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Mechanisms of Photochemical Reactions in Solution. XXVI. Photosensitized Decomposition of Azo Compounds

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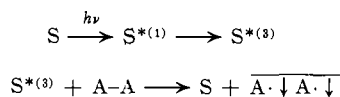
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Decomposition of an azoester (ethyl 2,2'-azobisisobutyrate), an azonitrile (azo-1-cyanocyclohexane), and the related ketenimine (N-(1-cyanocyclohexyl)pentamethyleneketenimine) has been carried out by energy transfer in solution and the results compared with data for thermolysis and direct photolysis of these compounds. Quantum yields for decomposition of the azoester have been measured using a variety of sensitizers and the results correlated with properties of their triplet states. Photodecomposition of the azonitrile and ketenimine has been effected under conditions where geminate recombination is the only source of 1,1'-dicyanobicyclohexyl. An explanation for the observed threefold decrease in yield of this product in sensitized as compared with unsensitized photodecomposition of ketenimine is sought, and the significance of the absence of such a decrease for the azonitrile is examined.

We have presented the results of a comparison of the efficiencies of radical production by thermolysis and direct photolysis of ethyl 2,2'-azobisisobutyrate (EAB) and concluded that the two modes become essentially identical decomposition processes by the time separation of geminate radicals can occur.¹ Further interest in the photolysis of azo compounds is aroused by the possibility of forming a triplet state prior to dissociation. We have already suggested that, in this situation, the amount of geminate recombination *might* be reduced since the radical pair should be produced with parallel electron spins.¹ The chances of observing such an effect would clearly be enhanced if spin transitions of the radical pair are slow compared to diffusive movements and also if the process referred to by Noyes² as secondary recombination is unimportant.

Such a triplet intermediate could be produced by direct photolysis of an azo compound if the excited state of the parent molecule were to undergo intersystem crossing to a triplet state before decomposition occurred. However, the quantum yield for the production of radicals from EAB in carbon tetrachloride is virtually unaffected by the addition of iodine.¹ Since iodine possesses a low-energy triplet state ($E_T = 34$ kcal./mole),³ the result implies either that triplets of the azo compound are not formed or that, if they are, their lifetimes must be very short. Otherwise transfer of triplet excitation to iodine should have occurred.

The problem should be susceptible to more definitive study if photolysis is accomplished by transfer of triplet excitation to an azo compound from a suitable sensitizer. We have recently observed several examples of photosensitized decomposition reactions in which energy transfer apparently involves bond-breaking in the acceptor.⁴



We will now report the results of a detailed study of the efficiency of radical production in photosensitized decomposition of EAB and two related compounds.

(1) G. S. Hammond and J. R. Fox, *J. Am. Chem. Soc.*, **86**, 1918 (1964).

(2) R. M. Noyes, *ibid.*, **77**, 2042 (1955).

(3) A. G. Porter and F. Wilkinson, *Proc. Roy. Soc. (London)*, **A264**, 1 (1961).

(4) G. S. Hammond, J. R. Fox, F. G. Moses, and W. Hardham, unpublished.

Results and Discussion

Quantum Yields for Photosensitized Decomposition of EAB.—Benzene solutions containing sensitizers and azoester were irradiated at 25° using 3130 Å. light isolated from the emission of a high-pressure mercury arc with suitable filters. Since the extinction coefficients of the sensitizers at that wave length range from 68 to 5000, whereas that of the azoester is 3.0, adjustment of sensitizer concentration ensured that 97.2 to 99.5% of the incident radiation was absorbed by the sensitizer. Results arising from the use of 3660 Å. light with anthracene ($\epsilon_{sens}/\epsilon_{EAB} = 78.1$ at 3660 Å) were not significantly different. Disappearance of EAB was followed spectrophotometrically at several wave lengths and light intensities were monitored using the ferrioxalate actinometer.⁵

Quantum yields for the decomposition of EAB, Φ_{EAB} , were recorded with different concentrations of one sensitizer (anthracene) and at different stages in many of the reactions. The results, which were found to be independent of both variables, are summarized in Table I where lowest triplet energies of the sensitizers (E_T), solution lifetimes of these states (τ), and efficiencies of intersystem crossing ($\Phi_{i.c.}$) are also shown where possible. Details of the individual measurements, from which these mean values of Φ_{EAB} were derived, are given in Table VI (Experimental).

Unfortunately, attempts to determine a value for the energy of the lowest triplet state of EAB were unsuccessful. However, assumption that EAB has the $n \rightarrow \pi^*$ configuration in its lowest triplet suggests that 70 kcal. per mole is a reasonable estimate of this quantity.⁶ Table I shows that the low-energy sensitizers, anthracene and 1,2-benzanthracene, promote EAB decomposition with high efficiency. Thus it would seem that EAB is an effective acceptor of energy from sensitizer triplets having insufficient excitation energy to promote the substrate to its spectroscopic triplet and that these systems involve energy transfer with nonvertical transitions.^{4,7}

There is interesting variation in the efficiencies of the sensitized reactions as is shown by quantum yields listed in Table I. Indeed, decomposition sensitized

(5) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956); see also footnote 11 of ref. 1.

(6) Estimated from the $n \rightarrow \pi^*$ absorption maximum at 3630 Å. (see ref. 1) and by assuming a singlet-triplet splitting of 3000 cm^{-1} .

(7) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2515, 2516 (1963).

TABLE I
QUANTUM YIELDS FOR PHOTOSENSITIZED DECOMPOSITION OF
EAB IN BENZENE^a AT 25°

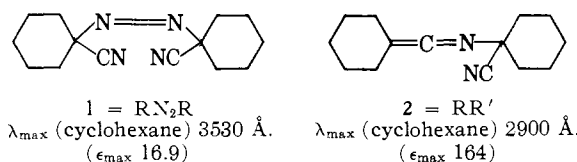
Sensitizer	[Sens.], mole l. ⁻¹	$E\tau$, kcal. mole ⁻¹	$10^{-4} \tau$, sec.	$\Phi_{i.o.}$	Φ_{EAB}
Anthracene	0.01, 0.05 ^b	42.0 ^c	9.1 ^e	...	0.18
1,2-Benzanthracene	0.01	47.2 ^c	1.6 ^e32
1-Naphthyl phenyl ketone	.01	57.5 ^d06
2-Acetonaphthone	.10	59.3 ^d	10 ^f10
Phenanthrene	.10	61.7 ^c	0.93 ^e	0.68 ^d	.30
Triphenylene	.10	68.0 ^c	0.56 ^e	0.95 ^d	.40
Benzophenone	.30	68.5 ^d	1.6×10^{-2g}	1.00 ^d	.06

^a All samples degassed; [EAB]₀ = 10⁻¹ mole l.⁻¹. ^b 3660 Å. irradiation. ^c Ref. 8. ^d Ref. 9. ^e Ref. 3. ^f Ref. 10. ^g Ref. 11.

by triphenylene approaches direct photolysis ($\Phi_{EAB} = 0.42$)¹ in efficiency. Two factors of obvious importance are the efficiencies of production of sensitizer triplets by intersystem crossing and the rate of unimolecular decay of the sensitizer triplets. Thus, the relatively low efficiency of benzophenone as a sensitizer may be attributed to the very rapid nonradiative decay of benzophenone triplets.¹¹ However, 2-acetonaphthone is relatively inefficient despite the fact that the triplets are relatively long lived in benzene solution.¹⁰ We hesitate to seek other explanations of the varying efficiencies of "nonclassical" energy transfer since the lifetimes of triplets in solution are poorly understood. In fact, Livingston and Ware¹² have recently suggested that unimolecular decay of triplets in solution is largely controlled by adventitious quenchers. If this is true, it is obvious that the quenching action cannot be predicted in any solution in which chemical changes are occurring.

Direct and Sensitized Photodecomposition of Azo-1-cyanocyclohexane and Related Ketenimine.—For the reasons already outlined, measurement of the extent of the cage effect in the sensitized decomposition of azo compounds was attempted. Of course, such a study requires that combination of kinetically free radicals be eliminated.

Scavenger Evaluation.—Conventional scavengers (e.g., iodine, α, α -diphenyl- β -picrylhydrazyl) are unsuitable for scavenging radicals produced by sensitized reactions since they may complex with solvent, absorb light, or interfere with the energy-transfer processes being studied. Our approach to this problem involved the use of cumene as both solvent and scavenger for the photodecomposition of azo-1-cyanocyclohexane (1) and the related ketenimine 2 in dilute solution (10⁻⁴ M).



Earlier studies^{13,14} showed that thermal decomposition of 1 and 2 in solutions containing low concentrations of reactive scavengers can be discussed in terms of

(8) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

(9) A. A. Lamola and W. G. Herkstroeter, unpublished.

(10) W. G. Herkstroeter, unpublished.

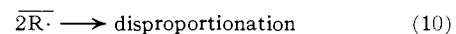
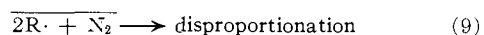
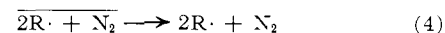
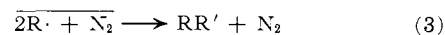
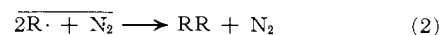
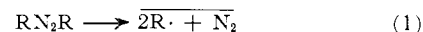
(11) H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

(12) R. Livingston and W. R. Ware, *J. Chem. Phys.*, **39**, 2593 (1963).

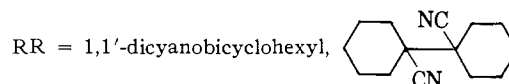
(13) C.-H. S. Wu, G. S. Hammond, and J. M. Wright, *J. Am. Chem. Soc.*, **82**, 5386 (1960).

(14) H. P. Waits and G. S. Hammond, *ibid.*, in press.

the mechanisms



S = a scavenger



Since we have demonstrated similarity between thermal and photochemical decomposition of EAB,¹ there is no reason to suppose that this general scheme is *fundamentally* changed in photolysis.

In order to demonstrate the efficacy of cumene as a scavenger of free radicals, formed in reactions 4 and 8, the yield of RR from the direct and complete photolysis of RN₂R (10⁻⁴ M) in cumene was measured by isotope dilution analysis, with and without the addition of an established scavenger, *n*-butyl mercaptan (10⁻³ M). The results are reported in Table II. Since 0.2 M *n*-butyl mercaptan is sufficient to scavenge all free radicals produced by thermal decomposition of an equimolar amount of another azonitrile,¹⁵ there can be no doubt that scavenging is complete in the present experiment involving mercaptan.

TABLE II
RR YIELDS FROM DIRECT PHOTOLYSIS^a OF RN₂R (10⁻⁴ M)
IN CUMENE AT 28°

% RR No addition ^b	% RR Addition of <i>n</i> -BuSH (10 ⁻³ M) ^c
19.00	18.66
19.24	18.43
18.97	18.85
19.47	19.13
19.39	19.18

^a Light of wave length greater than 3300 Å. employed. All samples degassed. ^b Mean value 19.2. ^c Mean value 18.9.

Comparison of the yields of RR in the two experiments shows that *cumene is a completely effective scavenger of free cyanocyclohexyl radicals.*

Ketenimine Formation.—Thermal¹⁶ and photochemical¹⁷ decomposition of azonitriles results in the formation of an isomeric coupling product ketenimine (RR' in the present system); RR' isomerizes thermally and photochemically to give the more stable RR (reactions 6 and 7). Thus, when making comparisons between thermal and photochemical experiments, it must be ensured that the isomerization of RR' is not allowed to

(15) G. S. Hammond, J. N. Sen, and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

(16) G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin, and R. T. Keys, *ibid.*, **82**, 5394 (1960), and cited references.

(17) P. Smith and A. M. Rosenberg, *ibid.*, **81**, 2037 (1959).

add to the amount of RR produced. Fortunately, this presents no problem in thermolysis and direct photolysis of RN_2R since the thermal experiments of Waits and Hammond¹⁴ were carried out in the presence of scavengers which destroy ketenimine and direct photolysis of the azo compound was accomplished selectively by use of a suitable filter. Following our observation that irradiation of sensitizers in the presence of RR' causes destruction of the latter, we determined to carry out the sensitized decomposition of RN_2R under conditions where RR' would be destroyed at birth. Experiments were carried out in the presence of dilute mineral acid, conditions expected to lead to rapid hydrolysis of the ketenimine.¹³ Control experiments showed that the yield of RR produced by direct and selective photolysis of RN_2R ($10^{-4} M$) in cumene at 28° was the same in the absence and presence of hydrogen chloride ($10^{-3} M$) and water ($5 \times 10^{-3} M$). Thus the addition of acid does not destroy components of the system other than RR' .

Photodecomposition of RN_2R .—Cumene solutions containing RN_2R ($10^{-4} M$), triphenylene ($10^{-3} M$) as sensitizer, and dilute acid were irradiated at 28° using predominantly 3130 Å. light. The yields of RR were measured by isotope dilution analysis and completeness of reaction was shown by the constancy of results after different periods of irradiation. Results are shown in Table III together with data for direct photolysis of RN_2R in the presence of acid and for thermolysis (80°) in chlorobenzene with low concentrations of bromine or iodine as scavengers.¹⁴

TABLE III

RR YIELDS FROM DECOMPOSITION OF RN_2R^a

Direct photolysis ^b (28°) in cumene	Sensitized photolysis ^c (28°) in cumene	Thermolysis ^d (80°) in chlorobenzene
$[RN_2R]_0 = 10^{-4}$	$[RN_2R]_0 = 10^{-4}$	$[RN_2R]_0 = 10^{-5}$
$[HCl]_0 = 10^{-3}$	$[HCl]_0 = 10^{-3}$	Low concentra-
$[H_2O]_0 = 5 \times 10^{-3}$	$[H_2O]_0 = 5 \times 10^{-3}$	tions of Br_2 or
	[Triphenylene] = 10^{-3}	I_2
% RR	% RR	% RR
20.03	17.65	
19.85	17.89	
19.91	17.52	
19.97		
19.87		
Mean 19.9	17.7	9.4

^a All samples degassed; units of concentration are mole l^{-1} .

^b Irradiation with light of wave lengths greater than 3300 Å.

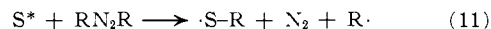
^c 2900–3500 Å. irradiation. ^d Ref. 14.

Various control experiments were also carried out. Triphenylene ($10^{-3} M$) was irradiated in cumene with and without the addition of RN_2R ($10^{-3} M$) and for a period corresponding to that required for complete decomposition of RN_2R . Comparison of ultraviolet absorption spectra before and after irradiation showed that the sensitizer was not consumed in either case. These experiments show that the sensitizer does not constitute part of any reaction product and that it is acting merely as an agent for energy transfer. They also show that this energy transfer is accomplished by triphenylene itself rather than by a derivative.

The absence of any marked difference between the yields of RR resulting from sensitized and un sensi-

tized decomposition of RN_2R (Table III) is suggestive of one of two circumstances. Either (1) both decompositions occur from the same electronically excited state or (2) the sensitized decomposition involves a triplet radical pair but the spin-inversion process is faster than the rate-determining step for formation of RR (presumably the ejection of N_2 from the cage). Since we have demonstrated similarity between thermolysis and direct photolysis of EAB¹ and inferred that direct photolysis of this azo compound does not involve a triplet intermediate (*vide infra*), we believe that the second alternative obtains.

An alternative mechanism for sensitized decomposition might be formulated using the generalized mechanism suggested by Schenck.¹⁹



Such mechanisms seem to be excluded by the observation that triphenylene survives unchanged when it functions as the sensitizer and by the fact that the efficiency of formation of R–R by geminate recombination is similar in direct and sensitized photolysis. If a different species, such as $\cdot S-R$, were involved in the reaction, the yield of RR by geminate recombination would surely be markedly reduced in the sensitized reaction.

The yield of cage coupling product from direct photolysis of RN_2R in cumene or chlorobenzene at 28° (19%) compares with a value of 9.4% for thermal decomposition in chlorobenzene at 80° . Since it has been concluded that the fundamental processes in thermolysis and direct photolysis of azo compounds are essentially identical, this would seem to afford a further example of the effect of temperature on diffusion of geminate radicals from the cage. Thus a change from 80 to 28° increases the yield of cage coupling product by a factor of two.

Photodecomposition of RR' .—Cumene solutions containing RR' ($1.43 \times 10^{-4} M$) were irradiated at 28° in the presence and absence of triphenylene ($10^{-3} M$) as sensitizer. Direct photolysis was effected with 3130 Å. light while the sensitized reaction was carried out with light of wave lengths greater than 3300 Å. to ensure that no radiation was absorbed directly by the ketenimine. Completeness of reaction was shown as before. The results are recorded in Table IV. Control experiments similar to those described in the previous section showed that the sensitizer was not consumed in the reaction.

TABLE IV

RR YIELDS FROM DECOMPOSITION^a OF RR'

Direct photolysis (28°) ^b in cumene	Sensitized photolysis (28°) ^c in cumene	Thermolysis ^d (80°) in chlorobenzene
$[RR']_0 = 1.43 \times 10^{-4}$	$[RR']_0 = 1.43 \times 10^{-4}$	$[RR']_0 = 1.72$
	[Triphenylene] = 10^{-3}	$\times 10^{-5}$
		Low concn. of DPFH
% RR	% RR	% RR
24.12	8.20	
24.05	8.32	
Mean 24.1	8.3	27.0

^a All samples degassed; units of concentration are mole l^{-1} .

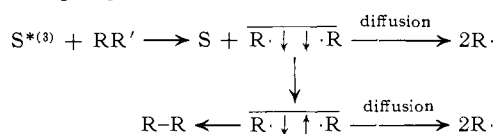
^b Irradiation with light of wave lengths greater than 2900 Å.

^c Above 3300 Å. ^d Ref. 14.

(18) M. Talát-Erben and S. Bywater, *J. Am. Chem. Soc.*, **77**, 3710 (1955). Our experiments showed hydrolysis in cumene to be virtually instantaneous.

(19) G. O. Schenck, I. von Wilucki, and C. H. Krauch, *Chem. Ber.*, **95**, 1409 (1962).

In contrast to the results observed with RN_2R , there is a threefold difference between the yields of RR in the sensitized and direct photolysis of RR' . The decrease in yield of the product of geminate recombination of radical pairs could be attributed to two classes of explanation. First, one might presume that fewer pairs of R· radicals are formed in the sensitized reaction. This would be reasonable grounds for invoking reactions analogous to 11 if it were not for the fact that the sensitizer is apparently unchanged during the reaction. A second kind of interpretation invokes the assumption that there is a special barrier to recombination of the radical pairs produced in the sensitized reaction. We favor the latter explanation and suggest that *the barrier arises because the radical pair is produced as a triplet*. Apparently the rate at which the radical pairs are separated by diffusive excursions is comparable to the rate of spin inversion which must precede coupling.



The implications of this postulate are interesting. We have inferred that the radical pairs produced in sensitized decomposition of RN_2R undergo spin inversion at a rate that is fast compared to the rate of diffusion. The principal difference between the two cases is the separation of the pair of R· radicals from the azo compound by a nitrogen molecule at the time of their genesis. We suggest that separation of the two radicals by an inert molecule results in a very weak interaction between the radicals. The separation between the triplet and singlet states of the radical pair will be very small if the interaction is weak; consequently the rate of spin inversion will be fast in comparison with the rate in radical pairs in which interactions are stronger. One might characterize the pair of radicals ($\overline{\text{R} \cdot \downarrow \downarrow \cdot \text{R}}$) produced by sensitized decomposition of RR' as a "tight" radical pair and designate the triplet aggregate ($\overline{\text{R} \cdot \downarrow \text{N}_2 \downarrow \cdot \text{R}}$) produced from RN_2R as a "loose" pair.

Another interesting feature of the results indicates the partial participation of a triplet mechanism in unsensitized photolysis. Thermal decomposition of RR' in chlorobenzene at 80° gives 27.0% RR while direct photolysis at 28° gives only 24.1%. In view of our conclusions concerning the effect of temperature on diffusion from the cage,¹ and the twofold difference in the corresponding values for RN_2R decomposition, the latter figure is lower than expected and by a factor of about two. It is tempting to speculate that this apparent discrepancy arises from competition between dissociation of excited singlets of RR' and intersystem crossing to triplet RR' . Dissociation of the latter would show the reduced cage effect found in sensitized reactions. Evidence for or against this explanation might be obtained by effecting photolysis in the presence of a triplet quencher since quenching of ketenimine triplets would favor singlet dissociation and give rise to an increase in the yield of cage coupling product. Unfortunately such an agent, which does not absorb light at 3130 Å. or shorter wave lengths, does not readily spring to mind.

Inclusion of molecular oxygen (*ca.* $10^{-3} M$) in the direct photolysis system described in Table IV reduces the yield of RR from 24.1 to 9.0%. This observation can be explained by the formation of peroxy radicals and their subsequent attack on ketenimine. This unwanted result is not surprising since the rate of thermal decomposition of the ketenimine derived from another azonitrile has been shown to be substantially increased in the presence of oxygen.²⁰

9,10-Dibromoanthracene as a Sensitizer.—The use of 9,10-dibromoanthracene as a sensitizer for the decomposition of RN_2R and RR' was also examined. Results of these experiments, given in Table V, show the same features as those involving the use of triphenylene as sensitizer. However, irradiation of 9,10-

TABLE V

RR YIELDS FROM DECOMPOSITION OF RN_2R AND RR' IN CUMENE AT 28° SENSITIZED BY 9,10-DIBROMOANTHRACENE ^a	
% RR from RN_2R ^b	% RR from RR'
20.50	6.08
20.10	6.02
20.15	6.11
19.97	6.01
Mean 20.2	6.1

^a All samples degassed; light of wave length greater than 3300 Å. employed in both cases. Substrate and sensitizer concentrations were the same as those in experiments reported in Tables III and IV. ^b In the presence of HCl ($10^{-3} M$) and H_2O ($5 \times 10^{-3} M$).

dibromoanthracene in cumene results in formation of an unidentified derivative which absorbs light in the same wave length region as its precursor. The ambiguity introduced by the operation of concurrent reactions, sensitized reaction and sensitizer destruction, makes further discussion of these results unprofitable.

Experimental

Solvents and Sensitizers.—Benzene (Baker Chemical Co., analyzed reagent grade, thiophene-free) and cumene (Matheson Coleman and Bell, reagent grade) were purified as described.¹ Anthracene (Matheson Coleman and Bell, reagent grade) was used without purification, m.p. 213.5–214°. 1,2-Benzanthracene (Eastman Kodak, white label) was purified by chromatography on alumina with benzene as solvent and eluent; m.p. 158.5–158.7°. Phenanthrene (Eastman Kodak, white label) was vacuum sublimed before use; m.p. 100.3–101°. Triphenylene (Aldrich, research grade) was vacuum sublimed before use; m.p. 197.6–198°. Benzophenone (Matheson Coleman and Bell, reagent grade) was recrystallized from ligroin (b.p. 60–70°); m.p. 48–48.5°. *n*-Butyl mercaptan (Matheson Coleman and Bell, reagent grade) was used without purification. 1-Naphthyl phenyl ketone was obtained from Dr. N. J. Turro, crystallized from benzene by Dr. J. Saltiel; m.p. 76.4–77.0°. 2-Acetonaphthone (Eastman Kodak, white label) was recrystallized from ligroin (60–70°) by Dr. J. Saltiel; m.p. 54.1–54.6°. 9,10-Dibromoanthracene was prepared by Dr. K. R. Kopecky and recrystallized three times from carbon tetrachloride by Mr. F. G. Moses; m.p. 219.2–219.8°.

Substrates.—Ethyl 2,2'-azobisisobutyrate (EAB) was prepared as described.¹ 1,1'-Azo(cyano-C¹⁴)cyclohexane ($\text{RN}_2\text{R}-\text{C}^{14}$), N-(1-cyano-C¹⁴-cyclohexyl)pentamethyleneketeneimine ($\text{RR}'-\text{C}^{14}$), and 1,1'-Dicyanobicyclohexyl (RR) were prepared by Dr. H. P. Waits, as described.¹⁴

Quantum Yields. Apparatus.—Sensitized photolysis of EAB was effected with light isolated from a Westinghouse (SAH 800-c) 800-watt short arc, medium pressure mercury lamp, housed in the apparatus described,²¹ with Corning filter No. 7–54 and an interference filter (Baird Atomic, Inc.) in series. Transmission

(20) G. S. Hammond, O. D. Trapp, R. T. Keys, and D. L. Neff, *J. Am. Chem. Soc.*, **81**, 4878 (1959).

(21) W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

of the filter system at 3130 Å. was 24%; at 3340 Å., 8.7%; at 3660 Å., 0.8%; and at 2537 Å., 0.8%. Corning filters No. 0-52 and 7-37 in series were used for the isolation of 3660 Å. light. Transmission of this system at various wave lengths has been reported.¹ All transmitted light was absorbed by the reactants.

Reaction Vessels and Degassing Procedure.—Quartz reaction vessels were prepared from clean quartz tubing, 15 mm. in external diameter. Graded seals joined the quartz tubes to Pyrex tops which contained small grease traps. Constant volumes of reactants were placed in the constricted tubes with a spring-loaded syringe and degassed (3 freeze-thaw cycles at *ca.* 10⁻⁴ mm.) by attaching to the vacuum system (standard taper joint). **Actinometry:** The potassium ferrioxalate system was employed.⁵ Quantum yield for ferrous ion production at 25° and 3130 Å. was taken as 1.24 and that at 3660 Å. as 1.21. Light intensities were monitored just before, during, and just after sample irradiation by exposure of the same volumes of ferrioxalate solution as were used in the decomposition experiments. Intensity decreased linearly with time, and mean intensities for the period of sample irradiation were employed in calculation of quantum yields. **Analysis:** Disappearance of EAB was measured spectrophotometrically as described.¹ Inclusion of sensitizer restricted measurement to wave lengths where no absorption by the sensitizer occurred. Optical densities of undiluted samples were measured every 10 or 20 Å. over the range 4000 to 4200 Å. where Beer's law was obeyed. Details of the measurements are given in Table VI.

TABLE VI
QUANTUM YIELDS FOR PHOTSENSITIZED DECOMPOSITION
OF EAB (Φ_{EAB}) IN BENZENE AT 25°^a

Sensitizer	[Sens.], mole l. ⁻¹	[EAB] ₀ , mole l. ⁻¹	10 ⁻¹⁵ I, qu. sec. ⁻¹	10 ² , sec.	% de- compn.	Φ_{EAB}
Anthracene	0.01	0.1304	11.2	68.6	45.5	0.17
Anthracene ^b	.05	.1499	1.43	23.7	2.5	.19
1,2-Benzanthra- cene	.01	.1224	3.11	145.2	49.7	.32
1-Naphthyl phenyl ketone	.01	.1215	3.92	92.7	8.0	.06
1-Naphthyl phenyl ketone	.01	.1215	3.80	92.7	7.3	.06
2-Acetonaphthone	.1	.1188	3.65	145.2	18.1	.10
Phenanthrene	.1	.1220	3.52	146.4	54.6	.31
Phenanthrene	.1	.1192	2.37	152.8	37.2	.29
Triphenylene	.1	.1190	3.53	146.4	72.4	.40
Triphenylene	.1	.1190	3.29	80.5	37.1	.40
Benzophenone ^c	.3	.1492	7.32	9.28	1.5	.06
Benzophenone ^c	.3	.1492	7.32	18.82	3.0	.06
Benzophenone ^c	.3	.1492	7.32	33.22	4.0	.05

^a 3130 Å. light, quartz reaction tubes, and ferrioxalate actinometry unless stated otherwise. ^b Using 3660 Å. light and Pyrex reaction tubes. ^c Using benzophenone-benzhydrol actinometry, with $\Phi = 0.74$.²²

(22) G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1148 (1962).

Yields of 1,1'-Dicyanobicyclohexyl (RR). **Counting Procedure.**—Radiocarbon analyses were performed with a Packard Tri-Carb liquid scintillation spectrometer, Model 314-Ex, as described.¹⁴ It was confirmed that RR did not affect the counting rate. RR-C¹⁴ was used as a radiation source in the calibration vials to correct for the scintillation effect of cumene in the measurement of total specific activity. Counting rates necessary for the calculation of yields were determined at the same time and were corrected for background radiation. Yields were calculated as before.¹⁴ **Degassing Procedure:** Ampoules were prepared by constricting 100 × 13 mm. Pyrex culture tubes. Solutions (3 ml.) were pipetted into the tubes which were then degassed (3 freeze-thaw cycles at *ca.* 10⁻⁴ mm.). **Irradiation Procedure:** Irradiation was carried out with an immersion lamp (Hanovia, 450-watt, medium pressure) at the center of a rotating turntable which carried many samples for simultaneous irradiation. This apparatus, designed by Mr. F. G. Moses, was immersed in a constant-temperature water bath. Three different filter systems were employed: (1) a cylindrical Pyrex filter opaque below 2900 Å., (2) a cylindrical uranium glass filter opaque below 3300 Å., and (3) a cylindrical Pyrex filter in series with a solution containing NiSO₄·6H₂O (230 g.) and CoSO₄·7H₂O (73 g.) per liter of distilled water (3 cm. path length). The latter system was opaque at 2900 Å. and below as well as at 3500 Å. and above. Filter systems used in particular experiments are indicated in table footnotes. Times necessary for complete reaction were determined initially by recovery of substrate and thereafter by comparison of RR yields in samples irradiated for different times. **Isotope Dilution Procedure:** Ampoules were removed from the reactor, cleaned, and immersed in a liquid nitrogen bath. After its contents had solidified, a tube was opened by removing the top. Both parts were then placed in an Erlenmeyer flask containing a known weight of RR, *ca.* 0.5 g., dissolved in 50 ml. of benzene. In the direct photolysis of RN₂R, the carrier solution also contained a drop of bromine to destroy RR'-C¹⁴ which might otherwise have produced additional RR-C¹⁴ in the subsequent work-up. Complete mixing was achieved by swirling the flask. The solutions were then evaporated to dryness on a steam bath and the residues crystallized from benzene (10 ml.). Analyses after one and two crystallizations showed that the latter procedure was unnecessary except when 9,10-dibromoanthracene was used as sensitizer. Here, two recrystallizations were adequate. The crystals of RR-C¹⁴ were filtered, dried under vacuum overnight, and weighed into scintillation vials.

Reaction Solutions.—Reaction solutions containing sensitizer or other additives were made from stock solutions of RN₂R-C¹⁴ and RR'-C¹⁴ in cumene by addition to weighed amounts in volumetric flasks. Thus total specific activities could be determined from samples of the stock solutions. In the oxygen experiment, a portion of the RR'-C¹⁴ solution was evaporated slowly at room temperature in a volumetric flask with a stream of very pure nitrogen. The flask was then made to the mark with cumene, saturated with oxygen. This solution was probably *ca.* 10⁻³ M in oxygen.²³

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