Mechanistic Studies in Organic Photochemistry. IV.[1] The Mechanism of the Photorearrangement of Bicyclo[2.2.2]octadienones to Tricyclo[3.3.0.0^{2,8}]octen-3-ones

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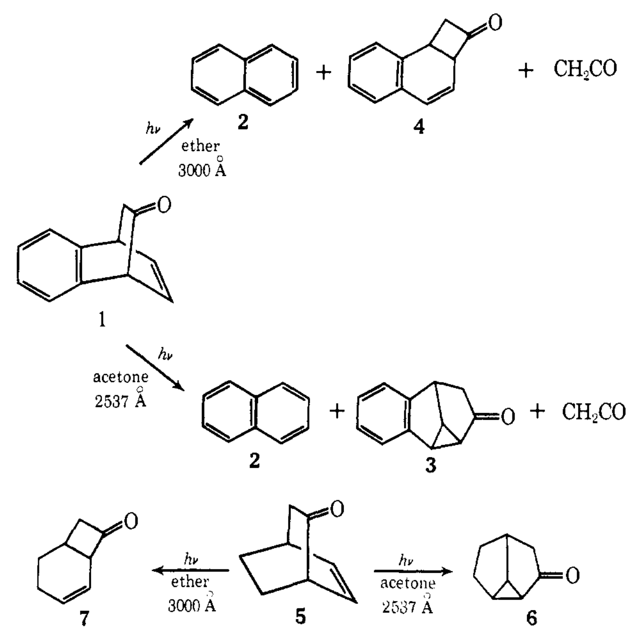
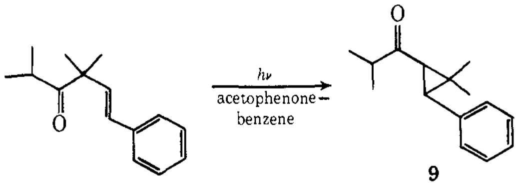
Abstract: Mechanistic studies on the photorearrangements of benzobicyclo[2.2.2]octadienone (**1**) and bicyclo[2.2.2]octenone (**5**) are reported. The limiting quantum yields for the singlet reaction of **1** are: $\Phi_{\text{dis}} = 0.50$; $\Phi_{\text{naphthalene}} = 0.45$; $\Phi_{\text{4,5-benzobicyclo[4.2.0]octa-2,4-dien-8-one}} = 0.10$. The limiting quantum yields for the acetophenone-sensitized reaction are: $\Phi_{\text{dis}} = 0.14$; $\Phi_{\text{naphthalene}} = 0.01$; $\Phi_{\text{benzotricyclo[3.3.0.0}^{2,8}\text{]octen-3-one}} = 0.12$. A deuterium labeling experiment established the 1,2-acyl migration mechanism for the photosensitized rearrangement of **1**. Finally, it was shown that the triplet reaction proceeded by a *concerted*, symmetry-allowed process by comparison with the photoisomerization of lactone **12**.

In the preceding paper,[1] we reported structural details and preliminary results on the direct and acetone-sensitized irradiations of benzobicyclo[2.2.2]octadienone (**1**) and bicyclo[2.2.2]octenone (**5**) (see Chart I). For the singlet reaction it was noted that the rearrangement proceeds by a concerted, symmetry-allowed 1,3-acyl shift to yield a cyclobutanone.

Chart I. Direct and Acetone-Sensitized Photorearrangements of Benzobicyclo[2.2.2]octadienone (**1**) and Bicyclo[2.2.2]octenone (**5**)



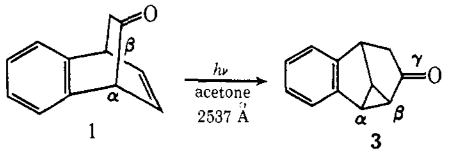
Of considerable interest are the rearrangements resulting from acetone sensitization. In an earlier communication[2] we suggested that these may result from the carbonyl analog of the divinylmethane photorearrangement. Subsequently, this di-π-methane process has been suggested[3] for the 1,2 migration of a benzoyl group for 1-phenyl-3,3,5-trimethylhex-1-en-4-one (**8**) to cyclopropyl ketone **9** (eq 1) (termed an "oxa-di-π-methane" rearrangement by Dauben[3]). Other accounts describing excited state carbonyl–vinyl bonding in photorearrangements have appeared.[4a-d]



8 **9** (1)

The mechanistic details of β,γ-unsaturated ketone photorearrangements have not been reported. We have studied the photorearrangements of the model systems bicyclo[2.2.2]octenone (**5**) and benzobicyclo[2.2.2]octadienone (**1**) in detail and our results are reported below.

The study of the triplet-sensitized rearrangement of benzobicyclo[2.2.2]octadienone demonstrated that the rearrangement involved the transposition of the carbonyl carbon from a position β to the aromatic ring to a position γ to the aromatic ring, *i.e.*



1 **3** (2)

Several mechanistic pathways have been suggested for this transformation including cleavage to acyl–allyl diradicals,[5] the well-known divinylmethane rearrangement,[1,5a] and, more recently, the di-π-methane rearrangement utilizing the carbonyl carbon[1,2] (the "oxa-di-π-methane" rearrangement[3]). These are shown in Chart II for the benzobicyclo[2.2.2]octadienone to benzotricyclo[3.3.0.0^{2,8}]octen-3-one rearrangement. A fourth alternative, the divinylmethane rearrangement initially uniting C-3 and C-8, was eliminated since this mechanism would predict benzotricyclo[3.3.0.0^{2,8}]octen-4-one instead of **3** as the photoproduct. However, the question remains as to which of the three

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[1] Paper III: R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, **93**, 3957 (1971).

[2] R. S. Givens and W. F. Oettle, *Chem. Commun.*, 1066 (1969).

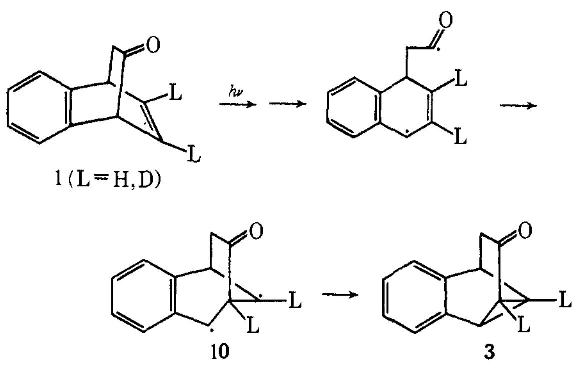
[3] W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 1786 (1970).

[4] (a) J. S. Swenton, *J. Chem. Educ.*, **46**, 217 (1969); (b) S. Domb, G. Bozzato, J. A. Saboz, and K. Schaffner, *Helv. Chim. Acta*, **52**, 2436 (1969); (c) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Aschaffenburg, Germany, 1970, p 96 ff; (d) D. M. Madigan and J. S. Swenton, *J. Amer. Chem. Soc.*, **92**, 7513 (1970).

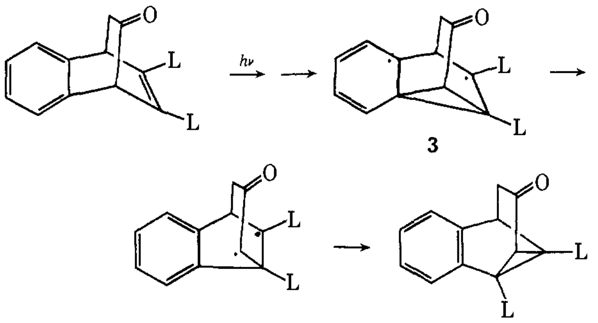
[5] (a) H. Hart and R. K. Murray, Jr., *Tetrahedron Lett.*, 379 (1969); (b) J. R. Williams and H. Ziffer, *Chem. Commun.*, 194 (1967).

Chart II. Suggested Mechanisms for the β,γ-Unsaturated Ketone to Cyclopropyl Ketone Photoisomerization

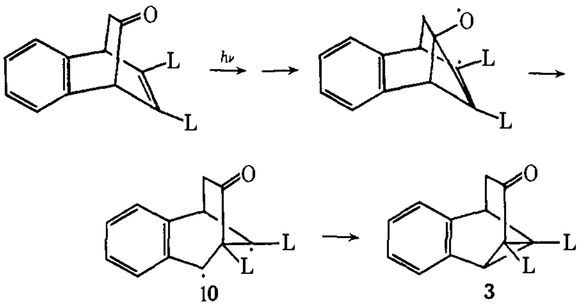
(a) acyl-allyl diradical



(b) divinylmethane



(c) di-π-methane or "oxa-di-π-methane"



alternative, stepwise mechanisms illustrated in Chart II may be operative. In addition, a concerted 1,2-acyl shift with cyclopropane formation is also possible.[4b,c,6]

Results and Discussion

In order to differentiate among the three stepwise mechanisms, a deuterium labeling experiment was run. The ethylene ketal of benzobicyclo[2.2.2]octadienone (**10**) was deuterated in the vinyl positions by an exchange reaction[7] with *N*,*N*-dideuteriocyclohexylamine–lithium cyclohexylamide (Chart III). During the work-up a small amount of exchange at the position α to the carbonyl was noted. The results (Table I) indicate that 77% of the vinyl hydrogens were exchanged for deuterium.

Chart III. Synthesis of Benzobicyclo[2.2.2]octadienone-2,3-d_2

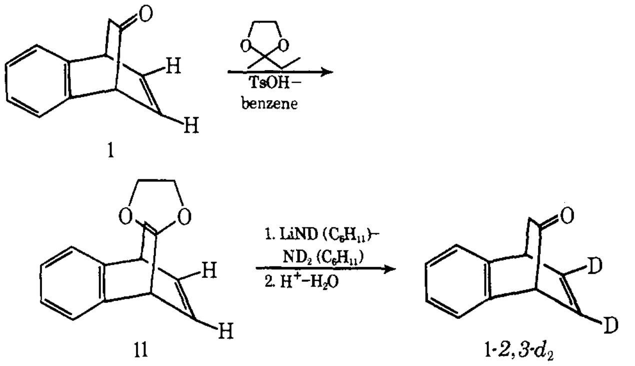


Table I. Hydrogen Atom Distribution in the Nonaromatic Positions in Benzobicyclo[2.2.2]octadienone-2,3-d_2 (**1**-2,3-d_2)

Signal position[a] (δ)	Signal description[b]	Hydrogen atom distribution[c] (error)
6.35–6.80	Vinyl m, H_2 and H_3	0.232 (±0.030)
4.20–4.40	Bridgehead, d of d, H_1	0.966 (±0.042)
3.95–4.20	Bridgehead, m, H_4	1.000 (assumed)
2.10 and 1.87	Methylene, 2 overlapping sets of d of d, H_5 and $H_{5'}$	1.782 (±0.037)

[a] 60- and 100-MHz nmr in CCl_4 with TMS as internal standard. [b] Assignments based on protiated benzobicyclo[2.2.2]octadienone. [c] Distributions determined by integration of the nmr signals and normalized to the bridgehead multiplet at δ 3.95–4.20. Error estimates are based on five or more integrations.

With labeled ketone, paths a and c can be distinguished from b by analysis of the nmr spectrum of the dideuteriobenzotricyclo[3.3.0.0^{2,8}]octen-3-one (**3**-d_2). The expected products are shown in Chart II (L = D) and the corresponding hydrogen atom distributions are given in Table II. Irradiation of **1**-2,3-d_2 in acetone under conditions identical with those used in the preparative studies[1] resulted in a mixture of labeled products and recovered **1**-2,3-d_2. Both products, naphthalene (**2**) and benzotricyclo[3.3.0.0^{2,8}]octen-3-one (**3**), were analyzed by 100-MHz nmr. Scrambling of the label was unimportant as shown by analysis of the recovered benzobicyclo[2.2.2]octadienone (**1**-2,3-d_2). The spectra were identical with those obtained from the starting ketone (**1**-2,3-d_2).

Inspection of Table II shows that the observed ratios for **3**-d_2 were in accord with mechanisms a or c but not with the divinylmethane pathway b. These results agree with those of Hart and Murray[5a] on the tetramethyl derivative of **1** and demonstrate that the benzo ring is not involved in the bonding processes during this rearrangement. The second product, naphthalene (**2**-d_2), also analyzed by 100-MHz nmr (Table III), must be formed by a photofragmentation reaction that does not involve any rearrangement of the C-1 through C-4 carbon skeleton.

Interestingly, both paths a and c involve an intermediate 1,3-diradical **10**. To test the hypothesis that diradical **10** was involved in this rearrangement, 6,7,8,9-tetrahydro-9-hydroxy-7-oxo-5,8-methano-5*H*-benzocycloheptene-10-carboxylic acid lactone (lactone

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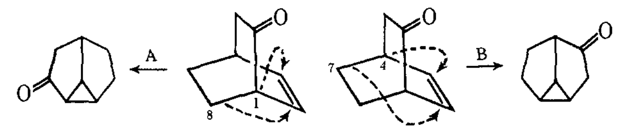
(6) Similar skeletal rearrangements are possible for **5**. For example, the σ electrons of the C_1–C_8 (C_4–C_7) bond could be involved in a 1,2 migration in a $[\pi 2_a + \sigma 2_a]$ type rearrangement,[4e] *i.e.*



However, this possibility seems unlikely in view of the selectivity of path A to the exclusion of B.

(7) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 6096 (1968).

Table II. Hydrogen Atom Distribution in the Nonaromatic Positions of Benzotricyclo[3.3.0.0^{2,8}]octen-3-one (**3**) from the Sensitized Irradiation of Benzobicyclo[2.2.2]octadienone-*2,3-d*$_2$ (**1**-*2,3-d*$_2$)

Signal position[a] (δ)	Signal description[b]	Hydrogen atom distribution[c] — Calcd for Mech a[c]	Hydrogen atom distribution[c] — Calcd for Mech b[d]	Hydrogen atom distribution[c] — Found (error)
3.74	ABX q, benzylic methine, H_5	1.000	1.000	1.000 (assumed)[e]
3.16	ABCD q, cyclopropylmethine, H_1	0.232	0.232	0.302 (±0.037)
2.74 and 2.78	Overlapping ABX q, H_4 and H_8	1.736	0.968	1.674 (±0.034)
1.88 and 2.18	Overlapping d and ABX q, $H_{4'}$ and H_2	0.968	1.736	0.998 (±0.094)

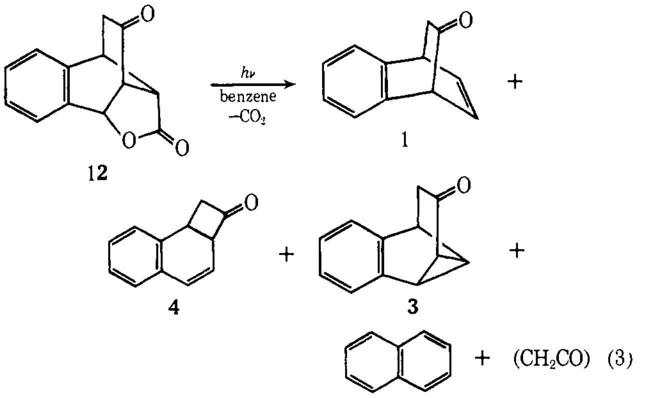
[a] 60- and 100-MHz nmr in CCl_4 with TMS as interal standard. [b] Assignments based on the protiated benzotricyclo[3.3.0.0^{2,8}]octen-3-one (**3**). [c] Distributions determined by nmr integrations and normalized to the benzylic proton (H_5). Error estimates are on five or more integrations. [d] Based on the distributions determined for benzobicyclo[2.2.2]octadienone in Table I. [e] Mechanisms a–c all predict that the bridgehead hydrogen H_4 will become the benzylic hydrogen H_5 in the transformation. Therefore, this hydrogen was assumed to be 1.000 also (see Chart II).

Table III. Hydrogen Atom Distribution in Naphthalene Obtained from the Sensitized Rearrangement of Benzobicyclo[2.2.2]octadienone-*2,3-d*$_2$

Signal position[a] (δ)	Signal description[b]	Hydrogen atom distribution[c] (error)
7.81	α hydrogens	1.000 (assumed)
7.46	β hydrogens	0.710 (±0.006)

[a] 60-MHz nmr in CCl_4 with TMS as internal standard. [b] Assignments based on those in Jackman and Sternhell (L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, London, 1969, p 205). [c] Distributions determined by integration of the nmr signals.

12) was photolyzed. Lactone **12** expelled carbon dioxide quantitatively upon irradiation and gave naphthalene (57%), benzotricyclo[3.3.0.0^{2,8}]octen-3-one (38%), benzobicyclo[2.2.2]octadienone (4%), and 4,5-benzobicyclo[4.2.0]octa-2,4-dien-8-one (1%) (eq 3).

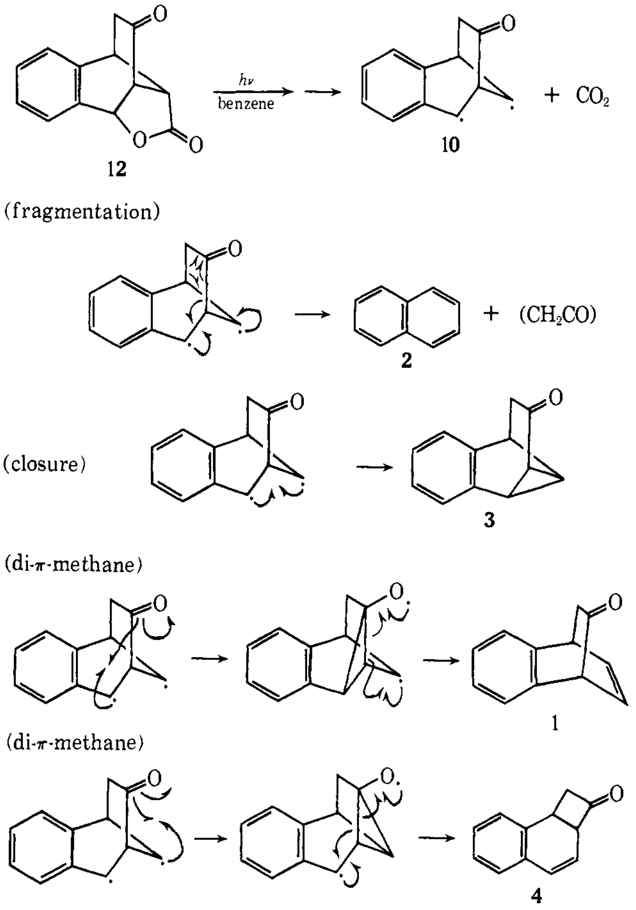


An economic and convenient mechanism for this transformation would be the initial formation of the 1,3-diradical **10** followed by a di-π-methane rearrangement to form **1**, a diradical closure to **3**, a di-π-methane rearrangement to **4**, and a fragmentation to naphthalene and ketene (see Chart IV).

Quantum Yield and Multiplicity Studies. The multiplicity of the excited state of **1** obtained on direct irradiation must be singlet. We have suggested that it rearranges by a *concerted* symmetry-allowed 1,3-acyl migration to yield **4**, and fragments to yield naphthalene and ketene. The efficiency of these two reactions is very high (the limiting quantum yields are 0.45 for naphthalene formation and 0.10 for the formation of **4** (see Table IV)). The excited singlet of **1** either reacts or returns to ground state by an alternate radiationless pathway. Intersystem crossing and radiative pathways were shown to be unimportant in the photochemistry of **1**.[8]

The triplet of **1** was generated by energy transfer from acetone and from acetophenone. Both sensitizers

Chart IV. Possible Mechanism of the Photorearrangements of **12** upon Direct Excitation in Benzene



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[8] Attempted fluorescence studies on **1** were unsuccessful. Only a weak, diffuse emission was found which could have resulted from trace impurities in solution.[5] We thank Professor R. B. Cundall for the fluorescence studies.

Table IV. Limiting Quantum Yields for the Direct and Sensitized Irradiations of **1**[a]

		Quantum yields				
		Disappearance of	Appearance of			
Run[b]	Sensitizer	1	2	3	4	2 + 3 + 4
1	None	0.50	0.45	None	0.10	0.55
2	Acetone	0.12	0.05	0.05	None	0.10
3	Acetophenone	0.14	0.01	0.12	None	0.13

[a] The quantum yields are determined by extrapolating the results of several conversions (ten or more determinations) to 0% conversion. [b] Run 1, in benzene, RPR 3000-Å lamps; run 2, in acetone solvent, RPR 2537-Å lamps; run 3, in benzene, sensitizer 0.2 *M*, RPR 3500-Å lamps.

Table V. Quenching Studies and Quantum Yields of Product Formation for the Photorearrangement of Lactone **12**

	Quencher concn, *M*			Appearance			
Run[a]	(1,3-cyclohexadiene)	Disappearance Φ_{12}	Φ_{CO_2}	Φ_1 (ϕ_0/ϕ)	Φ_2 (ϕ_0/ϕ)	Φ_3 (ϕ_0/ϕ)	Φ_4 $(\phi_0/\phi)^b$
1	None	0.175	0.148	0.020	0.046	0.061	*Ca.* 0.001
2	None			0.029 (1.00)	0.041 (1.00)	0.060 (1.00)	*Ca.* 0.002 (1.0)
3	0.0067			0.022 (1.32)	0.024 (1.71)	0.040 (1.50)	*c* (1.3)
4	0.0133			0.019 (1.53)	0.024 (1.70)	0.037 (1.60)	*c* (1.42)
5	0.0200			0.016 (1.81)	0.018 (2.22)	0.033 (1.81)	*c* (1.93)
6	0.0267			0.012 (2.42)	0.015 (2.74)	0.027 (2.26)	*c* (2.65)

In dioxane, RPR 3000-A lamps; analyzed by vpc (see Experimental Section). [b] Estimated by peak heights from vpc chromatogram. [c] Not determined.

gave the same products but the ratio of naphthalene to tricyclo[3.3.0.0^{2,8}]octen-3-one (**3**) varied. Thus, acetone sensitization gave a limiting quantum yield for appearance of 0.05 for both naphthalene and **3**. Acetophenone sensitization gave limiting appearance quantum yields of 0.01 for naphthalene and 0.12 for **3**. Attempts to sensitize this rearrangement with benzophenone were unsuccessful which places the triplet energy of ketone **1** below acetone (E_t = 79.5 kcal/mol[9]) and acetophenone (E_t = 74 kcal/mol[10a]) but above benzophenone (E_t = 68 kcal/mol[10a]).

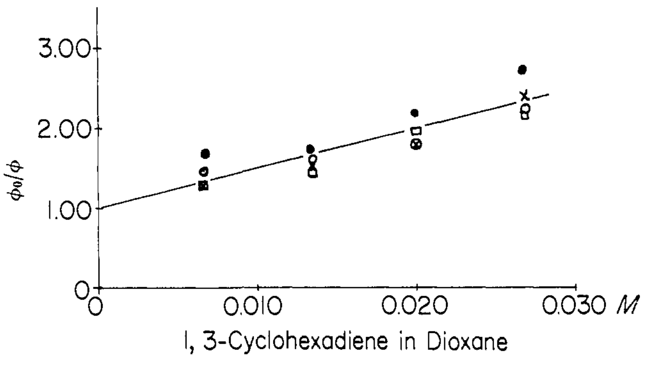

Figure 1. Stern-Volmer plot of the quenching of **1-4** in the photolysis of lactone **12**: ●, naphthalene (**2**); ○, benzotricyclo[3.3.0.0^{2,8}]-octen-3-one (**3**); ×, benzobicyclo[2.2.2]octadienone (**1**); □, benzobicyclo[4.2.0]octa-2,4-dien-8-one (**4**); slope = 102 l./mol.

A comparison of the photorearrangement of lactone **12** with the sensitized rearrangement of benzobicyclo[2.2.2]octadienone was of interest. The lactone rearrangement gave all of the products found from acetone-sensitized rearrangement of **1** although in different ratios. Table V compares the percentages and the quantum yields for production of the four products of the lactone photolysis. Also shown in Table V and Figure 1 are the results of quenching the lactone rearrangement with 1,3-cyclohexadiene. The reaction could be sensitized with acetone showing that this photorearrangement also must originate from an excited triplet (of **12**).

On closer inspection of Figure 1, it can be seen that all four products **1-4** are quenched with the same efficiency (τk_q = 102 l./mol, τ = 2.0 × 10^{-8} sec). This evidence is consistent with a common intermediate, the triplet of **12**, for all four products. Carbon dioxide is subsequently lost from the triplet as a ground-state singlet since the triplet energy of CO_2 (>120 kcal/mol[10b]) is prohibitively high. The remaining triplet diradical **10** then leads to the four products as pictured in Chart IV.

In contrast, the intermediate involved in the rearrangement of the triplet of ketone **1** *does not lead to the cyclobutanone* **4** (Chart I). Cyclobutanone (**4**) formation would be expected *via* mechanisms a and c (Chart II) based on the results from lactone **12**. This is direct evidence that the formation of cyclopropane must be concerted with acyl migration.

Finally, the acyl-migration step of mechanism a involves the same acyl-allyl diradical that was shown previously to lead only to naphthalene and ketene.[1] Thus, the evidence is consistent only with the di-π-methane rearrangement which should be pictured as a *concerted*[11] 1,2 migration with 1,3-bond formation *via* a 4n Hückel-type migration,[12] *i.e.*

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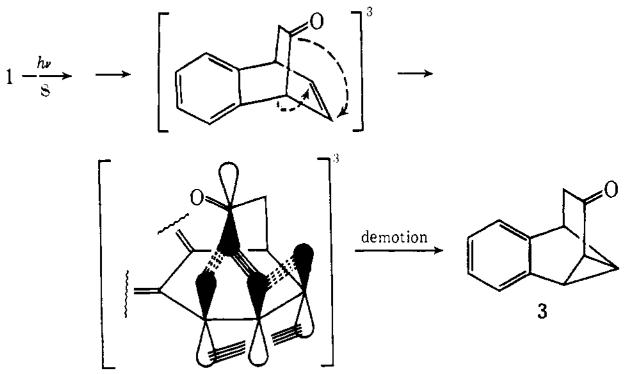
[9] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

[10] (a) J. G. Calvert and J. N. Pitts, Jr. "Photochemistry," Wiley, New York, N. Y., 1966, p 298; (b) p 223.

[11] Demotion and spin inversion could occur with concerted migration to give the ground state of **3**. This has been suggested for the divinylmethane rearrangements of barrelene and substituted barrelenes.[4c]

[12] H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1563, 1566 (1966).



The stepwise[13] di-π-methane mechanism does explain the overall reaction of **12**. Thus, *both the singlet and triplet rearrangements of these ketones proceed via concerted, symmetry-allowed processes.*

Experimental Section[14]

A. Preparation and Photorearrangement of Benzobicyclo[2.2.2]octadienone-2,3-d_2 (1). Ethylene Ketal of Benzobicyclo[2.2.2]octadienone (11). A solution of 1.3788 g (8.1 mmol) of **1**, 69.9 mg (0.4 mmol) of *p*-toluenesulfonic acid, and 15 ml of 2-ethyl-2-methyldioxolane[15] was heated at reflux for 1.5 hr. The mixture was distilled to remove the methyl ethyl ketone (bp 80-88°). The remaining dioxolane was removed by evaporation at reduced pressure and the residue was taken up in benzene, extracted with 5% sodium bicarbonate and water, and dried, and the solvent evaporated to yield 1.5704 g (7.3 mmol, 91%) of the ketal as a waxy off-white solid, mp 140-145°. The ketal was recrystallized from hexane to yield 799.2 mg of white solid, mp 143-145°. The infrared spectrum (CCl_4) showed bands at 3.28, 3.33, 3.40, 6.25 (w), several weak bands from 6.7 to 8.6 and 9.7 to 12.0, 8.95, 9.10, 9.35, 14.1, and 14.85 μ; nmr (CCl_4) δ 7.01 (s, 4 H, aromatic), 6.25-6.70 (m, 2 H vinyl), 3.55-3.95 (m, 6 H, bridgehead and dioxyethane), 1.5-2.1 (m, 2 H, C-5 methylene).

Deuterium Exchange.[7] To a solution of 700 mg (3.27 mmol) of the ketal in 25 ml of *N,N*-dideuteriocyclohexylamine, stirred under nitrogen for 1 hr, was added 3 ml of *n*-butyllithium (15.2% in hexane). The solution was stirred at 80° for 48 hr, quenched with D_2O, and added to 100 ml of water. The solution was extracted with 50 ml of ether (two times) and the combined ether extracts were washed with water and 5% HCl and water, dried over $MgSO_4$, and evaporated to yield 419.4 mg of a yellow semisolid residue. Chromatography on silica gel (Davison, grade 950, 60-200 mesh) using a 1 × 50 cm column slurry packed with 5% ether-hexane gave the following results (50-ml fractions): fractions 1-3, 5% ether-hexane, 148.8 mg (1.16 mmol, 35%) naphthalene; fractions 4-5, 5% ether-hexane, nil; fractions 6-7, 50% ether-hexane, nil; fractions 8-13, 50% ether-hexane, 146.4 mg (0.86 mmol, 31%) of benzobicyclo[2.2.2]octadienone-2,3-d_2 as a pale yellow oil. Rechromatography of 119.9 mg of the oil from fractions 8-13 employing the above conditions gave the following results: fractions 1-4, 5% ether-hexane, nil; fractions 5-12, 10% ether-hexane, nil; fractions 13-21, 10% ether-hexane, 80.7 mg (0.47 mmol, 67%) of crystalline benzobicyclo[2.2.2]octadienone-2,3-d_2, mp 53-54.5° (lit.[16] 56.5-58°). The infrared spectrum (CCl_4) showed a strong band at 5.78 μ (carbonyl of ketone **1**) and a weak band at 4.35-4.50 μ (C-D stretch); nmr (CCl_4) δ 7.18 (m, 4 H, aromatic), 6.4-6.8 (br t, 0.44 H, vinyl, J = 5.5 Hz), 4.29 (br s, 0.91 H, bridgehead), 4.10 (br d, 0.94 H, bridgehead, J = 2.5 Hz), 2.3-1.6 (m, 1.38 H, methylene) (see Table I). This indicated that 77% of the hydrogens at the vinyl positions had been exchanged for deuterium.

Acetone-Sensitized Photoisomerization of Benzobicyclo[2.2.2]octadienone-2,3-d_2. A solution of 72.0 mg (0.42 mmol) of **1**-2,3-d_2 in 15 ml of reagent acetone in a quartz tube was degassed for 1 hr with nitrogen and irradiated in the merry-go-round apparatus with the RPR 2537-Å lamps for 3 hr. Evaporation of solvent yielded 74.3 mg of a crude oil which was chromatographed on Davison silica gel column (1 × 50 cm) slurry packed with 5% ether-hexane to give the following results (50-ml fractions taken): fractions 1-3, 5% ether-hexane, 14.2 mg (0.111 mmol, 26%) of naphthalene; fractions 4-5, 5% ether-hexane, nil; fractions 6-12, 10% ether-hexane, nil; fractions 13-18, 10% ether-hexane, 16.7 mg (0.099 mmol, 24%) of benzobicyclo[2.2.2]octadienone-2,3-d_2; fractions 19-21, 10% ether-hexane, nil; fractions 22-23, 50% ether-hexane, nil; fractions 24-30, 50% ether-hexane, 15.4 mg (0.090 mmol, 21%) of benzotricyclo[3.3.0.0^{2,8}]octen-3-one (**3**). Each of the products had identical melting point and R_f values on tlc as the protiated products of the sensitized irradiation of benzobicyclo[2.2.2]octadienone. Nmr analysis of the individual products revealed the isotopic distributions indicated in Tables II and III.

B. Synthesis and Photoisomerization of 6,7,8,9-Tetrahydro-9-hydroxy-7-oxo-5,8-methano-5*H*-benzocycloheptene-10-carboxylic Acid Lactone (12). Synthesis of Lactone 12. This lactone was synthesized according to the method of Kitahonoki and Takano[16] with the following modification. A suspension of 240 g (0.95 mol) of 1,2,3,4-tetrahydro-9-oxo-1,4-ethanonaphthalene-2,3-*endo*-dicarboxylic acid[17] in 110 ml of dry pyridine and 1 l. of dry benzene was stirred under nitrogen for 2 hr. An exothermic reaction occurred after the addition of 440 g (0.99 mol) of lead tetraacetate and 0.100 g (0.5 mmol) of cupric acetate. The mixture was heated to 50-60° for 5 hr and cooled, and 2.5 l. of 5% nitric acid was added. The mixture was stirred for 7 hr, the precipitated lead salts were filtered, and the aqueous layer was separated and extracted with benzene. The combined benzene layers were washed with water, 20% potassium hydroxide, and water, and dried and evaporated to yield 39.0 g of a dark viscous oil. The oil was dissolved in 20 ml of chloroform and 5 g of the lactone precipitated as light tan crystals, mp 198-202° (lit.[16] 196-196.5°).

The remainder (33.2 g) was chromatographed on a 5 × 100 cm silica gel column (Davison, grade 950, 60-200 mesh) slurry packed in 5% ether-hexane (1-l. fractions taken): fractions 1-5, 5% ether-hexane, nil; fractions 6-7, 10% ether-hexane, nil; fractions 8-19, 10% ether-hexane, 22.6556 g (0.131 mol, 13.3%) of benzobicyclo[2.2.2]octadienone; fractions 20-28, 50% ether-hexane, nil; fractions 29-35, benzene, nil; fractions 36-45, 10% ethyl acetate-benzene, 10.250 g (0.047 mol, 5%) of lactone **12**, mp 198-202°. Recrystallization from chloroform-hexane gave a white crystalline solid, mp 197-199° (lit. 196-196.5°).

The infrared spectrum (KBr) showed bands at 3.28, 3.33, 5.69, and 5.58 (carbonyls), several small peaks from 6.7 to 7.8, 7.82, 8.70, 9.01, 10.4, 10.5, 10.65, 12.3, 12.8, and 14.3 μ; nmr ($CDCl_3$) δ 7.45-7.1 (m, 4 H, aromatic), 5.41 (d of d, 1 H, benzylic and α to COCOR), 4.05-3.50 (m, 3 H, bridgeheads), 3.1-2.2 (m, 2 H, methylene); uv (95% EtOH) λ_{max} 2737 (ϵ 152), 2688 (199), 2638 (211).

Photorearrangement of Lactone 12. A solution of 2.1008 g (9.7 mmol) of the lactone in 210 ml of benzene was degassed for 2 hr and irradiated for 6.5 hr with a 450-W Hanovia lamp fitted with a Pyrex filter. Aliquots were taken at 1, 2, and 6.5 hr and the progress of the reaction was followed by tlc and nmr. The solvent was removed and the 2.100 g of solid residue was chromatographed on a 3 × 60 cm column of silica gel (Davison, grade 950, 60-200 mesh) slurry packed with 5% ether-hexane giving the following results (250-ml fractions): fractions 1-4, 4% ether-hexane, 396.6 mg (3.1 mmol, 32%) of naphthalene; fractions 5-7, 4% ether-hexane, nil; fractions 8-12, 7% ether-hexane, nil; fractions 13-15, 10% ether-hexane, nil; fractions 16-20, 10% ether-hexane, 38.1 mg (0.22 mmol, 2.2%) of benzobicyclo[2.2.2]octadienone; fractions 21-31, 10% ether-hexane, nil; fractions 32-39, 50% ether-hexane, 340.3 mg (2.0 mmol, 21%) of benzotricyclo[3.3.0.0^{2,8}]octen-3-one; fractions 40-49, 50% ether-hexane, nil; fractions 50-60, benzene, nil; fractions 61-63, 5% ethyl acetate, nil; fractions 64-74, 10% ethyl acetate-benzene, 886.1 mg (4.1 mmol, 42.5%) of lactone **12**. Product identifications were made by comparison of spectral data, melting points, and mixture melting points with authentic samples.[18] The presence of 4,5-benzobicyclo[4.2.0]octa-2,4-dien-8-one (**4**) was shown by vpc separation of the photoproducts. The yield at low

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(13) Studies on substituted γ-butyrolactone photolyses show that cyclopropane formation occurs with little stereospecificity, indicating a lack of concerted bond formation with CO_2 expulsion (paper V: R. S. Givens and W. F. Oettle, *ibid.*, **93**, 3301 (1971)).

(14) Melting points were obtained on a hot-stage apparatus calibrated with known samples.

(15) H. J. Dauben, B. Loken, and H. J. Ringold, *J. Amer. Chem. Soc.*, **76**, 1359 (1954). Method B was employed for the ketalization.

(16) K. Kitahonoki and Y. Takano, *Tetrahedron Lett.*, 1597 (1963).

(17) R. C. Cookson and N. Waryar, *J. Chem. Soc.*, 2303 (1956).

(18) See previous paper for details of structure determinations of **1** and **3**.

conversion (to prevent secondary photolysis of **1**) was estimated to be *ca.* 1%. The production of CO_2 was demonstrated by passage of a stream of nitrogen through the photolysis solution. The exit stream carrying the CO_2 was then passed through a calcium hydroxide solution resulting in the precipitation of calcium carbonate.[19]

Acetone-Sensitized Irradiation of Lactone 12. A solution of 152.0 mg (0.71 mmol) of lactone **12** dissolved in 15 ml of acetone in a quartz tube was degassed for 20 min and irradiated with RPR 2537-Å lamps in a merry-go-round apparatus for 6.0 hr. The solvent was removed and the residue chromatographed on a 1.5 × 50 cm silica gel column (Davison, grade 950, 60–200 mesh) slurry packed in 5% ether–hexane (50-ml fractions): fractions 1–4, 5% ether–hexane, 16.6 mg (0.13 mmol, 18%) of naphthalene; fractions 5–13, 10% ether–hexane, nil; fractions 14–19, 10% ether–hexane, 8.8 mg (0.05 mmol, 7%) of benzobicyclo[2.2.2]octadienone; fractions 20–25, 50% ether–hexane, nil; fractions 26–31, 50% ether–hexane, 57.8 mg (0.34 mmol, 48%) of benzotricyclo[3.3.0.0^{2,8}]-octen-3-one; fractions 32–38, 10% ethyl acetate–benzene, 43.5 mg (0.21 mmol, 30%) of the starting lactone **12**.

C. Mechanistic Aspects. Quantum Yield Determinations. Quantum yield determinations were performed in the following general procedure. A solution of 0.71 mmol of the ketone or lactone in 15 ml of solvent in a quartz tube was degassed with purified nitrogen and placed in a merry-go-round apparatus. Irradiation was carried out either with the RPR 2537-, RPR 3000-, or RPR 3500-Å lamps, Southern New England Ultraviolet Co. (irradiations at 3000 and 3500 Å were done in Pyrex tubes). Light output was monitored by potassium ferrioxalate actinometry according to the method of Hatchard and Parker.[20]

Samples were removed and the contents determined by the following method: the solution was analyzed directly by vpc using an internal standard. A $^1/_8$ in. × 6 ft UCW 98 column in a HP 5750 thermal conductivity instrument was programmed at 100° (5 min), 15°/min to 250°, 250° (4 min). The carrier gas (He) flow rate was 30 cm^3/min. The results are compiled in Tables IV and V.

Sensitization and Quenching Experiments. Sensitizers and quenchers were purified before use. Samples of 0.71 mmol in 15 ml of solvent with sufficient sensitizer to capture >95% of the incident light were irradiated as described above. Quencher concentrations are given in Table V and were adjusted so that capture of incident light was <5%. In the case of cyclohexadiene, evidence of triplet quenching was confirmed by the detection of photodimers by vpc (conditions were the same as listed above) and comparison with an authentic sample. Analysis of the mixtures was accomplished by vpc.

Quantum Yield for CO_2 Evolution from Lactone 12. The quantum yield for carbon dioxide evolution from **12** was measured by passing the effluent gas from the photolysis vessel through a tared Ascarite–Anhydrone (magnesium perchlorate) trap. The value obtained was compared with the disappearance quantum yield as measured by quantitative vpc as above. The lactone (1.0047 g, 4.695 mmol) and cyclooctane vpc standard (0.5727 g, 5.113 mmol) were dissolved in 50 ml of dioxane, freshly distilled from LAH. The solution was placed in a 2 × 17 cm Pyrex vessel centered in the photochemical reactor and degassed 30 min with nitrogen (purified by passing through a drying tower filled with Ascarite–Drierite, 3:1). The effluent gas was passed through an ice–water cold trap and a Dry Ice–acetone trap. After degassing, the system was connected to a tared drying tube containing Ascarite and Anhydrone, and the sample was irradiated with the RPR 3000-Å lamps for 180 min with continuous nitrogen bubbling. After irradiation, the sample was degassed for another 15 min, the drying tube was disconnected and weighed, and the solution was analyzed by vpc as above. A blank CO_2 determination was run under identical conditions of time for degassing and irradiation and of rate of nitrogen flow. The light output was measured using ferrioxalate actinometry. The results are shown in Table V.

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(19) T. R. Hogness and W. C. Johnson, "Qualitative Analysis and Chemical Equilibrium," 4th ed, Holt, Rinehart and Winston, New York, N. Y., 1954, p 523.

(20) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).