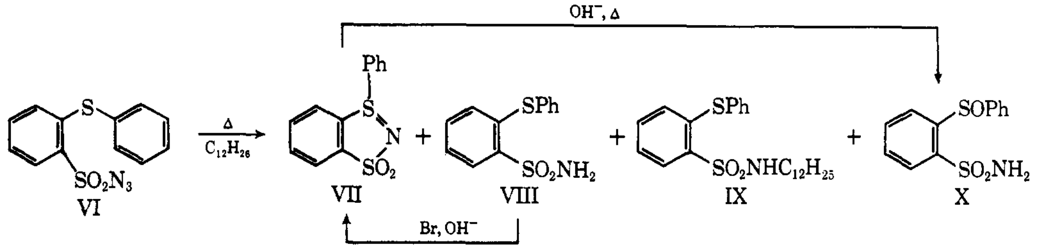

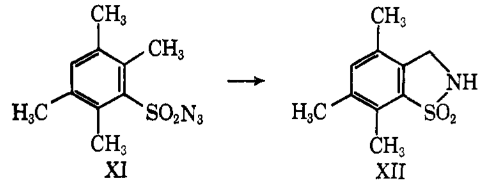

internuclear cyclization product was confirmed by the absence of an NH band in the infrared, by its methylation with dimethyl sulfate to give N,N-dimethyl-2-benzenesulfinylbenzenesulfonamide (82%), mp 120–122°, and by its synthesis from VIII with bromine and alkali. In one thermolysis only, some diphenylene disulfide (3%), mp 156.5–158° (lit.[7] mp 154°), was also obtained.

Thermolysis of diphenyl sulfone-2-sulfonyl azide, mp 99.5–100°, similarly did not yield the cyclic sulfonamide. In dodecane at 150°, the products formed were diphenyl sulfone (27%),[8] mp 125°, and diphenyl sulfone-2-sulfonamide (9%). In Freon E-4 at 150°, the products were diphenylene sulfone (1.3%),[8] mp 230°, and diphenyl sulfone-2-sulfonamide (1.5%), together with tars.

An attempt to effect intramolecular cyclization of a side-chain sulfonyl nitrene failed: thermolysis of $\alpha$-toluenesulfonyl azide, mp 53.5–54°, in dodecane gave $\alpha$-toluenesulfonamide (26.5%), mp 103.5–104.5°, and N-dodecyl-$\alpha$-toluenesulfonamide (41.8%), mp 99–101°. Photolysis or copper-catalyzed[10] decomposition of the azide with or without solvent also did not lead to cyclization, and it would appear as though geometrical restrictions do not permit the formation of the required aziridine intermediate[5] in this case. On the other hand, intramolecular insertion into an aliphatic side chain has been achieved: XI, mp 68.5°, was decomposed in dodecane at 150° to give a 10–15% yield of XII, mp 229.5–230°. No durene-3-sulfonamide was isolated.

The results can be explained if it is assumed that the species undergoing intramolecular aromatic substitution, attack upon divalent sulfur, and C–H insertion is the singlet sulfonyl nitrene, while that undergoing hydrogen abstraction from aliphatic hydrocarbons is the triplet. When the internuclear distance is large or the rotational conformation does not permit easy addition of the nitrene to the aromatic nucleus, it can either insert into a C–H bond, attack sulfur (to form a five-membered ring as is usually favored in nitrene cyclizations), or drop to the triplet ground state and undergo hydrogen abstraction.

**Acknowledgment.** This research was supported by a grant from the Warner-Lambert Research Institute, whom we thank.

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[7] E. D. Bergmann and M. Tschudnowsky, *Ber.*, **65**, 457 (1932).

[8] The formation of these products suggests the elimination of azide and $SO_2$ to give the aryl radical, which would have a parallel in the cleavage of sulfonyl chlorides.[9]

[9] F. A. Drahowzal in "Organic Sulfur Compounds," N. Kharasch, Ed., Vol. 1, Pergamon Press, New York, N. Y., 1961, p 372.

[10] H. Kwart and A. A. Kahn, *J. Am. Chem. Soc.*, **89**, 1951 (1967).

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## The Photochemistry of Aliphatic Azo Compounds. The Role of Triplets and Singlets in Their Photochemistry

*Sir:*

The gas-phase quantum yields of decomposition, $\Phi$(dec), of azo compounds have long been known to be pressure sensitive and have been explained in terms of the mechanism[1]

$$\text{azo} \underset{+\text{M}}{\overset{h\nu}{\rightleftharpoons}} \text{azo}^* \longrightarrow \text{products}$$

However, this simple scheme is not adequate; if it were it can readily be shown that azo compounds should not photolyze in solution, while they do so.[2] In agreement with this Wu and Rice[3] have recently observed curvature in the plot of $1/\Phi$(dec) *vs.* [M] for perfluoroazomethane. Moreover we have observed *cis–trans* isomerization of azomethane in solution using both polar and nonpolar solvents.[2] By analogy with other *cis–trans* systems we might expect that this isomerization proceeds *via* the triplet.[4] We have car-

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[1] H. Cerfontain and K. I. Kutscke, *Can. J. Chem.*, **36**, 344 (1958); W. C. Worsham and O. K. Rice, *J. Chem. Phys.*, **46**, 2021 (1967), and references therein.

[2] R. F. Hutton and C. Steel, *J. Am. Chem. Soc.*, **86**, 745 (1964); S. Kodama, S. Fujita, J. Takeishi, and O. Toyama, *Bull. Chem. Soc. Japan*, **39**, 1009 (1966).

[3] E.-C. Wu and O. K. Rice, *J. Phys. Chem.*, **72**, 542 (1968).

[4] Z. R. Grabowski and A. Bylina, *Trans. Faraday Soc.*, **60**, 1131 (1964); R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 165 (1964).

ried out work using mainly azoisopropane (AIP) which unifies these gas-phase and liquid-phase studies and preliminary data suggest that the results for azomethane and azoethane are similar.

*trans*-AIP was prepared in the usual way.[5] *cis*-AIP was prepared by irradiating ($\lambda_{\mathrm{irr}}$ 365 m$\mu$) degassed liquid *trans*-AIP and separating the photolysis mixture by gas chromatography. The nmr spectrum of *trans*-AIP, with respect to internal tetramethylsilane as standard, consists of a doublet centered at $\delta$ 1.1888, $J$ = 6.5, and a septet centered at $\delta$ 3.525, $J$ = 6.5 cps. In the case of *cis*-AIP $\delta$ (doublet) 1.229, $J$ = 6.5 cps, and $\delta$ (septet) 3.983, $J$ = 6.5 cps.

In aqueous solution both *trans*- and *cis*-AIP photoisomerize without decomposition just as azomethane does.[2] Starting from *trans*-AIP and using modified Fischer–Malkin[6] plots we find $\Phi_{365}{}^{trans}(cis) = 0.38 \pm 0.03$ and $\Phi_{365}{}^{trans}(trans) = 0.51 \pm 0.03$.[7] Starting from *cis*-AIP we get $\Phi_{365}{}^{cis}(trans) = 0.56 \pm 0.03$ and $\Phi_{365}{}^{cis}(cis) = 0.52 \pm 0.03$. We observed no effect of concentration ($10^{-3}$–$10^{-2}$ $M$) or of light intensity ($10^{-6}$ –$10^{-5}$ einstein/min) on these quantum yields. The fact that the quantum yields of *cis* and *trans* formation are about equal and add to unity is most readily explainable in terms of a common intermediate; a likely candidate is the $^3\pi,\pi^*$ state which should be twisted at 90° with respect to both isomers.[8] On the other hand, in the case of $^3$n,$\pi^*$ there should be two states, one with *cis* and one with *trans* geometry, separated from each other and from $^3\pi,\pi^*$ by an energy barrier, because in this case the N–N bond still has considerable double bond character.

In the gas phase at low pressures photolysis of *trans*-AIP yields no *cis*-AIP and *vice versa*, while in both cases $\Phi_{350}$(dec) = 1.0. As pressure is increased, however, by adding "inert" gas, M ($CO_2$), photolysis of one isomer yields the other and $\Phi_{350}$(dec) decreases. Thus for *trans*-AIP 0.248 torr and $CO_2$ 600 torr we obtain $\Phi_{350}{}^{trans}(\mathrm{dec}) = 0.18$, $\Phi_{350}{}^{trans}(trans) = 0.51$, $\Phi_{350}{}^{trans}(cis) = 0.31$, and for *cis*-AIP 0.09 torr and $CO_2$ 600 torr we obtain $\Phi_{350}{}^{cis}(\mathrm{dec}) = 0.27$, $\Phi_{350}{}^{cis}(cis) = 0.25$, $\Phi^{cis}(trans) = 0.48$. At very high pressures decomposition is even less. Thus in isooctane solution, which corresponds to a pressure of about 1000 atm, $\Phi_{365}{}^{trans}(\mathrm{dec}) = 0.025$ and isomerization is the major process, $\Phi_{365}{}^{trans}(cis) = 0.50$ (*trans*-AIP = $10^{-2}$ $M$). These results suggest two possible mechanisms. (1) At low pressure both *cis*- and *trans*-AIP dissociate from their $^1$n,$\pi^*$ states, but collision aids intersystem crossing to the $^3\pi,\pi^*$ state; from the latter there is no dissociation, but almost equal probability of return to the *cis*- or to the *trans*-ground state. There seems to be increasing evidence that pressure may aid intersystem crossing in the gas phase[9,10] and certainly crossing from $^1$n,$\pi^*$ to $^3\pi,\pi^*$ may be expected to be facile.[11] (2) The decrease in $\Phi$(dec) from 1.0 to 0.18 on the addition of 600 torr $CO_2$ shows that the lifetime of the state from which dissociation occurs has to be $>0.5 \times 10^{-9}$ sec. We have already remarked on the absence of fluorescence from AIP,[9] and recent work shows that $\Phi(\mathrm{fluor}) < 0.5 \times 10^{-5}$. As Collier, *et al.*,[12] have stated, this suggests that the actual lifetime of the singlet state is $<0.5 \times 10^{-10}$ sec since the natural radiative lifetime as calculated from the absorption spectrum is $1.0 \times 10^{-5}$ sec.[13] This calculation assumes that the radiative lifetimes of acyclic aliphatic azo compounds obey the standard formulas,[13] and there is evidence that this assumption is good at least for cyclic aliphatic azo compounds.[14] It is therefore quite possible that there is very rapid intersystem crossing to vibrationally excited levels of the triplet manifold, and it is from the latter that dissociation occurs. Collisional deactivation then occurs in the triplet manifold (see Figure 1).

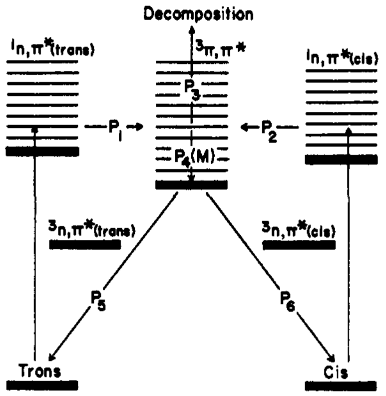

Figure 1. Possible states involved in the photochemistry of azoisopropane. $P_1$ is the probability of intersystem crossing from $^1$n,$\pi^*$ and so on. Thus $\phi^{trans}(cis) = P_1P_4(\mathrm{M})P_6$, etc. Typical $P$ values for (a) aqueous solution: $P_1 = P_2 = P_4(\mathrm{M}) = 1.0$, $P_3 = 0$, $P_5 = P_6 = 0.5$; (b) gas phase, (i) 0.2 torr, $P_1 = P_2 = P_3 = 1.0$, $P_4(\mathrm{M}) = P_5 = P_6 = 0$; (ii) 600 torr, $P_1 = P_2 = 1.0$, $P_3 = 0.2$, $P_4(\mathrm{M}) = 0.8$, $P_5 = 0.6$, $P_6 = 0.4$.

Engel[15] has recently carried out the photosensitization of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH), the cyclic analog of AIP, and has arrived at a value of 62–66 kcal mol$^{-1}$ for its triplet energy. Using benzene ($E_T$ = 84.0 kcal mol$^{-1}$) and benzophenone ($E_T$ = 68.5 kcal mol$^{-1}$) as sensitizers and *trans*-AIP ($2 \times 10^{-2}$ $M$) in methanol we found very little *cis* formation, $\Phi_{250}{}^{\mathrm{benz}}(cis) = 0.04 \pm 0.01$ and $\Phi_{303}{}^{\mathrm{benz}}(cis) = 0.06 \pm 0.02$, and practically no decomposition although we know from competitive quenching studies that *trans*-AIP is quenching the donor triplets at a rate which is close to diffusion controlled. Presumably sensitization produces *trans*-$^3$n,$\pi^*$ which is prevented from crossing to either $^3\pi,\pi^*$ or *cis*-$^3$n,$\pi^*$ by energy barriers.

However naphthalene ($E_T$ = 60.9 kcal mol$^{-1}$) sensitization caused very efficient isomerisation, $\Phi_{303}{}^{\mathrm{naph}}(cis) = 0.24$, and when photochemical equilibrium was reached 40% of the AIP was present as the *cis* isomer.

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(5) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

(6) S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).

(7) The symbolism is $\Phi_\lambda{}^{A}(B)$ = mol of product B formed per einstein of light absorbed by A when the latter is irradiated at $\lambda$ (m$\mu$).

(8) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1966, p 534.

(9) B. S. Solomon, T. F. Thomas, and C. Steel, *J. Am. Chem. Soc.*, **90**, 2249 (1968).

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(13) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).

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(15) P. S. Engel, *J. Am. Chem. Soc.*, **89**, 5731 (1967).

However in this case we found that *trans*-AIP quenched napthalene fluorescence in both methanol and isooctane at a rate close to the diffusion-controlled limit ($k_q = 1.14 \times 10^{10}$ sec$^{-1}$ $M^{-1}$ in isooctane) so that for azo $= 2 \times 10^{-2}$ $M$ $<4\%$ of the excited singlet naphthalenes cross into their triplet manifold. *cis*-AIP and DBH also quenched the naphthalene fluorescence at a similar rate, and there was efficient induced decomposition of the DBH, $\Phi_{303}{}^{\text{naph}}(\text{dec}) = 1.0$. Bartlett and Engel[16] have also recently observed the quenching of the fluorescence of aromatic compounds by azo compounds. Since the products and quantum yields for direct photolyses and the naphthalene-sensitized photolyses are so similar, it would appear that the latter is a case of singlet–singlet transfer.

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## The Preparation and Crystallographic Characterization of a Bridged Metallo-Carborane Complex Containing a Carbonium Ion Center: $(B_9C_2H_{10})_2CoS_2CH$

*Sir:*

In recent investigations of the chemistry of $(B_9C_2H_{11})_2M$ (M = transition metal) systems, we have attempted several Friedel–Crafts alkylations and have discovered a most unusual reaction, the product of which has been characterized by elemental analysis and a complete three-dimensional X-ray diffraction study.

When finely divided $K^+[(B_9C_2H_{11})_2Co]^-$ is stirred with several equivalents of aluminum chloride in carbon disulfide for 12 hr at room temperature, gas is evolved and the carbon disulfide acquires an orange color similar to that of the starting material. A fluffy yellow solid can be isolated in a highly variable yield from the filtered carbon disulfide solution. If a slow stream of hydrogen chloride is passed into the reaction mixture, however, the reaction time is halved, and a yield of 70% is consistently obtained.

Elemental analyses and a mass spectrometric molecular weight determination are consistent with the formulation of the complex as $(B_9C_2H_{10})_2CoS_2CH$. The $^1H$ nmr spectrum (acetone-$d_6$, 60 MHz) shows broad absorptions at $\delta$ 4.65 (4 H, cage C–H) and 11.5 (1 H, bridge C–H).

The molecular stereochemistry has been determined unambiguously by means of a single-crystal X-ray diffraction study.

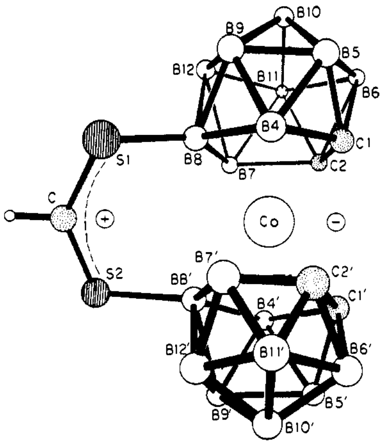

Figure 1. The $(B_9C_2H_{10})_2CoS_2CH$ molecule, projected onto the plane defined by Co, B(8), and B(8′). (Hydrogen atoms of the icosahedral cages are omitted for the sake of clarity.)

When $(B_9C_2H_{10})_2CoS_2CH$ is extracted with hexane in a Soxhlet extractor, it crystallizes as bright orange parallelepipeds in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ (no. 19) with $a = 10.92$, $b = 13.17$, $c = 12.87$ Å, $V = 1852$ Å$^3$. The observed density, $\rho_{\text{obsd}} = 1.421 \pm 0.0006$ g cm$^{-3}$, is in good agreement with the value calculated for $Z = 4$ ($\rho_{\text{calcd}} = 1.420$ g cm$^{-3}$). A set of X-ray diffraction data complete to sin $\theta = 0.42$ (Mo K$\alpha$ radiation) was collected with a 0.01° incrementing Buerger automated diffractometer, using a "stationary-background, $\omega$-scan, stationary-background" counting sequence. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. Using anisotropic thermal parameters for all nonhydrogen atoms, refinement converged to a discrepancy index of $R_F = 7.88\%$ for the 1557 independent, nonzero reflections. All atoms, including each of the 21 hydrogen atoms, have been located unambiguously. No attempt was made to determine the absolute configurations of the molecule, but it should be noted that since the space group is nonpolar, bond distances will not be affected by ignoring the imaginary part of the cobalt and sulfur scattering factors.

The geometry of the $(B_9C_2H_{10})_2CoS_2CH$ molecule is shown in Figure 1. The cobalt atom is "sandwiched" between the two mutually staggered carborane moieties and is symmetrically bonded to all five atoms of each basal pentagon. Cobalt–boron distances range from 2.02 to 2.13 Å (average 2.08 Å), and cobalt–carbon distances vary from 2.04 to 2.06 Å (average 2.05 Å). [These values are in good agreement with the mean Co–B (or C) distance of 2.07 Å in the disordered $Cs^+[(B_9C_2H_{11})_2Co]^-$.[1]

The two icosahedra which share the cobalt atom as a common apex are further linked *via* an S–CH–S bridge which spans B(8) and B(8′), *i.e.*, the central of the three boron atoms in each of the basal pentagons. Individual bond lengths within this bridge (in Å) are: B(8)–S(1) = 1.85 ± 0.02, S(1)–C = 1.71 ± 0.02, C–S(2) = 1.62 ± 0.02, S(2)–B(8′) = 1.90 ± 0.02; angles are [B(8)–S(1)–C] = 108 ± 1°, [S(1)–C–S(2)] = 133 ± 2°, and [C–S(2)–B(8′)] = 109 ± 1°. A comparison of the C–S(1) and C–S(2) distances shows

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