The conclusion that the k_3 step is rate determining can be represented in another way in terms of Scheme II. In the pH range 2–6, a thiol is more easily released from the hydrogen ortho thio ester, a tetrahedral intermediate, than water is. This agrees with the results of hydrolyses of thiol esters and ketene *O,S*-acetals.[11,45] Contribution from the protonated tetrahedral intermediate, which gives away water more easily, becomes appreciable only below pH 2.[45] That is, the explusion of water should be slower than that of thiol at pH >2.

General base catalysis of the hydration of carbenium ion is a problem of recent interest.[46-49] The less stable the carbenium ion, the less likely is its hydration subject to general base catalysis. The k_2 value was found to be seemingly independent of buffer concentrations. The catalysis must be weak, if the hydration of 1,1-bis(methylthio)ethyl cation is subject to general base catalysis. Furthermore, possible inverse solvent effects of the buffer component (carboxylic acid) on the rate (see solvent effects presented in Figure 1) may cancel the potential buffer catalysis. As a result k_{obsd} became approximately constant at limiting concentrations of buffer to give the constant k_{max}.

As a whole, the present observations indicate that the initial protonation of the ketene thioacetal is mostly rate determining at the zero buffer concentrations but is accelerated by the buffer to make the protonation reversible and the second step rate determining; furthermore, the addition of a thiol accelerates the second step to force the first step to be the slower step again. The rate-determining step of the reaction can thus be controlled by the addition of either buffer or thiol.

Acknowledgment. We are grateful to Professor A. J. Kresge for helpful discussions and examination of the manuscript.

Registry No. 9, 51102-74-0; 2-mercaptoethanol, 60-24-2.

Supplementary Material Available: Tables of observed first-order rate constants for the hydrolysis (Tables S1–S3) (3 pages). Ordering information is given on any current masthead page.

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Photochemical Transformations. 33. Some Studies of the Photorearrangements of Dibenzobarrelenes. A Novel Excitation-Transfer Relay Mechanism[1]

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Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80309. *Received September 7, 1982*

Abstract: The unsensitized and sensitized photorearrangements of 1-methyldibenzobarrelene (**4**) and 7-methyldibenzobarrelene (**5**) to 3-methyldibenzocyclooctatetraene (**12**) and, for the former case, mixtures of 2-methyldibenzosemibullvalene (**9**) and 5-methyldibenzosemibullvalene (**10**), and for the latter case, mixtures of 1-methyldibenzosemibullvalene (**11**) and 2-methyldibenzosemibullvalene (**9**), are reported. The unsensitized reactions gave largely cyclooctatetraene, while the triplet-sensitized reactions gave the semibullvalenes via di-π-methane rearrangements. The regioselectivity of the di-π-methane rearrangements did not vary with sensitizer, although the quantum yields did. The lack of dependence of product ratio upon sensitizer suggests that the product-determining step occurs after excitation transfer, rather than during it or in an exciplex containing triplet sensitizer and reactant. A similar conclusion may be tentatively reached by the fact that the quenchable triplet intermediate has the same lifetime (4 ± 1 ns) whether produced by acetone, acetophenone, or benzophenone sensitization of dibenzobarrelene (**1**), although the excitation-transfer rates from each of these sensitizer triplets to **1** vary substantially. In solutions of acetone and of **1** and **5** in acetonitrile, the ratio of dibenzocyclooctatetraene products to dibenzosemibullvalene products is much smaller than one would calculate from the fraction of the light absorbed by the dibenzobarrelene, when the solutions are irradiated at 254 nm. These results are rationalized by the assumption that an excitation-transfer relay mechanism exists, in which reactant absorbs light to give an excited singlet. This is followed by quenching by "sensitizer" to give its singlet. That singlet intersystem crosses to give a sensitizer triplet, which then delivers triplet excitation to reactant.

Since the first report[2a] of the photosensitizer-induced transformation of barrelene to semibullvalene and of the photoinduced transformation[2b] of polyphenyl-substituted propenes to cyclopropanes, there has been much interest in this class of reactions, now dubbed "di-π-methane reactions".[3] Study of dibenzobarrelene (**1**) and certain of its derivatives is particularly interesting, as Ciganek[4] showed that irradiation through Pyrex of an acetone solution of **1** gave dibenzosemibullvalene (**2**), while Friedman and co-workers[5] showed that irradiation of **1** in cy-

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[1] Paper 32: Cristol, S. J.; Dickenson, W. A.; Stanko, M. K. *J. Am. Chem. Soc.* **1983**, *105*, 1218. A portion of this work was described at the Spring 1982 meeting of the Americal Chemical Society in Las Vegas, Nev.

[2] (a) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183. (b) Griffin, G. W.; Covell, J.; Patterson, R. C.; Dodson, R. M.; Klose, G. *Ibid.* **1965**, *87*, 1410.

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[5] Rabideau, P. W.; Hamilton, J. B.; Friedman, L. *J. Am. Chem. Soc.* **1968**, *90*, 4466.

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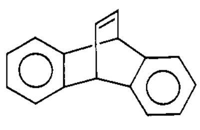
clohexane at 254 nm gave largely the dibenzocyclooctatetraene **3**. During this period, Brewer and Heaney[6] noted that tetrafluorobenzobarrelene had similar reactions; that is, acetone-sensitized irradiations in pentane gave the corresponding benzosemibullvalene, while in the absence of sensitizer the benzocyclooctatetraene was formed. The authors suggested that the triplet state of the barrelene species led to the semibullvalene, while the singlet state gave the octatetraene, a model accepted by Friedman and co-workers and one now generally accepted, for "rigid cyclic" systems at least.[3,7]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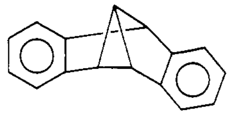
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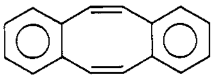
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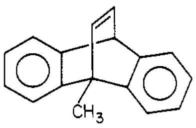
While the previous workers had used conditions where it was likely that the ketone sensitizers absorbed a large fraction of the light, in the course of our interest in the preparation of **2** for study of its ring-opening addition reactions,[8] we irradiated fairly concentrated solutions of **1** and of its 1-methyl (**4**) and 7-methyl (**5**) derivatives in acetone at 254 nm. The extinction coefficients of **1**, **4**, and **5** are such that irradiation at wavelengths of 300 nm or above (with reasonable amounts of ketone sensitizer present) does not lead to light absorption by these dibenzobarrelenes, but this is not necessarily the case with acetone ($\epsilon \sim 10$ M^{-1} cm^{-1}) and **1**, **4**, and **5** ($\epsilon \sim 10^3$ M^{-1} cm^{-1}) at 254 nm. Although, in these solutions, the substrates absorbed the major portion of the light, the products observed were those of the triplet reaction, i.e., the semibullvalenes, rather than those of the singlet reaction.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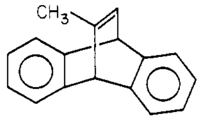
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It seemed possible to us that the results we observed could be rationalized by a relay process (Scheme I). The (ultimate) reactant (R) absorbs light, is converted to its excited singlet, and, in the absence of acetone, is converted largely to singlet product(s) P$_1$ (eq 1 and 2). In the presence of acetone (S) in concentration high enough[9] such that k_5[S] has a nonnegligible value compared with $k_2 + k_3 + k_4$, excitation transfer from ^{1}R to acetone might be expected to occur[11] to give ground-state reactant and singlet excited acetone. Put another way, if the lifetime of ^{1}R is long enough to allow for singlet quenching by acetone (eq 5), the formation (eq 2) of the cyclooctatetraene (P$_1$) would correspondingly be quenched. Intersystem crossing of singlet excited acetone to its triplet (eq 6), followed by triplet excitation transfer to give ^{3}R (eq 7), would lead to the triplet product, P$_2$. The amount of P$_2$ would be, in general, increased over that resulting from the intersystem crossing of ^{1}R to ^{3}R. We now wish to report results which make such a relay process[13] reasonable, and to give data from which one can approximate values of the singlet and triplet lifetimes of the excited states of **1** and **5**, i.e., $1/(k_2 + k_3 + k_4)$ and $1/(k_8 + k_9)$, as well as the rate constants of excitation transfer (k_7) from triplet acetone, acetophenone, and benzophenone to **1**. In addition we report data on the effect of various sensitizers on the ratios of the two sets of possible triplet products from **4** and from **5** and on the question of the location of the branching steps and of the energy-wasting step.

Scheme I

$$\mathrm{R} + h\nu \rightarrow {}^1\mathrm{R} \tag{1}$$

$${}^1\mathrm{R} \xrightarrow{k_2} \mathrm{P}_1 \tag{2}$$

$${}^1\mathrm{R} \xrightarrow{k_3} {}^0\mathrm{R} \tag{3}$$

$${}^1\mathrm{R} \xrightarrow{k_4} {}^3\mathrm{R} \tag{4}$$

$${}^1\mathrm{R} + \mathrm{S} \xrightarrow{k_5} {}^0\mathrm{R} + {}^1\mathrm{S} \tag{5}$$

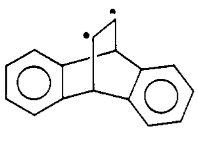
$${}^1\mathrm{S} \rightarrow {}^3\mathrm{S} \tag{6}$$

$${}^3\mathrm{S} + \mathrm{R} \xrightarrow{k_7} {}^3\mathrm{R} + \mathrm{S} \tag{7}$$

$${}^3\mathrm{R} \xrightarrow{k_8} \mathrm{P}_2 \tag{8}$$

$${}^3\mathrm{R} \xrightarrow{k_9} {}^0\mathrm{R} \tag{9}$$

Before we discuss the relay mechanism, let us first consider the other problems mentioned immediately above. At one time or another,[3ab,7] investigators have proposed that sensitization produces a triplet 1,2-biradical, such as **6**, which then rearranges to a 1,4-biradical (which is, of course, delocalized in **7**), which then continues its rearrangement to a 1,3-biradical such as **8**, thus leading to product[18] such as **2**. At other times, it was suggested that sensitization produced the 1,4-biradical directly, without the intervention of the 1,2-biradical. Several modes of approaching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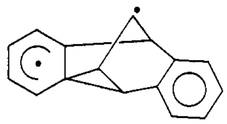
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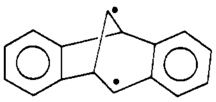
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[6] Brewer, J. P. N.; Heaney, H. *J. Chem. Soc., Chem. Commun.* **1967**, 811.

[7] Turro, N. J. "Modern Molecular Photochemistry"; Benjamin-Cummings: Menlo Park, Calif., 1978; p 497.

[8] Cristol, S. J.; Lim, W. Y.; Dahl, A. R. *J. Am. Chem. Soc.* **1970**, *92*, 4013.

[9] It is recognized that, in acetone solvent, or in solvents containing very high concentrations of acetone, rate expressions, in particular those involving "diffusion-controlled" rates, cease to have precise meanings as the first layer of the solvent cage surrounding the excited species will very likely contain an acetone molecule.[10]

[10] See ref 7, pp 317–319.

[11] The singlet energies of **1** and acetone differ by about 15 kcal/mol, as judged by their absorption spectra.[12]

[12] (a) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966; p 337. (b) Arganbright, R. P. Ph.D. Dissertation, University of Colorado, 1956, p 52.

[13] A similar relay process has been suggested[14] for the intervention of benzophenone in the dimerization of coumarin but has been subjected to question.[15] An analogous set of possibilities has been demonstrated[16] for intramolecular excitation exchanges in bichromophoric molecules, using emission techniques, and a case has been described[17] where an efficient singlet reaction has been converted to an inefficient one giving the same product, but, to the best of our knowledge, there are no authenticated cases in which the excitation-transfer relay converts one efficient chemical reaction into another, although doubtless many others remain to be discovered.

[14] Hammond, G. S.; Stout, C. A.; Lamola, A. A. *J. Am. Chem. Soc.* **1964**, *86*, 3103.

[15] (a) Morrison, H.; Curtis, H.; McDowell, T. *J. Am. Chem. Soc.* **1966**, *88*, 5415. (b) Hoffman, R.; Wells, P.; Morrison, H. *J. Org. Chem.* **1971**, *36*, 102.

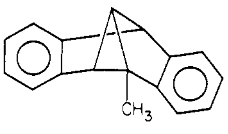
[16] Lamola, A. A.; Leermakers, P. A.; Byers, G. W.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 2322.

[17] Zimmerman, H. E.; Dürr, H. G.; Givens, R. S.; Lewis, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 1863.

[18] The stage at which intersystem crossing occurs is not known, but obviously singlet **8** is required to give the product **2**.

these problems occurred to us, which seemed likely to shed some light on this question. First, we thought it possible that, if rearrangement accompanied excitation transfer, a dibenzobarrelene which could give a mixture of products might give different mixtures with different sensitizers. This would, of course, also be true if rearrangement occurred in an exciplex of sensitizer and reactant. On the other hand, complete excitation transfer to give a sensitizer-free 1,2-biradical must give the same triplet product mixture with all sensitizers. Second, if the reactions gave a triplet species which could be quenched to reactant and whose lifetime could be measured, different sensitizers might lead to species of differing lifetimes, if rearrangement occurred in exciplexes rather than in free triplet species.

Although Ciganek had studied the regiochemistry of the rearrangements of the 1-methoxycarbonyl and 7-methoxycarbonyl derivatives of **1** and observed overwhelming regioselectivity, early work in this laboratory[19] indicated that irradiation of **4** in acetone gave an approximately 60:40 mixture of **9** and **10** and that a similar mixture of **11** and **9** arose from **5** when the dibenzobarrelenes were irradiated in acetone. These compounds then seemed to be reasonable substrates for testing and were therefore studied.



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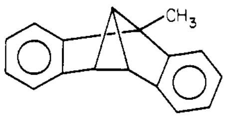

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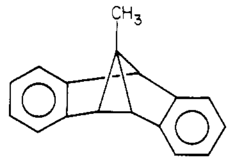

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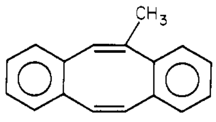

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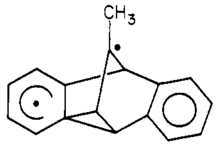
When 0.02 M **4** was irradiated in acetonitrile with 0.016 M benzophenone (300 nm), 0.06 M *p*-dimethoxybenzene (300 nm), 50% acetone (254 nm), 2.7 M acetone (254 nm), or 6.9 M chlorobenzene (254 nm), the mixture of the dibenzomethylsemibullvalenes **9** and **10** were all in the ratio 1.3 ± 0.1:1.0. There was thus no indication of a sensitizer effect upon regioselectivity in this reaction. Pursuant to the question of singlet–triplet reactivity, the benzophenone experiment showed less than 2% of 3-methyldibenzocyclooctatetraene (**12**), the dimethoxybenzene about 2% of **12**, the chlorobenzene experiment about 20%, and the 2.7 M acetone experiment no more than 4%. One can compute that the acetone absorbed about 40% of the light in this latter experiment. Irradiation of **4** in cyclohexane at 254 nm gave about 89% of **12** and 11% of **9** and **10**.

When **5** was irradiated in acetonitrile with benzophenone sensitizer (350 nm), or in *tert*-butyl alcohol with xanthone (300 nm), *p*-dimethoxybenzene (300 or 350 nm), or acetone (300 nm), the resulting mixture of **11** to **9** was 1.4 ± 0.1 to 1.0. Again, within the limits of our analytical procedure, there was no sensitizer effect upon regioselectivity, and thus, as with **4**, there is no evidence for participation of sensitizer at the rearrangement step, either in an exciplex or outside of one. Irradiation of **5** in acetonitrile at 254 nm gave 66% of **12** and 34% of **11** and **9**.

There may be some reason to wonder why there is not greater regioselectivity in the reaction of **5** than in that of **4**. In the rearrangement of the former, whatever the detailed process, the formation of **13** competes with that of **14**, and we might anticipate that the methyl at the tertiary site of the radical **13** would be substantially more effective than that at the cyclopropane ring site in **14**, but nonetheless, radical **13** is favored over **14** by less than 1.5 to 1.0. The corresponding competition from **4** is between **16** and **15** with **16** favored over **15** by 1.3 to 1.0. Little is known about stabilities of substituted cyclopropylcarbinyl radicals, nor do we have information about the possible reverse rearrangements of the 1,4-biradicals to the 1,2-biradicals or to the starting materials (the quantum yields of these reactions are all less than 0.7, so reversibility may be possible; see below for energy wastage discussion). The results suggest that the transition state for the biradical rearrangements to the 1,4-biradicals is not very far along the reaction coordinate.



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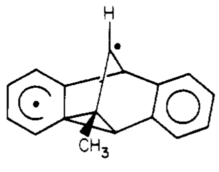

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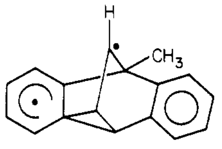

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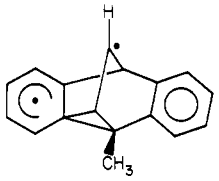

16

The second test we have proposed for the question of rearrangement coincident with sensitization was lifetime measurement. Several years ago, workers in this laboratory[20] developed a quenching procedure for triplet-sensitized reactions by which one can determine the ratio of rate constants for excitation transfer beween sensitizer and quencher (k_{SQ}) and between sensitizer and reactant (k_{SR}), as well as the product of the rate constant for excitation transfer between reactant and quencher (k_{RQ}) and the lifetime ($\tau_{^3R}$) of the triplet reactant leading to product. Since then we have considered the possibility of triplet sensitizer reacting with ground-state reactant to give not only triplet reactant and ground-state sensitizer (energy transfer), but also both reactant and sensitizer in their ground states (energy annihilation). This idea is expressed in eq 10 and 11. We now recommend the

$$^0R + {}^3S \xrightarrow{k_{SR^*}} {}^0S + {}^3R \qquad (10)$$

$$^0R + {}^3S \xrightarrow{k_{SR^0}} {}^0S + {}^0R \qquad (11)$$

incorporation of this additional idea into the above-mentioned quenching procedure. This resulted in only a minor difference between the quenching expression (eq 12), which incorporates eq

$$\frac{\phi_0}{\phi_q} = \left[1 + \frac{k_{SQ}[Q]}{(k_{SR}{}^* + k_{SR}{}^0)[R]}\right] + \left[1 + \frac{k_{SQ}[Q]}{(k_{SR}{}^* + k_{SR}{}^0)[R]}\right] k_{RQ}\tau_{^3R}[Q] \qquad (12)$$

10 and 11, and the originally derived quenching expression, which ignored eq 11, in that k_{SR} in the original expression[20] is replaced by the sum of k_{SR^*} and k_{SR^0}. In the original treatment, all of the energy wastage not involved in decay of sensitizer would have to be accommodated by inefficiency in the transformation of triplet excited reactant to product. Thus differences in quantum yields with different sensitizers would require that products come, in part at least, from exciplexes containing both reactant and sensitizer. While this may be true, the present modification allows for inefficiency in the sensitization step itself, and therefore the modified expression (eq 12) is more generally applicable. If one makes appropriate assumptions regarding k_{SQ} and k_{RQ} (dienes are used as quenchers, so values of 5×10^9 L mol^{-1} s^{-1} are reasonable[21-23]), one may derive values for $k_{SR^*} + k_{SR^0}$ and for $\tau_{^3R}$.

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

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

(21) Turro, N. J.; Schore, N. E.; Steinmetzer, H.-C.; Yetka, A. *J. Am. Chem. Soc.* **1974**, *96*, 1936.

(22) Porter, G.; Yip, R. W.; Dunston, J. W.; Cessna, A. J.; Sugamori, S. E. *Trans. Faraday Soc.* **1972**, *67*, 3149.

Table I. Results from Diene Quenching of the Sensitized Di-π-methane Reaction of **1** Using Modified Ilenda–Daughenbaugh–Cristol[20] Kinetics

sensitizer[a]	quencher[b]	[R]/[Q]	$k_{SQ}/(k_{SR^0} + k_{SR^*})$	$(k_{SR^0} + k_{SR^*}) \times 10^8$, L s^{-1} mol^{-1}	$k_{RQ}\tau_{^3R}$, L mol^{-1}	$\tau_{^3R}$,[e] ns
A[c]	PD	52		2.4	neg slope	
A[c]	HD	21	15	3.4	14	3
A[d]	HD	21	36	1.4	20	4
AP[d]	PD	59	18	2.8	38	8
AP[d]	PD	20	16	3.1	14	3
BP[d]	HD	19	107	0.44	21	4

[a] A, acetone; AP, acetophenone; BP, benzophenone. [b] PD, 1,3-pentadiene; HD, 2,5-dimethyl-2,4-hexadiene. [c] Hexane solvent. [d] Acetonitrile solvent. [e] Assuming k_{RQ} is 5×10^9 L mol^{-1} s^{-1}.

Of course, one does not need precise values of $\tau_{^3R}$ if one wishes to compare only lifetimes of triplet R; rather, one needs only $k_{RQ}\tau_{^3R}$ values obtained in the same solvent systems. It is implicitly assumed that k_{RQ} will be the same regardless of the structure of R. This procedure was used with **1** in acetonitrile, with 2,5-dimethyl-2,4-hexadiene and 1,3-pentadiene as quenchers, and with acetone, acetophenone, and benzophenone as sensitizers (see Table I). The sensitizers transferred excitation (excitation transfer encompasses both energy transfer and energy annihilation) to **1** with significantly different rate constants, all substantially below that (5×10^9 L mol^{-1} s^{-1}) assumed for "diffusion-like" control. Acetone had a $k_{SR^*} + k_{SR^0}$ value of $24 \pm 10 \times 10^7$, acetophenone $30 \pm 2 \times 10^7$, and benzophenone 4.4×10^7 L mol^{-1} s^{-1}. It has previously been noted[24] that, while acetophenone has a lower triplet energy than acetone, it transfers excitation to norbornadiene faster, relative to its transfer rate to dienes, than does acetone, and the same is true with **1**.

Benzophenone was slower than either acetophenone or acetone with norbornadiene, and the same is true for transfer to **1**, with an even greater difference in relative excitation transfer rate constants. While the excitation transfer rate constants ($k_{SR^0} + k_{SR^*}$) thus differed significantly, values of $k_{RQ}\tau_{^3R}$ resulting from the three sensitizers gave indistinguishable lifetimes, within the limits of error of this method (±1–2 ns). Thus all three sensitizers gave quenchable intermediates with lifetimes ($1/(k_8 + k_9)$) in the range of 4 ± 1 ns. These results lend no support, then, to the idea that triplet exciplexes involving sensitizer and reactant are the quenchable species.

It is of interest that the maximum quantum yield of **2** from **1** with either acetone or acetophenone as sensitizer is 0.66–0.70, while that with benzophenone is only 0.19. The maximum quantum yield is reached when all of the sensitizer is quenched and may be noted experimentally when increasing the concentration of reactant no longer leads to an observable increase in the quantum yield of product. This is reached, in these experiments, at concentrations of about 0.1 M for acetone, and about 0.03 for acetophenone and benzophenone. The fact that both acetone and acetophenone have identical values of 0.66 may mean that each quenching encounter of **1** with either of these ketones has a 2/3 probability of giving a triplet which leads completely to rearrangement and 1/3 probability of giving unexcited reactant and ground-state sensitizer (an energy-wasting process). An alternative interpretation is that a single triplet is produced, which has two decay paths, 2/3 to product **2** and 1/3 to starting material, i.e., steps 8 and 9 in Scheme I. The latter interpretation is reasonable, but, on the other hand, the significantly lower quantum yield observed with benzophenone is consistent only with an assumption that most of the energy-wasting occurs at the stage of interaction of triplet benzophenone and dibenzobarrelene. This may result, as suggested in eq 11, in the direct formation of ground state **1** and of sensitizer, or perhaps in the formation of a "hidden triplet", which does not have sufficient energy to rearrange and thus decays to product.[25] Another possibility involves the reaction of triplet benzophenone with **1** to give a cycloadduct, such as would be expected from a Paterno–Büchi reaction, in competition with energy transfer. This, however, does not seem plausible, since little, if any, of the cycloadduct is formed in the benzophenone-sensitized reaction of **1** in acetonitrile. The adduct is formed in benzene, however.

Let us now return to the question of the excitation-transfer relay mechanism described in Scheme I. If one makes the assumption that the fraction of light absorbed by each component in a solution of dibenzobarrelene (**1**) and acetone in a nonreactive and nonabsorbing solvent is proportional to the products of the appropriate extinction coefficients and concentrations,[26] then, if no excitation transfer from singlet excited **1** to acetone occurred, the relative quantum yield of **3** (ϕ_{P_1}) would be given by the expression

$$\phi_{P_1} = \phi_{P_1}{}^0 F_1 \tag{13}$$

where $\phi_{P_1}{}^0$ is the quantum yield of **3** in the absence of acetone (0.28–0.32), which of course is given by the expression $k_2/(k_2 + k_3 + k_4)$ (here it is assumed that **3** and P_1 are identical), and F_1 is the fraction of light absorbed by **1**. Likewise the quantum yield of **2** (ϕ_2) would be given by the expression

$$\phi_{P_2} = \phi_{P_2}{}^0 F_A \tag{14}$$

where $\phi_{P_2}{}^0$ is the quantum yield for the acetone-sensitized reaction (0.7), given by the expression $k_8/(k_8 + k_9)$ if all of the excited sensitizer is quenched by **1**, and F_A is the fraction of light absorbed by the acetone. In eq 14 it is assumed that **2** and P_2 of eq 8 are identical.

If one adds acetone quenching to this system, the expression for the quantum yield of P_1 (**3**) becomes

$$\phi_{P_1}{}^S = F_1 \frac{k_2}{k_2 + k_3 + k_4 + k_5[S]} \tag{15}$$

so that the quantum yield ($\phi_{P_1}{}^S$) of singlet product P_1 becomes negligible when the effective value[9] of k_5[S] becomes much greater than k_2. Likewise, one may deduce that the quantum yield ($\phi_{P_2}{}^S$) of triplet product P_2 is given by the relationship

$$\phi_{P_2}{}^S = \left\{F_A + F_1\left[1 - \frac{k_2 + k_3 + k_4}{k_2 + k_3 + k_4 + k_5[S]}\right]\right\}\left\{\frac{k_8}{k_8 + k_9}\right\} \tag{15a}$$

which approaches $k_8/(k_8 + k_9)$ or ϕ_{P_2} when k_5[S] becomes much greater than $k_2 + k_3 + k_4$. (One must, of course, correct for ^{3}R produced by intersystem crossing.) While we hesitate to predict[9] that these equations will be followed quantitatively over the range of acetone concentrations utilized, one would expect changes in product composition consistent qualitatively, at least, with these relationships.

As one may perceive by inspection of the data in Table II regarding irradiations of **1** and in Table III regarding irradiations of **5**, quantum yields of the dibenzocyclooctatetraenes decreased with increasing acetone concentration, and those of the di-

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(24) Cristol, S. J.; Kaufman, R. L. *J.* Photochem. **1980**, *12*, 207.

(25) We have recently noted the existence of such species in the photosolvolyses of benzylic halides. Cristol, S. J.; Bindel, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 7287.

(26) The precise validity of Beers' law in solutions containing high concentrations may be debated, but the validity at low absorbances is probably high, and at high concentrations the assumption that this is a reasonable approximation seems justifiable.

Table II. Effect of Acetone Concentration on the Quantum Yields of Dibenzocyclooctatetraene (**3**) and Dibenzosemibullvalene (**2**) upon Irradiation of 0.2 M Dibenzobarrelene (**1**) in Acetonitrile at 254 nm

[acetone]		fraction of light absorbed by:[a]		quantum yield of			
				3		**2**	
M	vol %	reagent (F_1)	acetone (F_A)	calcd[b]	found	calcd	found
0	0	1.00	0.00		0.24		0.29
0.20	1.5	1.00	0.005	0.24	0.21	0.03	0.15
0.27	2.0	0.99	0.007	0.24	0.22	0.03	0.18
0.41	3.0	0.99	0.010	0.24	0.19	0.03	0.23
0.68	5.0	0.98	0.017	0.24	0.16	0.03	0.29
0.82	6.0	0.98	0.020	0.24	0.16	0.03	0.33
1.1	8.0	0.97	0.028	0.23	0.13	0.04	0.35
1.4	9.9	0.97	0.034	0.23	0.12	0.04	0.41
1.6	12	0.96	0.041	0.23	0.12	0.04	0.46
2.0	15	0.95	0.050	0.23	0.11	0.05	0.51
2.7	20	0.94	0.061	0.23	0.098	0.07	0.58

[a] Assuming that the fractions are proportional to extinction coefficients and molar concentrations. [b] Assuming that quantum yields are related to fraction of light absorbed.

Table III. Effect of Acetone Concentration on the Quantum Yields of 3-Methyldibenzocyclooctatetraene (**12**) and Methyldibenzosemibullvalene (**9** and **11**) upon Irradiation of 0.13 M 7-Methyldibenzobarrelene (**5**) in Acetonitrile at 254 nm

[acetone]		fraction of light absorbed by:[a]		quantum yield of:			
				12		**9** + **11**	
M	vol %	reagent (F_1)	acetone (F_A)	calcd[b]	found	calcd	found
0	0	1.0	0.00		0.44		0.013
0.27	2.0	0.99	0.008	0.44	0.42	0.02	0.078
0.41	3.0	0.99	0.014	0.44	0.38	0.02	0.098
0.68	5.0	0.98	0.023	0.43	0.36	0.03	0.14
0.82	6.0	0.98	0.025	0.43	0.36	0.03	0.17
1.1	8.0	0.97	0.032	0.43	0.33	0.03	0.20
1.4	9.9	0.96	0.041	0.42	0.33	0.04	0.24
1.6	12	0.95	0.053	0.42	0.30	0.05	0.26
2.0	15	0.93	0.067	0.41	0.27	0.05	0.29
2.7	20	0.92	0.081	0.40	0.24	0.06	0.34
3.4	25	0.91	0.091	0.40	0.24	0.07	0.40

[a] Assuming that the fractions are proportional to extinction coefficients and molar concentrations. [b] Assuming that quantum yields are related to fraction of light absorbed.

benzosemibullvalenes increased. The changes observed are substantially greater than those calculated for light absorption, and thus these experiments would appear to give considerable credence to the excitation-transfer relay mechanism of Scheme I.

It has recently been reported[27] that acetone quenches benzene fluorescence with rate constants equal or slightly greater than those of diffusion control in solvents such as acetonitrile. If one uses the Debye equation[28] for computation of diffusion rate constants for two components, an approximate radius for **1** of 5.6 Å, and that for acetone of 2.5 Å, one[29] may compute a value for the diffusion-controlled rate constant in acetonitrile at 25 °C of 2×10^{10} L mol^{-1} s^{-1}, and presumably this value may be a reasonable one for k_5 of Scheme I.

When appropriate corrections are made for the fraction of light absorbed by the acetone (or for the dilute cases, ignoring it), one can combine eq 13 and 15 to get the Stern–Volmer expression:

$$\phi_{P_1}/\phi_{P_1}{}^{S} = 1 + k_5\tau_{^1R}[\text{acetone}] \qquad (16)$$

In this way, and by using values at the lower range of acetone concentrations, it is possible to compute values for the lifetime of the excited singlet leading to dibenzocyclooctatetraene. These are rough, as no attempt has been made to correct for possible quenching by the dibenzocyclooctatetraene or dibenzosemibullvalene products. Nonetheless, the data show that the quenchable species which lead to dibenzocyclooctatetraenes have lifetimes in the range 10–40 ps, and, as the quantum efficiencies for these reactions are in the range 0.28–0.54, the rate constants are all in the range 7 to 54×10^9 s^{-1} for the transformations of the quenchable singlet to the cyclooctatetraene itself or to an intermediate no longer observably quenchable to ground-state reactant.

Table IV

compd	lifetime, ps	
	Stern–Volmer	double reciprocal
1	27	55
1	36	50
1	39	70
1	41	50
5	18	27
5	12	23

Singlet excited **5** was found to be shorter lived (12–18 ps) than the corresponding state of **1** (27–41 ps). A comparison of the quantum yields of cyclooctatetraene formation for **1** (0.28–0.32) and **5** (0.37–0.54) leads one to believe that the decrease in the lifetime of singlet-excited **5**, relative to that of **1**, is due, in part or entirely, to an increase in the rate constant for cyclooctatetraene formation.

If there is a relay mechanism operating in the irradiation of **1**, **4**, and **5** in the presence of acetone, one can write an expression relating ϕ_{P_2} to the concentration of acetone, such as eq 17, assuming that the P_2 derived from intersystem crossing of ^{1}R is negligible or very small.

$$\phi_{P_2} = \left(\frac{k_5[S]}{k_5[S] + k_2 + k_3 + k_4}\right)(\phi^{S}{}_{isc})\left(\frac{k_7[R]}{k_7[R] + k_{sd^0}}\right)\left(\frac{k_8}{k_8 + k_9}\right) \qquad (17)$$

As $\phi^{S}{}_{isc}$ is 1.0 for acetone[30] and as, at concentrations of R giving complete energy transfer, $k_7[R]/(k_7[R] + k_{sd})$ is also 1, eq 17 reduces to

$$\phi_{P_2} = \left(\frac{k_5[S]}{k_5[S] + k_2 + k_3 + k_4}\right)\left(\frac{k_8}{k_8 + k_9}\right) \qquad (18)$$

If one rearranges eq 18 to

$$\frac{1}{\phi_{P_2}} = \left(\frac{k_8 + k_9}{k_8}\right)\left(1 + \frac{k_2 + k_3 + k_4}{k_5[S]}\right) \qquad (19)$$

it can readily be seen that $\phi_{P_2}{}^{-1}$ is linearly related to $[S]^{-1}$. Thus a plot of $\phi_{P_2}{}^{-1}$ vs. $[S]^{-1}$ from such an experiment should give a straight line whose quotient of intercept and slope will be $k_5/(k_2 + k_3 + k_4)$ or its equivalent $k_5\tau_{^1R}$. The singlet lifetime derived from such an experiment should match that derived from the Stern–Volmer quenching of P_1 by acetone if a relay mechanism is operating.

Of course, an experiment such as the one just described is more complicated in reality, since one must correct for absorption of light by acetone and by the photoproducts along with a minor correction for that amount of P_2 derived from intersystem crossing of ^{1}R.

Experiments of this type were carried out with surprising success, in view of all the corrections that were necessary. The double reciprocal plot for the product P_2 derived from **1** gave a singlet lifetime of about 55 ps, and for **5**, a singlet lifetime of about 25 ps. The lifetimes derived from the double-reciprocal treatment

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are consistently higher, by about 30 to 50%, than the lifetimes derived from the Stern–Volmer treatment (see Table IV). This indicates to us that there is an inherent error in the treatment of the data, thus preventing exact agreement.

In conclusion, it appears that a relay mechanism, such as that described in Scheme I, adequately explains the photochemistry of compounds such as **1** in the presence of acetone.

Experimental Section

General. All melting points were determined with a Thomas-Hoover apparatus. Proton nuclear magnetic resonance (^{1}H NMR) spectra were taken on a Varian Associates EM-390 instrument. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were taken on a Varian MAT CH-5 mass spectrometer. Gas chromatographic (GC) analyses were performed with a Hewlett-Packard 5754B gas chromatograph linked to either a Hewlett-Packard 3380S or 3380A integrator. The GC columns used were a 3 m × 3 mm glass (treated with dichlorodimethylsilane (CMS)) 5% Carbowax 20M on 100/120 mesh Chromosorb W column (column A), a 3 m × 3 mm glass (treated with CMS) 5% QF-1 on 100/120 mesh Chromosorb W column (column B), a 3 m × 3 mm aluminum 5% SE-30 on 80/120 mesh Chromosorb W column (column C), a 3 m × 3 mm aluminum 5% DC-710 on 100/120 mesh Chromosorb W column (column D), and a 0.2 mm × 25 m fused silica OV-1 column (column E). High-pressure liquid chromatographic (HPLC) analyses were carried out on a Waters Associates system including dual 6000A pumps, UKS universal injector, and 660 solvent programer. A Beckman Model 25 ultraviolet (UV) spectrometer equipped with a Waters Associates microcell apparatus was used as the detector for the HPLC system. The columns used for the HPLC analyses were either two Waters Associates 30 cm × 40 mm μ-Porasil columns or two Whatman 50 cm × 9.4 mm Partisil M950 columns connected in series. A mixture of hexanes and isooctane (1:1) with isopropyl ether (0.05–0.2%) was usually used as a mobile phase. UV spectra were taken on a Cary 219 UV–vis spectrometer (extinction coefficients given in units of L mol^{-1} cm^{-1}). Elemental analyses were performed by Galbraith Laboratories, Inc.

Irradiations. Irradiations were carried out in either a Rayonet RPR-100 reactor or in the apparatus described earlier,[23] which was used primarily for quantum-yield determinations. Each apparatus was equipped with either 350-, 300-, or 254-nm lamps. Generally, samples were degassed (10^{-5} torr) by the freeze–pump–thaw method before irradiation. This procedure was always used for quantum-yield determinations. Pyrex sample tubes were used for irradiations with 350- or 300-nm light and Vycor with 254-nm light. Cyclopentanone actinometry[31] was used to measure the light flux of the 300- and 254-nm lamps.

Materials. Fisher spectral grade acetone and Eastman spectro acetonitrile were used without further purification.

2,3:5,6-Dibenzobicyclo[2.2.2]octa-2,5,7-triene (1) was synthesized according to the procedure of Cristol and Lim:[32] UV (4:1 hexanes/isooctane) 280 nm (ϵ 4000, max), 272 (2330, max), 254 (1000); UV (acetonitrile) 254 nm (ϵ 970).

7-Methyl-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene (5). 7-Methylene-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene[33] (**17**) (0.17 mol, 37 g), *N*-bromosuccinimide (35.5 g, 0.2 mol), and 450 mL of CCl_4 were placed into a 1-L flask equipped with a mechanical stirrer and a reflux condenser. The mixture was stirred and exposed to irradiation with a 200-W light bulb for 5 h, which caused the solution to reflux. Most of the light from the bulb was diverted to the flask by means of aluminum foil. The solution was allowed to cool and the succinimide was filtered off. The solvent was removed in vacuo and the residue was chromatographed on 500 mL of silica gel 60 (Merck) with Skellysolve B. Starting material (1.5 g) and the product, 7-methylene-8-bromo-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (**18**) (43 g, 85%), were eluted from the column. The bromo compound was recrystallized from Skellysolve, mp 116–118 °C: ^{1}H NMR (CCl_4) δ 7.4–6.9 (m, 8 H, aromatic H), 5.25 and 5.1 (d, d, 2 H, J = 2 Hz, CH_2=), 4.7 (m, 1 H, H-8), 4.55 (s, 1 H, H-1), 4.35 (d, 1 H, J = 3 Hz, H-4).

Sodium borohydride (2.5 g, 65 mmol) was added gradually to a solution of compound **18** (2.24 g, 7.5 mmol) in 50 mL of 80% aqueous diglyme. The reaction mixture was stirred at 50 °C for 3 days. Water was then added and the products were extracted with Skellysolve B. The solution was dried (molecular sieves 4A), filtered, and distilled in vacuo. ^{1}H NMR showed a mixture that contained compound **5** and compound **17** in a ratio of 3:1, respectively. This mixture was separated by chromatography on silica gel with hexanes. **17** was eluted first. Fractional recrystallization from ethanol gave analytically pure **5** (mp 116.5–117.0 °C), which was used for irradiations: ^{1}H NMR ($CDCl_3$) δ 7.3–6.8 (dm, 8 H, aromatic H), 6.4 (m, 1 H, J = 5 Hz, H-8), 4.8 (d, 1 H, J = 5 Hz, H-4), 4.55 (d, 1 H, J = 1.5 Hz, H-1), 1.85 (s, 3 H, CH_3); UV (CH_3CN) 280 nm (ϵ 4400, max), 277 (1800, max), 273 (2600, max), 254 (1190); UV (hexanes) 280 nm (ϵ 4800, max), 277 (1600, max), 273 (2700, max), 254 (1100). Anal. Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found C, 93.63; H, 6.59. When a crude sample of the **18** was used in place of the pure compound, there was obtained, besides **5**, a new compound, 7-bromo-8-methyl-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene, mp 188–190 °C (recrystallized from ethanol): ^{1}H NMR ($CDCl_3$) δ 7.6–7.0 (dm, 8 H, aromatic H), 5.05 (s, 1 H, H-1), 4.9 (s, 1 H, H-4), 1.95 (s, 3 H, CH_3); mass spectrum, *m/e* (rel intensity) 296 (0.4), 298 (11), 217 (100).

1-Methyl-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene (4) was synthesized according to the procedure of Cristol, Perry, and Beckley.[34]

3,4:6,7-Dibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (2) was synthesized substantially as described by Ciganek:[4] UV (0.8% isopropyl ether–hexanes) 300 nm (ϵ 7), 282 (1700, max), 274 (2280, max), 254 (1380).

1,2:5,6-Dibenzocycloocta-1,3,5,7-tetraene (3) was synthesized in a manner similar to that described by Friedman and co-workers:[5] UV (CH_3CN) 254 nm (ϵ 10 500).

3-Methyl-1,2:5,6-dibenzobicycloocta-1,3,5,7-tetraene (12). A solution of **4** (0.15 M) in benzene was degassed and irradiated in Vycor tubes with 254-nm light. The crude product, obtained after the benzene had been removed in vacuo, was more than 90% **12** but had traces of **9** and **10**. The derived compound was recrystallized from ethanol, mp 77–78 °C: ^{1}H NMR ($CDCl_3$) δ 7.3–6.9 (m, 8 H, aromatic H), 6.77 (s, 2 H, H-7 and H-8), 6.60 (q, 1 H, $J \simeq$ 1.5 Hz, H-4), 2.17 (d, 3 H, $J \simeq$ 1.5 Hz, CH_3); mass spectrum, *m/e* (rel intensity) 218 (77), 219 (15), 217 (24), 215 (22), 204 (18), 203 (100), 202 (56), 189 (9), 101 (17); UV (1:1 hexanes/isooctane) 236 nm (ϵ 28 000, max), 254 (7030). Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. found: C, 93.52; H, 6.46.

2-Methyl- (9) and 5-Methyl-3,4:6,7-dibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (10). A solution of **4** (0.15 M) in acetone was degassed and irradiated in Vycor with 254-nm light. ^{1}H NMR indicated that the reaction had gone to completion and that the ratio of **9**:**10** was approximately 1.5:1. Analytically pure samples of **9** and **10** were obtained by HPLC with two Whatman Partisil columns, with 0.05% isopropyl ether in a 1:1 mixture of hexanes and isooctane: retention volumes, **10** $\simeq$ 200 mL; **9** $\simeq$ 212.5 mL. Compound **9** was recrystallized from hexanes, mp 98–99 °C: ^{1}H NMR ($CDCl_3$) δ 7.5–7.0 (m, 8 H, aromatic H), 4.46 (d, 1 H, $J \simeq$ 6.0 Hz, H-5), 3.3 (t, 1 H, J = 6.0 Hz, H-1), 2.92 (d, 1 H, J = 6.0 Hz, H-8), 1.68 (s, 3 H, CH_3); mass spectrum, *m/e* (rel intensity) 218 (52), 219 (9), 217 (16), 215 (16), 204 (17), 203 (100), 202 (50), 189 (7), 179 (3), 177 (3), 101 (6.4); UV (1:1 hexanes/isooctane) 251 nm (ϵ 1880), 282 (1870, max), 274 (2530, max). Compound **10** was recrystallized from hexanes, mp 84–85 °C: ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, 8 H, aromatic H), 3.42 (t, 1 H, J = 6.0 Hz, H-1), 3.1 (d, 2 H, J = 6.0 Hz, H-2 and H-8), 1.81 (s, 3 H, CH_3); mass spectrum, *m/e* (rel intensity) 218 (47), 219 (9), 217 (14), 215 (13), 204 (18), 203 (100), 202 (47), 189 (5), 179 (3), 177 (3), 101 (7); UV (1:1 hexanes/isooctane) 254 nm (ϵ 1140), 282 (1930, max), 274 (2460, max).

1-Methyl- (11) and 2-Methyl-3,4:6,7-dibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (9). A solution of **5** (0.2 M) in acetone was degassed and irradiated for 44 h in a quartz tube with 254-nm light. ^{1}H NMR indicated that the reaction had gone to completion and that the ratio of **11**:**9** was 1.3:1. The acetone solvent was removed in vacuo and the residue was recrystallized twice from a 9:1 mixture of hexanes and isopropyl ether. The compound was identified as **11**, mp 147–9 °C: ^{1}H NMR (CCl_4) δ 7.3–6.8 (m, 8 H, aromatic H), 4.02 (s, 1 H, H-5), 2.71 (s, 2 H, H-2 and H-8), 1.50 (s, 3 H, CH_3); mass spectrum, *m/e* (rel intensity) 218 (79), 219 (13), 217 (20), 215 (15), 204 (15), 203 (100), 202 (57), 189 (7), 179 (12), 177 (4), 101 (9); UV (1:1 hexanes/isooctane) 282 nm (ϵ 1850), 274 (2520), 254 (1800).

4,4-Diphenyl-7,8:9,10-dibenzo-3-oxatricyclo[4.2.2.0^{2,5}]deca-7,9-diene (19). A solution of **1** (0.2 M) and benzophenone (3 parts to 4 parts **1**) in benzene was degassed and irradiated in Pyrex tubes for 20 h with 350-nm light, after which time the solution was orange in color. HPLC analysis of the reaction mixture (25% $CHCl_3$ in hexanes; two μ-Porasil columns connected in series) indicated, in addition to benzene, benzophenone, and **2**, the presence of a significant amount of an unknown compound. This compound was isolated by preparative HPLC in 30% yield, recrystallized from hexanes/$CHCl_3$, and identified as **19**, mp 188–190 °C: ^{1}H NMR (CCl_4) δ 7.5 (dd, 2 H, $J \simeq$ 10 Hz, J = 2 Hz, aromatic H), 7.35–6.6 (m, 14 H, aromatic H), 6.41 (td, 1 H, J = 6.5 Hz, J = 1.5 Hz, aromatic H), 6.04 (d, 1 H, J = 6.5 Hz, aromatic H), 4.9

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(dd, 1 H, $J = 6.5$ Hz, $J = 4.5$ Hz, H-4), 4.45 (d, 1 H, $J = 4.5$ Hz, H-5), 4.33 (d, 1 H, $J = 3.5$ Hz, H-8), 3.28 (dd, 1 H, $J = 6.5$ Hz, $J = 3.5$ Hz, H-3); mass spectrum, m/e (rel intensity) 386 (4), 387 (2), 384 (4), 358 (8), 357 (17), 278 (36), 203 (24), 178 (100). Anal. Calcd for $C_{29}H_{22}O$: C, 90.12; H, 5.74. Found: C, 90.10; H, 5.82. This product was not formed in measurable amounts in acetonitrile.

Sensitized Irradiations of 7-Methyl-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene (5). In general, degassed solutions of **5** (0.02 M) and some sensitizer, in *tert*-butyl alcohol, were irradiated with 300-nm light. These irradiated samples were GC analyzed for the photoproducts on column A (*n*-hexadecane as internal standard).

Acetone Sensitization. Two 1-mL samples of the above solution (0.27 M acetone) were irradiated, one for 90 min (sample 1) and the other for 8 min (sample 2). Analysis for the photoproducts gave compounds **11** and **9** produced in ratios of 1.4:1 (sample 1) and 1.6:1 (sample 2), respectively.

Benzophenone Sensitization. A 1-mL sample of **5** in acetonitrile with benzophenone (0.016 M) was irradiated for 45 min with 350-nm light. Analysis (column B; *n*-octadecane) for the photoproducts gave compounds **11** and **9** produced in a ratio of 1.4:1, respectively.

Xanthone Sensitization. Four 2-mL samples of a solution of **5** (0.01 M) and xanthone (0.02 M) were irradiated and analyzed. The ratios of the amounts of **11** to **9** were found to be 1.46, 1.42, 1.44, and 1.42.

***p*-Dimethoxybenzene Sensitization.** Two 1-mL samples of the solution of **5** containing 0.0015 M *p*-dimethoxybenzene were irradiated for 15 min. Compounds **11** and **9** were produced in a ratio of 1.6:1 for both samples. Another 1-mL sample was irradiated with 350-nm light and the photoproducts, **11** and **9**, were found in a ratio of 1.4:1, respectively.

Sensitized Irradiation of 1-Methyl-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene (4). In general, degassed samples of solutions of **4** (0.02 M) and some sensitizer, in acetonitrile, were irradiated with 300-nm light. These irradiated samples were GC analyzed for the photoproduct on column B (0.001 M *n*-octadecane as internal standard).

Benzophenone Sensitization. Three 1-mL samples of a solution of **4** and benzophenone (0.016 M) were degassed and irradiated for 65 min. Compounds **9** and **10** were found to be produced in ratios of 1.3, 1.2, and 1.3:1, respectively. There was less than 2% of **12** produced.

***p*-Dimethoxybenzene Sensitization.** A 1-mL sample of a solution of **4** and *p*-dimethoxybenzene (0.006 M) was irradiated for 25 min. Analysis gave the ratio of **9**:**10** as 1.3:1. About 2% of **12** was produced.

Chlorobenzene Sensitization. A 3-mL sample (6.9 M chlorobenzene) was irradiated with 254-nm light for 1 h. Compounds **9** and **10** were produced in a ratio of 1.3:1, respectively. About 20% of the photoproduct was **12**.

Acetone Sensitization. Four 3-mL samples (2.7 M acetone) were irradiated with 254-nm light for 20 min. In all of the samples the ratio of **9** and **10** was found to be 1.3. No more than 4% of the photoproduct was **12**.

Irradiation of 4 in Cyclohexane. Two samples of a solution of **4** (0.15 M) in cyclohexane were deaerated with N_2 and irradiated in a quartz tube with 254-nm light. The cyclohexane solvent was allowed to evaporate off leaving a residue which was taken up in $CDCl_3$. The solutions were analyzed by ^1H NMR. The relative amounts of photoproducts, in each solution, was determined from the integration area of the methyl signal for each compound. Each sample had gone to about 69% completion. One of the samples analyzed as follows: 90% of the products were **12**, 4% were **10**, and 6% were **9**. The other sample analyzed as follows: 87% **12**, 5% **10**, and 8% **9**.

Complete Energy Transfer Experiments for Sensitized Irradiations of 1. For each experiment a range of concentrations of **1** was made. A sample of each concentration was irradiated in Pyrex with 300-nm light. The samples were analyzed for the content of **2** by HPLC or GC (column C, *n*-hexadecane internal standard). When analyzed by GC, duplicate injections of each sample were made. Plots were made of the quantum yield of **2** vs. the concentration of **1**. From this ϕ_{max} (maximum quantum yield of **2**) and the lowest concentration of **1** giving ϕ_{max} and c_{max} were obtained.

Acetone Sensitized. Three-milliliter samples of solutions of **1** (0.00078–0.10 M) in 20% acetone–hexane solvent were irradiated for 0.5 h. Each sample was then reduced in volume and analyzed by HPLC (μ-Porasil column). The peak areas were measured by triangulation. ϕ_{max} and c_{max} were found to be about 0.66–0.70 and 0.10 M, respectively.

Acetophenone Sensitized. Three-milliliter samples (0.25 M acetophenone in acetonitrile, 0.0020–0.25 M **1**) were irradiated for various lengths of time (0.25 to 2 h). ϕ_{max} and c_{max} were found to be 0.67 ± 0.04 and 0.03 M, respectively.

Benzophenone Sensitized. Three-milliliter samples (0.018 M benzophenone in acetonitrile, 0.0019–0.25 M **1**) were irradiated for various lengths of time (0.25 to 9.5 h). ϕ_{max} and c_{max} were found to be 0.19 and 0.03 M, respectively.

Ilenda–Daughenbaugh–Cristol Quenching Studies of 1. For each quenching experiment a range of concentrations of **1** and the quencher, either 1,3-pentadiene (PD) or 2,5-dimethyl-2,4-hexadiene (HD), was made such that the quotient of the concentrations of **1** and quencher (R/Q) was constant through the range. The concentration of **1** was always greater than c_{max}. The 3-mL sample of each concentration was irradiated with 300-nm light. These samples were analyzed by GC (column C, *n*-hexadecane internal standard) for the content of **2**. Duplicate injections were made for each sample. A plot of the results ϕ_0/ϕ_q for **2** vs. the concentration of the quencher gave straight-line plots. The slope and intercept of these plots were determined using least-squares analysis. In cases where **1** absorbed an appreciable amount of light, the quantum yields were corrected in such a way as to account for this.

Acetone Sensitized. Three Ilenda–Daughenbaugh–Cristol (IDC) studies were carried out. In the first, R/Q was 52, quencher was PD, and the concentration of **1** varied from 0.06 to 0.5 M in 25% acetone–hexane solvent. Treatments of the data as described above gave a slope and intercept of -20 ± 15 M^{-1} and 1.4 ± 0.08, respectively. A second study (R/Q of 21, quencher HD, and a concentration range of 0.19 to 0.59 M for **1** in 40% acetone–hexane solvent) gave a slope and intercept of 24 ± 10 M^{-1} and 1.7 ± 0.2, respectively. The last study (R/Q of 21, quencher HD, and a concentration range of 0.083 to 0.49 M for **1** in 30% acetone–acetonitrile solvent) gave a slope and intercept of 55 ± 2 M^{-1} and 2.7 ± 0.06, respectively, after analysis on column D.

Acetophenone Sensitized. Two quenching studies, with acetophenone (0.19 M in acetonitrile) as the sensitizer, were carried out. The first study (R/Q of 20, the quencher PD, and a concentration range of 0.25–1.1 M for **1**) gave a slope and intercept of 25 ± 2 M^{-1} and 1.8 ± 0.5, respectively. The second study (R/Q of 59, quencher PD, and a concentration range of 0.19–0.58 M for **1**) gave a slope and intercept of 50 ± 23 M^{-1} and 1.3 ± 0.2, respectively.

Benzophenone Sensitization. A quenching study, with benzophenone (0.020 M) in acetonitrile, with HD as the quencher, an R/Q of 19, and a concentration range for **1** of 0.10–0.59 M, gave a slope and an intercept of 139 ± 44 M^{-1} and 6.5 ± 0.6, respectively.

Acetone-Quenching Studies of the Irradiations of 1 and 5 in Acetonitrile. General. Solutions of **1** or **5**, containing a range of concentrations of acetone, in acetonitrile were made. A 2-mL sample of each solution was degassed and irradiated with 254-nm light. The samples were either analyzed directly on column E or worked up and analyzed in the following fashion. Each irradiated sample was transferred to a 2-mL volumetric flask. The solvent in each flask was allowed to evaporate with the aid of a stream of nitrogen. The resulting residue was dissolved in enough hexanes to give a 2-mL solution. Each solution was analyzed by HPLC according to the following procedures. A precisely measured volume (usually about 50 μL) of each solution was injected onto the Partisil M950 column. The starting material and photoproducts were collected separately (except for photoproducts **9** and **11**, which were collected together) into volumetric flasks for each injection. Generally, only one injection per sample was made. Each volumetric flask was diluted to the appropriate volume and then analyzed by UV spectroscopy. The absorbance of each solution was measured at a wavelength corresponding to one of the maxima in the absorption spectrum. In the case of the semibullvalenes and barrelenes, an absorption between 250 and 300 nm was used. For the cyclooctatetraenes, the absorption at about 236 nm was used. From the absorbance of the solution and the molar extinction coefficient of the compound being analyzed, the number of moles of compound injected was determined. From this the number of moles of compound in the original irradiated solution was determined. If the total number of moles of compounds in an irradiated sample did not equal the number of moles of barrelene that was in the sample before irradiation, the moles of each compound was adjusted so that the total moles of compounds would be the same as the number of moles of barrelene before irradiation. In the case of either analysis (GC or HPLC), the quantum yields of the photoproducts were corrected for absorption of light by the photoproducts and acetone ($\epsilon_{254} = 5$ L mol^{-1} cm^{-1}) during the irradiations. The fraction of light absorbed by the barrelene before and at the end of the irradiation was calculated. The average fraction of light absorbed by the barrelene was assumed to be equal to half of the sum of the fractions of light absorbed before and at the end of the irradiation. The corrected quantum yield is the quotient of the quantum yield before correction and the average fraction of light absorbed by the barrelene.

Irradiations of 1. Solutions of 0.2 M **1** were made, irradiated (5.01 × 10^{-5} Einstein), and analyzed on column E as described above. The quantum yields of **3** and **2**, before correction for absorption of light by

Table V. Corrected Data for the Quantum Yields of **2** and **3** from Irradiations Described in Table II (Analysis by Gas Chromatography)

[acetone], M	[1], M	ϕ_2	ϕ_3
0	0.202	0.033	0.28
0.20	0.208	0.17	0.24
0.27	0.208	0.21	0.25
0.41	0.198	0.26	0.21
0.68	0.201	0.33	0.18
0.82	0.207	0.37	0.18
1.1	0.194	0.40	0.14
1.4	0.195	0.48	0.14
1.6	0.194	0.53	0.14
2.0	0.192	0.59	0.13
2.7	0.208	0.68	0.12

Table VI. Corrected Data for the Quantum Yields of **2** and **3** from Duplicate Irradiation of **1** (Analysis by Gas Chromatography)

[acetone], M	[1], M	ϕ_2	ϕ_3
0	0.204	0.034	0.29
0.20	0.205	0.15	0.22
0.27	0.202	0.15	0.20
0.41	0.199	0.21	0.19
0.68	0.203	0.34	0.19
0.82	0.202	0.38	0.18
1.1	0.205	0.42	0.15
1.4	0.203	0.48	0.14
1.6	0.205	0.46	0.12
2.0	0.206	0.58	0.12
2.7	0.205	0.68	0.11

Table VII. Corrected Data for the Quantum Yields of **2** and **3** from Irradiation of **1** in Acetonitrile at 254 nm (Analysis by HPLC)

[acetone], M	F_A	ϕ_2	ϕ_3
0	0.00	0.04	0.32
0.20	0.004	0.28	0.24
0.27	0.006	0.26	0.23
0.41	0.008	0.27	0.24
0.68	0.012	0.46	0.22
0.82	0.016	0.46	0.19
1.1	0.022	0.53	0.17
1.4	0.027	0.60	0.16
1.6	0.033	0.59	0.13
2.0	0.040	0.67	0.15
2.7	0.053	0.78	0.12

photoproducts, are presented in Table II. The calculated quantum-yield values of **3**, in Table II, were found from the product of F_1 and 0.24 (the quantum yield of **3** found in the absence of acetone). The calculated quantum-yield values of **2**, in Table II, were found from the sum of the product of F_A and 0.71 (the maximum quantum yield of **2** in the acetone-sensitized irradiations) and the product of F_1 and 0.029 (the quantum yield of **2** found in the absence of acetone). The quantum yields after correction for absorption of light by photoproducts appear in Table V. A plot of ϕ_0/ϕ_q for **3**, where ϕ_0 is the quantum yield of **3** in the absence of acetone and ϕ_q is the quantum yield in the presence of acetone vs. acetone concentration was made. Linear regression analysis, by least squares, gave an intercept of 1.1, a slope of 0.53 M^{-1}, and a correlation coefficient (ρ) of 0.97 The quantum yields of **2** were corrected for the formation of **2** from both direct absorption of light by acetone and from intersystem crossing of the excited singlet of **1**. The corrected quantum yields (ϕ_{P_2}') were calculated from eq 20, where ϕ_{P_2} is the quantum yield

$$\phi_{P_2}' = \phi_{P_2} - F_A\phi_{P_2}{}^s - \phi_{P_1}\phi_{P_2}{}^0/\phi_{P_1}{}^0 \qquad (20)$$

of **2** before correction, F_A is the fraction of light absorbed by acetone, $\phi_{P_2}{}^s$ is the maximum quantum yield for the acetone-sensitized formation of **2**, ϕ_{P_1} is the quantum yield of **3** for the particular acetone concentration in question, $\phi_{P_2}{}^0$ is the quantum yield of **2** in the absence of acetone, and $\phi_{P_1}{}^0$ is the quantum yield of **3** in the absence of acetone. A value of 0.7 was used for $\phi_{P_2}{}^s$. A plot of $1/\phi_{P_2}'$ vs. the reciprocal of the acetone concentration was made. Linear regression analysis gave an intercept of 1.37, a slope of 1.23 M ($k_q\tau = 1.1$), and a ρ of 1.0. Another study of **1** (0.2 M) was carried out (6.0×10^{-5} Einstein of light) as described above. The results (quantum yields, have been corrected for absorption of light by photoproducts) of the irradiations are presented in Table VI, where ϕ_2 and ϕ_3 are the quantum yields of **2** and **3**, respectively.

Table VIII. Corrected Data for the Quantum Yields of **2** and **3** from Irradiation of **1** in Acetonitrile at 254 nm (Analysis by HPLC)

[acetone], M	F_A	ϕ_2	ϕ_3
0	0	0.06	0.30
0.14	0.003	0.18	0.26
0.20	0.005	0.24	0.25
0.27	0.007	0.21	0.24
0.41	0.010	0.32	0.21
0.55	0.014	0.30	0.21
0.68	0.017	0.35	0.22
0.82	0.020	0.33	0.18
1.1	0.027	0.45	0.18
1.4	0.033	0.44	0.15
1.6	0.039	0.47	0.14
2.0	0.049	0.48	0.10
2.7	0.064	0.57	0.094

Table IX. Corrected Data for Quantum Yields of **9** + **11** and **12** from Irradiations of **5** in Acetonitrile at 254 nm (Analysis by HPLC)

[acetone], M	F_A	ϕ_{9+11}	ϕ_{12}
0	0.00	0.04	0.37
0.20	0.004	0.19	0.34
0.41	0.011	0.26	0.32
0.60	0.017	0.29	0.27
1.1	0.030	0.33	0.25
1.3	0.036	0.37	0.28
1.7	0.045	0.47	0.29
2.0	0.053	0.40	0.23
2.6	0.067	0.45	0.22
3.3	0.082	0.52	0.20
3.8	0.096	0.55	0.20
4.5	0.114	0.55	0.14
6.8	0.162	0.71	0.10

Table X. Corrected Data for Quantum Yields of **9** + **11** and **12** from Irradiations of **5** Described in Table III (Analysis by Gas Chromatography)

[acetone], M	[5], M	ϕ_{9+11}	ϕ_{12}
0	0.144	0.016	0.54
0.27	0.140	0.096	0.52
0.41	0.124	0.12	0.47
0.68	0.124	0.18	0.45
0.82	0.135	0.21	0.45
1.1	0.137	0.25	0.41
1.4	0.133	0.30	0.42
1.6	0.123	0.34	0.38
2.0	0.119	0.38	0.34
2.7	0.129	0.45	0.31
3.4	0.142	0.51	0.31

ϕ_0/ϕ_q for **3** was plotted against the acetone concentration. The best line was drawn with an intercept of 1.0. This line has a slope of 0.72 M^{-1}. Another plot, $1/\phi_{P_2}'$ vs. reciprocal of the acetone concentration, was made. The best line was drawn with an intercept of 1.4. This line had a slope of 1.4 M ($k_q\tau = 1.0$). Solutions of 0.2 M **1** were made, irradiated, and analyzed by HPLC. The corrected quantum yields are presented in Table VII. The data were plotted in terms of the Stern–Volmer and double-reciprocal plots (quantum yields of **2** were corrected with eq 20). For the Stern–Volmer plot, the best line having an intercept of 1.0 was found to have a slope of 0.78 M^{-1}. For the double reciprocal plot, the best line having an intercept of 1.4 (neglecting the point with an acetone concentration 0.20 M) had a slope of 0.97 M ($k_q\tau = 1.4$). Another study (HPLC) of **1** (0.2 M) was conducted. The corrected quantum yields are presented in Table VIII. A linear regression analysis, by least squares, of the Stern–Volmer plot gave an intercept of 0.97, a slope of 0.82 M^{-1}, and a ρ of 0.97. The quantum yields of **2** were corrected with eq 20 in the same way as described above. A plot of the reciprocal of the corrected quantum yield vs. the reciprocal of the acetone concentration was made. The best line was drawn by inspection, with the points corresponding to the two lowest acetone concentrations neglected. The resulting line had an intercept of 1.4 and a slope of 1.4 M ($k_q\tau = 1.0$).

Irradiation of 5. A complete energy-transfer experiment was conducted with **5** similar to the one described above for **1**. The value for c_{max}

was found to be about 0.1 M. Solutions of 0.15 M **5** were made, irradiated, and analyzed (HPLC) as described above. The quantum yields *of* **9**, **11**, *and* **12**, *after correction for absorption of light by photoproducts,* are presented in Table IX. A linear regression analysis, by least squares, of the plot of ϕ_0/ϕ_q for **12** vs. the concentration of acetone gave a slope of 0.36 M^{-1} an intercept of 0.90, and a ρ of 0.96. The sum of the quantum yields of **9** and **11** were corrected with eq 20 as described above. A value of 0.7 was used for $\phi_{P_2}{}^{s}$. A plot of the reciprocal of the corrected sum vs. the reciprocal of the acetone concentration was made. A line having an intercept of 1.4 was drawn by inspection. The slope of this line was 2.6 M ($k_q\tau = 0.54$). Solutions of **5** in acetonitrile/acetone were made, irradiated (2.91×10^{-5} Einstein), and analyzed as described above with colume E. The quantum yields of **12** and of **9** + **11** are presented in Table III. The quantum yields were corrected with respect to light absorption by photoproducts (see Table X for corrected quantum yields). A Stern–Volmer plot of **12** was made. Linear regression analysis gave an intercept of 1.02, a slope of 0.24 M^{-1}, and a ρ of 0.98. Also a double *reciprocal plot of* **9** + **11** *was made. Linear regression gave an intercept* of 1.5, a slope of 3.3 M ($k_q\tau = 0.45$), and a ρ of 1.0.

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Registry No. 1, 2734-13-6; **2**, 2199-28-2; **3**, 262-89-5; **4**, 58426-49-6; **5**, 82201-51-2; **9**, 85029-18-1; **10**, 85029-19-2; **11**, 85029-20-5; **12**, 85029-21-6; **17**, 19978-14-4; **18**, 85029-22-7; **19**, 85029-23-8; 7-bromo-8-methyl-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene, 85029-24-9.

9a-Hydro-9a-methyl-9-anthracenone—A Molecule with Fused Blocked Aromatic Rings

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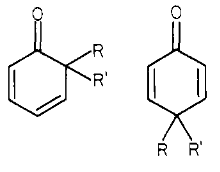
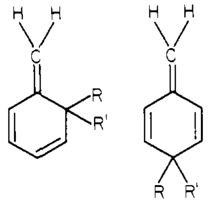
Abstract: The title compound (**1**), which contains fused semibenzene and cyclohexadienone rings, was prepared from the adduct of butadiene and 1,4-naphthoquinone in five steps. It is stable to base and undergoes dimerization, rather than rearrangement, in acid. Thermolysis leads to dimerization and to aromatization via a semibenzene rearrangement, yielding 10-methyl-9-anthrone. Photoisomerization results in a series of electrocyclic "aromaticity-switching" steps leading to quantitative formation of 4-methyl-9-anthrone.

We define a "blocked aromatic molecule" as a molecule in which a nonaromatic ring may be converted to an aromatic ring by a change in the location of a single substituent or hydrogen atom. Blocked aromatic molecules commonly contain cyclohexadienone or methylenecyclohexadiene ("semibenzene") rings.



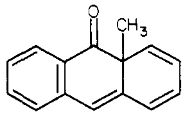
cyclohexadienones



semibenzenes

Rearrangements of cyclohexadienones under thermal, acid-catalyzed, and base-catalyzed conditions have been extensively investigated.[1] Not surprisingly, these processes almost always result in conversion of the cyclohexadienones to aromatic isomers (phenols or aryl ethers). They are often unusually rapid reactions and may involve mechanistic pathways which are not commonly observed in ketones which cannot be directly isomerized to aromatic molecules.[1b] Semibenzenes similarly undergo thermal rearrangments to aromatic isomers.[2] These rearrangements are often so rapid that the intermediate formation of semibenzenes can only be inferred, rather than detected.[2f] Several semibenzene rearrangements have been demonstrated to proceed by free radical chain mechanisms,[2d-g] although concerted paths appear to be followed when the structures of the semibenzenes allow immediate aromization by such routes.[2g]

In molecules with fused blocked aromatic rings, the presence of a single blocking substituent might prevent simultaneous aromatization of two or more nonaromatic rings. Until our preliminary report of part of this work,[3] no examples of such molecules had been described. In this paper we report the synthesis and a study of some of the properties of 9a-hydro-9a-methyl-9-anthracenone (**1**), which contains fused semibenzene and cyclohexadienone rings.



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