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SENSITIZATION AND QUENCHING IN THE CONVERSION OF LIGHT ENERGY INTO CHEMICAL ENERGY

MASTER

Progress Report

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Abstract of second progress report on:

SENSITIZATION AND QUENCHING IN THE CONVERSION OF LIGHT ENERGY INTO CHEMICAL ENERGY

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Extensive data from Stern-Volmer, Lamola-Hammond, and Ilenda-Daughenbaugh-Cristol quenching kinetics have now been accumulated on photosolvolysis in t-butyl alcohol for benzyl chloride and a number of meta and para substituted benzyl chlorides. Evidence for the existence of two triplet states, one relatively short-lived (τ 0-2 nsec) which gives solvolysis product and a second, relatively long-lived (τ 5-26 nsec), which does not give product, but instead is energy wasting, has been accumulated. The system, p-acetobenzyl chloride, has been investigated in detail. A method for quenching of singlet states for measurement of singlet lifetimes in the 100 picosecond to nanosecond range is being developed. Preliminary work on benzyl acetate photosolvolysis has been conducted. Some work on the geometrical requirements for intra-molecular excitation transfer in bichromophoric molecules has been conducted.

Several dienes related to norbornadiene have been prepared and preparative photoisomerizations to quadricyclene analogues have been carried out. Considerable attention has been given to certain di-π-methane rearrangements, work on most of which is still in progress. One system, the ethyl ester of dibenzobarrelene-7-carboxylic acid, has been scrutinized in detail.

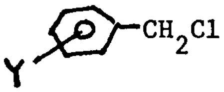
I. INTRODUCTION

The contract under which the research described in this report is supported had a starting date of February 1, 1979, and a first progress report was prepared in September 1979 describing work done during the first half year of the contract term. This report, which is being prepared in August, 1980 .

II. RESEARCH AREAS INVESTIGATED

A. Reaction of Benzylic Halides

T. H. Bindel continued his work on the ketone-sensitized reactions of benzyl chlorides and some meta- and para-substituted benzyl chlorides (1) in text-butyl alcohol, as well as of the corresponding unsensitized reactions. His earlier work had involved chemical and quantum yield measurements of the photosolvoysis ("ionic") products (the text-butyl ethers 2 and the benzylic alcohols 3 resulting from capture of the benzylic cation by the acetone used in the sensitized reactions) and the homolysis ("radical") products 4, 5, and 6 in both sensitized and unsensitized photoreactions. This work has now been published (S. J. Cristol and T. H. Bindel, I. Org. Chem., 45, 951, 1980). During the period of the DOE research support, Bindel has extended this work to several more compounds. Confirming and extending his earlier studies, he found that sensitized irradiations give higher chemical and quantum yields of ionic products then of radical products and that opposite is time for direct irradiations.



1

$ArCH_2Ot\text{-}Bu$

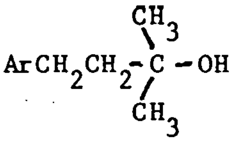
2

$ArCH_2OH$

3

$ArCH_2CH_2Ar$

4



$$ArCH_2CH_2-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

5

$ArCH_2CH_2CO\ CH_3$

6

Of perhaps more interest, Bindel's work during the last year has given us significant insight into details of these reactions that were not apparent to us from the earlier results. Although these photosolvolysis (and homolysis) reactions are not related to energy storage, we decided to use them, as we had so much background information on them, as substrates to test our method (C. J. Ilende, R. J. Daughenbaugh, and S. J. Cristol, Mol Photochem., 7, 287, 1976) for measuring triplet lifetimes of species produced by sensitization and for measuring rates of excitation transfer from sensitizer to reactant. We hoped to see if any structure/rate correlations might be apparent from such data. Further we hoped to correlate data obtained by our method for sensitized reactions with lifetimes (of triplets produced by intersystem crossing and measured by Stern Volmer product quenching procedures (Physik. Zeitschrift, 20, 183, 1919) or by the Lamola-Hammond procedure (J. Chem. Phys., 43, 2129, 1965) involving piperylene isomerization. We anticipated that the triplets produced by intersystem crossing would be identical to those produced by excitation transfer (sensitization) although the possibility of excited-state complex (exciplex) intervention in the latter situation was not excluded from our thinking.

Bindel's preliminary data were indicated in our September 1979 report, and his work has been extended to several additional compounds as well as to replication. We had prepared a manuscript last year, but did not submit it for publication, as it was clear to us that it would be more reasonable to delay publication until more data were available. An enlarged manuscript is now almost ready for final typing and will be submitted for publication at about the time this report is submitted to DOE. As that manuscript will contain almost all of the data presently available and related to this work, with the exception of work with p-chloromethylbenzophenone (p-1-COPh, which will be reported separately) the data are not reproduced in detail herein. Instead, only a summary of results and the conclusions we have drawn are included.

Bindel, using the Ilenda-Daugheinbaugh-Cristol procedure, found that the lifetimes of those triplets produced by either acetone or acetophenone sensitization, which lead to solvolysis product were in the 0.4 to 1.5 nsec range. The compounds studied were 1-H, p-1-Cl, p-1-t-Bu and m-1-OCH_3. The method, we believe, has a reliability of only ± 2 nsec, so that, from the point of view of structure-reactivity correlations, our results were disappointing. On the other hand, however, it is clear that the triplets produced by sensitization and leading to solvolysis products are extremely short-lived.

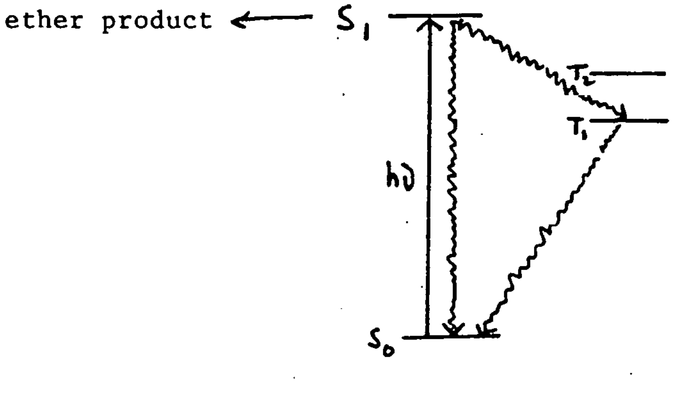
Stern-Volmer quenching by cis-piperylene of ether formation in direct irradiations was conducted with 1-H, m-1-OCH_3, p-1-$COCH_3$, and p-1-COPh. If it is assumed that products arise from triplet states, they had lifetimes in the

-0.5 to 1.2 nsec range, again all within the range of experimental error. Again the results, while not allowing structure/reactivity correlation, showed that the product-forming triplets were all extremely short-lived (or that products came directly from singlet states - see below).

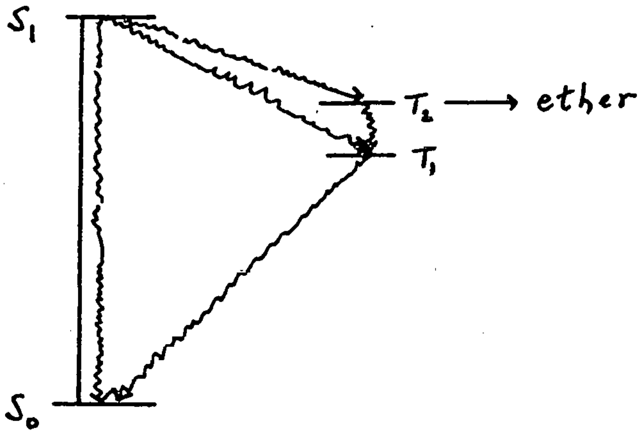
Lamola-Hammond quenching studies were carried out with 1-H, p-1-OCH$_3$, m-1-OCH$_3$, p-1-t-Bu, p-1-Cl, p-1-COCH$_3$, and p-1-COPh in t-butyl alcohol. This method gives both quantum yield of conversion of singlet produced by direct irradiation to piperylene-quenchable triplet and the lifetime of that species (that is the piperylene-quenchable triplet). The quantum yields for intersystem crossing varied from 0.05 to 0.6, with irradiation at 254 nm, but the triplets which were produced by intersystem crossing had lifetimes in the range of 5 to 26 nsec, well above those of the species which gave solvolysis products.

The results of the study of the three types of quenching imply that at least two triplets are produced in the benzyl chloride solvolyses. One of these, a relatively short-lived and (presumably always) higher energy species is reactive and leads to photosolvolysis products, while the other (longer-lived) one seems not be reactive, but rather decays to the ground-state so that it is "hidden," except in the Lamola-Hammond procedure. Its formation is, of course, an energy-wasting process. As we cannot tell, from our data, whether the ether produced in the direct irradiation process is the result of reaction from the excited singlet state or from the upper triplet state (we know only that the progenitor state is non-quenchable or barely quenchable), the results may be diagrammed either as Scheme I or Scheme II (for the non-keto benzyl chlorides) as plausible minimum paths.

Scheme I - Plausible Mechanism for Benzyl Chloride Photolysis.



Scheme II - Plausible Mechanism for Benzyl Chloride Photosolvolysis.

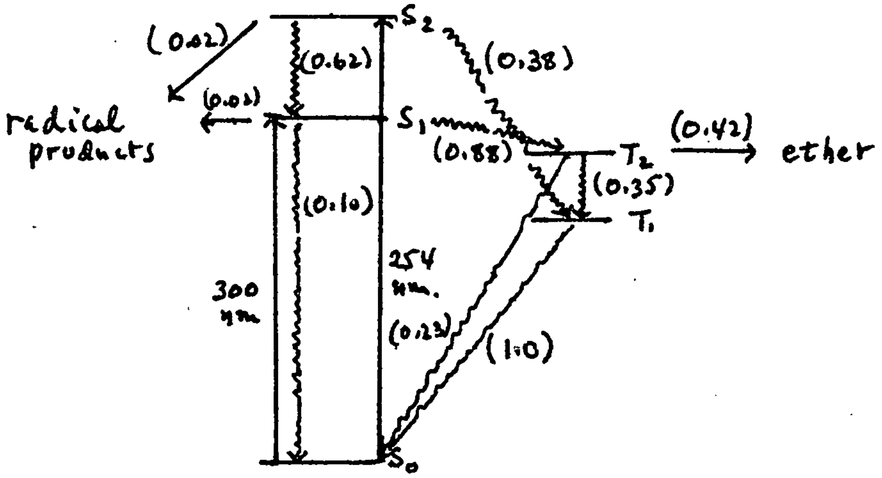


In Scheme I, we assume that an excited singlet state leads both to product and to the lower "hidden" triplet state (T_1) and that the upper triplet state is not accessible from the singlet state, possibly due to energy considerations, but more likely due to symmetry considerations. In Scheme II, the excited singlet-state crosses to T_2 and T_1, leading to product from T_2 and to energy wastage via T_1. The fact that the quantum yield of ether for direct irradiation is almost always (the exception is discussed below) lower than that of the sensitized irradiation is consistent with either scheme.

If, as we suggest, there are two triplets, of which T_2 gives product and T_1 is energy wasting, both may be accessible by sensitization. Put another way, higher energy sensitizers may be anticipated to give a larger ratio of T_2 to T_1 than lower energy sensitizers, even though the lower energy sensitizer may be completely quenched by the reactant. This is a different rationalization of lower quantum yields from low energy sensitizers; it is generally assumed that low quantum yields result from failure to effect excitation transfer rather than transfer to an inert excited state. Bindel observed that use of benzophenone (E_T 69 kcal/mol) as sensitizer gave ϕ_{max} values for m-methyoxybenzyl chloride about 1/20th that of acetone (E_T 80 kcal/mol) or acetophenone (E_T 74 kcal/mol). He then showed that this halide quenched the benzophenone-benzohydrol reaction to give benzopinacol, a result consistent with the idea of a T_1 state of energy close to 70 kcal/mol.

p-Acetobenzyl chloride is an interesting substrate, in that it shows a large wavelength dependence upon ether formation and upon T_1 formation. Thus irradiation at 254 nm leads to ether with a ϕ_{max} of 0.23 and to T_1 with a ϕ_{max} of 0.57, while irradiation at 300 nm gave ϕ_{max} of ether formation of 0.37 and Lamola-Hammond triplet yield of 0.31. The fact that the upper excited state S_2 (a $\pi - \pi^*$ state) gives less ether and more T_1 than does S_1 suggests that S_2 correlates with T_1 and S_1 with T_2. These are shown in Scheme III, in which the possibility of ether formation from singlet states is ignored. The efficiencies for all of the processes are given in parentheses in the Scheme, and we have used the quantum yield measured for acetone sensitization (0.42) to establish the high efficiency (0.88) of intersystem crossing from S_1 to T_2. Thus, using Scheme III, we have succeeded in accounting for almost all of the light absorbed in the direct irradiations, which is an unusual accomplishment.

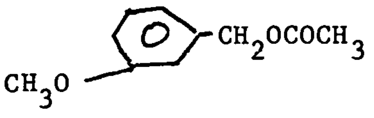
<u>Scheme III - Fates of Various Excited States of p-Acetobenzyl Chloride</u>.



K. M. Cruz has begun a study of the quenching of the benzyl chlorides to benzyl t-butyl ethers with acetone. In the experiment which she devised, she subjected benzyl chloride to irradiation at 254 nm, used acetone as a singlet quencher, in the presence of enough piperylene to quench the triplet acetone produced by intersystem crossing. We believe that this is the first use of such a procedure, which may be useful for measuring lifetimes of relatively long-lived singlets, although it is difficult to make an appropriate literature search. In any case, she obtained an excellent correlation line, giving a $k_Q\tau$ of 1.1, which implies a lifetime for the singlet antecedent to the benzyl t-butyl ether of about 100 picoseconds. We hope to test this procedure in other systems.

B. Benzyl Acetate Preliminary Work.

As the chlorides all had reactive triplet lifetimes too short to measure with any degree of accuracy for structure-reactivity correlations, and as H. E. Zimmerman and V. Sandel (J. Am. Chem. Soc., 85, 915, 1963) had reported that certain benzyl acetates including m-methoxybenzyl acetate (7) photosolvolyze readily in aqueous dioxane, we decided to study benzyl acetates in t-butyl alcohol. When 7 was irradiated



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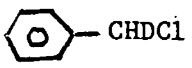

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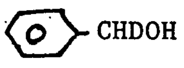

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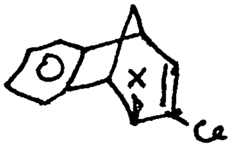
directly at 254 nm in t-butyl alcohol or sensitized with acetone in t-butyl alcohol (irradiation at 300 nm), only products resulting from homolysis of the benzyl-oxygen bond resulted. Repetition of the Zimmerman-Sandel experiment with 7 in aqueous dioxane confirmed their report that photosolvolysis accompanied a lesser amount of homolysis and we showed, as well, that the reaction stopped when irradiation was discontinued. Bindel then showed that, while irradiation of 7 in t-butyl alcohol did not give photosolvolysis, irradiation in aqueous t-butyl alcohol did, and that the ratio of ether plus alcohol to radical products increased with increasing water content in the solvent. Furthermore, photosolvolysis (along with homolysis) was observed upon irradiation in methanol, to give the methyl ether. The formation of ether products showed that Zimmerman and Sandel were correct in their assumption that heterolysis of the benzyl oxygen bond occurred. The solvent effect suggests a correlation between solvent ionizing power and solvolysis, just as in ground-state reactions. This was not observed with the chlorides.

These preliminary results encourage us to continue with work on other acetates, as well as to begin work on lifetime and other quantitative measurements. These are discussed in the proposal for continuation.

Vanessa Waite, a volunteer undergraduate student, who was attempting the preparation of chiral α-deuteriobenzyl chloride (8) succeeded in preparing the alcohol 9 and developing an analytical method for determining enantiomeric purity, but did not develop a method for the chloride. In view of the fact that we are now planning to switch to a study of solvolysis of the acetates, her work will be of use to us, as transformation of the chiral alcohol to the acetates should present no problem.

C. Other Photosolvolyses and Related Reactions.

Earlier work in our laboratory had shown that, while the chloride 10-Cl, dichloroacetate (10-OCOCHCl$_2$) and methanesulfonate (10-OSO$_2$CH$_3$) all gave Wagner-Meerwein rearrangement to 11-X compounds and solvolysis to 10-NHCOCH$_3$ upon direct irradiation, the acetate 10-OAc and the alcohol 10-OH gave only di-π-methane rearrangement to the corresponding 12 isomers. 12 isomers were producedfrom all 10-X species in sensitized reactions.



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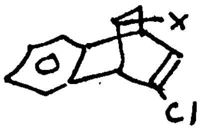

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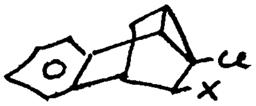

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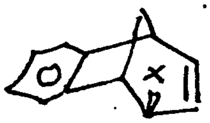

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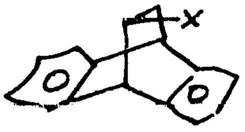
Cruz has begun a study of the quantitative aspects of these observations, planning to use quenching procedures to measure lifetimes of intermediates (and corresponding excited-state reaction rates) to attempt to rationalize these results. She has found that, in acetic acid, the photoreaction is diverted by almost 50% from 12-OAc to 11-OAc, suggesting (compare S. J. Cristol and R. D. Daussin, J. Am. Chem. Soc., 102, 2866, 1980) that acid catalysis converts the acetoxy group to a good nucleofuge, thereby favoring the "ionic" reaction route. On the other hand, she found that the dechloro analogue (13-OAc) was not diverted from the di-π-methane path in acetic acid. We hope that Stern-Volmer, Ilenda-Daughenbaugh-Cristol and Lamola-Hammond quenching experiments will enable us to begin to understand these peculiar structural effects, by giving us rate data which we can interpret. Furthermore we will have a chance to test our method against the others in systems where presumably only one triplet may be involved and in systems where singlets and triplets clearly give dissimilar products.

W. Szalecki prepared the quaternary ammonium salt 10-$N^+(CH_3)_3\ Cl^-$. Irradiation of this salt in acetic acid at 254 nm showed that it was photoactive, but a mixture containing over ten compounds was produced, none in substantial yield. He also prepared the quaternary ammonium compound 14-$^+N(CH_3)_3Cl^-$, but it was stable to irradiation. Work on quaternary ammonium compounds has been discontinued.



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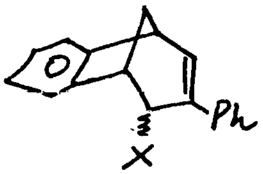

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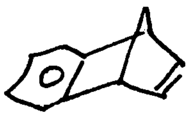

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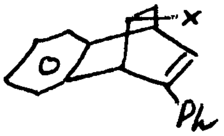

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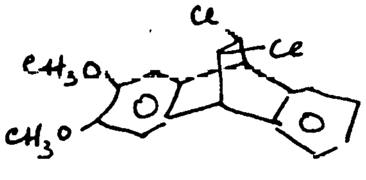
As part of our attempt to explore the nature of the chlorine effect in 10 and 13 compounds, Szalecki prepared some derivatives of 15. Attempts to prepare 15-Cl by addition of phenylchlorocarbene from phenylchlorodiazirene to benzonorbornadiene (16) were unsuccessful but the preparation of 15-OH from 10-OH with lithium diphenylcuprate was successful. This seems to be the first example of replacement of an ethylenic chlorine atom in such a reaction. A similar reaction to give 17-OH seems to be working. Irradiation of these compounds and of the corresponding chlorides is planned.

Bindel prepared compound 18, which has absorption at 310 nm, a point well beyond where the analog 19 is transparent. The principal products of



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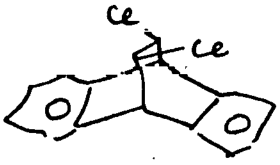

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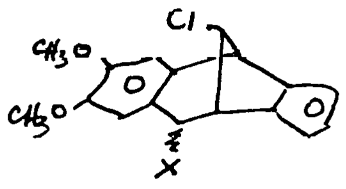

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irradiation in acetic acid of 18 at 300-310 nm were the acetates 20-OAc and the chlorides 20-Cl. This is an especially interesting experiment, as it shows that excitation transfer from the dimethoxybenzo ring chromophore activates the anti chlorine atom rather than the syn one, presumably by overlap of the π or π^* orbital of the ring with the σ^* orbital of the carbon-anti-chlorine bond, and that the non-activated syn ring (unsubstituted) migrates. These results were unforeseen and may have general inplications in terms of geometric requirements for intramolecular energy or electron transfer between chromophores in polychromophoric molecules. This work, plus work supported by NSF on two other systems which also demonstrate anti activation (excitation transfer) and syn migration and our attempt to rationalize these, has been written up and submitted as a Communication to the Editor. A copy of the manuscript has been sent to Dr. Kandel.

D. Photochemical Intramolecular [2 + 2] Cycloadditions.

The use of the photorearrangement of norbornadiene (21) to quadricyclene (22) and the reverse thermal (catalytic) reaction remains of active interest as an energy-storing model. Work on this system is conducted largely at Boston University (G. Jones, II) and at the University of Georgia (C. Kutal, B. King, R. Hautala). Our initial work with R. L. Kaufman on excitation-transfer rates from ketone sensitizers to norbornadiene and comments on lifetime measurements has been published (J. Photochem., 12, 207, 1980). We have not yet done more work with norbornadiene itself.

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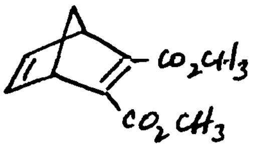

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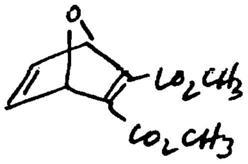

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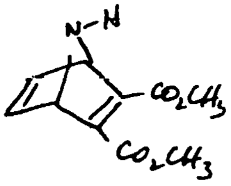

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D. Dorman has prepared 23, and its oxa (24) and aza (25) analogues and has photoisomerized them to the corresponding quadricyclenedicarboxylic ester and its oxa and aza analogues. With these materials in hand, Dorman is now working on the development of methods for the quantitative analysis of mixtures of the diene-quadricyclic components. When these methods are perfected, he will be in a position to begin work on the quantitative aspects of the sensitized and unsensitized photorearrangements. This should be carried out in the next year.

Dorman is also attempting the preparation of the unsubstituted 7-oxa and 7-azanorbornadienes (26 and 27). These compounds are very sensitive to acid reagents and have proven to be quite elusive. Work on the myrcene (28) to 29 photorearrangement has been deferred, due to lack of time.

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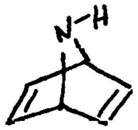

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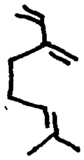

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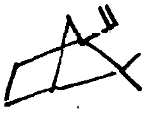

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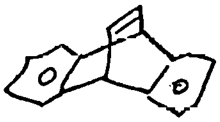
E. Di-π -methane Rearrangements.

We reported in 1979 that M. Hill (an undergraduate student) had succeeded in developing a gas chromatographic technique for the separation of dibenzobarrelene (30), dibenzosemibullvalene (31), and dibenzocyclooctatetraene (32), but, to our dismay, neither he nor W. Szalecki were able to reproduce the column to get decent separation. Szalecki has now developed a high pressure liquid chromatographic separation procedure for these compounds, so that he is now able to proceed to investigate the



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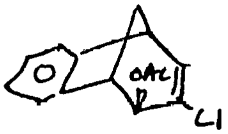

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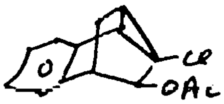

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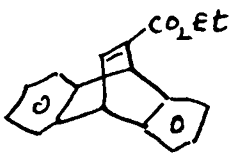
pressumed "relay" mechanism and the benzophenone sensitization energy wastage described in the proposal for continued work.

K. Cruz has measured quantum yields for the di-π-methane rearrangement of 33 to 34, both upon direct irradiation at 254 nm (ca 0.002) and upon acetone sensitization (ca 0.02). She now is in a position to do quenching studies for lifetime measurements for these triplet and/or singlet reactions.

J. Hager investigated the photorearrangement of ethyl 9,10-dihydro-9,10-ethenoanthracene-11-carboxylate (35) to the corresponding dibenzosemibullvalenecarboxylate (36). Previous work at duPont by E. Ciganek (J. Am. Chem. Soc., 88, 2882, 1966) indicated that 35 was converted in high yield to 36 upon irradiation in acetone, and preliminary work by G. Mayo in our laboratory had indicated that both direct irradiation and acetone sensitization of 35 gave 36, without measurable amounts of the other semibullvalene isomer 37 or the cyclooctatetranene isomer 38. Thus this system seemed a useful candidate for testing of the various quenching procedures. A liquid chromatographic method was developed for the analysis of 35 and 36 mixtures.



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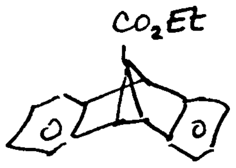

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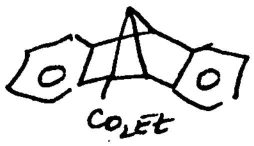

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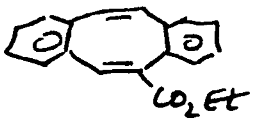

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Hager first looked at the Stern-Volmer product quenching procedure, using direct irradiation of solutions of 35 in acetonitrile and quenching with cis-piperylene. The levels of ϕ_o/ϕ_q which he obtained were very good straight lines, but the slopes were very small. Values for ϕ_o of 0.105, 0.116, and 0.119 (ave 0.11 ± 0.01) and slopes which led to values for $k_{RQ}\tau_{^{3}R}$ of 0.89, 0.80, and 0.74 (ave 0.8 ± 0.1) L/mol, assuming that a triplet state of 35 was being quenched, were obtained. If one assumes that k_{RQ} (the rate constant for excitation transfer from triplet 35 to piperylene is 5×10^9 L/sec/mol, a lifetime (τ_{3_R}) for triplet 35 of ca.200 psec may be computed. We do not have enough experience to know whether this result is reliable enough to indicate that a very short-lived triplet intermediate is produced, or whether a nonquenchable singlet is involved.

Lamola-Hammond quenching, measured by isomerization of cis-piperylene, was then carried out. Plots of $1/\phi_{\text{cis-trans}}$ vs 1/[piperylene] gave intercepts of 8.01 ± 0.19 and 7.70 ± 0.12 (ave 7.9 ± 0.2) and slopes of 1.60 ± 0.17 and 1.71 ± 0.09 (ave 1.7 ± 0.1). Computations fom these results gave values of ϕ_{isc} of 0.23 and 0.23 (arc 0.23 ± 0.01) and $k_{RQ}\tau_{3_R}$ of 5.0 and 4.5 (ave 5 ± 1). If these results are reliable, τ_{3_R} may be computed to be 1 nsec. This value seems to us to be too close to that of the Stern-Volmer method or of the Ilenda-Daughenbaugh-Cristol method (given below) to allow the discrimination of two triplet states, as was described above for the benzylic chloride solvolyses.

Preparatory to the use of the Ilenda-Daughenbaugh-Cristol method, Hager studied the effect of concentration of 35 on the quantum yield of 36, using benzophenone as sensitizater in acetonitrile solvent. Irradiation at 350 nm was chosen, as 35 has measurable absorbance at 300 nm, and benzophenone was chosen as sensitizer, as acetone has too low an absorbance at 350 nm and acetophenone interfered with analysis for 36. The quantum yield leveled out at 0.47 for ϕ_{max} at approximately 0.04 M in 35. A plot of $1/\phi$ vs 1/[35] had an intercept of 2.15 ± 0.04 and a slope of 0.0125 ± 0.0012. From the intercept, $\phi_{max} = 0.47$ and from the intercept/slope, $k_{SR}\tau_{3_S} = 170 \pm 30$. Unfortunately the lifetime for triplet benzophenone (T_{3_S}) in acetonitrile is apparently not known, and indeed values for T_{3_S} invarious solvents from 1 to 12 x 10^{-6} sec are given in the literature. If one uses the value reported for benzene solvent (F. S. Dainton, J. Kemp, G. A. Salmon, and J. P. Keene, Nature, 203, 1050, 1964, and G. Porter and R. Topp, Proc. Roy. Soc., Ser. A, 315, 163, 1970) of 3 x 10^{-6} sec, one gets a value for k_{SR} of 6 x 10^7 L/sec/mol.

This value is approximately 1/100th that of diffusion control, and we thought that this might be due to reversible excitation transfer. If that were the case, increasing the concentration of benzophenone sensitizer should decrease the quantum yield of 36. When Hager varied the concentration of benzophenone over the range 0.20 to 3.0 molar, the quantum yield was invariant within experimental error, indicating that reversible excitation transfer is not an important factor in this system.

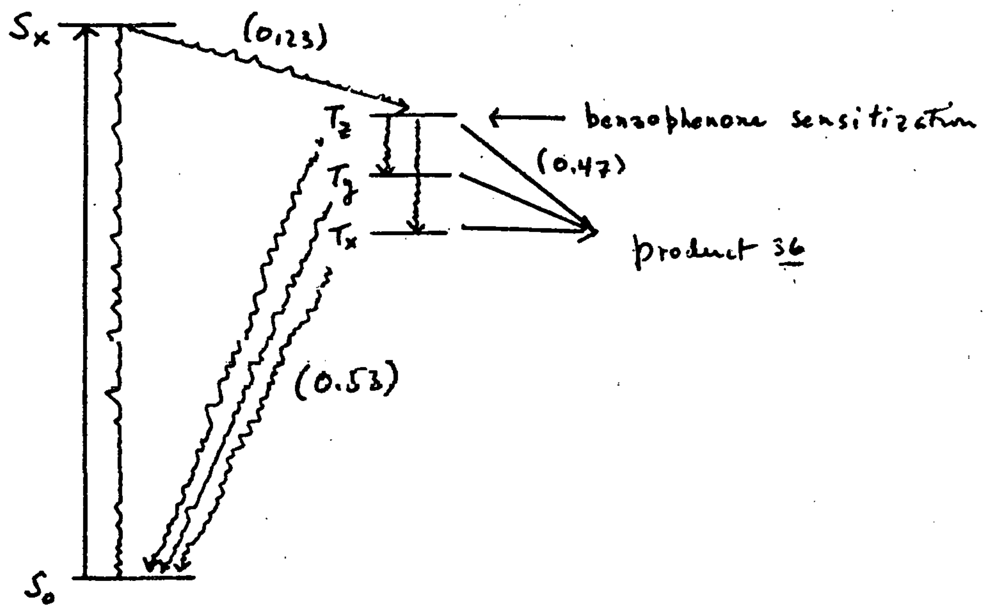
Two runs were made using Ilenda-Daughenbaugh-Cristol (IDC) quenching kinetics. The first run at a ratio of (35) to (piperylene) of 4.2 gave a slope of 20 and an intercept of 6.0, from which one may compute values of k_{SR}/k_{SQ} of 21 and $k_{RQ}\tau_{SR}$ of 3.3 M^{-1}. The second, run at a ratio of 20.5, gave rise to a line with slope 5.0 and intercept 1.8, from which one gets k_{SR}/k_{SQ} = 17 and $k_{RQ}\ \tau_{^3R}$ = 2.8 M^{-1}. With the usual assumptions of values for k_{SQ} and k_{RQ} equal to 5×10^9 L/mol/sec, one obtains values of $k_{SR} = 2.6 \times 10^8$ L/mol/sec and $\tau_{^3R}$ = 0.6 nsec.

The value of k_{SR} of 2.6×10^8 L/mol/sec is about 4 times that (6×10^7 L/mol/sec) computed from the sensitization data. Obviously the larger result has an assumption regarding k_{SQ} and the latter one regarding the lifetime of triplet benzophenone in acetonitrile. If we can get set up to measure this lifetime, we will have a base for all of the values we obtain. This is planned for the coming year.

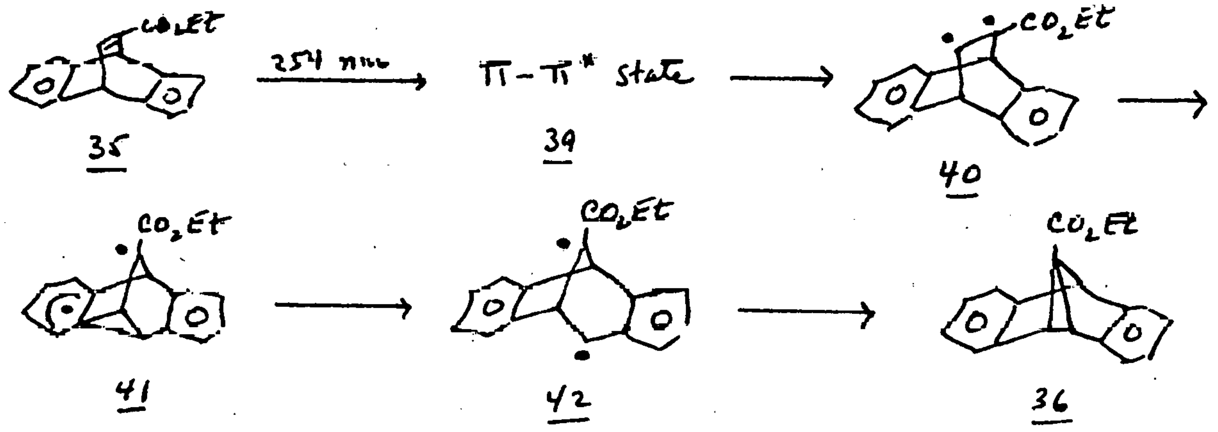
The three different methods for lifetimes of triplet 35 all give very disappointingly short lifetimes, possibly all identical within experimental error. Stern-Volmer results give $T_{^3R}$ of 0.2 nsec, IDC, 0.6 nsec, and Lamola-Hammond, 1.0 nsec. These values are all smaller than that reported by R. L. Kaufman (Ph.D. dissertation, University of Colorado) for dibenzobarrelene itself (30), using IDC kinetics, which Szalecki is planning to check and expand.

The Lamola-Hammond results certainly indicate that a triplet quenchable by piperylene, is formed by intersystem crossing from direct irradiation and that it is formed in a quantum yield of 0.23. It may not be a coincidence that the quantum yield of product (0.12) is approximately equal to this intersystem crossing efficiency (0.23) times the quantum yield (0.47) of 36 produced by benzophenone sensitization. This would give rise to the minimum Scheme IV for this over-all process.

Scheme IV Plausible Path for Photoisomerization of 35 to 36.



A serious problem with this system is that the mechanism commonly invoked to rationalize the di-π-methane rearrangement involves a variety of "intermediates" (see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, Chem. Rev., 73, 531, 1975). Such a path, from 35, might be as follows:



The "intermediates" shown may or may not be minima on the hypersurface leading from the excited state of reactant to the ground state of the product, although similar structures of monoradicals are energy minima in radical rearrangements. A principal difficulty with this scheme is that one cannot guess at which stage or stages intersystem crossing occurs, or whether sensitization (excitation transfer) leads to a triplet earlier or later in the reaction scheme than does direct irradiation and intersystem crossing. Further, one might guess that 39 and 40, if quenchable triplets, would be quenchable back to reactant 35, but that 42 would quench to product 36, and 41 might give both 35 and 36. These problems are obviously a good deal more complex than we anticipated, but working with compounds with longer triplet lifetimes may shed some light on how to treat such systems.

III. PERSONNEL INVOLVED

The work described above was conducted by post-doctoral, graduate, and undergraduate students at the University of Colorado. Some of the students received salaries (as noted) during the period indicated; where this is not indicated, chemicals and equipment were provided by our DOE contract. Except as noted, each individual is presently at the University of Colorado.

Thomas H. Bindel, B.S., University of Colorado at Denver; Ph.D. University of Colorado, Boulder, 1980; salary, March 1979 - August 1980; now acting assistant professor, University of Colorado, Boulder.

Katherine M. Cruz, B.S., University of New Orleans; salary, August 1979 - present.

David C. Dorman, B.S., University of San Diego; salary, summers 1979, 1980.

Matthew J. Hill, undergraduate student, University of Colorado.

Wojceich Szalecki, Ph.D., University of Lodz (Poland); post-doctoral stipend 1980.

Vanessa Waite, undergraduate student, work-study support, Summer, 1979; graduate student, Rice University.

The principal investigator on this contract is Stanley J. Cristol.

IV. ADDENDUM TO PUBLICATION LIST OF PROFESSOR STANLEY J. CRISTOL

The March 1978 proposal listed 186 publications appearing through 1977, and the September 1979 report listed five additional publications. Publications since that date are as follows:

188. S. J. Cristol and R. J. Daughenbaugh, "Photochemical Transformations. 23. β-Substituent Effects in the Photorearrangement-Cyclizations of Allylic Chlorides to Cyclopropyl Chlorides," J. Org. Chem., 44, 3434 (1979).

193. S. J. Cristol and R. M. Strom, "Photochemical Transformations. 24. Comparison of 'Ionic' Intermediates Produced Photochemically with Corresponding Ground-State Intermediates. Initial Studies in Some Chlorobenzooctadienyl Systems," J. Am. Chem. Soc., 101, 5707 (1979).

194. S. J. Cristol and R. L. Kaufman, "Photochemical Transformations. 25. Quenching Experiments in the Triplet-Sensitized Conversion of Norbornadiene to Quadricyclene," J. Photochem., 12 (1980) 207-213.

195. S. J. Cristol and T. H. Bindel, Photochemical Transformations. 26. Sensitized and Unsensitized Photoreactions of Some Benzyl Chlorides in tert-Butyl Alcohol," J. Org. Chem., 45, 951 (1980).

196. S. J. Cristol and R. D. Daussin, "Photochemical Transformations. 27. Acid-Catalyzed Photosolvolytic Reactions and Rearrangements. Evidence for Heterolytic Photochemical Bond Cleavage," J. Am. Chem. Soc., 102, 2866 (1980).

V. OTHER ACTIVITIES OF PRINCIPAL INVESTIGATOR

The principal investigator has eight manuscripts in various stages of publication or process. Of these, three are in press, two others have been submitted for publication, one is in final draft stage prior to submission, one has an initial draft typed and one is in preparation. Since September 1979, the principal investigator presented papers at the First Kyoto International Conference on New Aspects of Organic Chemistry and at the DOE Fourth Solar Photochemistry Research Conference at Notre Dame in June. He attended the Sixth IUPAC Conference on Organic Photochemistry in Seefeld, Austria in July and the Third International Conference on Solar Photochemistry in Boulder in August. His students presented five papers at the Spring 1980 meeting of the Colorado-Wyoming Academy of Sciences in Denver.

The principal investigator was honored by the awarding of a Faculty Fellowship (research sabbatical leave) by his University for the 1981 calendar year and by the John Simon Guggenheim Memorial Foundation of a Guggenheim fellowship for the same period. His present plans are to spend most of this time in Boulder with his research group and writing manuscripts, although tentative plans are being made to spend short stays (4 - 6 weeks) in Lausanne and in London.