epimeric CH_3), 1.30–0.80 (m, 10 H, $CH(CH_3)CH_2CH_2CH_2$). Anal. ($C_{18}H_{32}O_5{\cdot}0.25H_2O$): C, H.

[(2*RS*,5*SR*)-5-(5-Hydroxy-4,8-dimethyl-8-nonenyl)-5-methyl-1,4-dioxan-2-yl]acetic Acid (3b). Fractional crystallization of **15** from Et_2O/hexanes gave **16a** (43% from **15**; mp 61–62 °C) which was converted to **3b** (21.2%) according to the same procedure described for compound **21**: IR (neat) 3420, 1730, 1105 cm^{-1}; NMR ($CDCl_3$) δ 6.27 (br, 2 H, OH and COOH), 4.73 (br, 2 H, CH_2=), 3.83–3.27 (m, 6 H, C-2, C-3, C-6 H, and CHO), 2.48 (d, $J = 6$ Hz, 2 H, CH_2CO_2), 2.20–1.97 (m, 2 H, vinyl CH_2), 1.77 (s, 3 H, vinyl CH_3), 1.65–1.23 (m, 9 H, allylic CH_2 and $CHCH_2CH_2CH_2$), 1.07 (s, 3 H, C-5 CH_3), 0.60 (d, $J = 6$ Hz, 3 H, side-chain CH_3). Anal. ($C_{18}H_{32}O_5{\cdot}0.25H_2O$): C, H.

[(2*RS*,5*SR*)-5-(5-Hydroxy-4,8-dimethyl-7-nonenyl)-5-methyl-1,4-dioxan-2-yl]acetic Acid (3a). The double bond isomerization of **3b** was carried out as described for **21**. The crude reaction product was purified free of residual **3b** by chromatography (silica gel impregnated with 20% $AgNO_3$; Et_2O/petroleum ether/AcOH, 20:20:1), giving **3a** as a colorless oil: 34%; IR (neat) 3400, 2950, 1730 cm^{-1}; NMR ($CDCl_3$) δ 6.30 (br, 2 H, OH and COOH), 5.18 (m, 1 H, CH=), 3.77–3.28 (m, 6 H, C-2, C-3, C-6 H, and CHO), 2.48 (d, $J = 6$ Hz, 2 H, CH_2CO_2), 2.17 (m, 2 H, vinyl CH_2), 1.77 and 1.68 (2 s, 3 H each, 2 vinyl CH_3), 1.38 (m, 7 H, $CHCH_2CH_2CH_2$), 1.08 (s, 3 H, C-5 CH_3), 0.93 (d, $J = 6$ Hz, 3 H, side-chain CH_3). Anal. ($C_{18}H_{32}O_5{\cdot}0.25H_2O$): C, H.

Acknowledgment. We thank E. Deegan for the preparation of some of the intermediates, Dr. M. L. Cotter for spectroscopic results, and C. Shaw for GC/MS data. We are also in debt to Dr. S. D. Levine for constant encouragement and interest in this work and to Professor J. A. Marshall for helpful discussions.

Registry No. 3a, 84143-14-6; **3b**, 85665-05-0; **6**, 1071-73-4; **6** benzyl ether, 13329-18-5; (±)-**7**, 85665-06-1; (±)-**8**, 85665-07-2; **9**, 85665-08-3; (±)-**10**, 85665-09-4; **11**, 85665-10-7; **12**, 85665-11-8; **13**, 85665-12-9; **14**, 85665-13-0; **15**, 85665-14-1; (±)-**16a**, 85665-15-2; **17**, 85665-16-3; **18**, 85665-17-4; (±)-**19**, 85665-18-5; **20**, 85665-19-6; **22**, 84143-14-6; $BrCH_2CH_2(OEt)_2$, 2032-35-1; $Ph_3P{=}CHCO_2Et$, 1099-45-2.

Photochemical Transformations. 34. Some Studies on the Di-π-methane Rearrangement of 7-(Ethoxycarbonyl)dibenzobarrelene[1]

Stanley J. Cristol* and James W. Hager

Department of Chemistry, University of Colorado, Boulder, Colorado 80309

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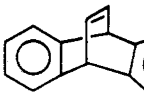
A detailed study of the rearrangement of 7-(ethoxycarbonyl)dibenzobarrelene to 1-(ethoxycarbonyl)dibenzosemibullvalene has been carried out. Lifetimes of the triplet intermediate(s) were measured by three quenching techniques and were in the 0.2–0.9-ns range in both direct and benzophenone-sensitized photoreactions. Difficulties in discussion of mechanism in systems that have a number of excited-state intermediates on the path from reactant to product are discussed.

Our group has been interested for some time in the measurements of rate constants for excitation transfer between triplet sensitizers and acceptor molecules and of lifetimes of triplets produced by sensitization.[2] It is necessary, in order to test various quenching techniques[1,3] for such measurements, to have a system where intersystem crossing from the directly excited singlet state of a substrate occurs to give a triplet species identical with that formed by sensitization.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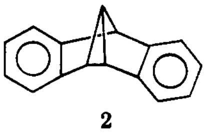
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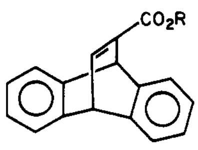

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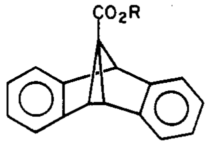

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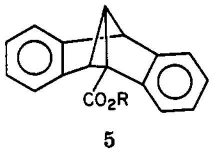

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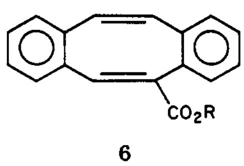

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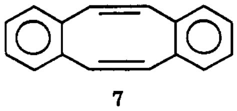
7

Among the most studied reactions[4–6] in photochemistry is the di-π-methane rearrangement. The rearrangements of dibenzobarrelene (**1**) and its derivatives to corresponding dibenzosemibullvalenes **2** represents some of the early examples[7] of this reaction. A detailed study of the conversion of **1** to **2**, which is a triplet reaction, has recently been carried out in our laboratory.[1] Ciganek[7] reported that the methoxycarbonyl derivative (**3**-CH_3) rearranged to the semibullvalene derivative (**4**-CH_3) upon direct irradiation in hydrocarbon solvents or upon acetone sensitization, without the formation of the other isomeric semibullvalene **5**-CH_3 or of the dibenzocyclooctatetraenecarboxylic ester **6**-CH_3, and this was confirmed by Friedman and coworkers.[8] Thus, unlike the parent dibenzobarrelene (whose excited singlet leads irreversibly to the intermediate

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(1) Paper 33: Cristol, S. J.; Kaufman, R. L.; Opitz, S. M.; Szalecki, W.; Bindel, T. H. *J. Am. Chem. Soc.*, in press.

(2) Ilenda, C. S.; Daughenbaugh, R. J.; Cristol, S. J. *Mol. Photochem.* **1976**, *7*, 287.

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(8) Rabideau, P. W.; Hamilton, J. B.; Friedman, L. *J. Am. Chem. Soc.* **1968**, *90*, 4466.

from which dibenzocyclooctatetraene is derived more rapidly than it intersystem crosses to its triplet[1,8]), the excited singlet of **3** presumably suffers intersystem crossing to the triplet more rapidly than it sets onto the path that would lead to **6**.[8,9] Accordingly, this seemed a good system to study.

A high-pressure liquid chromatographic method was developed for the analysis of **3**-Et[10] and **4**-Et.[11] When **3**-Et was irradiated in acetonitrile at 254 nm, it was converted to the semibullvalene **4**-Et in a quantum yield of 0.12 ± 0.01, without the formation of observable byproducts. We then studied the quenching of the formation of **4**-Et, using the Stern–Volmer[12] method, with *cis*-piperylene as quencher. The initial concentration of **3**-Et was 0.045 M, and that of piperylene varied from 0 to 0.18 M. The lines resulting from plots of ϕ_0/ϕ_q vs. piperylene concentrations had slopes that led to values of $k_{RQ}\tau_{3_R}$ of 0.89, 0.80, and 0.74 (average 0.8 ± 0.1) L mol^{-1}, where k_{RQ} is the rate constant for quenching of excited reactant R by quencher Q and τ_{3_R} is the lifetime of the (presumable) triplet state of R quenched. The reasonable[3,13] assumption that k_{RQ} has a value of 5×10^9 L s^{-1} mol^{-1} gives a value of ca. 0.2 ns for τ_{3_R}.

As sensitization conditions, we used 350-nm light and benzophenone as sensitizer in acetonitrile solvent. Compound **3**-Et has inconsequential absorbance at 350 nm. Plots of the dependence of quantum yield of **4**-Et vs. [**3**-Et] reached an asymptote of 0.47 (ϕ_{max}) at a concentration of about 0.04 M **3**-Et. A plot of $1/\phi$ vs. 1/[**3**-Et] had an intercept of 2.15 ± 0.04 and a slope of 0.0125 ± 0.0012. From the intercept, ϕ_{max} had a value of 0.47, and from the intercept/slope, a value for $k_{SR}\tau_{3_S}$ of 170 ± 30 L mol^{-1} was obtained, where k_{SR} is the constant for excitation quenching of triplet benzophenone by **3**-Et and τ_{3_S} is the lifetime of triplet benzophenone. Unfortunately, the lifetime for triplet benzophenone in acetonitrile at room temperature is not reported, and there is a large solvent variation in its values,[14] ranging from 0.5 to 20 μs, with a variety of aromatic solvents. These values result in a possible range for k_{SR} of 8×10^6 to 3×10^8 L mol^{-1} s^{-1}. All of the values in this range are well below that of diffusion control, and it seemed possible to us that this might be due to reverse energy transfer.[15] Should that be the case, increasing benzophenone concentration should decrease the quantum yield of **4**-Et. When the quantum yield of **4**-Et was measured, by using a range of benzophenone concentrations from 0.20 to 3.0 M, it was invariant (0.46 ± 0.01). This indicates that reversible energy transfer from reactant to sensitizer is not an important factor in this system.

Two experiments were carried out by using the method developed in this laboratory[1,2] for sensitized systems, in which eq 1 is the key equation. When values of ϕ_0/ϕ_q,

$$\frac{\phi_0}{\phi_q} = \left(1 + \frac{k_{SQ}[Q]}{k_{SR}[R]}\right) + \left(1 + \frac{k_{SQ}[Q]}{k_{SR}[R]}\right)k_{RQ}\tau_{3_R}[Q] \qquad (1)$$

measured with different concentrations of quencher Q but with constant ratios of concentrations of reactant R to quencher, are plotted against [Q], one may determine the ratio k_{SQ}/k_{SR} from the intercept and $k_{RQ}\tau_{3_R}$ from the slope divided by the intercept. One run, at an [R]/[Q] ratio of 4.2, gave a line of slope 20 and intercept 6.0, from which one may compute values for k_{SQ}/k_{SR} of 21 and for $k_{RQ}\tau_{3_R}$ of 3.3 L mol^{-1}. The second run, with an [R]/[Q] ratio of 20.5, gave a line with slope 5.0 and intercept 1.8, from which one gets values for the k_{SQ}/k_{SR} of 17 and $k_{RQ}\tau_{3_R}$ of 2.8. Averaging these values and assuming[13] values for k_{SQ} and k_{RQ} of 5×10^9 L mol^{-1} s^{-1}, one gets values of 2.6×10^8 L mol^{-1} s^{-1} for k_{SR} and a triplet lifetime for **3**-Et of 0.6 ns. The value of k_{SR} is at the upper end of the values computed from the double-reciprocal plot of the sensitization data and from values of benzophenone triplet lifetimes, but the correspondence is probably satisfactory, as the lifetimes of benzophenone triplets decrease as the polarity of the solvents increase, in those solvents studied by Schuster.[14] Considering the uncertainties inherent in the Ilenda–Daughenbaugh–Cristol (IDC) procedure,[2,3] as well as those in the Stern–Volmer (SV) procedure, the values of $k_{RQ}\tau_{3_R}$ of 0.8 (SV) and 3.0 (IDC) L mol^{-1} are identical, within experimental error (note that both lead to lifetimes well below 1 ns).

We have also used the Lamola–Hammond technique,[16] in which the isomerization of *cis*- to *trans*-piperylene is used as a tool to determine the extent of intersystem crossing (triplet yield), as well as the lifetime of the triplet quenched by piperylene. Duplicate values of the triplet yield (ϕ_{ISC}) were 0.23 ± 0.01 and of $k_{RQ}\tau_{3_R}$ were 4.4 and 4.7 ± 1.0 L mol^{-1}. If, again k_{RQ} is assumed to be 5×10^9 L mol^{-1} s^{-1}, a lifetime of 0.9 ns may be computed. This value for τ_{3_R}, again below 1 ns, is probably close enough to those of the other methods that one cannot assume that the triplet intercepted by piperylene in the Lamola–Hammond treatment is not the same as the product-determining intermediate.[17] This is particularly true, as is the case in this system, when the intersystem crossing yield (0.23) times the measured quantum yield of the triplet-sensitized reaction (0.47) is identical with the quantum yield (0.12) of the direct-irradiation process.

It is of interest to compare the results of **3**-Et with those[1] of dibenzobarrelene (**1**) itself. In the direct irradiation of **1**, very little dibenzosemibullvalene (**2**) is formed; the product is almost entirely the cyclooctatetraene **7**. On the other hand, **3** gives entirely semibullvalene species; obviously both the singlet and the triplet of **3** give **4**, or intersystem crossing of the singlet to the triplet is rapid enough to avoid the formation of **6**. Our data are compatible with the latter interpretation but do not rule out the former, except the linearity observed in the Stern–Volmer study demonstrates that **4** cannot arise in the direct irradiation from an unquenchable singlet *and* a quenchable triplet. Data[1] on the singlet lifetime of dibenzobarrelene (**1**) itself give values in the 50-ps region, with approximate quantum yields of 0.04 for **2** and 0.32 for **7**. These data fit an intersystem crossing rate constant of about 5×10^8 s^{-1}, assuming that all of the semibullvalene comes from the triplet and that the yield of **2** from the triplet is about 0.7. Put another way, if the excited singlet of **1** had no fates other than intersystem crossing and decay

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(9) The alternative that **4** is a singlet-derived product is considered below. 2,3-Naphthobarrelene, like **3**, gives the semibullvalene upon both direct irradiation and benzophenone sensitization, and evidence is good that both processes involve the T_1 state.[4c]

(10) Sheenoy, P. K. Ph.D. Thesis, University of Arizona, 1966.

(11) Mayo, G. O., private communication.

(12) Stern, O.; Volmer, M. *Phys. Z.* **1919**, *20*, 183.

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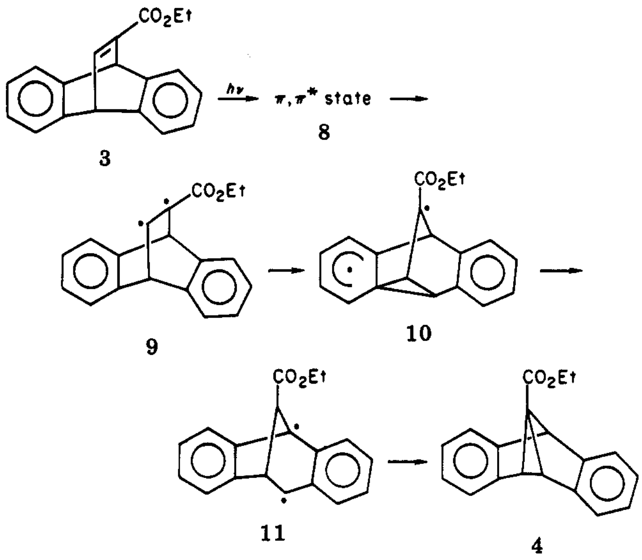
(15) Sandros, K.; Bäckström, H. L. J. *Acta Chem. Scand.* **1962**, *16*, 958. Sandros, K. *Ibid.* **1964**, *18*, 2355.

(16) Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129.

(17) One should note that, when two triplets are produced by intersystem crossing, unless special techniques are used, only the longer lived species will be observed.[3,18]

(18) Wagner, P. J.; Chen, C.-P. *J. Am. Chem. Soc.* **1976**, *98*, 129. Wagner, P. J.; Scheve, B. J. *Ibid.* **1979**, *99*, 1857. Wagner, P. J. *J. Photochem.* **1979**, *10*, 287.

Scheme I



to S_0, it would have a lifetime of ca. 2 ns. The failure[7,11,19] to see any dibenzocyclooctatetraene product **6** from **3** suggests, if similar assumptions are made, that the excited singlet of **3** has a lifetime well below 100 ps.

Some interesting questions arise in a process such as the di-π-methane reaction, where the mechanism commonly invoked[5] involves a number of "intermediates". A path, from **3**, could be as shown in Scheme I, in which we have illustrated all of the "intermediates" that might be conceived as being involved, although it is possible that irradiation of **3** at 300 nm might bypass the π,π* state **8**. The "intermediates" shown may or may not be minima on the hypersurface leading from the vertical excited state of reactant to the ground state of products, but some are similar to known excited states of aromatic compounds or of olefins, and the others have structures, similar to those of monoradicals, which are energy minima in radical rearrangements. Consideration of this scheme evokes the principal difficulty that one cannot guess at which stage or stages intersystem crossing occurs or whether sensitization (excitation transfer) leads to a triplet earlier or later than does direct irradiation and intersystem crossing. Further, one might guess that **8** and **9**, if quenchable triplets, would be quenched to reactant **3** but that **11** would be quenched to product **4**, while **10** might give **3** and/or **4**.[20] If more precise data were available (and for this, with quenching techniques, significantly longer lifetimes would be required), one could perhaps answer these questions.

Experimental Section

Materials. **3**-Et was prepared by the Diels–Alder reaction of ethyl propiolate and anthracene in benzene solution, as described by Sheenoy.[10] The *cis*-piperylene (10% trans isomer) was obtained from Chemical Samples Co. Benzophenone was obtained from Aldrich Chemical Co.

General Procedures. Irradiations were performed with 2-mL solutions in either 13 mm × 100 mm Pyrex tubes (350-nm light) or 13 mm × 120 mm Vycor tubes (254-nm light) in the apparatus described earlier.[21] Samples were degassed by the freeze–pump–thaw method several times at 2×10^{-5} torr prior to irradiation. All irradiations were carried out on acetonitrile solutions.

High-pressure liquid chromatographic analyses were carried out a Waters Model 6000A instrument using a silica gel column and a 10% THF/hexanes mixture as eluent. Fractions containing products were detected at 254 nm with a Beckman Model 25 spectrophotometer and collected; concentrations were determined by measurements of the absorption at 272 nm with a Cary Model 14 spectrophotometer.

Gas chromatographic analyses were performed with a Hewlett-Packard 5754-B gas chromatograph, using flame ionization detection, linked to either a Hewlett-Packard 3380S or 3380A integrator. The GC column used was a 7.5 m × 3 aluminum column containing 15% β,β′-oxydipropionitrile on 100–120 mesh Chromosorb W.

The amount of light absorbed by each sample during the course of irradiation was determined by cyclopentanone actinometry.[22]

Data obtained by the Stern–Volmer, Lamola–Hammond, and Ilenda–Daughenbaugh–Cristol techniques were fit to least-squares lines by the conventional method.[23]

Stern–Volmer Quenching Studies. A range of concentrations of *cis*-piperylene (0–0.18 M) was used as the quencher of the photorearrangement of **3**-Et to **4**-Et in acetonitrile solution. The concentration of **3**-Et (0.045 M) was set such that it absorbed ≥98.5% of the light. No evidence for an unquenchable singlet direct progenitor of **4**-Et (deviation from linearity at higher concentration of piperylene) was observed.

Triplet Energy Transfer from Benzophenone. Benzophenone (0.50 M) in acetonitrile solution was used as the triplet sensitizer. The concentration of **3**-Et was varied from 0.050 to 0.180 M. Under these conditions, the sensitizer absorbed >99% of the 350-nm light.

Ilenda–Daughenbaugh–Cristol Quenching Studies. Solutions of **3**-Et and quencher (*cis*-piperylene) were prepared over a range of concentrations such that the [R]/[Q] ratio was constant. For this study, a 1 M solution of benzophenone was used as the sensitizer. The following are the [R]/[Q] values and range of [Q].

$[R]/[Q] = 4.2 \quad [Q] = 0.009\text{–}0.062$ M

$[R]/[Q] = 20.5 \quad [Q] = 0.001\text{–}0.014$ M

Lamola–Hammond Quenching Studies. A range of concentration of *cis*-piperylene for a given concentration of **3**-Et was prepared such that the **3**-Et absorbed ≥99% of the light. Samples were analyzed by gas chromatography for the amount of cis to trans isomerization of the piperylene.

Reversible Energy Transfer Studies. Solutions containing a fixed **3**-Et concentration and varying benzophenone concentrations were prepared in acetonitrile solution and irradiated at 350 nm and the resulting amounts of **4**-Et determined by HPLC.

Acknowledgment. We are indebted to the Office of Basic Energy Sciences, U.S. Department of Energy, for support of this work under Contract DE-AC02-79ER-10366.

Registry No. **3**, 27649-95-2; *cis*-piperylene, 1574-41-0; benzophenone, 119-61-9.

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[19] This work.

[20] The quenching of excited-state species to products or to mixtures of reactants and products has been observed in other systems.[21]

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