of benzophenone is a triplet. It is reasonable to expect that transfer of energy from benzophenone triplets to other molecules will excite the latter to triplet states. In fact, the observation that just such a process occurred with biacetyl was a key part of the study by Bäckström and Sandros,[2] who observed induced phosphorescence of biacetyl. The use of benzophenone and other sensitizers to effect selective excitation of other molecules to triplet states offers both a new tool for the study of mechanism and the possibility of effecting new photochemical reactions. A nice example seems to be provided by the recent report by Schenck and Steinmetz[3] that benzophenone serves as a photosensitizer for the addition of maleic anhydride to benzenoid nuclei.

Table I contains the results of a series of experiments in which solutions of ethyl pyruvate were irradiated (a) with no other solute present, (b) in the presence of excess benzophenone and (c) in the presence of both benzophenone and benzhydrol. Appropriate filters were used, and concentrations were adjusted so that 5% or less of the light was absorbed by ethyl pyruvate in the experiments with benzophenone. Sensitized decomposition of ethyl pyruvate not only occurs but has a higher quantum yield than the direct excitation process. Decomposition of the ester must involve triplet states in the sensitized experiment, and the evidence that direct photolysis follows the same path is presumptive. It is also certain that production of the triplet state of ethyl pyruvate by energy transfer from benzophenone triplets is a more efficient process than the intersystem crossing from the excited singlet produced by direct excitation of the ketoester. Additional evidence for the efficiency of intermolecular energy transfer is quenching of photoreduction of benzophenone by benzhydrol in the presence of ethyl pyruvate. The quantum yield for disappearance of benzophenone becomes immeasurably small in the presence of 0.050 M ethyl pyruvate.

TABLE I

DIRECT AND SENSITIZED PHOTOLYSIS OF ETHYL PYRUVATE IN BENZENE SOLUTION

Ethyl pyruvate mole l.$^{-1}$	Benzophenone mole l.$^{-1}$	Benzhydrol mole l.$^{-1}$	ϕ_{ketone}	ϕ_{ester}
0.050	none	none	...	0.17
.050	none	none	...	.14
.050	0.100	none	...	.32
.010	.050	0.50	0.11	.27
.050	.100	.50	.00	.31
none	.100	.50	.80	...

A corollary of the theory presented is the prediction that triplet states which have excitation energies much lower than ethyl pyruvate triplets should be incapable of acting as sensitizers.[4] The phosphorescence of β-acetonaphthone is green (maximum at 5100 Å.) so the triplets must lie lower than ethyl pyruvate triplets. Irradiation of a benzene solution containing ethyl pyruvate and excess β-acetonaphthone results in no decomposition of the ketoester. The ketone acts only as an internal filter, thereby preventing direct photolysis of the ester.

Experimental: Determination of Quantum Yields.—The apparatus has been described previously.[1] The filter system consisted of a Corning 7–54 glass filter in series with a solution containing nickel sulfate and cobaltous sulfate. The transmission maximum is close to 3100 Å.; 2% of incident 3660 Å. light is transmitted. All reaction mixtures were degassed. Residual ethyl pyruvate was determined by vapor chromatography and benzophenone was determined spectrophotometrically.

Reaction Products.—One hundred milliliters of a solution containing 0.2 M benzophenone and 0.1 M ethyl pyruvate in toluene was irradiated in a Hanovia Type S 200-watt quartz immersion apparatus for 4 hr. using a filter with a cutoff at 2800 Å. A total of 175 ml. of gas, non-condensable at −78°, was collected. Infrared analysis of the gas showed it to be 90% carbon monoxide and 10% carbon dioxide. The liquid residue then was warmed to 40°, causing distillation of a volatile liquid which was shown by infrared analysis to be acetaldehyde. In other experiments the liquid residue was sampled directly and analyzed by vapor chromatography. Only one new constituent, acetaldehyde, was detected.

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(3) G. O. Schenck and R. Steinmetz, *Tetrahedron Letters*, No. 21, 1 (1960).

(4) It is entirely possible that even though energy transfer is slightly uphill, the process may still be fairly efficient. We know only that benzophenone and ethyl pyruvate triplets have similar energies because of the qualitative similarity in the color (but not intensity) of their phosphorescence.

PHOTOSENSITIZED *CIS-TRANS* ISOMERIZATION OF THE PIPERYLENES

Sir:

We have observed that a number of carbonyl compounds may be used as efficient photosensitizers for the *cis-trans* isomerization of piperylene (1,3-pentadiene). Thus, irradiation of a benzene solution originally containing 0.12 M benzophenone and 0.20 M *cis*-piperylene in a Hanovia quartz immersion reactor, using a filter with a cutoff at 2800 Å., converts the diene to a photostationary mixture within three hours. In this mixture the *trans*/*cis* ratio is about 1.3. A solution containing 0.05 M benzophenone and 0.10 M *cis*-diene was irradiated in the apparatus used in quantitative studies[1] for a time sufficient to convert 21% of the *cis*-diene to its *trans* isomer. The quantum yield calculated from the data was 0.29. The actual quantum yield must be slightly higher since the reverse reaction reduces the amount of net conversion. A similar mixture, except for the inclusion of 0.5 M benzhydrol, was irradiated and the rate of disappearance of benzophenone measured. The quantum yield for ketone destruction was 0.09

(1) G. S. Hammond and W. M. Moore, *J. Am. Chem. Soc.*, **81**, 6334 (1959); G. S. Hammond, W. M. Moore and R. P. Foss, *ibid.*, in press.

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 photostationary 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.

TABLE I

SENSITIZED *cis-trans* ISOMERIZATION OF PIPERYLENE

Carbonyl compound	*trans/cis* ratio at the stationary state	Phosphorescence O → 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 0→0 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–T_1 transition of *cis*-piperylene lies at slightly longer wave length than that of *trans* isomer.[7] Since 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–T_1 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 positive[8] and negative[9] 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 Tulupov[8] 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.

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

(3) H. L. J. Bäckstrom 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.

(8) N. I. Shuikin and V. A. Tulupov, *Vestnik Moskow. 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 CH_2 "radicals" produced by decomposition of diazomethane has been an exceptionally active field during recent years.[1–8] Doering[1] first noted the exceedingly indiscriminate action of methylene produced by photolysis of diazomethane, and Skell[3] inferred on a semi-intuitive basis that the stereospecificity of the reaction of the addition of CH_2 to olefins indicated that the fragment was produced in a singlet state. Herzberg[4] reported incontrovertible evidence that vapor phase photolysis of diazomethane produces singlet CH_2 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).