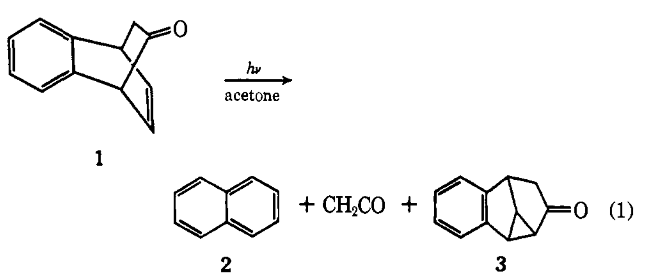
Mechanistic Studies in Organic Photochemistry. III.[1] The Photochemistry of Bicyclo[2.2.2]octenone and Benzobicyclo[2.2.2]octadienone

Richard S. Givens,* W. Frederick Oettle, Rick L. Coffin, and Robert G. Carlson[2]

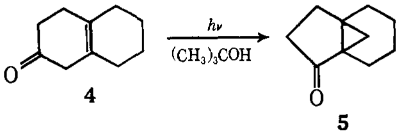
Contribution from the Department of Chemistry, the University of Kansas, Lawrence, Kansas 66044. *Received November 6, 1970*

Abstract: The photochemical rearrangements of benzobicyclo[2.2.2]octadienone (**1**) and bicyclo[2.2.2]octenone (**6**) have been investigated in detail. The product of the direct irradiation of **6** was bicyclo[4.2.0]oct-2-en-8-one (**7**), resulting from a 1,3-acyl shift. Similarly, **1** gave 4,5-benzobicyclo[4.2.0]octa-2,4-dien-8-one (**9**) as the minor product and naphthalene (**2**) as the major product of the direct irradiation. In contrast, the acetone-sensitized rearrangements of **6** and **1** gave tricyclo[3.3.0.0^{2,8}]octan-3-one (**8**) and benzotricyclo[3.3.0.0^{2,8}]octen-3-one (**3**), respectively, as major products. Evidence is presented which indicates a concerted rearrangement is occurring in the singlet reaction. The details of the product identifications are also given.

Previously, we reported the acetone-sensitized photorearrangement of benzobicyclo[2.2.2]octadienone (**1**) to naphthalene (**2**), ketene, and benzotricyclo[3.3.0.0^{2,8}]octen-3-one[1] (**3**) as shown in eq 1. Other reports on the photoisomerization of this[3] and a related[4] ketone indicate that this reaction might be general for bicyclic β,γ-unsaturated ketones. However, direct irradiation of **1** was reported to give only naphthalene (**2**) and ketene.[3]



Several investigators have reported the photoisomerization of β,γ-unsaturated ketones to cyclopropyl ketones *via* photosensitization with triplet sensitizers.[1,3–12] In contrast, Williams and Ziffer[13–15] and Tenney, *et al.*,[16] report that this type of photoisomerization occurs upon direct irradiation. For example, Williams and Ziffer found that 3,4,5,6,7,8-hexahydronaphthalen-2-(1*H*)-one (**4**) rearranges to tricyclo[4.3.1.0^{1,6}]decan-7-one (**5**) in *tert*-butyl alcohol upon direct irradiation[13] (eq 2). No systematic study of these interesting rearrangements has been reported.



(2)

In view of the wide interest in the photochemistry of β,γ-unsaturated ketones,[1,3–22] we have studied in detail the model systems bicyclo[2.2.2]octenone (**6**) and benzobicyclo[2.2.2]octadienone (**1**) to determine the generality and mechanistic details of this rearrangement. Bicyclo[2.2.2]octenone (**6**) and benzobicyclo[2.2.2]octadienone (**1**) were chosen because (1) they are rigid β,γ-unsaturated ketones, (2) they can be readily prepared in quantity, and (3) they represent two potentially interesting variations of the β,γ-unsaturated ketone chromophore. Examination of Dreiding models indicates that bicyclo[2.2.2]octenone is rigid and that interaction of the π orbitals of the double bond and the carbonyl should be extensive. This is supported by the ultraviolet spectra of both ketones. For example, the n-π* transition of **1** has ϵ values of 210 (320 mμ), 372 (306), 354 (296), and 265 (288), as compared with 30–50 for most saturated ketones. This is commonly observed in β,γ-unsaturated ketones[23] and electric dipole coupling of the excited states has been suggested by Moscowitz.[24] Finally, the introduction of the benzo substituent provides potentially alternate pathways for the rearrangements[25a] not available to **6** (see Chart I).

---

(1) For part II, see R. S. Givens and W. F. Oettle, *Chem. Commun.*, 1164 (1969).

(2) Alfred P. Sloan Foundation Fellow, 1970–1972.

(3) J. Ipaktschi, *Tetrahedron Lett.*, 215 (1969).

(4) (a) R. K. Murray, Jr., and H. Hart, *ibid.*, 4995 (1968); (b) H. Hart and R. K. Murray, Jr., *ibid.*, 379 (1969).

(5) J. Griffiths and H. Hart, *J. Amer. Chem. Soc.*, **90**, 5296 (1968).

(6) K. Kojima, K. Saki, and K. Tanabe, *Tetrahedron Lett.*, 1925 (1969).

(7) J. Ipaktschi, *ibid.*, 2153 (1969).

(8) E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969).

(9) S. Domb, G. Bozzato, J. A. Saboz, and K. Schaffner, *Helv. Chim. Acta*, **52**, 2436 (1969).

(10) H. Hart, R. K. Murray, Jr., and G. D. Appleyard, *Tetrahedron Lett.*, 4785 (1969).

(11) P. S. Engel and H. Ziffer, *ibid.*, 5181 (1969).

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

(13) J. R. Williams and H. Ziffer, *Chem. Commun.*, 194 (1967).

(14) J. R. Williams and H. Ziffer, *ibid.*, 469 (1967).

(15) J. R. Williams and H. Ziffer, *Tetrahedron*, **24**, 6725 (1968).

(16) L. P. Tenney, D. W. Boykin, Jr., and R. E. Lutz, *J. Amer. Chem. Soc.*, **88**, 1835 (1966).

(17) L. A. Paquette, R. F. Eizember, and O. Cox, *ibid.*, **90**, 5153 (1968).

(18) L. A. Paquette and G. V. Meehan, *J. Org. Chem.*, **34**, 450 (1969).

(19) F. A. L. Anet and D. P. Mullis, *Tetrahedron Lett.*, 737 (1969).

(20) R. G. Carlson and D. E. Henton, *Chem. Commun.*, 674 (1969).

(21) W. Kothe, *ibid.*, 5201 (1969).

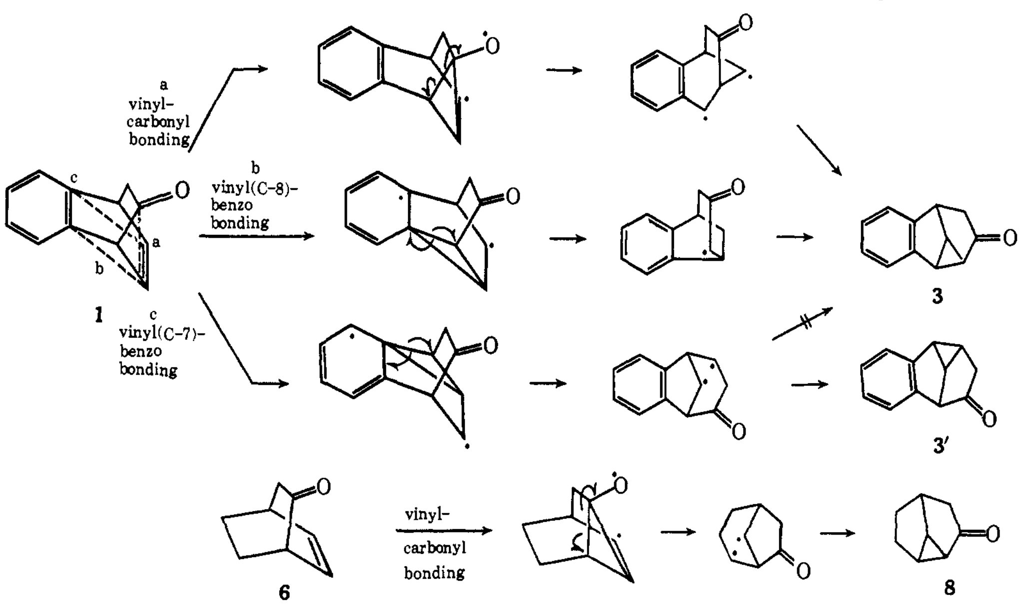
(22) See also R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Aschaffenburg, Germany, 1970, p 96 ff, for orbital symmetry considerations of the photorearrangements of β,γ-unsaturated ketones.

(23) R. C. Cookson and N. S. Warujcer, *J. Chem. Soc.*, 2302 (1956).

(24) A. Moscowitz, *Proc. Roy. Soc., Ser. A*, **297**, 40 (1967).

(25) (a) Such alternatives were suggested and sought in the bicyclo[2.2.2]octatriene (barrelene) to semibullvalene photorearrangement: H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 6096 (1968); (b) R. S. Givens and W. F. Oettle, *ibid.*, **93**, 3963 (1971).

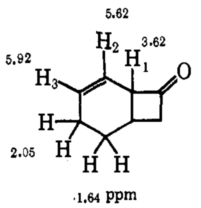
Chart I. Some Possible Di-π-methane Pathways Available to Bicyclo[2.2.2]octenone (6) and Benzobicyclo[2.2.2]octadienone (1)



Structural details and sensitization results are presented below, while the mechanistic details are presented in the following article.[25b]

Results

Direct Irradiation of 6. Bicyclo[2.2.2]octenone[26] (6) upon irradiation in ether employing 3000 Å light yielded a single, isomeric product. Isolation of this product by column chromatography gave a clear oil which showed infrared absorption at 5.62 μ, indicative of a cyclobutanone. The 100-MHz spectrum showed two one-proton multiplets at δ 5.62 and 5.92 indicating the presence of vinyl hydrogens. A 1 H multiplet at δ 3.62 was assigned to a methine hydrogen flanked by a carbonyl and a double bond. Broad 2 H singlets at δ 2.05 and 1.64 indicated methylene groups on a cyclohexene ring, the low-field absorption due to an allylic methylene.[27] Based on the spectral data, bicyclo[4.2.0]oct-2-en-8-one (7) was assigned as the structure of the photoproduct as indicated below. Confirmatory evidence for the assignments of H_1, H_2, and H_3 was provided by nmr double irradiation experiments. Irradiating at δ 3.62 led to partial collapse of both the δ 5.62 and 5.92 multiplets. Rearrangements of this type have also been observed for norbornenone by Schuster[28] and for several monocyclic, β,γ-unsaturated ketones.[29]

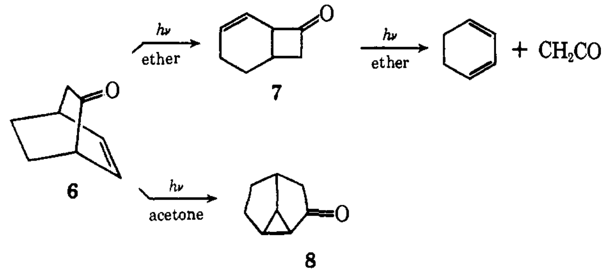


7

In a separate experiment the photoproduct, bicyclo[4.2.0]oct-2-en-8-one (7), was irradiated in ether in a NaCl cavity cell. Disappearance of the 5.62-μ band was noted along with the appearance of a band at 4.68 μ (ketene). No new bands appeared in the 5.8–5.9-μ range. Thus, the photochemical isomerization was shown not to be reversible.

Sensitized Irradiation of 6. To determine the influence of triplet sensitizers on the reaction, bicyclo[2.2.2]octenone (6) was irradiated in acetone using 2537 Å light. Again only a single, isomeric product could be detected, but the chromatographic behavior on both tlc and vpc was different from that of 7. The 100-MHz nmr spectrum showed no vinyl protons and a very complex multiplet from δ 1.4 to 3.1. The infrared spectrum showed a carbonyl at 5.80 μ indicating a cyclohexanone or cyclopentanone conjugated with a cyclopropane ring.[30a] These data suggested that the product was tricyclo[3.3.0.0^{2,8}]octan-3-one[30a] (8), and spectral comparison with an authentic sample[30b] firmly established this structure. The direct and acetone-sensitized photorearrangements for bicyclo[2.2.2]-octenone are summarized in Chart II.

Chart II. Sensitized and Direct Irradiations of Bicyclo[2.2.2]octenone (6)



---

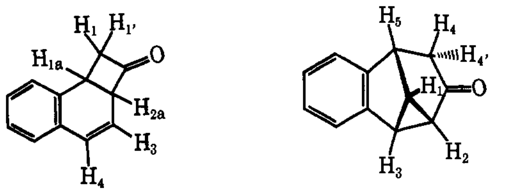
(26) W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, **19**, 381 (1954).

(27) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," 2nd ed, International Series of Monographs in Organic Chemistry, Vol. 5, Pergamon Press, Oxford, 1969, p 188.

(28) D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Lett.*, 1911 (1963).

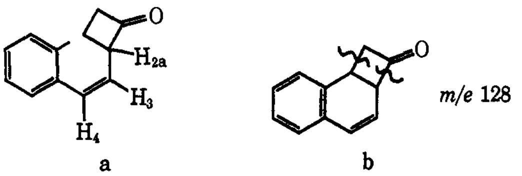
(29) For example, R. G. Carlson and J. Bateman, *ibid.*, 4151 (1967); L. A. Paquette and R. F. Eizember, *J. Amer. Chem. Soc.*, **89**, 6205 (1967); J. K. Crandall, J. P. Arrington, and J. Hen, *ibid.*, **89**, 6208 (1967).

(30) (a) S. A. Monti, D. J. Burcheck, and J. C. Shepard, *J. Org. Chem.*, **34**, 3080 (1969). (b) We thank Professor Monti for a sample of ketone 3 for comparison.



9 **3**

Figure 1. Structures and proton assignments for the photoproducts of the direct (*i.e.*, **9**) and acetone-sensitized (*i.e.*, **3**) rearrangements of **1**.



a b

Figure 2. Partial structure and fragmentation pattern of photoproduct **9**.

Direct Irradiation of 1. An ether solution of **1** was irradiated with a 450-W medium-pressure Hanovia lamp fitted with a Pyrex filter. At 50% disappearance of **1**, as monitored by vpc, two products were detected. The major product (>80% of the product mixture) was naphthalene, as identified by its physical properties and by spectral comparison with an authentic sample.

The minor component (*ca.* 10% yield, depending on the conditions) was obtained as a clear oil after molecular distillation. It was isomeric with **1** (mass peak 170 *m/e*) and its infrared spectrum displayed a strong absorption at 5.61 μ, indicating a cyclobutanone. By analogy with the direct photoisomerization of **6**, the structure of the photoproduct should be 2(1*H*)-oxo-1a,-2a-dihydrocyclobuta[*a*]naphthalene (4,5-benzobicyclo-[4.2.0]octa-2,4-dien-8-one (**9**)).

The structure **9** was firmly established by analysis of the nmr and mass spectra of the photoproduct. Thus the 100-MHz nmr spectrum showed, in addition to the four aromatic protons at δ 6.9–7.1, absorptions at δ 6.43, 5.67, and 4.08–4.35 (broad multiplet) for single protons and a broad, three-proton multiplet from δ 3.13 to 3.85. Table I and Figure 1 give the nmr data and proton assignments for the photoproduct **9**. As in cyclobutanone **7**, obtained from the direct irradiation of **6**, the chemical shift of the 1 H multiplet at δ 4.08–4.35 is indicative of a bridgehead methine flanked by a double bond and a carbonyl. Double irradiation experiments (see Experimental Section) showed that H_{2a} was coupled to H_3 (J = 4.5 Hz) and H_4 (J = 2.0 Hz). This leads to a partial structure shown in Figure 2a. Finally, the position of attachment to the cyclobutanone ring is indicated by the mass spectrum fragmentation pattern. The molecular peak at *m/e* 170 is very small (~0.1%) whereas the base peak is at *m/e* 128 due to the loss of ketene. The remainder of the fragmentation pattern was very similar to that of naphthalene. This confirms structure b (Figure 2), 4,5-benzobicyclo[4.2.0]octa-2,4-dien-8-one, as the photoproduct **9**.

Table I. 100-MHz Nmr Data for Photoproducts of the Direct (**9**) and Acetone-Sensitized (**3**) Rearrangements of **1**

Signal position δ, ppm	Signal description[a] (coupling constants, Hz)	Rel area
	9	
6.9–7.1	Complex m (arom H's)	4
6.43	ABX q (J = 9.5, 2.0) (vinyl H, H_4)	1
5.67	ABX q (J = 9.5, 4.5) (vinyl H, H_3)	1
4.08–4.35	Complex m (bridgehead H, H_{2a})	1
3.13–3.85	Complex m (cyclobutyl protons, H_1, $H_{1'}$, and H_{1a})	3
	3	
6.80–7.28	m (arom H's)	4
3.74	ABX q (J = 8.0, 5.2) (benzyl methine, H_5)	1
3.16	ABCD q (J = 5.2, 5.2, 5.2) (cyclopropyl methine, H_1)	1
2.78	ABX q (J = 16, 8.0) (methylene H, H_4)	1
2.74	ABX q (J = 5.2, 9.0) (benzylic cyclopropyl H, H_8)	1
2.18	ABX q (J = 5.2, 9.0) (cyclopropyl H adj to a carbonyl, H_2)	1
1.88	d (J = 16) (methylene H, $H_{4'}$)	1

[a] See Figure 1 for proton assignments.

In a separate experiment the appearance of ketene, trapped by ethanol to yield ethyl acetate, was followed by nmr as shown in Figure 3. The disappearance of **9** with extended irradiation was also noted in this experiment and may explain the absence of **9** in an earlier report of this reaction.[3] Continued irradiation led to the complete disappearance of **9** and gave only naphthalene as the photoproduct.

Sensitized Irradiation of 1. An acetone solution of **1** was irradiated with a Hanovia 450-W medium-pressure lamp for 12 hr. Tlc analysis indicated the presence of naphthalene and one other product, which was characterized by nmr and infrared spectroscopy. The 100-MHz nmr spectrum (Table I) showed, in addition to the four aromatic protons, a well-resolved proton spectrum for an additional six protons. Assignments were based on an analysis of the coupling constants and double irradiation experiments (see Experimental Section). The mass spectrum showed a molecular ion at *m/e* 170 and the infrared, a strong carbonyl absorption at 5.78 μ. By analogy with the sensitized photolysis of **6**, the structure of the photoproduct was assigned as benzotricyclo[3.3.0.0^{2,8}]octen-3-one (**3**). In order to confirm this structure, the photoproduct was degraded to the known hydrocarbon 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene[31] (**11**) as outlined in Chart III.

Ketone **3** was hydrogenated with 10% Pd/C in isopropyl alcohol to the dihydro photoketone **10**, mp 33–34°. The basic ring system was then established by a Wolff–Kishner reduction of **10** to the known hydrocarbon **11**.[31] In order to determine the carbonyl position, an exchange experiment in methanol-*O-d* was run. Of the three possible structures, for the dihydro photoproduct (**10**, **12**, and **13**), only **10** can deuterium exchange four protons under the mild base conditions employed. The fourth possibility, **14**, was ruled out from the ir of the dihydro photoketone (C=O, 5.73 μ).

---

[31] We thank Professor H. E. Zimmerman for copies of the nmr and ir spectra of 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene (11).

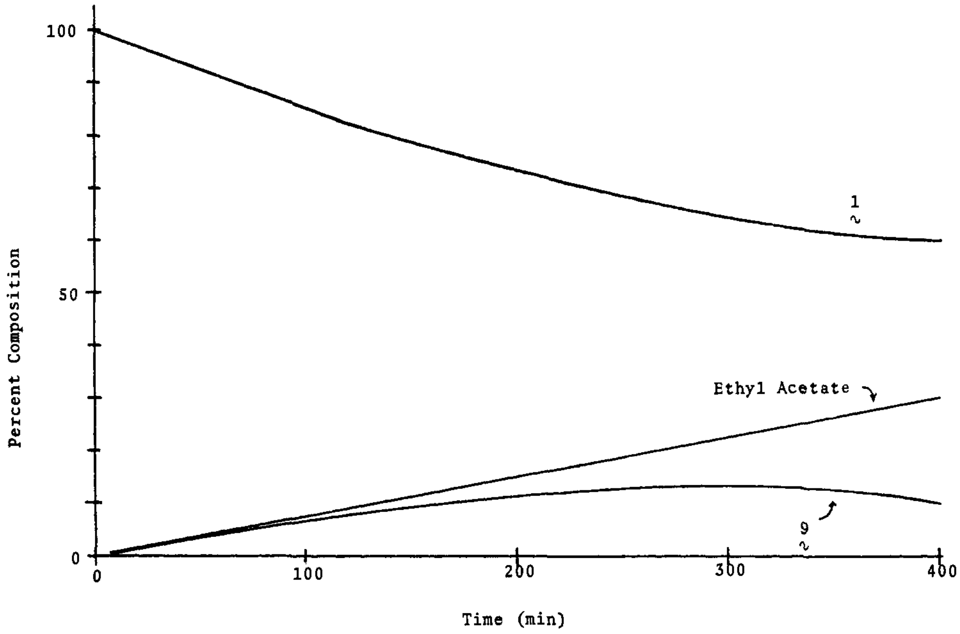
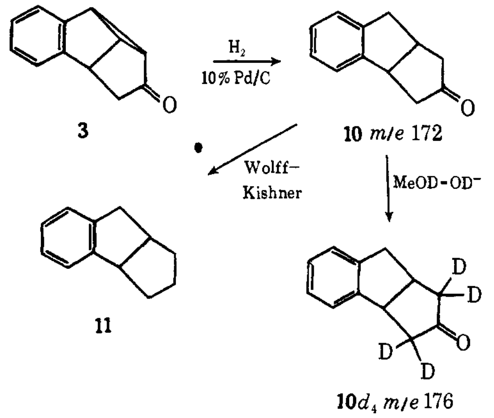
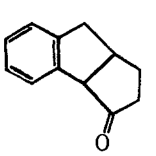


Figure 3. Per cent composition *vs.* irradiation time of the benzene solution photolysis of benzobicyclo[2.2.2.]octadienone (**1**). The percentages were determined by nmr integration (see Experimental Section).

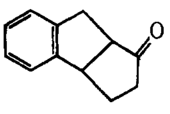
Chart III. Degradative Scheme for Benzotricyclo[3.3.0.0^{2,8}]octen-3-one (**3**)



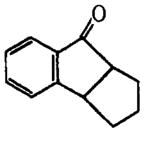
The dihydro photoketone exchanged four deuterium atoms/molecule in base as determined by nmr and mass spectral analysis, thus establishing the structure as **10**.



12, known[32]



13, unknown



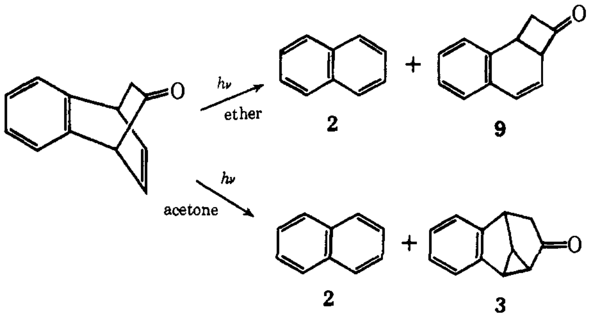
14, known[25b]

In turn, then, this firmly establishes the structure of the photoproduct as benzotricyclo[3.3.0.0^{2,8}]octen-3-one (**3**). The photochemical rearrangements for the direct and acetone-sensitized reactions are outlined in Chart IV.

Discussion

Clearly, the direct and acetone-sensitized irradiations of bicyclo[2.2.2]octenone (**6**) are in sharp contrast.

Chart IV. Photoproducts from the Sensitized and Direct Photolyses of **1**



Attempts to detect **8** in the product mixtures from direct irradiations were unsuccessful at all conversions. Since **8** is formed from **6** *via* triplet sensitization, the inability to detect **8** in direct irradiations indicates that intersystem crossing must be unimportant in **6**. A similar result is found for benzobicyclo[2.2.2]octadienone (**1**); *i.e.*, the benzo substituent does not alter the intersystem crossing efficiency. This inability of a benzene ring to influence intersystem crossing efficiency has been noted in at least two previous studies by Zimmerman, *et al.*,[25b] and by Edman.[33]

Two additional products, naphthalene and ketene, were found in the direct irradiations of benzobicyclo[2.2.2]octadienone (**1**). In fact, naphthalene was the major product of the direct irradiation. Thus, although the benzo substituent does not effect the intersystem crossing efficiency, it greatly alters the fate of the singlet excited state. Hart and Murray[4] found that tetramethylnaphthalene was the sole product of direct irradiation of the hexamethyl derivative of **1** even at −100°. We find[34] that 3,4-benzobicyclo[4.2.0]octa-

---

(32) S. Julia, C. Huynh, and J. Olivie, *Bull. Soc. Chim. Fr.*, 147 (1966).

(33) J. R. Edman, *J. Amer. Chem. Soc.*, **91**, 7103 (1969).

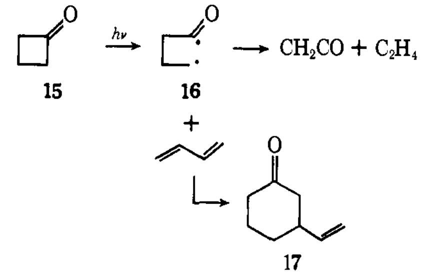
(34) We thank Dr. O. L. Chapman and Dr. J. D. Lassila, Iowa State University, for preliminary low-temperature studies. A full report on our continuing work at reduced temperatures will appear at a later time.

2,4-dien-8-one (**9**) is an important product at both -170 and 20°. The corresponding fragmentation was not observed from the singlet state of **6**. Upon extended irradiation, ketene was observed but its appearance was shown to originate from the photofragmentation of **7**.[35]

Since several β,γ-unsaturated ketones have been shown to undergo a reversible 1,3-acyl shift,[8,29] bicyclo[4.2.0]oct-2-en-8-one (**7**) was irradiated in an attempt to observe the reverse of the **6** → **7** conversion. However, irradiation of **7** gave only ketene (and cyclohexadiene). Analysis of the ir spectrum showed that no bicyclo[2.2.2]octenone was formed, indicating that the reaction is not reversible.

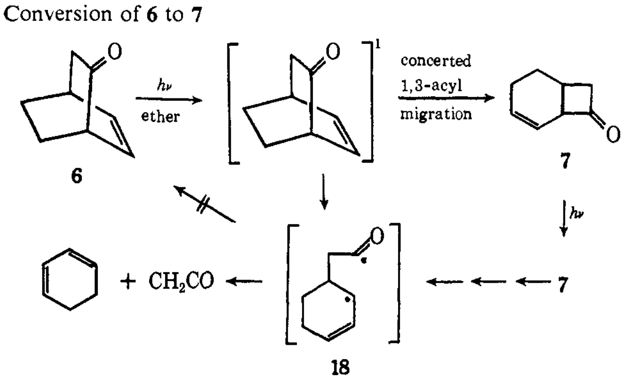
A more fundamental question is the nature of the intermediate or transition state in the **6** → **7** rearrangement. Indirect information (the photorearrangement of **7** to ketene and cyclohexadiene) bears on this question. Recently, Dowd and coworkers[36] have shown that cyclobutanone (**15**) undergoes a type I fragmentation to a 1,4-diradical **16** en route to ketene and ethylene (Chart V). This diradical was trapped with butadiene to yield 3-vinylcyclohexanone (**17**) to the exclusion of ketene formation.

Chart V. Trapping of the 1,4-Diradical in the Photolysis of Cyclobutanone



It is reasonable, then, to postulate the same type I cleavage to diradical **18** for the photolysis of bicyclo[4.2.0]oct-2-en-8-one to ketene and cyclohexadiene. Because ketene and cyclohexadiene are not primary photoproducts of **6**, this same diradical, **18**, cannot be involved in the 1,3-acyl shift of **6** to **7** (see Chart VI).

Chart VI. Possible Routes for the Direct Irradiation Conversion of 6 to 7



This suggests, then, that the 1,3-acyl migration occurs by a concerted, symmetry-allowed process.[22] Furthermore, other 1,3-acyl shifts (for a few examples, the photorearrangements of 1-phenyl-3,3,5-trimethylhex-1-en-4-one to 4-phenyl-2,6-dimethylhept-2-en-5-one,[12] 2,2-dimethyl-3-cycloheptenone to 2-isobutenylcyclopentanone,[17] 1-methoxy-8-phenylbicyclo[4.2.0]octa-3,7-diene-2,5-dione to 8-methoxy-7-phenylbicyclo[4.2.0]octa-3,7-diene-2,5-dione,[19] and 2-ethynylcycloheptanone to 2,3-cyclononadienone[20]) may also occur *via* a concerted 1,3-acyl shift. Work is in progress to test this hypothesis.

Finally, the triplet rearrangements of **1** and **6** are of interest. In both cases, the cyclopropyl ketones are the major products. However, naphthalene and ketene are also important products of the triplet of **1**. Again, the benzo substituent does alter the rearrangement pathway though its effect is less significant than in the direct irradiation.

Benzotricyclo[3.3.0.$0^{2,8}$]octen-3-one (**3**) may have resulted from a di-π-methane rearrangement *via* path a or path b but not *via* path c (Chart I). Although in a related system path a was established,[4b] further study is required to differentiate between these paths and to assess the influence of the benzo substituent on the possible di-π-methane rearrangements for benzobicyclo[2.2.2]octadienone.

Experimental Section[37]

A. Synthesis and Photorearrangement of Bicyclo[2.2.2]octenone. Synthesis of Bicyclo[2.2.2]octenone (6). The method of Wildman and Saunders[26] was employed without modification.

Direct Irradiation of Ketone 6. A solution of 313.6 mg (2.56 mmol) of **6** in 15 ml of anhydrous ether was degassed for 15 min with purified nitrogen. The sample was irradiated in a Pyrex vessel placed in a merry-go-round apparatus using RPR 3000-Å lamps (Southern New England Ultraviolet Co.) for 123 min. Aliquots were removed at 17, 62, 93, and 123 min and analyzed by infrared for the appearance of the band at 5.62 μ (cyclobutanone carbonyl). The solvent was then evaporated to yield 250.4 mg of a pale yellow liquid. Column chromatography (1.5 × 60 cm) using deactivated silica gel (Davison, grade 950, 60–200 mesh) gave the following (75-ml fractions): fractions 1–4, hexane, 1.5-mg residue; fractions 5–12, 5% ether–hexane, 9.2-mg residue; fractions 13–15, 10% ether–hexane, 39.2 mg (0.32 mmol) of cyclobutanone **7** as a clear oil; fractions 16–25, 10% ether–hexane, 100 mg (0.82 mmol) of bicyclo[2.2.2]octenone (**6**) as a waxy solid.

Characterization of Bicyclo[4.2.0]oct-2-en-8-one (7). The clear oil from fractions 13–15 was characterized by nmr and ir spectra. HA-100 nmr (CCl_4) showed complex multiplets at δ 1.64 (2 H), 2.05 (2 H), 2.47–3.20 (3 H), 3.62 (1 H), 5.62 (1 H), and 5.92 (1 H). Irradiation of the δ 3.62 multiplet led to a partial collapse of the 5.62 and 5.92 multiplets, indicating that the δ 3.62 proton is flanked by both a double bond and a carbonyl. The ir spectrum (CCl_4) showed absorptions at 3.29 (m), 3.35, 3.40, 3.50, 5.62 (s, cyclobutanone carbonyl), 6.10 (w), 6.95, 7.19, 7.25, 7.40, 8.95 9.50, and 14.5 μ (s). The mass spectrum (100°, 70 eV) showed a mass peak at *m/e* 122 with prominent peaks at 80 (loss of ketene), 79, 78, 77, 39, 32, 31, and 29.

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.68; H, 8.40.

Direct Irradiation of Bicyclo[4.2.0]oct-2-en-8-one (7). A solution of $\sim$5 mg of **7** in 0.1 ml of anhydrous ether was placed in a NaCl cavity cell and irradiated with unfiltered light from a 200-W Osram lamp for 2.5 min. A new peak appeared at 4.68 μ, attributed to ketene. No new band appeared at 5.85 μ (the C=O of **6**).

Acetone-Sensitized Irradiation of Bicyclo[4.2.0]oct-2-en-8-one (7). A solution of 10.7 mg (0.09 mmol) of **7** in 6 ml of reagent acetone was degassed for 10 min and irradiated in a quartz tube with RPR 2537-Å lamps in the merry-go-round apparatus for 149 min. Analysis of the sample by vpc (6 ft UCW 98, 100°) and infrared indicated a loss of **7** but only polymer was recovered.

---

(35) Preliminary studies on **9** indicate that it also fragments to ketene (and naphthalene) on direct irradiation and does not form **1**.

(36) P. Dowd, A. Gold, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5724 (1970).

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

Acetone-Sensitized Irradiation of Bicyclo[2.2.2]octenone (6). A solution of 410 mg (3.36 mmol) of **6** in 30.0 ml of reagent acetone was placed in three quartz tubes, degassed for 15 min, and irradiated with RPR 2537-Å lamps in the merry-go-round apparatus. After 4 hr, one tube analyzed by vpc (6 ft UCW 98 at 100°) and nmr showed the reaction was 70% completed. The remaining two tubes were photolyzed for an additional 3 hr. The solvent was evaporated and the crude oil (240 mg) was distilled with a microstill to yield 92.2 mg of a clear, colorless oil. The ir and nmr were identical with those of an authentic sample of tricyclo-[3.3.0.0^{2,8}]octan-3-one[30] (**8**).

B. Synthesis and Photochemistry of Benzobicyclo[2.2.2]octadienone. Synthesis of Benzobicyclo[2.2.2]octadienone (1). This was synthesized according to the method of Kitahonoki and Takano[38] as modified by Zimmerman.[25]

Direct Irradiation of Benzobicyclo[2.2.2]octadienone (1). A solution of 2.058 g (11.8 mmol) of ketone **1** in 230 ml of anhydrous ether, degassed for 20 min, was irradiated for 2 hr with a Hanovia 450-W medium-pressure lamp fitted with a Pyrex filter. The solvent was removed, yielding 1.7950 g of a pale yellow solid residue. Nmr and ir analysis indicated >65% conversion. The residue was chromatographed on deactivated Davison silica gel (grade 950, 60–200 mesh) slurry packed with 5% ether–hexane; 150-ml fractions: fractions 1–2, hexane, nil; fractions 3–6, hexane, 1.2700 g (9.9 mmol, 84%) of naphthalene; fractions 7–11, 1% ether–hexane, nil; fractions 12–30, 2% ether–hexane, nil; fractions 31–40, 2% ether–hexane, 88.0 mg (0.52 mmol, 4%) of an oil (*vide infra*); fractions 41–47, 2% ether–hexane, nil; fractions 48–51, 10% ether–hexane, 205.2 mg (1.2 mmol, 10%) of the starting ketone **1**.

The oil obtained from fractions 31–40 was distilled with a short-path still to yield a colorless oil. The infrared spectrum (CCl_4) showed bands at 3.30, 3.42, 5.61, 6.13, several bands between 6.7 and 9.0, 9.18, 9.60, 9.83, 10.41 (w), 10.65 (w), 11.65, 14.10, and 14.40 μ (sh); the 100-MHz nmr data are listed in Table I. Double resonance was performed; only those bands which were affected are included. Irradiation of H_{2a} at 414 Hz resulted in collapse of the H_3 ABX quartet and the upfield half of the H_4 ABX quartet; irradiation of the H_{2a} multiplet at 417 Hz resulted in the collapse of the H_3 ABX quartet and the downfield half of the H_4 ABX quartet; irradiation of H_4 resulted in the collapse of H_3 and irradiation of H_3 resulted in the collapse of H_4. Mass spectrum showed a molecular ion at *m/e* 170 and prominent peaks at 129, 128 (base peak), 127, 126, 102, 101, 78, 77, 76, 75, 74, 64, 63, 51, 50, and 42; uv (cyclohexane) λ_{max} 273 (8300), 265 (8100), 227 (19,800), and 221 (22,000). These data are consistent only with 2(1*H*)-oxo-1a,2a-dihydrocyclobuta[*a*]naphthalene (**9**).

Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.55; H, 6.19.

Trapping of Ketene. In a separate experiment, ketene was trapped with ethanol to yield ethyl acetate. A solution of 300.9 mg (1.76 mmol) of **1** in 1.0697 g of benzene and 24 mg of absolute ethanol was placed in an nmr tube and photolyzed with a Hanovia 450-W lamp fitted with a Pyrex filter sleeve. The nmr tube was removed and analyzed at 63, 109, 172, 252, 324, and 386 min. Integration of the signals for the bridgehead proton (H_1) on **4** at δ 4.37, the methylene of ethyl acetate at δ 4.03, and a methine of **9** at δ 3.03 gave the relative percentages of each present. A plot of the results is given in Figure 3.

Sensitized Irradiation of Benzocyclo[2.2.2]octadienone (1). A solution of 1.9283 g (11.3 mmol) of ketone **1** dissolved in 520 ml of reagent acetone and degassed for 1 hr was irradiated with an unfiltered Hanovia 450-W lamp. Aliquots were taken at 60, 121, 323, 423, 667, and 723 min. Tlc analysis showed the appearance of two new spots. The acetone solution was evaporated to yield 1.8241 g of a yellow-orange oil. The residue was chromatographed (3 × 75 cm column) on Davison silica gel (grade 950, 60–200 mesh) slurry packed with 5% ether–hexane (250-ml fractions were taken): fraction 1, 5% ether–hexane, 7.9 mg, residue; fractions 2–4, 5% ether–hexane, 406.1 mg (3.2 mmol, 28%) of a white waxy solid (mp 79–80°); fractions 5–7, 10% ether–hexane, nil; fractions 8–15, 10% ether–hexane, 684.4 mg (4.0 mmol, 35%) of a white solid (mp 51–53°); fractions 16–17, 50% ether–hexane, nil; fractions 18–23, 50% ether–hexane, 534.5 mg (3.14 mmol, 27%) of an oil. Fractions 2–4 were shown to be naphthalene by spectral comparison and by melting point and mixture melting point. Fractions 8–15 were shown to be starting ketone **1** by spectral comparison. The oil obtained from fractions 18–23 was crystallized from hexane (mp 63.5–64°) and characterized as **3** (*vide infra*).

Characterization of Benzotricyclo[3.3.0.0^{2,8}]octen-3-one (3). The infrared spectrum (CCl_4) showed bands at 3.25, 3.28, 3.30, 3.35, 3.45, 5.78, (s), 6.78, 6.85, 7.13, 7.83, 8.62, 9.42, 10.55 μ; uv$_{max}$ (cyclohexane) 322 (ϵ 14), 314 (30), 300 (39), 279 (935), 273 (870), 263 mμ (625); mass spectrum (70 eV) molecular ion *m/e* 170. The 100-MHz data are given in Table I. Double resonance was performed; only those bands which were affected are included. Irradiation of H_5 collapsed H_1 and H_4; H_1 irradiated, H_5, H_2, and H_8 collapsed; H_2 irradiated, H_1 and H_8 collapsed; $H_{4'}$ irradiated, H_4 collapsed. All irradiations were done at 200 mV.

Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.39; H, 5.81.

Degradation of Benzotricyclo[3.3.0.0^{2,8}]octen-3-one (3). Hydrogenation of 508 mg (2.98 mmol) of **6** over 508 mg of 10% Pd/C in isopropyl alcohol at 60 psi of hydrogen for 2 hr, filtration, and evaporation of the solvent yielded a light yellow oil. Nmr, ir, and tlc analysis indicated a single product with the carbonyl still intact. Molecular distillation at 120° (44 mm) gave 354 mg (2.06 mmol, 69%) of a clear liquid which crystallized on standing (mp 33–34°). The infrared spectrum (CCl_4) showed bands at 3.22, 3.25 (sh), 3.28, 3.36 (s), 3.41, 3.47, 5.73 (cyclopentanone, C=O), a series of bands from 6.7 to 8.0, 8.7 (s), 8.92, 9.70, 10.55, 13.90 μ; nmr ($CDCl_3$) δ 7.15 singlet (4 H, aromatic), 4.0–3.6 multiplet (1 H), and 3.4–1.5 multiplet (7 H); mass spectrum (70 eV) showed a molecular ion at *m/e* 172 with the base peak at *m/e* 129.

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.61; H, 6.78.

The 2,4-dinitrophenylhydrazone derivative was prepared[39] (mp 141.5–143°).

Deuterium Exchange of the Hydrogenation Product (10). A solution of 41.1 mg (0.24 mmol) of the hydrogenation product **10** in sodium methoxide–methanol-*O-d* prepared from 31.1 mg (1.4 mg-atoms) of sodium metal in 10 ml of methanol-*O-d* was stirred for 12 hr, quenched with D_2O containing two drops of HCl, and extracted with ether to yield 26 mg of a yellow oil. Chromatography on an 0.8 × 16 cm silica gel column (Davison, grade 950, 60–200 mesh) with 10% ether–hexane gave 11.3 mg (25%) of a clear oil. The nmr spectrum (CCl_4) showed bands at δ 7.11 (s, 4 H, aromatic) and 3.95–2.62 (m, 4 H, alkyl) indicating that four alkyl hydrogens were exchanged. Mass spectral determination confirmed that four hydrogens had been exchanged: (70 eV) molecular ion shifted to *m/e* 176 (calcd: d_0, 0%; d_1, 0%; d_2, 0%; d_3, 11%; d_4, 89%).

A second deuterium exchange was performed using NaOD in a methanol-*O-d*–D_2O mixture and gave identical exchanged ketone. These results rule out 1,2,8,8a-tetrahydrocyclopent[*a*]-inden-3(3a*H*)-one as the hydrogenation product **10**.

Wolff–Kishner Reduction of Hydrogenation Product 10. A solution of 147 mg (0.86 mmol) of ketone **10**, 2.5 ml of hydrazine hydrate, and 2.5 g of KOH in 14 ml of triethylene glycol was refluxed for 48 hr, the reaction mixture was added to 125 ml of 20% HCl and extracted with 100 ml of ether (four times), and the ether extract was washed with water, dried, and evaporated to yield 95 mg of crude product. Column chromatography (1 × 52 cm column) eluting with hexane (50-ml fractions) gave 45 mg (33%) of a pale yellow oil in fractions 7–11. Molecular distillation (46°(0.3 mm)) gave 33.8 mg of a clear liquid. The nmr and ir spectra of this material were identical with those of 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene (**11**) supplied by Professor H. E. Zimmerman.[31]

Direct Irradiation of Benzotricyclo[3.3.0.0^{2,8}]octen-3-one (3). A solution of 114.7 mg (0.67 mmol) of ketone **3** in 15 ml of benzene in a Pyrex tube was degassed for 1 hr and irradiated for 11.7 hr with a 450-W Hanovia lamp fitted with a Pyrex filter. Evaporation of the solvent yielded 117.4 mg of an oil. Nmr and infrared analysis indicated no new products (*i.e.*, only the starting ketone was present).

Acknowledgment. Support of this research by National Institutes of Health Grant No. GM 16611-02, the Research Corporation, and the Petroleum Research Fund, administered by the American Chemical Society (1070-G1), is gratefully acknowledged.

---

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

(39) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1962, p 219.