

as compared to 0.80 for photoreduction of the ketone by benzhydrol in similar solutions containing no diene.

Use of other compounds as sensitizers gives very interesting results. β -Acetonaphthone and α -naphthaldehyde sensitize isomerization but give photo-stationary mixtures that are much richer in *trans*-diene. Dibenzalacetone, on the other hand, is essentially inert as a sensitizer. The data are summarized in Table I.

Carbonyl compound	<i>trans/cis</i> ratio at the stationary state	Phosphorescence O \rightarrow O Band ²
Acetophenone	1.23	3850
Benzophenone	1.30	4100
Benzil	2.25	4630
β -Acetonaphthone	2.50	4830
α -Naphthaldehyde	13	5100
Dibenzalacetone	No isomerization	5400

Sensitized isomerization almost certainly involves energy transfer from the triplet state of the carbonyl compound^{1,3} to the diene with production of a triplet state of the diene. There is no report in the literature of observation of phosphorescence of simple, conjugated dienes; therefore, it is quite possible that the excited singlet states, produced by light absorption, do not decay by way of triplet levels. Consequently, the sensitized reactions are of considerable interest for two reasons: First, a method is now available for the production of a new group of potentially valuable chemical intermediates. Second, the use of a suitably graded series of carbonyl compounds should provide an easy method for estimation of the energies of the triplet states of dienes, a matter of substantial theoretical interest.⁴

It probably is safe to assume that energy transfer will not occur if the diene triplet lies much above the triplet state of the sensitizer, and it is likely that the efficiency will be low if the O \rightarrow O band in the spectrum of the sensitizer lies at longer wave length than the corresponding transition of the diene.^{5,6} Characteristics of the phosphorescence spectra of the various carbonyl compounds are included in Table I. Since acetophenone and benzophenone give close to the same stationary state compositions, we infer that their triplets are above the transition energies of both *cis*- and *trans*-piperylene. β -Acetonaphthone and α -naphthaldehyde establish stationary states in which the *trans* isomer predominates. We therefore infer that the S_g-T₁ transition of *cis*-piperylene lies at slightly longer wave length than that of *trans* isomer.⁷ Since

(2) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

(3) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

(4) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(5) At 0°, the temperature at which most of our experiments have been carried out, there is a reasonable possibility that energy transfers which are slightly "uphill" may occur. These activated processes could take place between the triplet and vibrationally excited diene molecules.

(6) C. Reid, "Excited States in Chemistry and Biology," Butterworth Scientific Publications, London, 1957.

(7) Since energy transfer to the *trans* isomer has become relatively inefficient.

dibenzalacetone shows no sensitizing action, both of the diene transitions must be at shorter wave lengths than 5400 Å. This estimate agrees very well with the results of Evans,⁴ who observed a broad band in the 3500-5000 Å. region (O-O band at 4800 Å.) in the spectrum of butadiene in the presence of oxygen. The agreement is important since it establishes the fact that S_g-T₁ transitions observed by the oxygen-perturbation method are not significantly altered by strong interactions between oxygen and the perturbed molecule.

Attempts to isomerize piperylenes by direct irradiation have given both positive⁸ and negative⁹ results. Apparently the process was slow, even in the successful experiments, although the results are difficult to interpret without a complete description of the light sources and other equipment. Shuikin and Tulupov⁸ reported that the stationary state contained 73% *cis*- and 27% *trans*-diene. The result may indicate that excited singlet and triplet states partition themselves differently between *cis* and *trans* ground states when they decay.

We wish to acknowledge stimulating and helpful discussion with Professor G. W. Robinson and Dr. M. F. A. El-Sayed.

(8) N. I. Shuikin and V. A. Tulupov, *Vestnik Moskov. Univ.*, **9**, No. 8, *Ser. Fiz-Mat. i Estestven. Nauk*, No. 5, 91-5 (1954); *C.A.*, **49**, 3776 (1955).

(9) R. L. Frank, R. D. Emmick and R. S. Johnson, *J. Am. Chem. Soc.*, **69**, 2313 (1947).

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THE TRIPLET STATE OF METHYLENE IN SOLUTION

Sir:

Study of the chemistry of the CH₂ "radicals" produced by decomposition of diazomethane has been an exceptionally active field during recent years.¹⁻⁸ Doering¹ first noted the exceedingly indiscriminate action of methylene produced by photolysis of diazomethane, and Skell³ inferred on a semi-intuitive basis that the stereospecificity of the reaction of the addition of CH₂ to olefins indicated that the fragment was produced in a singlet state. Herzberg⁴ reported incontrovertible evidence that vapor phase photolysis of diazomethane produces singlet CH₂ that decays to a triplet in the presence of high pressures of an inert gas. Chemical evidence for the decay mechanism has been harder to obtain since the gas phase studies are complicated by the fact the product formed by addition of singlet methylene to an olefin is a "hot"

(1) W. v. E. Doering, R. G. Buttery, R. G. Laughlin and N. Chanduri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(2) W. v. E. Doering and P. La Flamme, *ibid.*, **78**, 5447 (1956).

(3) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959).

(4) G. Herzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959).

(5) H. M. Frey, *Proc. Roy. Soc. (London)*, **A251**, 575 (1959).

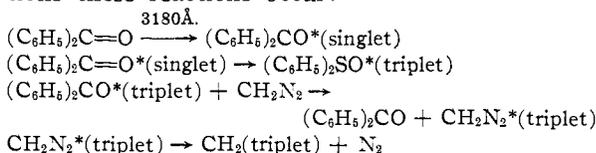
(6) D. B. Richardson, M. C. Simmons and I. Dvoretzky, *J. Am. Chem. Soc.*, **82**, 5001 (1960).

(7) F. A. L. Anet, R. F. W. Bader and A. M. Van der Auwera, *ibid.*, **82**, 3217 (1960).

(8) H. M. Frey, *ibid.*, **82**, 5947 (1960).

cyclopropane that can isomerize if it is not deactivated rapidly.^{5,9} Reactions in solution are simpler since deactivation of hot products must occur very rapidly; however, no one has thus far been able to "cool" singlet methylene to the triplet state in solution before it undergoes chemical reaction.

We have succeeded in producing a selective form of methylene by photosensitized decomposition of diazomethane. The spectrum of diazomethane shows virtually no absorption in the 3130 Å. region, so it is possible to selectively activate benzophenone in the presence of diazomethane. Suitable filters are used to eliminate virtually all of the radiation between 3660 and 7000 Å. from a high pressure mercury arc. Under these conditions these reactions occur:¹⁰



We have studied the decomposition of diazomethane in cyclohexene under a variety of conditions. The C₇ products are not resolved completely by our vapor chromatographic procedures. Norcarane and 1-methylcyclohexene are well separated from each other and from a mixture of 3- and 4-methylcyclohexene, which appears as a single, symmetrical peak in the chromatograms. As has been reported previously, direct photolysis gives a mixture of all products as does uncatalyzed thermal decomposition. Photosensitized decomposition and decompositions catalyzed by copper powder and ferric dipivaloylmethide give different results as indicated in Table I.

TABLE I

	Relative Yields		
Direct photolysis	1.0	0.24	1.3 ^a
Thermal decomposition at 265°	1.0	0.43	1.7
Sensitized photolysis	1.0	Trace	0.42 ^a
Thermal decomposition catalyzed by Fe(DPM) ₃	1.0	~0	~0
Thermal decomposition catalyzed by copper powder	1.0	~0	~0

^a Infrared analysis indicates that approximately equal amounts of 3- and 4-methylcyclohexene are produced.

We also have studied the reactions of methylenes, produced in various ways, with *cis*- and *trans*-2-butene in octane solution. Direct photolysis in the presence of *trans*-2-butene produces *trans*-dimethylcyclopropane and the expected products of insertion reactions. Under the same conditions *cis*-2-butene gives *cis*-dimethylcyclopropane along with at least one olefin which is not separated from the cyclopropane by our vapor chromatographic procedures. The results are in agreement with

(9) B. S. Rabinovitch and D. W. Setzer, *J. Am. Chem. Soc.*, **83**, 750 (1961).

(10) For an account of the photochemistry of benzophenone see G. S. Hammond and W. M. Moore, *ibid.*, **81**, 6334 (1959), and H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

previous reports^{2,3,5} Photosensitized decomposition in the presence of *cis*-2-butene produces *cis*- and *trans*-dimethylcyclopropane in a 2:1 ratio. A small amount of another non-olefinic compound, known not to be any product yet reported from the reactions of CH₂ with the butenes, also is produced. Photosensitized decomposition in the presence of *trans*-2-butene gives *trans*-dimethylcyclopropane, a small amount of *cis*-dimethylcyclopropane, and a trace of an olefinic compound. Decomposition of diazomethane induced by Fe(DPM)₃ and copper powder produces a species that reacts with the butenes to give only the cyclopropanes expected from stereospecific addition.¹¹ In the photosensitized, iron chelate- and copper powder-catalyzed decompositions the yields of products from reaction with the butenes are low; virtually no attack on the solvent, octane, occurs. Considerable amounts of polymethylene and low molecular weight hydrocarbons are formed, indicating that attack on diazomethane is the principal reaction of the selective reagents. There is no detectable isomerization of the butene under the experimental conditions, and no benzophenone is consumed when it is used as a photosensitizer.

Photosensitized decomposition surely produces the triplet state of CH₂; the chemical behavior of the species is close to that predicted by Skell³ and observed in the vapor phase by Frey.⁸ The results are explicable by assuming that methylene triplet adds to double bonds to produce a very short-lived biradical in which the electron spins are unpaired. Internal rotation before spin inversion occurs would lead to over-all, non-stereospecific addition. However, it is noteworthy that *cis*- and *trans*-2-butenes do not give the same product mixture. This result shows that spin inversion must be a very fast process in solution. The small yield of methylcyclohexenes produced in the photosensitized reaction comes from a trace of singlet decomposition, a result of inefficient light filtering.

The results also show that decompositions induced by copper powder and the ferric chelate do not produce either form of free methylene. Since the general reactivity of the reagent formed in the chelate-catalyzed reactions resembles that of the triplet, we are tempted to formulate the species as a charge-transfer complex of triplet CH₂ with the metal chelate. Delivery of the CH₂ fragment to an olefin would produce the biradical *in the field of a paramagnetic, heavy metal*. In such an environment spin relaxation should be essentially instantaneous. A similar account could be given to the effects of copper except that in this case it seems logical to formulate the intermediate as copper methylene as Yates¹² has done in discussing copper-catalyzed decomposition of diazoketones.

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(11) Professor W. v. E. Doering (Yale) and Professor P. S. Skell (Penn State) have informed us that work in their respective laboratories with decompositions catalyzed by cupric ion (Yale) and metallic copper (Penn State) give results similar to ours.

(12) P. Yates, *J. Am. Chem. Soc.*, **74**, 5376 (1952).