of configuration. These include: (a) the addition of bromine to 9,10-dehydrodianthracene,[15] (b) the addition of chlorine to nortricyclene,[16] and (c) the addition of bromotrichloromethane to dibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene.[17] Clearly, only the latter two investigations may be relevant with regard to the mechanism(s) of homolytic attack on cyclopropane and structurally simple cyclopropanes. The degree of relevance can be questioned since both nortricyclene and dibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene are tricyclic systems of considerable structural complexity. The importance of our study lies in the fact that 1,1-dichlorocyclopropane is a monocyclic system of relative structural simplicity and the only monocyclic system examined to date.

We propose, in view of the results obtained for 1,1-dichlorocyclopropane and the tricyclic systems, that the radical-induced ring opening of cyclopropanes will, for the majority of cases, occur preferentially *via* an inversion process. To confirm this proposal a greater variety of radical–cyclopropane systems will need to be examined. Our work in this area is continuing.

Acknowledgments. Our gratitude is expressed to Dr. Joseph Dadok of Mellon Institute for the spin-decoupling work and Drs. Jack Hausser and Kurt C. Schreiber for helpful discussions.

[15] D. E. Applequist and R. Searle, *J. Amer. Chem. Soc.*, **86**, 1389 (1964).

[16] M. L. Poutsma, *ibid.*, **87**, 4293 (1965).

[17] B. B. Jarvis, *J. Org. Chem.*, **35**, 924 (1970).

[18] NDEA Predoctoral Fellow, 1969–present.

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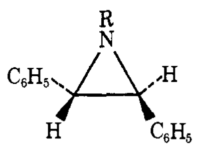
Received September 13, 1971

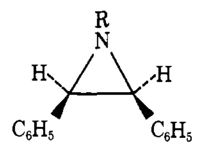
Photochemical Behavior of Certain N-Substituted Diphenylaziridines. The Question of Isomerization *vs.* Fragmentation

Sir:

The photochemistry of phenylated epoxides has attracted considerable mechanistic and synthetic attention in recent years.[1] While it is agreed that electronic excitation of such substances leads for the most part to molecular fragmentation into a carbene and a ketone (or aldehyde) the mechanistic details of the fragmentation process have been the subject of considerable discussion and there appears to be disagreement as to whether these substances undergo C–C[1,2] or C–O[3] bond scission on excitation.[4] Presently we briefly describe our findings with certain select N-substituted 2,3-diphenylaziridines which, we believe, bear on this question and which provide some insight into the photochemical behavior of phenylated three-membered heterocycles in general. The three stereoisomeric pairs employed in the present study are shown in **1** and **2**.[5]



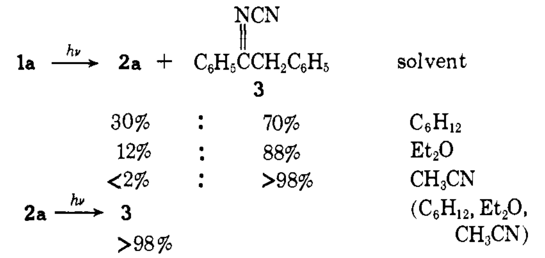
1a, R = CN
b, R = $COOC_2H_5$
c, R = $CON(CH_3)_2$



2a, R = CN
b, R = $COOC_2H_5$
c, R = $CON(CH_3)_2$

In the case of the **1a**,**2a** pair,[6] irradiation at 2537 Å (quartz optics) in solution and at ambient temperature leads not to fragmentation but rather to clean isomerization, the results of a few representative runs being detailed in Scheme I.[7] It is thus seen that while both stereoisomers rearrange to **3**[8] on illumination only the trans isomer undergoes detectable stereoisomerization to the cis counterpart under the same conditions.[9] Further, the product distribution in the photolysis of **1a** appears to exhibit strong solvent dependence whereby the proportion of **3** in the photolysate invariably increases with enhanced solvent polarity.

Scheme I



$$\mathbf{1a} \xrightarrow{h\nu} \mathbf{2a} + C_6H_5\overset{NCN}{\overset{\|}{C}}CH_2C_6H_5 \;(\mathbf{3})$$

			solvent
30%	:	70%	C_6H_{12}
12%	:	88%	Et_2O
<2%	:	>98%	CH_3CN

$$\mathbf{2a} \xrightarrow{h\nu} \mathbf{3}$$

>98% (C_6H_{12}, Et_2O, CH_3CN)

Under similar photolysis conditions the stereoisomeric urethanes **1b** and **2b**[10] undergo clean geo-

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[1] P. C. Petrellis, H. Dietrich, E. Meyer, and G. W. Griffin, *J. Amer. Chem. Soc.*, **89**, 1967 (1969), and references listed therein.

[2] T. DoMinh, A. M. Trozzolo, and G. W. Griffin, *ibid.*, **92**, 1402 (1970).

[3] R. S. Becker, J. Kolc, R. O. Bost, H. Dietrich, P. Petrellis, and G. W. Griffin, *ibid.*, **90**, 3292 (1968); R. S. Becker, R. O. Bost, J. Kolc, N. R. Bertoniere, R. L. Smith, and G. W. Griffin, *ibid.*, **92**, 1302 (1970).

[4] For a timely and comprehensive review of the subject, see: G. W. Griffin, *Angew. Chem., Int. Ed. Engl.*, 537 (1971).

[5] The compounds shown in **1** were prepared on treatment of *trans*-2,3-diphenylaziridine (A. Weissberger and H. Bach, *Chem. Ber.*, **64**, 1095 (1931)) with either cyanogen bromide, ethyl chloroformate, or *N*,*N*-dimethylcarbamoyl chloride while those depicted in **2** were synthesized on treatment of *cis*-2,3-diphenylaziridine (K. Kotera, S. Miyazaki, H. Takahashi, T. Okada, and K. Kitahonoki, *Tetrahedron*, **24**, 3681 (1968)) with the same reagents.

[6] **1a** showed: mp 81–82°; $\nu_{CN}{}^{KBr}$ 2180 cm^{-1}; λ_{max} (C_6H_{12}) 271 (ϵ 545), 265 (868), 258 nm (885); nmr ($CDCl_3$) τ 2.60 (10 H, singlet), 6.05 (2 H, singlet). **2a** showed: mp 115–116°; $\nu_{CN}{}^{KBr}$ 2190 cm^{-1}; λ_{max} (C_6H_{12}) 270 (sh) (ϵ 228), 264 (423), 259 (476), 253 nm (402); nmr ($CDCl_3$) τ 2.85 (10 H, singlet), 5.72 (2 H, singlet). In addition, these substances gave correct elemental analyses.

[7] Each tabulated run is one of several conducted by varying the irradiation time from 5 to 30 min. Brief irradiation proved necessary in order to prevent photodecomposition of **3** which sets in on longer exposure to light. The amount of unreacted aziridine contained in the mixtures listed in Scheme I ranged from 65 to 80%. In each case the photolysate was analyzed immediately, by nmr, employing both $CDCl_3$ and benzene-d_6 as solvents.

[8] Alkylidene cyanamide **3** was characterized on the basis of its nmr ($CDCl_3$) spectrum (τ 1.9–2.2 (2 H, multiplet), 2.5–2.8 (8 H, multiplet), and 5.52 (2 H, singlet)) and through its ready conversion to deoxybenzoin on treatment with moist alumina.

[9] It was pointed out by a referee that the implication that **1a** can form **3** as a primary photoproduct, without going through **2a**, is not demanded by the information collected in Scheme I. While we cannot categorically state that **3** materializes directly from **1a** we draw attention to the fact that **2a** photolyzes exclusively to **3** under the same conditions. When viewed in light of the fact that (a) the photostationary state in the case of the **1b**–**2b** and **1c**–**2c** pairs consists of **2** (cis) and **1** (trans) in a ratio of *ca.* 9:1 (*vide infra*) and (b) the steady-state concentration of **2a** (cis) in the photolysis of **1a** (trans) amounts to only *ca.* 8% of the total mixture (**1a** + **2a** + **3**), this observation is, we believe, best accommodated by a scheme whereby initially formed **1a** is drained irreversibly into **3** at a steady-state concentration which is much too low (<1%) for detection by nmr spectroscopy.

[10] **1b** showed: mp 56–57°; $\nu_{CO}{}^{KBr}$ 1710 cm^{-1}; λ_{max} (C_6H_{12}) 273 (ϵ 427), 266 (807), 260 nm (955); nmr ($CDCl_3$) τ 2.66 (10 H, singlet), 6.02 (2 H, quartet), 6.23 (2 H, singlet), 9.50 (3 H, triplet). **2b** showed: mp 54–55°; $\nu_{CO}{}^{KBr}$ 1715 cm^{-1}; λ_{max} (C_6H_{12}) 270 (sh) (ϵ 234), 265 (390), 260 (466), 253 nm (392); nmr ($CDCl_3$) τ 2.87 (10 H, singlet), 5.78 (2 H, quartet), 6.08 (2 H, singlet), 8.73 (3 H, triplet). In addition, these substances gave correct elemental analyses.

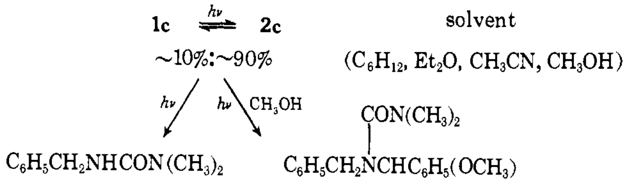
metrical isomerization without any detectable fragmentation. Specifically, exposure to 2537-Å radiation of either **1b** or **2b** for *ca.* 65 min in either C_6H_{12}, CH_3CN, or even CH_3OH[11] generates a two-component mixture consisting (nmr) of *ca.* 10% **1b** and 90% **2b** and resisting any further change on prolonged (*ca.* 5 hr) illumination.

Scheme II

$$\begin{array}{cc} \mathbf{1b} \overset{h\nu}{\rightleftharpoons} \mathbf{2b} & \text{solvent} \\ 10 \pm 3\% : 90 \pm 3\% & C_6H_{12},\ CH_3CN,\ CH_3OH \end{array}$$

Stereoisomerization to a mixture consisting (nmr) of *ca.* 90% cis and 10% trans isomer is also activated on brief (*ca.* 30 min) illumination at 2537 Å of either **1c** or **2c**[12] in a variety of solvents (C_6H_{12}, Et_2O, CH_3CN). However, the rearrangement here is further complicated by a competitive, albeit slightly less efficient, fragmentation process which invariably leads to **4**[13] as the only tractable product of prolonged (*ca.* 16 hr) irradiation. It is also worth noting in this connection that the same photoinduced stereoisomerization obtains in CH_3OH[11] as well but fragmentation is fully suppressed in this medium, the only substance formed here on prolonged photolysis being **5**,[14] *i.e.*, the product of methanol-assisted C–C bond scission.

Scheme III



4 **5**

It is abundantly clear from *all* the data recorded herein that the chemical fate of an electronically excited aziridine is a particularly sensitive function of N substitution.[15] For the most part the observed differences are best reasoned in terms of variations in substituent electronegativity, bearing in mind that the electron-withdrawing capacity of the R substituents examined here is in the order CN > $COOC_2H_5$ > $CON(CH_3)_2$. This "electronegativity" effect best manifests itself in the unique tendency of **1a**,**2a** among the three pairs studied to yield a substance such as **3**, *i.e.*, to isomerize through obvious scission of the strongly polarized aziridine $C(\delta^+)–N(\delta^-)$ link. Conversely, molecular fragmentation, which judging from the structure of **5** very likely materializes through initial C–C bond cleavage, appears to be chiefly triggered by enhanced involvement of the nitrogen lone pair, for it obtains only in the case of the **1c**,**2c** pair. In fact the notion that the nitrogen pair is somehow involved in the fragmentation process receives added credence from the recently reported[16] ready photofragmentation of 1,2,3-triphenylaziridine, *i.e.*, **1**, **2** (R = C_6H_5). Further, the results of HMO calculations on a hypothetical 4π 2-heterotrimethylene species, *i.e.*, C–X–C, which very likely intermediates the fragmentation process, clearly point to progressive weakening of the C–C bond with increased availability of the lone pair for π delocalization.[17]

Finally, a brief comment concerning the stereoisomerization process. In principle, this type of rearrangement could involve either a C–C bond or a C–N bond. In practice, the first possibility, *i.e.*, involvement of the homopolar C–C link, appears more realistic in view of (a) the total suppression of this process, in favor of **3**, on increasing the polarity of the solvent in the photolysis of **1** (Scheme I) and (b) the obvious inability of methanol to arrest this change (Scheme II). Further, the overwhelming predominance of the cis isomer in the photostationary composition irrespective of N substitution is, we believe, best accounted for in terms of the symmetry-controlled conversion of **1** to **7** and of **2** to **8** shown in Scheme IV

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(11) Spectral grade, freshly distilled over calcium hydride.

(12) **1c** showed: mp 101–102°; ν_{CO}^{KBr} 1650 cm^{-1}; λ_{max} (C_6H_{12}) 274 (ϵ 480), 265 (sh) (1060), 259 nm (sh) (1480); nmr ($CDCl_3$) τ 2.64 (10 H, singlet), 6.16 (2 H, singlet), 7.22 (6 H, singlet). **2c** showed: mp 143–144°; ν_{CO}^{KBr} 1660 cm^{-1}; λ_{max} (C_6H_{12}) 271 (sh) (ϵ 250), 266 (sh) (393), 263 (sh) (426), 261 (491), 255 nm (442); nmr ($CDCl_3$) τ 2.86 (10 H, singlet), 6.10 (2 H, singlet), 7.0 (6 H, singlet). In addition, these substances gave correct elemental analyses.

(13) This substance (mp 77°; ν_{CO}^{KBr} 1640 cm^{-1}; nmr ($CDCl_3$) τ 2.70 (5 H, singlet), 5.25 (1 H, exchangeable, multiplet), 5.62 (2 H, singlet), 7.12 (6 H, singlet)) was characterized on direct spectral (ir, nmr) comparison with an authentic sample (mp 77–78°) prepared from benzylamine and *N*,*N*-dimethylcarbamoyl chloride. Very likely, **4** is produced on photoreduction of an initially generated alkylidene. Experiments designed to assess the exact source of **4** and also characterize the alternate fragment (C_6H_5CH ?) are currently in progress here.

(14) This compound (mp 63–64°) was characterized both spectrally (ν_{CO}^{KBr} 1640 cm^{-1}, *m/e* 298 (P^+, 2.5%), 121 (100%), 72 (27%); nmr ($CDCl_3$) τ 2.3–2.8 (10 H, multiplet), 4.10 (1 H, singlet), 5.73 (1 H, singlet), 5.86 (1 H, singlet), 6.50 (3 H, singlet), 7.14 (6 H, singlet)) and through its conversion to benzaldehyde dimethyl acetal (ir, nmr) and **4** on treatment with anhydrous methanolic HCl. These two substances were also generated on photolysis of either **2c** or **5** in spectral grade methanol which was *not* subjected to calcium hydride treatment.

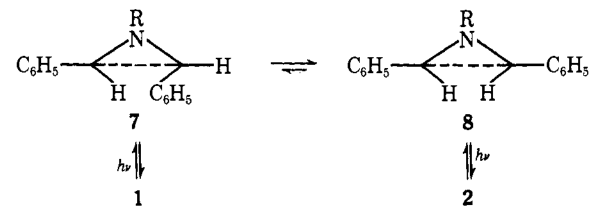
(15) Simple inspection of the uv data relating to **1** (**a**, **b**, **c**) and **2** (**a**, **b**, **c**) reveals the presence of an absorption manifold which is obviously benzenoid in character. Hence, our mechanistic comparison of the three distinct N-substituted systems studied here appears valid at least to the extent that electronic excitation at 2537 Å is in each case introduced into the system *via* the benzene chromophore. With regard to electronic multiplicity we should point out that we find **1**, **2**, and **3** to be unresponsive to prolonged sensitized (benzophenone) radiation (3500 Å). Therefore, it appears likely that singlet rather than triplet excited states are primarily responsible for the observed transformations.

(16) H. Nozaki, S. Fujita, and R. Noyori, *Tetrahedron*, **24**, 2193 (1968). Preliminary experiments in our laboratories appear to indicate that photofragmentation here occurs without prior stereoisomerization.

(17) The variation in heteroatom (X) electronegativity was introduced in the usual manner, *i.e.*, through the relation $\alpha_X = \alpha_C + h\beta$. For each h there was obtained a set of ground-state π binding energies (BE_π) by varying the value of the β_{CC} term in the calculation. The following results are representative of this treatment: (a) when $h = 1.5$, $BE_\pi = 5.00\beta$ for $\beta_{CC} = \beta$ (sharp angle) and 4.40β for $\beta_{CC} = 0.2\beta$ (wide angle) and (b) when $h = 0.5$, $BE_\pi = 3.00\beta$ for $\beta_{CC} = \beta$ and 3.14β for $\beta_{CC} = 0.2\beta$. Thus, a reduction in the effective electronegativity of X leads to a widening of the C–X–C angle of minimum π energy and consequently to a decrease in the 1,3-π-overlap within the 2-heterotrimethylene. Our reluctance to formulate the 2-heterotrimethylene as a dipolar species stems from the fact that this latter arrangement is but a resonance contributor to the general singlet wave function of the system, the other significant contributor being of course the diradical form whereby the nitrogen lone pair is largely localized and each of the two π carbons is associated with just one electron. Thus, while description of this fleeting intermediate by a dipolar arrangement appears, for obvious electronic reasons, justified in the case of *N*-aryl-2,3-dicarbalkoxyaziridines,[18a] similar formulation in the case of the diphenylaziridines studied here appears less straightforward. Indeed the pronounced substituent effect revealed by the present work is clearly suggestive of the importance of the dipolar contributor in the case where electronic excitation leads to fragmentation, *e.g.*, R (**1**, **2**) = C_6H_5, $CON(CH_3)_2$, and of the predominance of the diradical variant for the instance where photoexcitation leads solely to stereoisomerization, *e.g.*, R (**1**, **2**) = $COOC_2H_5$.

(18) For a description of the profound control that orbital symmetry appears to have on the thermal electrocyclization of related systems, see: (a) R. Huisgen and H. Mäder, *J. Amer. Chem. Soc.*, **93**, 1777 (1971); (b) J. H. Hall, R. Huisgen, C. H. Ross, and W. Scheer, *Chem. Commun.*, 1188 (1971), and references therein. Excited-state ring opening of these systems has also been reported: (c) R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967); (d) R. Huisgen and H. Mäder, *Angew. Chem., Int. Ed. Engl.*, 604 (1969); (e) Th. DoMinh and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **92**, 6997 (1970); (f) H. Herman, R. Huisgen, and H. Mäder, *ibid.*, **93**, 1779 (1971).

Scheme IV



where dotted lines are employed to indicate strong π interaction. For obvious steric reasons rotational interconversion between **7** and **8** ought to favor the latter and thus ultimately generate a mixture rich in **2**.[19] It is hoped that studies with optically active **1**, currently in progress within our laboratories, will shed further light into the mechanistic picture of the stereoisomerization process.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (GP 9404, GP 26347).

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(19) Within the frame of the scheme shown in IV, this conclusion is of course only valid if the σ–π interconversions shown occur in the excited state. It is also perhaps interesting to note that the observed interconversion between **1** and **2** may also be rationalized through the initial excited state generation of **7** and **8** depicted in Scheme IV followed by electronic deactivation of these species and subsequent *thermal*, symmetry-controlled, closure to **2** and **1**, respectively. Nonetheless, we tend to favor the mechanistic interpretation of Scheme IV owing to the obvious inability of the "thermal" process to readily accommodate the substantial photostationary predominance of the cis isomer irrespective of N substituent.

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Received September 15, 1971

Steric Hindrance in the Transfer of Singlet Electronic Energy

Sir:

Despite the rather large number of studies in recent years on electronic energy transfer, there have been no systematic investigations of the effect of variations of molecular structure, *i.e.*, variations which do not involve changes in the nature of the acceptor chromophore, on the transfer of singlet electronic energy in gas phase interactions. Work on the transfer of triplet energy in the gas phase from acetone to olefins[1] and from benzene to olefins[2] has been reported, but in both cases the transfer process is inefficient and the triplet energy levels of the olefins vary. Also, singlet energy transfer from benzene to a variety of accepters in the gas phase has been reported,[3] but, again, the singlet energy levels of the acceptors vary over a substantial range. In the liquid phase, quenching of fluorescence from a variety of ketones by olefins[4] has been studied as a function of ketone structure, but the process appears to involve a chemical reaction which can lead to new products rather than an electronic energy transfer.

Subtle structural variations which do not significantly alter the electronic energies of the donor and/or acceptor species should, in our opinion, provide a useful probe of the detailed nature of energy transfer mechanisms, particularly those which occur over molecular distances and which are relatively efficient. As a result we have been prompted to investigate the structural parameter in the exothermic transfer of singlet energy from benzene to various aliphatic ketones in the gas phase. The preliminary results reported in this communication confirm that structural dependencies in energy transfer can be measured and, to the best of our knowledge, provide the first quantitative study of steric hindrance in singlet electronic energy transfer in the gas phase.

The bimolecular rate constants and the corresponding hard-sphere effective quenching cross sections for the process singlet benzene + ketone → singlet ketone + benzene are shown in Table I.

Table I. Summary of Fluorescent Quenching Data[a]

Ketone	k_q, M^{-1} sec^{-1} × 10^{-10}	σ^2, Å^2
Acetone	8.27 ± 0.47	10.4 ± 0.6
2-Butanone	8.09 ± 0.23	10.4 ± 0.3
3-Pentanone	9.77 ± 0.52	13.1 ± 0.7
2,4-Dimethyl-3-pentanone	6.24 ± 0.49	8.92 ± 0.7
2,2,4,4-Tetramethyl-3-pentanone	2.03 ± 0.27	3.02 ± 0.4

[a] λ_{ex}, 253.7 nm; [benzene], 15 Torr; temperature, 25°.

The rate constants for bimolecular quenching, k_q, were determined in the standard manner[5] from least mean squares analysis of linear Stern–Volmer plots of $\phi_f{}^0/\phi_f$ *vs.* [ketone]. The singlet lifetime τ_s of benzene was taken to be 75 nsec.[6] Ketone pressures were measured with an MKS Baratron capacitance manometer using a 3-Torr head while the benzene pressure was measured with a mercury manometer. The 253.7-nm line from a Hanovia SH-100 medium-pressure Hg lamp was isolated with a Bausch and Lomb 500-mm grating monochromator using 2-mm slits, and the fluorescence was measured in a standard T-shaped cell. Scattered light corrections were made by totally quenching the benzene fluorescence with O_2. The individual values are averages of at least four independent determinations and the uncertainties indicate the average deviation from the mean in each case. The cross sections can be compared with those obtained by Lee and coworkers[7] of ~13–14 Å^2 for cyclobutanone, cyclopentanone, and cyclohexanone at benzene pressures of 2.5 Torr.

Since the benzene singlet lifetime has been independently measured by five laboratories using three different techniques, it seems safe to conclude that the bimolecular rate constants closely approximate absolute values for the conditions of these experiments.

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(1) R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **87**, 5569 (1965).

(2) For a summary see E. K. C. Lee in "Excited State Chemistry," J. N. Pitts, Jr., Ed., Gordon and Breach, New York, N. Y., 1970, pp 59–91.

(3) (a) A. Morikawa and R. J. Cvetanović, *J. Chem. Phys.*, **49**, 1214 (1968); (b) E. K. C. Lee, M. W. Schmidt, R. G. Shortridge, Jr., and G. A. Hanniger, Jr., *J. Phys. Chem.*, **73**, 1805 (1969).

(4) (a) N. J. Turro, J. C. Dalton, G. Farrington, M. Niemczyk, and D. M. Pond, *J. Amer. Chem. Soc.*, **92**, 6978 (1970); (b) G. D. Renkes and F. S. Wettack, submitted for publication.

(5) J. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 663.

(6) 75 ± 5 nsec appears to encompass the values of τ_s obtained by several laboratories for conditions similar to those used in these experiments. See, for example, (a) T. Chen and E. W. Schlag, in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 381; (b) G. M. Breuer and E. K. C. Lee, *J. Chem. Phys.*, **51**, 3615 (1969); (c) N. Nishikawa and P. K. Ludwig, *ibid.*, **52**, 107 (1970); (d) B. K. Selinger and W. R. Ware, *ibid.*, **53**, 3160 (1970); (e) C. S. Burton and H. E. Hunziker, *ibid.*, **52**, 3302 (1970).

(7) (a) H. A. Denschlag and E. K. C. Lee, *J. Amer. Chem. Soc.*, **90**, 3628 (1968); (b) E. K. C. Lee, *J. Phys. Chem.*, **71**, 2804 (1967); (c) R. G. Shortridge and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 2228 (1970).