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Photodecarboxylation of *N*-Phthaloyl-α-amino Acids[1]

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N-Phthaloylglycine (**1a**) was irradiated with a high pressure mercury lamp to give *N*-methylphthalimide (**2a**) in an excellent yield. *N*-Phthaloyl derivatives **1b**—**k** of other α-amino acids also afforded the decarboxylated products **2b**—**k**. In the cases of *N*-phthaloylserine (**1l**) and di-phthaloylcystine (**1m**), *N*-vinylphthalimide (**3**) was isolated as a major product. On the other hand, *N*-phthaloylmethionine (**11a**) and methyl *N*-phthaloylmethionate (**11b**) were treated in the same manner to give the aza-thiacycloheptanol derivatives **12a**—**b** having a new ring system. Solvent effects and possible pathways of these reactions were examined.

Keywords——*N*-phthaloyl-α-amino acid; photolysis; decarboxylation; cyclization; efficiency; solvent effect; ζ-hydrogen abstraction

One of the most common photoreactions of carboxyl derivatives is decarboxylation.[2] The nature of the carboxyl group and the substituents attached to it influence the photoprocesses as well as the fate of the intermediates generated by the loss of carbon dioxide. Although it has been reported that α-amino acids are decarboxylated by heating at 200—250°C,[3] little is known about the photodecarboxylation of α-amino acid derivatives. We have previously reported that *N*-phthaloyl-α-amino acids undergo facile decarboxylation on ultraviolet irradiation,[4] and full details are now presented in this paper.[1,5]

In a typical experiment, a solution of *N*-phthaloylglycine (**1a**) in acetone was irradiated with a 400 W high pressure mercury lamp at room temperature for 3 h in an atmosphere of argon. An oily product obtained on removal of the solvent *in vacuo* was purified by preparative thin layer chromatography (TLC) (silica gel, chloroform) to give *N*-methylphthalimide (**2a**) in 89% yield. In a similar manner, the *N*-phthaloyl derivatives of common α-amino acids (**1**) (L or DL) gave rise to the corresponding decarboxylated products **2** as shown in Chart 1 and Table I. The *N*-phthaloyl derivatives of other α-amino acid analogs such as phenylglycine (**1h**) and *O*-methyltyrosine (**1i**) also afforded corresponding decarboxylated products (**2h** and **2i**). The above products were identified either by direct comparison with authentic specimens or on the basis of their spectral and analytical data. From *N*-phthaloylserine (**1l**), the *N*-vinylphthalimide (**3**) was isolated as a result of concomitant elimination of a hydroxyl group, in place of a normally decarboxylated product. Likewise, di-phthaloylcystine (**1m**) also gave **3**. From *N*-phthaloylleucine (**1d**), a minor product **4a** was isolated in addition to the normal one **2d**. It is interesting that the acetone-adduct structure was assigned to the compound **4a**. An alternative structure **4b** was excluded based on comparison of the ^{13}C-nuclear magnetic resonance (NMR) data of the product with those of a reference compound **4c** prepared by irradiation of *N*-isopropoxymethyl phthalimide in acetone.[6] The quaternary carbon* of **4a**, substituted by a hydroxyl group, shows a similar chemical shift to that of **4c** (96.1 ppm for **4a** and 95.9 ppm for **4c**). By contrast, in the structure **4b**, this particular carbon* is substituted by three hetero atoms, so, the peak would appear at a lower field.[7] The stereochemistry of **4a** is still uncertain.

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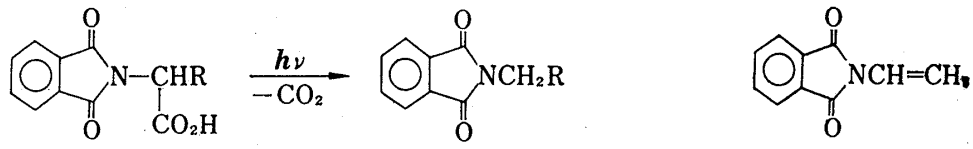
TABLE I. Photodecarboxylation of *N*-Phthaloyl-α-amino Acids

Substrate[a] 1		Solvent[b] for TLC	R	2 Yield[c] (%)	2 mp or bp (°C)/Torr found (reported)	3 Yield (%)	3 mp (°C)
a	Phth–GlyOH	A	H	89.4 (83.0)	132—133 (134[16])		
b	Phth–AlaOH	A	Me	38.3[d]	76—77 (78[16])		
c	Phth–ValOH	A	$CH(Me)_2$	26.7[d]	93—94 (93[17])		
d	Phth–LeuOH	A	$CH_2CH(Me)_2$	46.5 (42.1)	126—128/2 (308/760[18])	[**4a** (2.5%)][e]	
e	Phth–AspOH	C	CH_2COOH	(36.7)	148—150 (151[19])		
f	Phth–AsnOH	A	CH_2CONH_2	62.2 (47.7)	193—194 (204[20])		
g	Phth–PheOH	A	CH_2Ph	65.2 (57.2)	130—131 (130[17])		
h	Phth–pGlyOH	A	Ph	31.6	115—116 (115[21])		
i	Phth–TyrOH(Me)	B	CH_2–C$_6$H$_4$–OMe	10.8	134—136 (140[22])		
j	Phth–HisOH	D	CH_2–imidazole	29.8	186—187 (190[23])		
k	Diphth–LysOH	A	$(CH_2)_4$–Phth	33.6	175—178 (188[24])		
l	Phth–SerOH	A				30.0	88—86 (86[25])
m	Diphth–CysOH	A				40.9	

a) Phth=phthaloyl; Phth-pGly=phthaloyl phenylglycine.
b) The following abbreviations are used; A=$CHCl_3$; B=benzene: AcOEt (4: 1); C=$CHCl_3$: AcOH: MeOH (95: 3: 10); D=$CHCl_3$: AcOH: MeOH (20: 1: 3).
c) The values in parenthesis are yields when acetonitrile is used as the solvent.
d) Negligible amounts of the acetone adducts were isolated.
e) mp 165—166°C.



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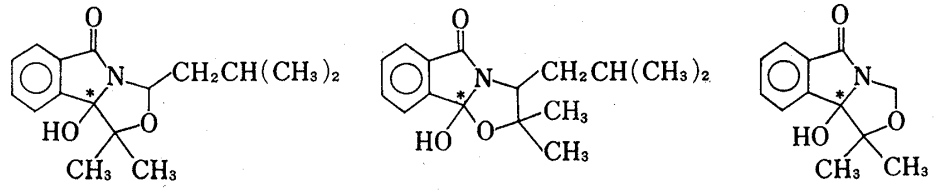

4a 4b 4c

Chart 1

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Photolysis of *N*-phthaloylglycine (**1a**) was examined under various conditions and the results are listed in Table II. Irradiation experiments using a high pressure mercury lamp with or without a Pyrex filter, and a low pressure lamp were all effective for the decarboxylation. Since photoreaction of the sodium salt of **1a** proceeded at a much slower rate, the reactive species of this reaction appears to the free carboxylic acid. As expected, the methyl ester was unchanged on irradiation.

Table II. Photodecarboxylation of *N*-Phthaloylamino Acids under Various Conditions

Phthaloylamino acid	Solvent	Irradiation[a] time (h)	Method	Yield **2a** (%)	Recovery of starting material (%)
1a	CH_3CN	1	B	94	—
	CH_3CN	1[b]	C	92	—
	Dioxane	1	B	89	—
	CH_3OH	3[c]	A	42	43
	50% aq. CH_3OH	3[c]	A	16	68
	90% aq. CH_3CN	0.25	A	71	28
Phth–GlyONa	90% aq. CH_3CN	0.25	B	23	68
Phth–GlyOMe	CH_3COCH_3	3[c]	A	—	97
Phth–β-AlaOH	CH_3CN	3	B	—	99
	CH_3COCH_3	3[c]	A	—	97
1a+Isobutene	CH_3CN	8	B	2	90
1a+*cis*-1,3-pentadiene	CH_3CN	0.3[c]		24	45

The following lamps were used for irradiation; *a*) 500 W HP, *b*) 120 W LP, *c*) 400 W HP.

The solvent effects on this reaction were examined (Table III). The tendency for relative efficiency to decrease in aprotic solvents suggests an important role of intramolecular hydrogen bonding in **5** between the carboxyl and the imide carbonyl groups. The fact that *N*-phthaloyl-β-alanine is photostable (Table II) is consistent with an intramolecular nature of the participating hydrogen bond as postulated in **5**. Although acetonitrile gave the best results among the solvents examined, (Table III), acetone was employed for the preparative photolysis because significant coating of the lamp was observed with acetonitrile as a solvent in the preparative apparatus.

Table III. Solvent Effects on the Photodecarboxylation of *N*-Phthaloylglycine

Solvent	CH_3CN	CH_2Cl_2	Acetone	*tert*-BuOH	H_2O
Relative efficiencies	1.00	0.80	0.35	0.41	0.05

As can be seen in Table II, the photodecarboxylation reaction of **1a** was significantly prevented by adding either isobutene or *cis*-1,3-pentadiene. Since the triplet energy of isobutene, 81 kcal·mol^{-1},[8] is about 10 kcal·mol^{-1} higher than that of the imide which is estimated to be *ca.* 70 kcal·mol^{-1} from the O–O band of the phosphorescence spectrum (ethanol, 77° K), energy transfer is unlikely as a mechanism for the quenching by isobutene. Instead, an electron transfer from the diene to the imide may be responsibible for the quenching since such electron transfer is often of importance in the photoreactions of phthalimides and olefins and dienes.[9] In contrast to this, it is interesting that the photodecarboxylation of *N*-benzoylglycine,[1b] a closely related analog of the phthaloyl derivatives, is sensitized by acetone, suggesting the involvement of an excited triplet intermediate.

Intramolecular hydrogen abstraction of the excited imide carbonyl from the carboxyl group to generate directly a carboxyl radical **6** would be energetically unfavorable. Low

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efficiency of phthalimide type II reaction[10] and no substantial depression of the formation of **2a** in the presence of a good hydrogen donor (dioxane; Table II) also tend to exclude this radical mechanism.

Although the detailed mechanistic features of this reaction are not yet clear, plausible pathways are illustrated in Chart 2. Initial proton transfer from the hydrogen-bonded carboxyl group of **5** to the imide carbonyl leads to the formation of a zwitterion intermediate **7**, which would be decarboxylated to give a biradical **8** followed by hydrogen transfer to **2**. Formation of **4a** is supported by the trapping of a relatively long-lived secondary radical **8** by a solvent (acetone). An isomeric product **4b**, even if formed, would be readily decomposed due to its hemiacetal-like instability. It is also conceivable that 1,3-dipolar addition of a zwitterionic intermediate **9** would give a similar product. In such a polar addition, however, the alternative isomer **4b** would be a more plausible product through a nucleophilic attack of the carbonyl oxygen of acetone at the imide carbonyl group in **9b**. The formation of *N*-vinylphthalimide (**3**) is explained in terms of concerted heterolytic elimination of an appropriate leaving group **10** (X=–OH and –S–S–), in accord with the postulation of the zwitterion intermediate **7**.

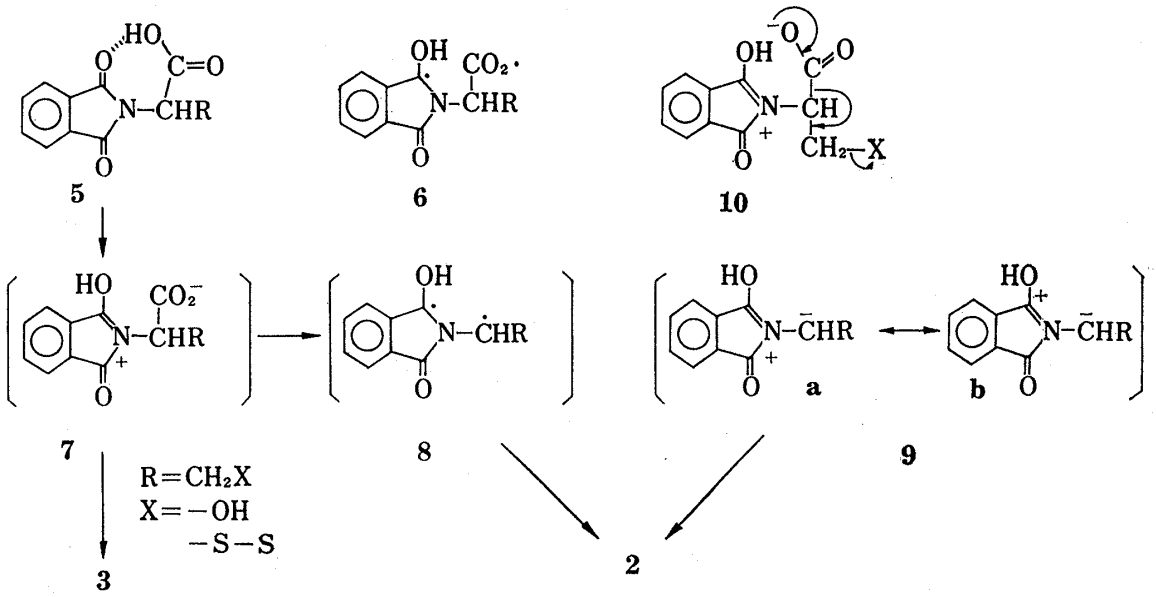

Chart 2

During the course of this study, an unexpected product **12a** (61%) was isolated on irradiation of *N*-phthaloylmethionine (**11a**) in acetone solution.[11] The ^{1}H-NMR spectrum of **12a** showed a new peak of a methylene moiety [3.43 (d, 15 Hz), 3.01 (d, 15 Hz); δ, $CDCl_3$] in place of the original *S*-methyl group in **11a** indicating that cyclization had occurred at the thioether methyl group in addition to decarboxylation. All other spectral and analytical data supported the structure **12a**. In a similar manner, irradiation of methyl *N*-phthaloyl-L-methionate **11b** ($[\alpha]_D$ −46.2°) afforded the crystalline product **12b**, which was separated by silica gel preparative TLC into two optical isomers. They were the *trans* (*levo*-form, $[\alpha]_D$ −101.0°) and *cis* (*dextro*-form, $[\alpha]_D$ +132.8°) stereoisomers with regard to a hydroxyl group and a methoxycarbonyl group in the new ring, consistent with the assigned structure **12b**. The stereochemistry of the *trans* and *cis* isomers of **12b** was deduced from the infrared (IR) and ^{1}H-NMR spectral data. The IR signals of a hydroxyl group and a methoxycarbonyl group in **12b** appeared at ν 3370 (OH, sharp), 1750 ($COOCH_3$)cm^{-1} and 3620—3200 (OH, broad), 1740 ($COOCH_3$)cm^{-1}, for the *trans* and *cis* isomers, respectively. Namely, the absorptions of a hydroxyl group and a methoxycarbonyl group in **12b** *cis* appeared at lower frequency and as broader peaks

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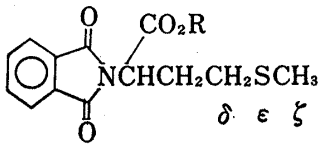
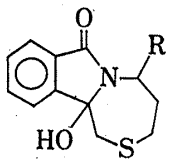
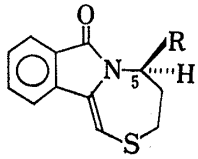
than those of the corresponding *trans* isomer, due to the participation of a hydrogen bond of a hydroxyl group and a methoxycarbonyl group in **12b** *cis* (Chart 3). In the ^{1}H-NMR spectrum ($CDCl_3$), a new peak of a methylene group of **12b** *trans* appeared as a singlet at δ 3.19, whereas that of **12b** *cis* appeared as ABq type at δ 2.98 and 3.35 (J=15 Hz, each), due to the participating hydrogen bond (fixed conformation) as illustrated in Chart 3. On treatment with acid, **12a** and **12b** (*trans* and *cis*) were readily converted into the dehydrated products, **13a** and **13b** in good yields, respectively, in support of the tertiary hydroxyl structure of **12**. On the other hand, the configuration of C_5 in **12b** (*trans* and *cis*) is correlated with that of L-methionine. The methoxycarbonyl group in the *trans* and *cis* isomers of **12b** was unchanged on dehydration to give the same **13b** of *levo*-form ($[\alpha]_D$ $-365\pm3°$), respectively. Therefore, the configuration of the dehydrated compound is represented by **13b**, in which the asymmetric carbon (C_5) has *S*-configuration.



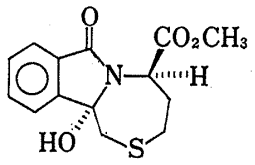
11a : R=H
11b : R=CH_3



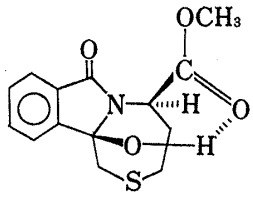
12a : R=H
12b : R=CO_2CH_3



13a : R=H
13b : R=CO_2CH_3



12b *trans*



12b *cis*

Chart 3

Since γ-hydrogen abstraction is a major path for simple carbonyl systems,[8,12] it is interesting that in these examples the aza-thiacycloheptanol derivatives **12**, corresponding to ζ-hydrogen abstraction,[11] were produced easily. In fact, this finding of a special "cyclophilic nature" of the phthalimides with a thioether in their side chain led us, in an extensive study of applications of this system, to develop novel photochemical macrocyclic syntheses.[5,13]

Experimental

Melting points are uncorrected. For vapor-phase chromatography (VPC, FID detector) a column of 1% Fluoxylate K on Uniport HP (Gasukuro Kogyo Co., Ltd., Japan), 3 mm×2 m, was used. NMR spectra were obtained in $CDCl_3$ solution with JEOL JNM-FX 100, and JEOL JNM 60 spectrometers, unless otherwise noted, and are given in δ (ppm) from internal tetramethylsilane. Coupling constants (J) are given in Hz and the following abbreviations are used; s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. Infrared spectra (IR) were obtained with a Hitachi 215 spectrometer. Mass spectra (MS) were taken on a Hitachi RMU-6M spectrometer. Phosphorescence spectra were recorded on a Hitachi 650-60 fluorescence spectrophotometer. *N*-Phthaloyl-α-amino acids were prepared by the methods reported in the literature and procedures cited therein.[14,15]

Methyl *N*-Phthaloyl-L-methionate (11b)——A mixture of L-methyl methionate·HCl 10.0 g (0.05 mol), *N*-carbethoxyphthalimide 11.0 g (0.05 mol) and Na_2CO_3 5.03 g (0.05 mol) in 50% aqueous $CHCl_3$ (100 ml) was stirred at 25°C for 2 h. The reaction mixture was acidified with dil. HCl and extracted with $CHCl_3$. The extract was dried and concentrated *in vacuo* to give 13.5 g (92.0%) of product, colorless prisms from hexane–isopropyl ether, mp 33—34°C. $[\alpha]_D^{22}$ $-46.2°$ (c=1.0, $CHCl_3$). IR ν_{max}^{Nujol} cm^{-1}: 1780, 1745, 1715. MS m/e: 293 (M^+). ^{1}H-NMR: 2.08 (3H, s), 2.40—2.70 (4H, m), 3.78 (3H, s), 4.97—5.28 (1H, m), 7.80—8.10

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(4H, m). *Anal.* Calcd for $C_{14}H_{15}NO_4S$: C, 57.33; H, 5.16; N, 4.78; S, 10.91. Found: C, 57.52; H, 5.12; N, 4.96; S, 11.10.

Photolysis of *N*-Phthaloylamino Acids——Method A: Solutions (300 ml) of **1** [1.2 g (3—6 mmol)] in acetone were irradiated for 3 h with a 400 W high pressure mercury lamp in an atmosphere of argon, unless otherwise specified. Products obtained on removal of the solvent *in vacuo* were purified by silica gel preparative thin layer chromatography (TLC) to give **2**. The results are listed in Table I, with the solvents used and physical data for the products.

Method B: Solutions (300 ml) of **1a**, the sodium salt of **1a** or *N*-phthaloyl-*β*-alanine (3 mmol) were irradiated using a 500 W high pressure mercury lamp with a Pyrex filter under continuous bubbling of nitrogen. After removal of the solvent, the residue was passed through a silica gel short column to give **2a** (benzene: EtOH=10: 1) or the starting material ($CHCl_3$: MeOH: AcOH=50: 4: 1). The results are listed in Table II.

Method C: The same procedure as above was used except that a 120 W low pressure mercury lamp was used for irradiation (Table II).

***N*-Isopentyl-phthalimide (2d) and 9b-Hydroxy-3-isobutyl-5-oxo-1,3,5,9b-tetrahydro-oxazolo[4,3-*a*]isoindole (4a)**——A solution of *N*-phthaloyl-L-leucine **1d** in acetone was irradiated in a manner similar to that described for method A to give 462 mg (46.5%) of **2d** and 31 mg (2.5%) of **4a**, respectively. **2d**: Colorless oil of bp 126—128°C/2 Torr (lit.[18] bp 308°C/760 Torr). **4a**: Colorless needles of mp 165—166°C from $CHCl_3$–hexane. IR ν_{max}^{Nujol} cm^{-1}: 3230, 1677, 1609. UV λ_{max}^{EtOH} mμ (ε): 245 (5050), 276 (1450), 283 (1100). MS *m/e*: 275 (M^+). ^{1}H-NMR: 0.68 (3H, s), 0.97 (3H, d, J=6 Hz), 1.02 (3H, d, J=6 Hz), 1.53 (3H, s), 1.77 (2H, m), 1.65—2.10 (1H, m), 3.10—3.45 (1H, br), 5.21 (1H, t, J=5 Hz), 7.35—7.75 (4H, m). ^{13}C-NMR: 21.8 [q, $-CH(\underline{C}H_3)_2$ or $-C(\underline{C}H_3)_2$], 22.9 [q, $-C(\underline{C}H_3)_2$ or $-CH(\underline{C}H_3)_2$], 24.3 [d, $-\underline{C}H(CH_3)_2$], 46.1 (t, CH_2), 82.4 [s, $-\underline{C}(CH_3)_2$], 84.8 (d, N–$\underline{C}$H–O), 96.1 (s, –C–OH), 122.0, 123.9, 130.1, 132.7, 133.2 and 144.5 (aromatic carbons), 170.7 (s, carbonyl carbon). *Anal.* Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.84; H, 7.61; N, 5.10.

3-Phthalimido-propionamide (2f)——The same procedure as above (method A) was used for irradiation. The crystalline residue obtained on removal of the solvent under reduced pressure was recrystallized from EtOH to give 414 mg (62.2%) of **2f** as colorless needles of mp 193—194°C (lit.[20] mp 203—204°C). IR ν_{max}^{Nujol} cm^{-1}: 3390, 3290, 3190, 1768, 1700, 1645. MS *m/e*: 218 (M^+). ^{1}H-NMR (DMSO-d_6): 2.46 (2H, t, J=7 Hz), 3.82 (2H, t, J=7 Hz), 6.50—7.00 (1H, br), 7.15—7.60 (1H, br), 7.80 (4H, s). *Anal.* Calcd for $C_{11}H_{10}N_2O_3$: C, 60.54; H, 4.62; N, 12.84. Found: C, 60.72; H, 4.60; N, 12.99.

1,5-Bis(phthalimido)pentane (2k)——Colorless needles of mp 175—178°C (lit.[24] mp 188°C) from MeOH. This compound was identical with an authentic sample as judged by direct comparison.

1,3,4,5,7,11b-Hexahydro-11b-hydroxy-[1,4]thiazepino[3,4-*a*]isoindol-7-one (12a)——A solution (300 ml) of *N*-phthaloyl-L-methionine **11a**[26] (1.2 g, 4.3 mmol) in acetone was irradiated for 3 h as described for method A. The residue was subjected to preparative TLC ($CHCl_3$: EtOH=20: 1) to give 606 mg (60.6%) of **12a**, colorless prisms from EtOH, mp 188—190°C. IR ν_{max}^{Nujol} cm^{-1}: 3265, 1665. MS *m/e*: 235 (M^+). ^{1}H-NMR ($CDCl_3$–DMSO-d_6, 100 Mc): 1.70—2.30 (2H, m), 2.40—3.00 (3H, m), 3.01, 3.43 (1H each, a pair of AB type, J=15 Hz), 3.70—4.20 (1H, m), 6.33 (1H, br s), 7.30—7.76 (4H, m). *Anal.* Calcd for $C_{12}H_{13}NO_2S$: C, 61.27; H, 5.57; N, 5.96; S, 13.61. Found: 61.36; H, 5.68; N, 5.82; S, 13.81.

3,4,5,7-Tetrahydro-[1,4]thiazepino[3,4-*a*]isoindol-7-one (13a)——A mixture of **12a** (700 mg), conc. HCl (4 drops) and MeOH (20 ml) was refluxed for 3 h. After removal of the solvent under reduced pressure, the residue was subjected to silica gel preparative TLC ($CHCl_3$) to give 582 mg (90.0%) of **13a** as a pale yellow oil. IR ν_{max}^{film} cm^{-1}: 1700. MS *m/e*: 217 (M^+). ^{1}H-NMR: 2.00—2.50 (2H, m), 3.10—3.40 [2H, m (t-like)], 4.15—4.50 [2H, m (t-like)], 6.37 (1H, s), 7.35—8.00 (4H, m). *Anal.* Calcd for $C_{12}H_{11}NOS$: C, 66.35; H, 5.10; N, 6.45; S, 14.75. Found: C, 66.50; H, 5.07; N, 6.72; S, 14.60.

Methyl 1,3,4,5,7,11b-Hexahydro-11b-hydroxy-7-oxo-[1,4]thiazepino[3,4-*a*]isoindole-5-carboxylate (12b) (*trans* and *cis*)——A solution (300 ml) of methyl *N*-phthaloyl-L-methionate **11b** (1.2 g, 4.1 mmol) in benzene was irradiated for 3 h as described for method A. The residue was subjected to silica gel preparative TLC ($CHCl_3$: AcOEt=2: 1) to give two compounds.

12b (*trans*): 458 mg (38.2%), colorless needles from AcOEt–hexane, mp 130—131°C. $[\alpha]_D^{22}$ −101.0° (c=1.0, $CHCl_3$). IR ν_{max}^{Nujol} cm^{-1}: 3370, 1750, 1685. MS *m/e*: 293 (M^+). ^{1}H-NMR: 2.25—2.85 (4H, m), 3.19 (2H, s), 3.72 (3H, s), 4.55—5.10 (1H, m), 5.17—5.50 (1H, m), 7.30—7.85 (4H, m). *Anal.* Calcd for $C_{14}H_{15}NO_4S$: C, 57.33; H, 5.16; N, 4.78; S, 10.91. Found: C, 57.49; H, 5.22; N, 4.73; S, 11.01.

12b (*cis*): 330 mg (27.5%), colorless prisms from AcOEt–hexane, mp 212—215°C. $[\alpha]_D^{22}$ +132.8° (c=1.0, $CHCl_3$). IR ν_{max}^{Nujol} cm^{-1}: 3600—3200, 1740, 1675. MS *m/e*: 293 (M^+). ^{1}H-NMR: 2.25—2.90 (4H, m), 2.98, 3.35 (1H each, a pair of AB type, J=15 Hz), 3.67 (3H, s), 3.90—4.20 (1H, m), 4.25—4.80 (1H, m), 7.40—7.85 (4H, m). *Anal.* Calcd for $C_{14}H_{15}NO_4S$: C, 57.33; H, 5.16; N, 4.78; S, 10.91. Found: C, 57.07; H, 5.31; N, 4.58; S, 10.66.

In the Case of *tert*-Butanol as the Solvent: A solution of **11b** (1.20 g, 4.1 mmol) in *tert*-BuOH (300 ml) was treated by a procedure similar to that mentioned above and **12b** (*trans*), 214 mg (17.8%), and **12b** (*cis*), 380 mg (31.6%), were obtained from the residue.

Methyl 3,4,5,7-Tetrahydro-7-oxo-[1,4]thiazepino[3,4-*a*]isoindole-5-carboxylate (13b)——From **12b** (*trans*): A mixture of **12b** (*trans*) (7.5 g, 0.026 mol), *p*-toluenesulfonic acid (0.6 g) and CH_2Cl_2 (60 ml) was refluxed

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for 2 h. After removal of the solvent under reduced pressure, the residue was subjected to silica gel chromatography (benzene: AcOEt=14: 1) to give 4.92 g (70.0%) of **13b**, colorless prisms from AcOEt–hexane, mp 118—119°C. $[\alpha]_D^{22}$ −362.4° (c=1.0, $CHCl_3$). IR ν_{max}^{Nujol} cm^{-1}: 1738, 1680, 1620. MS m/e 275. ^{1}H-NMR: 3.00—3.40 (4H, m), 3.75 (3H, s), 5.50—5.70 [1H, m (q-like)], 6.40 (1H, s), 7.60—8.00 (4H, m). *Anal.* Calcd for $C_{14}H_{13}NO_3S$: C, 61.09; H, 4.76; N, 5.09; S, 11.64. Found: C, 61.25; H, 4.71; N, 5.28; S, 11.82.

From **12b** (*cis*): A mixture of **12b** (*cis*) (750 mg), *p*-toluenesulfonic acid (40 mg) and CH_2Cl_2 (10 ml) was treated by a procedure similar to that mentioned above to give 560 mg (80.0%) of **13b**. $[\alpha]_D^{22}$ −367.6° (c=1.0, $CHCl_3$).

Irradiation of 1a in the Presence of Isobutene——A solution of **1a** (2.05 g, 10 mmol) and isobutene (11 g, 0.2 mol) in acetonitrile (100 ml) was irradiated in a procedure similar to method B for 8 h to give 40 mg (2%) of **2a**, and 1.85 g of the starting material was recovered (90%).

Irradiation of 1a in the Presence of *cis*-1,3-Pentadiene——A solution of **1a** (0.3 g, 1.5 mmol) and *cis*-1,3-pentadiene (108 mg, 1.6 mmol) in acetonitrile (230 ml) was irradiated by a procedure similar to method A for 20 min to give 57 mg (24.2%) of **2a**, and 134 mg (44.7%) of the starting material was recovered.

Irradiation of *N*-Benzoylglycine[1b]——*N*-Benzoylglycine (538 mg, 3 mmol) in acetonitrile or acetone was irradiated by a procedure similar to method B for 1 h to give 535 mg (99%) of the starting material (in acetonitrile) or 394 mg (97%) of *N*-methylbenzamide (in acetone).

Solvent Effects on Irradiation of 1a——Degassed solutions of **1a** (10 mM) in Pyrex tubes were irradiated on a merry-go-round using potassium chromate as a chemical filter to isolate 313 nm. The formation of **2a** was determined by vapar phase chromatography analysis using *m*-dinitrobenzene as an internal standard. The results are listed in Table III.

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