

The Photosensitized Decomposition of Peroxides¹

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*Diacyl peroxides, peresters, and hydroperoxides undergo photosensitized decomposition in the presence of benzophenone, many other carbonyl compounds, and anthracene. However, di-*t*-butyl peroxide is stable. Products are those expected of radical scission of the O-O bond, even for *trans*-4-*t*-butylcyclohexanecarbonyl peroxide which undergoes primarily heterolytic thermal decomposition. The technique accordingly provides a means of achieving radical decomposition of peroxides which otherwise undergo polar reactions. Analysis of the kinetics of the benzophenone-benzoyl peroxide system indicate energy transfer from benzophenone triplet with a rate constant of 3.2×10^6 l./mole/sec. However, only 25% of the resulting excited peroxide molecules decompose, either because of deactivation or cage recombination. Quantum yields for hydroperoxide decomposition are similar. Although the process follows different kinetics and its details are obscure, induced chain decomposition of the hydroperoxide is shown not to be significant.*

In 1955 Luner and Szwarc² showed that anthracene and certain other polynuclear hydrocarbons act as photosensitizers for the homolytic decomposition of acetyl peroxide and lead to the same products as in the thermal reaction. As far as we are aware, when the work described here was begun no further investigation of the photosensitized decomposition of organic peroxides had been reported, a rather surprising circumstance in view of the current intense activity in all phases of organic photochemistry. Subsequently Vasilev and Krongauz³ have concluded that the decomposition of benzoyl peroxide is sensitized by both toluene and 2,5-diphenyloxazole, and Ueberreiter and Bruns⁴ have reported that tetralin hydroperoxide, but not benzoyl peroxide, undergoes photosensitized decomposition in the presence of fluorenone. Our own study reported here includes a general survey of the scope of the photosensitization reaction, product studies in a few selected reactions, and a fairly detailed kinetic analysis of the benzophenone-benzoyl peroxide system.

Results

Survey of the Photosensitization Phenomenon. At the start of our study a series of qualitative experiments were carried out in which various peroxide-sensitizer combinations (in approximately 10:1 ratio) were irradiated at wave lengths $>3050 \text{ \AA}$. (Nonex glass filter) in sealed degassed tubes and decomposition rates compared with those of peroxide alone under comparable conditions. Several of the combinations were subse-

quently investigated more carefully with a more precise optical set-up, and all results are summarized in Table I. While results are qualitative, systems noted as showing photosensitization in general underwent complete photolysis in irradiation times which produced at most a few per cent decomposition of the peroxide alone.

Table I indicates that sensitization is a general phenomenon for acyl peroxides and peresters, with and without aromatic rings, and for hydroperoxides. On the other hand, we have not been able to sensitize the decomposition of di-*t*-butyl peroxide. Effective sensitizers include ketones such as benzophenone which yield $n \rightarrow \pi^*$ triplet states, and also 2-acetonaphthone and anthracene where triplet states represent $\pi \rightarrow \pi^*$ transitions. Among the ketones, however, there seems to be a level of triplet energy⁵ below which they are ineffective.

Products. Products of decomposition were investigated in a few cases to establish the homolytic nature of the photosensitized reaction and consumption, if any, of sensitizer. Photolysis of 0.02–0.1 *M* benzoyl peroxide solutions in benzene containing approximately 10% as much benzophenone gave quantitative recovery of benzophenone by gas-liquid chromatography (g.l.c.), 1.06 ± 0.04 moles of CO₂, 0.59 mole of organic acids (presumably chiefly benzoic), 0.3 mole of biphenyl, a trace of quaterphenyl, and only traces, if any, of phenyl benzoate, a product distribution very similar to that obtained from thermal decomposition at 70–100°.⁶

Results with *trans*-4-*t*-butylcyclohexanecarbonyl peroxide were somewhat more interesting. Thermal decomposition of this compound at 50° in *sym*-tetrabromoethane was reported by Lau and Hart⁷ to give a 90% yield of *trans*-4-*t*-butylcyclohexyl *trans*-4-*t*-butylcyclohexanecarboxylate. Subsequently it has been shown by Greene⁸ and in our laboratory⁹ that this ester arises by CO₂ loss from the corresponding carbonate anhydride, formed by a polar carboxyl inversion process. Some homolytic scission also takes place, and is apparently favored by elevated temperature, since Lau and Hart⁷ obtained a 3% yield of mixed *cis*- and *trans*-4-*t*-butylcyclohexyl bromides at 50°, while Greene¹⁰ reported a $\approx 20\%$ yield of the corresponding chlorides on conducting the decomposition in refluxing CCl₄ at 80°. In contrast to these results, benzophenone-sensitized photolysis of 0.044 *M* peroxide in CCl₄ at 0° gave a 40.5% yield of mixed *cis*- and *trans*-4-*t*-butylcyclohexyl chloride (ratio 23:77) and 66% C₂Cl₆. Other products

(5) See Table I, footnote a.

(6) Cf. for example, C. Walling and E. S. Savas, *J. Am. Chem. Soc.*, **82**, 1738 (1960).

(7) H. H. Lau and H. Hart, *ibid.*, **81**, 4897 (1959).

(8) F. D. Greene, H. P. Stein, C. C. Chu, and F. M. Vane, *ibid.*, **86**, 2080 (1964).

(9) C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, *ibid.*, **87**, 518 (1965).

(10) F. D. Greene, C. C. Chu, and J. Walia, *J. Org. Chem.*, **29**, 1285 (1964).

(1) Taken from the Ph.D. dissertation of M. J. Gibian, Columbia University, 1965. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) C. Luner and M. Szwarc, *J. Chem. Phys.*, **23**, 1978 (1955).

(3) I. N. Vasilev and V. A. Krongauz, *Kinetika i Kataliz*, **4**, 204 (1963).

(4) K. Ueberreiter and W. Bruns, *Makromol. Chem.*, **68**, 24 (1963).

Table I. Peroxide Decompositions Showing Photosensitization

Peroxide	Solvent	Sensitizer	Triplet Energy ^a	Sensitization ^b
Benzoyl peroxide	Benzene	Acetophenone	73.6	+
Benzoyl peroxide	Benzene	Benzophenone	68.5	+
Benzoyl peroxide	Cyclohexane	Benzophenone		+
Benzoyl peroxide	Benzene	<i>p</i> -Chlorobenzophenone		+
Benzoyl peroxide	Benzene	2-Acetonaphthone	59.3	+
Benzoyl peroxide	Benzene	2,3-Pentanedione	54.7	-
Benzoyl peroxide	Benzene	Benzil	53.7	-
Benzoyl peroxide	Benzene	Fluorenone	53.3	-
Benzoyl peroxide	Benzene	Anthracene	42	+
Benzoyl peroxide	Cyclohexane	Anthracene	...	+
<i>trans</i> -4- <i>t</i> -Butylcyclohexanecarbonyl peroxide	CCl ₄	Benzophenone	...	+
<i>t</i> -Butyl peracetate	Cyclohexane	Benzophenone	...	+
<i>t</i> -Butyl hydroperoxide	CCl ₄	Acetophenone	...	+
<i>t</i> -Butyl hydroperoxide	CCl ₄	Benzophenone	...	+
<i>t</i> -Butyl hydroperoxide	Benzene	Benzophenone	...	+
<i>t</i> -Butyl hydroperoxide	Chlorobenzene	Benzophenone	...	+
Cumene hydroperoxide	Cyclohexane	Benzophenone	...	+
Di- <i>t</i> -butyl peroxide	Cyclohexane	Benzophenone	...	-
Di- <i>t</i> -butyl peroxide	Benzene	Benzophenone	...	-

^a Energy of lowest triplet level of sensitizer: W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

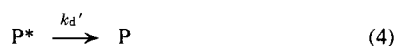
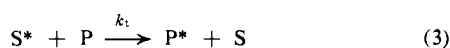
^b + indicates photosensitized decomposition; - indicates no significant difference from control.

were not identified, but the infrared spectra of the crude reaction mixture showed that the corresponding acid, ester, and carbonate anhydride were all absent. Accordingly we conclude that the photolysis takes place by a homolytic path, at least to the extent of 66% and probably entirely.

The photolysis of *t*-butyl hydroperoxide in benzene in the presence of benzophenone was also shown to be a true photosensitization since 20% benzophenone led to complete consumption of hydroperoxide, no benzohydroxide or benzopinacol could be detected, and the benzophenone was recovered quantitatively at the end of the reaction. The chief decomposition product of the hydroperoxide was *t*-butyl alcohol together with (at most) a trace of acetone. No water could be detected by the use of Karl Fischer reagent.

Kinetics. Quantum yields and rates of peroxide disappearance were investigated in some detail for the benzoyl peroxide-benzophenone system in benzene. Two sets of measurements were made, one using sealed degassed tubes under conditions of approximately equal illumination in a water bath, and the other with a thermostated optical cell and constant light source. Since the latter gave the more accurate data, only its results will be discussed in detail.

For analysis of data, the following kinetic scheme was assumed, paralleling other studies of triplet-sensitized processes. Reaction 1 represents conversion of benzo-



phenone to an excited state, assumed to be the lowest energy triplet, a process for which Φ' is essentially unity.⁵ The triplet then either decays *via* reaction 2 or

transfers its energy to peroxide in reaction 3. The excited peroxide, P^* , in turn, either decays, reaction 4, or decomposes, reaction 5. From this sequence we may write for Φ_{decomp} , the quantum yield for peroxide decomposition (assuming $\Phi' = 1$)

$$1/\Phi_{\text{decomp}} = (1 + k_{d'}/k_r)(1 + k_d/k_t[P]) \quad (6)$$

The quantity $\Phi_{\text{decomp}} = -d[P]/I_a dt$ and may be obtained directly from rates of peroxide decomposition and actinometry. Figure 1 shows some typical peroxide decomposition curves. Equation 6 predicts a linear relation between $1/\Phi_{\text{decomp}}$ and $1/[P]$. The intercept gives $k_r/k_{d'}$ and this ratio combined with the slope of the line gives k_d/k_t . The resulting plot is shown in Figure 2 and has a slope of 0.123, an intercept of 3.92, and a correlation coefficient of 0.998. Thus $k_{d'}/k_r = 2.92$, $k_d/k_t = 0.031$.

The foregoing analysis assumes that there is no induced decomposition of benzoyl peroxide brought about by radicals produced in the photolysis. The induced decomposition of benzoyl peroxide in benzene has been examined by Nozaki and Bartlett¹¹ at 60 and 80°. Extrapolation of their data to our temperatures and decomposition rates indicates that at our highest peroxide concentration induced reaction would account for less than 3% of the decomposition.

An attempt to apply a similar kinetic treatment to the sensitized decomposition of *t*-butyl hydroperoxide gave inconsistent results and indicated that a more complicated situation is involved. With 0.005 *M* benzophenone, Φ_{decomp} was 0.12 for 0.027 *M* hydroperoxide and 0.19 at 0.015 *M*, a lower concentration. Similar quantum yields were obtained in benzene and chlorobenzene and also in the presence of hydroquinone and *p*-cresol, observations discussed further below. A few experiments were run on other systems. 2-Acetonaphthone at a single concentration with benzoyl peroxide gave Φ_{decomp} of 0.034. Assuming $\Phi' = 0.84$ ¹²

(11) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

(12) A. A. Lamola, Ph.D. Thesis, California Institute of Technology, 1965.

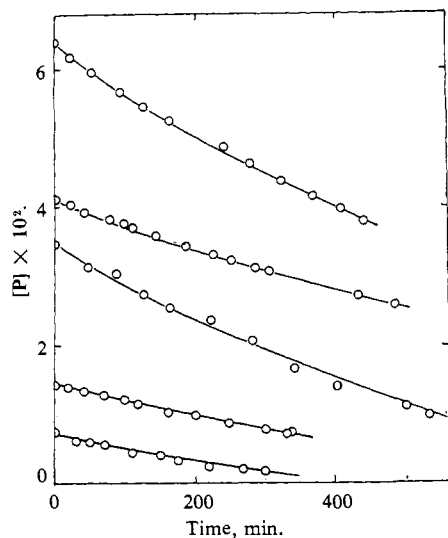


Figure 1. Photolysis of benzoyl peroxide, $5 \times 10^{-3} M$ benzophenone in benzene.

and our value of k_d'/k_r , this corresponded to $k_d/k_t = 0.074$. More qualitatively, *p*-chlorobenzophenone with benzoyl peroxide gave a quantum yield similar to benzophenone, and benzophenone-sensitized decompositions of benzoyl peroxide, *t*-butyl peracetate, *t*-butyl hydroperoxide, and cumyl hydroperoxide all occur at roughly the same rate.

Discussion

Our results indicate that photosensitized decomposition is a general process for acyl peroxides, peresters, and hydroperoxides, but fails to occur with di-*t*-butyl peroxide. In general products are those expected from homolytic scission of the O–O bond, as reported earlier by Luner and Szwarc for acetyl peroxide,² a result which parallels the recent findings of Hammond on sensitized photolysis of azo compounds.¹³ However, as we have shown, it provides a means of ensuring radical cleavage of peroxides which normally decompose *via* a polar path,¹⁴ and should be of use for this purpose.

Our evidence for the detailed nature of the photosensitized process comes from our study of the benzophenone–benzoyl peroxide system. Here at high peroxide concentrations Φ_{decomp} approaches 0.25 (from the intercept of Figure 2). Since the quantum yield for formation of the benzophenone triplet state is essentially unity, and the singlet state can only be intercepted by extremely reactive quenching agents,¹⁵ we conclude that the sensitization involves the benzophenone triplet state. It further seems certain that the sensitization reaction 3 is an energy transfer rather than chemical reaction. First, no sensitizer is consumed, and second, sensitizers with $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplets show similar efficiencies. A third argument may be based upon the actual rate of reaction 3. Bell and

(13) J. R. Fox and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4031 (1964).

(14) Some time ago we reported a similar phenomenon in the unsensitized photolysis of a peroxide analog, dibenzoylhydroxylamine. This compound decomposes thermally to phenyl isocyanate and benzoic acid with only a trace of radical production. On the other hand, photolysis yields typical radical products: C. Walling and A. N. Naglieri, *ibid.*, **82**, 1820 (1960).

(15) R. P. Foss, D. O. Cowan, and G. S. Hammond, *J. Phys. Chem.*, **68**, 3747 (1964).

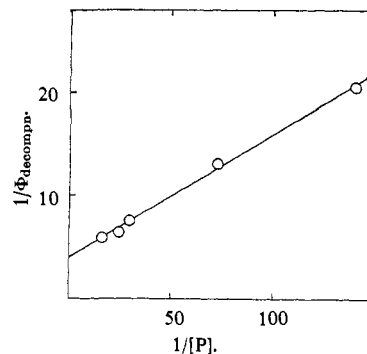


Figure 2. Photolysis of benzoyl peroxide, plot of eq. 6.

Linshitz¹⁶ have determined k_d for benzophenone in benzene as 10^5 sec^{-1} , so from our data $k_t = 3.2 \times 10^6$. On the other hand most rates of chemical reaction (hydrogen abstraction) for benzophenone triplet with a variety of substrates¹⁷ lie in the range 10^2 – 10^5 . Vasilev and Krongauz³ have also concluded that the photosensitized decomposition of benzoyl peroxide is an energy transfer process on the basis of similar limiting quantum yields with quite different sensitizers and with the unsensitized process, obtaining a value of 0.4, in reasonable agreement with ours (0.25).

At present there appears to be at least two mechanisms by which energy transfer from a triplet may occur: excitation of the quenching agent to a triplet state, which is generally a diffusion-controlled reaction with a rate constant of $\approx 10^9$ providing the process is not endothermic,¹⁸ and a slower “non-Franck–Condon process,” when a low-lying triplet state is not available, as in the sensitized conversion of quadricyclene to norbornadiene.¹⁹ Our value of k_t suggests the latter type of process, as does the fact that no low-lying triplet state of acyl peroxides has been reported and the lack of any simple correlation between photosensitization and sensitizer triplet energy (Table I, where we see that, while there is an apparent cut off for ketones with low triplet energies, anthracene is still effective).

Finally, our value of k_d'/k_r requires discussion since it indicates that only 25% of the benzoyl peroxide which reacts with the benzophenone triplet undergoes decomposition. Two possibilities exist²⁰ which are hard to distinguish: vibrationally excited peroxide molecules may be produced which in part dissipate their energy without dissociating, or benzoyloxy radicals may be produced efficiently, but most undergo recombination within the solvent cage. Our data provide no basis for distinguishing between the two processes, but O¹⁸-labeling experiments, at least in the thermal decomposition of acetyl peroxide at higher temperatures, have provided no evidence for such recombination, since undecomposed peroxide shows no “scrambling.”²¹

(16) J. Bell and H. Linshitz, *J. Am. Chem. Soc.*, **85**, 528 (1963).

(17) C. Walling and M. Gibian, *ibid.*, **87**, 3361 (1965).

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

(19) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Am. Chem. Soc.*, **86**, 2532 (1964).

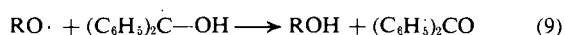
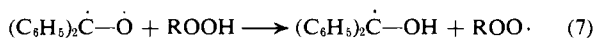
(20) A third possibility, back transfer of energy from excited peroxide to sensitizer, seems unlikely since it has been observed only with triplet–triplet energy exchanges which are initially endothermic or at least almost thermoneutral and shows a critical dependence on triplet energy which we do not observe.

(21) L. Herk, M. Feld, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

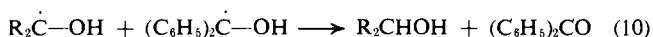
Presumably photosensitization of the decomposition of other acyl peroxides and peresters proceeds similarly. However, our results with *t*-butyl hydroperoxide, although hardly definitive, indicate a more complicated process with different kinetics, perhaps not a surprising finding in view of the known complexities of hydroperoxide decompositions and their tendency to form dimers and complexes with solvent.²² Although quantum yields are similar to the benzoyl peroxide decomposition, we must consider again the possibility of a less efficient primary process followed by an induced chain decomposition. Our results appear to rule this out, since phenols, which inhibit such chains, have no effect on the photolysis. Further, photolysis proceeds at the same rate in benzene and in chlorobenzene, although in the latter solvent the induced chains which accompany thermal decomposition are evidently much longer and should lead to more rapid over-all decomposition.²²

We are thus left again with two alternatives: energy transfer (presumably of the non-Franck-Condon type, since it is difficult to picture a low-lying hydroperoxide triplet) followed by O–O bond scission, or triplet attack on hydroperoxide hydrogen. The first would give rise to hydroxyl radicals which should be expected, at least in part, to end up as water, which we have been unable to detect. On the other hand, in aromatic solvents they chiefly undergo addition to yield eventually phenols and polyphenyls,²³ and some phenol formation could account for the absence of induced hydroperoxide decomposition just mentioned.

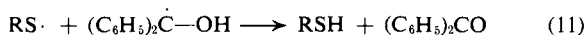
Hydrogen abstraction, analogous to that occurring in the photoreduction of benzophenone, would account for the nonreactivity of di-*t*-butyl peroxide, but requires a reaction for the regeneration of benzophenone which we have shown not to be consumed. Here a possible sequence is the following (eq. 7–9). Evidence



against the analogous carbon-radical reaction (eq. 10)



comes from the lack of racemization of optically active secondary alcohols during their photooxidation by benzophenone,²⁴ but the thiyl radical reaction (eq. 11)



may be involved in the mercaptan inhibition of photoreduction studied by Cohen,²⁵ and a similar hydrogen transfer (eq. 12) has been suggested by Huyser²⁶ as a



step in the induced decomposition of di-*t*-butyl peroxide in the presence of alcohols. Although further work will be required to distinguish between these alterna-

(22) C. Walling and L. Heaton, *J. Am. Chem. Soc.*, **87**, 38, 48 (1965).

(23) *Cf.*, for example, L. M. Dorfman, I. A. Taub, and D. A. Harter, *J. Chem. Phys.*, **41**, 2954 (1964).

(24) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Marton, *J. Am. Chem. Soc.*, **81**, 1068 (1959).

(25) S. G. Cohen, D. A. Laufer, and W. V. Sherman, *ibid.*, **86**, 3060 (1964).

(26) E. S. Huyser and C. J. Bredeweg, *ibid.*, **86**, 2401 (1964).

tives,²⁷ our results leave no doubt about the occurrence of a relatively efficient photosensitized decomposition of hydroperoxides and provides a basis for further study.

Experimental

Photolyses. Preliminary and semiquantitative experiments were carried out in sealed, degassed tubes arranged concentrically in a water bath around a 450-w., medium-pressure mercury arc with Nonex glass filter placed in a Vycor immersion well. The tube holder was rotated periodically to ensure equal illumination, and approximate light intensities were determined by measuring rates of photoreduction of benzophenone at the same concentration in isopropyl alcohol in similar tubes. Tubes with and without sensitizer were run together for equal times and then analyzed for unreacted peroxide. Only slight or no decomposition was noted in unsensitized systems.

Quantitative kinetic runs were carried out with an assembly consisting of a 1000-w., high-pressure mercury arc and reflector, filters (25 mm., 10% CuSO₄ solution plus 4.8-mm. Corning No. 5970 glass), and a thermostated cell with quartz faces, arranged for flushing with argon or nitrogen and for magnetic stirring, from which aliquots of solution could be withdrawn for titration with a hypodermic syringe. Light intensity and light absorption were determined by uranyl oxalate actinometry²⁸ using a similar cell placed before the reaction cell before and after a run and behind the cell while a run was in progress. In a typical experiment showing a peroxide decomposition rate of 1.72×10^{-5} mole/l./min., actinometry gave 41.2×10^{-5} and 40.2×10^{-5} einstein/l./min. in front and 5.1×10^{-5} behind the reaction cell, whence $\Phi_{\text{decomp}} = 0.048$. With the exception of di-*t*-butyl peroxide, which was determined by g.l.c. analysis, peroxide consumption was followed by conventional iodimetry, using appropriate modifications for acyl peroxides,²⁹ hydroperoxides,³⁰ and peresters.³¹ Rates of decomposition were determined by least-squares fit to data such as appear in Figure 1, using a machine program, and the final fit of eq. 6 was determined similarly.

Product Analyses. Benzophenone concentrations after reaction were measured by g.l.c. against calibrated standards, CO₂ was determined gravimetrically, benzoic acid was determined by titration, and biphenyl was determined by g.l.c. In experiments with *trans*-4-*t*-butylcyclohexanecarbonyl peroxide, 25 ml. of CCl₄ containing 0.402 g. of peroxide and 0.0446 g. of benzophenone was irradiated at -10 to $+5^\circ$ until the peroxide had disappeared (12 hr.), and a similar sample decomposed thermally at 40° . Comparison of infrared spectra showed that peaks characteristic of ester (5.78μ), anhydride (5.52 and 5.73μ), acid (5.90μ), and carbonate anhydride (5.55 and 5.69μ) were all ab-

(27) Recent experiments by J. Azar in these laboratories show that decomposition of *t*-butyl hydroperoxide is sensitized by 2-acetonaphthone and phenanthrene, but less efficiently than by benzophenone, suggesting that both paths may be involved.

(28) P. A. Leighton and G. S. Forbes, *J. Am. Chem. Soc.*, **52**, 3139 (1930).

(29) K. Nozaki, *Ind. Eng. Chem. Anal. Ed.*, **18**, 583 (1946).

(30) C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 979 (1947).

(31) L. S. Silbert and D. Swern, *ibid.*, **30**, 385 (1958).

sent from the products of the photosensitized decomposition, although a single, sharp, unidentified peak at 5.86μ was observed. Yields of 4-*t*-butylcyclohexyl chloride and C_2Cl_6 were determined by g.l.c. vs. *o*-dichlorobenzene as standard. Calibration for the cyclohexyl chloride was made using authentic material pre-

pared from 4-*t*-butylcyclohexanol. *cis* and *trans* isomers appeared as separate peaks, area ratio 23:77. The thermal decomposition products showed the expected infrared absorption for the carbonate anhydride and a much lower yield of chlorides by g.l.c., although products were not determined quantitatively.

The Photoisomerization of the 2,3-Dihydrooxepin Ring. Long-Range Coupling in Some 2-Oxabicyclo[3.2.0]hept-6-enes¹

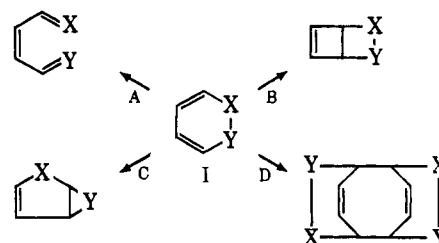
Leo A. Paquette,^{2a} James H. Barrett,^{2b} Robert P. Spitz,^{2c} and Ross Pitcher

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio, and the Varian Associates Application Laboratory, Pittsburgh, Pennsylvania. Received April 23, 1965

2,3-Dihydrooxepins undergo light-induced valence tautomerism to 2-oxabicyclo[3.2.0]hept-6-enes, a previously unknown class of compounds. Chemical structure proof of the irradiation products was obtained by hydrogenolysis to 2-cyclobutylethanol, whose independent synthesis was also achieved. Double-resonance techniques have been applied to the n.m.r. spectra of the photoisomers; complete chemical shift and coupling constant assignments have been derived. The relatively large upfield shift of the vinyl proton of Va relative to Vb has been analyzed by means of a \cos^2 dependence upon the neighbor-anisotropy effect of the carbon-chlorine bond.

The effect of ultraviolet irradiation on conjugated cyclic dienes has been found to vary with the particular system under study. Derivatives of 1,3-cyclohexadiene (I), for example, have been transformed into a vast array of photoproducts *via* ring-opening processes (A, most frequently observed),³ valence-bond tautomerism reactions (B),⁴ bond-switching mechanisms (C),⁵ and dimerization pathways (D).⁶ On the other hand, 1,3-cycloheptadienes have been shown⁷ to be much more

consistent in their photochemical behavior. Valence-bond isomerization to bicyclo[3.2.0]heptenes has been observed in all instances with but one exception, namely,



the fragmentation of 3,5-cycloheptadienones to carbon monoxide and 1,3,5-hexatriene.⁸ More recent studies with heterocyclic derivatives of this seven-membered ring system⁹ did not give evidence of a reaction pathway other than the bridging reaction. With 1,3-cyclooctadiene, irradiation likewise effects valence isomerization to bicyclo[4.2.0]octene.¹⁰ The uniform behavior in the medium-sized rings can be readily attributed to the fact that simple ring cleavage is impossible when the diene chromophore is joined at its extremities by more than two atoms.

With a desire to discover new photochemical reaction pathways of appropriate 1,3-cycloheptadienes, we have examined the irradiation of the 2,3-dihydrooxepin ring system (II). Our reasons for this choice were twofold, each based on recognition of the fact that II

(1) Part XVIII of the series on unsaturated heterocyclic systems. For part XVII, see L. A. Paquette, *J. Org. Chem.*, **30**, 2107 (1965).

(2) (a) Alfred P. Sloan Foundation Research Fellow; (b) National Science Foundation Summer Fellow, 1964; (c) undergraduate research participant, 1964.

(3) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959); D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960); P. de Mayo and S. T. Reid, *Quart. Rev. (London)*, **15**, 393 (1961), and additional pertinent references cited therein; E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961); E. Havinga, *Chimia (Aarau)*, **16**, 146 (1962).

(4) W. G. Dauben and R. M. Coates, *J. Am. Chem. Soc.*, **86**, 2490 (1964); H. Prinzbach and J. H. Hartenstein, *Angew. Chem.*, **74**, 651 (1962); **75**, 639 (1963); E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **85**, 3297 (1963).

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