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Studies on the *N*-Oxides of π-Deficient *N*-Heteroaromatics. XXXVI.[1,2] Photochemical and Thermal Michael Reactions of Alcohols with Methyl 2-Phenyl-3,1-benzoxazepine-5-carboxylate and Its Derivatives

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Irradiation (≥300 nm) of methyl 2-phenyl-3,1-benzoxazepine-5-carboxylate in an alcohol afforded the *Z*-isomer of methyl 3-alkoxy-2-(2-benzamidophenyl)-acrylate as the major addition product. In contrast, thermal reaction of the oxazepine with a primary alcohol in the presence of triethylamine led to the exclusive formation of the corresponding *E*-isomer. The same kinds of Michael addition products were also obtained stereoselectively from 3,1-benzoxazepines having an acetyl group at the 5-position under these conditions.

The interrelation between the stereoisomers obtained from the oxazepine and an alcohol under these two conditions was established by photochemical equilibration, and the stereochemistry of the two isomers was determined by proton magnetic resonance spectroscopy.

An explanation is proposed for the observed stereoselectivities in the two kinds (photochemical and thermal) of reactions.

Keywords——photochemical Michael reaction; *E–Z* photoisomerization; reaction mechanism; PMR spectroscopy; stereoselective reaction; methyl 3-alkoxy-2-(2-benzamidophenyl)-acrylates and related compounds

The photochemical reaction of 3,1-benzoxazepines in an aprotic solvent resulted in the predominant formation of indole derivatives and was explained in terms of 3*H*-indole derivatives as key intermediates.[3] In the previous paper of this series,[4] we reported that this photochemical ring-contraction reaction was a quite general phenomenon among oxazepine derivatives under irradiation at 254 nm, and demonstrated the intermediacy of 3*H*-indole species by the actual isolation of methyl 3-acetyl-2-phenyl-3*H*-indole-3-carboxylate from the photoreaction of methyl 4-methyl-2-phenyl-3,1-benzoxazepine-5-carboxylate. During these studies, it was also found that 4-unsubstituted methyl 2-phenyl-3,1-benzoxazepine-5-carboxylate (II) was converted to methyl 2-phenylindole-3-carboxylate (III) even by irradiation at ≥300 nm in an aprotic solvent.

In the present paper, a novel photochemical reaction of methyl 2-phenyl-3,1-benzoxazepine-5-carboxylate (II) in an alcoholic solvent giving stereoselectively the *Z*-isomer (*Z*-IV) of methyl 3-alkoxy-2-(2-benzamidophenyl)-acrylate is reported. In contrast, it was also found that a thermal Michael addition of an alcohol to the same oxazepine (II) led to the *E*-isomers (*E*-IV) of the acrylate. The same kinds of ring-opened addition products were likweise obtained with corresponding stereoselectivities under these two conditions from related 3,1-oxazepines if they had an electron-withdrawing substituent at the 5-position.

The stereochemistries of both kinds of isomers (*E*- and *Z*-isomers) were established and probable mechanisms accounting for the observed stereoselectivities in the two kinds of reaction were proposed.

Results and Discussion

Photochemical Michael Addition of an Alcohol to Methyl 2-Phenyl-3,1-benzoxazepine-5-carboxylate (II)

Since 3,1-benzoxazepines were prepared, in high yields from quinoline 1-oxides by irradiation at $\geq$300 nm,[5] it was expected that these oxazepines would be stable to further irradiation. Our recent studies,[3,4] however, revealed that most of the oxazepines suffered photochemical ring-contraction on irradiation at 254 nm to give indoles, and methyl 2-phenyl-3,1-benzoxazepine-5-carboxylate (II) afforded a ring contraction product, methyl 2-phenylindole-3-carboxylate (III), even on irradiation at $\geq$300 nm.

Here, we report on a new type of reaction of this oxazepine (II), *i.e.*, a photochemical Michael addition of an alcohol to II, which occurs in an alcohol solvent at a much faster rate than that of the afore-mentioned ring-contraction reaction leading to III. Thus, irradiation ($\geq$300 nm) of II in methanol afforded, after silica gel chromatography, the ring-opened addition products in 89% yield as a mixture of *Z*- and *E*-isomers of methyl 3-methoxy-2-(2-benzamidophenyl)-acrylate (IV), together with 4% of the indole[4] (III). Prolonged irradiation after the complete consumption of II caused an increase of the *E*-isomer content to the point where the ratio of *E*: *Z* reached *ca.* 5: 2. When, irradiation was terminated as soon as all of II was consumed, predominant formation of the *Z*-isomer resulted, and the pure *Z*-isomer (*Z*-IVa) was obtained in *ca.* 50% yield by direct recrystallization of the whole addition product.

The infrared (IR) spectrum of *Z*-IVa indicated the presence of an amide (3425 and 1670 cm^{-1}) and a conjugated ester group (1710 cm^{-1}). The structure of *Z*-IVa was supported by the proton magnetic resonance (PMR) spectrum, which showed three sharp singlets, δ 3.76 (3H), 3.86 (3H), 6.70 (1H), one broad singlet, 8.80 (NH), and complex signals due to aromatic protons between 7.0—8.1 (9H). The position of the vinylic proton signal (δ 6.70) was at much higher field region than expected for the corresponding *E*-isomer.[6,7]

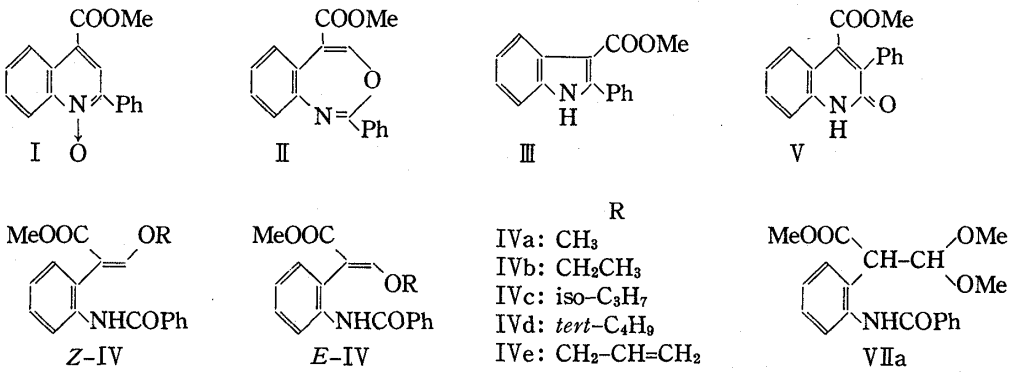

Fig. 1

Irradiation of II in ethanol under the same conditions yielded 81% of an adduct (*Z*-IVb) contaminated with an appreciable amount of the *E*-isomer, and 7% of III. Spectral data of the major addition product obtained after recrystallization were quite similar to those of *Z*-IVa, and the structure *Z*-IVb was deduced. It should be noted that the same kind of addition product (*Z*-IVd) was also formed from II by irradiation in *tert*-butanol and this resultindicates that this photo-addition reaction occurs irrespective of the kind of alcohol used.[8]

More conveniently, these alcohol addition products were obtained in satisfactory yields (*ca.* 70%) by irradiation of 4-methoxycarbonyl-2-phenylquinoline 1-oxide (I) in a mixed solvent composed of an alcohol and dichloromethane (ROH: CH_2Cl_2=5: 95 v/v).[9] In this case, due to the solvent effect on the photochemical reaction of aromatic amine oxides,[5] a small amount (less than 5%) of the 2(1*H*)-quinolone (V) was also formed[10] in addition to the simple

deoxygenation product (methyl 2-phenylquinoline-4-carboxylate: VI, *ca.* 8%). Use of the mixed solvent is also applicable to II and seems worthwhile when an alcohol is inappropriate for use as an irradiation solvent due to a high boiling point or limited availability. For example, on irradiation of I in a mixed solvent (allyl alcohol-dichloromethane 5: 95 v/v), 71% of the addition product (*Z*-IVe, contaminated with *E*-IVe) was obtained together with III (13%), V (4%), and VI (9%).

In the photolyses of II, almost pure *Z*-isomers (*Z*-IVa—d) were obtained upon termination of irradiation when *ca.* one-third of II was consumed. This result indicates that the addition of an alcohol to II proceeds in a stereoselective manner to give the *Z*-isomers in all cases, and the *E*-isomers were formed from *Z*-IVa—d upon longer irradiation (*vide infra*).

Thermal Michael Addition of a Primary Alcohol to Methyl 2-Phenyl-3,1-benzoxazepine-5-carboxylate (II)

Though the oxazepine (II) was stable in an alcohol at room temperature in the dark, the presence of triethylamine caused a slow addition of the alcohol to II. Thus, on standing II in methanol in the presence of triethylamine at room temperature for 4 h, 75% of an addition product (*E*-IVa) was obtained in addition to 23% of the starting material (II). In a similar manner, the ethanol addition product (*E*-IVb) was obtained from II as the sole product. The isomeric nature of these products (*E*-IVa, b) with respect to *Z*-IVa, b was indicated by the close similarity of their UV and IR spectra and finally confirmed by the PMR spectra. In the spectrum of *E*-IVa, the following signals were observed: δ 3.78 (3H, s), 3.88 (3H, s), 7.73 (1H, s), 7.2—7.6 (4H, m), 7.0—7.25 (2H, m), 7.7—7.9 (2H, m), 8.16 (1H, d, J=8 Hz), and 8.28 (NH). As expected, the spectrum is similar to that of *Z*-IVa, except for the olefinic signal (δ 7.73), which appears at lower field than that (6.70) of the *Z*-isomer.

The two acrylates, *E*-IVa and its isomer (*Z*-IVa), were found to be stable under the reaction conditions; no isomerization of these compounds could be detecetd by PMR spectroscopy over a 5—10 h period in the dark in triethylamine–methanol. Though the 1: 2-addition product (VIIa) was formed upon longer standing with consumption of the 1: 1-addition product (*E*- or *Z*-IVa), this 1: 2-addition product was stable under the above reaction conditions. It is clear from these results that neither the 1: 2-addition product (VIIa) nor *Z*-IVa was the precursor of *E*-IVa in this thermal Michael reaction. Addition of *tert*-butanol to II occurred in the same way. However, since the reaction is quite slow (*e.g.*, more than 50% of II was recovered unchanged in *tert*-butanol-triethylamine after 1 week), it is more convenient to prepare the *E*-isomers having a secondary or tertiary alcohol function (*E*-IVc, d) from the corresponding *Z*-isomers (*Z*-IVc, d) by photochemical equilibration followed by silica gel column chromatography.[11]

Photoequilibrium between the *E*- and *Z*-Isomers (*E*-IV and *Z*-IV) and Their Stereochemistries

It was found that irradiation at $\geq$300 nm of each isomer (*Z*- or *E*-IV) in an aprotic solvent caused *E*-*Z* isomerization and finally afforded a photo-equilibration mixture composed of both isomers. This photochemical $E \rightleftarrows Z$ isomerization was easily carried out in a PMR tube using $CDCl_3$ as a solvent, and the reaction was followed by periodical external irradiation and

Table I. Melting Points of Addition Products (*Z*-and *E*-IVa-d) and Chemical Shifts (δ) of Their Olefinic Protons[a]

	a	b	c	d
Z-IV mp	143—145°C	127—128°C	134—135°C	141—142°C
δ	6.70	6.75	6.80	6.90
E-IV mp	99—101°C	111—112°C	140—142°C	131—133°C
δ	7.73	7.75	7.82	7.98

a) Measured in $CDCl_3$.

subsequent measurements of PMR spectra of the sample. By this technique, it was found that the *E*–*Z* ratio in the equilibrium state was approximately 2—2.5: 1 for all of the addition products (IVa—d) and no other reaction occurred during the irradiation.

Since all geometrical isomers of the addition products have been synthesized, we could compare the PMR spectra of each set (*Z*- and *E*-isomers) of IVa—d in order to determine the stereochemistries. Table I shows the olefinic proton signals of these addition products. The olefinic protons in the *E*-isomer would only be deshielded by the carbonyl group, leading to resonance at lower field than in the *Z*-isomer.[12]

Since the *Z*-isomers assigned as above are formed from II by photochemical reaction and the *E*-isomers (*E*-IV) by thermal reaction, it is clear that the stereoselectivities in both reactions are independent of the kind of alcohol, but dependent upon the type of reaction.

Mechanisms Accounting for the Observed Stereoselectivities in the Two Kinds of Reaction

Although additional work is required for a detailed mechanistic proposal, our results are consistent with the premise that the formation of *E*-IV under thermal conditions proceeds by a triethylamine-catalyzed *trans* addition of an alcohol (either concerted or stepwise) to give an intermediate[13] (*trans*-VIII) which undergoes a *cis* elimination through a conformer depicted by the formula *trans*-VIII-A. Inspection of a molecular model of *trans*-VIII-A indicates that this conformer should be stable and has an orbital array suitable for a retro ene reaction,[14] as indicated by the formula (*trans*-VIII-A). An alternative pathway involving the *cis* addition intermediate (*cis*-VIII) should not occur (at least under such mild conditions), because the conformers (*cis*-VIII-B or -C) would have to take an energetically unfavorable state in order to gain coplanarity in the reaction site to ensure subsequent *trans* elimination.

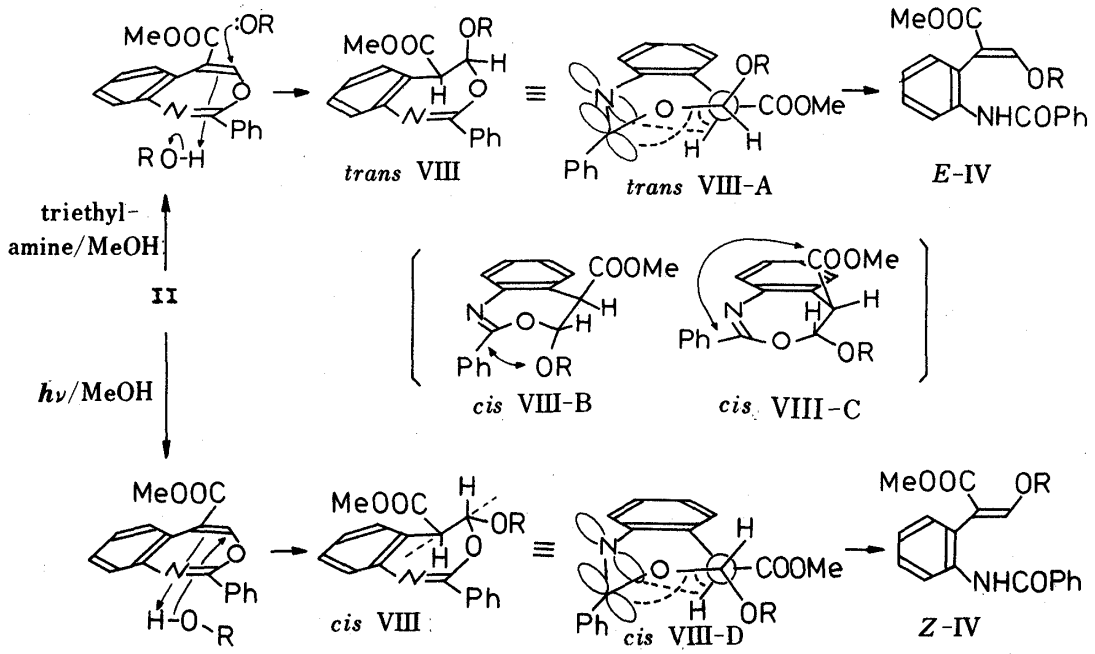

Chart 1

For the photochemical formation of *Z*-IV, the stereochemistry of the products offers two pathways (i and ii), namely: i) *trans* addition followed by *trans* elimination and ii) *cis* addition followed by *cis* elimination. We prefer the pathway ii for two reasons. First, it is difficult to explain why the *E*-isomer is not formed at all as the primary photo-product (as mentioned, the formation of *E*-IV from *trans*-VIII should be a facile process). Second, a *cis* addition of a σ-component ($_{\sigma}2_{s}$) to a double bond ($_{\pi}2_{s}$) is a photochemically allowed pericyclic reaction[15]

and if the addition product (*cis*-VIII) is formed, it would, like *trans*-VIII-A, be expected to give the *Z*-isomer by retro ene reaction *via* the conformer (*cis*-VIII-D).

It seems noteworthy that II reacted with methanol in the absence of triethylamine only after prolonged refluxing (*ca.* 10 h) to give methyl 2-phenylindole-3-carboxylate (III) in quantitative yield. This reaction probably proceeds by initial attack of methanol on the azomethine function of II followed by ring-opening and recyclization as depicted in Chart 2. Such ring-contraction reactions are quite common in solvolyses of the related oxazepines.[5]

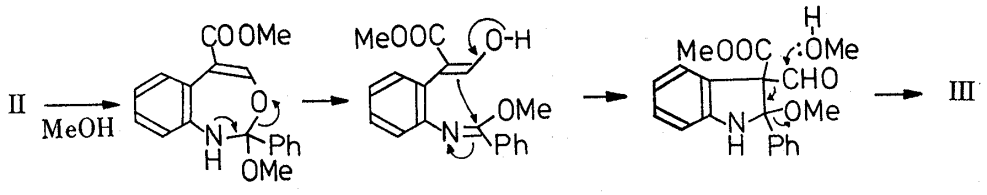

Chart 2

Photochemical and Thermal Michael Addition Reactions of Alcohols to the Oxazepines Related to II

Photo-addition products similar to IV were also formed directly from 4-methoxycarbonyl-2-methylquinoline 1-oxide (IX) by irradiation in *tert*-butanol.[16] In this photolysis, the major product (57%) was the ring-contraction product (methyl 2-methylindole-3-carboxylate: XI) and the combined yield of the addition products (*Z*- and *E*-XII) was only 28% (Chart 3).

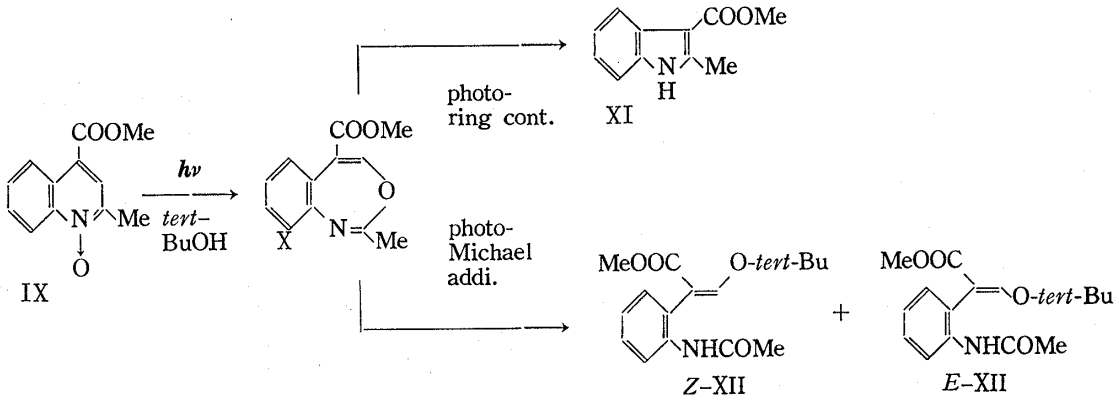

Chart 3

These Michael addition reactions were successfully extended to 3,1-benzoxazepines having an acetyl function at the 5-position. Thus, irradiation of 5-acetyl-2-phenyl-3,1-benzoxazepine (XIV) or the corresponding quinoline 1-oxide (XIII) in an alcohol afforded the addition products (XV) as the major products (Chart 4). If the N-oxide (XIII) was used as a starting material in the photolyses using methanol or ethanol as a solvent, two 2-quinolones (XVII and XVIII) were obtained concomitantly. In all cases, the yield of the ring contraction product (3-acetyl-2-phenylindole: XVI) was quite low (less than 5%). All of the addition products (XVa—d) could be separated by chromatography over silica gel and the stereostructures (*E*- and *Z*-configurations) of the purified products were determined from the PMR spectra, as shown in Table II.

In contrast to the behavior of IV, the addition products (XV) obtained from XIV did not show $E \rightleftarrows Z$ isomerization upon irradiation,[17] but the *Z*-isomers (*Z*-XV) slowly isomerized irreversibly to the *E*-isomers at room temperature in the dark. For example, *Z*-XVa in $CDCl_3$ gave *E*-XVa in quantitative yield at room temperature in the dark after 5 days. Taking

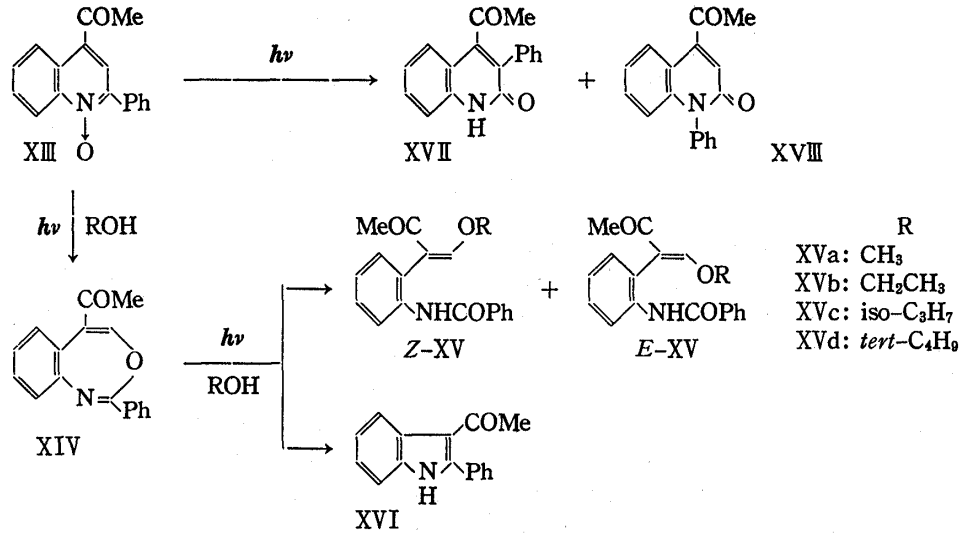

Chart 4

TABEL II. Melting Points of Addition Products (*Z*- and *E*-XVa—d) and Chemical Shifts (δ) of Their Olefinic Protons[a)]

	a	b	c	d
Z-XV mp	oil	109—110°C	117—119°C	155—156°C
δ	6.78	6.85	6.92	7.17
E-XV mp	158—159.5°C	113—114.5°C	85—87°C	120—121°C
δ	7.58	7.59	7.63	7.85

a) Measured in $CDCl_3$.

this result into consideration, as well as the inconsistent *E*/*Z* ratios after chromatographic separation over silica gel, we believe that the primary product is also the *Z*-isomer in this case. The fact that rapid work-up after the irradaiation increased the relative amount of the *Z*-isomer over the *E*-isomer supported this view.

Reaction of XIV in methanol in the presence of triethyamine gave *E*-XVa exclusively. Therefore, it is clear that the thermal reaction proceeds with reverse stereoselectivity compared to that in the photochemical reaction, as in the case of the formation of IV from II.

The assigned configurations of XV (*cf.* Table II) were also supported by the irreversible isomerization from the *Z*-isomers to the *E*-isomers mentioned above, because it is well known that the *E*-isomer is thermodynamically more stable than the *Z*-isomer in related compounds.[18)]

The irreversible thermal isomerization from *Z*- to *E*-isomers in *Z*-XVa—d (but not in *Z*-IV) is probably due to the stronger electron-withdrawing nature of an acetyl group over a methoxycarbonyl group, which would facilitate the formation of a zwitterionic intermediate (XIX) which would be responsible for the isomerization.

In accordance with the proposed mechanism for the formation of these addition products (IV and XV), the oxazepine (XX) afforded XXI in quantitative yield on treatment with methanol containing triethylamine. Irradiation of the same oxazepine (XX) in methanol

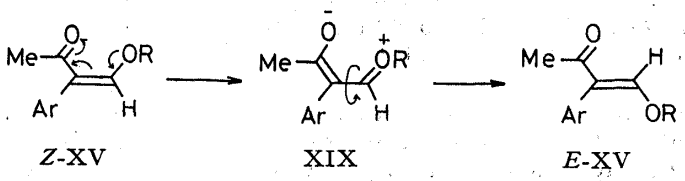

Fig. 2

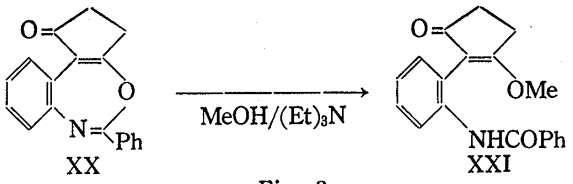

Fig. 3

resulted in the formation of intractable tars and no addition product was detected in the reaction mixture. This probably reflects the fact that it is impossible to form the expected product (formally categorized as a Z-isomer) since the olefinic moiety is involved in a five-membered ring.

Conclusions

In this paper, Michael-type addition reactions of alcohols to the 4,5-double bond in oxazepine derivatives under photochemical and thermal conditions are reported. Since such additions have not been observed previously, an essential requisite for their occurrence seems to be the presence of an electron-withdrawing group at the 5-position in the oxazepine system.[19]

This report provides the first example of work on stereochemical aspects of both photochemical and thermal Michael additions of alcohols to one substrate at the same time,[20] and the results are noteworthy in that exactly reverse stereo-pathways of the reactions operate under photochemical conditions and under thermal conditions.

Experimental

All melting points are uncorrected. Infrared absorption spectra (IR) were recorded on a Shimadzu IR-420 spectrometer, UV spectra with a Hitachi 320 spectrometer, and PMR spectra on a JEOL JNM-C60 spectrometer (with tetramethylsilane as an internal standard). Mass spectra (MS) were obtained with a JEOL-JNM-01SG spectrometer with a direct inlet system.

Photolyses were carried out in a Pyrex immersion apparatus equipped with a Toshiba 400P high-pressure mercury lamp (this corresponds to irradiation at $\geq$300 nm) cooled internally with running water. All irradiations were carried out under argon or nitrogen with stirring.

2-Substituted 4-Methoxycarbonylquinoline 1-Oxides (I and IX) and the Oxazepines (II)——These compounds were prepared according to the procedure described in the previous paper.[4]

4-Acetyl-2-phenylquinoline 1-Oxide (XIII)——To a mixture of sodium methoxide in methanol (prepared by adding 0.96 g of sodium in 5 ml of ab. methanol) and 12 ml of toluene was added 7.75 g of 4-methoxycarbonyl-2-phenylquinoline 1-oxide (I) and 17 ml of methyl acetate. The mixture was refluxed for 13 h. After the reaction, the reaction mixture was poured into 100 ml of ice water and the whole was acidified by the addition of 10% aq. HCl. The residue obtained after extraction with CH_2Cl_2 followed by drying over Na_2SO_4 and concentration was separated by silica gel column chromatography. Elution with hexane–ether (2: 1 v/v) gave first, 400 mg (4%) of 4-methoxycarbonylacetyl-2-phenylquinoline (oil) and then 8.3 g (93%) of the 1-oxide, mp 83—86°C (recrystallized from methanol). *Anal.* Calcd for $C_{19}H_{15}NO_4$: C, 71.02; H, 4.71; N, 4.36. Found: C, 70.96; H, 4.90; N, 4.48. MS *m/z*: 321 (M^+).

A solution of 4-methoxycarbonylacetyl-2-phenylquinoline 1-oxide (2.0 g) in 30 ml of 25% aq. sulfuric acid was heated on a boiling water bath for 7 h. After cooling, the reaction mixture was made alkaline (pH 9) by the addition of saturated aq. Na_2CO_3 and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and the solvent was evaporated off. The residue was recrystallized from methanol to give 1.50 g (91.5%) of 4-acetyl-2-phenylquinoline 1-oxide (XIII), mp 95—96°C (recrystallized from methanol). *Anal.* Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.50; H, 4.86; N, 5.53. MS *m/z*: 263 (M^+).

5-Acetyl-2-phenyl-3,1-benzoxazepine (XIV)——A solution of the *N*-oxide (XIII; 445 mg) in 300 ml of acetone was irradiated at $\geq$300 nm for 10 min. After removal of the solvent by evaporation, the residue was chromatographed on a silica gel column (35 g). Elution with hexane–ether (3: 1 v/v) afforded 14 mg (3%) of the deoxygenated base (4-acetyl-2-phenylquinoline), mp 71—72°C, and then 236 mg (53%) of the oxazepine (XIV), mp 78—79°C. PMR (CCl_4) δ: 2.31 (3H, s), 7.16 (1H, s), 7.0—7.5 (8H, m), and 8.06 (1H, m). IR ν_{max}^{KBr} cm^{-1}: 1660. MS *m/z*: 263. *Anal.* Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.43; H, 5.04; N, 5.38.

Elution with hexane–ether (1: 2 v/v) gave a small amount of 3-acetyl-2-phenylindole (XVI) (6 mg: (1.5%). Elution with ether afforded 145 mg (32.5%) of the unchanged 1-oxide (XIII).

3-(2-Carboxyethyl)-2-phenylquinoline-4-carboxylic Acid——A solution of 12 g of isatin and 16 g of γ-benzoylbutanoic acid in 100 ml of 30% aq. KOH solution was refluxed on an oil bath for 12 h. The precipi-

tates that appeared after acidification with acetic acid were collected and washed with water. Recrystallization from methanol afforded 25.7 g (93%) of 3-(2-carboxyethyl)-2-phenylquinoline-4-carboxylic acid, mp 277—280°C.[21]

Methyl 3-(2-Methoxycarbonylethyl)-2-phenylquinoline-4-carboxylate——(a) With Dimethyl Sulfate in the Presence of Sodium Methoxide: The acid (2.0 g) was dissolved in methanol containing sodium methoxide (prepared from 0.3 g of Na in 18 ml of ab. methanol). After the addition of 1.0 ml of dimethyl sulfate, the mixture was refluxed for 2 h. Removal of the solvent by evaporation followed by addition of aq. K_2CO_3 and extraction with CH_2Cl_2 gave *ca.* 140 mg of the residue, which afforded 92.2 mg (4.2%) of the dimethyl ester after recrystallization from CH_2Cl_2–hexane. The sample was identical with that obtained in (b).

(b) With Dimethyl Sulfate in Acetone in the Presence of K_2CO_3: The diacid (1.0 g) was suspended in 20 ml of anhydrous acetone. After addition of 1.0 ml of dimethyl sulfate and 1.0 g of finely powdered K_2CO_3, the reaction mixture was refluxed vigorously for 5 h (the bath temperature was held at about 120°C). The neutral fraction obtained after the usual work-up gave, after recrystallization from CH_2Cl_2–hexane, 369 mg (34%) of methyl 3-(2-methoxycarbonylethyl)-2-phenylquinoline-4-carboxylate, mp 147—150°C. PMR ($CDCl_3$) δ: 2.33 (2H, t, J=8.0 Hz), 3.13 (2H, t), 3.53 (3H, s), and 4.03 (3H, s). IR ν_{max}^{KBr} cm^{-1}: 1720. *Anal.* Calcd for $C_{21}H_{19}NO_4$: C, 72.19; H, 5.48; N, 4.01. Found: C, 72.15; H, 5.53; N, 3.89. MS *m/z* 349 (M^+).

4-Methoxycarbonyl-3-(2-methoxycarbonylethyl)-2-phenylquinoline 1-Oxide——The diester (475 mg) was dissolved in 10 ml of acetic acid containing 2 ml of 30% aq. H_2O_2 solution and the mixture was heated on a water bath (90°C) for 6 h. After addition of 20 ml of water, the mixture was concentrated under reduced pressure. After basification of the residue by the addition of aq. K_2CO_3 solution, the product was extracted with CH_2Cl_2 and dried over $MgSO_4$. Removal of the solvent by evaporation followed by recrystallization of the residue from ether–hexane afforded 365 mg (73.5%) of the 1-oxide, mp 130—131.5°C. UV λ_{max}^{MeOH} nm: 238, 331, 345. MS *m/z* 365 (M^+). *Anal.* Calcd for $C_{21}H_{19}NO_5$: C, 69.03; H, 5.24; N, 3.83. Found: C, 68.86; H, 5.31; N, 3.79.

2,3-Dihydro-1-oxo-4-phenyl-1*H*-cyclopenta[*c*]quinoline 5-Oxide——a) Dieckmann Condensation of 4-Methoxycarbonyl-3-(2-methoxycarbonyl-ethyl)-2-phenylquinoline 1-Oxide: The diester (600 mg) was refluxed in 20 ml of toluene containing sodium methoxide (prepared from 0.1 g of Na in 5 ml of methanol) for 6 h. The residue obtained after removal of the solvent by evaporation was extracted with CH_2Cl_2 and the extract was dried over $MgSO_4$. The neutral fraction obtained after usual work-up was separated by silica gel column chromatography to give 43.1 mg (8%) of the cyclopentanone ester, mp 163—165°C (recrystallized from methanol). UV λ_{max}^{MeOH} nm: 258, 271, 355 (sh.), and 372. MS *m/z* 333. From a more polar fraction, the starting material was recovered (133 mg: 22%).

From the acidic fraction of the residue, the corresponding diacid [3-(2-carboxyethyl)-1-oxido-2-phenylquinoline-4-carboxylic acid] was obtained (237 mg: 43%).

b) Hydrolysis of the Cyclopentanone Ester and Subsequent Decarboxylation: The cyclopentanone ester (86 mg) was refluxed in 15 ml of methanol containing 5 ml of 10% aq. HCl solution. The methanol was evaporated off, and the residue was basified by the addition of K_2CO_3 and extracted with CH_2Cl_2. The residue obtained after removal of the solvent was chromatographed on a silica gel column. Elution with hexane–ether (3: 1 v/v) afforded 38.0 mg of 2,3-dihydro-1-oxo-4-phenyl-1*H*-cyclopenta[*c*]quinoline 5-oxide, mp 169.5—171°C. PMR ($CDCl_3$) δ: 2.81 (2H, t, J=8.4 Hz), 2.88 (2H, t), and 7.4—9.0 (9H, m). MS *m/z* 275. *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.45; H, 4.80; N, 4.98.

Photochemical Transformation of 2,3-Dihydro-1-oxo-4-phenyl-1*H*-cyclopenta[*c*]quinoline 5-Oxide to the Oxazepine (XX)——A solution of the 5-oxide (150 mg) in 200 ml of acetone was irradiated at $\geq$300 nm under an argon atmosphere for 30 min. The acetone was evaporated off, and silica gel column chromatography of the residue with hexane–ether (2: 1 v/v) gave 93.6 mg (62.5%) of the oxazepine (XX), mp 104—105°C (recrystallized from hexane–ether). PMR ($CDCl_3$) δ: 2.65 (4H, s) and 7.05—8.15 (9H, m). MS *m/z* 275 (M^+). *Anal.* Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.39; H, 4.82; N, 4.97.

Reactions of 2,3-Dihydro-1-oxo-5-phenyl-1*H*-cyclopenta[*d*]-3,1-benzoxazepine (XX)——(a) Thermal Reaction with Methanol in the Presence of Triethylamine: A solution of the oxazepine (XX: 30 mg) in 5 ml of methanol containing 0.5 ml of Et_3N was kept standing at room temperature for 4 h. The solution was concentrated, and recrystallization of the residue from methanol gave the methanol addition product (XXI) in quantitative yield, mp 223—226°C. PMR ($CDCl_3$) δ: 2.73 (4H, A_2B_2 pattern), 3.96 (3H, s), 7.0—7.6 (6H, m), 7.8—8.0 (3H, m), and 9.51 (1H, bs, which disappeared on the addition of D_2O). MS *m/z* 307 M^+. *Anal.* Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.39; H, 5.62; N, 4.49. On treatment with 10% HCl–methanol, the adduct (XXI) afforded 3,4-dihydrocyclopent[*b*]indol-1(2*H*)-one[22] in 65% yield, mp 250—252°C (dec.). PMR (DMSO-d_6): 2.90 (4H, A_2B_2 pattern) and 6.95—7.75 (4H, m). MS *m/z* 171 (M^+).

(b) Irradiation in Methanol: Irradiation of the oxazepine (XX) in methanol at $\geq$300 nm resulted in the formation of intractable tars.

Irradiation of 4-Methoxycarbonyl-2-phenylquinoline 1-Oxide (I) in Methanol——A solution of the *N*-oxide (1.75 g) in 880 ml of methanol was irradiated at $\geq$300 nm for 4 h. The residue obtained after removal of the solvent was chromatographed over silica gel (40 g). Elution with hexane–ether (7: 3 v/v) afforded 185 mg (11%) of the deoxygenated base (methyl 2-phenylquinoline-4-carboxylate) and 80 mg (5.1%) of the

indole (III). Elution with hexane–ether (1: 2 v/v) gave 1.08 g (55.5%) of a mixture of *E*- and *Z*-isomers of methyl 3-methoxy-2-(2-benzamidophenyl)-acrylate (IVa). Elution with CH_2Cl_2–methanol (95: 5 v/v) gave 430 mg (24.5%) of 4-methoxycarbonyl-3-phenyl-2(1*H*)-quinolone (V: mp 273—276°C). The structure of V was deduced from the spectroscopic data [IR ν_{max}^{KBr} cm^{-1}: 1740, 1660; UV λ_{max}^{MeOH} nm: 223, 288, and 341, and PMR (DMSO-d_6) δ: 3.70 (3H, s), 7.1—7.8 (9H, m), and 12.2 (1H, bs; which disappeared on the addition of D_2O)] and by its synthesis from 3-phenyl-2-quinolone-4-carboxylic acid.[3]

The relative amount of the addition products increased with decreasing polarity of the alcohol used as the irradiation solvent. Thus, for example, irradiation of the *N*-oxide (I) in isopropanol resulted in the formation of 81.5% of the addition product (again as a mixture of *E*- and *Z*-isomers of IVc) and the yield of the oxygen-rearrangement product (V) decreased to 1.9%. In contrast to the above result, irradiation in *tert*-butanol gave only 67.5% of the addition products (*Z*- and *E*-IVd), 14.9% of the indole (III), and a trace (0.8%) of V. The remarkable increase in the yield of III indicated that the addition of *tert*-butanol to the excited II was inhibited somewhat by the bulkiness of the reactant and as a result, the formation of the photo-ring contraction product[4] (III) competed with that of the addition product (IVd).

All of the addition products (IV) gave methyl 1-benzoylindole-3-carboxylate[2] (mp 124.5—125.5°C) in nearly quantitative yield upon treatment (60°C, 10 min) with aq. 10% HCl in methanol. All of the crystalline adducts gave satisfactory analytical data and the structures of oily adducts were supported by the presence of M^+ ions in the mass spectra (see Table III).

Irradiation of the Oxazepine (II) in Methanol——Irradiation of a 0.2% solution of II in methanol until it had been consumed completely (30 min for 1 l of solution) resulted in an 89% yield of a mixture of *E*-IVa and *Z*-IVa (*ca.* 1: 3, as judged from PMR), together with 4% of III, after silica gel column chromatography. Repeated recrystallization of the adducts from hexane–ether afforded a 45% yield of pure *Z*-IVa. UV λ_{max}^{MeOH} nm (log ε): 229 (4.39) and 255 sh (4.22). For other data, see Tables I and III.

Table III. Elemental Analyses and Mass Spectral Data of the Adducts (IV)

Adduct	Molecular composition (M.W.)	Analysis (%) Calcd C	H	N	Found C	H	N	M^+ (in m/z)[a]
Z-IVa	$C_{18}H_{17}NO_4$	69.44	5.50	4.50	69.34	5.60	4.46	311
E-IVa	(311)							311
Z-IVb	$C_{19}H_{19}NO_4$	70.14	5.89	4.31	70.36	6.01	4.54	325
E-IVb	(325)							325
Z-IVc	$C_{20}H_{21}NO_4$	70.78	6.24	4.13	70.78	6.24	4.13	339
E-IVc	(339)							339
Z-IVd	$C_{21}H_{23}NO_4$	71.37	6.56	3.96	71.53	6.63	4.15	—[b]
E-IVd	(353)				71.50	6.59	4.01	—[b]

a) All mass spectra showed the following fragment ions as common peaks: 279, 175, 105, and 77.
b) The molecular ions (*m/z* 353) were not observed for *Z*- and *E*-IVd.

Irradiation of 4-Methoxycarbonyl-2-phenylquinoline 1-Oxide (I) in Dichloromethane Containing Allyl Alcohol——A solution of the *N*-oxide (I: 560 mg) in 300 ml of a mixture composed of allyl alcohol and dichloromethane (5: 95 v/v) was irradiated at $\geq$300 nm until I had disappeared (*ca.* 1 h). The residue obtained after removal of the solvent by evaporation was chromatographed over silica gel (30 g). Elution with hexane–ether (7: 3 v/v) afforded 42.2 mg (8%) of the deoxygenated base and 65.5 mg (13%) of the indole (III). Elution with hexane–ether (1: 2 v/v) gave 480 mg (71%) of the addition product, which on recrystallization from hexane–ether gave 280 mg of the pure *Z*-isomer of methyl 3-allyloxy-2-(2-benzamidophenyl)-acrylate (*Z*-IVe), mp 92—93°C. PMR ($CDCl_3$) δ: 3.78 (3H, s), 4.52 (2H, d, J=6 Hz), 5.2—5.5 (2H, m), 5.96 (1H, m), 6.72 (1H, s), 7.1—7.6 (6H, m), 7.8—8.0 (2H, m), 8.11 (1H, d, J=8 Hz), and 8.88 (NH). MS *m/z*: 337. *Anal.* Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.18; H, 5.73; N, 4.06.

Elution with CH_2Cl_2–methanol (95: 5 v/v) gave 17 mg (3%) of the 2-quinolone (V).

Irradiation of 4-Methoxycarbonyl-2-methylquinoline 1-Oxide (IX) and Its 2-Ethyl Derivative in *tert*-Butanol——A solution of the *N*-oxide (IX: 730 mg) in 300 ml of *tert*-butanol was irradiated at $\geq$300 nm for 1.5 h. The residue obtained after removal of the solvent was chromatographed over silica gel (35 g). Elution with hexane–ether (1: 1 v/v) afforded 363 mg (57.1%) of methyl 2-methylindole-3-carboxylate[3,16] (XI, mp 160—162°C). Elution with ether gave 275 mg (28.1%) of a mixture of the methanol adducts (*Z*- and *E*-XII). Rechromatography of the adduct fraction over silica gel with hexane–ether (2: 3 v/v) gave first *Z*-XII and then *E*-XII in an approximate ratio of 3: 2. *Z*-XII, mp 120—122°C. NMR ($CDCl_3$) δ: 1.45 (9H, s), 2.12 (3H, s), 3.78 (3H, s), 6.94 (1H, s; the olefinic proton), 7.1—7.5 (3H, m), 7.90 (NH, bs), and 8.0 (1H, d, J=8.0

Hz). MS *m/z*: 291 (M^+). *Anal.* Calcd for $C_{16}H_{21}NO_4$: C, 65.95; H, 7.27; N, 4.81. Found: C, 65.86; H, 7.40; N, 4.87. *E*-XII, mp 127—129°C. NMR ($CDCl_3$) δ: 1.37 (9H, s), 2.09 (3H, s), 3.71 (3H, s), 7.0—7.5 (4H, m), 7.91 (1H, s; the olefinic proton), and 7.97 (1H, d, J=8.0 Hz). MS *m/z*: 291 (M^+), *Anal.* Calcd for $C_{16}H_{21}NO_4$: C, 65.95; H, 7.27; N, 4.81. Found: C, 65.79; H, 7.38; N, 4.75.

Irradiation of 2-ethyl-4-methoxycarbonylquinoline 1-oxide in *tert*-butanol under the same conditions as above gave, in addition to 62.0% of methyl 2-ethylindole-3-carboxylate [mp 72—73°C, NMR ($CDCl_3$) δ: 1.34 (3H, t, J=8.0 Hz), 3.20 (2H, q, J=8.0 Hz), 3.95 (3H, s), 7.1—7.4 (3H, m), 8.10 (1H, m), and 8.52 (NH, bs). UV λ_{max}^{MeOH} nm (log ε): 214 (4.56), 228 (4.26), 255 (3.94), 282.5 (4.05), and 287 sh (4.08); the spectrum is almost identical with that of methyl 2-methylindole-3-carboxylate. MS *m/z* 203 (M^+)], 25.9% of a mixture of the corresponding *tert*-butanol adducts, from which the pure *Z*- and *E*-isomers were obtained by rechromatography. *Z*-isomer, mp 103—104°C. NMR ($CDCl_3$) δ: 6.88 (1H, s; the olefinic proton). MS *m/z* 305 (M^+). *Anal.* Calcd for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59; N, 4.59. Found: C, 66.73; H, 7.71; N, 4.54. *E*-isomer, mp 127.5—128.5°C. NMR ($CDCl_3$) δ: 7.92 (1H, s, the olefinic proton). MS *m/z* 305 (M^+).

Irradiation of 4-Acetyl-2-phenylquinoline 1-Oxide (XIII) in Methanol——A solution of the *N*-oxide (XIII: 525 mg) in 300 ml of methanol was irradiated for 45 min. The residue obtained by removal of the solvent was chromatographed over silica gel (30 g). Elution with hexane–ether (2: 1 v/v) afforded 37 mg (7.5%) of the deoxygenated base and then 92 mg (17.5%) of the oxazepine (XIV: mp 78—79°C). Elution with hexane–ether (1: 1 v/v) gave 11 mg (2.3%) of 3-acetyl-2-phenylindole [XVI, mp 219—221°C. NMR (DMSO-d_6) δ: 2.07 (3H, s), 7.1—7.7 (8H, m), 8.17 (1H, m), and 11.91 (NH). MS *m/z* 235 (M^+)], 40 mg (6.8%) of *Z*-XV (R=Me; oil), 61 mg (11.6%) of 4-acetyl-1-phenyl-2(1*H*)-quinolone (XVIII, mp 160—162°C), and 127 mg (21.6%) of *E*-XV (R=Me: mp 158—159.5°C). Elution with methanol–CH_2Cl_2 (5: 95 v/v) gave 4-acetyl-3-phenyl-2(1*H*)-quinolone (XVII, mp >300°).

Both of the 2-quinolones showed an acceptable parent ion (*m/z* 263) in the mass spectra and typical 2(1*H*)-quinolone absorptions (XVII; λ_{max}^{MeOH} nm: 227, 288, and 341, and XVIII; λ_{max}^{MeOH} nm: 213, 282, and 345) in the UV spectra. The appearance of a singlet at δ 7.02 in the NMR spectrum of XVIII indicated that XVIII had an 4-acetyl-1-phenyl-2(1H)-quinolone structure.

The use of isopropanol or *tert*-butanol as an irradiation solvent increased the yields of the addition products (as a mixture of the two stereoisomers) to 73.1 or 75.0%, respectively. The structures of all the adducts were supported by the presence of the molecular ion peaks in the mass spectra and all the crystalline adducts gave acceptable analytical data (see Table IV).

Table IV. Elemental Analyses and Mass Spectral Data of the Adducts (XV).

Adduct	Molecular composition (M.W.)	Analysis (%) Calcd C	H	N	Found C	H	N	M^+ (in *m/z*)[a]
Z-XVa	$C_{18}H_{17}NO_3$	73.20	5.80	4.74	73.17	5.92	4.58	295
E-XVa	(295)				73.13	5.94	4.67	295
Z-XVb	$C_{19}H_{19}NO_3$	73.76	6.19	4.53	73.61	6.28	4.40	309
E-XVb	(309)							309
Z-XVc	$C_{20}H_{21}NO_3$	74.28	6.55	4.33	74.19	6.73	4.19	323
E-XVc	(323)							323
Z-XVd	$C_{21}H_{23}NO_3$	74.75	6.87	4.15				337
E-XVd	(337)				74.90	6.96	3.98	337

a) All mass spectra showed the following fragment ions as common peaks: 263, 159, 144, 105, and 77.

Reaction of Methyl 2-Phenyl-1,3-benzoxazepine-5-carboxylate (II) with Methanol in the Presence of Triethylamine——A solution of the oxazepine (II, 229 mg) in 30 ml of methanol containing 1 ml of triethylamine was kept standing at room temperature for 5 h. The residue obtained after removal of the solvent by evaporation was chromatographed over silica gel (15 g). Elution with hexane–ether (1: 1 v/v) afforded 54.2 mg (23.7%) of the starting material (II) and then 17.4 mg (5.8%) of the di-methanol adduct (VIIa: mp 144—146°C. NMR ($CDCl_3$) δ: 3.46 (3H, s), 3.60 (3H, s), 3.78 (3H, s), 4.19 (1H, d, J=8.0 Hz), 5.03 (1H, d, J=8.0 Hz), 7.1—7.7 (6H, m), 8.0—8.2 (3H, m), and 9.52 (NH, bs). *Anal.* Calcd for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16; N, 4.08. Found: C, 66.51; H, 6.23; N, 4.01) and 148 mg (58.0%) of the mono-methanol adduct (*E*-IVa: mp 99—101°C).

Reaction of 5-Acetyl-2-phenyl-1,3-benzoxazepine (XIV) with Methanol in the Presence of Triethylamine——A solution of the oxazepine (XIV: 38.5 mg) in 3 ml of methanol containing 0.1 ml of triethylamine was kept standing at room temperature for 16.5 h. The solution was concentrated and the residue was chromatographed over silica gel with hexane–ether (1: 1 v/v) to afford 28.0 mg (58.5%) of the di-methanol adduct

[oil, MS *m/z* 327 (M^+). NMR ($CDCl_3$) δ: 2.09 (3H, s), 3.37 (3H, s), 3.46 (3H, s), 4.09 (1H, d, J=6.0 Hz), 4.89 (1H, d, J=6.0 Hz), 7.0—7.6 (6H, m), 7.75—8.0 (3H, m), and 9.33 (NH, bs).] and then 17 mg (39.4%) the mono-methanol adduct (*E*-XV: R=Me, mp 158—159.5°C).

Photochemical Equilibrium between *E*- and *Z*-Isomers of IV——Both isomers of IV were stable in solid form as well as in organic solvents. However, on irradiation at ≥300 nm, and equilibrium mixture composed of *E*- and *Z*-isomers in *ca.* 5: 2 ratio was obtained. This experiment can be carried out using pure *Z*- (or *E*-) isomer of IV in $CDCl_3$ solution in an NMR tube with periodic external irradiation (Pyrex-filtered light, Toshiba 400P lamp as a light source) followed by NMR measurements.

Irreversible Thermal Isomerization of *Z*-XV to *E*-XV——The methanol adduct (*Z*-XVa) obtained from XIV by irradiation in methanol was dissolved in $CDCl_3$ containing a small amount of tetramethylsilane and the whole was sealed in an NMR tube and stored in the dark with periodic measurements of NMR spectra. After 5 h, the spectrum had changed completely to that of the corresponding *E*-isomer (*E*-XVa). Four weeks are needed for the complete conversion of *Z*-XVd to *E*-XVd under these conditions. Both isomers (*Z*- and *E*-XV) decomposed quite rapidly on irradiation at ≥300 nm. However, no isomerization between *E*- and *Z*-forms was observed.[17]

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References and Notes

1) Part XXXV: C. Kaneko, W. Okuda, Y. Karasawa, and M. Somei, *Chemistry Lett.*, **1980**, 547. This paper also forms Part XII of "Studies on Oxazepine Derivatives." Part XI: S. Kawai and C. Kaneko, *Heterocycles*, **14**, 47 (1980).
2) A part of this work has been published as a communication: M. Somei, R. Kitamura, H. Fujii, K. Hashiba, S. Kawai, and C. Kaneko, *JCS Chem. Comm.*, **1977**, 899.
3) C. Kaneko and R. Kitamura, *Heterocycles*, **6**, 111 (1977); *idem*, *ibid.*, **6**, 117 (1977); R. Kitamura, H. Fujii, K. Hashiba, M. Somei, and C. Kaneko, *Tetrahedron Lett.*, **1977**, 2911.
4) C. Kaneko, H. Fujii, S. Kawai, A. Yamamoto, K. Hashiba, T. Kimata, R. Hayashi, and M. Somei, *Chem. Pharm. Bull.*, **28**, 1157 (1980).
5) C. Kaneko, *J. Syn. Org. Chem. Japan*, **26**, 758 (1968).
6) According to the equation derived by Pascual *et al.*, the calculated value for the *Z*-isomer is 7.16: C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966). See also, L.M. Jackman and S. Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry," 2nd Ed., Pergamon Press, N.Y., 1969, p. 184.
7) As will be described later, final confirmation of the stereochemistry of the product was obtained by direct comparison of the PMR spectra of the *Z*- and *E*-isomers.
8) It seems noteworthy that the ratio of IV/III decreased in the order of MeOH>EtOH>iso-PrOH>*tert*-BuOH. This trend probably reflects the fact that the photo-addition is slower in *tert*-BuOH than in MeOH.
9) The ratio of IV/III decreased as the proportion of the alcohol in the mixed solvent decreased. Use of distilled CH_2Cl_2 afforded an appreciable amount (*ca.* 40%) of IVa due to the presence of a small amount of methanol used as a stabilizer. Hence, for mixed solvents, acid-treated CH_2Cl_2 was used throughout.
10) While the use of isopropanol or *tert*-butanol as an irradiation solvent for I did not result in the formation of V in any significant amount due to their low polarity, use of methanol as the solvent caused an increase of the yield of V to *ca.* 10%.
11) Though the two isomers of IVa,b behave almost identically, *E*- and *Z*-isomers of IVc,d can be separated by silica gel column or thin layer chromatography, in which the *Z*-isomers are found to be less polar than the *E*-isomers.
12) This conclusion was also supported by the ^{13}C-NMR spectra of these addition products: Y. Itatani, R. Hayashi, H. Fujii, and C. Kaneko, the 45th Meeting of the Hokuriku Branch, Pharmaceutical Society of Japan, Kanazawa, November 1977. Abstracts, p. 6. The results of this study will be published separately.
13) Reaction of [*E*]-*O*-methylbenzohydroximoyl chloride with methoxide ion under conditions comparable with ours leads to complete inversion; the product being [*Z*]-*O*-methylbenzohydroxime methyl ether. A mechanism (*trans* addition of methanol to the *E*-isomer followed by *trans* elimination of HCl) has been proposed: J.E. Johnson, E.A. Nalley, and C. Weidig, *J. Am. Chem. Soc.*, **95**, 2051 (1973).
14) The retro ene reaction is a thermally allowed pericyclic reaction ($_\sigma 2_s + _\pi 2_s$), and pyrolyses of ester and xanthogens are the classic examples of this kind of reaction. The reaction becomes more feasible when hetero atoms are involved in the system: H.M.R. Hoffmann, *Angew. Chem.*, **81**, 587 (1969) and references cited therein.

15) R.B. Woodward and R. Hoffmann, *Angew. Chem. Engl.*, **8**, 781 (1969).
16) The formation of the oxazepine (X) as a primary product from IX was confirmed as follows: the spectral change of IX in $CDCl_3$ caused by external irradiation was followed by PMR spectroscopy; signals assignable to X; δ 7.16 (H-4, s), 3.76 (3H, s), and 2.21 (3H, s), appeared with the disappearance of those of IX. An attempted isolation of X failed due to its facile solvolysis to indole derivatives by moisture. It seems noteworthy that irradiation of IX in methanol gave no addition product and afforded only indole derivatives and carbostyrils. The formation of indoles is caused by the solvolysis of X by methanol prior to the photo-addition reaction. The details of this work have been published: C. Kaneko, T. Naito, M. Hashiba, H. Fujii, and M. Somei, *Chem. Pharm. Bull.*, **27**, 1813 (1979).
17) Irradiation of *E*-XVd or *Z*-XVd in $CDCl_3$ and the direct determination of the spectral change revealed new signals [δ 10.20 (1H, s), 2.74 (3H, s), and 1.28 (9H, s); the latter signal is identical with that of *tert*-butanol] with complete disappearance of those of XVd. Since 3-formyl-2-methylindole (mp 198—200°C)[3] was obtained after basic hydrolysis of the product, the product was tentatively assigned as 1-benzoyl-3-formyl-2-methylindole.
18) C. Kaneko, S. Kawai, and M. Somei, *Chem. Lett.*, **1978**, 1281.
19) A weak electron-withdrawing substituent, COOH instead of COOR in II, still gave a similar photo-addition product, though in low yield.[2,3]
20) Photochemical Michael-type additions of alcohols to related compounds, *e.g.*, α,β-unsaturated ketones,[a] their enol esters,[b] and α,β-unsaturated carboxylic acids,[c] are known. However, the stereochemical features of these reactions have not been studied; *a*) T. Matsuura and K. Ogura, *J. Am. Chem. Soc.*, **88**, 2602 (1966); *b*) P. DeMayo and J.S. Wasson, *J.C.S. Chem. Comm.*, **1967**, 970; *c*) R. Stoermer and H.S. Stockmann, *Chem. Ber.*, **47**, 1786 (1914).
21) J. Braun and L. Brauns, *Chem. Ber.*, **60**, 1253 (1927).
22) Y. Oikawa and O. Yonemitsu, *J. Org. Chem.*, **42**, 1213 (1977).