chervinsky and Oref;⁵¹ in fact, there is recent evidence that for a bicyclo[2.2.2]azoalkane, the decomposing state precedes the fluorescing state.⁵⁷ The bicyclic compound is admittedly very different from the acyclic ones under discussion here, but this result is consistent with residual direct photolysis originating from an energy-localized ¹(n,π*) state. It is conceivable that intersystem crossing (isc) occurs in the gas phase but not in solution but this trend would be opposite to the previously reported effect of pressure on isc yield in another system.⁵⁸

As mentioned above, triplet-sensitized decomposition of acyclic azoalkanes is well known in the gas phase but the same process in solution³¹ does not occur in the case of azomethane, AIP, and ATB (cf. Table I). On the other hand, four azoal-

kanes which produce resonance-stabilized radicals do decompose on triplet sensitization in solution; one of these (EAB, Table I) was reported¹⁸ 14 years ago but the results were not well accepted on account of the confusion introduced by singlet sensitization.¹ The failure of the simple aliphatic azo compounds to respond to triplet sensitization in solution is not caused by their inability to quench triplets;²⁰ neither is it due to rapid triplet-sensitized trans \rightarrow cis isomerization.³¹ Why, then, does the triplet state decompose in some cases but not in others?

There is rather good evidence that gas-phase triplet sensitization proceeds through a vibrationally excited azoalkane triplet (T_1^v).⁵² Thus all azoalkanes which have been studied³¹ exhibit an activation energy for decomposition of T_1 ranging from 5.0 kcal mol⁻¹ for azoethane to 8.8 kcal mol⁻¹ for AIP.⁵⁰ In the gas phase at ambient temperatures, azoalkanes quench both acetone⁵⁴ and biacetyl triplets, but decomposition ensues only in the former (higher triplet energy) case.⁵² We postulate that the potential energy surfaces for S_0 and T_1 appear as in Figure 1. According to theoretical calculations,⁵⁹ T_1 of azoalkanes crosses the ground-state surface at a considerably distorted geometry in which the molecule is twisted out of plane or one nitrogen has become linear. Although both of these motions provide an efficient channel for radiationless decay of T_1 , we have chosen the twisting option because it appears to be of lower energy. To explain the existence of an activation energy for photosensitized decomposition, a dissociative curve is shown for ATB crossing the bound T_1 state at a rather high vibrational level. In solution, triplet ATB is quenched vibrationally before it can get onto the dissociative curve even if it has sufficient energy to do so; hence it undergoes twisting and rapid radiationless decay. For a molecule such as **1**, the allylic radical produced is resonance stabilized so that its dissociative curve lies lower than the one for ATB. The intersection of this curve with T_1 occurs at a low vibrational level; so even in solution some of the vibrationally equilibrated triplets are able to dissociate before they undergo twisting. In accord with this suggestion, the apparent activation energy for triplet-sensitized photolysis of **2**, as calculated from the data in Table II, is only 1.5 kcal mol⁻¹, substantially lower than any such value measured previously. Additional evidence that the triplet state of **1** undergoes rapid vibrational relaxation in solution prior to surmounting the small barrier for decomposition is the fact that Φ_{N_2} does not exceed 0.14, regardless of sensitizer triplet energy.

It is of interest that the quantum yields for **1** and **2** are nearly identical, despite their greatly different thermal stability. We take this as evidence that triplet-sensitized photolysis in solution requires only one weak C-N bond. To conserve spin, the species produced on decomposition must then be a triplet diazenyl-dimethylallyl pair, which would surely exhibit a repulsive potential curve of the type shown (Figure 1).

Fate of Radical Pairs. The data in Table IV show quite clearly that the cage effect is much lower for sensitized photolysis of **1** than for direct photolysis. The same trend becomes apparent on examination of the products obtained from **2** under these two decomposition modes. As shown in Scheme IV, escape of methyl and dimethylallyl radicals from the solvent cage leads to hydrocarbon dimers **3** plus methane, whereas cage recombination produces the two C₆ olefins. Sensitized photolysis of **2** at -80 °C gave more than twice as much methane (Table II) and a far greater ratio of **3** to C₆ hydrocarbons (Table VII) than direct irradiation under the same conditions. These results from **1** and **2** support the idea that the pathways for direct and sensitized photolysis do not merge; that is, both do not proceed via a triplet or via the cis isomer. The same conclusion is derived from the CIDNP experiments in which only triplet sensitization produced significant peak intensity changes.

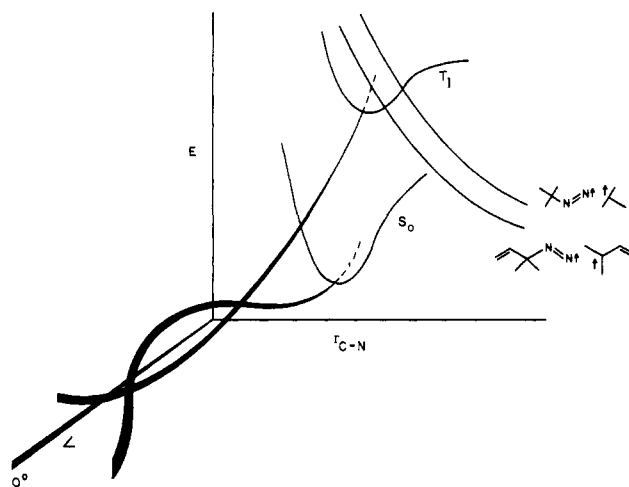
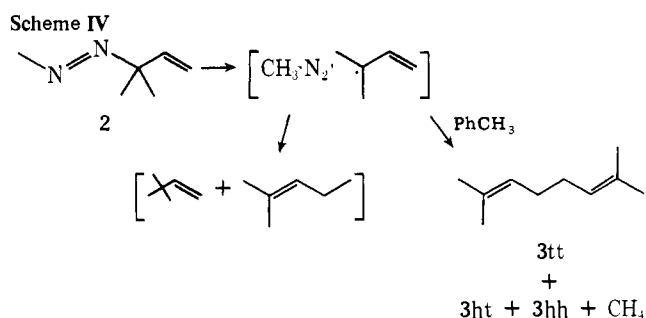


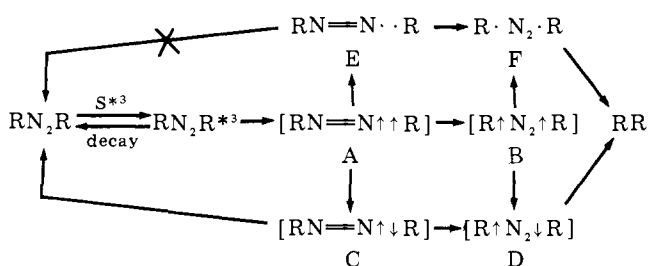
Figure 1. Potential energy curves for ground-state and triplet azoalkanes. The axis coming out of the plane represents the C-N=N-C dihedral angle.



Despite considerable experimental error, it is also apparent that the cage effect for photolysis of **1** at 12 °C is higher than that for thermolysis at 54 °C. This difference is not of profound origin for the cage effect is known to decrease at higher temperatures. Using Nelsen and Bartlett's¹⁹ observed activation energy difference between diffusion and cage recombination of 1.3 kcal mol⁻¹, we calculate that a cage effect of 0.44 at 54 °C corresponds to 0.59 at 12 °C, in good agreement with the observed value of 0.61. Thermal and photochemical cage effects at 25 °C were also similar for EAB (cf. Table I),⁶⁰ but two other studies claimed greater¹⁹ and lesser⁶¹ cage effects for the two decomposition modes. In all cases, thermolysis is a reaction of trans azoalkane whereas photolysis is primarily thermolysis of the cis isomer. Thus thermolysis of both isomers of **1** gives the same radical pair and no concerted extrusion mechanism operates in the cis azoalkane.⁶²

It is tempting to conclude that the lower cage effect in the sensitized photolysis of **1** is a spin correlation effect; however, two other explanations are possible. Since sensitized decomposition is a true photolysis, the radical pairs produced are "hot", causing them to diffuse from the cage more rapidly than in direct photolysis, which is actually thermolysis of cis. If kinetic energy of the radicals were the most important factor, however, residual direct photolysis of azomethane ought to show a low cage effect. In fact, α for this case is in the region of 70%¹ and is invariant with photolysis wavelength (254, 313, or 366 nm).^{63,64} A second explanation for our results is rather attractive, namely, that triplet-sensitized photolysis proceeds by breakage of only one C-N bond. Nitrogen could be lost after the alkyldiazenyl radical diffuses from the solvent cage, resulting in a low cage effect for C₁₀ hydrocarbons.⁶⁵ This possibility forces us to consider the decomposition process in greater detail, which is done in Scheme V.

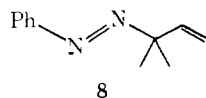
Scheme V



On the basis of the above discussion, it is likely that triplet azoalkane is formed with high efficiency, but that most of it decays radiationlessly to starting material. Stepwise cleavage to give radical pair A is consistent with two important observations: the quantum yield for triplet-sensitized photolysis of **1** is the same as that for **2** (see above) and CIDNP is seen in the C₁₀ hydrocarbons arising from triplet-sensitized photolysis of **1**. A net effect in CIDNP is not obtained when two reacting radicals have the same *g* value, as in the 1,1-dimethylallyl radicals produced by decomposition of **1**. Spin polarization must therefore arise in radical pair A, with a "memory effect"⁶⁶ accounting for the CIDNP seen in the C₁₀ hydrocarbon products RR.⁷⁰ Applying Kaptein's rule⁴³ for the net effect to intermediate A, we obtain

$$\Gamma_{nc} = \mu\epsilon\Delta gA_i = +++++ = +$$

where μ is + for a triplet precursor, ϵ is + for recombination product, Δg is + because *g* (dimethylallyl) > *g* (diazanyl),⁷¹ and A_i is + for the methyl groups on the α carbon of an alkyl radical.⁷⁴ Hence, we predict that Γ_{nc} is +, so that the methyl protons should show enhanced absorption while the methylene protons⁷⁴ of the dimethylallyl radical should exhibit emission. These expectations correspond exactly to the observed CIDNP spectrum in the triplet-sensitized photolysis of **1**. Neither thermolysis nor direct photolysis of **1** or of any symmetrical azoalkane studied previously⁷⁶ shows a net effect in high-field CIDNP. Thus stepwise cleavage occurs only from the triplet state of **1**; however, there is good evidence for stepwise cleavage of azo compounds when one radical is phenyl or norbornyl.^{68,73} Polarization of the starting azoalkane was observed in those cases, demonstrating the reversibility of single C-N bond cleavage. Since we do not see any unusual change in the NMR signal intensity of **1** during triplet-sensitized photolysis, the initial cleavage must not be reversible. One would hardly expect A to return to **1** but it does not even undergo spin inversion to C, in which recombination is spin allowed. Further evidence against the process A → C is the absence of turnaround compound **7** in all decomposition modes of **2** (thermolysis and direct and sensitized photolysis). Azoalkane **1** is even less likely to give turnaround product than is **2** because loss of nitrogen from the dimethylallyldiazanyl radical should be faster than the same process in methyl-diazanyl. Interestingly, compound **8** does undergo the turnaround reaction.⁷⁸ The process A →



C might occur and still be consistent with the results just presented if C loses nitrogen rapidly to give D. However, D is the singlet radical pair which also arises from direct photolysis. If A → C → D were rapid, both direct and sensitized decomposition would give the same cage effect, contrary to our results (Table IV).

Having ruled out C and D as important intermediates in the decomposition of triplet **1**, we must now consider whether RR is formed via B or E. If free diazenyl radicals are involved, they do not revert to azoalkane, based on the same arguments

which ruled out C. On the other hand, radical pair A must live for at least 10⁻¹⁰ s in order to observe CIDNP.⁴³ Therefore, some diazenyl radicals are expected to escape the cage, but they must all lose nitrogen (E → F) before finding a new R· with which to recombine. Although the process A → E → F accounts for all of our observations, a classical spin correlation effect should involve triplet radical pair B. It is clear that the spin multiplicity of a radical pair precursor (**1**) determines the cage effect, but the reason seems to be a special decomposition mechanism of the triplet state rather than a SCE.

Some insight into the question of *why* triplet acyclic azoalkanes decompose stepwise is provided by a recent calculation on *cis*-diimide.⁷⁹ Comparison of one bond cleavage with concerted elongation of both NH bonds revealed that the activation energy for crossing of the ³n,π* state with the dissociating ³π,π* state is much lower in the stepwise mechanism. If these results hold for *trans* azoalkanes, the dissociative curve in Figure 1 can be identified with the ³π,π* state, which becomes degenerate with the ground state at large separation of the diazenyl and alkyl fragments. The prediction⁷⁹ that direct irradiation should lead to decomposition via a triplet state seems not to be borne out by our experiments (see discussion of residual direct photolysis above).

Turning now to the product distribution from **1** and **2**, we note from Table V that the ratio of the three recombination products **3** is seen to depend weakly on the temperature at which decomposition was carried out with the trend of the three photochemical runs extrapolating nicely to the thermal run at 50 °C. This constitutes further evidence that thermolysis of *cis*- and *trans*-**1** gives the same radical pair. Since the amount of 3hh increases at the expense of 3tt at lower temperature, it appears that movement of the radicals within the solvent cage is diminished. A similar study of AIBN³⁴ showed little change of product distribution with temperature though disproportionation and carbon-carbon radical recombination increased while ketimine decreased in a frozen glass compared with fluid solution. Thus the main factor responsible for the changing product distribution in Table V is probably greater solvent viscosity at the lower temperatures. Recently, another case in which equilibration of the two ends of an allylic radical was inhibited by a frozen matrix was reported.⁸⁰

The caged methyl-dimethylallyl radical pair from thermolysis of **2** (Table VI) undergoes recombination at the tail end of the delocalized radical 5.2 times as often as at the head end. This ratio agrees rather well with the value 5.7 obtained from the gas-phase photolysis of olefins⁸¹ and again speaks for the importance of steric factors in radical recombination. The total yield for hydrocarbons is 44% of the evolved nitrogen; however, this figure represents only caged hydrocarbons. In fact 0.44 is a reasonable value for the cage effect for **2** at 138 °C. Some isoprene was detected in the thermolysis of **2** but its amount is meaningless on account of its probable reaction with benzoquinone. The low yield of methane demonstrates that cage disproportionation is unimportant in this radical pair; hence, virtually all of the methane in Table II must arise from reaction of free methyl radicals with toluene. The ratio of methane to nitrogen in the gases produced on warming irradiated solutions of **2** (thermolysis of *cis*-**2**) was 0.23. If one assumes that thermolysis of *cis*-**2** occurred at 7 °C,²⁶ the known¹⁹ temperature dependence of the cage effect predicts a value of 0.09 at -80 °C, which compares nicely with the experimental value of 0.12 (Table II). The key point about Table VII has already been discussed, namely, that the cage effect is greater for direct photolysis at -80 °C than for sensitized. Irradiation at ambient temperature gave a rather complex mixture, though none of the products is especially surprising. The high quantum yield (0.47) for ambient temperature photolysis coupled with a lower cage effect leads to more radical-radical reactions⁸² and probably to more attack

of radicals on products. For the latter reason, we are reluctant to interpret product ratio.

Summary

Moderate quantum yields were obtained for triplet-sensitized photolysis of acyclic azoalkanes which give resonance-stabilized free radicals. Use of ketone sensitizers avoided the complication of singlet sensitization. Triplet-sensitized photolysis was shown by low-temperature NMR and nitrogen evolution experiments not to proceed via the thermally labile cis isomers. Since these observations were an auspicious omen that a spin correlation effect might be observable, cage effects were determined for **1** under direct and sensitized irradiation, using the deuterium labeling technique. It was apparent that the two photolysis modes gave a large difference in cage effect for both **1** and **2**, demonstrating that solution-phase direct photolysis of these azoalkanes does not proceed via the triplet manifold. This conclusion was supported by CIDNP studies, which further suggested that the reason for the lower cage effect in the triplet state was stepwise C-N bond breakage. Analysis of the products revealed no unusual chemistry and none of the turnaround azoalkane **7**. A simple diagram (Figure 1) was presented to rationalize the photolability of triplet **1** and **2** by assuming decomposition of a thermally equilibrated triplet state in solution.

Experimental Section

Material and Equipment. Melting points and boiling points are uncorrected; melting points were obtained with a Mel-Temp apparatus. NMR spectra were obtained on a Varian XL-100, A-56/60, or EM-390 spectrometer using 10% solutions of material in CDCl₃ with Me₄Si as an internal standard unless otherwise indicated. IR spectra were obtained on a Beckman IR-8, UV spectra on a Cary 17 spectrophotometer, and mass spectra on a Finnigan Model 3300 mass spectrometer. VPC was carried out on a Hewlett-Packard Model 700 chromatograph and on a Barber-Coleman Electra Series 5000 flame ionization chromatograph. Hydrogenations were run both in a standard Parr apparatus and in a microhydrogenator. Photochemical experiments were carried out on a merry-go-round using as a light source a 450-W Hanovia lamp with an inner NiSO₄ filter and an outer K₂CrO₄ filter solution to isolate 313 light. Other experiments employed a 500-W point source mercury lamp with the same type of filter solutions.

Reagent quality benzene and toluene were dried over LiAlH₄ overnight, then distilled from LiAlH₄ through a 6-in. glass helices packed column. 3-Amino-3-methyl-1-butyne (Aldrich Chemical Co.) was swirled with solid KOH until an aqueous layer separated, whereupon the aqueous layer was discarded. After this process was repeated several times, the amine was distilled from KOH pellets through a 6-in. glass helices column. Methylamine hydrochloride was dried overnight under vacuum with P₂O₅; SO₂Cl₂ was used without purification. Toluene-*d*₈ was distilled from LiAlH₄ and AIBN was recrystallized from diethyl ether and ethanol.

Purification of Sensitizers. Anthraquinone was successively recrystallized from benzene and CHCl₃ (40 mL/g). Benzophenone was recrystallized from hexane. Michler's ketone was recrystallized three times from ethanol. β -Acetonaphthone was recrystallized from ethanol-H₂O and then from hexane. Acetophenone was dried over CaSO₄, then distilled twice. *p*-Methoxyacetophenone was distilled through a Vigreux column, then recrystallized from ether-pentane. Thioxanthone was purified by dry column chromatography with chloroform as eluent followed by recrystallization from ethanol. 9-Fluorenone was recrystallized from ethanol.

3-Amino-3-methyl-1-butyne (5). 3-Amino-3-methyl-1-butyne (**4**, 10.0 g, 120 mmol) was hydrogenated using Lindlar catalyst⁸³ as described by Freifelder,⁸⁴ except that the hydrogenation was carried out at 1 atm in a microhydrogenator. The reaction was monitored by VPC on a 250-ft capillary SF-96 column and was stopped after the 3-amino-3-methyl-1-butyne peak disappeared. The catalyst was removed by filtration and the reaction mixture was distilled through a 4-in. glass helices column (bp 72–74 °C): yield 5.2 g (51%); NMR δ 0.99 (s, 2 H), 1.15 (s, 6 H), 4.95 (m, 2 H), 5.95 (m, 1 H). It was later

found on similar compounds that distillation under N₂ dramatically improved yields.

N,N'-Bis-3-(3-methyl-1-butenyl)sulfonamide (6) and Related Compounds. A 250-mL RB3N flask, equipped with a mechanical stirrer, addition funnel with a drying tube, and a tube extending 1 in. into the flask, and a N₂ inlet was placed under a brisk flow of N₂ and warmed thoroughly with a heat gun. The system was then allowed to cool under the N₂ flow. A solution of 3-amino-3-methyl-1-butyne (5.00 g, 58.7 mmol) and triethylamine (6.5 g, 64.2 mmol) in 20 mL of CH₂Cl₂ was placed in the flask. After the RB flask was cooled with a dry ice-acetone bath and vigorous stirring was commenced, a solution of sulfuryl chloride (3.80 g, 28.2 mmol) in 20 mL of CH₂Cl₂ was added dropwise to the solution. After 15 min, the addition was complete, and the solution was stirred for an additional 2–3 h at –78 °C. The cooling bath was removed and the solution was stirred overnight.

A 2 M HCl solution (50 mL) was added to the reaction flask and the solution was allowed to stir for 0.5 h, then the two layers were separated. The organic layer was washed one more time with 2 N HCl, then once with H₂O and with NaCl solution. After each separation, the aqueous layer was always washed with a small portion of CH₂Cl₂ which was then combined with the main organic layer. The organic layer was dried over K₂CO₃, then the CH₂Cl₂ was removed by rotary evaporation. The resultant white solid was dried in a vacuum desiccator to remove the last traces of CH₂Cl₂ or H₂O: yield 5.6 g (85%); mp 84.2–86.2 °C; NMR δ 1.43 (s, 12 H), 4.42 (br s, 2 H), 5.10 (m, 4 H), 6.04 (m, 2 H).

1,1,1,2,2,2-Trideuterio-3-amino-3-methyl-1-butyne (4-*d*₃). To a 100-mL RBSN flask, that had been previously heated in an oven and flushed thoroughly with N₂, was added a saturated K₂CO₃-D₂O solution (37 mL) and 3-amino-3-methyl-1-butyne (15.1 g, 181.5 mmol). This solution was stirred rapidly under N₂ for 15 h. The layers were separated and the whole process repeated for 3.0 h. The layers were separated again and the organic material was then distilled through a 2-in. glass helices packed column: bp 80–81 °C; yield 11.5 g (73%); NMR δ 1.43 (s).

1,1,2,2,2,2-Pentadeuterio-3-amino-3-methyl-1-butyne (5-*d*₅). was prepared from **4-*d*₃** as described above for the *h*₅ analogue substituting D₂ instead of H₂: yield 7.7 g (64%); bp 73.0–74.5 °C; NMR δ 1.23 (s); other small peaks due to a small amount of back exchange appeared at δ 4.50, 5.10, and 6.03.

N,N'-Bis-3-(1,1,2-trideuterio-3-methyl-1-butenyl)sulfonamide (6-*d*₆). was prepared from the deuterated amine (1.5 g, 16.7 mmol) as described above for the *h*₆ analogue. The deuteriums on the nitrogens were lost during the workup: yield 1.6 g (81%); mp 83.8–85.0 °C; NMR δ 1.44 (s, 12 H), 4.42 (broad s, 2 H), plus small peaks at δ 5.10 and 6.05 due to incomplete deuteration.

Azobis-3-(methyl-1-butene) (1) was prepared as described previously:²⁶ yield 1.4 g (79%); NMR δ 1.22 (s, 12 H), 5.02 (m, 4 H), 5.98 (m, 2 H); UV (hexane) λ_{\max} 366 nm (ϵ 29.6).

Methyl azo-1,1-dimethyl-2-propene (2) was prepared by the method of Ohme⁸⁵ and also by the method of Baldwin.⁸⁶ The azo compound was purified by preparative VPC on a 1/4 in. \times 20 ft 8% OV-17 on Chromosorb W 70/80 mesh column, followed by a short-path distillation: yield 0.487 g (19%); bp 45–50 °C (30 mm); NMR δ 1.22 (s, 6 H), 3.63 (s, 3 H), 4.90 (m, 2 H), 5.90 (m, 1 H); UV (hexane) λ_{\max} 363 nm (ϵ 17.0).

Quantum Yields. The azoalkanes were photolyzed in solution using a merry-go-round apparatus in an insulated, cooled water bath. A Hanovia 450-W lamp in a quartz immersion well with a dual filter train of NiSO₄-K₂CrO₄ was used to irradiate the solutions. Quantum yields were determined by measuring the amount of N₂ evolved with a Töpler pump-gas buret system. In the case of **2**, the total amount of N₂ and methane was measured. The relative amount of each gas was then determined by VPC according to the method of Charlier and Obermiller.⁸⁷ Solutions of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) in benzene with absorbance between 2.0 and 3.0 at 313 nm were employed as the actinometer.

For the determination of a set of quantum yields, a stock azoalkane solution was prepared (usually in benzene) such that the azo absorbance at 313 nm was below about 0.15. The appropriate amounts of sensitizers were weighted into volumetric flasks such that the sensitizer absorbance at 313 nm was about 2.9, thus making the total absorbance about 3. Portions (20 mL) of these solutions and of the actinometer solutions were then syringed into their respective irradiation tubes and degassed four times before being sealed with a torch.

The tubes were irradiated for a preset amount of time in the merry-go-round apparatus and the amount and composition of the gases were determined by the Töpler buret-VPC system. Values of Φ_{N_2} were based upon $\Phi_{N_2} = 1.0$ for DBH.⁸⁸

Cage Effect Determinations. The sulfonimides of **1-h₆** and **1-d₆** were oxidized separately using conditions similar to that for the synthesis of the isolated **1** with the following exceptions: (1) no pentane was added to the oxidation mixture (the reaction mixture was washed instead with benzene to extract the azoalkane from the aqueous layer); and (2) the temperature of the reaction was constantly monitored to ensure that **1** did not decompose during its preparation.

After benzene solutions of **1-h₆** and **1-d₆** were obtained, their absorbance was reduced by dilution to a value between 0.10 and 0.15. The absorbance of the two solutions was equalized by addition of small amounts of benzene, then equal amounts of the two solutions were mixed together to make the stock solution for the cage effect experiment. In each experiment, a small portion of the **1-h₆** and **1-d₆** solutions was kept separate to be photolyzed as a reference standard. Sensitizers were weighed into volumetric flasks and made up to the mark with the azoalkane stock solution. A 3.0-mL portion of each solution was syringed into irradiation tubes, degassed five times, and sealed with a torch. The tubes were then exhaustively irradiated (5–7 h) on the photochemical merry-go-round. As in the case of the quantum yields, the tubes were kept cool (11–15 °C) to prevent complications from concomitant thermolysis. After irradiation, the solutions were stored in vials at –20 °C. In an early experiment, the amount of gas evolved from each tube was measured; 95–100% of the expected N₂ was collected.

Analysis of the hydrocarbon mixtures was performed on a Finnigan mass spectrometer using a 250-ft SF-96 capillary column to separate all products. Conditions were adjusted to maximize the molecular ions. At least two runs were performed for each tube. After the raw data were obtained, corrections and calculations were made as described in the Results section and in the supplementary material.

A control experiment consisted of thermolyzing separate equimolar solutions of **1** and **1-d₆** at 60 °C overnight. Equal amounts of the resultant solutions of **3-h₆** and **3-d₆** were then mixed together and to portions of this mixture was added the appropriate amount of sensitizer. The resultant sensitizer-hydrocarbon solutions were then syringed into an irradiation tube, degassed five times, sealed with a torch, and irradiated for about 6 h. Analysis of these solutions on the GC/MS demonstrated the absence of any label scrambling during the photoreaction.

Low-Temperature Φ_{N_2} Determination. These experiments were carried out in a specially constructed photolysis cell connected to a Töpler buret-VPC system via a cold trap with a side arm for convenient addition and withdrawal of solutions. The cell was cooled by refluxing Freon-13 (bp ~ –80 °C); the pressure above the Freon was controlled by a 29-cent orange party balloon.

Direct and triplet-sensitized quantum yields at low temperature were determined as follows. A solution of **2** in dry toluene was made at the concentration appropriate to the experiment (direct photolysis, 202.3 mg/3.1 mL toluene; triplet-sensitized photolysis, 15 mg/3.1 mL toluene), whereupon 3.0 mL of solution was syringed into the trap through the side arm. For the triplet-sensitized reaction, the *p*-methoxyacetophenone (12.2 mg) was introduced into the cell. The solution in the trap was degassed five times. Freon 13 was condensed into the low-temperature apparatus using liquid N₂ as a cooling medium; the solution was then distilled into the cell. After the system had equilibrated, it was irradiated by a 500-W mercury lamp through a NiSO₄-K₂CrO₄ dual filter train for a known amount of time. The product gases were then collected with the Töpler pump, a process which required about 3 h. The total amount of gas was measured in the buret, and it was then analyzed by VPC as described above. The buret was evacuated, the Freon removed by distillation, and the contents of the cell allowed to warm up. After the thermally labile intermediates had decomposed, the contents of the cell was distilled back into the trap and the resultant gases were measured and analyzed by VPC.

Low-Temperature NMR Experiment. A 10.1-mg portion of **2** was weighed into a 1.00-mL volumetric flask, which was made up to the mark with toluene-*d*₈ plus a few drops of Me₄Si. A 0.50-mL portion of the solution was syringed into an NMR tube attached to a 7/22 standard taper joint. To the remaining solution was added *p*-methoxyacetophenone (29.8 mg) and the mixture was diluted to the 1.00-mL mark. The sensitizer-azoalkane solution (0.5 mL) was syringed

into an NMR tube like the first. Both tubes were degassed five times and sealed with a torch. NMR spectra were taken on the tubes, which were then irradiated at –78 °C in a dry ice–2-propanol bath for about 1 h; then NMR spectra were again run at about –50 °C. The tubes were warmed to room temperature and allowed to stand for a few minutes to thermolyze any labile intermediates, especially *cis*-**2**. Warm spectra were then run on the tubes.

Low-Temperature Product Study. Two NMR tubes with solutions similar to those in the previous experiments were made. Both tubes were irradiated for 2–3 h, whereupon NMR spectra at –50 °C demonstrated the absence of any **2** (either *cis* or *trans*). The contents of the tube was analyzed by VPC using a 250-ft SF-96 capillary column and a temperature program (30 min isothermal at 40 °C; 0.5 °C rise/min up to 120 °C). Peaks were identified by injection of authentic samples of various compounds and by obtaining mass spectra of the various compounds as they eluted from a Finnigan GC/MS system under similar GC conditions.

Acknowledgment. The authors wish to thank the National Science Foundation, The Robert A. Welch Foundation, and the Alfred P. Sloan Foundation for their generous support of this work.

Supplementary Material Available: A description of our work with **1-d₂** and a discussion of the procedure for correcting the mass spectral data in Table III to obtain cage effects (5 pages). Ordering information is given on any current masthead page.

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- Although the discrepancy between two runs with the same sensitizer is considerable (e.g., no. 4 and 9 in Table III), the first set of experiments (runs 1–4) gave consistently lower cage effects than the second set (runs 5–10).

- Most of this variation is undoubtedly due to the analytical method but acetophenone gave a lower yield of all hydrocarbons, probably because it reacted photochemically with the product hydrocarbons.
- (39) The isotopic purity of 1- d_6 must be at least as great as that of the hydrocarbons **3** arising from its decomposition. Of these hydrocarbons, 38% were d_6 and 62% were d_8 , giving an isotopic purity of 94%.
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Single-Electron Oxidation Equilibria of Tetraalkylhydrazines. 2. Tetraalkyl-2-tetrazenes as Models for Steric Effects, and the Importance of Alkyl Group Charge Delocalization Anisotropy

S. F. Nelsen,* V. E. Peacock, and C. R. Kessel

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received April 3, 1978

Abstract: Vapor phase vertical ionization potentials (IP_1) were determined by PE spectroscopy for 17 tetraalkyltetrazenes and 14 tetraalkylhydrazines in addition to those previously reported. E^0 vs. SCE values were determined for the tetrazenes and hydrazines in acetonitrile, and for 12 of the tetrazenes, in methylene chloride. From comparisons of these data, it is documented that the charge-stabilizing ability of an asymmetric alkyl group depends on its steric environment, a conclusion supported by MINDO/3 calculations on ethylamine and its cation radical. The 2-tetrazenes are argued to be reasonable steric models for the flattening which occurs at nitrogen upon removal of an electron from a hydrazine. By comparing tetrazene with hydrazine data, it is concluded that the energy for eclipsing the two sets of methyl groups of tetramethylhydrazine in going from the neutral form to the radical cation is about 5 kcal/mol, and that the wide variation in tetraalkyltetrazene E^0 values arises principally because of differences in steric strain between the neutral and radical cation forms.

In a previous paper¹ we reported standard oxidation potentials, E^0 ,² for several tetraalkylhydrazine-tetraalkylhydrazine radical cation (I, I^+) redox couples (see eq 1) as measured by cyclic voltammetry (CV). These E^0 values seem best considered as a series of $\Delta(\Delta G^\circ)$ values for various I, I^+ equilibria, compared to ΔG° for the parent compound, te-

