

single fraction at 96–101° (20 mm) weighing 13.6 g (77%): ν 2230 cm^{-1} (acetylenic). An analytical sample was purified by preparative gc.

Anal. Calcd for $\text{C}_{10}\text{H}_{10}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.70.

1-(*m*-Methylphenyl)-2-methylcyclopropene-3-carboxylic Acid.—Using procedure A, 16.4 g (0.14 mol) of ethyl diazoacetate was added to 37.5 g (0.29 mol) of 1-(*m*-methylphenyl)propyne in the presence of 0.029 g of anhydrous CuSO_4 over 2 hr. The reaction was started at 135° and then quickly lowered to 110–115°. The reaction mixture was hydrolyzed, using 40 g of NaOH in 500 ml of 90% ethanol. Work-up gave a heavy oil which was dissolved in 100 ml of benzene and passed through silica gel using benzene as the eluent. Vacuum evaporation left a heavy oil which was crystallized from ether–pentane at –78°. Recrystallization twice from benzene–heptane and twice from acetone–heptane gave 0.7 g of white crystals (3%): mp 125.6–126.4°; nmr (CCl_4) δ 7.35 (m, 4, aromatic), 2.32, 2.36, 2.38 (3 s, 7, C–H, ArCH_3 , cyclopropene CH_2); ν (hexachloro-1,3-butadiene mull) 2950, 1895, 1845, 1675, 1480, 1415, 1370, 1125, 1110, 1285, 1270, 1240, 1105, and 1025 cm^{-1} ; other ν (Nujol mull) 1180, 950, 900, 880, 850, 780, 725, and 680 cm^{-1} ; uv absorbance (1.5×10^{-5} M

in absolute ethanol at 261 μm (ϵ 19,000) with shoulders at 227 (21,000) and 219 (25,300) on uv maximum <210.

Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2$: C, 76.57; H, 6.43; neut equiv, 188.2. Found: C, 76.80; H, 6.41; neut equiv, 187.3, 186.8.

Instrumentation.— pK_a determinations in 50.0% (v/v) aqueous ethanol were carried out as previously reported.³ Proton nmr were run at 100 MHz.

Registry No.—1-Phenyl-2-methylcyclopropene-3-carboxylic acid, 18826-56-7; 1-(*p*-chlorophenyl)-2-methylcyclopropene-3-carboxylic acid, 18826-55-6; 1-(*p*-methoxyphenyl)-2-methylcyclopropene-3-carboxylic acid, 18826-57-8; 1-(*m*-chlorophenyl)-2-methylcyclopropene-3-carboxylic acid, 18826-58-9; 1-(*p*-fluorophenyl)propyne, 18826-59-0; 1-(*p*-fluorophenyl)-2-methylcyclopropene-3-carboxylic acid, 18826-60-3; 1-(*m*-methylphenyl)-2-propanone, 18826-61-4; 1-(*m*-methylphenyl)propyne, 18826-62-5; 1-(*m*-methylphenyl)-2-methylcyclopropene-3-carboxylic acid, 18826-63-6.

Photocycloaddition Reactions of Some 3-Substituted Cyclohexenones¹

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The photochemical cycloaddition reactions of 3-methyl-, 3-phenyl-, and 3-acetoxycyclohexenones with the substrates cyclopentene, isobutene, 1,1-dimethoxyethylene, ethoxyethylene, *cis*- and *trans*-dichloroethylene, and acrylonitrile have been studied. These enones add to the various substrates bearing electron-donating substituents to give, sometimes accompanied by other products, bicyclo[4.2.0]octan-2-ones in which the orientation of the substituents is, in most cases, that predicted by the Corey rule of the oriented π complex. Irradiation of 3-acetoxy- and 3-methylcyclohexenone with isobutylene yielded, in addition, significant quantities of the 8,8-dimethylbicyclo[4.2.0]octan-2-one derivatives, indicating that steric factors can sometimes outweigh mild electronic demands in a substrate. The relative rates of addition of the various enones to each substrate were determined. These vary over one order of magnitude and are suggestive of processes involving diradical-like intermediates with a low degree of charge separation.

The photochemical cycloaddition of α,β unsaturated ketones to carbon–carbon double bonds has been the subject of much recent investigation.² Cyclic enones add to cyclic and acyclic olefins, alkynes,^{3b} allenes,^{3b,4} and to themselves to give cyclobutane derivatives. The cycloaddition reaction has been applied fruitfully to the preparation of key intermediates in total syntheses of natural products^{5–7} and unusual cage-like molecules.^{8–10}

A significant amount of evidence regarding the mech-

anism of the reaction has been gathered. Since the cycloaddition of enones proceeds when Pyrex-filtered light ($>2900 \text{ \AA}$) is used, an initial $n \rightarrow \pi$ excited singlet state must be formed. This initial excited state could give rise to either an $n \rightarrow \pi^*$ triplet or $\pi \rightarrow \pi^*$ triplet. It is now generally agreed, on the basis of experiments involving sensitizers and quenchers and on studies of emission spectra, that the reactive excited states in dimerizations and crossed cycloadditions are $n \rightarrow \pi^*$ triplets.^{11–14} DeMayo has concluded that one or more triplet states other than that of lowest energy (T_1) are involved in the photocycloadditions of cyclopentenone.¹⁴ Very recently Chapman has presented evidence that two different triplets are involved in photocycloadditions of isophorone and 4,4-dimethylcyclohexenone.¹⁵ A considerable amount of the evidence so far available on the details of the mechanism of the cycloaddition process itself has been provided by Corey and coworkers, who studied the orientation and stereochemistry of the addition of cyclohexenone to several olefins.⁴ Among

(1) Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) For a critical review of recent work and leading references see (a) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968); (b) R. O. Kan, "Organic Photochemistry," McGraw-Hill Publishing Co., New York, N. Y., 1966, Chapters V and VI.

(3) (a) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2454 (1962); (b) P. E. Eaton, *Tetrahedron Letters*, 3695 (1964); (c) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

(4) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964).

(5) (a) E. J. Corey, R. B. Mitra, and H. Uda, *ibid.*, **86**, 485 (1964); (b) E. J. Corey and S. Nozoe, *ibid.*, **87**, 5733 (1965).

(6) J. D. White and D. N. Gupta, *ibid.*, **88**, 5364 (1966).

(7) R. W. Guthrie, Z. Valenta, and K. Wiesner, *Tetrahedron Letters*, 4045 (1966).

(8) P. E. Eaton and T. W. Cole, *J. Am. Chem. Soc.*, **86**, 962 (1964).

(9) R. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3043 (1964).

(10) R. Cookson, R. R. Hill, and J. Hudec, *ibid.*, 3062 (1964).

(11) (a) J. L. Ruhlen and P. A. Leermakers, *J. Am. Chem. Soc.*, **88**, 5671 (1966); (b) *ibid.*, **89**, 4944 (1967).

(12) P. E. Eaton and W. S. Hurt, *ibid.*, **88**, 5038 (1966).

(13) E. Y. Lam, D. Valentine, and G. S. Hammond, *ibid.*, **89**, 3482 (1967).

(14) P. DeMayo, J.-P. Pete, and P. M. Tahir, *ibid.*, **89**, 5712 (1967).

(15) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *ibid.*, **90**, 1657 (1968).

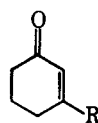
the significant features of their results are (1) *trans*-bicyclo[4.2.0]octanones were usually obtained, sometimes as the major product; (2) the orientational mode of the addition is apparently governed by the electron demands of the substituents on the olefin; and (3) the relative rate of addition of various olefinic substrates were dependent on the electron-donating power of substituents on the substrates. These workers proposed a mechanism in which an intermediate π complex is formed between an enone in an excited state and a ground-state olefin molecule. The orientation in the π complex is governed by the electronic demands of the olefin, the more electron-rich carbon atom of the olefin being adjacent to the α -carbon of the enone. This π complex collapses to a diradical intermediate which subsequently closes to the cyclobutane. In support of the hypothesis of a diradical intermediate was the observation that *cis*- and *trans*-2-butene give identical product mixtures, the steric identity of the substrate being lost in the course of the addition. The possibility of a zwitterionic intermediate is militated against by the low orientational selectivity observed in the additions of cycloalkenones to the weakly polarized olefins isobutylene⁴ and propene.¹⁶ Further, the differences in the relative rates of addition of cyclohexenone to olefins bearing groups of greatly different electronic character are too small to be consistent with an intermediate bearing a great deal of charge separation. Several subsequent reports of photocycloadditions of enones present results which are consistent with the Corey mechanism.^{7,15,17}

Reports of photocycloadditions of enones bearing functional groups on the π system are limited to cases involving the enol acetates of cyclohexenone and cyclopentenone,¹⁸ chromone¹⁷ (formally a β -alkoxyenone), and bicyclic vinylogous imides (formally β -amidoenones).¹⁹ Several of the products thus obtained were of value as synthetic intermediates. The effects of the substituents on the addition process were not dramatic; however, it seems possible that cases where a particular enone gave products not synthetically useful may have gone unpublished.

The research described below has been concerned with the photochemical cycloaddition of several substituted cyclohexenones with various olefins. This work was undertaken with several goals in mind: (1) to elucidate the structures of the products obtained and thereby extend the synthetic usefulness of the cycloaddition reaction; (2) to use the knowledge gained of the orientations and stereochemistries of the adducts to more clearly delineate the mechanism of the addition process; and (3) to determine the relative rates of reaction of various substrates with each enone in order to gain information on the electrical and steric effects of the substituents and on the degree of charge separation in the excited states and intermediates involved.

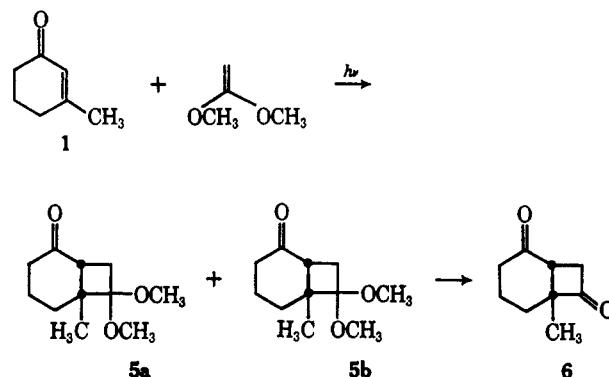
Results

Described below are studies on the photochemical cycloaddition reactions of the following 3-substituted cyclohexenones: 3-methyl (1), 3-acetoxy (2), and 3-phenyl (3). The products resulting from each enone will be described separately. All of the photochemical reactions described herein were performed using as the light source a 450-W medium-pressure mercury arc (Hanovia 679A-36) in a quartz well. A Corex filter was placed between the lamp and the well to prevent reactions arising from $\pi \rightarrow \pi^*$ excited states of the enones. The reaction vessel was cooled externally by water at 6–8°; the same water was circulated through the annular space in the well.



- 1, R = CH₃
- 2, R = Ph
- 3, R = OAc
- 4, R = OCH₃

A. Products from 3-Methylcyclohexenone.—The photocycloaddition of 3-methylcyclohexenone (1) to 1,1-dimethoxyethylene proceeded readily to yield **5a** and **5b** in yields of 26 and 38%, along with several minor products in yields of less than 4% each. The analytical and molecular weight data and the absence of vinyl hydrogen signals in the nmr spectra indicate that **5a** and **5b** are the expected 1:1 cycloadducts. That the methoxyls are at C-7 rather than C-8 was shown by the isolation, after gentle acid hydrolysis, of the dione **6**.



This is the γ -diketone shown and not the isomeric β -diketone, since it is nonenolic (infrared, nmr, negative FeCl₃ test), is not hydrolyzed by base, and shows normal cyclobutanone and cyclohexanone carbonyl infrared stretching bands. Exposure of **5a** to cold methanolic sodium methoxide effected isomerization to **5b**. The compounds are therefore epimeric at C-1 and **5a** must be the more strained *trans*-fused isomer.

The photocycloaddition of 1 to ethoxyethylene proceeded quickly and cleanly, giving a mixture of two cycloadducts, **7a** and **7b** (26 and 65%). Base treatment of **7a** and **b** caused no change; the compounds probably possess a *cis* ring fusion and are epimeric at the ethoxyl-bearing carbon. The adduct mixture (**8**) from 1 and benzyloxyethylene was shown to possess the 7-benzyloxy structure by chemical means. The benzyl group was removed by hydrogenolysis (palladium-charcoal); oxidation of the resulting alcohol mixture

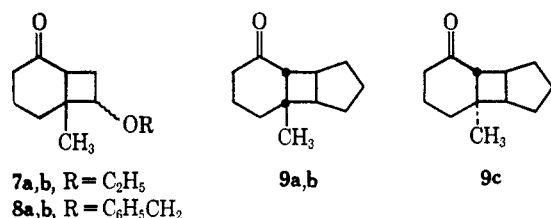
(16) P. E. Eaton, unpublished results cited in ref 2a.

(17) J. W. Hanifin and E. Cohen, *Tetrahedron Letters*, 5421 (1966).

(18) (a) P. DeMayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963); (b) P. DeMayo and H. Hikino, *J. Am. Chem. Soc.*, **86**, 3582 (1964); (c) P. E. Eaton 140th National Meeting of the A.C.S., San Francisco, Calif., April 1, 1968.

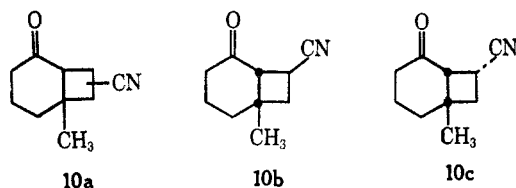
(19) (a) E. H. W. Bohme, A. Valenta, and K. Wiesner, *Tetrahedron Letters*, 2441 (1965); (b) K. Wiesner, I. Sirkovsky, M. Fishman, and C. A. J. Williams, *ibid.*, 1523 (1967).

with Jones reagent gave, after careful purification, the dione **6**, identical with the sample obtained previously. The position of the ethoxyls in **7a** and **7b** is therefore probably C-7 also.



Irradiation of 3-methylcyclohexenone in the presence of excess cyclopentene under the standard conditions gave three products, **9a-c** (4.8, 32, and 34%) whose analytical and spectral data indicated they were the expected cycloadducts. Compound **9c** was converted to **9a** on treatment with sodium methoxide and is therefore probably one of the two isomers possessing the *trans* stereochemistry at the 6-4 ring juncture. The inertness to base of **9a** and **9b** suggests they are the two *cis*-fused isomers. A definite assignment of stereochemistry to **9a** and **b** was not possible on the basis of the available data, including the nmr coupling constants. Others have observed the *cis* and *trans* coupling constants between vicinal hydrogens in fused cyclobutane derivatives vary widely and are frequently of comparable magnitude.^{3c,20} However, it seems likely that the major isomer **9b** is the *cis,anti,cis* compound and **9a** the *cis,syn,cis* by analogy with the addition of cyclopentene to cyclopentene, in which the *anti* isomer is formed exclusively.

Photocycloaddition of **1** to acrylonitrile proceeded surprisingly rapidly and led to the formation of three isomeric cyanobicyclo[4.2.0]octanones (**10a-c**) (9, 17,

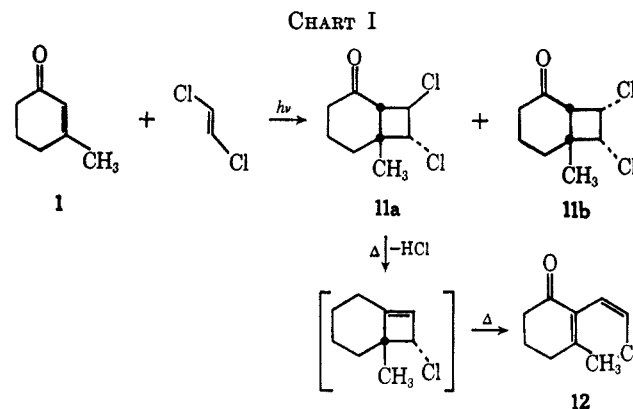


and 29%). Compound **10a** was difficult to separate from **10b** and was not obtained in a pure state. Compounds **10b** and **10c** are believed to be 8-cyanobicyclo[4.2.0]octan-2-ones; in the nmr spectra of these products the signals due to the hydrogens on C-1 were sharp doublets (see Experimental Section) and those of the hydrogens α to the cyano group were eight-line multiplets. These are the multiplicities expected for the 8-cyano compounds, whereas the corresponding hydrogens of the 7-cyano isomers should both show pairs of doublets. Exposure to methoxide converts **10c** to **10b**. Since the chemical shifts of H-1 in the two isomers are almost identical, whereas those of H-8 differ by 0.4 ppm, it appears that **9b** and **c** differ in configuration at C-8 rather than at C-1. The relative stability of the compounds suggests that **10b** is the less hindered *exo*-cyano isomer and **10c** the *endo*-cyano compound.

Irradiation of **1** in the presence of *cis*- or *trans*-1,2-

(20) J. W. Hanifin and G. O. Morton, *Tetrahedron Letters*, 2307 (1967).

dichloroethylene gave two major products (**11a** and **11b**) (Chart I) and three unidentified minor products.

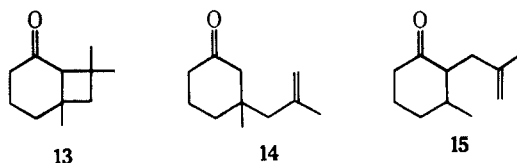


The yields of **11a** and **11b** from *trans*-dichloroethylene were 48 and 33%, and from *cis*-dichloroethylene, 22 and 51%. Compound **11a** proved to be rather prone to undergo thermal elimination of hydrogen chloride and its structure was inferred indirectly. Treatment of mixtures of **11a** and **11b** with mild base followed by fractional distillation, or more simply, preparative gas chromatography effected elimination of hydrogen chloride from **11a** to give the monochloro ketone **12**. The structure of **12** followed from its analytical and spectral data. The vinyl hydrogens' nmr signal was a clean AB quartet, the size of the coupling constant (13.2 Hz) indicating the *cis* geometry. According to the Woodward-Hoffmann orbital symmetry rules governing electrocyclic reactions **12** is formed in a conrotatory process and the methyl group and chlorine atom in the presumed cyclobutene intermediate must therefore be *trans* to each other. The ready thermal elimination of hydrogen chloride from **11a** suggests that H-1 and the chlorine on C-8 are *cis*;²¹ since **11a** is formed in greater amount from the *trans*-dichloroethylene, the chlorines are most likely *trans* and **11a** is assigned the structure shown. Compound **11b**, mp 53-55°, is stable to heat and to mildly basic conditions. This suggests that H-1 and the C-8 Cl are *trans*, and that the ring juncture is *cis*. Together with the observation that **11b** is the major product from the *cis* olefin,²² this evidence suggests the stereochemistry shown above for **11b**.

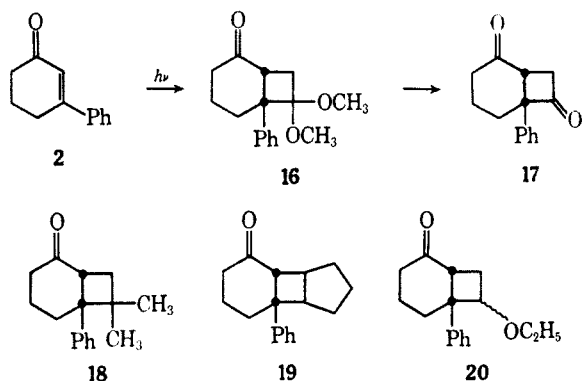
The products of irradiation of 3-methylcyclohexenone in the presence of isobutene have been described by Corey,⁴ who reports the isolation of 6,8,8-trimethylbicyclo[4.2.0]octan-2-one (**13**), 3-(β -methallyl)-3-methylcyclohexanone (**14**), and 2-(β -methallyl)-3-methylcyclohexanone (**15**) in unstated yields. The reaction in our hands gave these products in yields of 14, 50, and 27%.

(21) (a) Unimolecular gas-phase eliminations of a molecule of hydrogen halide, a carboxylic acid, etc., to form C-C double bonds are generally thought to proceed *via* cyclic four- or six-membered transition states and thus to be possible only when the hydrogen atom and the other departing atom or group are *cis* to each other and coplanar or nearly so.^{21b} Although an analogy with gas-phase eliminations may be tenuous, we feel that since **11a** and **b** differ so greatly in the ease of elimination of HCl under nonbasic conditions, that the assignments given for the stereochemistry at C-8 are justified. (b) A. MacColl in "Studies on Chemical Structure and Reactivity," J. A. Ridd, Ed., John Wiley & Sons, Inc., New York, N. Y., 1966, Chapter 4.

(22) The photocycloaddition of indene to *trans*- and *cis*-1,2-dichloroethylene is reported to lead to adduct mixtures in which compounds with the chlorine atoms *trans* and *cis*, respectively, predominate: W. Metzner, *Tetrahedron Letters*, 1321 (1968).



B. Products from 3-Phenylcyclohexenone.—The photoaddition of 3-phenylcyclohexenone (**2**) to 1,1-dimethoxyethylene gave a single addition product, 6-phenyl-7,7-dimethoxybicyclo[4.2.0]octan-2-one (**16**, 71%), mp 54°. Hydrolysis of the cyclobutanone ketal function of **16** with dilute mineral acid afforded the non-enolic γ -diketone **17**. The methoxyls of **16** are therefore



located at C-7 and not C-8. The nmr spectrum of the lactone derived from **16** by Baeyer-Villiger exhibits an overlapping pair of doublets at τ 5.68 ($J \sim 7$ Hz), the region expected for $-\text{COOCH} <$. Evidently the *cis* and *trans* couplings between vicinal hydrogens on the cyclobutane ring of the lactone are of comparable magnitude. There are several well-documented examples of bicyclo[4.2.0]octane derivatives in which the *cis* and *trans* vicinal hydrogen couplings constants are both 7–10 Hz.²⁰ Exposure of **16** to sodium methoxide caused no change; we therefore tentatively assign the *cis* ring fusion shown.

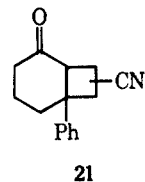
The photoaddition of **2** to isobutylene appears to follow the orientation scheme observed for dimethoxyethylene, the sole tractable product isolated being 6-phenyl-7,7-dimethylbicyclo[4.2.0]octan-2-one (**18**, 45%). Lactonization by the Baeyer-Villiger reaction by *m*-chloroperbenzoic acid gave a product which showed in the region of the nmr expected for hydrogen α to oxygen a one-hydrogen apparent triplet (τ 5.25, $J = 7.2$ Hz) from splitting by the two adjacent hydrogens on C-8 (*vide supra*). The methyls of **18** are thus probably at C-7, as the corresponding hydrogen signal in the lactone derived from the 8,8-dimethyl isomer should be a singlet. The ring fusion of **18** is assigned as *cis* on the basis of its stability to base.

Irradiation of 3-phenylcyclohexenone in the presence of excess cyclopentene gave, in addition to considerable quantities of intractable high molecular weight material, the adduct **19** in 38% yield. The 6–4 ring fusion is probably *cis*, as treatment with sodium methoxide produced no change.

Photoaddition of 3-phenylcyclohexenone to ethoxyethylene proceeded rapidly and gave a mixture of two products (**20**) in 78% combined yield. The adducts are assumed to be epimeric at the ethoxyl-bearing carbon and this position is assumed to be C-7 by analogy

with the adducts of **2** with dimethoxyethylene and isobutylene.

On irradiation of mixtures of 3-phenylcyclohexenone and acrylonitrile there was produced considerable quantities of polymer and an adduct (**21**) which was not

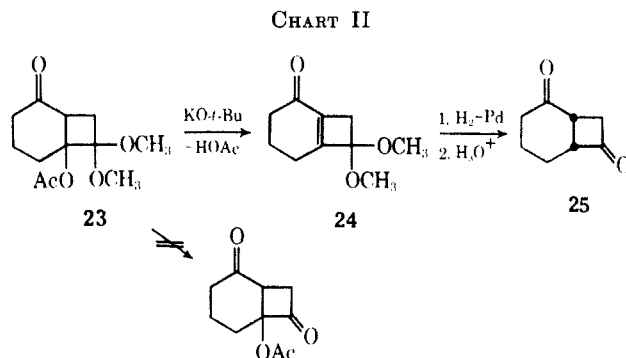


obtained analytically pure. The reasons for the difference in behavior of **1** and **2** on irradiation in acrylonitrile are not known.

Irradiation of 0.4 *M* solutions of 3-phenylcyclohexenone with no olefins present resulted in the isolation of a dimer, mp 194–195° (**22**). This compound has been mentioned briefly²³ and has been assigned the *syn*, head-to-head structure.

C. Products from 3-Acetylcyclohexenone.—3-Acetylcyclohexenone (**3**) was selected for study as an example of an enone with a mild electron-withdrawing group in the β position of the enone system, and because the adducts are potentially useful synthetic intermediates.¹⁸ The additions of **3** were much slower than those of the other enones studied here and those of the parent cyclohexenone, typically requiring 15–40 hr for consumption of 0.03 mole of starting material.

The photoaddition of 3-acetylcyclohexenone to 1,1-dimethoxyethylene gave a single adduct, 6-acetoxy-7,7-dimethoxybicyclo[4.2.0]octan-2-one (**23**), in 44% yield. The position of the methoxyls in **23** was established by the degradative sequence shown in Chart II. Meth-



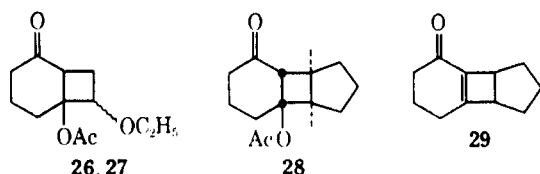
oxide-induced elimination of acetic acid from **23** gave the enedione monoketal **24**, characterized by spectral means. Hydrogenation of **24** followed by hydrolysis of the ketal function gave the previously known *cis*-dione **25**, identical with a sample prepared by hydrolysis of the adduct from 2-cyclohexenone and 1,1-dimethoxyethylene.⁴

The ketal function of **23** resisted all attempts at hydrolysis. A variety of acids in aqueous-organic solvents at temperatures up to 50° gave no reaction; higher temperatures caused decomposition to tarry material. Evidently the carbonyl oxygen of the nearby

(23) Reference 40 in P. Yates and M. J. Jorgenson, *J. Am. Chem. Soc.*, **85**, 2956 (1963).

acetoxyl group is a stronger base than the ketal oxygens and is preferentially protonated.²⁴

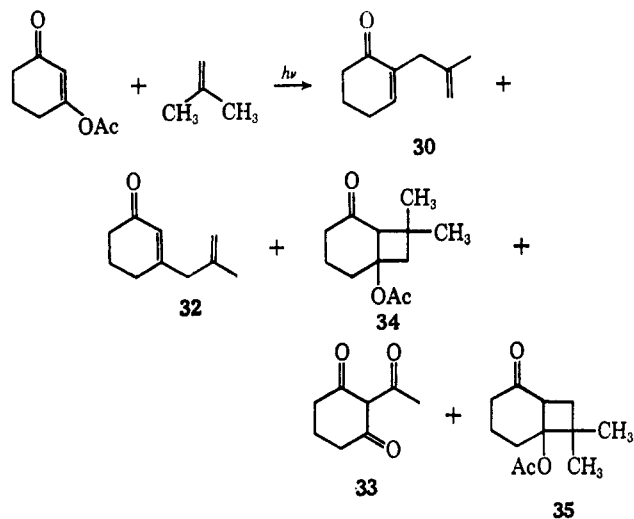
Photocycloaddition of 3-acetoxycyclohexenone to ethoxyethylene gave two isomeric adducts in 44 and 17% yields (**26** and **27**). The location of the ethoxyl group in these compounds at C-7 was established by the observation that the nmr signal due to the hydrogen on the ethoxyl-bearing carbon is a pair of doublets due to splitting by the adjacent methylene hydrogens. If the ethoxyl were at C-8, the C-8 hydrogen signal should be eight lines, as is the C-8 hydrogen of **10c**. It has previously been shown that the products from addition of methoxyethylene to cyclohexenone are 7-methoxybicyclooctanones.⁴



The irradiation of mixtures of 3-acetoxycyclohexenone and cyclopentene led to an especially clean photoaddition process which gave 7-acetoxycyclohexenone (**28**) in 68% yield (by gc, 43% isolated). This crystalline adduct, mp 58°, probably possesses a *cis* 6-4 ring juncture since it proved to be resistant to the effects of base. Prolonged treatment with potassium *t*-butoxide effected elimination of acetic acid, giving the enone **29**. Since the 5-4 ring fusion of **28** is almost certainly *cis*, this compound is assigned the *cis,anti,cis* stereochemistry.

The photoreaction of 3-acetoxycyclohexenone with isobutene was complete after 40 hr and gave a mixture of six products which were separated by preparative gc (Chart III); of these, two proved to be cycloaddi-

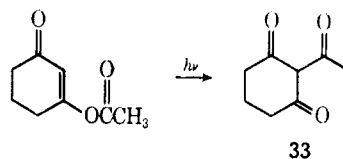
CHART III



tion products. The products and respective yields, in order of elution from a Carbowax 20-M column, are (1) 2-(β -methallyl)cyclohexenone (**30**, 17%), *x*-(β -methallyl)cyclohexenone (**31**, 6%), (3) 3-(β -

methallyl)cyclohexenone (**32**, 21%), (4) 2-acetyl-1,3-cyclohexanedione (**33**, 13%), (5) 6-acetoxy-8,8-dimethylbicyclo[4.2.0]octan-2-one (**34**, 25%), and (6) 6-acetoxy-7,7-dimethylbicyclo[4.2.0]octan-2-one (**35**, 13%). The enones **30** and **32** were identified by means of analytical and spectral data; the position of the β -methallyl group in the compounds followed from the chemical shift of the ring vinyl hydrogen of each isomer (τ 3.31 in **30** and 4.16 for **32**). The 3-substituted isomer **32** was conclusively identified by comparison with a sample prepared by reaction of β -methallylmagnesium chloride with 3-ethoxycyclohexenone. Compound **31** was obtained in an amount too small for positive identification, but appears to be a β -methallylcyclohexenone on the basis of infrared spectra. Trione **33** was identified by means of analytical, and infrared, ultraviolet, nmr, and mass spectral data, and by the blue copper complex, mp 264–266°, which it formed on treatment with cupric acetate.²⁵ This trione, isomeric with the starting enone, could be isolated in ~60% yield after irradiation of solutions of **3** in the absence of a substrate. This type of photoisomerization of enol esters, involving O-to-C acyl migration, has been previously observed in simpler enol acetates.²⁶ No **30** was observed among the products of irradiation of **3** with the more electron-rich olefins. Addition of the excited state of **3** to the relatively unreactive isobutylene is sufficiently slow that the unimolecular isomerization can compete with addition. The structural assignments of the cycloaddition products **34** and **35** rest on analytical and spectral data, particularly the nmr signal of the C-1 hydrogen in the ketones and the corresponding lactones derived by Baeyer–Villiger oxidation. In the spectrum of **34**, and the lactone derived therefrom, the signal is a sharp singlet (τ 7.29 in **31**, 5.64 in the lactone), whereas in the spectrum of **35** the signal is an apparent triplet (τ 6.96, $J = 10.2$ cps; τ 5.52 in the lactone) from splitting by the two hydrogens on C-8. As in all of the cycloadducts of **3**, the ease of elimination of acetic acid precluded assignment of the stereochemistry of the ring fusion.

Photoaddition of 3-acetoxycyclohexenone to the isomers of 1,2-dichloroethylene proceeded so slowly that the major product of irradiation of mixtures of **3** and the dichloroethylenes was the trione **33**. There could also be isolated a small amount of an adduct mixture of uncertain composition.



Irradiation of mixtures of 3-acetoxycyclohexenone and acrylonitrile led only to a low yield of trione **30** and to acrylonitrile polymers.

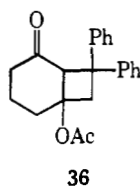
Photoaddition of 3-acetoxycyclohexenone to 1,1-diphenylethylene gave a single crystalline adduct (**36**, mp 172–173°) in low yield. The structure of **36** was deduced from the analytical and spectral data; in particular, the location of the phenyls at C-8 followed from

(24) Bicyclic diazaketals have recently been reported which were unusually resistant to hydrolysis: (a) E. L. Allred and C. Anderson, *J. Org. Chem.*, **32**, 1874 (1967); (b) N. P. Marullo and J. A. Alford, *ibid.*, **33**, 2368 (1968).

(25) H. Smith, *J. Chem. Soc.*, 803 (1953).

(26) A. Yogev, M. Gorodetsky, and Y. Mazur, *J. Am. Chem. Soc.*, **86**, 5208 (1964).

the observation that the signal for H-1 was a singlet (τ 6.32) rather than a multiplet, and that the methylene hydrogens appeared as a simple AB quartet ($J = 14$ Hz).



Sensitization Experiments.—Enones **1**, **2**, and **3** were irradiated in the presence of excess cyclopentene and in the presence of an equimolar amount of xanthone ($E_t = 74$ kcal) using a Pyrex filter, so that essentially all of the incident light was absorbed by the sensitizer. The extent of conversion of photoadducts after irradiation compared to the conversion in the absence of a sensitizer (Φ_s/Φ_0) was 0.54, 0.38, and 0.45 for **1**, **2**, and **3**, respectively. Although the cycloadditions proceeded somewhat less efficiently in the sensitized reactions, the results do indicate that the processes proceed *via* an initial triplet excited state, probably of the $n \rightarrow \pi^*$ type.

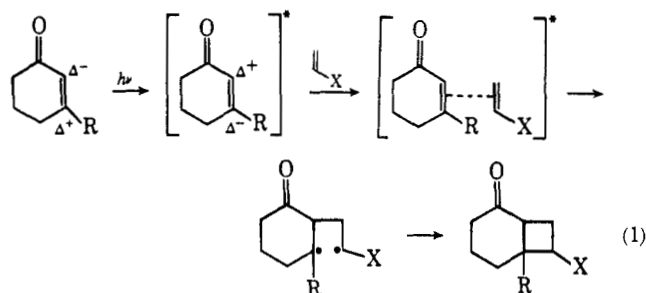
D. Competition Studies.—The results of competition studies in which an enone was irradiated in the presence of an equimolar mixture of two olefins are given in Table I. The reactions were followed gas chromatographically and checked to see that the ratio of products from the two substrates did not change during the course of the reaction.

Of interest is the surprisingly rapid reaction of 3-methylcyclohexenone with acrylonitrile. Corey found acrylonitrile to react far slower than any other substrate in his study on the parent cyclohexenone. The unusually rapid reaction with 3-methylcyclohexenone may be due to sensitization by the acrylonitrile. This olefin absorbs the major part of the incident light in the concentrations used in these experiments and may be acting as a singlet or triplet sensitizer. Another possibility is that reaction involves attack of an excited acrylonitrile molecule on a ground-state 3-methylcyclohexenone molecule. However, the reason for the difference in behavior of cyclohexenone and 3-methylcyclohexenone is not clear.

Discussion of Results

This study of the product structures and reactivity ratios in photocycloadditions of β -substituted enones has produced results which are, in general, consistent with the Corey hypothesis of an oriented π complex of excited enone and ground-state olefin being formed and subsequently collapsing to an intermediate which is of

predominantly diradical character. The orientation of the enone and substrate in the complex, and subse-



quently in the adduct, is governed mainly by the electron distribution in the substrate, with the more electron-rich carbon of the substrate being adjacent to the α -carbon of the enone. The cycloadditions are generally believed to proceed *via* an $n \rightarrow \pi^*$ excited state of the enone; these states possess relatively electron-rich β -carbons. For the parent cyclohexenone⁴ and for the substituted enones studied here, the course of addition to the olefins 1,1-dimethoxyethylene, ethoxyethylene, and benzyloxyethylene is that leading to the 7-substituted bicyclooctanones. However, the reverse orientation is observed in the addition of isobutylene to 3-methyl- and 3-acetoxycyclohexenone. Since isobutylene is less electron rich than the substrates mentioned, and might be expected to be the least subject to the electronic control of the enone excited state during the formation of the π complex, it seems possible that the steric interference that would be encountered by the two methyls approaching the β -substituent of **1** and **3** might outweigh the electronic effect and that the opposite orientation to that shown in eq 1 might be preferred. In accordance with this picture is the recent report by Eaton^{2a} that photocycloaddition of cyclopentenone to propene gives an adduct mixture in which the products predicted by eq 1 predominate by a factor of only 1.2:1. The observation in the present study that a 3-phenylcyclohexenone appears to add in the manner predicted by eq 1 may be the result of coplanarity of the phenyl and enone moieties in the excited state of **2**; a coplanar phenyl would not be expected to exert a large blocking effect.

The relative rates of addition of the various olefins to each enone vary over about one order of magnitude and support the view of intermediates and transition states with a low degree of charge separation. The mildly electron-withdrawing acetoxy group and the electron-donating methyl thus exert no dramatic effect on the course and nature of the reaction. It will be interesting to determine the effect of extremely strongly electron-

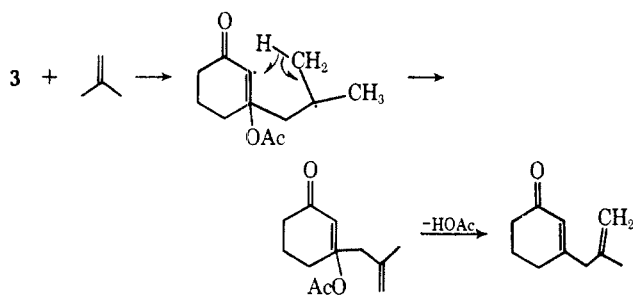
TABLE I

3-Methylcyclohexenone		3-Acetylcyclohexenone		3-Phenylcyclohexenone	
Olefin	Rel rate	Olefin	Rel rate	Olefin	Rel rate
Acrylonitrile	7.68	1,1-Dimethoxyethylene	4.40	1,1-Dimethoxyethylene	~18
Ethoxyethylene	1.96	Ethoxyethylene	3.48	Ethoxyethylene	~5.3
1,1-Dimethoxyethylene	1.27	Cyclopentene	1.00 ^a	Cyclopentene	1.00 ^a
		Isobutene ^b	0.47, 0.28 ^b	Isobutene	0.61
Cyclopentene	1.00 ^a				
Isobutene	0.59 ^a				
<i>trans</i> -1,2-Dichloroethylene	0.40				

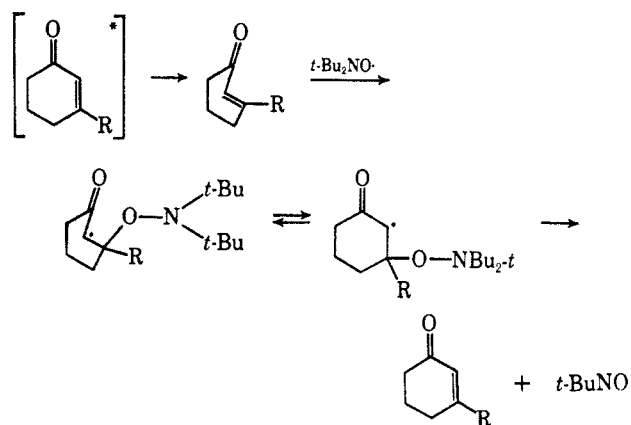
^a The reactivities of cyclopentene and dichloroethylene are corrected by a factor of 2, since they have two reactive centers which lead to the same product. ^b 0.47 for production of **32** and **34**, 0.28 for production of **30** and **35**.

donating and -withdrawing groups. Such studies are presently in progress.

Compounds **30** and **32** apparently arise from **3** and isobutene *via* a hydrogen-transfer process to give saturated β -acetoxy ketones which are 3,4-addition products of a Michael-type addition of isobutene to **3**. Elimination of acetic acid would give **30** and **32**. Such a facile elimination of acetic acid would be unexpected; however, the formation of 3,4-addition products has been previously observed in the photoaddition of isobutene to 2-cyclohexenone and its 3-methyl derivative (**1**).⁴ Indeed, in our hands, the major photoproducts from **1** and isobutene are the 3,4 and 4,3 addition products. Meinwald and Schneider²⁷ have proposed a rationalization for these and other 3,4 photoadditions on the basis of rates of hydrogen transfer from the intermediate diradicals, 3,4 addition predominating when the intermediate radical is tertiary and cycloaddition predominating when it is secondary. Since in the addition of isobutene to **1** and **3**, the radical resulting from attack of isobutene at C-3 is secondary and cycloaddition is more rapid; when attack is at C-2, the radical at C-3 is tertiary, hydrogen transfer is more rapid, and 3,4 addition predominates.



Still unaccounted for are the observations that cyclohexenone and 3-methylcyclohexenone give both *cis* and *trans* ring-fused adducts, whereas the 3-phenyl- and 3-acetoxycyclohexenone apparently give only cycloadducts possessing a *cis* fusion. Recently it was shown¹⁵ that di-*t*-butyl nitroxide quenched the formation of *cis* and *trans* cycloadducts of 4,4-dimethylcyclohexenone with different efficiencies. The authors argue that the *cis* and *trans* adducts arise from two different triplet states, possibly differing in geometry. The evidence available permits an alternative explanation, namely, that *trans*-fused adducts may arise from a highly strained ground state *trans*-cyclohexenone. *trans*-2-Cycloheptenones have been observed at low temperatures and shown to undergo a thermal 2 + 2 cycloaddition.²⁸ Although *trans*-2-cyclohexenones were not detected, it seems possible that they could be the precursors of the *trans*-fused cycloadducts from some cyclohexenes. Because of the enormous strain of the *trans* double bond in a six-membered ring, reaction could occur with di-*t*-butyl nitroxide to give an intermediate species which could undergo bond rotation, followed by dissociation. The quenching action of the nitroxide would thus be accounted for by a Schenck-type mechanism. Unfortunately, the data provided here do not permit a distinction to be made between the



intermediary of a second triplet and a strained ground-state enone. Experiments designed to answer this question are now under way.

Experimental Section

General Procedure for Irradiations.—The apparatus consisted of a cylindrical Pyrex irradiation vessel which surrounded a quartz immersion well and was fitted by means of side arms with a cold-finger condenser and a small serum bottle cap. Chilled water at 5–8° was passed through the annular space of the quartz well and also through an external bath in which the entire apparatus was immersed. For those reactions in which low-boiling substrates such as isobutene were employed, an ethylene glycol–water mixture cooled to –20° was passed through the well and through a cooling coil in an external glycol–water bath. Solutions of the enones and substrates in dry ethyl ether were placed in the vessel and were deoxygenated by flushing with purified nitrogen for 1.5 hr. A slight positive pressure of nitrogen was maintained throughout the irradiations. The solutions were irradiated by a Hanovia Type L medium-pressure 450-W mercury arc. A Correx filter sleeve was employed unless otherwise stated. This filter is opaque to light of wavelength shorter than 250 nm. The progress of the reaction was monitored by removing aliquots 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) 5 ft × 0.25 in. 5% Carbowax 20-M on Chromosorb P (column B), and (3) 12 ft × 0.25 in. 10% QF-1 fluoro-silicone rubber on Chromosorb W (column C). Preparative gas chromatographic separations were accomplished using either a 10 ft × 3/8 in. 20% Carbowax on Chromosorb P (column D) or a 12 ft × 3/8 in. 10% QF-1 on Chromosorb P (column E). Nuclear magnetic resonance spectra were obtained on a Varian A56-60A instrument operating at 38°.

Photoaddition of 3-Methylcyclohexenone (1) to 1,1-Dimethoxyethylene.—A solution of 3-methylcyclohexenone (5.47 g, 0.050 mol) and 1,1-dimethoxyethylene (45 g, 0.52 mol) in dry ether (170 ml) was irradiated under the standard conditions for 2.5 hr. Evaporation of the solvent and distillation of the residue gave two fractions: (1) bp 59–74° (0.15 mm), 1.3 g; gc analysis on column A showed >95% of starting enone **1** present; (2) 4.2 g, bp 84–105° (0.15 mm), analysis on column A showed two major peaks comprising 86% of the total area and five minor peaks comprising 14% of the total area. The two major components were isolated by preparative gc on column E. The faster moving major component had a retention time of 17.4 min at 180° and was identified as 6-methyl-7,7-dimethoxy-*cis*-bicyclo[4.2.0]-octan-2-one (**5b**, 38% based on unrecovered **1**): ir (film), 1702 (C=O) cm⁻¹; nmr (CCl₄), τ 6.86 and 6.90 (s, 3 H each, OCH₃), and 8.76 (s, 3 H, CCH₃). *Anal.* Calcd for C₁₁H₁₈O₂: C, 66.65; H, 9.14. Found: C, 66.37; H, 9.05.

The second major peak, of retention time 19.5 min at 180°, was found to be 6-methyl-7,7-dimethoxy-*trans*-bicyclo[4.2.0]-octan-2-one (**5a**, 26% based on unrecovered **1**): ir (film), 1718 (C=O) cm⁻¹; nmr (CCl₄), τ 6.76 and 6.90 (s, 3 H each, OCH₃) and 9.03 (s, 3 H, CCH₃). *Anal.* Found: C, 67.00; H, 9.21.

Epimerization of 5a to 5b.—A solution of 0.10 g of the *trans* isomer **5a** (0.50 nmol) and sodium (*ca.* 0.01 g) in methanol

(27) J. Meinwald and R. A. Schneider, *J. Am. Chem. Soc.*, **89**, 2023 (1967).

(28) (a) E. J. Corey, M. Tada, R. LeMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965); (b) P. E. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965).

(2 ml) was stirred under nitrogen at room temperature for 2 hr. The solution was poured into water and extracted twice with pentane. The combined pentane extracts were washed with water, dried, and evaporated. The faintly yellow oil remaining showed one gc peak on column A with the same retention time as 5b; the ir spectrum was identical with that of authentic 5b.

Hydrolysis of 5b to the Diketone 6.—A solution of 0.20 g (1.01 mmol) of a mixture of 5a and 5b was treated with sodium methoxide as described above. The material was added to a mixture of tetrahydrofuran (3 ml) and water (2 ml) containing 3 drops of concentrated hydrochloric acid and stirred at room temperature for 4 hr. Neutralization and work-up gave a yellow oil (0.18 g) which was distilled in a short-path apparatus to give colorless 6-methylbicyclo[4.2.0]octane-2,7-dione (6): bp 50–60° (bath temperature, 0.4 mm); ir (film), 1779 and 1700 (cyclohexanone and cyclobutanone C=O) cm^{-1} ; a ferric chloride test was negative. *Anal.* Calcd for $\text{C}_9\text{H}_{12}\text{O}_2$: C, 71.05; H, 7.89. Found: C, 70.81; H, 7.97.

Baeyer-Villiger Oxidation of 5a and 5b.—A solution of 5a (0.10 g, 0.50 mmol) and *m*-chloroperbenzoic acid (0.12 g, 0.65 mmol) in methylene chloride (5 ml) was allowed to stand at room temperature for 3 days. Filtration of the *m*-chlorobenzoic acid and evaporation of the solvent gave a semisolid residue containing unreacted peracid. This was extracted three times with pentane and the pentane extracts were evaporated to give the ϵ -lactone as a viscous oil: ir (film), 1738 cm^{-1} ; nmr (CCl_4), τ 5.86 (1 H, 2 doublets, $J = 9.2$ Hz, $J' = 8.4$ Hz, $>\text{CHOCO}$), 6.61 and 6.70 (3 H each, singlets, OCH_2), and 8.89 (3 H, s, CCH_3).

Lactonization of 5b in the same manner gave a colorless oil which appeared to be the expected ϵ -lactone: ir (film), 1731 ($\text{C}=\text{O}$) cm^{-1} ; nmr (CCl_4), τ 5.99 (1 H, apparent triplet, $J = 4.8$ Hz, CH_2CHOO), 6.82 and 6.94 (3 H each, s, OCH_2), and 8.75 (3 H, s, CCH_3).

Photoaddition of 3-Methylcyclohexenone to Cyclopentene.—A solution of 3-methylcyclohexenone (6.0 g, 0.054 mol) and cyclopentene (48 g, 0.70 mol) in ether (430 ml) was irradiated 2 hr using the standard conditions. The solvent was evaporated and the residue distilled to give the adduct mixture as a faintly yellow oil, 6.9 g (0.039 mol, 73%), bp 86–98° (0.15 mm). Analytical gc on column C showed three major peaks amounting to 91% of the total area. These are, in order of retention times at 160°, 9a (7.1 min, 6% of area, 4.8% yield), 9b (8.4 min, 32% yield), and 9c (9.2 min, 44% yield). The isomers were isolated by preparative gc on column E at 170°. Compound 9a was available only in very small amount and was not obtained analytically pure; ir (film), 1705 ($\text{C}=\text{O}$) cm^{-1} ; nmr (CCl_4), τ 8.77 (3 H, s, CCH_3). Isomer 9b was obtained as a colorless oil: ir (film), 1694 ($\text{C}=\text{O}$) cm^{-1} ; nmr (CCl_4), τ 7.78 (1 H, d, $J = 7.0$ Hz, CHCHCO), and 8.65 (3 H, s, CCH_3); no nmr signals below τ 6.5. Compound 9b is thus considered to be one of the stereoisomers of 7-methyltricyclo[6.3.0.0^{2,7}]undecan-3-one. *Anal.* Calcd for $\text{C}_{12}\text{H}_{18}\text{O}$: C, 80.91; H, 10.11. Found: C, 80.67; H, 10.04.

Compound 9c was obtained as white prisms from ether-pentane; mp 34–35°; ir (film), 1698 cm^{-1} ; nmr (CCl_4), τ 8.00 (1 H, d, $J = \sim 6$ Hz) (CHCHCO) and 9.02 (3 H, s, CCH_3); no signals below τ 7.0. A 2,4-dinitrophenylhydrazone of 9c, prepared in the standard fashion, had mp 162–163°. *Anal.* Found: C, 81.13; H, 10.27.

Epimerization of 9c.—A solution of the mixture of 9a, b, and c (0.10 g, 0.62 mmol) obtained directly by distillation was stirred with sodium methoxide (20 mg) in methanol (3 ml) for 5 hr. Neutralization of the reaction mixture and work-up afforded a colorless oil which analysis on column C showed to contain only 9a and 9b in a ratio of 52:48. The nmr spectrum of the product showed no CH_2 singlet at 9.02, whereas the signal due to 9a at 8.77 was greatly increased in size. Evidently 9c is converted to 9a by base.

Lactonization of 9b and 9c.—Samples of 9b and 9c were treated with *m*-chloroperbenzoic acid in 20% excess, in methylene chloride solution, for 4 days to effect Baeyer-Villiger oxidation. Work-up as described previously for 5a and 5b gave the ϵ -lactones derived from 9b and 9c as oils. The 9b-lactone showed the following spectral properties: ir (film), 1739 (lactone $\text{C}=\text{O}$) cm^{-1} ; nmr, τ 5.83 (1 H, 2 doublets $J = 7.8$ Hz, $J' = 2.0$ Hz, $>\text{CHOCO}$), and 8.78 (3 H, singlet, CH_3). The 9c-lactone data are ir (film), 1740 cm^{-1} ; nmr (CCl_4), τ 5.86 (1 H, doublet, $J = 5.2$ Hz, $>\text{CHOCO}$) and 9.00 (3 H, singlet, CH_3).

Photoaddition of 3-Methylcyclohexenone to Ethoxyethylene.—

A solution of 3-methylcyclohexenone (1, 5.0 g, 0.046 mol) and ethoxyethylene (50 g, 0.70 mol) in ether (160 ml) was irradiated under the standard conditions for 5 hr. Evaporation of the solvent and distillation of the residue gave the adduct mixture (5.8 g) as an oil, bp 83–110° (0.2 mm). Analysis on column B showed two major peaks (7a and b) representing 22 and 65% of the total peak area. Treatment of the mixture with sodium methoxide in methanol caused no change in composition as shown by gc and nmr. A sample of the mixture was redistilled for analysis, bp 60–70° (bath) (0.15 mm). *Anal.* Calcd for $\text{C}_{11}\text{H}_{18}\text{O}_2$: C, 72.53; H, 9.90. Found: 72.16; H, 9.64.

Photoaddition of 3-Methylcyclohexenone to Benzyloxyethylene.—A solution of 3-methylcyclohexenone (5 g, 0.046 mol) and benzyloxyethylene (67 g, 0.50 mol) in ether (150 ml) was irradiated using the standard conditions for 4.5 hr. Distillation of the residue gave, after 53 g of recovered benzyloxyethylene, the adduct mixture 8 as a viscous oil, bp 173–210° (0.1 mm), 4.1 g (39%). The crude mixture of 8a and b showed ir maximum (film) at 1703 cm^{-1} and in the nmr three broad singlets in the region τ 5.5–5.9 (methylene of benzyloxy). No olefinic hydrogen signals appeared in the nmr spectrum after base treatment, indicating that the benzyloxy groups of the isomer were in the 7 position. However, the number of peaks in the 5.5–5.9 region was reduced, probably because a *trans*-fused isomer was being epimerized to *cis*.

A sample of the crude mixture of isomers was degraded to the dione 6 by the following procedure. A solution of 8a, b (2.0 g, 8 mmol) and sodium methoxide (0.5 g) in methanol (50 ml) was stirred for 3 hr. The solution was neutralized and evaporated to dryness. The residue was extracted three times with 4:1 pentane-ether; the combined extracts were evaporated and the viscous oily residue was dissolved in ethyl acetate (70 ml) and hydrogenated over 10% palladium-charcoal under 15 psig hydrogen pressure. After the catalyst was removed by filtration and the product was recovered by evaporation of the solvent. The infrared spectrum of the oil thus obtained showed a broad, strong band at ~ 3400 cm^{-1} and a ketonic band at 1710 cm^{-1} , in agreement with expectation for 6-methyl-7-hydroxybicyclo[4.2.0]octan-2-one.

This material was dissolved in acetone (40 ml) and oxidized with Jones reagent (8 N chromic acid) at 20°. Evaporation of most of the acetone, addition of sodium chloride solution, and extraction with ether gave, after washing the extracts with bicarbonate solution, drying, and removal of solvent, a yellow oil which was distilled to afford 0.34 g of the diketone 6 (bp 50–60° at 0.15 mm). This material was chromatographed on a 20 \times 120 mm silica gel column and eluted with chloroform-hexane mixtures. Evaporation of the 1:2 chloroform-hexane fractions gave diketone 6 as a colorless oil (0.28 g), identical (ir and gc) with a sample previously obtained as described above.

Photoaddition of 3-Methylcyclohexenone to Acrylonitrile.—A solution of 3-methylcyclohexenone (5.0 g, 0.046 mol) and acrylonitrile (41 g, 0.75 mol) in ether (160 ml) was irradiated using the standard conditions for 2.5 hr. After filtration to remove some acrylonitrile polymer and evaporation of the solvent, the residue was distilled to give the adduct mixture as a viscous oil, bp 104–115° (0.15 mm), 4.9 g (64%). A viscous orange residue (1.6 g) remained in the distilling flask. Analysis on column C showed three major peaks (10a–c). Compounds 10b and 10c were isolated by preparative gc on column E at 195°; we were unable to obtain 10a free of 10b since none of the columns tried gave a clean separation. Compound 10c (retention time 13.0 min at 195° on column C; 17% by gc peak areas) was obtained as a colorless oil: ir (CCl_4), 2236 ($\text{C}=\text{N}$) and 1696 ($\text{C}=\text{O}$) cm^{-1} ; nmr (CCl_4), τ 6.58 (1 H, eight-line pattern which is the A portion of an ABXY multiplet; $J_{AB} = 10.4$ Hz, $J_{AX} = 8.5$ Hz, $J_{AY} = 7.5$ Hz, $>\text{CHCHCNCH}_2$), 7.28 (1 H, doublet, B portion of ABXY pattern where $J_{AB} = 10.4$ Hz, $J_{BX} = J_{BY} = 0$ Hz, COCHCHCN) and 8.73 (3 H, s, CCH_3). *Anal.* Calcd for $\text{C}_{10}\text{H}_{13}\text{NO}$: C, 73.61; H, 7.98. Found: C, 73.42; H, 8.24.

Compound 10b (retention time 11.0 min at 195° on column C; 29% yield by gc) was collected from column E as a colorless oil, contaminated with ca. 30% of 10a; ir (film), 2240 ($\text{C}=\text{N}$) and 1707 ($\text{C}=\text{O}$) cm^{-1} ; nmr (CCl_4), τ 6.83 (1 H, eight lines which are the A portion of an ABXY multiplet, $J_{AB} = 6.6$ Hz, $J_{AX} \sim 8$ Hz, $J_{AY} \sim 6$ Hz, CHCN), 7.24 (1 H, doublet, B half of AB pattern, $J = 6.6$ Hz, $\text{COCHCH}(\text{CN})$ —), and 8.58 (3 H, s, CH_3). *Anal.* Found: C, 73.18; H, 7.69.

Isomer 10a (retention time 10.4 min at 195° on column C;

11% by gc) was isolated only as mixtures with **10b**. It showed the following spectral properties: ir (film), 2240 and 1701 cm^{-1} .

Epimerization of Adduct 10c.—A solution of mixture as obtained directly from distillation (0.10 g), sodium methoxide (0.025 g), and methanol (3 ml) was stirred at room temperature for 6 hr. Neutralization with Dry Ice and work-up gave a yellow oil (0.083 g) which showed peaks for **10a**, **b**, and **c** in the ratio 23:70:7; the ratio before base treatment was 18:52:30. The nmr spectrum of the product mixture showed no signal for the methyl of **10c** at 8.73, whereas the methyl signal at 8.58 was of increased intensity.

Baeyer-Villiger Oxidation of 10b and 10c.—Samples of **10b** and **10c** (0.10 g each) and *m*-chloroperbenzoic acid (0.14 g for each ketone) were refluxed in methylene chloride for 3 days. The reaction mixtures were filtered and examined by nmr directly. In the spectrum of the lactone derived from **10b**, the doublet at τ 7.24 had almost vanished and was replaced by a new doublet at 5.90 ($J = 7.6$ Hz, CHOCO); the multiplet at 7.24, due to H-8, did not change position. In the spectrum of the **10c**-lactone, the doublet at τ 7.28 was missing and replaced by a broadened doublet at 5.87. The multiplet for H-8 appeared at 6.62.

Photoaddition of 3-Methylcyclohexenone to *cis*- and *trans*-1,2-Dichloroethylene.—A solution of 3-methylcyclohexenone (5.00 g, 0.046 mol) and *trans*-1,2-dichloroethylene (60 g, 0.62 mol) in dry ether (150 ml) was irradiated for 7 hr, using the standard conditions. Evaporation of the solvent and excess dichloroethylene gave the adduct mixture as a golden oil which underwent partial decomposition on attempted distillation. Analysis on column C showed two major components, **11a** and **11b**, in 48 and 33% yield and a number of minor components (17% total). Preparative gc on column E caused elimination of hydrogen chloride from **11a** and to the isolation of monochloro ketone **12** and dichloro ketone **11b**. After short-path distillation **12** was a colorless oil: ir (film), 1688 (conj $\text{C}=\text{O}$) cm^{-1} ; nmr (CCl_4), τ 3.08 and 3.62 (2 H, AB quartet, $J = 13$ Hz, *cis* $\text{CH}=\text{CH}$), and 8.00 (3 H, s, $\text{C}=\text{CCH}_3$); uv (CH_3OH), 267 nm (ϵ 7300). Accurate analytical data could not be obtained as **12** decomposed on storage.

Compound **11b** was isolated either by preparative gc on column E or, in larger amount, by stirring the crude adduct mixture at 5° with 0.3 equiv of triethylamine and fractional distillation of the product. After **12**, bp 65–80° (0.2 mm) there was obtained **11b** as a yellow oil, bp 116–121° (0.2 mm), which solidified in the receiver. Recrystallization from ether–pentane gave pure **11b** as white prisms: mp 53–55°; ir (CCl_4), 1710 ($\text{C}=\text{O}$) cm^{-1} ; nmr (CCl_4), τ 5.82 and 5.98 (2 H, five-line multiplet, AB portion of ABX pattern in which $J_{\text{AX}} = 0$ Hz, $J_{\text{AB}} = 8.0$ Hz, $J_{\text{BX}} \sim 8$ Hz, CHClCHCl), 7.49 (1 H, doublet, $J = 8$ Hz, COCH —), and 8.66 (3 H, s, CH_3). Anal. Calcd for $\text{C}_9\text{H}_{12}\text{Cl}_2\text{O}$: C, 52.42; H, 5.34. Found: C, 52.74; H, 5.57.

Photoaddition of 3-Phenylcyclohexenone to 1,1-Dimethoxyethylene.—A solution of 3-phenylcyclohexenone (3.44 g, 0.020 mol) and 1,1-dimethoxyethylene (27 g, 0.30 mol) in dry ether (180 ml) was irradiated 3 hr using the standard conditions, except that a Pyrex filter was employed. Distillation of the ether and excess dimethoxyethylene gave a viscous yellow oil which was evaporatively distilled in a short-path apparatus at 0.05 mm (bath temperature 70–80°). There was thus obtained a viscous oil (4.4 g, 87%) which showed two peaks on column C at 200° in the ratio 97:3. The material eventually solidified on standing in the refrigerator. Recrystallization from ethyl acetate–hexane at 5° gave pure 6-phenyl-7,7-dimethoxybicyclo[4.2.0]octan-2-one as colorless, chunky prisms: mp 55–56°; ir (CCl_4), 1698 ($\text{C}=\text{O}$), 1039 and 1070 (CO) cm^{-1} ; nmr (CCl_4), τ 2.82 (5 H, s, C_6H_5), 6.67 and 7.05 (3 H each, s, OCH_3). Compound **16** was recovered unchanged after exposure to methanolic sodium methoxide. Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$: C, 73.85; H, 7.68. Found: C, 73.59; H, 7.39.

Hydrolysis of 16 to Diketone 17.—A solution of adduct **1** (0.27 g, 1.0 mmol) and concentrated hydrochloric acid (3 drops) in 80% aqueous dioxane (5 ml) was stirred 2 hr at room temperature. The solution was neutralized, poured into water, and extracted with ether. The ether extracts were washed four times with saturated sodium chloride solution, dried MgSO_4 , and evaporated to give a yellow oil which was short-path distilled, bp 80–90° (0.3 mm), to give 6-phenylbicyclo[4.2.0]octane-2,7-dione (**17**) as a colorless oil: ir (film), 1781 (4-ring $\text{C}=\text{O}$) and 1708 (6-ring $\text{C}=\text{O}$) cm^{-1} ; nmr (CCl_4), τ 2.7–2.9 (5 H, multiplet, C_6H_5) and 7.6–8.2 (9 H, multiplets, aliphatic H). A

ferric chloride test was negative. No enolic hydrogen signal was observed in the nmr or ir spectrum. A 2,4-dinitrophenylhydrazone prepared in the usual manner showed mp 151–154°. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.51; H, 6.54. Found: C, 78.75; H, 6.33.

Photoaddition of 3-Phenylcyclohexenone to Isobutene.—A solution of 3-phenylcyclohexenone (3.44 g, 0.020 mol) and isobutene (30 g, 0.53 mol) in dry ether (180 ml) was irradiated at –20° through a Pyrex filter for 5 hr. Evaporation of the ether and excess isobutene followed by vacuum distillation gave a clear viscous oil (2.1 g, 45%), bp 94–100° (0.15 mm). A considerable amount of nonvolatile residue remained in the distillation flask. Analysis on columns A and C showed a single peak. The oil was taken to be the cycloadduct, 6-phenyl-7,7-dimethylbicyclo[4.2.0]octan-2-one (**18**): ir (CCl_4), 1694 ($\text{C}=\text{O}$) and 1600 (C_6H_5) cm^{-1} ; nmr (CCl_4), τ 2.8–3.15 (5 H, broad, C_6H_5), 6.77 (1 H, apparent triplet, $J = 9.8$ Hz, CH_2CHCO), 8.73 and 9.27 (3 H each, s, $\text{C}(\text{CH}_3)_2$). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2$: C, 84.22; H, 8.77. Found: C, 83.97; H, 8.91.

Two days exposure to methoxide was without effect; **18** is therefore considered to possess a *cis* ring fusion. That the proton on C-1 of **18** indeed exchanged under these conditions was demonstrated by the disappearance of the triplet at τ 6.77 in the nmr after treatment with $\text{CH}_3\text{ONa}-\text{CH}_3\text{OD}$. The incorporation of ~3 atoms of deuterium/molecule was shown by mass spectrometry.

Baeyer-Villiger Oxidation of Adduct 18.—A solution of adduct **18** (0.23 g, 1.0 mmol) and *m*-chloroperbenzoic acid (0.22 g, 1.2 mmol) in methylene chloride (5 ml) was stored at room temperature 3 days. Evaporation of the methylene chloride, extraction of the residue with three portions of pentane, and evaporation of the pentane extracts gave the ϵ -lactone as a viscous oil: ir (film), 1743 cm^{-1} ; nmr (CCl_4), τ 5.25 (1 H, apparent triplet, $J = 7.2$ Hz, COCHCH_2).

Photoaddition of 3-Phenylcyclohexenone to Cyclopentene.—A solution of 3-phenylcyclohexenone (3.44 g, 0.020 mol) and cyclopentene (21 g, 0.31 mol) in ether (180 ml) was irradiated through a Pyrex filter for 8 hr. The residue remaining after evaporation of the ether and excess cyclopentene was subjected to short-path distillation. There was obtained the adduct, 7-phenyltricyclo[6.3.0.0^{2,7}]undecan-3-one (**19**) as a viscous colorless oil, bp 100–110° (bath temperature) (0.3 mm), 1.86 g, 38%. A considerable amount (2.1 g) of nonvolatile orange gum remained in the distillation apparatus. The oil showed one spot on tlc (silica gel G, benzene) and one peak on gc columns B and C; ir (CCl_4), 1695 ($\text{C}=\text{O}$) cm^{-1} ; nmr (CCl_4), τ 2.8–3.2 (5 H, multiplets, C_6H_5), and 7.08 (1 H, s, COCHCH). Exposure of **19** to methanolic methoxide caused no change as shown by gc and nmr. Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}$: C, 85.03; H, 8.33. Found: C, 84.71; H, 8.77.

Photoaddition of 3-Phenylcyclohexenone to Ethoxyethylene.—A solution of 3-phenylcyclohexenone (3.44 g, 0.020 mol) and ethoxyethylene (25 g, 0.34 mol) in ether (180 ml) was irradiated 5 hr through Pyrex. Evaporation of the ether and excess olefin, followed by distillation, gave the adduct mixture (**20**) as a pale yellow oil, bp 80–103° (0.2 mm), 3.96 g (79%). Analysis on column B at 190° showed two components in the ratio 72:28. Exposure on base caused no change and the isomers are probably epimeric at the ethoxyl-bearing carbon. The mixture shows an ir maximum (CCl_4) at 1706 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2$: C, 78.33; H, 8.46. Found: C, 78.02; H, 8.32.

Photoaddition of 3-Phenylcyclohexenone to Acrylonitrile.—Irradiation of 3-phenylcyclohexenone (1.72 g, 0.01 mole) and acrylonitrile (40 g) in ether (170 ml) for 7 hr through Pyrex gave, after filtration of polymer and evaporation of solvent and excess acrylonitrile, a very viscous yellow syrup which afforded 0.6 g of faintly yellow oil on short-path distillation; bp 120–130° (0.2 mm). Tlc on silica gel G indicated the presence of several overlapping spots; the nmr spectrum was not sufficiently well resolved to yield information other than the presence of phenyl and CHCN hydrogen signals.

Photoaddition of 3-Acetoxycyclohexenone to 1,1-Dimethoxyethylene.—A solution of 3-acetoxycyclohexenone (3.54 g, 0.023 mol) and 1,1-dimethoxyethylene (43 g, 0.48 mol) in dry ether (160 ml) was irradiated 6 hr using the standard conditions. Distillation of the ether and excess dimethoxyethylene gave an oil which was distilled to yield two fractions: (a) 0.75 g, bp 60–75° (0.2 mm), >95% recovered **3** by gc; and (b) 2.98 g, bp 96–110° (0.2 mm); gc on column B indicates this fraction is composed of two components: unchanged **3** and the adduct **23**

in a 11:89 ratio. The total yield of **23** was 2.69 g (48%) by gc. Attempted fractional distillation or preparative gc of distillation fraction b led to considerable loss by thermal decomposition. Eventually, the fraction partially crystallized; recrystallization from ethyl acetate-hexane at 0° gave the pure adduct, 6-acetoxy-7,7-dimethoxybicyclo[4.2.0]octan-2-one (**23**) as colorless prisms: mp 58–59°; ir (film), 1737 (ester C=O), 1711 (ketone C=O), and 1235 (C—O) cm⁻¹; nmr (CCl₄), τ 6.72 and 6.79 (3 H each, s, OCH₃), 7.18 (1 H, 2 d, $J = 10.4$ Hz; $J' = 8.8$ Hz, COCHCH₂), and 8.00 (3 H, s, OCOCH₃).

Anal. Calcd for C₁₂H₁₈O₅: C, 59.49; H, 7.44. Found: C, 59.11; H, 7.30.

Photoaddition of 3-Acetoxy-cyclohexenone to Ethoxyethylene.—

A solution of 3-acetoxy-cyclohexenone (8.78 g, 0.057 mol) and redistilled ethoxyethylene (94.5 g, 1.31 mol) in dry ether (110 ml) was irradiated 18 hr using the standard conditions. Removal of the ether and excess ethoxyethylene under reduced pressure and distillation of the residue gave a mixture of adducts (**26** and **27**) as a viscous oil, bp 115–138° (0.2 mm), 7.8 g, 65%. Analysis on column B showed three peaks in area ratio 66:25:8, corresponding to yields of 44, 16, and 5%. The two major components were isolated by collection from column D at 210°. The major isomer (retention time 12.3 min) **26** was a viscous oil: ir (CHCl₃), 1740 (ester C=O) and 1709 (ketone C=O) cm⁻¹; nmr (CCl₄), τ 6.01 (1 H, 2 d, $J = 5$ Hz, $J' = 4.5$ Hz, COCHCH₂), 6.43 and 8.85 (2 and 3 H, q and t, OCH₂CH₃), and 7.94 (3 H, s, OOCCH₃). Anal. Calcd for C₁₂H₁₈O₄: C, 63.71; H, 7.98. Found: C, 63.27; H, 8.28.

The isomer of retention time 14.8 min (**26b**) possessed ir (film) 1709 (C=O) cm⁻¹; nmr (CCl₄), τ 5.90 (1 H, apparent triplet, $J = 9.5$ Hz, COCHCH₂), 6.35 and 8.78 (q and t, $J = 7$ Hz, OCH₂CH₃), and 7.97 (3 H, s, OOCCH₃). Anal. Found: C, 62.78; H, 8.13.

Photoaddition of 3-Acetoxy-cyclohexenone to Cyclopentene.—

A solution of 3-acetoxy-cyclohexenone (8.45 g, 0.055 mol) and cyclopentene (55 g, 0.74 mol) in dry ether (400 ml) was irradiated 28 hr, using the standard conditions. After distillation of the ether and excess cyclopentene at atmospheric pressure, the residue was fractionated *in vacuo* to give unreacted starting enone (bp 35–76° at 0.1 mm) (1.15 g) and the adduct **28** (bp 94–112° at 0.1 mm) (7.08 g) as a colorless oil which partially solidified on standing. Recrystallization from ethyl acetate-hexane gave pure **28** as white chunky prisms, mp 48–49°. The yield of recrystallized **28** was 43%. Analysis on column B of the second distillation fraction indicated it contained only starting enone and **28**; the yield of **28** by gc was 68%, based on unrecovered enone. Compound **28** exhibited the following spectral properties: ir (CHCl₃), 1738 (ester C=O), 1709 (ketone C=O), and 1230 and 1245 (CO) cm⁻¹; nmr (CCl₄), 7.79 (1 H, d, $J = 5.4$ Hz, COCHCH), and 8.04 (3 H, s, OOCCH₃). Anal. Calcd for C₁₁H₁₆O₃: C, 70.27; H, 8.11. Found: C, 70.34; H, 8.19.

Exposure of **28** to basic alumina or sodium methoxide at 5° caused no change. Treatment with methoxide at room temperature and work-up in the usual manner gave an oil whose spectral data [ir (film) 1674 cm⁻¹; no acetyl singlet at 7.5–8.5 region in nmr] suggested it was the product of elimination of acetic acid. The material gave a red 2,4-dinitrophenylhydrazone, mp 146–147°.

Conversion of **28** to the corresponding ϵ -lactone was accomplished by allowing a solution of **28** (21 g, 1.0 mmol) and *m*-chloroperbenzoic acid (1.8 g, 1.1 mmol) in methylene chloride (9 ml) to stand 96 hr at room temperature. Filtration and evaporation of the solvent gave a viscous colorless oil, whose ir spectrum [ν_{\max} (film) 1729 cm⁻¹] indicated that ~90% conversion to the lactone had taken place. The nmr (CCl₄) spectrum showed, *inter alia*, signals at τ 6.23 (1 H, d, $J = 5.5$ Hz, COOCHCH) and 8.01 (3 H, s, OOCCH₃).

Baeyer-Villiger Oxidation of Adduct 23.—A solution of the adduct **23** (0.17 g, 0.70 mmol) and *m*-chloroperbenzoic acid (0.22 g, 0.9 mmol) in methylene chloride (5 ml) was refluxed 72 hr. Cooling, filtration, evaporation of solvent, and short-path distillation gave the ϵ -lactone as a colorless viscous oil: bp 100–110° (0.15 mm); ir (CCl₄), 1736 (ester C=O and lactone C=O) cm⁻¹; nmr (CCl₄), τ 6.74 (1 H, 2 d, $J \sim 10$ Hz, $J' \sim 8$ Hz, COOCHCH₂).

Elimination of Acetic Acid from 23. Formation of 24.—A solution of adduct **23** (0.12 g, 0.45 mmol) and sodium (ca. 20 mg) in methanol (3 ml) was stored at room temperature 2 hr. Neutralization, extraction, and work-up gave a yellow

oil which was distilled to give pure 7,7-dimethoxybicyclo[4.2.0]oct-1(6)-en-2-one (**24**): bp 55–58° (0.1 mm) (0.063 g, 70%); ir (film), 1684 (conj C=O) cm⁻¹; nmr (CCl₄), τ 6.72 (6 H, s, 2 OCH₃) and 7.30 (2 H, s, CH₂C). A 2,4-dinitrophenylhydrazone prepared in the standard fashion crystallized from ethyl acetate-ethanol as red leaflets, mp 126–128°. Anal. Calcd for C₁₀H₁₄O₃: C, 66.92; H, 7.89. Found: C, 66.56; H, 8.21.

Hydrogenation-Hydrolysis of 24 to Diketone 25.—A solution of dimethoxy ketone **24** (0.040 g, 0.22 mmol) in ethyl acetate was hydrogenated (5 psig) for 75 min; filtration and evaporation of the solvent gave the saturated ketal-ketone, ν_{\max} 1710 cm⁻¹. Hydrolysis of the ketal function was accomplished by stirring the crude product with one drop of concentrated hydrochloric acid in 80% aqueous tetrahydrofuran. Dilution with water and continuous extraction with ether, followed by evaporation of the ether extracts, gave the diketone **25** as an oil, bp 40–50° (0.2 mm), identical (gc, ir) with a sample prepared by hydrolysis of the cyclohexenone-dimethoxyethylene photoadduct mixture as described by Corey, *et al.*⁴

Photocondensation of 3-Acetoxy-cyclohexenone and Isobutene.—A solution of 3-acetoxy-cyclohexenone (12.2 g, 0.080 mol) and isobutene (~130 ml, ~1.6 mol) in dry ether (440 ml) was irradiated 36 hr at ~-15°. A cold (-20°) ethylene glycol-water mixture was circulated through the jacket of the immersion well and through an external cooling bath. After evaporation of the ether and excess isobutene, the residue was distilled to give the mixture of products as a yellow oil, bp 60–125° (0.1 mm), 14.1 g. Partial separation of the mixture could be effected by fractionation on a spinning-band column; however, some decomposition of the less volatile components usually occurred and preparative gc was used. Analysis on column B indicated the presence of six major components amounting collectively to 96% of the total area of the chromatogram. The components were collected in the effluent from column D at 220°.

Compound 30.—The material giving a peak of retention time 7.0 min was redistilled to give **30**, 2- β -methyl-2-cyclohexenone (17% of area, 14% yield): ir (film), 1672 (conj C=O) and 1614 (C=C) cm⁻¹; nmr (CCl₄), 3.3 (1 H, m, C=CH), 5.3 (2 H, m, C=CH₂), 7.15 (2 H, broad, =CCH₂C=C), and 8.34 (3 H, t, $J = 1$ Hz, C=CCH₃). Anal. Calcd for C₁₀H₁₄O: C, 80.00; H, 9.33. Found: C, 79.63; H, 9.51.

A 2,4-dinitrophenylhydrazone of **30** was prepared in the usual manner. Recrystallization from ethanol gave tiny red leaflets, mp 142–144°.

Compound 31.—The second peak (retention time 10.5 min), a viscous yellow oil, was not positively identified, but appears to be a β -methylcyclohexanone from its infrared (ν_{\max} 1702 and 903 cm⁻¹) and nmr (τ 5.3, 2 H, m, C=CH₂; no acetyl or vinyl signals).

Compound 32.—Collection of the third major peak (retention time 15.1 min) and redistillation gave **32**, 3-(β -methyl)-2-cyclohexenone (19% yield): ir (film), 1670 (conj C=O) and 1621 (C=C) cm⁻¹; nmr (CCl₄), τ 4.16 (1 H, m, COCH=C), 5.08 and 5.17 (2 H, broad s, C=CH₂), 7.09 (2 H, m, C=CCH₂C=C), and 8.28 (3 H, m, C=CCH₃). Anal. Calcd for C₁₀H₁₄O: C, 80.00; H, 9.33. Found: C, 79.67; H, 9.26.

A 2,4-dinitrophenylhydrazone of **32**, prepared in the standard β -methyl chloride (4.5 g, 0.05 mol) and magnesium (1.3 g) in dry ether (80 ml) for 20 hr was treated with 3-ethoxycyclohexenone (6.0 g, 0.043 mol) and the solution was stirred and refluxed 6 hr. Hydrolysis with ice and aqueous hydrochloric acid followed by the usual work-up gave **32**, bp 73–76° (0.3 mm), identical (ir, nmr, gc) with the sample obtained as described previously.

Compound 33.—The fourth major component was collected from column D (retention time 23.5, 13% of area, 10% yield) as a yellowish solid. Recrystallization from ether-benzene gave pure trione **33**, mp 25–27°, identical (ir, gc, nmr) with a sample prepared by photoisomerization of **3** in the absence of a substrate (*vide infra*).

Compound 34 was collected from the effluent of column D (retention time 36 min, 25% of area, 21% yield), or with less thermal decomposition, from a 5 ft \times $\frac{3}{8}$ in. Carbowax 20M on Chromosorb P column (column F) (retention time 22 min). Redistillation gave the analytical sample of **33**, 6-acetoxy-8,8-dimethylbicyclo[4.2.0]octan-2-one, as a colorless viscous oil: ir (CHCl₃), 1734 (ester C=O), 1700 (ketone C=O), and 1235 (CO) cm⁻¹; nmr (CDCl₃), τ 7.29 (1 H, s, COCH(CH₃)₂), 7.88

(2 H, AB, $\Delta\nu \approx 12$, $J = 11$ Hz, $(\text{H}_3\text{C})_2\text{CCH}_2\text{C}$), 8.02 (3 H, s, OOCCH_3), and 8.70 and 9.01 (3 H each, s, CCH_3). *Anal.* Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_3$: C, 68.57; H, 8.57. Found: C, 68.32; H, 8.73.

Adduct **34** was subjected to Baeyer-Villiger oxidation by treating a sample (40 mg) with *m*-chloroperbenzoic acid (50 mg) in methylene chloride solution in an nmr sample tube. After standing 3 days at room temperature the *m*-chlorobenzoic acid had settled to the bottom of the tube and the nmr spectrum of the ϵ -lactone was obtained directly; τ 5.64 (1 H, s, $\text{COOCH}(\text{CH}_3)_2$), 7.90 (1 H, d, lower limb of AB, $J = 11$ Hz), 7.96 (3 H, s, OOCCH_3), and 8.75 and 8.88 (3 H each, s, $\text{C}(\text{CH}_3)_2$).

Compound **35** underwent appreciable decomposition on column D because of its long retention time (~ 50 min) and was collected from column F (31 min, 13% of area, 10% yield). Micro short-path distillation gave pure **35**, 6-acetoxy-7,7-dimethylbicyclo[4.2.0]octan-2-one, as a colorless oil: ir (CHCl_3), 1731 (ester $\text{C}=\text{O}$), 1702 (ketone $\text{C}=\text{O}$), and 1240 ($\text{C}-\text{O}$) cm^{-1} ; nmr (CDCl_3), τ 6.96 (1 H, apparent triplet, $J = 10.3$ Hz, COCH_2CH_2), 8.03 (3 H, s, OOCCH_3), and 8.83 (6 H, broad s, $\text{C}(\text{CH}_3)_2$). *Anal.* Found: C, 68.19; H, 8.30.

Baeyer-Villiger oxidation of **35** proceeded only with difficulty; after 3 days of refluxing of a solution in methylene chloride with *m*-chloroperbenzoic acid, an nmr spectrum was obtained which suggested that a mixture of ketone and the corresponding ϵ -lactone in a ratio of ca. 60:40 was present. The spectrum exhibited, in addition to the singlets at τ 8.01 and 8.83 characteristic of the ketone **35**, new signals at 7.95 and 8.80, in the ratio 3:6. There was also a new apparent triplet at τ 5.52 ($J \sim 8$ Hz) ($\text{OOCCH}_2\text{CH}_2$).

Photoisomerization of 3-Acetoxy-cyclohexenone.—A solution of 3-acetoxy-cyclohexenone (5.0 g, 0.033 mol) in dry ether (225 ml) was irradiated under the standard conditions for 60 hr. Evaporation of the ether followed by vacuum distillation gave an oil (3.8 g), bp 88–90° (0.2 mm), which solidified in the receiver. Recrystallization from ether-benzene at 5° gave 2-acetyl-1,3-cyclohexanedione (**33**) as thick white prisms: mp 27–28° (lit. mp 28–29°); 2.97 g (60%); ir (CHCl_3), ca. 1560 (enolic β -diketone); nmr (CHCl_3), singlets at τ -1 (enol CH) and 7.48 (CCH_3). *Anal.* Calcd for $\text{C}_8\text{H}_{10}\text{O}_3$: C, 62.34; H, 6.48. Found: C, 62.09; H, 6.57.

Shaking an ether solution of **33** with saturated aqueous cupric sulfate gave the blue copper complex of **33**, mp 264–266°, after recrystallization from chloroform (lit.²⁵ mp 263–265°). This sample was identical with one prepared from **33** isolated from the irradiation of **3** in the presence of isobutylene (*vide supra*).

Photoaddition of 3-Acetoxy-cyclohexenone to Dichloroethylene.—A solution of 3-acetoxy-cyclohexenone (3.0 g, 0.020 mol) and *trans*-1,2-dichloroethylene (40 g, 0.42 mol) in ether (170 ml) was irradiated 50 hr under the standard conditions. Evaporation of the excess dichloroethylene gave a viscous oil (3.2 g). Analysis on column C indicated the presence of $\sim 20\%$ unchanged starting material, 50% of the photoisomer **33**, and $\sim 10\%$ of unknown material of short retention time. The remaining 20% of the material showed two broad peaks of approximate retention times 28 and 31 min. These are evidently photoadducts. Attempts to isolate these peaks by fractional distillation and preparative gc were unsuccessful because of decomposition of the compounds.

Photoaddition of 3-Acetoxy-cyclohexenone to 1,1-Diphenylethylene.—A solution of 3-acetoxy-cyclohexenone (2.0 g, 0.013 mol) and 1,1-diphenylethylene (27 g, 0.15 mol) in ether (180 ml) was irradiated 18 hr through Pyrex. Distillation of the ether

at atmospheric pressure and the excess diphenylethylene under reduced pressure gave a yellow syrup (3.1 g) which partially crystallized on trituration with ether-pentane. The crude product, after filtration, was recrystallized from ethyl acetate-hexane to give the adduct **36** as white prisms, mp 172–173° (0.41 g, $\sim 10\%$). Chromatography of the mother liquors on silica gel gave no further crystalline material; considerable quantities of polar, high molecular weight material adhering strongly to the column were present. Compound **36** showed the following spectral data: ir (KBr), 1720, 1738 (cm^{-1}); nmr (CDCl_3), τ 2.3–2.8 (10 H, m, C_6H_5), 6.32 (1 H, s, COCHCPh_2), and 8.18 (3 H, s, OAc). *Anal.* Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_3$: C, 79.31; H, 6.59. Found: C, 79.01; H, 6.56.

Competition studies were performed by irradiating an enone in the presence of an equimolar amount of each of two olefins, usually a tenfold excess of each being employed. The reactions were monitored by gc to ensure that the ratios of the two sets of products did not change appreciably during the course of the reactions. The area of the peaks corresponding to the sets of products from the two substrates were measured and the ratios were considered to represent the relative reactivities. Each value in Table I is the average of at least two determinations.

Sensitization Experiments.—Solutions of 0.02 mol of each enone, 0.02 mol of xanthone, and 0.4 mol of cyclopentene in ether (160 ml) were irradiated under the standard conditions using a 2-mm Pyrex filter. It was calculated that the sensitizer absorbed $>99\%$ of the incident light in the experiment with **1** to **3** and over 95% in the case of **2**. After 4 hr of irradiation the conversion of **1** to adducts **9a** and **b** was 38% (gc) as compared to 70% in the unsensitized experiments; the ratio of **9a** to **9b** was the same as in the absence of a sensitizer. Similarly, the conversion of **2** to **19** was 30% complete after 6 hr, compared to 78%, and the conversion of **3** to **28** was 38% after 20 hr, compared to 82% with no sensitizer. The identity of the products was checked by infrared.

Registry No.—**5a**, 18944-87-1; **5a** (ϵ -lactone), 18944-88-2; **5b**, 18926-75-5; **5b** (ϵ -lactone), 18926-76-6; **6**, 18933-52-3; **7a, b**, 18926-87-9; **8a, b**, 18926-88-0; **9a, b**, 18926-77-7; **9c**, 18926-78-8; **10b**, 18926-79-9; **10c**, 18926-80-2; **11a**, 18926-81-3; **11b**, 18926-82-4; **12**, 18926-83-5; **16**, 18926-84-6; **17**, 18926-85-7; **18**, 18926-86-8; **19**, 18926-89-1; **20**, 18926-90-4; **23**, 18926-91-5; **23** (ϵ -lactone), 18926-92-6; **24**, 18926-93-7; **24** (2,4-dinitrophenylhydrazone), 18926-94-8; **26**, **27**, 18926-95-9; **28**, 18926-96-0; **28**, 18926-96-0; **28** (ϵ -lactone), 18926-97-1; **30** 18926-98-2; **30** (2,4-dinitrophenylhydrazone), 18944-89-3; **32**, 18926-99-3; **32** (2,4-dinitrophenylhydrazone), 18927-00-9; **33**, 4056-73-9; **34**, 18927-02-1; **34** (ϵ -lactone), 18926-63-1; **35**, 18927-03-2; **36**, 18944-90-6.

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