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Photo-induced Polar Addition of Protic Solvents to Cycloalkenones. Evidence for the Ground-state *trans* Isomers as Chemically-reactive Intermediates[1]

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The photo-induced reaction of cyclic α,β-unsaturated ketones with protic media is described. The irradiation of 2-cycloheptenone or 2-cyclooctenone in various protic solvents (alcohols, acetic acid, water, and diethylamine) results in the formation of Michael-type solvent adducts. The chemically-reactive species have been demonstrated to be the highly strained *trans* isomers in a ground state. The irradiation of *cis*-2-cyclononenone affords the stable *trans* isomer, which reacts in the dark with methyl alcohol at an elevated temperature to give 3-methoxycyclononanone. The irradiation of 2-cyclohexenone in methyl alcohol yields 3-methoxycyclohexanone in a poor yield. The possible existence of *trans*-2-cyclohexenone is discussed.

In recent decades the photochemistry of cyclic α,β-unsaturated ketones has received considerable attention.[2] Particularly interesting is the fact that the reaction course is profoundly influenced by the ring size. Diphenylcyclopropenone, the smallest cyclic enone, suffers photochemical decarbonylation to give tolan.[3] Cyclobutenone derivatives afford ketenes under electrocyclic ring opening.[4] The five- and six-membered homologs can undergo intermolecular photoreactions. 2-Cyclopentenone, upon irradiation, leads to the cyclobutane dimers in good yields,[5] while in the presence of an excess of cyclopentene [2+2] cross-cycloaddition takes place.[6] 2-Cyclohexenone shows a reactivity qualitatively parallel to that of 2-cyclopentenone in cycloaddition.[7] Certain 4,4-disubstituted 2-cyclohexenones are known to rearrange to the bicyclo[3.1.0]hexan-2-ones with group migration.[8] Throughout these intra- and intermolecular reactions, two points are noteworthy: (1) mechanistically, most of these reactions have been believed to occur in an electronically-excited state (either a singlet or a triplet), and (2) formally, the reactions are regarded as being a nonpolar (nonionic) process. In striking contrast, as will be shown below, upon irradiation seven- and eight-membered cyclenones can undergo polar (ionic) reactions arising from a highly reactive ground-state molecule. The mechanisms of the related polar reactions of 2-cyclohexenones are also a subject of our interest.

Results and Discussion

The photo-induced reactions of alcohols across a carbon—carbon double bond may be divided into the two classes depicted in Chart 1. Path *a* is a radical process and involves a fission of a weak C–H bond bearing an OH function (bond energy ~92 kcal/mol[9]). The second pathway, *b*, defined as a polar addition, involves a rupture of the stronger (~102 kcal/mol[9]), more ionic O–H bond.[10]

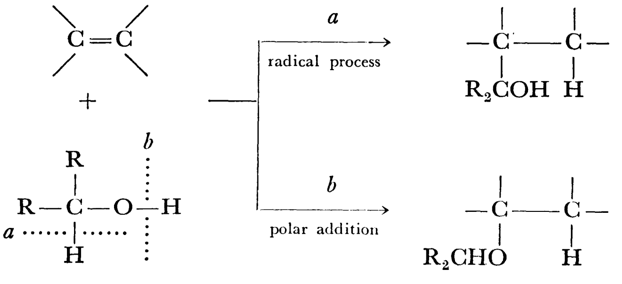


Chart 1.

The irradiation of 2-cycloheptenone (I)[11] with a high-pressure mercury arc in such protic solvents as alcohols, acetic acid, water–acetonitrile, and diethylamine at room temperature afforded the corresponding polar adducts, II. The results are given in Table 1. In certain cases, considerable amounts

Table 1. Irradiation of 2-cycloheptenone in protic solvents[a]

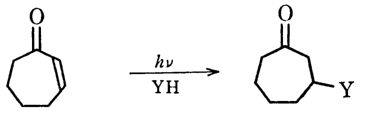
Solvent	Conversion %[b]	Yield of II %[b,c]
Methyl alcohol	68	86
Ethyl alcohol	66	73
Isopropyl alcohol	54	50[d]
tert-Butyl alcohol	40	3[d]
Acetic acid	34	23[d]
Water-acetonitrile (1 : 5)	61	27[d]
Diethylamine	80	55[e]

a) Irradiation was effected on 1.0% solution at room temperature for 15 min. b) Determined by glpc. c) Based on the consumed enone. d) Considerable amounts of cyclodimers were obtained.[12] Irradiation of I in cyclohexane gave cyclobutane dimers in 88% yield. e) Photolysis was performed at 0 °C and yield was determined by NMR analysis.

Table 2. Photolysis of 2-cyclooctenone in protic solvents[a]

Solvent	Irradiation time, min	Conversion %[b]	Yield of IV %[b,c]
Methyl alcohol	10	92	72
Isopropyl alcohol	150	90	43
Acetic acid	150	58	76
Water-acetonitrile (1 : 5)	75	81	25
Diethylamine	30[d]	85	66[e]

a) All photolyses were performed in a 1.0% solution at room temperature. b) Determined by glpc. c) Based on the consumed III. d) Irradiation was carried out at 0°C. e) Determined by NMR analysis.



I II a: $Y=OCH_3$ e: $Y=OCOCH_3$
b: $Y=OC_2H_5$ f: $Y=OH$
c: $Y=OCH(CH_3)_2$ g: $Y=N(C_2H_5)_2$
d: $Y=OC(CH_3)_3$

of cyclodimers[12] were also formed. No products were obtained *via* a radical process. A similar photo-induced polar addition of protic solvents was observed for 2-cyclooctenone (III),[11] as is summarized in Table 2. The structural determination of the photoproducts was made on the basis of elemental analyses and spectral data (Table 3). The structure of the β-ketols, IIf and IVd, was confirmed by converting them to the acetates, IIe and IVc, respectively.

The photo-induced polar addition reaction of the protic solvents mentioned here provides a new synthetic means of introducing oxygen or nitrogen functions to the β position of a carbonyl group under neutral or comparatively mild reaction conditions.

The observed photo-induced reaction could be interpreted in various ways. As the product-forming species, the π,π* triplet states of the enones[13,14] or, alternatively, the highly strained ground-state molecules derived therefrom may be involved. Oxabicyclobutanes[7b,12a,15] or enones containing a *trans* double bond[1,12,14,16] would be the candidates in the latter case (Chart 2). The reaction could also be accounted for by assuming the intervention of the polar state, a hypothetical dipolar species first suggested by Chapman.[17] We have examined in detail the behavior of I and III and found that their *trans* isomers are the product-determining intermediates.

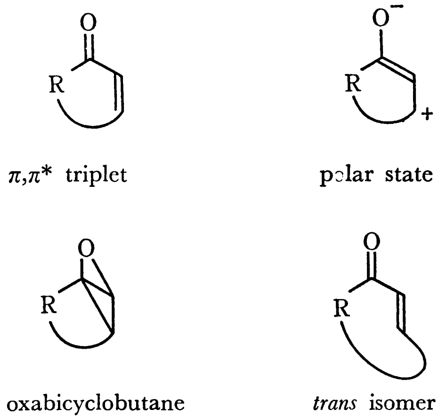
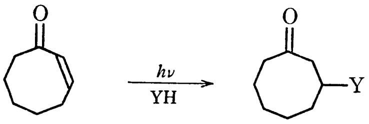
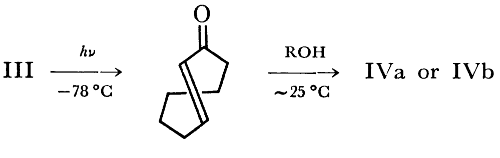


Chart 2. Possible reactive species.

Eaton and Lin observed that the photolysis of the medium-sized enone III causes a *cis-trans* isomerization, thus establishing an equilibrium between III and V (*ca.* 20 : 80 ratio).[16] The moderate thermal stability of the *trans* cyclenone, V, permitted low-temperature studies of its chemical behavior. The enone III was irradiated in 2-methyltetrahydrofuran at −78 °C for 15 min. After the light source had then been turned off, the photolysate was poured into an excess of cold (−78 °C) methyl alcohol and allowed to warm up to room temperature in the dark, thus producing the corresponding alcohol adducts, IVa, in a 43% yield. The starting enone, III, was recovered in a 41% yield. When isopropyl alcohol was used in place of methyl alcohol, IVb was obtained in a 24% yield. The irradiation of III in isopropyl alcohol under the same conditions, followed by treatment with a large excess of methyl alcohol in the dark, gave almost exclusively the methyl alcohol adduct, IVa (80%). Only a very small amount of the isopropyl alcohol adduct, IVb (<1%), if any, was formed. Apparently the polar addition to the photo-excited states is not significant.

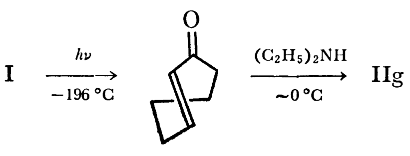


III IV a: $Y=OCH_3$ d: $Y=OH$
b: $Y=OCH(CH_3)_2$ e: $Y=N(C_2H_5)_2$
c: $Y=OCOCH_3$



V

The more strained *trans*-2-cycloheptenone (VI) can also be generated by the irradiation of the *cis* enone I.[12] Because of the much reduced stability, however, it was difficult to demonstrate that the ground-state molecule, VI, is involved in the photo-induced polar addition of alcohols. The irradiation of I in EPA at the temperature of liquid nitrogen was followed by turning the lamp off, the addition of cold (−78 °C) methyl alcohol, and a gradual warming to room temperature. Only cyclodimers of I[12] were obtained, however. No methyl alcohol adduct could be detected in the reaction mixture. The irradiation of I in methyl alcohol at −196 °C, followed by warming up to room temperature, also failed to produce the adduct IIa. Fortunately, however, a proof was obtained using diethylamine, a more efficient nucleophile. Thus, the addition of diethylamine to the photolysate of I at −196 °C (EPA glass), followed by warming up to 0 °C, led to the formation of the Michael-type adduct IIg in a 25% yield. A control experiment showed that the *cis* enone I gives no trace of the adduct IIg under these thermal conditions.[18]



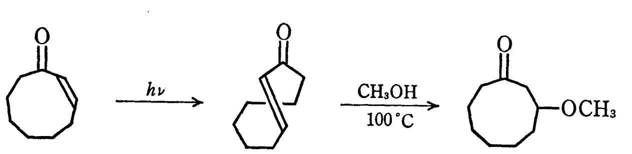
VI

The irradiation of a nine-membered cyclenone, *cis*-2-cyclononenone (VII) in methyl alcohol or cyclohexane below room temperature afforded a mixture of VII and the *trans* isomer, VIII. The latter was stable enough to be isolated by a usual work-up. The enone VIII in methyl alcohol remained unchanged at

Table 3. Spectral properties of polar addition products

Adduct	IR, cm^{-1}[a] (assignment)	NMR, δ ppm from TMS[b]				
		$C(2)H_2$	$C(3)H$	$C(4—n)H_2$	$C(n+1)H_2$	others
IIa	1700 (C=O) 1090 (COC)	2.70 m[c]	3.45 m	1.6—1.9 m	2.38 m	3.30 s (CH_3)
IIb	1700 (C=O) 1085 (COC)	2.65 m[c]	3.65 m	1.5—2.0 m	2.40 m	1.15 t $(CH_2C\underline{H}_3)$[d] 3.47 q $(C\underline{H}_2CH_3)$[d]
IIc	1700 (C=O) 1060 (COC)	2.70 m[c]	3.70 m	1.5—2.0 m	2.46 m	1.15 d $(CH(C\underline{H}_3)_2)$[e] 3.65 m $(C\underline{H}(CH_3)_2)$[e]
IId	1700 (C=O) 1050 (COC)	2.55 m[c]	3.80 m	1.6—1.9 m	2.32 m	1.16 s $(C(CH_3)_3)$
IIe	1740 (OC=O) 1700 (C=O) 1240 $(OCOCH_3)$	2.68 d[e]	5.00 m	1.6—1.9 m	2.40 m	2.00 s (CH_3)
IIf	3450 (OH) 1695 (C=O) 1040 (COH)	2.70 d[f]	4.00 m	1.6—2.0 m	2.45 m	4.05 s (OH)
IIg[g]	1695 (C=O)	2.59 m	2.80 m	1.3—2.0 m	2.35 m	1.02 t $(CH_2C\underline{H}_3)$[d] 2.42 m $(C\underline{H}_2CH_3)$[d]
IVa	1700 (C=O) 1095 (COC)	2.60 m[c]	3.38 m	1.1—2.1 m	2.25 m	3.30 s (CH_3)
IVb	1700 (C=O) 1065 (COC)	2.61 m[c]	3.47 m	1.3—2.1 m	2.25 m	1.10 d $(CH(C\underline{H}_3)_2)$[e] 3.69 q $(C\underline{H}(CH_3)_2)$[e]
IVc	1738 (OC=O) 1700 (C=O) 1240 $(OCOCH_3)$	2.60 d[d]	5.12 m	1.2—2.0 m	2.30 m	1.98 s (CH_3)
IVd	3460 (OH) 1695 (C=O) 1055 (COH)	2.62 m[c]	3.92 m	1.2—2.1 m	2.32 m	3.52 s (OH)
IVe[g]	1695 (C=O)	2.60 m	2.90 m	1.3—2.1 m	2.35 m	1.06 t $(CH_2C\underline{H}_3)$[d] 2.55 m $(C\underline{H}_2CH_3)$[d]
IX	1700 (C=O) 1095 (COC)	2.65 m[c]	3.50 m	1.3—2.2 m	2.35 m	3.26 s (CH_3)
XI	1710 (C=O) 1100 (COC)	2.52 m[c]	3.70 m	1.7—2.1 m	2.30 m	3.32 s (CH_3)

a) Neat liquid film. b) Taken in 5—10% CCl_4 solutions. Splitting patterns are designated as s, singlet; t, triplet; q, quartet; m, multiplet. The number *n* is 6 (II), 7 (III), 8 (IX), or 5 (XI). c) An AB part of ABX system. d) $J=7$ Hz. e) $J=6$ Hz. f) $J=5$ Hz. g) NMR spectrum was measured in $CDCl_3$ solution.



VII VIII IX

0 °C, but heating the solution at 100 °C gave rise to the adduct IX in a high yield. The spectral data are given in Table 3.

Thus, the photo-induced polar addition of cyclic enones proved to consist of two chemical reactions, *i. e.*, a prior *photochemical* isomerization to the *trans* isomers and a subsequent *thermal* reaction with nucleophilic solvents. The protic solvent addition to six-,[19] seven-,[19] and eight-membered cycloalkenes[20] under irradiation has been previously reported. The reaction was proposed to proceed by a sequence; (1) a photochemical *cis-trans* isomerization of the olefins, (2) protonation to the strained *trans* olefins to produce cycloalkyl cations, and (3) nucleophilic capture by the solvent. In the present case, however, the nucleophilic attack of the solvent takes place directly on the carbon—carbon double bond of the strained enones.

The relationship between the reactivity and the ring size of cyclic enones could be inferred from the potential energy curves of the twisted olefins (Fig. 1). The twist angle, ϕ, indicates the deviation from the normal $C(sp^2)=C(sp^2)$ plane. An electronically-excited olefin (either S_1 or T_1) should prefer a rotation about the $C(sp^2)-C(sp^2)$ single bond to afford an orthogonal geometry ($\phi=90°$), thus minimizing the mutual repulsive interactions of the π and π^* electrons.[21] Decay by either internal conversion[22] or intersystem crossing leads to the *cis* or *trans* ground state, in which ϕ is 0° or 180° respectively. With rather small ring olefins,

Table 4. IR-, UV-, and NMR-spectroscopic data of 2-cycloalkenones

2-Cycloalkenone	IR, cm^{-1} a) C=O	IR, cm^{-1} a) *trans* CH=CH	UV, nm b) $\lambda_{\max}^{\pi\to\pi^*}$ (ε)	UV, nm b) $\lambda_{\max}^{n\to\pi^*}$ (ε)	NMR, δ ppm from TMS, J in Hz c,d) H$_\alpha$	H$_\beta$	$J_{H\alpha H\beta}$	$J_{H\beta H\gamma}$
2-Cyclopentenone	1720 e)	—	217 (10, 200) d)	304 (65) d)	6.28	8.01	6.0	2.8
2-Cyclohexenone (X)	1691 e)	—	225 (13, 800) e)	— —	5.90	6.90	10.3	3.9
cis-2-Cycloheptenone (I)	1669 d)	—	227 (10, 220) f)	317 (52) f)	6.03	6.60	11.7	5.4
trans-2-Cycloheptenone (VI)	1715 g)	1010 g)	— —	— —	—	—	—	—
cis-2-Cyclooctenone (III)	1664 d)	—	230 (7, 700) h)	310 (80) h)	5.96	6.32	12.5	6.4
trans-2-Cyclooctenone (V)	1715 g)	1008 g)	— —	283 (70) g,i)	—	—	18 j)	
cis-2-Cyclononenone (VII)	1667 d)	—	231 (8, 100) d) 223 (8, 800) i,k)	318 (86) d) 332 (47) i,k)	5.95	6.20	12.5	8.6
trans-2-Cyclononenone (VIII)	1692 i,k)	980 i,k)	221 (7, 700) i,k)	327 (47) i,k)	5.95 k)	6.35 k)	16.0 k)	8.0 k)
cis-2-Cyclododecenone	1695 l)	—	228 (5, 250) l)	320 (47) l)	6.21	5.69	11.6	7.5
trans-2-Cyclododecenone	1669 l) 1695	990 l)	230 (11, 200) l)	321 (174) l)	6.22	6.65	15.9	7.0

a) Neat liquid film. b) Unless otherwise stated, UV-data were taken in C_2H_5OH. c) Taken in CCl_4. d) M. Regitz and J. Rüter, *Chem. Ber.*, **102**, 3877 (1969). e) H. N. A. Al-Jallo and E. S. Waight, *J. Chem. Soc.*, *B*, **1966**, 73. f) See Ref. 11. g) See Ref. 12b. h) A. C. Cope, M. R. Kinter, and R. T. Keller, *J. Amer. Chem. Soe.*, **76**, 2757 (1954). i) Taken in C_6H_{12}. j) See Ref. 16. k) This work. l) See Ref. 23a.

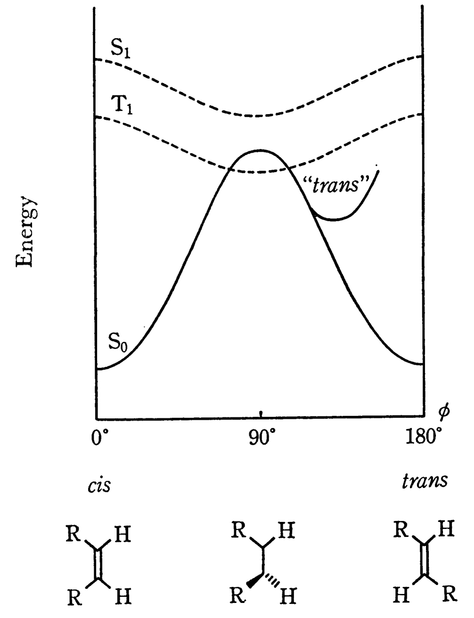
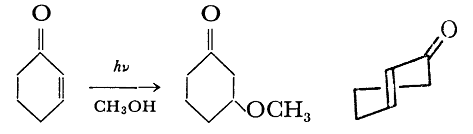


Fig. 1. Energy for the twisting of various electronic states of 1,2-disubstituted olefin. $\phi = \angle C(sp^2)-C(sp^2)$

however, a complete twisting ($\phi > 90°$) is sterically impossible; consequently, their *cis* to *trans* isomerization is precluded. In contrast, open-chain or sufficiently large-membered cyclic olefins undergo the geometrical isomerization facilely. Seven- and eight-membered cyclic olefins are located intermediate between the two extremes. Obviously, a coplanar *trans* double bond ($\phi = 180°$) could not be accommodated, but a 90°-twisted conformation can be adopted and further twisting to a ground-state isomer ($90° < \phi < 180°$) with minimized energy could occur. Such molecules are conventionally referred to as *trans* isomers. Table 4 compares the spectral data of certain *cis* and *trans* cyclenones. The degree of the conjugation of the C=C bond with the C=O group in the seven- and eight-membered *trans* enones (VI and V) is markedly decreased as compared with that of the *cis* isomers. These *trans* double bonds suffer enough torsional strain to provide effective strain-releasing reactions. Apparently the nine-membered *trans* enone VIII is sterically less constrained and, consequently, undergoes the addition of methyl alcohol under only forcing thermal conditions. Both *cis*- and *trans*-2-cyclododecenones,[23] enones free from torsional strain, were inert under these reaction conditions. Electron-deficient olefins including α,β-unsaturated ketones are susceptible to nucleophilic reagents (alcohols, water, primary and secondary amines, *etc.*) under basic conditions and afford Michael-type addition products.[24] A similar type of the addition of acids is also known.[25] Therefore, the above findings are not surprising. The *trans* cyclenones, even though torsionally strained, conform electronically to a ground-state singlet; therefore, they exhibit reactivities understandable on the basis of our knowledge of classical organic chemistry.

In principle, the reactivities of *cis* and *trans* double bonds are identical in type; they are different from each other only in a quantitative way. If this were generally the case for cyclenones, the photolysis in turn in protic solvents might serve as a probe for the chemical detection of the elusive *trans*-2-cyclohexenone. This assumption prompted us to examine the behavior of 2-cyclohexenone (X). In the dark X did not react with freshly-distilled methyl alcohol below 100 °C. Upon the irradiation of a 0.1% solution of X in methyl alcohol at room temperature, 3-methoxycyclohexanone (XI) was obtained, though in a low yield (0.7%) (see Table 3). The major products were its cyclodimers.[7] Thus, the formation of the polar adduct, XI, may suggest the existence of *trans*-2-cyclohexenone (XII),



X XI XII

Table 5. Analytical data of the polar adducts[a)]

Compound	Bp, °C/mmHg (mp, °C)	Molecular formula	Found (Calcd), % C	Found (Calcd), % H
3-Ethoxycycloheptanone (IIb)	65/3	$C_9H_{16}O_2$	69.43 (69.19)	10.37 (10.32)
3-Isopropoxycycloheptanone (IIc)	70/3	$C_{10}H_{18}O_2$	70.47 (70.54)	10.94 (10.66)
3-*tert*-Butoxycycloheptanone (IId)	110—120/10	$C_{11}H_{20}O_2$	71.88 (71.69)	10.82 (10.94)
3-Acetoxycycloheptanone (IIe)	80/3	$C_9H_{14}O_3$	63.76 (63.51)	8.22 (8.29)
3-(*N*,*N*-Diethylamino)cycloheptanone (IIg) picrate[b)]	(103—107)	$C_{17}H_{24}O_8N_4$	49.55 (49.51)	5.94 (5.86)
3-Isopropoxycyclooctanone (IVb)	70/3	$C_{11}H_{20}O_2$	71.52 (71.69)	11.10 (10.94)
3-Acetoxycyclooctanone (IVc)	105—110/3	$C_{10}H_{16}O_3$	65.27 (65.19)	8.85 (8.75)
3-(*N*,*N*-Diethylamino)cyclooctanone (IVe) picrate[b)]	(102—106)	$C_{18}H_{26}O_8N_4$	50.89 (50.70)	6.07 (6.15)

a) Microanalyses were performed at the Elemental Analyses Center of Kyoto University. b) IIg (bp, 83 °C/3 mmHg) and IVe (bp, 90 °C/3 mmHg) afforded a correct molecular peak in mass spectrum at *m/e* (70 eV) 183 and 197, respectively.

though attempted low-temperature experiments had failed to demonstrate the formation of the highly-reactive enone.[12)] Although Hammond showed that the photodimerization of X proceeded *via* the triplet state,[7c)] the problem of whether or not the ground-state molecule, XII, can be derived therefrom has remained unsolved. In the literature, we can find various examples of a similar type of polar photoreaction: the alcohol addition to Pummerer's ketone,[26)] the reaction of cyclohexenone derivatives in aqueous acetic acid,[17)] the *tert*-butyl alcohol addition to 5,5-dimethyl-2-cyclohexenone,[27)] and the alcohol addition to acetylcyclohexene.[14)] As to the behavior of 2-cyclohexenone (X) itself, irradiation in a phosphate buffer solution forming 3-hydroxycyclohexanone has been recorded.[13)] Finally, it is worth pointing out that 2-cyclopentenone reacts with alcohols photochemically *via* only a radical process (*cf.* Chart 1).[28)]

Experimental

Instrumentation. The IR spectra were taken on a JASCO DS-402G or a Shimadzu IR-27-G spectrophotometer. The UV spectra were recorded on a Perkin-Elmer Model 202 spectrophotometer. The NMR spectra were measured with a Jeol JNM C-60H spectrometer, using tetramethylsilane (TMS) as the internal standard. The mass spectra were obtained with a Hitachi RMU-6C spectrometer. The gas-chromatographic analyses (glpc) were performed on a Yanagimoto Model G-8 chromatograph equipped with a column of Apiezon L on Chromosorb (10% or 30%, 2 mm × 2 m) or one of PEGS on Neosorb (5%, 2 mm × 2 m), and a flame ionization detector, using nitrogen as the carrier gas. The preparative work was done on a Yanagimoto Model GCG-3D instrument with a thermal conductivity detector and using helium as the carrier gas. Columns of Apiezon L on Chromosorb (30%, 5 mm × 2 m) and of PEGS on Neosorb (5%, 5 mm × 2 m) were employed. Analytical and preparative thin-layer chromatography (tlc) was carried out on silica-gel plates (Merck silica gel GF_{254}, buffered at pH 7; 0.25 mm and 1.00 mm thickness respectively).

Materials and Solvents. The 2-cyclohexenone, 2-cycloheptenone, and 2-cyclooctenone were prepared as has been reported by Garbisch.[11)] The 2-cyclononenenone[29)] was obtained by the oxidation[30)] of 3-hydroxycyclononene.[31)] S.P.- (methyl alcohol, acetonitrile, and cyclohexane) or G.R.-grade solvents (other alcohols, acetic acid, diethylamine, and isopentane) were purchased from Nakarai Chemicals, Ltd., Kyoto, and were used for photochemical studies without further purification. The 2-methyltetrahydrofuran, ether, and water were used after distillation.

General Procedure for Preparative Scale Irradiations. A solution of the cyclic enones (3.6—15 mmol) in various solvents (10—400 ml) was placed in Pyrex tubes (15 × 180 mm), flushed with purified nitrogen for 15 min, and then irradiated externally using a 200 W high-pressure mercury arc for 0.5—24 hr at room temperature. The progress of the reaction was monitored by the glpc analysis of aliquots removed from the reaction vessel. The removal of the solvent, followed by rough distillation, gave a crude oil. Pure materials were obtained by preparative glpc (Apiezon L 30%, 150—180 °C). The spectral properties of the polar adducts are given in Table 3, while the analytical data of new compounds are summarized in Table 5. The fairly unstable adducts, IIg and IVe, were analyzed after their conversion to crystalline picrates.

The treatment of two labile hydroxy ketones, IIf and IVd (0.5—1.6 mmol), with a 1 : 3 mixture of acetic anhydride and pyridine (1.3—2.5 ml) at 100 °C for 1.5 hr, followed by a usual work-up, gave the respective acetoxy ketones, IIe and IVc; they were identified by means of the IR spectra and the retention times of glpc.

All the 3-methoxycycloalkanones were compared with authentic samples.[29b,c)]

Irradiation for Analytical Purposes (Tables 1 and 2). A

1.0% solution (2.5—20 ml) of the enones was placed in a quartz tube (10×80 mm) or a Pyrex tube (15×180 mm) and irradiated externally with a 200 W high-pressure mercury lamp through a Pyrex filter at a distance of 15 mm at room temperature or 0 °C under a nitrogen atmosphere. The irradiation was continued for the stated time, and then the yield of polar adducts was determined by glpc (Apiezon L 30% or 10%).

Low-temperature Photolysis of 2-Cyclooctenone (III). (a) In 2-Methyltetrahydrofuran: The enone III (13.6 mg, 0.11 mmol) was dissolved in 2-methyltetrahydrofuran (1.5 ml) containing cyclododecane (14.9 mg, 0.09 mmol) as an internal standard for glpc analysis. The solution was then divided into two parts and irradiated in Pyrex tubes (10×80 mm) at −78 °C (Dry Ice–CH_3OH bath) for 15 min under nitrogen, using a 200 W high-pressure mercury arc. After the lamp had then been turned off, each photolysate was poured into methyl alcohol and isopropyl alcohol (1.0 ml), respectively, each of which had been cooled to −78 °C and flushed with dry nitrogen. The methyl alcohol solution was then allowed to warm spontaneously to room temperature in the dark. The solvent was removed *in vacuo*,. The glpc analysis of the residue showed two peaks of retention times identical with those of the starting ketone, III, (41%) and IVa (43%). A similar work-up of the isopropyl alcohol solution, followed by glpc analysis, demonstrated the existence of III (60%) and IVb (24%).

(b) In Isopropyl Alcohol: A solution of III (10.2 mg, 0.08 mmol) and cyclododecane (11.0 mg, 0.07 mmol), an internal reference for glpc analysis, in isopropyl alcohol (1.0 ml) was flushed with dry nitrogen and irradiated at −78 °C as has been described above. After 15 min, the lamp was turned off and the photolysate was treated with an excess of cold methyl alcohol (5.0 ml) in the dark. The mixture was then allowed to warm up to room temperature. Subsequent glpc analysis revealed the existence of only two components, with reaction times identical with those of III and IVa (17 and 80% yields respectively). The isopropyl alcohol adduct, IVb, could not be detected over 1%, if at all.

Low-temperature Photolysis of 2-Cycloheptenone (I). (a) In Methyl Alcohol: A solution of the enone I (100 mg, 0.91 mmol) in a 1 : 1 mixture of methyl alcohol and 2-methyltetrahydrofuran (10.0 ml) was irradiated at −196 °C (liq. nitrogen) for 3 hr. After the lamp had then been turned off, the reaction mixture was allowed to warm up to room temperature. The residue obtained after the removal of the solvents was analyzed by glpc and mass analyses. Although the starting material was consumed (30%), no methyl alcohol adduct was obtained.

(b) In EPA: A solution of I (142 mg, 1.29 mmol) in a 5 : 5 : 2 mixture of ether, isopentane, and ethyl alcohol (EPA) (2.0 ml) was irradiated at −196 °C for 3 hr, after which the lamp was turned off. To the cold photolysate we then quickly added diethylamine (1.8 ml) in EPA (4.0 ml) which had been chilled at −78 °C. The solution was allowed to warm to 0 °C while the vessel was caused to vibrate. The subsequent careful removal of the solvents at 0 °C *in vacuo* gave an oily residue; an NMR analysis of this residue showed that 3-(*N,N*-diethylamino)cycloheptanone (IIg) was afforded in a 25% yield (40%, based on the consumed enone I).

The treatment of I (116 mg, 1.05 mmol) with a 1 : 10 mixture of diethylamine and EPA (11.0 ml) at 0 °C for 3 hr in the dark did not produce IIg, as ascertained by NMR analysis. The heating of I in diethylamine at 60 °C for 3 hr gave IIg in a 30% yield.

Irradiation of cis-*2-Cyclononenone (VII) in Cyclohexane.* A solution of VII (1.0 g, 7.25 mmol) in cyclohexane (100 ml) was divided into five portions, and each aliquot was irradiated in a Pyrex tube (15×180 mm) affixed to the extension of the lamp at room temperature. After 30 min, the solvent was removed at room temperature under reduced pressure. The residual oil was shown by NMR analysis to consist of the starting enone, VII, and a *trans* isomer, VIII (45 : 55 ratio). Preparative scale tlc (*n*-hexane : ether=4 : 1, three developments) afforded pure VIII. Mass spectrum: *m/e* 138 (M^+). The IR-, UV-, and NMR-spectral data are given in Table 4.

The heating of a solution of VIII (200 mg, 1.47 mmol) in methyl alcohol at 100 °C for 1 hr, followed by the evaporation of the solvent, gave 65 : 35 mixture of 3-methoxycyclononanone (IX) and the *cis* enone, VII (by glpc analysis). The IR and NMR spectra (Table 3) were identical with those of an authentic sample.[29c)]

Irradiation of VII in Methyl Alcohol. A solution containing VII (42.6 mg, 0.32 mmol) in methyl alcohol (5.0 ml) was irradiated at 0 °C for 30 min. The subsequent careful removal of the solvent at 0 °C under reduced pressure gave a residue which was found, by NMR and glpc analyses, to contain no methyl alcohol adduct, IX. The oil consisted of only VII and VIII (46 : 54 ratio).

Photolysis of 2-Cyclohexenone (X) in Methyl Alcohol. A dilute solution of X (345 mg, 3.69 mmol) in freshly-distilled methyl alcohol (400 ml) was irradiated in an immersion well at room temperature under nitrogen for 3 hr. By glpc, 70% of the enone X was found to be consumed. The subsequent careful removal of methyl alcohol at 0 °C *in vacuo*, followed by distillation, afforded an oily product (45 mg). Glpc and NMR analyses showed that 3-methoxycyclohexanone (XI) was produced in a 0.7% yield. Glpc examination revealed that no trace of XI was found in the dark under the above-described conditions.

An authentic sample of XI was obtained according to the known procedure.[28c)] The IR and NMR spectral data are given in Table 3.

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