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# A Study on the Photochemistry of α,β-Unsaturated γ-Lactones. II. Photoisomerization of 3-Ethylidene-4,5-dihydro-2(3*H*)-furanone[1]

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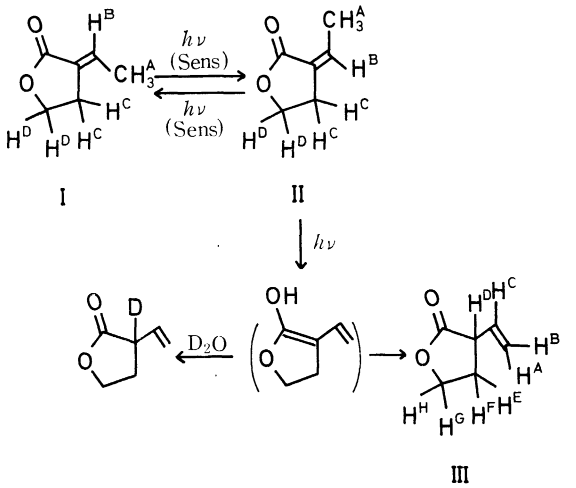
On irradiation of *cis*-3-ethylidene-4,5-dihydro-2(3*H*)-furanone with 2537 Å light, both the *cis-trans* isomerization of the exocyclic double bond and transformation into the β,γ-unsaturated isomer, 3-vinyl-4,5-dihydro-2(3*H*)-furanone, were observed. By the use of sensitizers such as acetone, acetophenone, *p*-methoxyacetophenone and benzophenone, it was possible to induce *cis-trans* isomerization exclusively. On the basis of the solvent effect and the wavelength dependence of the reactions, transformation into the β,γ-unsaturated isomer and *cis-trans* isomerization were suggested to proceed *via* $T_2(n,\pi^*)$ and $T_1(\pi,\pi^*)$ states, respectively.

In contrast to the case of α,β-unsaturated ketones, information on the excited states of α,β-unsaturated esters and their analogues is scarce on account of the fact that systematic studies have not been made on the photochemistry of the latter.[2] The n,π* absorption bands of esters and their analogues are extremely blue-shifted from those of the corresponding α,β-unsaturated ketones as a result of conjugation between the carbonyl group and the adjacent hetero atom.[3] Hence, one may expect the photochemical behaviors ascribable to the n,π* excited state to differ considerably. We reported on the photodimerization of 2(5*H*)-furanone where no significant difference in stereo-selectivity and solvent effects on the yield were observed as compared with those of 2-cyclopentenone.[4] On irradiation of 2(5*H*)-furanone in 2-propanol, we obtained the same type of compound as in the case of the photoaddition of 2-cyclopentenone to 2-propanol;[5] the yield of the adduct in the former system, however, was very large in contrast to that of the latter system.[6] In order to investigate the photochemical behaviors of α,β-unsaturated lactones, we synthesized 3-ethylidene-4,5-dihydro-2(3*H*)-furanone, which is a new α,β-unsaturated lactone having a carbon-carbon double bond exocyclic to the lactone ring. The photochemical reactions of this compound are dealt with in this paper.

## Results and Discussion



*Synthesis and Identification of Starting Materials and Reaction Products.* In order to synthesize the starting material, *trans*-3-ethylidene-4,5-dihydro-2(3*H*)-furanone (I), some modifications were made in the method by Zimmer and Rothe who mainly prepared 3-benzylidene derivatives of 4,5-dihydro-2(3*H*)-furanone.[7] The product contained at least two impurities which could not be removed by either repeated distillation or preparative vapor phase chromatography (vpc). The benzene solution was then irradiated in the presence of acetone as a sensitizer to yield *cis*-3-ethylidene-4,5-dihydro-2(3*H*)-furanone (II), which was readily isolated by preparative vpc. By the use of either acetone or benzophenone as a sensitizer, II was further photoisomerized back to I. Isolation of I from a small amount of the by-product III was achieved by the use of preparative vpc. The IR and NMR spectroscopic data of I and II given in Table 1 are in line with those of the isomeric 3-ethylidene-4,5-dihydro-2(3*H*)-furanones. The mass spectra and results of elementary analyses are in agreement with the assigned structure. A large difference in the chemical shift of methyl and methine protons on the exocyclic double bond can be seen in the NMR spectra. In the case of five- or six-membered ketones or lactones with structures analogous to compounds I and II, the methine proton signals for the *trans*-isomer are observed at lower field than those for *cis*-isomer, while a reverse tendency is observed for methyl proton signals.[8] Hence, compounds I and II were assigned to *trans*- and *cis*-3-ethylidene-4,5-dihydro-

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Table 1. NMR[a] and IR[b] spectra of the three isomers (I, II, and III)

| Compound | Chemical shifts ($\delta$, ppm) | | Coupling constants (Hz) | | | Characteristic IR absorptions ($\text{cm}^{-1}$) | |
|---|---|---|---|---|---|---|---|
| I | $H^A$ 1.87 | | | $J_{AB}$ 7.1 | | $\nu_{C=O}$ | 1753 |
| | $H^B$ 6.81 | | | $J_{AC}$ 2.0 | | $\nu_{C-O-C}$ | 1215 |
| | $H^C$ 2.85 | | | $J_{BC}$ 3.0 | | $\nu_{C=C}$ | 1681 |
| | $H^D$ 4.38 | | | $J_{CD}$ 7.3 | | $\nu_{CH}$ | 3015 |
| II | $H^A$ 2.17 | | | $J_{AB}$ 7.2 | | $\nu_{C=O}$ | 1752 |
| | $H^B$ 6.36 | | | $J_{AC}$ 2.4 | | $\nu_{C-O-C}$ | 1211 |
| | $H^B$ 2.92 | | | $J_{AC}$ 2.3 | | $\nu_{C=C}$ | 1673 |
| | $H^D$ 4.33 | | | $J_{CD}$ 7.4 | | $\nu_{CH}$ | 3015 |
| III | $H^A$ 5.28[c] | $H^E$ 2.20 | $J_{AB}$ 1.5[c] | $J_{CD}$ 5.9 | $J_{EH}$ 8.1 | $\nu_{C=O}$ | 1771 |
| | $H^B$ 5.30[c] | $H^F$ 2.48 | $J_{BC}$10.5[c] | $J_{DE}$10.0 | $J_{FG}$ 6.4 | $\nu_{C-O-C}$ | 1218 |
| | $H^C$ 5.92[c] | $H^G$ 4.27 | $J_{AC}$17.5[c] | $J_{DF}$ 8.5 | $J_{FH}$ 4.5 | $\nu_{C=C}$ | 1646 |
| | $H^D$ 3.27 | $H^H$ 4.38 | $J_{AD}$ 1.5 | $J_{EF}$13.0 | $J_{GH}$ 9.0 | $\nu_{CH}$ | 3080 |
| | | | $J_{BD}$ 1.6 | $J_{EG}$ 8.6 | | $\delta_{CH}$ | 1005<br>927 |

a) Obtained in $CDCl_3$ with TMS as an internal standard.
b) Liquid sample.
c) Obtained by the simulation of the vinyl proton signals (ABC type) of III, deuterated at the $\alpha$-position.

2(3*H*)-furanones, respectively. In the following experiments, the *cis*-isomer II (prepared as described above) was used as the starting material for photochemical investigations.

In addition to the *trans*-isomer I, another compound III was also produced when the acetonitrile solutions of isomer II in a sealed quartz tube was irradiated with a high-pressure mercury lamp. Compound III was isolated by preparative vpc, and the mass spectra as well as the result of elementary analysis indicate that III is another isomer. The spectral data are also summarized in Table 1. The wave number of the carbonyl absorption band (1771 $\text{cm}^{-1}$) indicates that the structure of $\gamma$-lactone is still retained in III but the carbonyl group is not conjugated with the carbon-carbon double bond. The IR spectra suggest the presence of a terminal vinyl group ($\delta_{CH}$, 1005, 927 $\text{cm}^{-1}$). This was confirmed by the observation of ABC-type proton signals ascribable to the vinyl group in the NMR spectra of the sample, which was deuterated at the $\alpha$-position with respect to the carbonyl group. Compound III was thus assigned to $\beta,\gamma$-unsaturated 3-vinyl-4,5-dihydro-2(3*H*)-furanone($\beta,\gamma$-isomer).

*Direct Irradiation of* cis-*Isomer II.* Acetonitrile solutions of II were irradiated with a low-pressure mercury lamp in nitrogen atmosphere. The variation of each component with time was monitored by the use of vpc (Fig. 1). A very small amount of an unidentified compound (X) is produced together with the main products (I and III). The NMR spectra of the irradiated solution also indicates that isomers I and III are absolutely predominant reaction products and that the formation of X is negligible compared with those of I and III. The absorption maximum in the UV spectra shifted to shorter wavelength and the absorbance decreased with time. These changes can be accounted for by the formation of $\beta,\gamma$-unsaturated isomer III. Thus we see that the direct excitation of II induces both *cis-trans* isomerization between I and II and transformation from II to III.

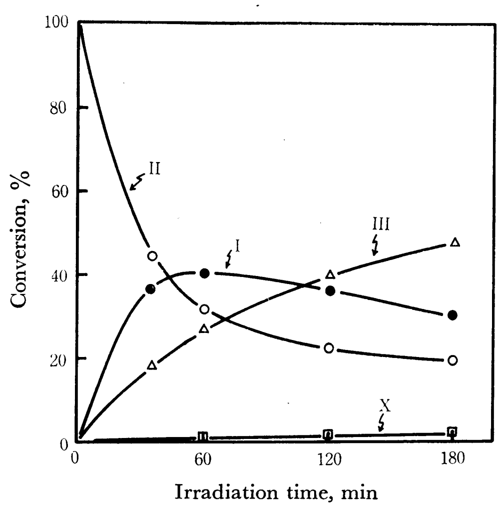

Fig. 1. Variation in the population of each component during the direct irradiation of II in acetonitrile $(3\times10^{-3}\text{M})$.

When irradiation was carried out in $D_2O$–acetonitrile mixed solvent (4: 1), the methine group $\alpha$ to the carbonyl group of III was deuterated up to 89% as determined by NMR spectra. The formation of III is considered to proceed through an enol intermediate produced by the intramolecular hydrogen abstraction in analogy with the isomerization of $\alpha,\beta$-unsaturated esters[9] or 5-methyl-3-hexen-2-one.[10]

*Photosensitized* cis-trans *Isomerization.* In Fig. 2 is shown the variation of isomer ratio with irradiation time, when either the *cis*- or *trans*-isomer was irradiated with a high-pressure mercury lamp in the presence of

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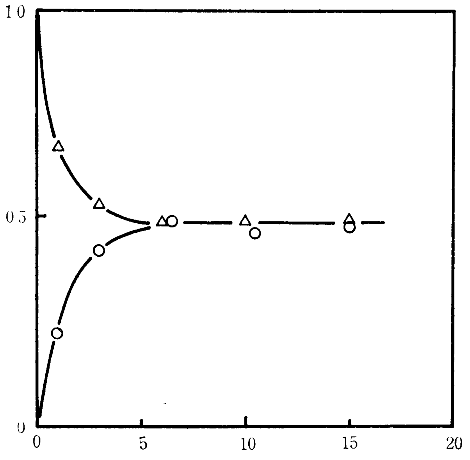

Fig. 2. Variation of the isomer ratio along the elapsed time in the acetophenone photosensitized isomerization of I and II.

Table 2. The isomer ratio at the photostationary state in the photosensitized isomerization between I and II[a)]

| Sensitizer | [Sensitizer] M | $E_T$ of the sensitizer kcal/mol | Isomer ratio[b)] I/II |
|---|---|---|---|
| Acetone | 0.11 | 80 | 1.0 |
| Acetophenone | 0.01 | 74 | 0.96 |
| *p*-Methoxy-acetophenone | 0.01 | 72 | 1.0 |
| Benzophenone | 0.01 | 69 | 1.7 |

a) The concentrations of both I and II were $2.0\times10^{-2}$M. The reactions were carried out in an ordinary glass sample tube except for the case of acetone sensitization where a Pyrex tube was utilized.

b) Average values for the two reactions started from the pure sample of either of the two isomers. The errors are within 5%.

acetophenone as a sensitizer. The isomer ratio was determined by vpc analysis, assuming that both isomers can be detected with equal sensitivity. The isomer ratios at the photostationary states in the presence of a series of sensitizers were investigated in a similar way and the results are summarized in Table 2. The relationship between the triplet energy of the sensitizer and the isomer ratio at the photostationary state indicates that the triplet energy of the *cis*-isomer is lower than that of the *trans*-isomer estimated to be approximately 70 kcal/mol.

On direct excitation of the *cis*-isomer with 2537 Å light, the $\beta,\gamma$-isomer was obtained in 45% yield of the *trans*-isomer. In the case of the photosensitized reaction, the formation of the $\beta,\gamma$-isomer was completely suppressed. Thus, the excited precursor of the $\beta,\gamma$-isomer seems to differ from that of the *trans*-isomer. Since it is clear that *cis-trans* isomerization proceeds *via* the lowest triplet state ($T_1$) in the photosensitized reaction, the excited precursor leading to the $\beta,\gamma$-isomer seems to be either an excited singlet state ($S_1$) or the second-lowest triplet state ($T_2$) located above the triplet energy of acetone.

*Solvent Effects of the Relative Yields of the β,γ-Isomer on the Direct Excitation of the cis-Isomer.* When the *cis*-isomer in various solvents was irradiated with 2537 Å light, the relative quantum yield of the $\beta,\gamma$-isomer varied considerably with solvent polarity (Table 3), while that of the *trans*-isomer was unaffected by the change of solvent. The quantum yield of the $\beta,\gamma$-isomer in cyclohexane is reduced to a value less than 50% of that in either methanol or acetonitrile (Table 3).

Table 3. Solvent effects on the relative quantum yields of the *trans*-isomer and the $\beta,\gamma$-isomer in the direct excitation of the *cis*-isomer

| Solvent | $[II]\times10^2$ M | Product yield (%) I | III | $\Phi_I$ in solv.[a)] / $\Phi_I$ in $C_6H_{12}$ | $\Phi_{III}$[b)] / $\Phi_I$ |
|---|---|---|---|---|---|
| $C_6H_{12}$ | 2.07 | 6.4 | 1.1 | 1.0 | 0.18 |
| $CH_3CN$ | 2.08 | 5.6 | 2.6 | 1.0 | 0.45 |
| $CH_3OH$ | 2.04 | 5.5 | 2.3 | 1.0 | 0.41 |

a) The relative quantum yield for the formation of I in the given solvent with respect to that in cyclohexane.

b) The relative quantum yield for the formation of III with respect to that of I.

A similar solvent effect has been reported also on the photoisomerization of $\alpha,\beta$-unsaturated esters: conversion of ethyl *trans*-crotonate into the $\beta,\gamma$-unsaturated isomer proceeds much more easily in ethanol than in *n*-hexane.[9d)] This is explained by the effect of crossing between the $\pi,\pi^*$ triplet and the $n,\pi^*$ triplet levels on the change of solvents. The $n,\pi^*$ triplet seems to be the reactive species responsible for the formation of the $\beta,\gamma$-isomer.

It is quite likely that the solvent dependence of the quantum yield can also be explained by assuming the crossing of two closely separated energy levels with different reactivities. The plausibility of this speculation was further examined by studying the electronic absorption spectra. The UV-spectra of the *cis*-isomer II are shown in Fig. 3. The strong absorption band at the shorter wavelength is assigned to $\pi,\pi^*$ absorption in analogy with the case of $\alpha,\beta$-unsaturated esters.[3)] We see that a week absorption band is superimposed on the tail of the $\pi,\pi^*$ absorption band in the cyclo-

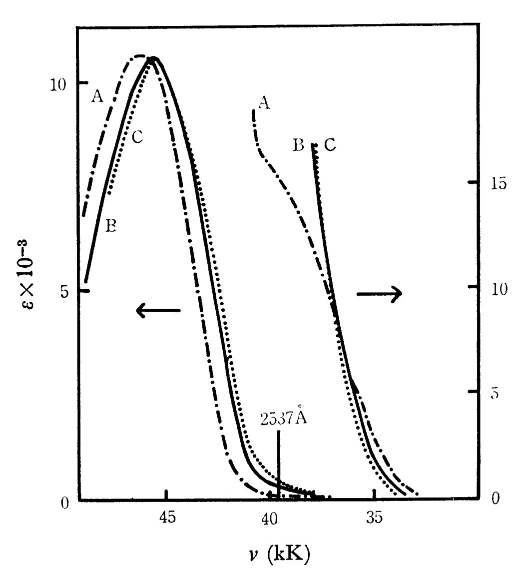

Fig. 3. UV absorption spectra of the *cis*-isomer II. A, in cyclohexane,; B in acetonitrile; C, in methanol.

hexane solution. On closer examination it can be seen to be associated with a series of broad vibrational structures frequently observed with n,$\pi$* absorptions. The weak absorption band observed in cyclohexane is concealed under the red-shifted $\pi$,$\pi$* absorption in acetonitrile and methanol. Hence, the weak absorption band is suggested to be either unaffected or slightly blue-shifted in polar solvents. We thus assigned the weak absorption band to the n,$\pi$* transition of the *cis*-isomer II. As far as the singlet states of the *cis*-isomer II are concerned, the energy level of the lowest n,$\pi$* excited state is concluded to be very close to that of the lowest $\pi$,$\pi$* excited state in both acetonitrile and methanol. The 2537 Å exciting light is situated in the middle of the region where the n,$\pi$* transition is superposed on the tail of the $\pi$,$\pi$* transition (Fig. 3). Hence, the ratio in population between the n,$\pi$* singlet and the $\pi$,$\pi$* singlet species obtained in the excitation should vary with solvent. This might be why the relative yield of the $\beta$,$\gamma$-isomer considerably varies with the solvent while that of the *trans*-isomer remains the same (Table 3).

It should be noted, however, that the solvent effect on the yield of Norrish type II photolysis of valerophenone has been explained as being due to stabilization of the hydroxyl biradical intermediate which is capable of making a hydrogen bonding with the polar solvent molecules.[11] An *enol* type intermediate is suggested to be involved in the isomerization from II to III. The solvent effect on the secondary processes after the photoexcitation might be partly responsible for the variation in the relative yield of the $\beta$,$\gamma$-isomer with the change of solvent.

*Dependence of the Relative Quantum Yields on the Wavelength of the Exciting Light.* If the solvent effect on the relative yield of the $\beta$,$\gamma$-isomer is due to the change in population ratio between the n,$\pi$* singlet and the $\pi$,$\pi$* singlet just after excitation, the yield should show an appreciable variation with the wavelength of the exciting light, when examined in the absorption edge of the sample in a given solvent. The experiment was carried out under two different irradiation conditions: (a) with 2537 Å light from a low-pressure mercury lamp and (b) with a xenon short arc lamp filtered through carbon tetrachloride layer of 15 mm thickness, the incident lights being limited to be those with wavelength longer than 260 m$\mu$. The results are summarized in Table 4. In cyclohexane, the ratio of the relative yield of the $\beta$,$\gamma$-isomer to that of the *trans*-isomer under conditions (b) is reduced to 35% of that under conditions (a). The isomer ratio ($\beta$,$\gamma$-isomer/*trans*-isomer) in acetonitrile under the same conditions varies only by 20%. The n,$\pi$* absorption band of the *cis*-isomer in cyclohexane appears as a clear shoulder superimposed on the tail of the $\pi$,$\pi$* absorption band (Fig. 3). Hence the longer the wavelength of the excitation light, the larger the population ratio between the $S_1$(n,$\pi$*) and $S_2$($\pi$,$\pi$*). Thus, the rapid decrease in the isomer ratio in cyclohexane is nicely correlated to the increase in the relative population of the first n,$\pi$* singlet state. Analogously, the small wavelength dependence of the isomer ratio in the acetonitrile solution is suggested to correspond to the fact that the n,$\pi$* absorption band is located in almost the same wavelength region where the $\pi$,$\pi$* absorption is observed. It is thus difficult to enhance selectively the relative population of the n,$\pi$* excited species only by selection of the wavelength of exciting light.

TABLE 4. DEPENDENCE OF THE RATIO OF THE RELATIVE QUANTUM YIELDS (III/I) ON THE WAVELENGTH OF THE EXCITING LIGHT ($\lambda$)[a)]

| Solvent | $\lambda$>260 m$\mu$[b)] | $\lambda$=254 m$\mu$ |
|---|---|---|
| $C_6H_{12}$ | 0.059 | 0.17 |
| $CH_3CN$ | 0.33 | 0.41 |

a) The relative yield was estimated from the vpc chart by assuming that the molar sensitivities of the two isomers are the same.

b) Obtained by the use of Xe lamp in combination with $CCl_4$.

*Proposal of a Reaction Scheme.* As regards solvent effects and wavelength effects on the relative quantum yields of the $\beta$,$\gamma$- and the *trans*-isomer, we might suggest that the former mainly comes from the $\pi$,$\pi$* singlet state and the latter from the n,$\pi$* singlet state. The relative heights of the n,$\pi$* and $\pi$,$\pi$* singlet energy levels can be determined from the UV absorption spectra of the *cis*-isomer (Fig. 3). We have no data for the location of the triplet energy levels. However, the following theoretical consideration can be given.

On spectroscopic evidences, Marsh *et al.* have shown that the energy of n,$\pi$* triplet state of steroidal enones is very close to that of the $\pi$,$\pi$* triplet state.[12] This may be also true for other $\alpha$,$\beta$-unsaturated ketones in general. In the case of esters and lactones, the conjugation between the carbonyl group and the adjacent oxygen atom raises the n,$\pi$* state considerably and leaves the $\pi$,$\pi$* state almost unchanged in comparison with those of the corresponding ketones or aldehydes.[13] The lowest n,$\pi$* triplet state of an ester or a lactone is thus expected to be located much above the lowest $\pi$,$\pi$* triplet state so that the change of solvents can not reverse the relative heights of these energy levels. A schematic energy-level diagram for the relevant states of the *cis*-isomer is shown in Fig. 4.

Intramolecular hydrogen abstraction is generally considered to take place at the n,$\pi$* excited state. In the present experiment, however, $S_1$(n,$\pi$*) species is considered to hardly contribute to the hydrogen abstraction reaction since the relative yield of the $\beta$,$\gamma$-isomer decreases on irradiation of the *cis*-isomer in cyclohexane with the longer wavelength light which predominantly induces n,$\pi$* transition. Formation of the $\beta$,$\gamma$-isomer should be correlated to the population of $S_2$($\pi$,$\pi$*) species, since the relative quantum yield on the irradiation with 2537 Å light decreases in cyclohexane, where an appreciable blue shift of the $\pi$,$\pi$* absorption band

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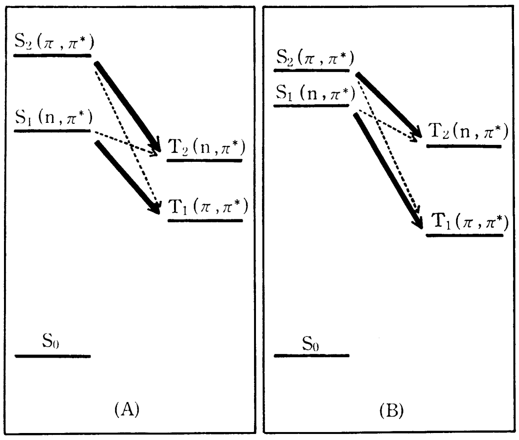

Fig. 4. Schematic energy level diagram for the relevant states of the *cis*-isomer: A (in cyclohexane) and B (in acetonitrile). The solid and dotted arrows represent the intersystem crossing manifolds with the higher- and the lower-efficiency, respectively.

is observed. The quantum yield of the *cis-trans* isomerization, in turn, should be related to the population of $S_1(n,\pi^*)$ species. However, it is rather unusual that the *cis-trans* isomerization takes place directly at the $S_1(n,\pi^*)$ state, since this type of reaction is known to proceed *via* $\pi,\pi^*$ state. Taking into account the fact that *cis-trans* isomerization is sensitized by the triplet sensitizers, and that the lowest triplet state is estimated to be a $\pi,\pi^*$ state, it is more likely that *cis-trans* isomerization takes place at $T_1(\pi,\pi^*)$ state which mainly comes from $S_1(n,\pi^*)$ state even in direct excitation. The results on the formation of the $\beta,\gamma$-isomer, are well accounted for if we consider that the hydrogen abstraction reaction takes place at $T_2(n,\pi^*)$ state which mainly comes from $S_2(\pi,\pi^*)$ state. This is in accordance with the general principle on the reactive species in the photochemical hydrogen abstraction reactions.

On the basis of theoretical arguments and experimental observations on the radiation yields of ketones, El-Sayed proposed a selection rule for the intersystem crossing at the excited states: the intersystem crossing between the levels of different nature [$S(n,\pi^*)\rightarrow T(\pi,\pi^*)$ and $S(\pi,\pi^*)\rightarrow T(n,\pi^*)$] should be faster than those between the levels of the same nature [$S(\pi,\pi^*)\rightarrow T(\pi,\pi^*)$ and $S(n,\pi^*)\rightarrow T(n,\pi^*)$] by a factor of $10^3$.[14] If this selection rule holds also in the case of the photoexcited states of II, the routes for photoisomerization can be reasonably accounted for as shown in Fig. 4, where the intersystem crossing with higher efficiency is denoted by a broad solid arrow, and that with lower efficiency by a dotted arrow.

In order to confirm the reaction scheme, we made several attempts to quench the excited states in the photoisomerization of II on direct excitation. However, no positive results were obtained. This is understandable from the fact that the lifetimes of the concerned states are expected to be extremely short in the present case. We can not completely disregard the contribution of singlet species to isomerization on direct excitation at this stage. The present model might be adopted as reasonable means for explaining the characteristics of the photoisomerization of $\alpha,\beta$-unsaturated $\gamma$-lactones.

## Experimental

*Instrumental Analysis.* The NMR spectra were measured with a Varian Model A-60 analytical spectrometer. The IR, UV, and mass spectra were recorded on a JASCO Model DS-301 IR spectrometer, a Shimadzu Model UV-200 spectrophotometer, and JEOL Model JMS-01SG mass spectrometer, respectively. Vapor phase gas-chromatography for qualitative analysis was carried out by the use of a Shimadzu Model GC-2C chromatograph equipped with a thermal conductivity detector. Analysis was carried out by the use of a column (2.25 m × 3 mm) with packings made by coating polyphenyl ether 5-rings (10%) on Chamelite CS (DMCS-treated Celite 545) support. The column temperature was kept to 175 °C. The preparative vpc was also carried out under the same conditions. The quantitative analyses were carried out at either 120 or 130 °C by the use of a Shimadzu Model GC-3BF gas chromatograph equipped with a flame ionization detector.

*Preparation of* trans-*3-Ethylidene-4,5-dihydro-2(3*H*)-furanone (I).* Preparation of I was carried out by a modification of the method reported by Zimmer and Rothe.[7] Acetaldehyde (18 g) and $\gamma$-butyrolactone (70 g) in benzene (500 ml) were maintained at 5 °C in the presence of powdered sodium ethoxide for 1.5 hr, and the reaction was completed by heating the solution up to 45 °C for 15 min. Dilute sulfuric acid (10%, 360 ml) was added to the solution, and the organic layer was separated from the aqueous phase. The aqueous phase was extracted with 350 ml of benzene, and the extract was combined with the previously separated organic layer. The benzene solution was successively washed with water, aqueous sodium hydroxide and finally with water. Benzene was removed by distillation and the succeeding distillate was collected (up to 114 °C/6 mmHg). The same procedure was repeated and crude products were combined (21.7 g), which yielded 6.2 g of the final product (72.5—76.0 °C/5 mmHg) after fractional distillation. In addition to the main product I, several other byproducts were involved in the collected distillate. Preparative vpc was then applied to obtain I, which was still accompanied by small amounts of two other impurities difficult to separate. An attempt was also made to prepare I according to Pinder's method[15] for the preparation of the benzylidene analogue of I, but the yield was too small for the method to be adopted.

*Preparation of* cis-*3-Ethylidene-4,5-dihydro-2(3*H*)-furanone (II).* The *trans*-isomer I (1.8 g), together with small amounts of accompanying impurities were dissolved in 100 ml of benzene. Acetone (10 g) was added as a sensitizer, and the solution was internally irradiated with a high-pressure mercury lamp (Riko-Sha UVL-700P) equipped with a pyrex water-jacket in nitrogen atmosphere for 21 hr. According to the vpc analysis, the *cis*-isomer II was the sole product. The *cis*-isomer was isolated by fractional distillation followed by preparative vpc. Yield, 325 mg; $m/e = 112$ ($M^+$). Found: C, 64.18; H, 7.28%. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19%.

*Photosensitized Reaction of* cis-*3-Ethylidenedihydro-2(3*H*)-furanone (II).* *(A) Preparation of the Authentic Sample of* trans-*Isomer (I):* The *cis*-isomer II (179 mg) and benzophenone (5 mg) were dissolved in 1 ml of benzene. The

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solution was placed in a pyrex tube which was sealed after evacuation under nitrogen atmosphere. The sample was externally irradiated with a high-pressure mercury lamp (Toshiba H-400P) for 22 hr at room temperature. The NMR and vpc of the irradiated sample indicated that the *trans*-isomer I was formed together with a small amount of III. Preparative vpc was applied to isolate I. Yield, 39 mg; $m/e=112$ ($M^+$); Found: C, 64.05; H, 7.37%. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19%.

*(B) Determination of the Isomer Ratio between I and II at the Photostationary State*: Acetone was purified by treating with potassium permanganate followed by fractional distillation. Acetophenone (reagent grade) was also purified by fractional distillation under reduced pressure just before use. *p*-Methoxyacetophenone was recrystallized from *n*-hexane–benzene mixed solvent (mp 39.1—40.1 °C). Benzophenone was recrystallized from methanol (mp 51.2—51.5 °C). Each sample tube was sealed after flushing with nitrogen and irradiated with a high-pressure mercury lamp (Riko-Sha UVL-700P) equipped with a pyrex glass filter. The reaction was carried out at 20.2 °C, and the products were analyzed by vpc at 130 °C.

*Direct Irradiation of* cis-*Ethylidene-4,5-dihydro-2(*3H*)-furanone II.* *(A) Preparation of β,γ-Unsaturated 3-Vinyl-4,5-dihydro-2(*3H*)-furanone III*: The *cis*-isomer II (73 mg) was dissolved in 0.5 ml of acetonitrile, and the solution was irradiated in a quartz tube under exactly the same conditions, as for the preparation of I, except for the absence of the sensitizer. The main products were isomers I and III, the latter being isolated by distillation under reduced pressure followed by vpc in a preparative scale. Yield, 20 mg; $m/e=112$ ($M^+$); Found: C, 63.89; H, 7.28%. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19%.

*(B) Variation of UV Spectra during Irradiation*: Acetonitrile solution of II ($3\times10^{-3}$M, 150 ml) was internally irradiated with a low-pressure mercury lamp (Riko-Sha UVL-303Q) under nitrogen atmosphere at room temperature. Four ml of the sample was periodically extracted from the irradiated solution, and a quarter of the sample was used for measurement of the UV spectra after being diluted with acetonitrile to one hundredth of the initial concentration. The remaining 3 ml of the sample was concentrated to approximately one twentieth in volume, and was analyzed by vpc. After irradiation for 3 hr most of the acetonitrile was removed by distillation under reduced pressure and the residue was analyzed by NMR spectroscopy. No absorption was observed due to the compound other than the three isomers.

*(C) Irradiation in $D_2O$-Acetonitrile System*: Approximately 60 mg of the *cis*-isomer was dissolved in a mixed solvent consisting of $D_2O$ (0.8 ml) and acetonitrile (0.2 ml). A quartz tube containing the solution was sealed under reduced pressure, after the remaining oxygen had been replaced with purified nitrogen. The sample was externally irradiated for 12 hr with a high-pressure mercury lamp. After irradiation was completed, the products were extracted into benzene (20 ml), and successively distilled under reduced pressure. The NMR spectra in deuterochloroform indicated the isomers I, II, and III to be 24, 9, and 67%, respectively.

*Solvent Effect on the Quantum Yield of the Isomers on the Irradiation of II with 2537 Å Light.* The *cis*-isomer was purified by vpc on a preparative scale and successive distillation under reduced pressure (2 mmHg) so that it gave a single peak in the vpc. The purified *cis*-isomer was dissolved in solvents of spectrograde purity. Eight ml of each solution was pippetted into a quartz tube (15 mm inner diameter), fused to a pyrex tubing of the same diameter with a graded seal. The air inside the sample tube was purged by a stream of purified nitrogen, and the tube was sealed under reduced pressure (2 mmHg) after it was cooled by being dipped into dry ice–methanol mixture. In the case of the acetonitrile and methanol solutions, the samples were also prepared by the use of a vacuum line (less than $10^{-4}$ mmHg) for degassing. Good agreement was observed with the pair of samples prepared by the above two methods. Each sample tube was set in a cylindrical glass holder, mounted on a turn table with a radius of 12 cm. A square window ($10\times30$ mm) on the wall of the holder allowed more than 99% of the incident 2537 Å light to be absorbed in the sample at the concentration of the experiment. At the center of the turn table was placed a low-pressure mercury lamp (Riko-Sha UVL-303Q), surrounded by a layer of aqueous 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene perchlorate filter solution (175 mg/l)[16] of approximately 2 cm thickness. Under such conditions, the sample absorbs only 2537 Å light from the low-pressure mercury lamp since no absorption band is observed for the *cis*-isomer at the wavelength longer than 300 mμ. The characteristic of each sample tube was calibrated in advance by monitoring the change in the potassium ferrioxalate actinometer solution in each tube when it was irradiated by the light filtered through an aqueous solution containing $NiSO_4\cdot xH_2O$ (450 g), $CoSO_4\cdot 6H_2O$ (150 g), and 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene perchlorate (175 mg).[17] The relative quantum yield of each isomer was determined after irradiation of the sample for 1,5 hr. The reaction was carried out at 20.0 °C by immersing the whole irradiation unit in a thermostat bath. The content of the sample tube was concentrated, under nitrogen stream, down to approximately one tenth of the initial volume and the residue was analyzed by vpc in the presence of β-methylnaphthalene as an internal standard. On irradiation of the cyclohexane solution, small amounts of a by-product other than the three isomers were also detected. No further attempt was made to identify the by-product since the yield was extremely small.

*Determination of the Relative Quantum Yield on Irradiation of Light with Wavelength longer than 260 mμ.* Either acetonitrile solution ($2.2\times10^{-2}$M) or cyclohexane solution ($2.18\times10^{-2}$M) was placed in a cylindrical cell, ($25\phi\times10$ mm) which was sealed under reduced pressure (2 mmHg) after being flushed with nitrogen. The light beam from a xenon lamp (Ushio UXL-500D) was filtered through a layer of carbon tetrachloride (15 mm), and was irradiated on the optically flat surface of the cylindrical cell. Irradiation was continued for 4.5 hr at a constant temperature (19—20 °C), and the product was analyzed by vpc.

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