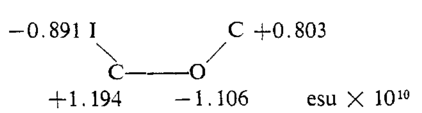
discrepancy between the theoretical and the experimental values. Assigning a dielectric constant to the bonds will reduce the attraction between nearest neighbor bonded atoms, while the repulsion of alternate nonbonded atoms will remain unchanged. Using the C–I and C–O bond-refractive indices of Creswell, *et al.*,[9] the overall electrostatic interaction is reduced to 2 kcal/mol repulsion. We can eliminate the discrepancy between our calculated attraction and the experimental value by assigning a bond refractive index of n = 1.15 to the O–CI bond, compared to 1.51 measured for dimethyl ether. Our calculations assume a dielectric constant of 1 for the repulsions of like charges on alternate atoms. With a larger ϵ than 1, we can assign a value for n of the O–CI bond more like that of the parent ether, and obtain good agreement with the experimental value.

As an alternative to increasing the dielectric constant between the partial charges, we can reduce the degree of additivity of the partial charges. For example, using the partial charges shown below, and a uniform dielectric constant of unity, we calculate 2.5-kcal/mol attraction in the *gauche* conformation.



Conclusion

By assuming an electrostatic model, the relative stability of iodoacetone has been calculated with good agreement to that found experimentally. Partial charges were calculated from group dipole moments and potentials obtained by simple coulombic interaction. Similar calculations for iodomethyl methyl ether are complicated as the interacting dipoles are not separated by at least one bond. Assuming that the partial charges are additive and with a uniform dielectric constant of 1, the predicted relative stability is too high. Good agreement is obtained with the experimental value by introducing a dielectric constant for potentials along bonds, or by a mutual reduction from simple addition of concurrent dipole charges.

Both refinements can be determined experimentally from the bond-refractive indices and overall dipole moments of iodo compounds. However, this information is not available at present. On a qualitative basis, a system of alternate positive and negative partial charges imparts stability to a molecule, while destabilization is associated with adjacent like charges. From Table II it may be seen that, relative to the parent hydrogen compound, the most stable iodo compound is acetyl iodide. The negative iodine atom is adjacent to the positively polarized carbon atom of the carbonyl group.

The entropy and enthalpy of $ICH_2COCH_3(g)$ has been calculated as $S°_{298}$ = 85.7 ± 2.0 gibbs/mol and $\Delta H_f°_{298}$ = −31.0 ± 1.5 kcal/mol. From these results we can obtain the group contribution of the iodo ketone group.[11]

	$\Delta H_f°_{298}$, kcal/mol	$S°_{298}$, gibbs/mol
C—(CO)(I)(H_2)	10.6	42.5

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(11) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

The Photochemistry of 2,6-Cyclooctadienone and 2,4-Cyclooctadienone[1]

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Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. *Received December 19, 1969*

Abstract: Irradiation of 2,6-cyclooctadienone (**1**) in inert solvents affords in modest yield tricyclo[3.2.1.$0^{2,6}$]-octan-8-one, whose structure was proven by chemical degradation. Irradiation of **1** in reactive solvents such as methanol or furan gives addition products derived from a ground-state intermediate, 2-*trans*,6-*cis*-cyclooctadienone. Photolysis of 2,4-cyclooctadienone, **2**, in inert solvents gives low yields of the *trans*, head-to-head, 2 + 2 dimer, **16**, resulting from dimerization at the α,β positions of each dienone molecule. In methanol and furan adducts resulting from trapping of a mono-*trans*-dienone are formed. Possible pathways for the formation of the various products are discussed.

As part of the tremendous amount of investigation into the photochemistry of carbonyl compounds, cyclic enones of various ring sizes have received considerable attention.[2] Recent studies of the photochemical behavior of medium-ring unsaturated ketones have uncovered a multitude of interesting transformations. The eight-membered ring conjugated enones 2-cycloocten-1-one[3] and 2,4,6-cyclooctatrien-1-one[4] have been found to undergo isomerization to strained *trans* enones, which in turn undergo thermal cycloadditions and dimerizations, and in the latter case,

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(1) Supported in part by a grant from the Robert A. Welch Foundation.

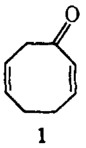
(2) See, for example, R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, Chapters 3 and 4.

(3) (a) P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, **86**, 2087 (1964); (b) R. Noyori, A. Watanabe, and M. Kato, *Tetrahedron Lett.*, 5443 (1968).

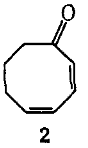
(4) L. L. Barber, O. L. Chapman, and J. Lassila, *J. Amer. Chem. Soc.*, **91**, 531 (1969).

electrocyclic closure to bicyclic products. The cross-conjugated 2,7-cyclooctadienone is noteworthy in that it is photolytically transformed to an intermediate, the nature of which is not yet clear, which can be trapped by protic solvents or by dienes to give bicyclo[3.3.0]-octane derivatives.[5] From irradiation of the β,γ-unsaturated ketone 3-cycloocten-1-one there is formed 6-vinylcyclohexanone, evidently arising from an initial type I cleavage at the C_1–C_2 bond, followed by allylic rearrangement.[6] Photolysis of 2-cyclodecenone gives vinylcyclooctanone, evidently the product of a similar rearrangement of initially produced 3-cyclodecenone.[7a]

It was deemed of interest to investigate the photochemical behavior of 2,6-cyclooctadienone (**1**) and 2,4-cyclooctadienone (**2**) since there existed, *a priori*, a large number of possible reaction pathways which the excited states of **1** and **2** might follow.



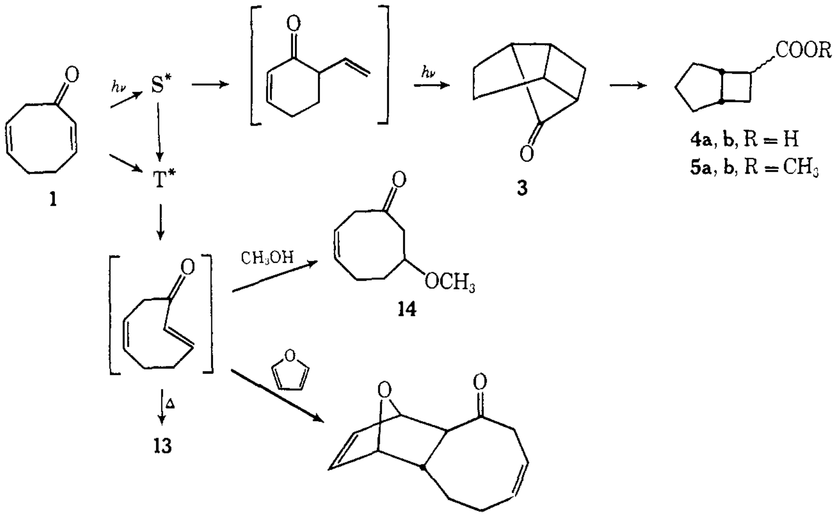
1



2

Results

Compound **1**, 2,6-cyclooctadien-1-one, was prepared from the known 3-bromo-1,5-cyclooctadiene[8] by successive treatments with silver acetate, lithium aluminum hydride, and chromium trioxide (Jones reagent). The identity of **1** was established by its infrared, ultraviolet, nuclear magnetic resonance, and mass spectral data (see Experimental Section). Irradiation of 0.5% solutions of **1** in ether or pentane at 10° (Hanovia 450-W medium-pressure mercury arc) through Pyrex resulted in slow conversion ($\sim$8–12 hr) to an isomer of shorter gc retention time. The progress of the reaction was conveniently monitored by gas chromatography (or, less successfully, by infrared). The major product of irradiation was a sticky, colorless gum, evidently polymeric. By distillation, followed by gas chromatography, there was isolated compound **3**. There was also obtained by further distillation $\sim$20% of a noncrystalline dimer mixture, which will be discussed later. That **3** was isomeric with the starting ketone was evident from its analysis and mass spectrum. The infrared spectrum of **3** showed a carbonyl stretching band at 1756 cm^{-1}, indicative of a somewhat strained five-membered ring ketone.[9] This information, together with the absence of signals in the vinyl region (τ 2.5–5.5) of the nmr spectrum, favored structure **3**, tricyclo-[3.2.1.0^{2,6}]octan-8-one, for the photoisomer.



Chemical proof of structure **3** was obtained by a combination of chemical degradation and synthesis. Cleavage of **3** at the bonds α to carbonyl was accomplished by using the Gassman–Zalar modification of the Haller–Bauer reaction.[10] This involves treatment of a nonenolizable ketone with potassium *t*-butoxide in ether or dimethyl sulfoxide containing a trace of water; the active species is believed to be unsolvated hydroxide ion. Application of this method to **3** gave a mixture of *endo*-(major) and *exo*-bicyclo[3.2.0]heptane-6-carboxylic acid (**4a** and **4b**), which was directly esterified to give the methyl esters **5a** and **5b**. The ester mixture showed a single sharp peak on four gc columns of widely varying polarity. However, lithium aluminum hydride reduction of the ester mixture gave the mixture of *endo*- and *exo*-bicyclo[3.2.0]heptane-6-carbinol (**6a** and **6b**), which proved to be easily separable by preparative gc. Authentic samples of **6a** and **6b** were prepared by the route shown. Thus, photocycloaddition of 2-cyclopentenone to acrylonitrile proceeded readily to give a mixture of at least three adducts, as shown by gc. The absence of vinyl hydrogen signals in the nmr spectrum of the adduct mixture (no signals below τ 5.5) indicates that all three are epimers of 6- or 7-cyanobicyclo[3.2.0]heptan-2-one (**7**). The position of the cyano group in the isomers is not known; however, it seems likely that 6-cyano

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(5) (a) J. K. Crandall and R. P. Haseltine, *J. Amer. Chem. Soc.*, **90**, 6251 (1968); (b) R. Noyori and M. Kato, *Tetrahedron Lett.*, 5075 (1968).

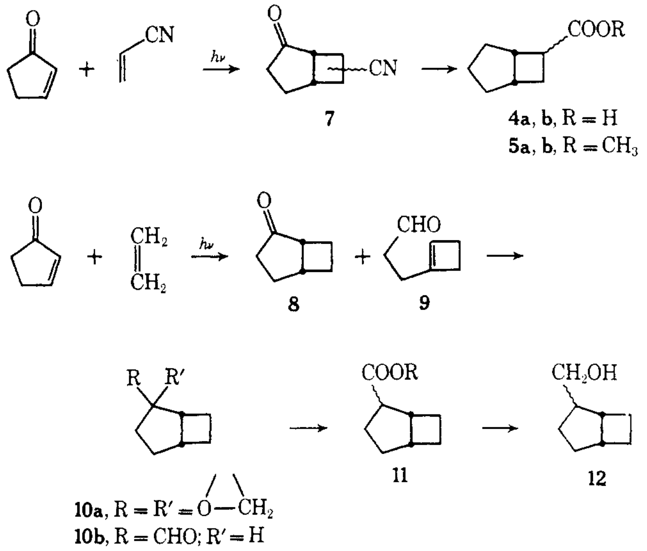
(6) (a) L. A. Paquette and R. F. Eizember, *J. Amer. Chem. Soc.*, **89**, 6205 (1967); (b) J. K. Crandall, J. P. Arrington, and J. Hen, *ibid.*, **89**, 6208 (1967).

(7) (a) R. G. Carlson and J. H. Bateman, *Tetrahedron Lett.*, 4151 (1967); (b) for a still more recent example of a related cleavage, see W. F. Erman and T. W. Gibson, *Tetrahedron*, **25**, 2493 (1969).

(8) A. C. Cope and F. A. Hochstein, *J. Amer. Chem. Soc.*, **72**, 2515 (1950).

(9) The carbonyl stretching bands at norbornen-2-one and bicyclo-[3.2.1]octan-8-one are reported to occur at 1757 cm^{-1}: C. S. Foote, *ibid.*, **86**, 853 (1964).

(10) P. G. Gassman, J. T. Lumb, and F. V. Zalar, *ibid.*, **89**, 946 (1967).



isomers predominate, since in the photocycloaddition of cyclohexenone[11a] and 3-methylcyclohexenone[11b] to acrylonitrile the major products are believed, on the basis of spectral data, to possess the structures in which the cyano-bearing carbon of acrylonitrile is bonded to C-2 of the enone moiety. The orientation of the adducts is actually of no consequence for our purposes, since the carbonyl group is removed in succeeding steps. Hydrolysis of the cyano groups of the adduct mixture and Wolff–Kishner removal of the carbonyl function was accomplished by following the normal Huang–Minlon procedure, with the incorporation of some water at the beginning of the preliminary reflux period, before addition of hydrazine. The acid mixture thus obtained was esterified with diazomethane and then reduced with lithium aluminum hydride to give the epimers of **6** in an *endo–exo* ratio of 14:86. The vigorous basic conditions of the Wolff–Kishner reduction evidently effect equilibration at C-6 and the thermodynamically more stable *exo* isomer predominates. The minor carbinol, thus synthesized, apparently the more crowded and less thermodynamically stable *endo* isomer, was identical (ir, gc on three columns, nmr) with the major carbinol obtained by cleavage of **3**, as were the opposite components in the two mixtures. A small amount of a third compound which was present in the mixture of acids obtained by cleavage of **3** and which was detected as a very small third peak on the gas chromatograph of the carbinol mixture is believed to be the result of cleavage of the other bond α to carbonyl, *viz.*, bicyclo[3.2.0]heptane-2-carboxylic acid (**12**). The epimers of **12** were prepared by the route shown, involving an initial photocycloaddition of 2-cyclopentenone to ethylene. This addition proceeds rapidly at −50° to give the desired bicyclo[3.2.0]heptan-2-one (**8**) in 71% yield, accompanied by 6% of 3-(1-cyclobutenyl)-propionaldehyde (**9**), the product of type I cleavage of **8**, followed by abstraction of hydrogen γ to carbonyl.[12] The structures of **8** and **9** were readily ascertained from the spectral and analytical data on the two compounds (see Experimental Section). Treatment of **8** with dimethyl sulfoxonium methylide[13] gave the spiro epoxide **10a**, which on treatment with boron trifluoride etherate without purification was converted to the bicyclic aldehyde mixture **10b**. Oxidation with silver oxide followed by diazomethane esterification furnished the esters of **11**. Reduction by lithium aluminum hydride gave the carbinols **12** in a 68:32 ratio. The minor carbinol exhibited the same gc retention time as a third peak in the chromatogram of the carbinol mixture derived from cleavage of **3**, amounting to ∼1% of the total area; insufficient material was available for direct comparison. The reasons for the unexpectedly high degree of specificity in the basic cleavage of **3** are not clear.

Irradiation of **1** in methanol results in rapid (∼1 hr) disappearance of starting material and formation of 7-methoxy-3-cycloocten-1-one (**14**, 71%) along with small amounts of **3** (∼10%). The structure of **14** was deduced from analytical and spectral data, including infrared bands at 1702 and 1666 cm^{-1} (saturated carbonyl and nonconjugated double bond). The nmr spectrum showed a two-hydrogen multiplet at τ 4.3, indicative of vinyl hydrogens on a double bond not conjugated with a carbonyl group. The structure of **14** was established with certainty by catalytic hydrogenation to 3-methoxycyclooctanone, whose identity with an authentic sample[14] was shown by comparison of infrared spectra, gc retention times, and melting points of 2,4-dinitrophenylhydrazones. That **14** is the product of thermal addition of methanol to a reactive ground-state species, probably *trans*-2-*cis*-6-cyclooctadienone, was demonstrated by low-temperature studies in inert solvents. Thus, irradiation of **1** in ether at −70° for 0.5 hr, turning the lamp off, addition of methanol, and gradual warming to room temperature gave a solution consisting of 58% **14**, 4% **3**, and 38% unchanged **1**. Low-temperature infrared studies on 2-cycloocten-1-one have demonstrated the formation of the *trans*-enone on irradiation[3a] and it appears to be the precursor to 3-methoxycyclooctanone, the product of irradiation of 2-cyclooctenone in methanol.[3b]

Irradiation of **1** in 1:1 ether–furan gave an inseparable mixture of two Diels–Alder adducts, assigned gross structure **15** on spectral grounds, particularly helpful being infrared bands at 1724 and 1703 (saturated ketone) and 1633 (nonconjugated olefin) cm^{-1} as well as nmr signals (*inter alia*) at τ 3.3–5.0 for four vinyl hydrogens and at 5.2 and 5.6 attributable to two hydrogens on oxygen-bearing carbons.

Catalytic hydrogenation of the adduct mixture gave a mixture of tetrahydro derivatives which was compared with the mixture obtained by reduction of the adducts derived by addition of furan to photochemically produced *trans*-2-cyclooctenone.[3] The latter mixture consisted of two components in a 62:38 ratio, whereas the reduction product of **15** contained the same two components in a 47:53 ratio.[15] It was previously shown[3a] that the adducts from photochemically pro-

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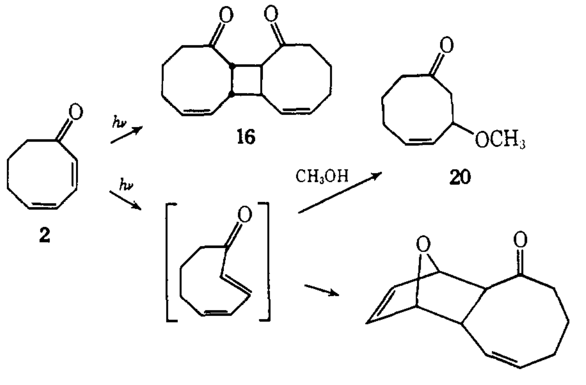
(11) (a) E. J. Corey, J. D. Bass, R. LaMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); (b) T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, **34**, 509 (1969).

(12) Unsaturated aldehydes are frequently observed products in the solution-phase irradiation of cyclic ketones: R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1964).

(13) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1341 (1965).

(14) Prepared by photochemically induced addition of methanol to 2-cycloocten-1-one; see ref 2b.

(15) Comparison by gc on three columns (one capillary column) and tlc in two solvent systems. The infrared spectra were quite similar and the same peaks were present in both, albeit sometimes of different intensity; this seems consistent with the presence of the same two components in a slightly different ratio.

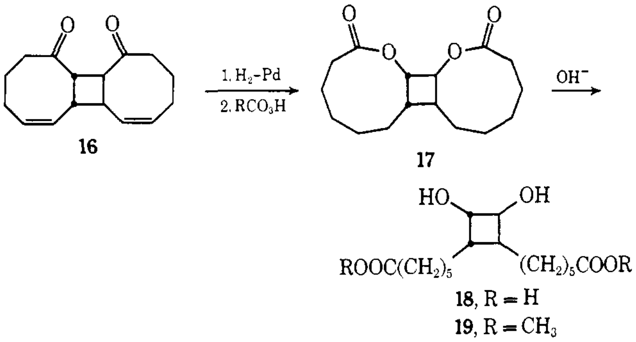


duced *trans*-2-cyclooctenone and furan possess *trans* ring fusions.

The irradiation of **1** in ether or pentane for several hours gave, besides isomer **3**, 20–30% of a noncrystalline dimer mixture **13**. The infrared (ν_{max} 1698 cm^{-1}), nmr (four vinyl hydrogens at τ 4.0–4.5), and mass (parent ion peak at *m/e* 244; base peak at *m/e* 122) spectral data on the dimer mixture indicate that the components are cyclobutane-type dimers. Irradiation of **1** at *ca.* −50° for 1 hr, turning the lamp off, and warming the reaction mixture to room temperature, gave a mixture consisting of 53% recovered **1**, 5% **3**, and 26% dimers **13** (plus intractables). The dimers therefore appear to be derived from a ground-state intermediate, the *trans–cis* isomer of **1**. Catalytic hydrogenation of the dimer mixture gave a mixture of tetrahydro dimers whose components possessed tlc retention times in several solvent systems identical with those of the cyclooctenone dimers[3a] whose exact structures have not been established with certainty, but which are cyclobutane-type dimers derived from the *trans*-enone.[16] Finally, examination of the infrared spectrum at −70° of a solution of **1** which had been irradiated through Pyrex at this temperature revealed the presence of a new band at 1708 cm^{-1}, in addition to the strong carbonyl band of **1** at 1665 cm^{-1}. This band can be assigned to the reactive 2-*trans*-6-*cis*-cyclooctadienone, in which the orthogonality of the *trans* double bond and carbonyl function prevents effective conjugation between these two groups.

Photochemistry of 2,4-Cyclooctadienone. Irradiation of **2**[17] (0.2% in ether or pentane) through Pyrex led to rapid (~1 hr) disappearance of starting material and formation of dimer **16** (8–10%), mp 174°, along with large quantities of high molecular weight gums. The elemental analysis and mass spectrum of **16** (*m/e* 244, P) established that it was a dimer of **2**. The dimer exhibits infrared absorption characteristic of saturated carbonyl groups (1701 cm^{-1}) and nonconjugated *cis* double bonds (688 and 721 cm^{-1}); it displayed nmr signals for four vinyl hydrogens (τ 7.2, M portion of AA'MM'XX'), *inter alia*, and must therefore be one of the isomeric cyclobutane-type dimers produced by bridging at C-2 and C-3 of each molecule of **2**. That compound **16** was recovered unchanged after treatment with methanolic sodium methoxide for 24 hr at 40° indicates that the 8–4 ring fusions are *cis;* it has been previously observed that *trans*-fused bicyclo[*n*.2.0]-alkanones (where n = 3–6) readily epimerize to the corresponding *cis*-fused ketones under such conditions.[3a,11] That **16** is one of the two head-to-head dimers of the gross structure shown follows from the multiplicity of the nmr signals for the hydrogens to carbonyl; the six-line pattern observed corresponds well to that calculated for the A portion of an AA'XX' system (here it is actually AA'MM'XX') where $J_{AX} \sim$ 10 Hz, $J_{AX'} \sim 0$, and $J_{AA'} = J_{XX'} \sim 6$ Hz. The *anti* and *syn* head-to-tail isomers would show first-order multiplets for the corresponding hydrogens, *viz.*, two doublets and one doublet, respectively.[18]

The structure of **16** was confirmed chemically, by a degradative sequence similar to that previously applied to the photodimer of 3-phenylcyclohexenone.[19] Thus, catalytic hydrogenation of the double bonds of **16** followed by Baeyer–Villiger oxidation (*m*-chloroperbenzoic acid) of the resulting saturated diketone produced the oily dilactone **17**, ν_{max} 1724 cm^{-1}. Hydrolysis of **17** proceeded under mild conditions to give the crystalline dihydroxy dicarboxylic acid **18**, mp 137–138°. This material was a 1,2-diol as shown by oxidation of the dimethyl ester **19** by lead tetraacetate during 2 days to a dialdehyde hydrate. The relatively slow rate of cleavage of the ester by lead tetraacetate and the inertness of the diacid **18** to warm aqueous methanolic periodate indicate that the hydroxyls of **18** and **19** are *trans* to each other.



Photolysis of **2** in methanol gave, besides **16** (6–8%) and gummy polymers, adduct **20** (32%) whose structure was established by catalytic hydrogenation to 3-methoxycyclooctanone and comparison with an authentic sample. Similarly, irradiation of **2** in furan gave a mixture of two adducts, assigned structure **21** on the basis of spectral data including infrared bands characteristic of saturated carbonyl at 1701 cm^{-1} and nmr signals for four vinyl hydrogens at τ 3.4–5.0 (multiplets), and mass spectral molecular weight (parent ion at *m/e* 190). Confirmation of this assignment was through comparison of the saturated adduct mixture obtained on catalytic hydrogenation of **21** with the reduction product of the adduct mixture from 2-cyclooctenone and furan (*vide supra*). The reduction of **21** gave a mixture of the same two components (ir, gc on three columns) in the ratio 6:94. Adducts **20** and **21** probably arise from an intermediate 2-*trans*-4-*cis*-cyclooctadienone, as was shown to be the case for **14** and **15**. A search was made

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(16) Private communication from P. E. Eaton.

(17) Prepared by a modification of the procedure of Cope, *et al.*: A. C. Cope, S. Moon, C. H. Park, and G. L. Woo, *J. Amer. Chem. Soc.*, **84**, 4865 (1962); *cf.* S. Moon and C. R. Ganz, *J. Org. Chem.*, **34**, 465 (1969).

(18) For a discussion of the analogous case of the cyclopentenone photodimers, *cf.* P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2344 (1962).

(19) P. Yates, S. Ege, G. Büchi, and D. Knutsen, *Can. J. Chem.*, **45**, 2927 (1967).

for thermal dimers of such a *trans* species; however, none could be found.

Discussion

We have found here that excited **1** can undergo two concurrent reactions: (1) isomerization to *trans*-2-*cis*-6-cyclooctadienone, which dimerizes or reverts to **1** at room temperature unless captured by trapping agents, and (2) type I cleavage at the allylic bond α to carbonyl, followed by reclosure at C-6 to give 6-vinyl-2-cyclohexen-1-one, which undergoes intramolecular photochemical cycloaddition to the saturated tricyclic ketone **3**. The two processes may proceed from the same excited state of **1**, or, somewhat more likely, from two different excited states. On irradiation of **1** in methanol the isomer **3** and the adduct **14** were produced at relative rates of $\sim$1:7–10. Irradiation of **1** in the presence of sufficient xanthone to absorb over 90% of the incident light resulted in less than 2% of **3** and considerable gummy polymer. However, conducting the photolysis of **1** in the presence of 0.5–4.0 *M cis*-piperylene led to no decrease in the rate of formation of **3**. These results favor the intermediacy of singlet excited states in *both* steps leading to **3**, including the intramolecular cycloaddition of the presumed intermediate 6-vinyl-2-cyclohexenone. This is a somewhat surprising conclusion, since there is a large amount of existing evidence which implicates enone triplet excited states as intermediates in intermolecular cycloadditions.[20] However, we favor an alternate explanation; namely, that this and other intramolecular cycloadditions may proceed from excited triplets at rates too rapid for deactivation by quenchers.

Photolysis of **1** in methanol containing sufficient xanthone to absorb over 90% of the incident light led to production of adduct **14** at a nearly undiminished rate, indicating that the isomerization of **1** to the supposed mono-*trans* intermediate proceeds *via* an excited triplet state. It thus appears that **1** can undergo photochemical reactions from both singlet and triplet excited states. The singlet can undergo type I cleavage and allylic rearrangement, followed by intramolecular cycloaddition, probably *via* a triplet, to the isomer **3**. Competing with the cleavage of dienone singlet is intersystem crossing to the triplet state, which undergoes efficient conversion to ground-state *trans*,*cis*-2,6-cyclooctadienone. This strained species reverts thermally to *cis*,*cis*-**1** or can undergo thermal addition of alcohols or dienes when these are present.

Irradiation of **2** in the presence of xanthone resulted in formation of **16** and **20** at rates similar to those in the absence of sensitizer. The dimerization of **2** thus probably proceeds *via* addition of a molecule of excited triplet **2** to a second molecule of ground-state **2**, by analogy with the dimerizations of simple enones such as cyclohexenone and cyclopentenone.[21] The stereochemistry of **16** is the same as that of the sole photodimer of 3-phenylcyclohexenone,[19] the major photodimer of coumarin under conditions which produce coumarin triplets,[21d] and the major dimer of cyclohexenone.[21a] A thermal addition of a photochemically produced *trans*,*cis*-2,4-cyclooctadienone to a molecule of *cis*,*cis*-**2** is likely, since this process is predicted on the basis of orbital symmetry considerations to give *cis*,*anti*-*cis* (as in **16**) or *cis*, *syn*-*cis* dimers. A careful search was made of the reaction mixtures for other dimers, but none were found. If a thermal dimerization of a mono-*trans*-**2** were to proceed in concerted fashion, the products would have one or more *trans* ring fusions, which chemical and nmr evidence show to be absent in **16**. It thus appears that all of the observed photoproducts of **2** arise from triplet excited states, possibly the same triplet. The reasons for the large amounts of polymer produced on irradiation of **2** are not clear.

Experimental Section

General Procedure for Irradiations. The apparatus consisted of a cylindrical Pyrex irradiation vessel which surrounded a Pyrex immersion well and was fitted by means of side arms to a condenser and a small serum bottle cap. Ice water at 4–8° was passed through the annular space of the Pyrex well and also through an external bath in which the entire apparatus was immersed. Solutions of the enones or dienones were placed in the vessel and were deoxygenated by flushing with purified nitrogen for 1 hr. A slight positive pressure of nitrogen was maintained in the system throughout the irradiations. The solutions were irradiated by a Hanovia type L medium-pressure 450-W mercury arc. The progress of the reaction was monitored by removing aliquots from the reaction vessel with a syringe and examination by gas chromatography or infrared spectral means. Analytical gas chromatography was performed *on the following columns: (1) 5 ft × 0.25 in. 5% SE-30 silicone* rubber on Chromosorb P, column A; (2) ft × 0.25 in. 5% Carbowax 20M on Chromosorb P, column B; (3) 12 ft × 0.25 in. 10% QF-1 fluorosilicone rubber on Chromosorb W, column C; and (4) a 200 ft × 0.01 in. (i.d.) polyphenyl ether capillary column (D). Preparative gas chromatographic separations were accomplished on a 6 ft × 0.375 in. 5% SE-30 silicone rubber on Chromosorb P, column E. Gas chromatographic work was done on a Varian Aerograph Model 202-1B gas chromatograph utilizing a thermal conductivity detector. Infrared spectra were obtained on a Beckman IR-8 infrared spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian A56-60A instrument operating at 38°.

Preparation of 2,6-Cyclooctadienone (1). A solution of 1,5-cyclooctadiene (200 g, 1.85 mol) was refluxed with N-bromosuccinimide (245 g, 7.376 mol) and a catalytic amount of benzoyl peroxide in CCl_4 for 4 hr. Evaporation of the solvent and fractional distillation gave 2.87 g (83%) *of a mixture of isomeric bromo*-cyclooctadienes. This material was fractionally crystallized twice from ether to afford fairly pure 3-bromo-1,5-cyclooctadiene, mp $\sim$0°. This product was used directly in the next reaction.

The 3-bromo-1,5-cyclooctadiene (149.3 g, 0.80 mol) and silver acetate (170.0 g, 1.02 mol) were stirred for 24 hr at room temperature in glacial acetic acid in a flask covered with aluminum foil. The solution was filtered and the silver bromide was washed with fresh acetic acid; the solvent was then evaporated from the combined filtrates. The residue was taken up in ether and the remaining silver bromide was filtered. Evaporation of the solvent and distillation at 64° (0.4 mm) gave 90.5 g (67%) of 3-acetoxy-1,5-cyclooctadiene: ir (film) 1732 cm^{-1} (C=O). The nmr spectrum of the acetate showed a vinyl hydrogen pattern similar to that of the bromide; evidently, little allylic rearrangement had occurred.

A solution of 3-acetoxy-1,5-cyclooctadiene (90.5 g, 0.54 mol) in dry ether (300 ml) was added dropwise to a slurry of lithium aluminum hydride (21 g, 0.55 mol) in ether (700 ml). *After completion* of the addition reaction the mixture was refluxed for 12 hr. The excess hydride was destroyed by cautious addition of ethyl acetate; then water (60 ml) and 15% sodium hydroxide solution (30 ml) were added. The coagulated solid salt was filtered, washed three times with ether, and the combined ether solutions were dried (magnesium sulfate) and evaporated to give a colorless oil. Distillation of this material gave pure 1,5-cyclooctadien-3-ol: bp 45–48° (0.3 mm); 63 g (92%); ir (film) 3340 (br, OH); nmr (CCl_4) τ 4.1–4.5 (4 H, m, vinyl). *Anal.* Calcd for $C_8H_{12}O$: C, 77.42; H, 9.68. Found: C, 77.18; H, 9.83.

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(21) (a) E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 3482 (1967); (b) J. L. Ruhlen and P. A. Leermakers, *ibid.*, **89**, 4944 (1967); (c) P. E. Eaton and W. S. Hurt, *ibid.*, **88**, 5038 (1966); (d) C. A. Stout, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 3104 (1964).

To a stirred solution of 1,5-cyclooctadien-3-ol (63 g, 0.51 mol) in acetone (300 ml) was added dropwise a solution of chromium trioxide (40 g, 0.40 mol) in 8 *N* sulfuric acid (120 ml); the temperature was maintained at 15–20° by intermittent cooling. After addition was complete, most of the acetone was removed by evaporation and the reaction mixture was poured onto an ice–water slurry. The mixture was extracted five times with ether and the combined extracts were washed with 5% sodium bicarbonate and dried (magnesium sulfate). Evaporation of the ether and distillation of the residue through a Vigreux column gave 2,6-cyclooctadien-1-one (**1**, 35 g, 56%): bp 42–44° (0.4 mm); ir (film) 1665 (C=O) and 665 and 768 (C=C, m) cm^{-1}; nmr (CCl_4) τ 3.63 (2 H, broadened AB, $\Delta\nu$ = 29 Hz, J_{AB} = 12.5, H-2 and H-3), 3.1–4.3 (2 H, m, H-6 and H-7), 6.5–6.8 (2 H, m, H's on C-4), and 6.9–8.0 (4 H, m, H on C-4 and C-5); $\lambda_{\max}^{CH_3OH}$ 227 and 320 nm (ϵ 7200 and 75); mass spectrum *m/e* (parent)/122.

A 2,4-dinitrophenylhydrazone was prepared by the standard procedure and recrystallized from ethanol to give orange needles, mp 143–144°. *Anal.* Calcd for $C_{14}H_{14}O_4N_4$: C, 55.62; H, 4.65. Found: C, 55.89; H, 4.35.

Photolysis of 2,6-Cyclooctadienone (1) in Inert Solvents. A solution of 2,6-cyclooctadienone (**1**, 2.0 g, 0.016 mol) in dry ether (200 ml) was flushed with nitrogen and irradiated under the standard conditions for 7.5 hr. Filtration of a white, flocculent polymer, evaporation of the ether, and distillation gave slightly impure **3** (0.65 g, 32%), bp 38–43° (0.4 mm). Preparative gas chromatography on column E at 150° gave the pure photoisomer, tricyclo[3.2.1.0^{2,6}]octan-8-one: ir (film) 1765 (C=O) cm^{-1}; nmr(CCl_4) complex multiplets from τ 7.0 to 8.6; mass spectrum *m/e* (relative intensity) 122 (P, 98), 94 (31), 79 (100), and 66 and 67 (both 48). A 2,4-dinitrophenylhydrazone was prepared in the usual manner and was purified by chromatography on silica gel, eluting with chloroform–ethyl acetate (5:1). Recrystallization from ethanol–ethyl acetate (3:1) gave the pure derivative as yellow-orange prisms, mp 144–145° (admixture with the 2,4-DNP of **1** gave mp 127–130°). *Anal.* Calcd for $C_{14}H_{14}N_4O_4$: C, 55.62; H, 4.65. Found: C, 55.38; H, 5.00.

Short-path distillation of the residue remaining from the isolation of **3** gave a second fraction, a viscous syrup identified as the mixture of dimers **13**: bp 120–140° (bath) (0.2 mm); ir ($CHCl_3$) 1692 (C=O) and 1647 (C=C) cm^{-1}; nmr ($CDCl_3$) τ 4.0–4.5 (4 H, m) and 6.8–8.6 (16 H, m); mass spectrum *m/e* (relative intensity) 244 (P, 100), 122 (62), 91 (47), and 80 (66).

Hydrogenation of the dimer mixture **13** (0.40 g) in ethyl acetate solution over 10% palladium-charcoal at 10 psig hydrogen pressure led to the rapid uptake of 2 equiv of hydrogen. Filtration of the catalyst, evaporation of the solvent, and short-path distillation gave a viscous syrup, bp 130–140° (bath) (0.2 mm), whose infrared spectrum was essentially identical with that of the dimer mixture obtained from irradiation of *cis*-2-cyclooctenone in ether.

Cleavage of 3 to Bicyclo[3.2.0]heptane-6-carboxylic Acids (4). The reaction vessel, a 50-ml three-necked flask, was flamed thoroughly and flushed with dry nitrogen while cooling. To a stirred suspension of freshly sublimed potassium *t*-butoxide (2.01 g, 1.79 mmol) in dry ether (25 ml) was added successively distilled water (0.095 g, 5.3 mmol) and a solution of **3** (0.26 g, 2.1 mmol) in dry ether (5 ml) at *ca.* 5°. After both additions were completed, the ice bath was removed and the solution was allowed to stir at room temperature for 3 hr. The reaction mixture was again cooled in ice and water (10 ml) was added. The aqueous layer was acidified to pH 2 and extracted twice with ether. The combined ether solutions were dried (magnesium sulfate) and evaporated to give the crude acid epimers **4a** and **4b** as a faintly cloudy colorless oil, $\nu_{\max}$ 1710 cm^{-1}.

The crude acid, in 5 ml of fresh ether, was added to a fivefold excess of diazomethane in ether (prepared from N-nitrosomethylurea); vigorous gas evolution was observed. After the ether and excess diazomethane had been allowed to evaporate, the residue was distilled to afford the epimeric esters, **5**, as colorless oils: bp 71–75° (0.3 mm) (0.107 g, 34%); $\nu_{\max}^{film}$ 1732 cm^{-1}. *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.14; H, 9.08. Found: C, 70.46; H, 8.83.

Reduction of Bicyclo[3.2.0]heptane-6-carboxylic Ester (5) to Bicyclo[3.2.0]heptane-6-carbinol Epimers (6). To a slurry of lithium aluminum hydride (0.040 g) in dry ether (10 ml) was added dropwise a solution of the esters (0.029 g, 0.19 mmol) in ether (5 ml). The solution was refluxed for 5 hr and then was hydrolyzed by successive addition of water (28 μl), 15% sodium hydroxide (28 μl), and water (83 μl). The granular precipitate was filtered and washed with two portions of ether and the combined ether solutions were dried ($MgSO_4$). Evaporation of solvent followed by distillation afforded the epimers of carbinol **6** (0.020 g, 100%), ir (film) 3350 (OH) and 1030 (CO) cm^{-1}; *m/e* 126 (P). Analysis on column B showed the material to be a 97:3 mixture. The retention time of the major component on columns A and B was identical with that of the minor component of the mixture of the epimers of **6** prepared by synthesis (*vide infra*); the infrared spectrum of the present 97% pure material was identical with that of the minor component of the synthetic mixture, collected from column B. A very small third peak, representing ~1% of the total area, is believed to be the result of reduction of the product of cleavage at the other bond α to the carbonyl of **3**, *i.e.*, bicyclo[3.2.0]heptane-2-carbinol.

Photocycloaddition of Cyclopentenone to Acrylonitrile. A solution of 2-cyclopentenone (4.0 g, 0.050 mol) and acrylonitrile (40 g, 0.78 mol) in ether (160 ml) was irradiated through Pyrex for 4 hr. The solution was then filtered to remove some white flocculent polymer and ether and excess acrylonitrile were evaporated from the filtrate. Distillation of the residue gave the adduct mixture **7** as a pale yellow oil: bp 68–80° (0.3 mm) (4.3 g, 0.032 mol, 64%); ir (film) 1732 (C=O) and 2248 (CN) cm^{-1}; nmr (CCl_4) no signals in τ 2.5–5.5 region; broad signals at 6–8.5. Analysis on column A showed three partially resolved peaks in the approximate ratio 55:35:10. No further attempts at separation or characterization were made. *Anal.* Calcd for C_8H_9NO: C, 71.14; H, 6.68. Found: C, 70.83; N, 7.06.

Reduction and Hydrolysis of the Adduct Mixture 7. Synthesis of 5a and 5b. A solution of the adduct mixture, **7**, from cyclopentenone and acrylonitrile, obtained as described above (4.0 g, 0.028 mol), potassium hydroxide (3.0 g), water (5 ml), and diethylene glycol (20 ml) was refluxed under nitrogen for 2 hr. After the addition of hydrazine (6 ml) the solution was refluxed an additional 0.5 hr. Water and excess hydrazine were then removed by distillation, the temperature of the solution being allowed to rise to 200° and held there for 2 hr. The reaction mixture was cooled and poured into an ice–hydrochloric acid slurry; the resulting mixture was extracted with four 30-ml portions of ether. The combined ether extracts were washed with 5% sodium bicarbonate, with water, and dried ($MgSO_4$). Evaporation of the ether gave the crude acids **4** (2.9 g), ir (film) 3400–2600 (br, COOH), and 1700 (s, br, acid C=O).

The crude acid (2.9 g) in ether (50 ml) was added to excess diazomethane in ether and allowed to stand overnight at room temperature. Evaporation of the ether and excess diazomethane, followed by distillation, gave the mixture of *endo-* and *exo*-6-carbomethoxybicyclo[3.2.0]heptane (**5a** and **5b**) as a colorless oil, bp 83–88° (0.3 mm) (2.7 g), ir (film) 1732 cm^{-1}. Analysis on columns A and B, as well as a 5 ft × 0.25 in. column of 15% diethylene glycol succinate on Chromosorb W, and a 6 ft × 0.25 in. column packed with 15% XF-1150 on Chromosorb W showed one sharp peak, whose retention time was the same in all cases as that of the **5a** and **5b** mixture prepared by cleavage of **3**.

Reduction of the Synthetic Ester Mixture 5a and 5b to Bicyclo[3.2.0]heptane-6-carbinols (6). To a slurry of lithium aluminum hydride (0.20 g) in dry ether (30 ml) was added a solution of **5a** and **5b** (0.38 g) prepared synthetically as described above. The mixture was refluxed for 5 hr and was then hydrolyzed by successive addition of water (0.20 ml), 15% sodium hydroxide (0.20 ml), and water (0.34 ml). The granular precipitate was filtered and washed well with ether. The combined filtrate and washings were dried ($MgSO_4$) and evaporated to give the mixture of *endo-* and *exo*-carbinols **6** in almost pure condition (0.30 g, 95%). Analysis on column B showed the presence of two components in a ratio of 15:85. Collection of the pure components from the same column gave the pure *endo-* and *exo*-carbinols **6a** and **6b**. The infrared spectrum of the minor (*endo*) carbinol was identical with that of the 97% pure material obtained by degradation of **3** (*vide supra*); a mixture of the two samples showed a single sharp peak on columns A, B, C, and D (capillary).

Photocycloaddition of 2-Cyclopentenone to Ethylene. A solution of 2-cyclopentenone (5.0 g, 0.062 mol) in dry ether (400 ml) was saturated with ethylene and irradiated through Pyrex while being cooled with an external Dry Ice–chloroform bath. An ethylene glycol–water mixture precooled to −30° was circulated through the annular space of the immersion well; the average temperature of the solution inside the vessel was thereby maintained at −40 to −50°. After 3-hr irradiation the solution was allowed to warm while the excess ethylene evaporated; the ether was then removed on the rotary evaporator. Distillation of the residue gave a mixture of **8** and **9** as a colorless oil (4.8 g, 91:9 ratio, 61 and 6% yield, respectively), bp 50–67° (0.5 mm), as well as cyclopentenone dimers (0.8 g, bp 105–115° (0.4 mm)). Separation of **8** and **9** was readily achieved by preparative gc on column E. The pure compounds appeared as peaks of retention time 4.0 and 5.6 min, respectively, at 150°. The first peak was identified as 3-(1-cyclobutenyl)propionaldehyde (**9**): ir (film) 2740 and 2855 (CHO) and 1727 (C=O) cm^{-1}; nmr (CCl_4) τ 0.18 (1 H, t, J = 1.6 Hz, CHO) 4.27 (1 H, m, vinyl H), and 7.3–7.8 (8 H, saturated H). *Anal.* Calcd for $C_7H_{10}O$: C, 76.38; H, 9.08. Found: C, 76.25; H, 9.01. A 2,4-dinitrophenylhydrazone was prepared by the usual procedure and recrystallized from 95% ethanol to give orange prisms, mp 138–139°. The semicarbazone, mp 168°, was also prepared.

The second peak, of retention time 5.6 min, was the desired bicyclo[3.2.0]heptan-2-one (**8**): ir (film) 1730 (C=O) cm^{-1}; nmr (CCl_4) 6.8–8.4, multiplets; *m/e* 110 (parent). *Anal.* Found: C, 76.46; H, 9.90. The 2,4-dinitrophenylhydrazone was obtained as pale orange prisms, mp 155.5–157°, from 95% ethanol.

Conversion of Ketone 8 to Carbinol 13. To a solution of dimethylsulfoxonium methylide[13] prepared from 4.40 g (20 mmol) of trimethylsulfoxonium iodide, 480 g (20 mmol) of sodium hydride, and dimethyl sulfoxide (50 ml) was added dropwise, with stirring, over a 30-min period, a solution of the bicyclic ketone **8** (2.00 g, 18 mmol). The resulting red solution was heated to 60–70° for 1 hr, then cooled and poured into water. Extraction with pentane (four 50-ml portions), drying ($MgSO_4$), and concentration of the extract left 1.7 g of the epoxide **10** as a colorless oil which showed infrared absorption at 1100–1000 cm^{-1}; only weak carbonyl absorption was present. The nmr spectrum exhibited two overlapping AB quartets at *ca.* τ 7.3–7.4 ($J \sim 6$ Hz).

A solution of the epoxide **10a** (1.8 g, 15 mmol) in ether (30 ml) was treated at −15° with 2.2 g (17 mmol) of boron trifluoride etherate and the resulting solution was allowed to warm to 0° over a 30-min period, and then allowed to warm to room temperature. The resulting yellow solution was poured into water, and the ether layer was separated, combined with an ether extract of the aqueous layer, dried, and concentrated. The residue of the crude aldehyde **10b** (1.3 g) was a colorless oil with infrared bands at 2790 (aldehyde CH) and 1722 (C=O), and nmr signals at τ 0.22 (CHO); a 2,4-dinitrophenylhydrazone was prepared and recrystallized twice from ethanol to give yellow leaflets, mp 107–108.5°.

The crude aldehyde was dissolved in 50 ml of 60° ethanol containing 4.5 g of silver nitrate and to this solution was added during 20 min a solution of sodium hydroxide (2.0 g, 50 mmol) in 30 ml of water. The resulting suspension was stirred at room temperature for 14 hr, then filtered, extracted with ether, acidified with concentrated hydrochloric acid, and extracted three times with ether. The ether extract was dried and concentrated to leave the crude acid mixture **11** as a yellow oil (0.8 g) with infrared bands at 3200–2600 (carboxyl OH) and 1704 (C=O) cm^{-1}. Esterification of this material by treatment with excess ethereal diazomethane gave the mixture of *endo* and *exo* acids **12a** and **12b** (0.7 g). The ester mixture, bp 83–86° (0.2 mm), showed a single sharp peak on columns A, B, and C, as did the mixture of esters **5a** and **5b**. A sample of **12** was collected from column E for analysis. *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.14; H, 9.08. Found: C, 69.87; H, 9.40. The infrared spectrum exhibited a carbonyl band at 1730 cm^{-1} and showed distinct differences from the spectrum of the **6a** and **6b** mixture.

Irradiation of 2,6-Cyclooctadienone in Methanol. A solution of 2,6-cyclooctadienone (**1**, 1.57 g, 0.013 mol) in anhydrous methanol (200 ml) was irradiated under the standard conditions for 1.5 hr. Evaporation of the solvent and distillation gave crude 3-methoxy-6-cycloocten-1-one (**13**) as a colorless oil (1.68 g, 90% pure by gc, 71%), bp 70–75° (0.2 mm). A pure sample was obtained by collection from column E, and showed the following spectral properties: ir (film) 1700 (C=O) and 1095 (CO) cm^{-1}; nmr (CCl_4) τ 4.1–4.6 (2 H, multiplets, vinyl H), 5.6 (1 H, apparent quintet, $J \sim 5.5$ Hz, $-CHOCH_3$), 6.68 (3 H, singlet OCH_3), 7.0–7.7 (2 H, four doublets, AB portion of ABX, J_{AB} = 12, $J_{AX} = J_{AB} \approx 5.5$, CH_2CO), and 7.8–8.7 (6 H, multiplets). *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.14; H, 9.08. Found: C, 69.94; H, 8.76.

Hydrogenation of Methoxy Ketone 14. A solution of ketone **14** (0.35 g, 2.3 mmol) in ethyl acetate (50 ml) was shaken with 10% palladium-on-charcoal (50 mg) under 20 psig hydrogen pressure for 2 hr. Filtration of the catalyst, evaporation of the solvent, and distillation of the residual oil gave 3-methoxycyclooctanone as a colorless oil: bp 61–63° (0.3 mm) (0.28 g, 78%); ir (film) 1697 (C=O) and 1100 (CO) cm^{-1}; nmr singlet at τ 6.65 (OCH_3). This material exhibited an infrared spectrum identical with that of a sample obtained by irradiation for 2 hr of 2-cyclooctenone in methanol; a mixture of the two samples showed a single sharp peak on columns A, B, and C. A 2,4-dinitrophenylhydrazone was prepared from each sample. Both had mp 146–147°; a mixture melting point was undepressed.

Irradiation of 2,6-Cyclooctadienone in Furan. A solution of 2,6-cyclooctadienone (2.0 g, 1.7 mmol) in freshly distilled furan (125 ml) was irradiated under the standard conditions for 3 hr. Evaporation of excess furan and short-path distillation gave the adduct mixture as a viscous oil: bp (bath) 60–70° (0.2 mm); ir ($CHCl_3$) 1703 (C=O) cm^{-1}; nmr ($CDCl_3$) τ 3.3–5.0 (4 H, m, $-CH{=}CH-$), 5.2 and 5.6 (2 H, m, $-OCH-$), 7.0 (2 H, m), and 7.5–8.5 (6 H, m); *m/e* 190. *Anal.* Calcd for $C_{12}H_{14}O_2$: C, 75.79; H, 7.36. Found: C, 75.26; H, 7.61.

Analysis on columns A, B, or C showed only two poorly resolved peaks; attempted preparative scale gc was fruitless.

Hydrogenation of 1-Furan Adducts. A solution of the adduct mixture **15** described above (0.50 g) was shaken with 10% palladium–charcoal under 15 psig hydrogen pressure for 4 hr. Filtration of the catalyst, evaporation of the solvent, and distillation gave the tetrahydro adducts as a pale yellow viscous oil (0.33 g); ir (film) max 1690 (C=O) cm^{-1}. This material was analyzed on the capillary column D and exhibited two peaks of relative areas 47:53. The hydrogenation product of the 2-cyclooctenone–furan adduct mixture (*vide infra*) showed two peaks of identical retention times in a 62:38 ratio.

The infrared spectra of both samples exhibited the same bands, including significant ones at 2940, 2878, 1690, 1446, 1202, 990, and 932 cm^{-1}, the intensities of some of which were somewhat different, as expected for mixtures of the same components.

Irradiation of 2-cyclooctenone and furan[3a] gave an adduct mixture in *ca.* 60% yield which was reduced directly over palladium-on-charcoal; the saturated adduct mixture, bp 70–80° (bath) (0.2 mm), was shown by gc on the capillary column D, to exhibit two peaks of relative areas 62:38, of retention times identical with those of the hydrogenated 2,6-cyclooctadienone–furan adducts, described above. Admixture of the two samples gave only the same two peaks on columns A, B, and C, as well.

Preparation of 2,4-Cyclooctadienone (2). The conversion of 1,3-cyclooctadiene to 1,3-cyclooctadien-5-ol has been previously described.[17] The procedure of Cope, *et al.*, was followed with the modifications of using in the bromination double the stated amount of benzoyl peroxide and limiting the reflux period to 5 hr. The once-distilled product was treated with silver acetate in acetic acid as described to afford a material which showed two partially resolved peaks on column B in an 80:20 ratio. Comparison of the nmr spectrum of this mixture with that of authentic 2,7-cyclooctadien-1-ol suggested that the major component here was the unrearranged 2,4-cyclooctadien-1-yl acetate. Cleavage of the acetate function by lithium aluminum hydride proceeded smoothly to give the alcohol, bp 49–52° (0.3 mm), in 93% yield.

To a solution of 1,3-cyclooctadien-5-ol (15 g, 0.12 mol) in reagent grade acetone (200 ml) was added dropwise a solution of 12 g (0.12 mol) of chromium trioxide in 40% sulfuric acid (20 ml). The orange color was discharged by the addition of a small amount of isopropyl alcohol. The bulk of the acetone was then evaporated under reduced pressure and the residue was stirred with ice water (300 ml). The resulting mixture was extracted with five 100-ml portions of ether; the combined extracts were washed with 5% sodium bicarbonate and dried ($MgSO_4$). The ether was evaporated and the residue distilled to give **2**, 2,4-cyclooctadienone: bp 44–46° (0.7 mm) (11.6 g, 78%); ir (film) 1662 (C=O) and 1595 (C=C) cm^{-1}; nmr (CCl_4) τ 3.5–4.4 (4 H, m, $-CH{=}CH-$, [2 H observed as A part of AB at τ 4.32, J = 12.5)], 7.3–8.3 (6 H, multiplets). The 2,4-dinitrophenylhydrazone, red-orange prisms from 95% ethanol, exhibited mp 178–179° (lit.[17] mp 179–180°).

Irradiation of 2,4-Cyclooctadienone (2) in Ether. A solution of 2,4-cyclooctadienone (1.00 g, 0.079 mol) in dry ether (200 ml) was irradiated through Pyrex for 1.5 hr. Evaporation of the ether and trituration of the semisolid residue with ether–pentane gave three crops of nearly pure **16**, mp 171–173°. Recrystallization of the combined solid from ethyl acetate–benzene (1:1) afforded the pure dimer: mp 173–174° (0.10 g, 10%); ir (KBr) 1700 (C=O) and 722 and 687 (C=C) cm^{-1}; nmr ($CDCl_3$) τ 4.1–4.3 (4 H, multiplets (CH=CH), 6.6 (2 H, A part of AA′XX′, $J_{AX} \approx J_{A'X} \sim$ 10.1), 7.3 (2 H, multiplet, X part of AA′XX′YY′), and 7.4–8.6 (8 H, multiplets); *m/e* 244 (parent, 100), 188 (180), 160 (76), and 132 (120). A sample was sublimed at 150° (0.1 mm) for analysis. *Anal.* Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.32; H, 8.28.

Evaporation of the solvent from the mother liquors of **16** gave a colorless gum which was placed in a sublimation apparatus and heated to 100–120° while at 0.1 mm; only a trace of **16** sublimed onto the cold finger. Chromatography of the mother liquors from a similar irradiation gave, as before, no material other than a trace of **16**.

Degradation of Dimer 16. Conversion to 18. A solution of dimer **16** (1.20 g, 5.0 mmol) in ethyl acetate (200 ml) was shaken with 10% palladium-on-charcoal (300 mg) under 15 psig hydrogen pressure until no further uptake occurred (3 hr). Filtration of the reaction mixture and evaporation of the solvent gave the tetrahydro dimer as a colorless syrup in quantitative yield: ir (film) 1699 cm^{-1}; no nmr signals in the τ 2.0–5.5 region.

The tetrahydro dimer as obtained above was dissolved in chloroform (30 ml) and refluxed with *m*-chloroperbenzoic acid (1.20 g, 85% purity, 6.0 mmol) for 40 hr. The chloroform was evaporated and the residue was triturated with 4:1 hexane–chloroform and filtered. The solid was washed twice with fresh portions of 4:1 hexane–chloroform. The solvent was evaporated from the extracts to give dilactone **17** as a colorless, viscous oil: 1.04 g (76%); ir (film) 1724 (lactone C=O) and 1300–1100 (CO) cm^{-1}; nmr ($CDCl_3$) τ 5.8 (2 H, m) and 6.9–8.7 (22 H, m). The material gave only one spot on tlc on silica gel.

Hydrolysis of dilactone **17** was accomplished by stirring the compound (1.0 g) with 20% aqueous sodium hydroxide (20 ml) overnight. The reaction mixture was extracted twice with ether, acidified with concentrated hydrochloric acid, and extracted with three 30-ml portions of ether. The combined ether extracts were washed with 3% sodium bicarbonate, and saturated sodium chloride, then dried ($MgSO_4$) and evaporated to give crude **18** as a pale yellow solid. Recrystallization of the residue from ethyl acetate gave the diacid **18**, *trans,cis,trans*-3,4-bis(5-carboxypentyl)-1,2-cyclobutanediol as white prisms: mp 137–138° (0.80 g, 76%); ir (KBr) 3500–2600 (br, OH), 1700 (C=O), and 1070 (CO) cm^{-1}; nmr ($CDCl_3$) τ −1.6 (COOH); *m/e* (P) 316. *Anal.* Calcd for $C_{16}H_{28}O_6$: C, 60.77; H, 8.86. Found: C, 60.40; H, 8.99.

To a solution of dihydroxy diacid **18** (50 mg) in methanol–water (3:1, 3 ml) was added a solution of potassium periodate (100 mg) in water (1 ml) and the resulting solution was warmed to 40° during 3 hr. Cooling the solution, evaporation to *ca.* 1 ml, and cooling to 0° caused crystallization of a crop of crystals. These were filtered, dried, and showed mp 137–138°. This material was unchanged diacid, **18**, as shown by the identity of the infrared spectra of the recovered material with an authentic sample, and by the lack of depression of a mixture melting point.

The dihydroxy diacid **18** was converted to the corresponding dimethyl ester **19** by treatment with excess ethereal diazomethane. The resulting colorless viscous oil was distilled in a short-path apparatus to give pure **19**: bp 100–110° (0.1 mm); ir (film) 1730 (C=O) and ~1100 (CO) cm^{-1}; nmr ($CDCl_3$) τ 6.21 (s, OCH_3). A solution of diester **19** (0.10 g) in methylene chloride (10 ml) was treated with lead tetraacetate (0.22 g) in methylene chloride (10 ml) and the solution was stirred for 3 days. The brown precipitate which had gradually appeared was filtered and the filtrate was washed with sodium bisulfite solution, with water, and then dried ($MgSO_4$). Evaporation of the solvent gave an orange oil whose spectral data [ir (film) ~3600 (OH) and 1705 (C=O) cm^{-1}; nmr ($CDCl_3$) τ 6.2 (s, OCH_3) and 4.5 (d, $J \sim 5$)] and positive tests with 2,4-dinitrophenylhydrazone solution were consistent with the assignment of a dialdehyde hydrate, or tetrahydrofuran 2,5-diol structure. The material was not obtained crystalline.

Irradiation of 2,4-Cyclooctadienone in Methanol. A solution of 2,4-cyclooctadienone (**2**) (1.22 g, 10 mmol) in dry methanol (200 ml) was irradiated through a Pyrex filter under the standard conditions for 4 hr. Evaporation of the solvent and trituration of the residue with ethyl acetate gave 82 mg (6.5%) of crude dimer **16**. Evaporation of the solvents from the mother liquors and distillation of the residue gave 3-methoxy-4-cycloocten-1-one (**20**) as a colorless oil, bp 71–74° (0.3 mm) (0.48 g, 30%). A sample was collected from column E for analysis and exhibited the following spectral data: ir (film) 1704 (C=O), 740 (C=C), and 1110 and 1095 (C—O) cm^{-1}; nmr (CCl_4) τ 4.28 (2 H, m, -CH=CH), 5.59 (1 H, apparent pentet, $J \sim 5.5$, -C*H*OCH_3), 6.69 (3 H, s, OCH_3), and 7.1–8.6 (8 H, m). *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.14; H, 9.08. Found: C, 69.56; H, 8.91.

Hydrogenation of 3-Methoxy-4-cycloocten-1-one (20). A solution of **20** in ethyl acetate (50 ml) was shaken with 10% palladium-on-charcoal under 10 psig hydrogen pressure for 3 hr. After filtration of the catalyst and evaporation of the solvent, the residue was distilled to afford 3-methoxycyclooctanone in quantitative yield. The infrared spectrum of the material so obtained was identical with that of the authentic sample described earlier (*vide supra*). The melting point of the 2,4-dinitrophenylhydrazone of the present sample was undepressed on admixture with that of the authentic sample.

Irradiation of 2,4-Cyclooctadienone (2) in Furan. A solution of **2** (1.46 g, 10 mmol) in 125 ml of freshly distilled furan was irradiated under the standard conditions for 3 hr. Evaporation of the excess furan and evaporative distillation of the residue in a short-path apparatus gave the adduct mixture **21** as a viscous, pale yellow oil: bp 90–100° (bath) (0.1 mm); ir (film) 1692 (C=O) and (C=C) cm^{-1}; nmr ($CDCl_3$) τ 3.3–4.5 (4 H, m, -CH=CH-), 5.2 and 5.6 (2 H, -C*H*O- and 8 H, multiplets); mass spectral parent ion 190.

Hydrogenation of the above mixture of adducts from **2** and furan (15 psig hydrogen) for 3 hr gave, after filtration, evaporation of the solvent, and short-path distillation, a colorless oil, bp 90–100° (0.2 mm). Analysis on column D showed peaks in the ratio 6:94; the reduced adduct mixture from 2-cyclooctenone and furan showed the same two peaks (on the capillary column D, as well as columns A and B, on which the peaks were incompletely resolved) in the ratio 62:38 (*vide supra*). The infrared spectra of the two samples differed only in the intensities of the peaks.

Low-Temperature Photolysis of 1. Formation of 14 in a Dark Reaction. A solution of **1** (1.2 g) in dry ether (125 ml) was flushed with nitrogen for 1 hr and irradiated in a vessel immersed in a Dry Ice–acetone bath. Glycol–water at −30° was circulated through the Pyrex immersion well. After 45-min irradiation, the lamp was turned off. After the reaction mixture had been allowed to stand in the Dry Ice bath for 5 min, methanol (75 ml), which had been previously chilled to −70° and flushed with nitrogen was added, and the solution was allowed to warm spontaneously to room temperature. Evaporation of the ether and methanol under reduced pressure and analysis of the residue on column A at 170° showed three peaks, of retention times identical with photoisomer **3**, starting ketone **1**, and methoxy ketone **14**, in the ratio 3:37:60. Collection of the second and third peaks from column E provided samples which were identical in every respect with authentic samples of **1** and **14**, respectively.

Sensitization Experiments on 1 and 2. In the sensitized photolysis of **1**, a solution of **1** (0.61 g, 5 mmol) and xanthone (0.30 g, 1.5 mmol), $E_T = 74$ kcal, in ether (150 ml) was irradiated under the standard conditions. After 10 hr, over half of the starting dienone had been consumed in some undetermined reaction with the sensitizer, but only *ca.* 1% of **3** was detectable (gc). After 20 hr, **1** was completely consumed and only ~2% of **3** was detectable.

A similar irradiation of **1** (0.61 g) in the presence of *cis*-piperylene concentrations of 0.5, 1.5, and 4.0 *M* led to production of **3** to the extent of 5% after 2 hr and 20% after 9 hr, as shown by gas chromatography.

Irradiation of **1** (0.61 g) in methanol (75 ml) containing 0.098 g (0.5 mmol) of xanthone for 90 min gave 66% 3-methoxy-6-cycloocten-1-one (**14**), isolated by collection from column E, and 34% unchanged **1**.

A solution of **2** (0.48 g) and xanthone (0.10 g) in methanol (100 ml) was irradiated through Pyrex for 3 hr. Evaporation of the solvent, trituration of the residue with ethyl acetate, and filtration gave crude **16** (25 mg). Concentration of the mother liquors and examination by gc showed **2** and **16** to be present in the ratio 27:73.

Acknowledgment. The authors are grateful to Dr. M. R. Willcott for determining the 100-MHz nmr spectrum.