

The organic portion was extracted with ether and treated with acetic anhydride overnight. Concentrated hydrochloric acid was added, and the solution was extracted with ether to remove any undesired organic material. The amine was liberated from the aqueous solution with sodium hydroxide, separated by extraction with ether, and isolated by distillation.

trans-Azobenzene-¹⁵N was prepared by the reduction of nitrobenzene-¹⁵N with zinc in a basic methanol-water solution.

trans-Azoxybenzene-¹⁵N was prepared by treatment of *trans*-azobenzene-¹⁵N with acetic acid and 30% hydrogen peroxide at 55° for 24 hr. After 8 hr. and after 20 hr., additional hydrogen peroxide was added. Water was added and the product was isolated by extraction with 60–70° petroleum ether and evaporation of the solvent.

Hydrazobenzene-¹⁵N.—*trans*-Azoxybenzene-¹⁵N was heated with zinc in a basic ethanol-water solution at 100° for 1 hr. The mixture was filtered hot and the filtrate then placed in the refrigerator. The resulting solid was washed with 50% ethanol containing sodium bisulfite until white (m.p. 121.5–125°). The alcoholic solutions yielded *trans*-azobenzene after removal of most of the ethanol by distillation.

Benzamide-¹⁵N.—Benzoyl chloride in ether solution was cooled in a Dry Ice-acetone bath and treated over a 1.5-hr. period with ammonia-¹⁵N generated from ammonium-¹⁵N chloride and base. After 12 hr. at room temperature, the solution was filtered and the ammonium-¹⁵N chloride (collected quantitatively) was

washed with acetone. The filtrate was evaporated to incipient crystallization, treated with benzene, heated to boiling, and filtered hot. Benzamide was obtained in several crops from the benzene solution (89% yield).

Benzonitrile-¹⁵N was prepared from benzamide-¹⁵N by treatment with sodium aluminum chloride and distillation with a free flame.

Diphenylketimine-¹⁵N.—Phenylmagnesium bromide in ether was heated under reflux with benzonitrile-¹⁵N for 7 hr.; the complexes were destroyed with methanol, the slurry filtered, and the ketimine isolated by distillation.⁴⁰

Diphenylketimine-¹⁵N hydrochloride was prepared by bubbling dried hydrogen chloride gas through an ether solution of the parent ketimine in a nitrogen atmosphere; the solid was removed by filtration and dried under reduced pressure.

Glycine-¹⁵N (96% ¹⁵N) was obtained from Bio-Rad Laboratories.

Acetylglycine-¹⁵N was prepared from glycine-¹⁵N and acetic anhydride according to the procedure of Herbst and Shemin.⁴¹

Urea-¹⁵N₂ was prepared from ammonia-¹⁵N (*vide supra*) and diphenyl carbonate according to the procedure of Leitch and Davidson.⁴²

(40) P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, **26**, 4886 (1961).

(41) R. M. Herbst and D. Shemin, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 11.

(42) L. C. Leitch and W. M. Davidson, *Sci. Agr.*, **29**, 189 (1949).

[CONTRIBUTION FROM THE CONVERSE LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE, MASS. 02138]

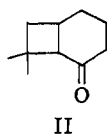
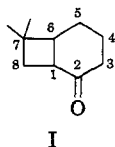
A Study of the Photochemical Reactions of 2-Cyclohexenones with Substituted Olefins¹

By E. J. COREY, J. DOLF BASS, RONALD LEMAHIEU, AND RAJAT B. MITRA

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The photochemical reactions of 2-cyclohexenone and other conjugated enones with a variety of unsaturated substances have been investigated to determine the scope, orientation, and stereochemistry of cycloaddition. The occurrence of marked orientational specificity is confirmed as is the frequent formation of *trans*-fused ring systems. The susceptibility of a number of olefinic substrates to attack by excited 2-cyclohexenone has been measured by competition experiments which establish the series: 1,1-dimethoxyethylene > methoxyethylene > cyclopentene > isobutylene > allene >> acrylonitrile. An hypothesis is advanced to explain (1) the observed orientational specificity, (2) the stereochemistry of photoaddition, and (3) the relative reactivity of different olefins with excited 2-cyclohexenone. Because orientational specificity and high olefin reactivity have been found to coincide and to appear with those olefins which are good π -donors, these factors are linked in the theory; for good π -donors an oriented π -complex is considered as an intermediate. The generation of a cyclobutane unit by cycloaddition seems to occur in two distinct stages with *sequential* formation of the two new carbon-carbon bonds, *i.e.*, via a 1,4-diradical system, at least in certain instances.

During the recent program of research in these laboratories on the total synthesis of caryophyllene,² an investigation was made of possible synthetic routes to the bicyclic ketone I and it was discovered that the photochemical cycloaddition of isobutylene and 2-cyclohexenone was an efficient and practical one-step procedure. This reaction which was effected by ultra-



violet excitation of 2-cyclohexenone in the presence of a high concentration of isobutylene (nonabsorbing at the ultraviolet wave lengths used) is formally analogous to a number of other cycloaddition processes which have been described in recent years.³ In general, these in-

volve the addition of a photoactivated double bond to an unactivated multiple bond which is not in the absorbing chromophore. Apart from being of great utility, the photoaddition of 2-cyclohexenone to isobutylene was of exceptional interest for other reasons. First, the major product I was formed in much larger amount than the alternative cycloaddition product II; in fact, in our early experiments the isomer II escaped detection. Second, both *cis* and *trans* forms of I were obtained with the latter predominating by a considerable margin even though it is a relatively strained system. At the time of our initial studies of this reaction there were no indications that photoaddition processes would involve such orientational and stereochemical effects. We have, therefore, investigated several

(1) This work was supported by the National Science Foundation (GP 221) and the National Institutes of Health (GM 7484).

(2) E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **86**, 485 (1964); **85**, 362 (1963).

(3) (a) G. Ciamician and P. Silber, *Ber.*, **41**, 1928 (1908); (b) G. Büchi and J. M. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957); (c) S. J. Cristol and R. L. Snell, *ibid.*, **76**, 5000 (1954); (d) R. C. Cookson and E. Crandwell,

Chem. Ind. (London), 1004 (1958); (e) H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 4791 (1960); (f) G. O. Schenck and R. Steinmetz, *Tetrahedron Letters*, **No. 21**, 1 (1960); (g) E. Grovenstein, Jr., and D. V. Rao, *ibid.*, **No. 4**, 148 (1961); (h) G. Büchi, paper presented at the Seventh Reaction Mechanisms Conference, University of Chicago, Sept. 5, 1958; (i) P. deMayo, H. Takeshita, and A. B. M. A. Sattar, *Proc. Chem. Soc.*, 119 (1962); (j) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2454 (1962); (k) P. deMayo, R. W. Yip, and S. T. Reid, *Proc. Chem. Soc.*, 54 (1963); (l) G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, **76**, 4327 (1954); (m) J. A. Barltrop and R. Robson, *Tetrahedron Letters*, **No. 9**, 597 (1963); (n) R. Robson, P. W. Grubb, and J. A. Barltrop, *J. Chem. Soc.*, 2153 (1964).

photoaddition reactions of 2-cyclohexenone and some substituted 2-cyclohexenones in order to gain an understanding of the factors which produce orientational and stereochemical selectivity and to define the scope of such processes as practical synthetic methods.

Results

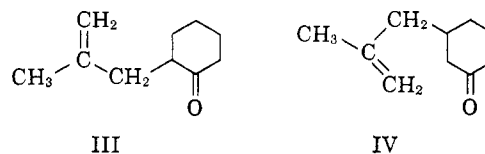
A. Products from 2-Cyclohexenone.—All the photochemical reactions described herein were conducted with a mercury arc lamp (Hanovia, Type L, 450 w.) housed in a water-cooled quartz well which was immersed in the reaction mixture. In addition a Corex glass filter (0% transmission below 250 m μ , 50% transmission at 290 m μ , and 100% transmission at 350 m μ) was employed to prevent reactions caused by $\pi \rightarrow \pi^*$ excitation of the conjugated ketone. In the reaction of isobutylene with 2-cyclohexenone [ultraviolet max. (methanol) 224, 321 m μ (ϵ 9680, 29); ultraviolet max. (cyclohexane) 218, 331, 343, 356, 375 m μ (ϵ 10,480, 23, 24, 17, 7)] the same reaction products were observed with Corex and Pyrex (0% transmission below 290 m μ) filters although the reaction was approximately half as fast in the latter case. The cell containing the reactants was cooled during irradiation by an external Dry Ice-ethanol bath. Usually a 15-fold excess of the olefinic component was used with pentane as solvent.

Since mention has already been made of the photochemical reaction of 2-cyclohexenone and isobutylene, this case will be considered first. The conditions and procedure used for the experiments were those which have been described previously.² The various reaction products were isolated in pure condition by a combination of distillation, chromatography on silica gel, and vapor phase chromatography (v.p.c.) as detailed in the Experimental part. The most satisfactory column for the resolution of these mixtures by v.p.c. was a column of fluorosilicone (Dow Corning FS 1265) (10%) on Diatoport S (available from F and M Scientific Co.),⁴ a special property of which is that it does not effect the isomerization of *trans*-I to *cis*-I which had previously been observed.² Five substances have now been identified as reaction products and the yields from the reaction have been ascertained by a combination of vapor phase chromatographic and nuclear magnetic resonance (n.m.r.) analysis. The major product is *trans*-I which is formed in 26.5% yield (based on the amount of 2-cyclohexenone put into the reaction); the n.m.r. spectrum of this substance is characteristic and shows methyl peaks at 1.07 and 1.15 δ (δ = parts per million shift down field from tetramethylsilane as internal standard). The *cis* isomer of I is produced in smaller amount (6.5% yield) and as reported earlier, the ratio of *cis*- and *trans*-I is approximately 1:4; the n.m.r. spectrum of *cis*-I exhibits two methyl peaks at 0.97 and 1.15 δ . The alternative cycloaddition product, 8,8-dimethylbicyclo[4.2.0]octanone-2 (II) is formed as a minor product (yield ca. 6%), which has a much shorter retention time in v.p.c. and is lower boiling than *cis*- or *trans*-I. It was isolated by column chromatography of the reaction mixture on silica gel to remove two unsaturated ketones (see below) and subsequent separation from *cis*- and *trans*-I by preparative v.p.c.; the n.m.r. spectrum of ketone II exhibits methyl peaks at 0.96 and 1.23 δ . The two unsaturated ketones referred to above are

readily separated from the saturated ketones I and II by chromatography on silica gel (the unsaturated ketones are eluted most rapidly) and they can be separated easily from one another by v.p.c. They are isomeric and show very similar n.m.r. and infrared spectra which indicate for each the presence of the group



to $\text{C}=\text{CH}_2$, and 5.84 μ due to $\text{C}=\text{O}$; n.m.r. peaks due to two olefinic protons at 4.6–4.8 δ and a methyl group at 2.0 δ . The isomer which is the more rapidly eluted during v.p.c. with column D⁴ is 2-(β -methylallyl)cyclohexanone (III) as was shown by comparison with an authentic sample prepared from cyclohexanone and β -methylallyl bromide by alkylation *via* an enamine. The other olefinic ketone is assumed to be 3-(β -methylallyl)cyclohexanone (IV) on the basis of the physical and analytical data and the mode of formation.



On column D at 140° with a helium flow of 50 ml./min., the elution times of the above products were: II, 20.1 min.; III, 20.9 min.; *cis*-I, 28.7 min.; IV, 30.5 min.; and *trans*-I, 31.1 min. Some material (ca. 6% of the total (by weight)) was eluted at times between 10 and 20 min.

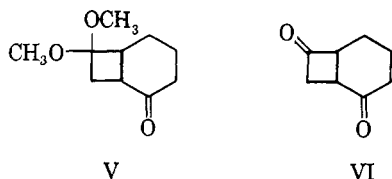
The assignment of formula II to the minor saturated photoaddition product rests on analytical and spectral data only and hence is not regarded as final. The compound which has been isolated resists isomerization by alumina (in contrast to *trans*-I) and appears to be the *cis* isomer on this basis. The n.m.r. peaks characteristic of the substance also appear in the spectrum of the photoproduct obtained after distillation but without further treatment; *cis*-II thus seems to be a primary reaction product.

A control experiment was performed to test the possibility that *trans*-I is formed by photochemical isomerization of *cis*-I, and it was discovered that this transformation did not occur under the conditions of the photoaddition reaction. Prolonged irradiation (pentane solution) did result in the partial conversion of *cis*-I to a nonketonic, hydroxylic material which appears to be a mixture of the corresponding secondary alcohols.

The photochemical reaction of 2-cyclohexenone with 1,1-dimethoxyethylene was also investigated. Under the standard conditions the reaction proceeded readily and afforded two major products along with a number of volatile by-products (yield of each less than 6%) as determined by v.p.c. using column D. The two major products are stereoisomeric as shown from the facile isomerization of one, a crystalline solid, m.p. 52.5°, to the other, which is a liquid, by treatment with alcoholic base at room temperature. The solid and liquid isomers, obtained in yields of 49 and 21%, respectively, are regarded as *trans* and *cis* forms (respectively) of 7,7-dimethoxybicyclo[4.2.0]octanone-2 (V). Infrared, n.m.r., and analytical data support the formulation of these compounds as bicyclic saturated ketones with

(4) This column is referred to as column D in the remainder of this paper.

intact dimethyl ketal grouping. A choice between the alternative 7,7- and 8,8-dimethoxy structures can be made on chemical grounds. Hydrolysis of the stereoisomeric ketals with dilute aqueous acid affords the diketone VI. This is obviously not a 1,3-diketone; it is nonenolic and it is not converted to a keto acid upon treatment with aqueous base under nitrogen. Further, the *cis* isomer of V is unchanged upon prolonged



treatment with sodium ethoxide in ethanol; the methoxy groups are not lost by elimination or exchange for ethoxy groups. The various minor products from the reaction which affords *cis*- and *trans*-V have not been investigated in detail, but it would appear from a v.p.c.-n.m.r. study that 8,8-dimethoxybicyclo[4.2.0]octanone-2 could only be present in small amounts, *i.e.*, not more than 3% of theoretical under our reaction conditions.

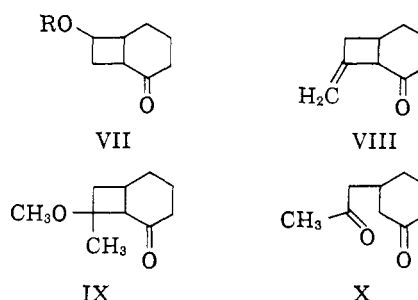
The photoreaction of 2-cyclohexenone and benzyl vinyl ether appears to follow the orientation scheme observed for 1,1-dimethoxyethylene, the major product being VII, R = CH₂C₆H₅. This material appears to be a mixture of stereoisomers; however, the aspect of stereochemistry was not investigated in this case. The photoaddition product as isolated by distillation appeared to consist largely of VII, R = CH₂C₆H₅, and none of the 8-substituted isomer could be detected by a chemical means. For example, the treatment of this product with 1% sodium methoxide in methanol for 1 hr. did not lead to any replacement of benzyloxy by methoxy (n.m.r. analysis) and did not lead to elimination of benzyloxy to form an unsaturated ketone. Hydrogenation of the adduct (after treatment with base to isomerize any *trans*-VII present) with palladium on carbon in ethyl acetate led to hydrogenolysis of benzyl (one equivalent of hydrogen absorbed) with the formation of a hydroxy ketone. Oxidation of this hydroxy ketone with chromic acid-acetone gave a diketone which was identical with the compound *cis*-VI described above. The yield of VII from the photoreaction is estimated to be approximately 65%.

The photoaddition of 2-cyclohexenone to methyl vinyl ether produced three stereoisomeric 7-substituted bicyclo[4.2.0]octanone-2 adducts (VII, R = OCH₃). Two of these differed at the ring fusion since one of the two could be isomerized to the other by exposure to neutral alumina. None of these compounds underwent loss of methoxy when treated with sodium ethoxide in ethanol, indicating that they are 7-methoxy derivatives.

Photoaddition of 2-cyclohexenone to vinyl acetate afforded three stereoisomeric acetoxy ketones formulated as VII, R = OCOCH₃, since these are converted to diketone VI by hydrolysis and oxidation.

The irradiation of mixtures of 2-cyclohexenone and allene led to an especially clean photoaddition process which gave 8-methylenebicyclo[4.2.0]octanone-2 (VIII) as the major product (55% yield). This product was obtained in pure form simply by distillation as judged

by v.p.c., n.m.r., and infrared data. The structure of the adduct follows from its conversion to a methoxy ketone (IX) by brief treatment with methanolic potassium hydroxide and to a diketone (X) after a longer re-

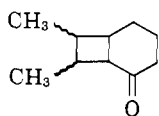


action time. The basis for the assignment of structures VIII, IX, and X to these compounds is presented in detail in the Experimental section. Obviously the data cannot be reconciled with the assumption that the photoproduct is the 7-methylene isomer. The geometry of the ring fusion in VIII has not yet been determined rigorously, but is probably *cis* since the photoproduct resists isomerization (*e.g.*, in pyridine at 25° for 3 weeks).

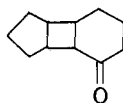
In order to study the stereochemistry of cycloaddition to the olefinic (nonketonic) component in these photochemical processes, the reactions of *cis*- and *trans*-2-butene with 2-cyclohexenone were studied with rather interesting results. Both reactions afforded saturated ketonic 1:1 adducts (XI) with no detectible unsaturated addition products (by n.m.r. analysis). Furthermore, both reactions yielded a mixture of products and in each case v.p.c. analysis (column D, 140°, helium flow rate 50 ml./min.) showed three major peaks at *ca.* 28.5, 31.3, and 37.5 min. with approximately the same relative intensities. The materials corresponding to each of these peaks were collected and it was shown that the infrared and the n.m.r. spectra of each peak from the reaction of *cis*-2 butene matched those of the corresponding peak from the reaction of *trans*-2-butene. As expected, the spectra of the total reaction mixtures in each case were essentially identical. The occurrence of products in the *trans*-bicyclo[4.2.0]octane series was tested by treatment of the total products from *cis*- and *trans*-2-butene with alumina under equilibrating conditions. Only very minor changes were observed in the n.m.r. and infrared spectra. These and other experiments show that the formation of three main products in each case does not reflect the presence of isomers differing only at the ring fusion and that the photoaddition process is not stereospecifically *cis* or *trans* relative to the olefin component; common intermediates are indicated for a major part of the reaction. In order to test the possibility that the 2-butenes might be subjected to equilibration under the conditions of the photoreaction, aliquots were withdrawn periodically from a reaction of *cis*-2 butene with 2-cyclohexenone and the butene fraction was analyzed (gas phase) by infrared. No isomerization of the butene was observed (upper limit 1%).

The photoaddition of 2-cyclohexenone to cyclopentene gave two stereoisomeric bicyclo[4.2.0]octanone-2 derivatives (XII) which differed only in geometry of the 6-4 ring fusion. By treatment with alumina one isomer (*trans* 4-6 fusion) was transformed into the

other (*cis* 4-6 fusion). Both reaction products must have the same geometry at the 4-5 ring fusion, presumably *cis*. The five- and six-membered rings in XII are probably *anti*.^{3j}



XI

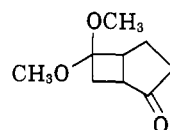


XII

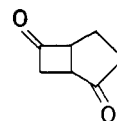
Irradiation of 2-cyclohexenone in the presence of acrylonitrile at 25° led to the formation of four stereoisomeric cycloaddition products all of which seem to possess the *cis* 4-6 fusion. Preliminary studies of these compounds indicate that the dominant mode of cycloaddition is that which produces 8-cyanobicyclo[4.2.0]octanone-2 structures. A noteworthy feature of this reaction is its slowness relative to the cases with other olefins which are mentioned above.

B. Products from Other Conjugated Enones.—

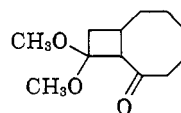
The photoaddition of 1,1-dimethoxyethylene to 2-cycloalkenones was studied to determine the influence of ring size on orientational and stereochemical specificity. This particular olefin was selected because of its reactivity (*vide infra*), because of the simplicity of structural analysis of the addition products, and because of the interesting results obtained with 2-cyclohexenone (orientational specificity, formation of both *trans*- and *cis*-bicyclo[4.2.0]octanones). From the photochemical reaction of 2-cyclopentenone with 1,1-dimethoxyethylene, a single addition product could be isolated—*cis*-6,6-dimethoxybicyclo[3.2.0]heptanone-2 (XIII) in 60% yield. In this case the orientational mode corresponds to that observed with 2-cyclohexenone and the specificity exceeds that observed previously in the reaction of 2-cyclopentenone with allene⁵ or 2-cyclopentenone (dimerization).⁶ The photoadduct XIII was recovered unchanged after treatment with sodium ethoxide in ethanol. The lack of replacement of methoxy by ethoxy indicates that the methoxy groups in XIII are not β to the carbonyl group; lack of isomerization demonstrates the *cis* ring fusion. Acid-catalyzed hydrolysis of XIII afforded the non-enolic diketone XIV. The irradiation of 2-cycloheptenone and 1,1-dimethoxyethylene under the standard conditions did not lead to isolable quantities of cycloaddition product. However, the irradiation of 2-cyclooctenone with this olefin gave an adduct which was shown to be XV (37% yield); here a different mode of addition occurs from that found with 2-cyclopentenone and 2-cyclohexenone. This striking difference was shown to be caused by a special reaction pathway for 2-cyclooctenone involving prior *cis* \rightarrow *trans* isomerization of the ketone followed by a thermal cycloaddition.⁷ Thus, irradiation of *cis*-2-cyclooctenone in pentane at Dry Ice temperatures until a photostationary state was reached, followed by discontinuation of irradiation, addition of 1,1-dimethoxyethylene, and reaction in the dark with gradual warming to room temperature, afforded the same adduct (XV) as obtained



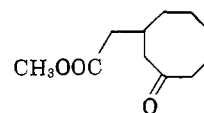
XIII



XIV



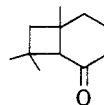
XV



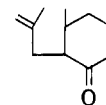
XVI

by irradiation of 2-cyclooctenone in the presence of 1,1-dimethoxyethylene. The structure of the adduct XV follows from its conversion with dilute aqueous acid to a keto ester XVI, and from its conversion with sodium ethoxide in ethanol to the corresponding diethyl ketal (XV, C_2H_5 in place of CH_3).

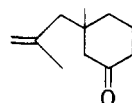
In order to gain some idea of the consequences of substitution of the enone component, a limited study has been made of the irradiation of mixtures of isobutylene with 2-methyl-2-cyclohexenone and 3-methyl-2-cyclohexenone. These have shown that with the former ketone the 2-methyl substituent greatly diminishes the rate of the photoreaction (relative to that of 2-cyclohexenone), and, furthermore, in this case the reaction product is a complex mixture. The substitution of a 3-methyl group in place of hydrogen, in contrast, does not seem to cause a significant rate retardation. The products obtained from 3-methyl-2-cyclohexenone and isobutylene were separated by v.p.c. and were identified as the saturated ketone XVII and the unsaturated ketones XVIII and XIX.



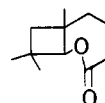
XVII



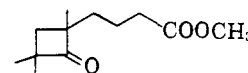
XVIII



XIX



XX



XXI

The structure of saturated ketone was determined from spectral data and from the conversion with peracetic acid to a lactone (XX) which showed in the n.m.r. spectrum one proton downfield (3.8 δ) in the region

expected for $-COO-CH$ as a sharp singlet. The lac-

tone XX was hydrolyzed to a hydroxy acid which was converted by oxidation and esterification with diazomethane to the keto ester XXI. The intermediate keto acid was clearly identified as a cyclobutanone by infrared carbonyl absorption at 5.65 ($C=O$) and 5.85 μ ($COOH$). The structural assignments for the unsaturated products were made from infrared and n.m.r. data. The saturated ketone XVII was the major product; next in amount was the β -substituted unsaturated ketone XIX, and finally the isomeric α -substituted unsaturated ketone XVIII was a minor component.⁸

C. Relative Rates of Reaction of Various Olefins with Excited 2-Cyclohexenone as Determined by Di-

(8) Much of the work on the identification of these products was kindly performed by Dr. K. Sestanj in these laboratories, to whom we express thanks.

(5) P. E. Eaton, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 4Q.

(6) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

(7) The photochemical *cis* \rightarrow *trans* isomerization of 2-cyclooctenone has recently been demonstrated by the elegant experiments of P. E. Eaton and K. Lin, *ibid.*, **86**, 2087 (1964).

rect Competition.—In order to determine relative rates of addition of various olefins with excited 2-cyclohexenone, a number of experiments were performed in which 2-cyclohexenone was irradiated in the presence of 9–10 molar equivalents of each of two olefins. The products of these reactions were determined quantitatively by v.p.c., and the ratio of the total products from one olefin to those from the other was taken to be a measure of relative rates. The results are summarized in Table I for a number of runs in which

TABLE I
COMPETITION BETWEEN CYCLOPENTENE AND VARIOUS
OLEFINS FOR EXCITED 2-CYCLOHEXENONE

| Olefin, O | Obsd. ratio of products from olefin O and cyclopentene | Rel. rate factor |
|-----------------------|--|--------------------------------------|
| 1,1-Dimethoxyethylene | 2.33 | 4.66 |
| Methoxyethylene | 0.785 | 1.57 |
| Cyclopentene | | 1.00 |
| Isobutylene | 0.266 | 0.40, ^b 0.13 ^c |
| Allene | 0.234 | 0.234 ^a |

^a Factors of two were applied to observed ratios in the case of cyclopentene and allene in which there are two modes of addition which lead to the same product. ^b Refers to formation of I + III. ^c Refers to formation of II + IV.

one of the olefins in each instance was cyclopentene. An additional fact which is not indicated in the table is that acrylonitrile is far less reactive than any of the olefins listed. In summary, the data on relative reactivities tend to characterize excited 2-cyclohexenone as a moderately electrophilic species in the reaction with olefins.

A single competition experiment was conducted with 2-cyclopentenone and a mixture of 1,1-dimethoxyethylene and cyclopentene. Interestingly, the relative rates of addition were essentially the same as observed for these two olefins with excited 2-cyclohexenone.

Discussion

The experimental results outlined above are relevant to both the theory and the practical synthetic aspects of the photoaddition of 2-cyclohexenone and related substances to unsaturated compounds. We shall deal first with the matter of synthesis. It was indicated earlier² that the photoaddition of 2-cyclohexenone to isobutylene is at present the only practical method for the synthesis of 7,7-dimethylbicyclo[4.2.0]octanone-2, a valuable intermediate for the construction of a number of interesting molecules. One of the important factors in determining the suitability of the photoaddition method in this and other applications is the selectivity between the various modes of addition which are possible and which lead to position and stereoisomers. From the present results it is clear that a high degree of orientational specificity can operate in the joining of the α - and β -carbons of the enone to the olefinic component and that in certain instances only one of the possible position-isomeric structures is produced; the outstanding cases from the present work are the reactions of 2-cyclohexenone with 1,1-dimethoxyethylene, allene, vinyl acetate, and methoxy- or benzyl-oxyethylene. In the case of 2-cyclohexenone, at least, it appears that both orientational specificity and ease of reaction can be expected with olefins having electron-supplying group(s) at the double bond; the dominant cycloaddition product is that in which the α -carbon of

the enone has attached itself to the carbon of the olefin which is most nucleophilic. In every case studied thus far in these laboratories, 1,1-dimethoxyethylene has reacted with excited enones in an orientationally specific manner. Even with 2-cyclopentenone, which is more prone to afford position isomers with other olefins (e.g., allene⁵) than is 2-cyclohexenone, only one product is formed in the addition of 1,1-dimethoxyethylene. It should be noted here that the ring size appears to be important in the case of cyclic enones not only in controlling the mode of addition, but also in determining the rate of addition relative to competing processes. Thus, 2-cycloheptenone was found to be inoperative in the photoaddition reaction under the standard reaction conditions for 2-cyclohexenone. Further, *cis*-2-cyclooctenone also did not appear to undergo direct photoaddition but rather prior isomerization to *trans*-2-cyclooctenone followed by nonphotochemical (thermal) addition in those cases where combination occurred. No photoaddition of 2-cyclooctenone to cyclopentene or allene could be observed under the standard conditions presumably because the excited enone decays rapidly to *trans*-2-cyclooctenone which is not sufficiently reactive to add to these unsaturated molecules.

It is still too early to reach a conclusion regarding the effect of methyl substituents in the enone system on the course of photoaddition. The present results with 2-methyl-2-cyclohexenone and isobutylene indicate that alkylation at C-2 of the enone is deleterious to the photochemical addition to an olefin, but more evidence on this point is required. Substitution of methyl at C-3 of the enone system evidently does not affect the reactivity of the enone adversely,⁹ but the results obtained in the reaction of 3-methyl-2-cyclohexenone (i.e., formation of XVII, XVIII, and XIX) imply that the replacement of hydrogen by a 3-methyl substituent can influence the orientational mode of the photochemical addition.

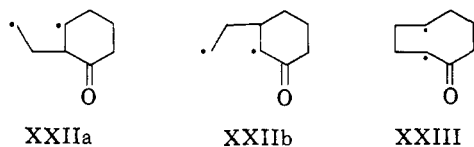
The formation of *trans* fused bicyclo[4.2.0]octanones appears not to be a peculiarity of isobutylene since this has now also been definitely observed in the reactions of, e.g., 1,1-dimethoxyethylene, methoxyethylene, cyclopentene, and tetramethylethylene with 2-cyclohexenone. The case of 1,1-dimethoxyethylene is noteworthy because of the ease of obtaining the *trans* fused adduct V in pure condition, and in this instance the photochemical synthesis is unique as a route to this hitherto inaccessible compound. The formation of 4–6-*trans* fused rings was also observed in the photoaddition of 3-methyl-2-cyclohexenone to 4,4-dimethylcyclopentene.⁹

The utility of the enone-olefin cycloaddition, which has been pointed out previously,^{3i,3j} can now be seen to extend to the specific synthesis of certain structures in preference to position isomers and also to the synthesis of certain unstable stereoisomers such as *trans*-bicyclo[4.2.0]octane derivatives.

The present results obviously do not define the exact nature of the excited ketonic species or the detailed mechanism of the photoaddition. However, the high orientational selectivity observed in several cases, the commonplace formation of *trans*-bicyclo[4.2.0]octanes,

(9) The photoaddition of 3-methyl-2-cyclohexenone to 4,4-dimethylcyclopentene, which proceeds very smoothly, was a key step in the recent synthesis of α -caryophyllene alcohol: E. J. Corey and S. Nozoe, *J. Am. Chem. Soc.*, **86**, 1652 (1964).

and the production of almost identical mixtures from *cis*- and *trans*-2-butenes would seem to provide an argument against certain alternative mechanisms which seemed to be reasonable possibilities *a priori*. The concerted *cis* addition of excited 2-cyclohexenone to the two olefinic carbons of the "unactivated" component is considered improbable since this was not observed in the case of the 2-butenes, which would appear to be models of good generality. A two-step addition, for example, *via* an intermediate of type XXIIa or b,

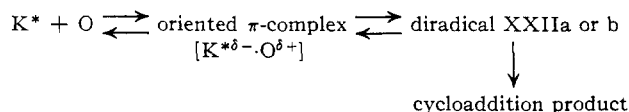


appears preferable.¹⁰ In this connection it might be noted that the concerted reaction of excited ketone (K^*) with olefin (O) to form cycloaddition product directly would be highly exothermic and would require that a large amount of energy be removed from the reacting pair during encounter.¹¹ A more probable mode of combination of K^* with O would be one that produces a high energy intermediate which does not contain all of the bonds which exist in the product, for example, the diradical XXIIa or b. It is estimated that these diradicals would be of roughly 60 kcal./mole higher energy than the cycloaddition product.¹² The energy of the $n-\pi^*$ excited singlet from 2-cyclohexenone is *ca.* 85 kcal./mole above the ground state, and the lowest triplet excited state can be expected to be of somewhat lower energy (perhaps by 10 kcal./mole). It is likely that either the first excited singlet or the lowest-lying triplet state is sufficiently energetic to give the diradical XXIIa or b and, further, the amount of energy which would have to be released in the process is not excessive. The formation of a cyclobutane ring from the 1,4-diradicals is supported by analogy.^{12,18} Although present evidence favors the two-step addition, further data (*e.g.*, on the stereochemistry of addition to other stereoisomeric olefins) are required before generality can be established.

Clearly, the formation of *trans*-bicyclo[4.2.0]octanone-2 derivatives is not inconsistent with the intermediacy of a diradical such as XXIIa or b. These intermediates are sufficiently energetic to produce the *trans* system which we estimate to be not more than 10 kcal./mole higher in energy than the *cis* fused form. The possibility that the *trans*-bicyclo[4.2.0]octanone-2 system is formed from a metastable form of the enone with *trans* oriented, out-of-plane hydrogens must also be considered,¹³ as must the alternative that *cis* and *trans*

fused adducts arise from different excited forms of the enone. The latter hypothesis is open to question because of the observation that the ratio of *cis* to *trans* adducts V from 2-cyclohexenone and 1,1-dimethoxyethylene is the same *with* and *without* competing cyclopentene. The alternative that the *cis*-bicyclo[4.2.0]octanones are intermediates in the formation of the *trans* isomers, *e.g.*, by a process through species such as XXIII, seems unlikely in view of the control experiment with *cis*-7,7-dimethylbicyclo[4.2.0]octanone-2 which has been mentioned in the foregoing section.

With regard to the orientational specificity in the coupling of excited ketone K^* to olefin O, there is clearly a need for much more experimental data. However, the striking effects noted in the present work encourage us to believe that the problem of explaining and predicting orientation may not be as difficult as might be expected on the basis of the highly energized state of K^* . In particular, there is one possibility which seems especially attractive and intriguing because of its simplicity and because it fulfills the requirement that a working hypothesis explain all the data at hand. In outline the process can be described



It is further assumed that the factor which controls orientation in the photoaddition process is the geometry of the intermediate π -complex, *i.e.*, that orientation is determined in a step prior to formation of diradical. The π -complex could reasonably be of the donor-acceptor type and presumably the excited ketone would function as acceptor and the olefin as donor (this is in agreement both with expectations and with the data on relative rates in Table I).¹⁴ In general, two types of donor-acceptor (DA) complexes are possible: (1) complexes in which the low-lying state is less polar than the higher-energy state reached by charge transfer and (2) complexes in which the reverse situation obtains. We consider that the former type of complex is appropriate here and, further, that the complex is more likely a less polar, "lower" state complex of the excited ketone and unexcited olefin rather than an "upper" state complex of the ground state ketone and ground state olefin¹⁵

available with the exception of the first excited $n-\pi^*$ singlet state of acrolein (see J. C. D. Brand and D. G. Williamson, *Discussions Faraday Soc.*, **35**, 184 (1963)) which appears to be a planar $C=C-CHO$ structure with a low energy barrier (7.8 kcal./mole) to rotation about the $C\alpha-C\beta$ bond. This reference should be consulted for other interesting details. A recent review on the structure of electronically excited organic molecules by the same authors appears in "Advances in Physical Organic Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1963, pp. 365-423. The equilibrium geometry of the $n-\pi^*$ triplet state of acrolein, a matter of great interest, is presently unknown.

(14) See (a) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962); and (b) G. Briegleb, "Electron-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin-Göttingen-Heidelberg, Germany, 1961.

(15) This last possibility can be formulated as mainly $K^+ \cdot O^-$ with a small contribution from $K \cdot O$. It is highly bonding since K and O are bound together by coulombic attraction and it is for this reason not unattractive as an intermediate in dimerization. However, we calculate that for the case in which the ionization potential of the donor exceeds the electron affinity of the acceptor by more than 8 e.v. at a donor-acceptor separation of 3.5 Å, more energy would be required to form such a complex than is available from the originally absorbed quantum. We do not at present know ($I_D - E_A$) values for the cases of interest here (because E_A is not known) but they probably cannot be much below 8 e.v. The rather modest differences in reactivity toward excited 2-cyclohexenone of allene ($I_D = 10.2$ e.v.) methoxy-ethylene (I_D 8.9 e.v.) and cyclopentene ($I_D = 9.2$ e.v.) tend to argue against a highly polar donor-acceptor complex.

(10) The formulas XXIIa and b are not intended to convey detail with regard to stereochemistry, charge distribution, or spin multiplicity.

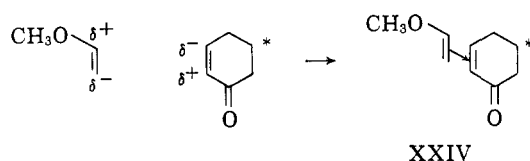
(11) The combination of two molecules of ethylene to form cyclobutane in the gas phase at 298°K. corresponds to a free energy change (ΔF) of -6.25 kcal./mole; see "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, 1953, p. 474, and G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5634 (1953). If the reaction of 2-cyclohexenone with an olefin in the ground state involves roughly zero free energy change, it is clear that the amount of energy to be dissipated during reaction of photoexcited 2-cyclohexenone is large, approximately the excess energy of the excited ketone.

(12) This estimate is made from kinetic measurements on the thermal decomposition and isomerization of cyclobutanes; see (a) C. T. Genaux, F. Kern, and W. D. Walters, *ibid.*, **75**, 6196 (1953); and (b) H. R. Gerberich and W. D. Walters, *ibid.*, **83**, 3935, 4884 (1961).

(13) Information concerning the equilibrium geometries of singlet and triplet excited states of α,β -unsaturated carbonyl compounds is not yet

which would be largely ionic. Assuming that the ketone component of the oriented complex is in the $n-\pi^*$ excited state and that the olefinic component is above the α,β -double bond of the ketone (four-center π -complex) an estimate can be made of preferred orientation in the π -complex. Recent calculations of charge distribution in the $n-\pi^*$ excited state of planar α,β -unsaturated ketone indicate that C_β is quite negative relative to C_α .^{16,17}

The orientation of the donor-acceptor π -complex from excited 2-cyclohexenone and methoxyethylene can be derived therefore as XXIV. This simple inter-



pretation explains the observed products from 2-cyclohexenone and 1,1-dimethoxyethylene, benzyloxy- and methoxyethylene, isobutylene, and allene. In the last case polarity is taken as $\text{CH}_2=\text{C}=\text{CH}_2$ since this follows from the greater electronegativity of sp -hybridized carbon over sp^2 -hybridized carbon. The formation of *anti*-XII in preference to *syn*-XII is another kind of orientational specificity which is predicted by the assumption of an intermediate π -complex of type XXIV.

It is likely that the oriented π -complex model cannot be extended to the photodimerization of enones.⁶ Here a complex of the type $\text{K}^*\cdot\text{K} \leftrightarrow \text{K}\cdot\text{K}^*$ seems possible and the orientational requirements, if any, are not clear. Also, more study is needed to determine whether the oriented π -complex idea pertains to the reaction of enones with olefins substituted by electron-withdrawing groups such as CN or COOR which are clearly not π -donors; *a priori* this extension also seems unwarranted.

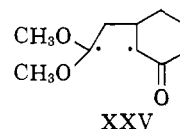
More detailed experimental studies on the effect of substituents in the enone system on orientation in photochemical cycloaddition reactions are required before these cases can be considered in general terms. Application of the hypothesis presented above also requires data on relative charge distribution of C_α and C_β in the various substituted enones. Lastly, a general assessment of steric factors must be made.

In order to evaluate the possibility (*cf.* ref. 3m and n) that photochemical addition of 2-cyclohexenone to olefins might involve light absorption from a donor-acceptor complex of ground state ketone and olefin, studies were carried out on the light absorption of 2-cyclohexenone dissolved in ethoxyethylene (which should be a good donor). No evidence of donor-acceptor complex formation was seen; the spectrum of the ketone was essentially the same in these solutions as in cyclohexane. Although this does not exclude the possibility that an extremely low concentration of charge transfer complex is responsible for photoaddition, it should be noted that photoaddition from a

ground state donor-acceptor complex does not predict correctly the observed orientational results.

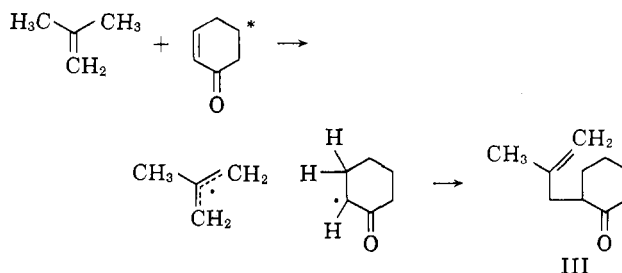
The alternative hypothesis that preferential diradical formation controls orientation in the photoaddition is subject to considerable difficulty. One proposition would be that the most stable diradical would predominate, *i.e.*, that diradical stability controls the product (application of this idea can be found in ref. 3l). Clearly this approach leads to incorrect conclusions; for example, with regard to the product from 2-cyclohexenone and 1,1-dimethoxyethylene which would be expected to be 8,8-dimethoxybicyclo[4.2.0]octanone-2 from the diradical XXV.

It should be noted, however, that the structure of the product of thermal cycloaddition of *trans*-2-cyclo-



octenone to 1,1-dimethoxyethylene is that expected from the diradical analogous to XXV.^{18,19} On the other hand, it might be considered that the high energy of the enone excited state would permit, and even favor,²⁰ the formation of one of the relatively less stable diradicals. The difficulty with this view, aside from the fact that it does not provide clearcut predictions, is that it does not explain the observed differences in reactivity of the various olefin components as summarized in Table I. These differences indicate that the excited ketone is fairly selective.

Diradical intermediates of type XXIIa or b can also be invoked to rationalize the formation of unsaturated adducts such as III and IV from 2-cyclohexenone and isobutylene. Alternatively these could arise from an initial hydrogen transfer from olefin to excited enone followed by combination of the two radicals which result.



We prefer the former mechanism partly because this provides a ready explanation for the absence of appreciable amounts of unsaturated adduct from the reaction of 2-cyclohexenone with cyclic olefins such as cyclopentene.

So far the discussion has avoided the problem of identifying the excited state(s) of the enone involved in photoaddition, although this is a matter of fundamental

(16) R. Hoffmann, personal communication. These calculations were performed using 2,5-cyclohexadienone as a model by the "extended Hückel method" already described: R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2480 (1964).

(17) See also H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964).

(18) For an elegant study of the mechanism of thermal cycloadditions of halo olefins *via* diradicals, see (a) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 616 (1964); (b) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964); and (c) P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964).

(19) An oriented π -complex of "ground state" *trans*-2-cyclooctenone and 1,1-dimethoxyethylene also would lead to the observed product in this case; this appears to us to be an attractive mechanism in this case. See S. Proskow, H. E. Simmons, and T. Cairns, *ibid.*, **85**, 2341 (1963).

(20) See G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

importance. There can be little doubt that the excited state initially formed from 2-cyclohexenone and related enones is the $n-\pi^*$ singlet. The $n-\pi^*$ band for cyclohexenone, centered at 3330 Å., has an oscillator strength, f , of $ca. 5.5 \times 10^{-4}$ (in cyclohexane solution), not very different from that in acetone ($ca. 4 \times 10^{-4}$), and this leads to a calculated radiative lifetime for the $n-\pi^*$ singlet of approximately 10^{-5} sec. which could be long enough to permit intermolecular addition before decay to the ground state. However, it seems to us likely for two reasons that the $n-\pi^*$ singlet is transformed into the $n-\pi^*$ triplet state. First, intersystem crossing between $n-\pi^*$ singlet and triplet states of ketones is common and, second, no fluorescence from the $n-\pi^*$ state of 2-cyclohexenone could be detected in dilute hydrocarbon solution.²¹ In general, the singlet-triplet energy gap for $n-\pi^*$ states appears to be 0.5 e.v. or less in the cases which have been studied (e.g., formaldehyde, 4000 cm^{-1} or 0.495 e.v.); this relatively small separation provides an indication that rapid intersystem crossing from the singlet to the triplet state ought to be fairly characteristic of $n-\pi^*$ states of carbonyl compounds.²² Unfortunately, we have not been able to detect phosphorescence from $n-\pi^*$ excited 2-cyclohexenone (in frozen methylcyclohexane),^{21,23} and consequently there is no direct evidence for the production of $n-\pi^*$ triplets. (Evidence for the formation of $\pi-\pi^*$ triplets also could not be obtained.^{24,25}) The formation and participation of $n-\pi^*$ or $\pi-\pi^*$ triplets in the photochemical reactions studied here remains sufficiently attractive to warrant further consideration and study, nonetheless.²⁶

As mentioned earlier, more than one kind of excited enone may be involved in the molecular combination which leads to photoadduct. At present there is no real

(21) Unpublished experiments by Mr. W. L. Mock in these laboratories.

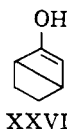
(22) The singlet-triplet energy difference is generally considerably larger for the lowest $\pi-\pi^*$ states (e.g., in the range 2.5–3.2 e.v. for ethylene, 1,3-butadiene, and benzene) owing to a much larger exchange interaction between the two electrons in half-filled orbitals (smaller average interelectronic distance, r_{12} , for $\pi-\pi^*$ than $n-\pi^*$ cases). See H. Hartman, *Adv. Chem. Phys.*, **5**, 1 (1962), for a simple formulation of this interaction in the general two-electron case. Consequently, one of the reasons why interstate crossing from singlet $\pi-\pi^*$ to triplet $\pi-\pi^*$ states is not as common as for the $n-\pi^*$ systems would appear to be the larger energy gap between the $\pi-\pi^*$ states.

(23) Dr. D. Arnold of the Union Carbide Research Laboratory at Tarrytown, N. Y., also has found that phosphorescence from $n-\pi^*$ excited 2-cyclohexenone is either lacking or extremely weak.

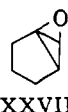
(24) There does not appear to be phosphorescence in the region expected for the lowest $\pi-\pi^*$ triplet.²¹ This triplet state is probably of comparable or somewhat lower energy than the $n-\pi^*$ triplet (we estimate²² the $\pi-\pi^*$ triplet to be $ca. 60$ kcal. or 2.6 e.v. above the ground state).

(25) M. H. Fisch and J. H. Richards, *J. Am. Chem. Soc.*, **85**, 3029 (1963), have previously referred to the possibility that the lowest $\pi-\pi^*$ triplet might be formed via the corresponding $n-\pi^*$ singlet and triplet states. The transition probability for $n-\pi^*$ triplet $\rightarrow \pi-\pi^*$ triplet is unknown, but seems likely to be quite small on symmetry grounds.

(26) The absence of phosphorescence from the $n-\pi^*$ triplet or $\pi-\pi^*$ triplet of 2-cyclohexenone could be attributed to rearrangement to form an energetic, unstable but ground state species, e.g., XXVI and XXVII. These



XXVI



XXVII

structures might revert to 2-cyclohexenone by nonradiative processes. Alternatively, it is possible that the triplet state is stabilized by a change of geometry (e.g., twisting about the α, β -bond) which serves to prevent radiative return to the ground state (Franck-Condon principle) and maintain the triplet state sufficiently long to allow deactivation by thermal or chemical modes. A structure analogous to XXVII is reported to be formed by irradiation of 3,5-cholestadiene; see W. G. Dauben and F. G. Willey, *Tetrahedron Letters*, No. 20, 893 (1962).

indication that such is the case, but the possibility cannot yet be discarded.

Experimental

General Procedure for Photochemical Reactions.—The general photocondensation procedure was essentially that described previously.² The apparatus consisted of an irradiation vessel fitted with a Hanovia quartz immersion well, magnetic stirring bar, a rubber stopple in one side arm, and a Dry Ice condenser leading to a three-way stopcock on the other side arm. Freshly distilled liquid reactants in pentane solution were placed in the reactor which was then evacuated of air and filled with argon six times. Gaseous olefins were condensed into the solution via the Dry Ice condenser and a needle was inserted through a stopple to provide a gas exit. Usually a 15-mole excess of the olefin was used. The vessel was wrapped well with aluminum foil and, with water running at a good rate through the cooling annulus, was immersed in a Dry Ice-ethanol bath. The stirred solution was irradiated by a Type L, 450-w. Hanovia mercury arc through a Corex filter. This cut out wave lengths shorter than 250 $\text{m}\mu$ and assured excitation of the $n \rightarrow \pi^*$ transition alone. This was found to occur at $\lambda_{\text{max}}^{\text{MeOH}}$ 321 $\text{m}\mu$ (ϵ 29.1) for cyclohexenone, 318 $\text{m}\mu$ (ϵ 39.1) for 2-methylcyclohexenone, and 311 $\text{m}\mu$ (ϵ 43.1) for 3-methylcyclohexenone.

The reaction was generally followed by removing aliquots with a syringe and measuring infrared absorption. The unsaturated ketone carbonyl peak gradually disappeared and was replaced by a nonconjugated carbonyl peak. Removal of the solvent was followed by distillation on a 46-cm. spinning band column, unless otherwise stated.

Analyses by v.p.c. were made using an F and M Model 300 gas chromatograph fitted with column A (8 ft., 20% Dow Corning FS 1265 on Chromosorb), column B (10 ft., 20% nitrile silicone on Diatoport), column C (8 ft., 5% Dow Corning FS 1265 on Diatoport S), or column D (12 ft., 10% FS 1265 on Diatoport S).⁴ Yields of photoproducts are based on starting cyclohexenone.

Some of the preparative v.p.c. work was carried out with a Wilkens Autoprep instrument using a 12-ft., 20% fluorosilicone 1265 Diatoport column in $3/8$ -in. diameter aluminum tubing.

The conditions for equilibration of *cis* and *trans* 4–6 fused ring ketones were as follows, unless otherwise specified. A solution of the ketone in ether was placed in contact with a column of Woelm activity I neutral alumina for 30 min., and the equilibrated material was subsequently eluted from the column with ether.

Photocondensation of 2-Cyclohexen-1-one with Isobutylene.—A solution of cyclohexenone (11.506 g., 0.12 mole), isobutylene (170 ml., 1.82 moles), and 150 ml. of pentane was irradiated 8.5 hr. and distilled to obtain 13.048 g. (71.6%) of photoproduct mixture I, b.p. 53–57° (0.45 mm.); 1.693 g. (9.3%) of a higher boiling yellow oil; and 0.778 g. (4.3%) of a gummy orange residue.

Careful refractionation of 9.419 g. of I on a 46-cm. spinning band column gave six colorless fractions: (1) 0.497 g., b.p. 50° (1.0 mm.), 53° (1.4 mm.); (2) 2.281 g., b.p. 55–58° (1.3–1.4 mm.); (3) 4.222 g., b.p. 58–58.5° (1.1 mm.); (4) 1.364 g., b.p. 58.5–60° (1.1 mm.); (5) 0.292 g., b.p. >60° (1.1 mm.); and (6) 0.392 g., b.p. >60° (1.1 mm.). Analysis of each fraction by v.p.c. (column D, 140°, helium flow 50 cc./min.) indicated photoproduct mixture I contained five major components with the following elution times: a, 20.1 min.; b, 20.9 min.; c, 28.7 min.; d, 30.5 min.; and e, 31.1 min. Three minor components were also found at 11.7, 16, and 18 min.

Substance a was identified as follows. Olefinic material (mainly b) was removed from distillation fractions 1 and 2 by chromatography on a 50-fold weight of 80–200 mesh silica gel. Elution with 2% chloroform in methylene chloride removed all olefin in the first seven fractions while the next twenty fractions, eluted with gradually increasing amounts of chloroform (to 25%), contained a, c, and e. These components were separated by passing the olefin-free fractions through the Autoprep instrument (145°, helium flow 200 cc./min.). The n.m.r. spectrum of a showed two methyl proton peaks at 0.96 and 1.23 δ (three protons each) and several sharp peaks in the methylene proton region with the expected integration for ten protons. The infrared spectrum showed a strong carbonyl peak at 5.89 μ and no indication of olefinic peaks. Since there was no change in the n.m.r. methyl proton peaks of a mixture of a and b after filtration through neutral alumina, a must be in its most stable conformation (probably with a *cis* ring fusion). The n.m.r. sample of pure a was injected on v.p.c. column D to prepare a specimen for analy-

sis. Since a is a saturated 1:1 adduct different from *cis*- or *trans*-I, it can reasonably be formulated *cis*-II.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.21; H, 10.34.

Substance b was identified as follows. A 0.87-g. portion of distillation fraction 4 was chromatographed on 52 g. of 80–200 mesh silica gel, by eluting with increasing proportions of chloroform in methylene chloride; v.p.c. analysis (column D, 140°, helium flow 50 cc./min.) of the seventh fraction (eluted with 10% chloroform) showed a single peak at 23.8 min. (corresponding to b) and a small shoulder at 22 min. (perhaps a). The infrared spectrum had strong bands at 5.84 (carbonyl), 8.83, and 11.2 μ (terminal methylene). An n.m.r. sample obtained *via* v.p.c. from fractions 7 through 9 showed a singlet at 1.67 δ (three protons, after correcting for background) and a multiplet at 4.67 δ (two protons), the pattern expected for a methyl group adjacent to a terminal methylene. Except for a trace of methyl proton impurity, b was identical spectrally and by v.p.c. with an authentic sample of 2-[β -methyl]cyclohexanone (III) described below. The analytical sample was prepared from the n.m.r. specimen by v.p.c.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.55; H, 10.61.

Identification of c.—Material collected by v.p.c. (column D, 125°, helium flow 50 cc./min.) from several injections of distillation fraction 1 was reinjected to obtain a sample of c containing about 12% e. The n.m.r. had two methyl proton peaks at 0.97 and 1.15 δ (three protons each if correction is made for the e impurity), a methylene region with the highest peak at 2.02 δ , and five multiplets in the 2.4 to 3.1 δ region totaling two protons. The infrared carbonyl absorption was at 5.87 μ (strong). An analytical sample was prepared by v.p.c. from the n.m.r. specimen. The n.m.r. thus identifies c as *cis*-7,7-dimethylbicyclo-[4.2.0]octanone-2 (*cis*-I) previously reported.²

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.80; H, 10.71.

Identification of d.—The twelfth fraction of the same silica gel chromatograph from which b was isolated gave a single peak at 35.6 min. by v.p.c. (column D, 140°, helium flow 50 cc./min.) accompanied by less than 2% of 24-min. eluate. Strong infrared absorption was observed at 5.84 (carbonyl), 8.16, and 11.18 μ (terminal methylene). An n.m.r. sample prepared *via* v.p.c. showed, besides trace amounts of c and e in the methyl proton region, a quartet, $J = ca. 0.6$ c.p.s. at 1.70 δ (three protons, after correction for background), a large methylene proton peak at 2.02 δ , and an olefin multiplet at 4.72 δ (two protons). The structure of 3-methylcyclohexanone (IV) is thus assigned to d since its spectra and v.p.c. behavior differ from that of the synthetic 2-methylcyclohexanone. The n.m.r. sample was purified for analysis by v.p.c.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.56; H, 10.32.

Identification of e.—Repeated injections of distillation fraction 1 were collected by v.p.c. (column D, 125°, helium flow 50 cc./min.) and reinjected to give e. Two sharp methyl peaks (three protons each) appeared in the n.m.r. spectrum at 1.08 and 1.15 δ . The infrared spectrum showed a strong carbonyl absorption at 5.81 μ and many lesser, yet well-defined peaks at longer wave lengths. There was no evidence to indicate the presence of olefin in either spectrum; v.p.c. collection of the n.m.r. sample provided a sample for analysis. This substance is converted to *cis*-I upon treatment with alumina and, hence, is formulated as *trans*-I.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.47; H, 10.26.

Equilibration of *trans*- and *cis*-I. (A) **By Filtration through Alumina.**—The equilibration of e (*trans* ring fusion) to c (*cis* ring fusion) under mild conditions was best illustrated by the following experiment. A 35-mg. sample of distillation fraction 6 was placed on a column of 2.3 g. of grade I neutral alumina and eluted with ether. Removal of solvent left 27 mg. of product. A comparison of n.m.r. spectra showed that the two equal-intensity methyl proton peaks at 1.08 and 1.15 δ of the starting material had been converted to two equal-intensity methyl proton peaks at 0.97 and 1.15 δ characteristic of *cis*-I. In addition, the peak at 2.02 δ had increased in intensity; v.p.c. analysis indicated that a starting material peak (90% of the sample) containing d and e had been converted to a product peak (90.7% of the sample) of shorter elution time containing c (pronounced shoulder) and d.

A sample of the starting material filtered through silica gel showed no conversion of the 1.08 and 1.15 δ n.m.r. peaks but again showed significant increase in the 2.02- δ peak.

(B) **By Treatment with Hydroxide.**—A 5.193-g. sample containing (by n.m.r.) e and c in the ratio of 5:1 was refluxed under nitrogen for 2 hr. with 38 ml. of 4% potassium hydroxide in methanol and 15 ml. of water. The usual work-up and distillation afforded 4.386 g. (85% conversion) of colorless liquid, b.p. 56–59° (0.3 mm.), showing the same shift of n.m.r. methyl proton peaks described in part A above.

(C) **By Acid Treatment.**—A 0.617-g. sample identical with that used in part B was refluxed 2 hr. in 30 ml. of benzene containing 21 mg. of *p*-toluenesulfonic acid monohydrate. The usual work-up and distillation gave 0.382 g. (62% conversion) of colorless liquid. The n.m.r. showed the same shift of methyl proton peaks noted in parts A and B.

(D) **By Heating.**—An n.m.r. sample tube containing 0.475 g. of material identical with that used in part B was degassed with shaking and filled with argon four times. A drop of tetramethylsilane was added and the tube sealed. Heating 40 min. in a 205° oil bath resulted in the disappearance of the 1.08- δ n.m.r. peak accompanied by decreases in peaks at 1.15 and 1.67 δ , and increases in peaks at 0.97 and 2.02 δ . This closely parallels the changes produced by base, even to the appearance of small peaks in the 2.5 to 3.1 δ region (noted for photoproduct c). It is therefore likely that e would be quickly equilibrated upon contact with the v.p.c. injection chamber at 235°. It is evidently stable to injection temperatures around 150°.

Irradiation of *cis*-I.—To test for the possibility of *trans*-I being formed under irradiation conditions from the *cis* isomer, a solution of 4.106 g. of base-equilibrated photoproduct mixture in 160 ml. of pentane was irradiated 6 hr. under the usual conditions. Removal of solvent followed by distillation gave after a small forerun: (a) 1.799 g. of colorless liquid, b.p. 49–51° (0.25 mm.); (b) 0.273 g. of nearly colorless liquid, b.p. 51–60° (0.2 mm.).

Neither fraction contained *trans*-I since no n.m.r. peak appeared at 1.08 δ ; v.p.c. analysis (column A, 175°, helium flow 51 cc./min.) showed fraction a was essentially unchanged starting material with peaks at elution times of 9 (9.8% of sample), 12.3 (15.2%, a and b), and 17 min. (52.5%, c and d). Fraction b, however, contained 70.5% of an 8.6-min. eluate (sh. 8.3 min.) and only 3.2 and 20.3% of the 12.7- and 17-min. eluates, respectively.

This 8.6-min. eluate was collected by double passage through v.p.c. column B. The infrared spectrum showed strong absorption at 2.95 (hydroxyl) and 9.47 μ . The n.m.r. spectrum had a pair of peaks at 0.87 and 1.13 δ and another pair at 0.93 and 1.20 δ , the ratio of the first pair to the second being about 1:3. A broad band with an integrated intensity estimated at about one-sixth that of the methyl proton region appeared at 3.6 δ . This sample is probably a mixture containing two alcohols corresponding to reduced *cis*-I and produced by this photoreaction in 91% yield. Reduction of *cis*-I by sodium borohydride in methanol-water furnished an alcohol which after distillation exhibited infrared peaks at 2.95 and 9.5 μ and n.m.r. peaks at 0.93 and 1.20 δ (attributed to methyl groups) and broad peaks at 3.6 and 4.07 δ , corresponding to those observed for one of the alcoholic products from the photoreaction.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.16; H, 11.75.

Quantitative Analysis of the Photoproduct from Isobutylene and 2-Cyclohexenone.—The photocondensation was repeated to obtain all products in a single distillation fraction. A solution of cyclohexenone (7.854 g., 0.082 mole), isobutylene (115 ml., 1.23 moles), and 210 ml. of pentane (purified by acid washing) was irradiated 6.5 hr. until cyclohexenone could no longer be detected by v.p.c. Removal of the solvent gave 10.794 g. (86.8%) of crude product, of which 8.915 g. was distilled on a 46-cm. spinning band column to afford 6.733 g. (75.4% recovery \times 86.8% = 65.5% yield based on starting cyclohexenone), b.p. 43–45° (0.2 mm.), and 1.384 g. of yellow residue. (An additional 0.216 g. of colorless distillate was recovered from the still head.) The distillate was then analyzed by v.p.c. (column D, 150°, helium flow 60 cc./min.). An average of the two best injections indicated 5.8% of the material in peak A (retention time, 8 min.), 31.6% in peak B (14 min.), and 62.6% in peak C (21 min. with a shoulder at 19.5 min.). These proportions multiplied by 65.5% yield gave the percentage yields of material represented by each peak as 3.8, 20.7, and 41.0% for A, B, and C, respectively. Samples of

material corresponding to the latter two peaks were prepared for n.m.r. analysis by double passage through the Autoprep unit. Since the fraction corresponding to peak B consisted only of II and 2-[β -methallyl]cyclohexanone (III) and that corresponding to C consisted only of *cis*-I and *trans*-I and 3-[β -methallyl]cyclohexanone, quantitative analysis by n.m.r. was straightforward. However, the ratio of *cis*-I to *trans*-I was taken from n.m.r. analysis of the original distilled photoproduct because of the problem of partial *trans* \rightarrow *cis* isomerization during v.p.c. The calculated yields of products were: 26.5% *trans*-I, 6.5% *cis*-I, 6% II, 14% III, and 8% IV.

2-[β -Methallyl]cyclohexanone (III).—A colorless solution of the morpholine enamine of cyclohexanone (8.009 g., 48 mmoles) and sodium iodide (0.782 g., 4 mmoles) in 50 ml. of acetonitrile was evacuated of air and filled with nitrogen six times. Freshly distilled methallyl chloride (4.529 g., 50 mmoles) was then added dropwise *via* syringe and a sodium chloride precipitate rapidly formed. The stirred mixture was refluxed under nitrogen 2.5 days during which time it gradually turned orange, then red. The cooled mixture was washed with portions of 1% hydrochloric acid, 10% sodium bisulfite, water, and saturated brine, dried over anhydrous sodium sulfate, and concentrated. The residual oil was distilled on a 46-cm. spinning band column to obtain 1.206 g. (16.4%) of colorless liquid, b.p. 38–39° (0.09 mm.). This was found to be identical by infrared, n.m.r., and v.p.c. analysis with photoproduct b. A sample of III was collected by v.p.c. for elemental analysis.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.79; H, 10.27.

1,1-Dimethoxyethylene was prepared by adding bromoacetaldehyde dimethylacetal (169 g., 1 mole) to a solution of potassium metal (39.1 g., 1 g.-atom) in 943 g. of α -terpineol which had previously been dried over anhydrous sodium sulfate and distilled from calcium hydride. The mixture was allowed to reflux under nitrogen for a few minutes at 120 to 200° and then distilled. The 60.7-g. fraction, b.p. 85–95°, was redistilled on a 46-cm. spinning band column to obtain 53.493 g. of colorless liquid, b.p. 88–91° (lit.²⁷ 89–91°). The n.m.r. spectrum showed two sharp peaks at 3.08 and 3.64 δ in the ratio 1:3.

Photocondensation of 2-Cyclohexen-1-one with 1,1-Dimethoxyethylene.—A solution of cyclohexenone (4.089 g., 0.043 mole), 1,1-dimethoxyethylene (53.493 g., 0.607 mole), and 270 ml. of pentane was irradiated 5 hr. and distilled. The forerun, 22.408 g. of recovered 1,1-dimethoxyethylene, b.p. 88–92°, was followed by the photoproduct collected in three fractions: (1) 1.238 g., b.p. 47–73° (0.25 mm.); (2) 2.800 g., b.p. 64° (0.02 mm.)–57° (0.01 mm.); (3) 3.132 g., b.p. 61–97° (0.01 mm.) (slightly yellow). Thus, 7.170 g. (91%) of distillate and 0.611 g. (7.8%) of brown oily residue were obtained.

Analysis of the distillates by v.p.c. (column C, 140°, helium flow 60 cc./min.) indicated product yields of components at the following elution times: 6.9% at 6.0 min., 21.3% *cis*-V (12.7 min.), and 48.6% *trans*-V (15.7 min.). Broader peaks indicated mixtures of other components: 6 (1.2 min.), 3.4 (3 min.), and 5% (27–34 min.). Spectra of the collected 6-min. eluate indicated it to be a mixture. A medium intensity carbonyl peak appeared in the infrared spectrum of this material at 5.82 μ and several stronger bands were found in the 8.0–11.5 μ region. A weak band at 2.83 μ indicated some hydroxyl. The n.m.r. spectrum had two strong methoxy peaks at 3.14 and 3.19 accompanied by multiplets at 3.69, 4.24, and 5.95 δ .

Distillation fractions 2 and 3 partially solidified. The solid was twice alternately recrystallized from pentane and evaporatively distilled (65°, 0.13 mm.) to give colorless irregular prisms, m.p. 51–52.5°, with an infrared spectrum (strong carbonyl absorption at 5.81 μ) identical with that of the 15.7-min. eluate, *trans*-V. The n.m.r. spectrum showed two equal peaks at 3.18 and 3.27 δ (6 methoxy protons) and a methylene region (10 protons).

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.01; H, 8.58.

Equilibration of 0.110 g. of the pure solid isomer *trans*-V on 8.0 g. of base-washed alumina gave 0.106 g. of *cis*-V identical by infrared and n.m.r. spectra with the 12.7-min. v.p.c. eluate. The infrared spectrum showed strong carbonyl absorption at 5.85 μ and the n.m.r. spectrum showed two poorly resolved peaks at 3.11 and 3.12 δ (6 methoxy protons); a small portion was distilled for an analytical sample.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.89; H, 8.54.

The solid isomer is thus assigned the *trans* ring fusion and the liquid the *cis* fusion. A 0.053-g. sample containing about equal amounts of these two isomers was stirred under nitrogen 1 hr. with a solution of 0.007 g. of sodium in 3 ml. of ethanol. The usual work-up provided 0.044 g. of light yellow liquid. The n.m.r. spectrum of this product showed it consisted mainly of *cis*-V with no indication of replacement of methoxy by ethoxy. This supports the assignment of these adducts as 7,7-dimethoxybicyclo[4.2.0]octan-2-ones (V).

Hydrolysis of *trans*-V to the Diketone VI.—A 0.156-g. portion of the *trans*-dimethoxyketone V was suspended in 10 ml. of water containing 2 drops of concentrated hydrochloric acid. While being stirred 1.5 days at room temperature, the crystals dissolved giving a colorless solution. Neutralization and work-up gave 0.114 g. (98%) of a light yellow oil which on distillation in a two-bulb tube gave 0.106 g. of colorless liquid VI, b.p. 70–90° (0.07 mm.), negative ferric chloride test. The v.p.c. curve (column C, 140°, helium flow 50 cc./min.) showed one peak at 20.7 min. with a small shoulder at 22 min. Collection of this peak gave an analytical sample.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.52; H, 7.19.

The infrared spectrum showed very strong absorption at 5.62 (cyclobutanone) and 5.83 μ (cyclohexanone) and weak absorption at 2.75 μ (hydroxyl). The n.m.r. spectrum was not readily analyzed owing to complex spin-spin splitting and overlapping of bands.

Hydrolysis of *cis*-V under the same conditions with acid afforded the same diketone.

Benzyl Vinyl Ether.—Benzyl vinyl ether was prepared by the transesterification method.²⁸ A mechanically stirred solution of benzyl alcohol (515 g., 4.76 moles), *n*-butyl vinyl ether (2979 g., 28.3 moles), and mercuric acetate (28.5 g., 0.09 mole) was heated at 88–95° for 9 hr. and then anhydrous potassium carbonate (21.22 g., 0.15 mole) was added and the mixture was distilled through a 15-in. column. The fraction, b.p. 70–85° (15 mm.), which consisted mainly of benzyl vinyl ether contaminated with benzyl alcohol (total 198 g.) was treated with 18 g. of sodium in small portions over 2 hr. and redistilled to give 52.5 g. of pure benzyl vinyl ether, b.p. 79–80° (15 mm.).

Photocondensation of 2-Cyclohexen-1-one with Benzyl Vinyl Ether.—A solution of cyclohexenone (4.855 g., 0.05 mole) and benzyl vinyl ether (44.265 g., 0.33 mole) in 270 ml. of purified pentane was irradiated for 4 hr. Solvent was removed and the unchanged benzyl vinyl ether (31 g.) was recovered by distillation; the last portion was removed at b.p. 30° (0.05 mm.). The 14.118 g. of light yellow viscous oil remaining was then distilled through a short pass still on a vacuum line at 10⁻⁶ mm. to obtain 0.769 g. of a very light yellow liquid, b.p. 102–117°, and 8.129 g. (70.5%) of light yellow liquid, b.p. 118–128°. The residue was 4.648 g. of orange viscous oil.

The main distillation fraction exhibited strong carbonyl absorption at 5.85 μ and intense bands at 8, 9, 13.5, and 14.3 μ . The n.m.r. spectrum showed an aromatic proton peak (7.25 δ), at least six peaks in the region 4.3–4.6 δ (methylene protons of the benzyloxy unit), and broad absorption further upfield attributed to protons attached to saturated carbon. Treatment of this material with sodium methoxide-methanol or alumina reduced the number of peaks in the n.m.r. spectrum at 4.3–4.6 δ ; a sharp peak at 4.33 δ and two relatively minor bands at 4.39 and 4.52 δ remained. No olefinic proton peaks appeared in the n.m.r. spectrum either before or after base treatment. The major fraction thus appears to consist of a mixture of isomeric saturated adducts with both *trans* and *cis* fused ring structures. An analytical sample was prepared by distillation at 130° (0.05 mm.); however, complete fractionation of the mixture was not attempted.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.51; H, 7.70.

In order to determine the position of the benzyloxy group in the components of the major distillation fraction, 202 mg. of the above product was treated with a solution of 50 mg. of sodium in 5 ml. of methanol under nitrogen at 25° for 1 hr. A stream of carbon dioxide (excess) was introduced to decompose sodium methoxide and the solution was evaporated to dryness at 20 mm. The residue was extracted repeatedly with *n*-pentane-ether (4:1)

(27) S. M. McElvain and G. R. McKay, Jr., *J. Am. Chem. Soc.*, **77**, 5601 (1955).

(28) W. H. Watanabe and L. E. Conlon, *ibid.*, **79**, 2828 (1957).

and the extracts were dried and concentrated to give 190 mg. of oil. This was examined by n.m.r. and found not to contain methoxy or olefinic protons indicating that very little 8-benzyl-oxybicyclo[4.2.0]octanone-2 was present in the original material. The base-treated material appeared to consist of one major component with a single sharp methylene peak at 4.33 δ in the n.m.r. spectrum as noted above. This is probably *cis*-7-benzyl-oxybicyclo[4.2.0]octanone-2 (VII, R = C₆H₅CH₂). From the n.m.r. data we infer that *trans*-7-benzyl-oxybicyclo[4.2.0]octanone-2 is present in the original photoproduct in amount roughly twice that of the *cis* isomer and that the benzyloxymethylene protons in this *trans* compound do not have the same n.m.r. chemical shift.

The photoproduct was correlated with V by conversion to the diketone VI as follows. The material from the sodium methoxide treatment described above (190 mg.) was hydrogenated with 30 mg. of 10% palladium on charcoal in 3 ml. of ethyl acetate. Absorption of hydrogen was rapid and 1.08 equiv. was taken up. The catalyst was removed by filtration and the product was recovered by evaporation of the solvent. The infrared spectrum indicated that the product was the desired 7-hydroxybicyclo[4.2.0]octanone-2, with absorption at 2.85 μ attributed to hydroxyl and at 5.85 μ to the ketonic function.

This material was oxidized in 15 ml. of acetone with 0.21 ml. of 8 N chromic acid solution (Jones reagent) at 25°. Evaporation of solvent, addition of saturated sodium sulfate solution, and extraction gave, after washing with bicarbonate and evaporation of the extracts, a colorless liquid. Distillation afforded 64 mg. of the *cis*-diketone VI, identical by infrared, n.m.r., and v.p.c. with a sample obtained by acid hydrolysis of *cis*-V as described above.

Photoaddition of Methoxyethylene to 2-Cyclohexenone.—A solution of 2.000 g. (0.02 mole) of cyclohexenone and 30 ml. (0.4 mole, density at 0° = 0.777 g./ml.) of methoxyethylene in 110 ml. of pentane was irradiated under argon in a Dry Ice bath under the usual conditions. After 3 hr. and 15 min., the reaction was complete and the pentane and methoxyethylene were removed *in vacuo*. Distillation of the liquid residue yielded four fractions: (1) b.p. 50–58° (0.1 mm.), 0.0305 g.; (2) b.p. 58–60° (0.1 mm.), 0.7873 g.; v.p.c. analysis on column D at 190° gave peaks at 8.2 (46%), 9 (42%), and 10.2 min. (12%); (3) b.p. 60–61° (0.1 mm.), 0.9767 g.; v.p.c. analysis showed peaks at 8.2 (37%), 9 (45%), and 10.2 min. (18%); and n.m.r. analysis showed three methoxyl peaks at 3.17, 3.20, and 3.30 δ ; (4) b.p. 61–62° (0.1 mm.), 0.2540 g.; v.p.c. analysis showed peaks at 8.4 min. (25%), 9 (45%), and 10.2 min. (30%). The three photoproducts (total yield 2.05 g., 67%) were separated for analysis by v.p.c. The products corresponding to peaks 1–3 showed carbonyl absorption in the infrared at 5.86 μ , 5.81, and 5.81 μ , respectively.

Anal. Calcd. for C₈H₁₄O₂: C, 70.09; H, 9.15. Found: Peak 1: C, 69.88; H, 9.12. Peak 2: C, 69.80; H, 9.05. Peak 3: C, 69.66; H, 9.00.

When an ethereal solution of 0.2035 g. of the above mixture from fraction 3 was placed on a column of 7 g. of Woelm neutral alumina (activity I) and eluted with ether, 0.1842 g. of a clear oil was obtained which by v.p.c. analysis consisted of only two components, those corresponding to peaks 1 and 2 above; in addition peak 1 was augmented by an amount corresponding to peak 3 in the starting mixture of adducts.

Treatment of the mixture of photoadducts with sodium ethoxide in ethanol (concentration 9.5 g. Na/l.) at 25° for 2 hr. under nitrogen did not cause elimination of methoxy groups or introduction of ethoxy groups as determined by n.m.r. These data indicate VII, R = OCH₃, as the structure of the isomeric photoproducts.

Photocondensation of 2-Cyclohexen-1-one with Allene.—This reaction presented more problems than others of this series because of the very low boiling point of allene (–32°). Thus, if the solution was not cold enough when allene was introduced, rapid ebullition could occur resulting in loss of sample. A solution of cyclohexenone (11.0 g., 0.1145 mole), allene (100 g., 2.5 moles), and pure pentane (530 ml.) was irradiated for 4.5 hr. The Dry Ice bath was sufficiently deep to cool the reaction vessel even above the level of internal liquid. At the end of the reaction a long hypodermic needle was inserted into the reaction mixture and a stream of nitrogen was passed through for ebullition. The cooling bath was slowly lowered and the allene was carefully distilled. Removal of the solvent and distillation gave 8.6 g. (55%) of adduct VIII, b.p. 43–45° (0.65 mm.). Analysis by v.p.c. (column D, 175°, helium flow 50 cc./min.) indicated the photoproduct consisted of one component eluted at 10.2 min. The infrared spectrum of VIII shows strong carbonyl absorption

at 5.87 μ and a broad terminal methylene band at 11.36 μ . The n.m.r. spectrum of VII shows a multiplet at 4.79 δ (2H) and another at 3.46 δ (1H), probably in the angular position between the carbonyl and terminal methylene groups and three more complex multiplets in the methylene proton region. An analytical sample was prepared by v.p.c.

Anal. Calcd. for C₉H₁₂O: C, 79.37; H, 8.88. Found: C, 79.22; H, 8.91.

Base Treatment of the VIII.—A homogeneous solution containing the allene photoproduct VIII (0.285 g., 2.09 mmoles), 1 ml. of 2% potassium hydroxide–methanol solution, 2 ml. of methanol, and 2 ml. of water was stirred 1 hr. at room temperature. After removal of most of the methanol, the residue was extracted with 1:1 pentane–ether and the combined extracts were washed with water, dried, and concentrated. The infrared spectrum of the resulting colorless liquid IX (0.270 g.) had strong bands at 5.90 (carbonyl), 8.11, 8.42, and 9.3 μ and a medium olefin absorption at 11.15 μ . Two new singlets of equal intensity appeared in the n.m.r. at 1.12 δ (methyl, 3H) and at 3.12 δ (methoxy, 3H) indicating that the elements of methanol had added across the carbon–carbon double bond. That this reaction occurred under such mild conditions suggests that the olefinic group had been in a position from which it could isomerize into conjugation with the carbonyl group as an intermediate step.

An analytical sample of this methoxy compound IX was prepared by treating 0.318 g. of allene photoproduct VIII with 0.011 g. of sodium dissolved in 5 ml. of methanol for 1 day under nitrogen. The usual work-up yielded 0.327 g. of crude products, portions of which were distilled to provide analytical and n.m.r. samples.

Anal. Calcd. for C₁₀H₁₆O₂: C, 71.39; H, 9.59. Found: C, 71.80; H, 9.55.

The product of the 1-hr. base treatment, which contained about 78% of methoxy compound with 22% of allene photoproduct, was treated for 4 hr. more with the same amounts of potassium hydroxide, methanol, and water. Work-up as before produced a new compound X with a very strong infrared absorption at 5.84 μ (carbonyl). The n.m.r. spectrum showed almost complete disappearance of the 1.12 and 3.12 δ peaks and the appearance of an intense new singlet at 2.07 δ (CH₃CO, 3H). A sample was distilled for analysis.

Anal. Calcd. for C₉H₁₄O₂: C, 70.10; H, 9.15. Found: C, 70.19; H, 9.23.

Hydrogenation of the Allene Photoproduct VIII.⁸—The photoketone VIII (0.508 g., 3.72 mmoles), stirred at room temperature with 0.050 g. of 10% palladium on charcoal in ca. 2 ml. of methanol, rapidly took up hydrogen to 95% of theory. Removal of catalyst and solvent gave 0.495 g. (96.3%) of light yellow liquid. The strong infrared band at 5.88 μ (carbonyl) was only slightly weaker than the 3.41 μ band (C–H stretching). The n.m.r. spectrum showed two peaks of equal intensity at 0.91 and 1.01 δ (3H) and four well-defined peaks at 3.08, 3.18, 3.24, and 3.32 δ (0.6 proton total; probably the angular proton adjacent to the carbonyl, split twice by adjacent single protons). These data show that the only unsaturation in the allene photoproduct is C=CH₂, as expressed by formula VIII.

Photoaddition of Vinyl Acetate to 2-Cyclohexenone.—A solution of 8.00 g. (0.08 mole) of 2-cyclohexenone and 103 g. (1.2 moles) of vinyl acetate (Eastman Kodak, stabilized and not distilled before use) in 450 ml. of pentane under argon was irradiated at room temperature through a Pyrex well and filter. After 8.5 hr., the reaction was complete and the vinyl acetate and pentane were removed *in vacuo* to yield 15.43 g. of colorless oil. A 4.92-g. portion was distilled through a Holzmann column to yield three fractions: (1) b.p. 80–83° (0.15 mm.), 0.0674 g.; (2) b.p. 83–84° (0.15 mm.), 0.895 g.; infrared absorption at 5.74, 5.79, and 5.84 μ ; n.m.r. peaks at 1.95, 1.97, and 2.06 δ attributed to acetyl; v.p.c. (20% fluorosilicon column at 195°) peaks at 23 (50%), 25 (20%), and at 29 min. (30%); (3) b.p. 84–88° (0.15 mm.) 1.355 g.; infrared absorption at 5.75, 5.80, and 5.85 μ ; v.p.c. peaks at 23 (35%), 25 (25%), and at 29 min. (40%). Samples were collected from the v.p.c. column for infrared spectra and analysis: component (1): 5.75, 5.85 μ ; component (2): 5.75, 5.79 μ ; component (3): 5.75, 5.86 μ .

Anal. Calcd. for C₁₀H₁₄O₃: C, 65.91; H, 7.74. Found: Component (1): C, 65.67; H, 8.12. Component (2): C, 65.69; H, 7.98. Component (3): C, 65.70; H, 7.85.

Equilibration of the Vinyl Acetate Adducts on Alumina.—A solution of 0.1942 g. of the vinyl acetate–cyclohexenone adduct (fraction 2) in ether was added to a column of 10 g. Woelm activ-

ity I alumina and left for 30 min. Elution with chloroform and concentration of the eluent yielded 0.2183 g. of a colorless oil (probably contains some chloroform), 5.75 and 5.87 μ ; v.p.c. analysis with a 20% fluorosilicon column at 195° gave peaks at 23 (67%), 25 (7%), and 29 min. (26%); n.m.r. gave two peaks for $\text{CH}_3\text{-COO-}$ at 1.95 and 1.98 δ and a complex multiplet between 4.55–5.05 for the hydrogen α to the acetoxy group. Apparently the 25-min. peak is *trans* fused compound and is isomerized to the 23-min. peak on alumina. The *trans* fused ketone band (5.79 μ) also disappears in the infrared spectrum after equilibration.

Conversion of the Vinyl Acetate Adducts to Diketone VI.—A solution of 0.5496 g. of the vinyl acetate-cyclohexenone adduct (fraction 3) and 0.25 g. of sodium hydroxide in 1 ml. of water and 5 ml. of ethanol was refluxed for 1 hr. After concentration *in vacuo* to remove most of the ethanol, 20 ml. of methylene chloride and 5 ml. of water were added. The aqueous layer was saturated with sodium chloride and extracted again with methylene chloride. After drying the combined extracts, it was concentrated *in vacuo* to yield 0.4688 g. of an oil; 2.90 and 5.88 μ .

The crude hydroxy ketone was taken up in 5 ml. of acetone and cooled in an ice bath while 1.5 ml. of Jones reagent (0.006 mole) was added dropwise with stirring. After stirring for 15 min., the mixture was concentrated *in vacuo* and the diketone was extracted with methylene chloride. The extract was dried and concentrated to yield 0.3041 g. of an oil (5.59 and 5.85 μ); v.p.c. on a 10% fluorosilicon column at 190° gave a single peak at 12.7 min. which was collected for an infrared spectrum. The v.p.c. retention time and the infrared spectrum were identical with those of authentic bicyclo[4.2.0]octan-2,7-dione.

Photocondensation of 2-Cyclohexen-1-one with *cis*-2-Butene.—A solution of cyclohexenone (5.173 g., 0.054 mole) and *cis*-2-butene (63.0 g., 1.12 moles) in 240 ml. of pentane was irradiated for 5 hr. Every hour an aliquot was withdrawn and injected into an evacuated flask sealed with a rubber septum and then allowed to come to room temperature. The vapors were then drawn into a gas cell (4-cm. path length) for infrared analysis. Spectra of the 0- and 5-hr. samples were identical except that a small absorption at 8.2 μ had disappeared and a strong absorption at 12.9 μ had greatly decreased. No *trans*-2-butene could be detected in these vapor spectra. The spectra of the liquid aliquots showed the normal disappearance of the cyclohexenone peak at 5.90 μ accompanied by formation of a new saturated ketone peak at 5.85 μ . Distillation of the reaction mixture provided 5.757 g. (73.1%) of adduct in two fractions, b.p. 40–48° (0.10 mm.), and 1.598 g. (20.3%) of residue; v.p.c. analysis of the distilled mixture (column D, 140°, helium flow 50 cc./min.) indicated yields of photoproducts (based on starting cyclohexenone) with the following elution times: 1.4% a (22–25.6 min.), 6.47% b (28.3–28.8 min.), 9.98% c (30.9–31.7 min.), and 55.5% d (36.8–37.9 min.). This last peak was shown by n.m.r. to contain two isomers. (See the section below comparing photoproducts of the *cis*- and *trans*-2-butene reactions.) Analytical samples were prepared by v.p.c.

Anal. Calcd. for $\text{C}_{10}\text{H}_{16}\text{O}$: C, 78.89; H, 10.59. Found for sample containing b and c: C, 78.62; H, 10.63. Found for sample of d: C, 78.77; H, 10.68.

Photocondensation of 2-Cyclohexen-1-one with *trans*-2-Butene.—A solution of cyclohexenone (7.690 g., 0.08 mole) and *trans*-2-butene (65 g., 1.16 moles) in 220 ml. of pentane was irradiated for 5.5 hr. and distilled on a 46-cm. spinning band column to obtain the colorless fractions: (1) 0.856 g., b.p. 35–42° (0.18 mm.); (2) 3.922 g., b.p. 44–47° (0.17 mm.); (3) 2.811 g., b.p. 45–46° (0.2 mm.); (4) 0.161 g., b.p. 52–63° (0.25 mm.), representing 63% yield. The yellow viscous residue amounted to 2.892 g. (23.7%); v.p.c. analysis of these distilled fractions (column D, 140°, helium flow 50 cc./min.) indicated yields of photoproducts with the following elution times: 1.8% a (21–25.6 min.), 6.89% b (28.3–29.4 min.), 4.10% c (31–32 min.), and 48.1% d. A comparison of the *cis*- and *trans*-2-butene photoproducts follows.

Comparative Study of the Photocondensation Products of 2-Cyclohexen-1-one with *cis*- and *trans*-2-Butene.—Preparative v.p.c. (Autoprep, 12 ft., 20% Dow Corning FS 1265 on Diatoport S, 120°, helium flow 150 cc./min.) was utilized to separate and collect components from the photoproduct mixtures for both the *cis*- and *trans*-2-butene reactions. The amounts of a collected were insufficient for spectral comparison. However, both the infrared and n.m.r. spectra were almost superimposable for each of the next three v.p.c. peaks b, c, and d collected from each of the two reaction mixtures. The n.m.r. spectra of the v.p.c. collected d were very similar but showed small differences in the methyl

proton region (as slight shoulders on the main peaks). Thus, the n.m.r. spectrum of a sample from *cis*-2-butene showed four peaks at 0.91 (sh. 0.92), 0.99, 1.02 (sh. 1.03), and 1.11 (sh. 1.14) δ , and the n.m.r. spectrum of a sample from *trans*-2-butene showed four peaks at 0.91, 1.00, 1.02, and 1.12 (sh. 1.14) δ .

These shoulders indicate the presence of minor component(s) in both samples of d. Treatment of these fractions of d with alumina under isomerizing conditions seemed to clean up the four principal methyl peaks indicating that minor amounts of a *trans* fused product might be present. The d fraction showed carbonyl absorption in the infrared at 5.87 μ .

The n.m.r. spectrum of product b had methyl proton peaks at 0.91, 0.98, 1.02, and 1.07 δ (six protons in a pair of doublets) and a quartet centered at 2.67 δ (one angular proton adjacent to the carbonyl group and split twice by adjacent protons). The infrared carbonyl absorption was at 5.89 μ .

The n.m.r. spectrum of product c showed a broad, poorly resolved methyl proton peak with crests at 1.01 and 1.06 δ (six protons) and a methylene proton region with an intense peak at 2.08 δ . The infrared absorption was at 5.81 μ .

Since olefinic photoproducts had been observed in the isobutylene reaction, a search was made for indications of the olefinic photoketones in the reactions of the 2-butenes. However, no appreciable peaks were observed in the olefinic proton region in the n.m.r. spectra of the materials a, b, c, or d described above.

Photoaddition of Cyclopentene to 2-Cyclohexenone.—A solution of 1.9966 g. (0.02 mole) of cyclohexenone and 23 g. (0.34 mole) of cyclopentene in 110 ml. of pentane under an argon atmosphere and cooled in a Dry Ice bath was irradiated with a high pressure mercury arc using a quartz well and Corex filter. After 75 min., the reaction was finished and the pentane and cyclopentene were removed by distillation to yield 4.0738 g. of colorless oil; v.p.c. of this on column D at 180° gave peaks at 16.5 (71%) (*cis* product) and at 19.1 min. (29%) (*trans* product). Distillation gave four fractions: (1) b.p. 57–64° (0.2 mm.), 0.0251 g.; v.p.c. on 5% fluorosilicon column at 150° gave peaks at 10 (90%) and at 11.6 min. (10%); (2) b.p. 63.5–64° (0.15 mm.), 1.7920 g., v.p.c. peaks at 10 (76%) and at 11.9 min. (24%); (3) b.p. 64–65° (0.15 mm.), 0.2879 g., v.p.c. at 10 (63%) and at 12 min. (37%); (4) rinsed from column, 0.0971 g., v.p.c. peaks at 10 (44%) and 12 min. (56%). The total yield was 2.202 g. (67%). Samples were collected by v.p.c. for infrared and elemental analysis. Infrared absorption for products corresponding to peaks 1 and 2 in the carbonyl region is at 5.88 and 5.82 μ , respectively.

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}$: C, 80.44; H, 9.82. Found: Peak 1: C, 80.62; H, 9.93. Peak 2: C, 80.63; H, 9.90.

A solution of 0.1036 g. of the cyclopentene adducts XII in ether was filtered through a column of 7 g. of activity I neutral Woelm alumina. Elution with ether and concentration of the eluent yielded an oil (0.1020 g.); 5.88 μ . Analysis by v.p.c. on column C at 150° gave a single peak at 10.3 min.; the later peak originally present had disappeared indicating that in the original mixture the material corresponding to peaks 1 and 2 are *cis*- and *trans*-fused isomers of XII, respectively.

Photoaddition of Acrylonitrile to 2-Cyclohexenone.—A solution of 2.002 g. (0.02 mole) of 2-cyclohexenone and 22.2 g. (0.4 mole) of freshly distilled acrylonitrile in 130 ml. of pentane under an argon atmosphere was irradiated at 25° with a high pressure mercury arc. (At –50° the reaction was exceeding slow; there was no detectable change after 4 hr.) A Pyrex well and filter were used. The infrared spectrum of a sample removed after 5 hr. indicated that the reaction was complete. The white polymer, which had deposited on the walls of the photochemical apparatus, was removed by filtration and the filtrate was concentrated *in vacuo* to remove pentane and excess acrylonitrile. Bulb-to-bulb distillation of the photoproduct yielded a colorless oil, 1.570 g. (53%), with infrared absorption attributed to cyano and keto groups at 4.46 and 5.83 μ ; v.p.c. analysis on column D at 225° revealed three peaks: one at 11.3 min. (61%), one at 12.0 min. (16%), and one at 16.2 min. (24%). The first and third peaks were collected from the column for analysis. Thin layer chromatography of the distilled photoproduct on silica gel using ether as eluent revealed three spots: (1) R_f 0.48 (50%), (2) R_f 0.42 (10%), and (3) R_f 0.26 (40%).

Anal. Calcd. for $\text{C}_9\text{H}_{11}\text{NO}$: C, 72.45; H, 7.43; N, 9.39. Found: Peak 1: C, 72.61; H, 7.56. Peak 3: C, 73.18; H, 7.60. Peaks 1 and 2: N, 9.20.

A solution of 0.2407 g. of the photoproduct was subjected to equilibration on alumina and eluted with chloroform to yield 0.2214 g. of colorless oil. Analysis by v.p.c. on column D at 225°

revealed three peaks; one at 11.3 min. (60%), one at 12.1 min. (19%), and one at 16.2 min. (21%). No appreciable amount of *trans* fused compound seems to be present in the photoproduct mixture.

The photoproduct mixture was separated on the Autoprep using a 20% fluorosilicon column at 210°. Under these conditions, components (1) and (2) are eluted together at 28 min., component (3) at 30 min., and component (4) at 44 min. Components (3) and (4) have the same R_f value and could not be separated by column chromatography. Components (1) and (2) could be separated by column chromatography on silica gel.

Components (1), (2), (3), and (4) must all be cyano ketones since they show ketonic carbonyl and cyano absorption in the infrared. Analysis of these compounds and the analogs containing deuterium substituents α to the carbonyl by n.m.r. suggests that (1) and (4) are 8-epimeric, 8-cyanobicyclo[4.2.0]octanones and that (2) is a 7-cyano position isomer. Component (3) was not obtained in sufficient amount and purity to permit study.

Approximate percentages of the photoproduct mixture are: component (1) = 49%, component (2) = 12%, component (3) = 15%, and component (4) = 24%.

Photoaddition of 1,1-Dimethoxyethylene to 2-Cyclopentenone.—A solution of 1.0139 g. (0.0124 mole) of redistilled cyclopentenone and 13.4151 g. (0.152 mole) of freshly distilled 1,1-dimethoxyethylene in 70 ml. of pentane under argon was cooled in a Dry Ice bath and irradiated using a high pressure mercury arc, quartz well, and Correx filter. The reaction was complete after 3 hr. and 40 min., and the pentane and excess 1,1-dimethoxyethylene were removed through a short Vigreux column. Distillation of the liquid residue yielded 1.53 g. of crude 6,6-dimethoxybicyclo[3.2.0]heptanone-2, b.p. 53–60° (0.03 mm.), infrared absorption attributed to carbonyl at 5.74 μ . This material was not homogeneous as shown by v.p.c. analysis which showed in addition to the major peak at 9.1 min. (column C, 140°, 60 ml./min. flow) two minor components as shoulders on either side of the main peak. Pure 6,6-dimethoxybicyclo[3.2.0]heptanone-2, m.p. 29–31°, was obtained by recrystallization from pentane at –70° or by v.p.c. purification. The yield of pure product is about 60%; its n.m.r. spectrum shows a single peak attributed to methoxy at 3.07 δ ; this is also the only methoxy peak in the n.m.r. spectrum of the crude product. The impurities appear to be unsaturated aldehydes with infrared absorption at 5.71 and 6.15 μ . An analytical sample of the solid product was obtained by v.p.c.

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.67; H, 8.30.

This product did not undergo isomerization when treated with alumina under the standard conditions for effecting epimerization of *trans* fused bicyclo[4.2.0]octanone-2 derivatives. Moreover, it did not undergo methoxy loss or replacement when treated with sodium ethoxide in ethanol.

Acid-Catalyzed Hydrolysis of 6,6-Dimethoxybicyclo[3.2.0]heptanone-2.—A heterogeneous mixture of 0.0659 g. of solid 6,6-dimethoxybicyclo[3.2.0]heptanone-2, 5 ml. of water, 1 ml. of tetrahydrofuran, and 2 drops of concentrated hydrochloric acid was stirred at room temperature for 10 hr. The homogeneous solution was concentrated *in vacuo* at room temperature to remove the tetrahydrofuran and most of the water. After taking up the liquid residue in 15 ml. of ether–pentane (1:1), the solution was washed with saturated brine, dried over magnesium sulfate, and concentrated *in vacuo* to yield bicyclo[3.2.0]heptanone-2,6 as an oil (0.0454 g.), 5.59 and 5.73 μ , homogeneous on column C at 125° giving a peak at 19 min. An analytical sample was collected from the v.p.c. column.

Anal. Calcd. for $C_7H_{10}O_2$: C, 67.73; H, 6.49. Found: C, 67.53; H, 6.57.

Photoaddition of 1,1-Dimethoxyethylene to 2-Cyclooctenone.—A solution of 2.0133 g. (0.016 mole) of 2-cyclooctenone and 27 g. (0.31 mole) of freshly distilled 1,1-dimethoxyethylene in 120 ml. of pentane under an argon atmosphere was irradiated with external Dry Ice cooling. The infrared spectrum of a sample taken after 4 hr. indicated the reaction was finished at this time. After removal of the pentane through a Vigreux column, 16 g. of 1,1-dimethoxyethylene was distilled at 25–27° (20 mm.) and the liquid residue was distilled to yield three fractions: (1) b.p. 31–32° (0.5 mm.), 0.4029 g. (2-cyclooctenone); (2) b.p. 32–75° (0.15 mm.), 0.0198 g.; and (3) b.p. 75–76° (0.15 mm.), 1.0282 g. The residue amounted to 1.1205 g. The yield of photoproduct based on consumed cyclooctenone was 37%. Analysis of fraction 3 by v.p.c. (column C at 170°) showed a single peak at 7.5 min. Fraction 3 exhibited a carbonyl band at 5.87 μ in the in-

frared spectrum and methoxyl resonances at 3.00 and 3.15 δ (total of six hydrogens) and no olefinic protons in the n.m.r. spectrum. An analytical sample was collected by v.p.c.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.49. Found: C, 67.85; H, 9.44.

Treatment of 10,10-Dimethoxybicyclo[6.2.0]decanone-2 with Ethanolic Sodium Ethoxide.—A solution of 0.0205 g. (0.9 mmole) of sodium in 6.5 ml. of absolute ethanol and 0.1514 g. (0.7 mmole) of 10,10-dimethoxybicyclo[6.2.0]decanone-2 was stirred under nitrogen at room temperature for 2.5 hr. Most of the ethanol was removed *in vacuo* and the liquid residue was taken up in 25 ml. of ether–pentane (1:1). After washing with water, the organic phase was dried over magnesium sulfate and concentrated *in vacuo* at room temperature to yield a light yellow oil (0.1246 g., infrared absorption 5.87 μ). The n.m.r. spectrum exhibited two C_2H_5O groups as a triplet at 1.13 δ (six hydrogens) and a quartet at 3.84 δ ; the two peaks attributed to methoxyl were removed almost completely. This material was homogeneous on column C at 170° giving a peak at 8 min. In order to remove the trace of starting material still present, the material was stirred with 0.0114 g. of sodium in 5 ml. of absolute ethanol at room temperature under nitrogen for 1 hr. and worked up as before to yield 0.111 g. of an oil; infrared absorption 5.77 (weak), 5.87 μ . The n.m.r. spectrum showed all the starting material was gone but a new peak (25%) appeared in the v.p.c. at 18 min. An analytical sample was collected by v.p.c.; the product clearly is 10,10-dimethoxybicyclo[6.2.0]decanone-2.

Anal. Calcd. for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: C, 70.10; H, 10.08.

Acid-Catalyzed Hydrolysis of 10,10-Dimethoxybicyclo[6.2.0]decanone-2.—A heterogeneous mixture of 0.1379 g. of 10,10-dimethoxybicyclo[6.2.0]decanone-2 in 10 ml. of water, 2 ml. of tetrahydrofuran, and 3 drops of concentrated hydrochloric acid was stirred for 15 hr. at room temperature. The reaction mixture became homogeneous and remained colorless. The tetrahydrofuran and most of the water were removed *in vacuo* at room temperature to yield an oil which was taken up in 20 ml. of ether–pentane (1:1) and washed with water. After drying the organic layer over magnesium sulfate and concentration *in vacuo*, a light yellow oil (0.0880 g.) was obtained with infrared absorption at 5.74 and 5.87 μ . The n.m.r. spectrum exhibited a sharp singlet at 3.58 δ (3 hydrogens). Analysis by v.p.c. on column C at 170° showed a single peak at 16.4 min. The analytical sample of XVI was obtained by v.p.c.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.78; H, 9.16.

Treatment of 10,10-Dimethoxybicyclo[6.2.0]decanone-2 with Alumina.—A solution of 0.0454 g. of 10,10-dimethoxybicyclo[6.2.0]decanone-2 in ether was placed on a column of 2.5 g. of Merck alumina (basic to wet pH paper). Elution with ether gave a colorless oil (0.0431 g.), 5.78 (med.) and 5.87 μ . The chemical shifts of the methoxyl groups in the n.m.r. spectrum and v.p.c. behavior were identical with those in the starting material indicating that isomerization at the ring fusion did not occur under these conditions.

In addition, no evidence of isomerization was found upon treatment of the adduct with sodium methoxide (from 14 mg. of sodium) in methanol (4 ml.) for 1 hr. at 25° using n.m.r. and v.p.c. analyses. It seems likely that the adduct from 1,1-dimethoxyethylene possesses the more stable 4–8 fusion; examination of models and consideration of the caryophyllene analogy suggests that the *trans* fusion may be more stable than *cis*.

Reaction of 1,1-Dimethoxyethylene with Preirradiated 2-Cyclooctenone (trans).—A solution of 0.9992 g. (0.008 mole) of *cis*-2-cyclooctenone in 120 ml. of pentane was irradiated under the usual conditions (Dry Ice bath). The infrared spectrum (5.81, 8.64, and 10.14 μ) after 30 min. indicated the *cis*-cyclooctenone was almost gone. Irradiation was continued for 15 min.; the mercury arc was shut off, the bath was removed, and 8.9818 g. (0.1 mole) of 1,1-dimethoxyethylene was injected immediately. The mixture was stirred and allowed to warm to room temperature. A sample removed after 45 min. exhibited infrared bands at 5.82, 6.00, 6.17, 8.64, and 10.13 μ . After stirring for 2 more hr., the reaction mixture was transferred to a flask and left at room temperature for 16 hr. The pentane was removed by distillation through a Vigreux column and the 1,1-dimethoxyethylene was distilled at 25–26° (20 mm.). The liquid residue was distilled in a bulb-to-bulb apparatus at 0.15 mm. with a bath temperature of 75–85° to yield a colorless oil, 0.7046 g., infrared absorption at 5.85 and 5.98 μ but no band at 10.15 corresponding

to *trans*-cyclooctenone; and a residue (0.5013 g., 5.88 μ). The *cis*-cyclooctenone was removed by distillation at 30–31° (0.5 mm.) (0.1461 g.) and the liquid residue was shown to be pure 10,10-dimethoxybicyclo[6.2.0]decanone-2 by infrared, v.p.c. analysis on a 5% fluorosilicon (C) column, and n.m.r. (two methoxyl peaks at 3.68 and 3.23 δ).

In a control experiment a solution of 0.2156 g. of cyclooctenone and 2.1107 g. of 1,1-dimethoxyethylene in 12 ml. of pentane was left at room temperature for 16 hr. and then concentrated *in vacuo*. Analysis of the liquid by v.p.c. on column C showed no peak corresponding to photoadduct and only the peak for cyclooctenone.

Irradiation of 2-Methyl-2-cyclohexenone with Isobutylene.—A solution of pure 2-methyl-2-cyclohexenone²⁹ (6.652 g., 0.06 mole), isobutylene (90 ml., 54 g., 0.915 mole), and 240 ml. of pentane was irradiated for 35 hr. Infrared spectra of aliquots removed at intervals from the reaction mixture showed that the extremely slow formation of saturated ketone was not accelerated by warming from –75 to –3°, by addition of 34 mg. of benzophenone, or by replacing the Corex filter with Vycor. At the end of 35 hr. the concentration of unsaturated ketone was estimated to have decreased by only about one-third. Distillation gave 22.4% recovered 2-methylcyclohexenone: 2.041 g. (20.4%) of yellow product mixture, b.p. 45° (0.13 mm.) to 75° (0.08 mm.); and 3.176 g. (31.8%) of reddish brown oily residue. Analysis by v.p.c. (column A, 200°, helium flow 60 cc./min., see Chart C) indicated a product yield of 10.9% of a mixture of at least seven components eluted in 1–7.5 min. and 8.4% of a material eluted at 8.5 min. This latter fraction was reinjected and again collected from the v.p.c. to obtain an analytical sample. The infrared absorption spectrum of this material indicated that saturated ketone (5.86 μ) and olefinic (3.28, 6.09, and 11.20 μ) groups were present. An n.m.r. spectrum showed broad peaks at 1.04 (doublet, J = 6.5 c.p.s.), 1.70, and 4.73 δ .

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.26; H, 10.81.

Photocondensation of 3-Methyl-2-cyclohexenone with Isobutylene.—A solution of 3-methyl-2-cyclohexenone³⁰ (5.926 g., 0.054 mole), isobutylene (75 ml., 45 g., 0.80 mole), and 250 ml. of pentane was irradiated for 6.25 hr., although infrared spectra indicated the reaction was essentially complete after 2 hr. Distillation afforded 4.633 g. (74.3%) of products, b.p. 35–66° (0.35 mm.), and 1.426 g. (16.0%) of yellow residue. The distillate was analyzed by v.p.c. using column D, and three components were detected with retention times (Autoprep instrument, 150°, flow 167 ml./min.) 27.5, 30, and 41 min. These were separated by preparative v.p.c.; they are referred to below as a, b, and c in order of elution.

The first component a was identified as 6,8,8-trimethylbicyclo[4.2.0]octanone-2. The n.m.r. spectrum showed sharp signals attributed to methyl groups at 1.25 (2CH₃) and 0.93 δ (1CH₃), a single proton at 2.24 δ and eight additional protons downfield—none of them far enough downfield to be olefinic. The infrared spectrum exhibited a carbonyl peak at 5.88 μ .

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.56; H, 10.99.

Reaction of component a with excess peracetic acid in methylene chloride at 25° for 50 hr. afforded the lactone XX which showed carbonyl absorption at 5.70 μ and sharp n.m.r. peaks at 3.8 (–CH–OCO–), 1.22 (2CH₃), and 1.18 δ (1CH₃). The fact

that the carbinol proton is unsplit allows the assignment of methyl group positions unequivocally.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.53; H, 9.98.

Hydrolysis of the lactone with aqueous alkali followed by acidification and extraction gave a hydroxy acid with infrared absorption at 2.2–4.0 μ attributed to hydroxyl and 5.83 μ to carboxyl. Oxidation of this acid with chromic acid–sulfuric acid in acetone produced a keto acid which showed carbonyl absorption at 5.65 (cyclobutanone) and 5.85 μ (carboxyl) which gave a keto ester

XXI with diazomethane. The keto ester absorbed in the infrared at 5.65 and 5.75 μ and exhibited sharp n.m.r. peaks at 3.65 (OCH₃), 1.22 (2CH₃), and 1.19 δ (1CH₃).

The n.m.r. spectrum of component b from the photoreaction showed a single methyl group as a doublet at 0.87 and 0.75 δ (therefore as >CH–CH₃), a methyl group attached to an olefinic linkage at 1.67 δ , and two olefinic protons at 4.62 δ . The infrared spectrum showed a carbonyl peak at 5.84 μ and terminal methylene bands at 6.08 and 11.25 μ . The substance b is therefore assigned the structure 3-methyl-2-[β -methylallyl]cyclohexanone.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.50; H, 10.94.

The third component, c, from the photoreaction was indicated clearly to be 3-methyl-3-[β -methylallyl]cyclohexanone from spectral data. The n.m.r. spectrum showed a sharp methyl peak at 0.94 δ , a broader methyl peak at 1.78 δ attributed to CH₃ attached to unsaturated carbon, two olefinic protons at 4.85 and 4.63 δ , and a total of 18 protons. The infrared spectrum of component c showed carbonyl absorption at 5.85 μ and terminal methylene absorption at 6.1 and 11.15 μ .

Competition Experiments. A.—A solution of 2.00 g. (0.02 mole) of cyclohexenone, 13.6 g. (0.2 mole) of cyclopentene, and 11.7 ml. (0.2 mole, density = 0.68 g./ml.) of allene in 100 ml. of pentane was irradiated under the usual conditions (Dry Ice cooling). The reaction was finished after 2.5 hr. and the excess allene was removed with a stream of nitrogen. Removal of the pentane and cyclopentene by distillation yielded a colorless oil (3.9028 g.). Analysis by v.p.c. on column C at 150° gave peaks at 3.4 (19%, allene adduct), at 9.7, and at 11.6 min. (81%, *cis*- and *trans*-cyclopentene adducts).

B.—A solution of 2.0079 g. (0.02 mole) of cyclohexenone, 13.6 g. (0.2 mole) of cyclopentene, and 17.5 ml. (0.2 mole, density = 0.64 g./ml. at –20°) of isobutylene was irradiated under the usual conditions (Dry Ice bath). After 3 hr., the reaction was complete and the isobutylene, cyclopentene, and pentane were removed by distillation to yield a colorless oil (3.3834 g.). Analysis by v.p.c. on column C at 150° gave peaks at 2.7, 4.3, and 6.0 min. (total of 21% isobutylene adducts) and at 11.6 and 13.8 min. (total of 79% cyclopentene adducts).

C.—A solution of 1.5432 g. (0.019 mole) of freshly distilled cyclopentenone, 10.23 g. (0.15 mole) of cyclopentene, and 13.22 g. (0.15 mole) of 1,1-dimethoxyethylene in 110 ml. of pentane under an argon atmosphere was irradiated with a high pressure mercury arc using a quartz well and Corex filter. Dry Ice cooling was used. After 2 hr., the reaction was complete and the pentane and cyclopentene were removed through a Vigreux column. The excess 1,1-dimethoxyethylene was distilled at 25–30° (30 mm.). Distillation of the liquid residue yielded a fraction, b.p. 54–59° (0.2 mm.), 1.7227 g., which was analyzed by v.p.c. on column C at 125° and gave peaks at 16 (72%, 1,1-dimethoxyethylene adduct) and at 17.7 min. (28%, cyclopentene adduct).

D.—A solution of 0.2957 g. (0.0031 mole) of cyclohexenone, 2.28 g. (0.026 mole) of 1,1-dimethoxyethylene, and 1.77 g. (0.026 mole) of cyclopentene in 15 ml. of pentane under an argon atmosphere was irradiated under the usual conditions (Dry Ice bath). After 1 hr., the reaction was complete and the pentane, cyclopentene, and 1,1-dimethoxyethylene were removed *in vacuo* at room temperature to yield an oil (0.6479 g.). Analysis by v.p.c. on column C at 180° gave peaks at 13.3 (21%, *cis*-1,1-dimethoxyethylene adduct), 15.8 (71%, *trans*-1,1-dimethoxyethylene adduct and *cis*-cyclopentene adduct (ratio 49:22, respectively)), and at 18.8 min. (8%, *trans*-cyclopentene adduct). Analysis by v.p.c. after equilibration on activity I Woelm alumina gave peaks at 13.5 (70%, *cis*-1,1-dimethoxyethylene adduct) and at 16.2 min. (30%, *cis*-cyclopentene adduct).

E.—A solution of 2.000 g. (0.02 mole) of cyclohexenone, 13.6 g. (0.2 mole) of cyclopentene, and 15 ml. (0.2 mole) of methyl vinyl ether was irradiated under the usual conditions. The reaction was complete after 2.5 hr. and the pentane and excess reagents were removed *in vacuo* to yield a clear liquid (2.9667 g.). Analysis by v.p.c. on column C at 150° gave peaks at 7.4, 8, and 9.5 min. (47% total, methyl vinyl ether adducts) and at 11.8 and 14 min. (53% total, cyclopentene adducts). Analysis by v.p.c. of the liquid obtained after equilibration on alumina gave peaks at 7.4 and 7.9 min. (44% total, *cis*-methyl vinyl ether adducts) and at 12 min. (56%, *cis*-cyclopentene adduct).

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