Transformation of Alkyl *N*-(Vinyloxy)benzimidates to Alkyloxazoles. Mechanism and Extension

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Transformation of alkyl *N*-(vinyloxy)benzimidates to alkyloxazoles proceeds through the intermediates: a charge-separated 1,2-oxazetidine derivative and then 1-hydroxy-2-[[methylthio(phenyl)methylene]imino]maleic acid diester, while their photochemical transformation takes place via a concerted [1,3] sigmatropic shift. As the extension of this reaction, the preparation of the precursor proposed for virginiamycin M2 synthesis and the reaction of *N*-analogs of alkyl *N*-(vinyloxy)benzimidates are described.

In previous papers,[1] we reported an unprecedented thermal and photochemical rearrangement which is the transformation of alkyl *N*-(vinyloxy)benzimidates to alkyloxazoles. Although the reaction mechanism has been proposed tentatively,[1b] we reinvestigated this reaction in detail because it seemed to provide an useful tool for the construction of many heterocycles. Especially, it has become important to develop a synthetic method of oxazoles since the appearance of useful natural products containing oxazole moiety,[2] even if there are many synthetic procedures.[3]

Results and Discussion

Thermal Reaction. The previously proposed mechanism is shown in Scheme 1. The initial cleavage of N–O bond of **1a** gives radical fragments **2**, which then form an intermediate **3**. The cyclization of **3** gives the oxazole **5a** via a dihydro compound **4** followed by elimination of ethanol.

This mechanism was proposed from the following facts: (1) The reaction also took place under photochemical conditions, and (2) coumarin was isolated as a by-product in the reaction of dimethyl (2*H*-[1]benzopyran-2-ylideneaminooxy)butenedioate to dimethyl 2-[2-(*o*-hydroxyphenyl)vinyl]-4,5-oxazoledicarboxylate. In order to confirm this mechanism, we carried out several experiments as described below.

Preparation of Intermediate 3: We attempted to isolate the intermediate **3** in this reaction, but it was unsuccessful. This may have been because **3** is not sufficiently tolerated under the present conditions which bring about the initial N–O bond cleavage for the formation of **5a**.

Therefore we tried to isolate a *S*-analog **9** corresponding to **3** from glycine ethyl ester by the procedure shown in Scheme 2. *N*-[Methylthio(phenyl)methylene]glycine ethyl ester (**8**) was treated with diethyl oxalate in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at room temperature to give diethyl 2-phenyl-4,5-oxazoledicarboxylate (**10**) quantitatively. This result shows that **8** changes to **10** via the expected intermediate **9**.

Crossover Experiment: We carried out a crossover experiment to confirm the generation of radical fragments **2**. The *o*-xylene solution involving an equimolar mixture of **1a** and its deutrated compound **1a-*D*** was refluxed for 4 h. Usual work-up gave **5a** and its deutrated compound **5a-*D*** in 50% yield. The crossover products ($m/z=266$ and 267) could not be detected (Scheme 3).

Thus, the existence of radical fragments **2** appears extremely doubtful. Because the diffusion rate of radicals (10^9—10^{10} $m^{-1}\,s^{-1}$) is much larger than their reaction rate (10^5—10^6 $m^{-1}\,s^{-1}$),[5] we wish to propose a charge-separated 1,2-oxazetidine derivative **11** instead of the intermediate **2** (Scheme 4).

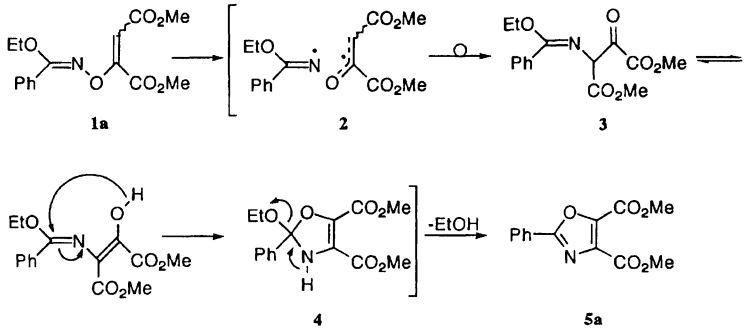
Solvent Effect: Thermal rearrangement of **1a** was carried out in various solvents (Table 1). Generally, the use of more polar solvents, especially such as diglyme, increased the chemical yield.

Reaction Rate: In order to obtain the thermodynamic parameters, the reaction of **1a** was carried out in toluene at three reaction temperatures in the usual way (Table 2). The activation energy ($\Delta E^{\ddagger}=64.9$ kJ mol^{-1}) and the activation entropy ($\Delta S^{\ddagger}=-154.0$ J K^{-1} mol^{-1}) are derived from the rate constants obtained in Table 2.

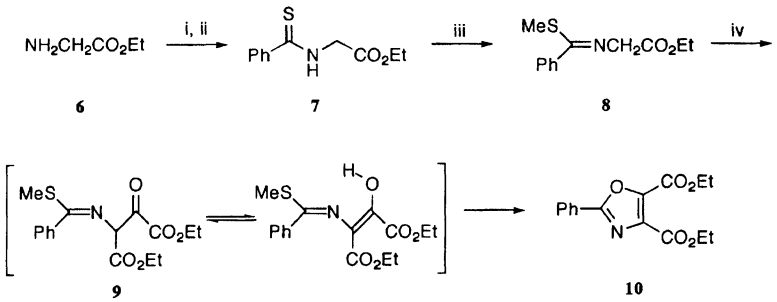
The fact that the $\Delta E^{\ddagger}$ is lower than the energy for N–O bond cleavage (221.8 kJ mol^{-1})[6] and $\Delta S^{\ddagger}$ has a large negative value can also support the process of **11**, which has a concerted character.

Substituent Effect: The yields of **5a**—**5e**, which have different para-substituted phenyl groups, were measured under reaction conditions (95 °C, toluene, 4 h) and their relative rates (Y_X/Y_H) are summarized in Table 3. No correlation was observed with regard to the electronic effect (δ) of substituent X.

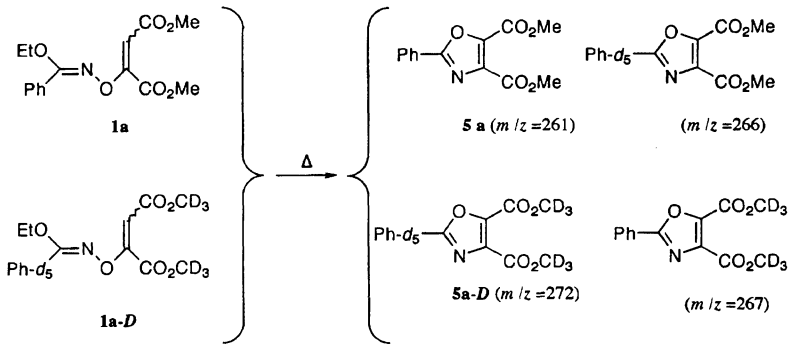
Judging from the above results, we think the reaction mechanism shown in Scheme 4 is reasonable. Radical fragments **2** are ruled out from the results of the crossover experiment. Further, the intermediate **11** is supported from evaluation of the kinetic parameters. Furthermore, the formation of **10** by the reaction of **8** with diethyl oxalate shows that this reaction proceeds via the intermediate **3**. The reason why the substituent effect of phenyl group does not act on the chemical yields may be based on a much larger electron-donating



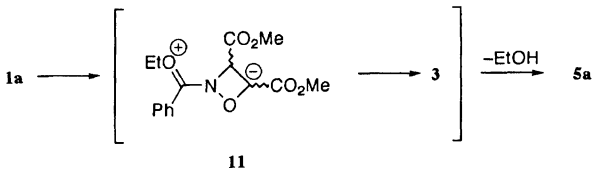
Scheme 1. Previously proposed mechanisms.



Scheme 2. Synthesis of **9**. (i) PhCOCl, Et_3N; (ii) Lawesson's reagent; (iii) Me_3OBF_4; (iv) DBU, $(CO_2Et)_2$.



Scheme 3. Crossover experiment.



Scheme 4. Reasonable reaction mechanism.

Table 1. Solvent Effect for Thermal Reaction of **1a**

Solvent	E_T(kcal mol^{-1})[4]	Yield (%)
CH_3CN	46.0	34.3
$(CH_3CO)_2O$	43.9	37.8
$(CH_3OCH_2)_2O$	38.2	50.0
$C_6H_5CH_3$	33.9	29.8
CCl_4	32.5	27.7

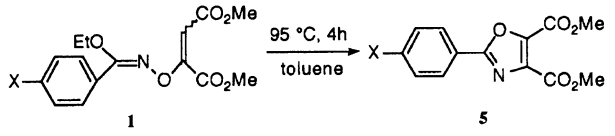
Table 2. Rate Constant for Thermal Reaction of **1a**

T(±1 °C)	k($\times 10^5 s^{-1}$)	Correlation coefficient (r)
91	2.64×10^{-5}	0.995
100	5.17×10^{-5}	0.994
119	5.17×10^{-5}	0.969

effect of ethoxyl group than that of phenyl group.

Photochemical Reaction. The present reaction was found to take place under photochemical conditions. This mechanism was elucidated. When the dichloromethane solution of **1a** was irradiated by a high-pressure Hg lamp under bubbling with oxygen as a radical quencher, **5a** was obtained in 9.3% conversion yield, while the nonbubbled experiment gave **5a** in 10.8% conversion yield. The dichloromethane solution of **1a** containing hydroquinone as the radical quencher was also irradiated in the same way to afford **5a** in 10% conver-

Table 3. Relative Rates (Y_X/Y_H) of Isolated Yield of **5**



1 **5**

Product	**5b**	**5c**	**5a**	**5d**	**5e**
X	MeO	Me	H	Cl	CN
Y_X/Y_H	1.00	0.78	1.00	0.79	0.98

sion yield. The same crossover experiment as described in the thermal reaction was carried out. In this experiment, we could not observe the crossover products (m/z=266 or 267) at all. These facts may rule out the radical mechanism involving the intermediate **2**. No solvent effect could be observed on the chemical yield of **5a** (Table 4). Therefore, the photochemical reaction is considered to occur via the concerted [1,3] sigmatropic process allowed by the Woodward–Hoffmann rule.

The [1,3] sigmatropic reaction mechanisms so far reported have been well summarized in the literature.[7] In a report relevant to the present reaction, the photochemical [1,3] sigmatropic reaction of benzyloxystyrene to 3-phenylpropiophenone was observed to proceed through a triplet state intermediate like **2** and 8% of crossover product.[8]

For Synthesis of Natural Product. As application of this reaction, we chose the synthesis of *t*-butyl 2-(phenylsulfonylmethyl)-4-oxazolecarboxylate (**18**), which was proposed as a starting material for the total synthesis of virginiamycin M2.[9] The synthetic procedure is summarized in Scheme 5.

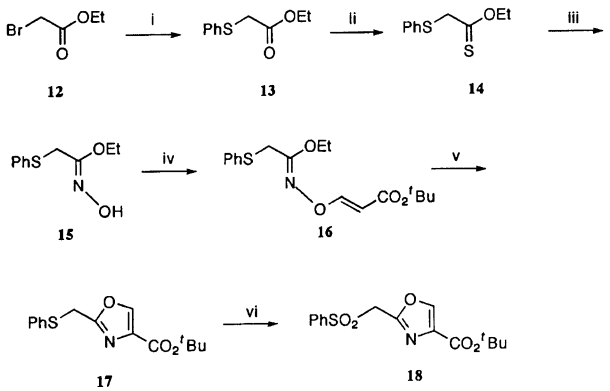
Ethyl (phenylthio)acetate (**13**) was prepared from ethyl bromoacetate (**12**) and then converted to ethyl (phenylthio)acetohydroximate (**15**) via *O*/*S* exchanged compound **14**. Compound **15** was derived to ethyl *N*-[2-(*t*-butoxycarbonyl)vinyloxy](phenylthio)acetimidate (**16**) by treatment with *t*-butyl propiolate. Then **16** was converted to *t*-butyl 2-(phenylthio)methyl-4-oxazolecarboxylate **17** by utilizing the present thermal rearrangement. Thus obtained **17** was easily oxidized by *m*-chloroperbenzoic acid (*m*-CPBA) to give the expected **18** in 12% overall yield based on **12**. Although the method starting from 2-methyl-4-oxazolecarboxylate has been known for the synthesis of **18**,[10] this affords another convenient method starting from an easily available compound such as **12**.

Extension to *N*-Analogs of Alkyl *N*-(Vinyloxy)benzimidate. As the extension of this reaction, some *N*-analogs of alkyl *N*-(vinyloxy)benzimidate were examined under thermal conditions. 1-Methyl-2-[(1,2-bis(methoxycarbonyl)vinyloxy]imino]pyrrolidine **19** was heated with benzoyl chloride for 3 h at 140 °C to afford an expected rearranged product, dimethyl 2-[3-(*N*-methylbenzoylamino)propyl]-4,5-oxazoledicarboxylate (**20**) in 39% yield (Scheme 6).

N^2-[1,2-bis(methoxycarbonyl)vinyloxy]benzamidine was heated with a mixture of acetic anhydride and toluene to give an unidentified product.

On the other hand, cyclic compounds **21** underwent a [3,3] sigmatropic reaction in heating acetic anhydride to afford **22** in moderate yield (Table 5).

This reaction is considered to proceed as shown in Scheme 7: Acetic anhydride reacts with 2-[[(*Z*)-1,2-bis(methoxycarbonyl)vinyloxy]imino]piperidine (**21c-*Z***) to give an isomeric mixture **23** which can be isolated. Thus obtained **23** rearranges to **24** via [3,3] sigmatropic shift. Next, compound **24** cyclizes with the elimination of acetic acid.



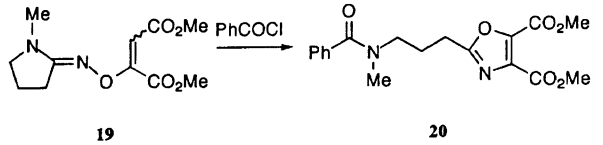
Scheme 5. Synthesis of **18**. (i) PhSH, pyridine, EtOH, rt, 2 h, 100%; (ii) Lawesson's reagent, *o*-xylene, Δ, 5 h, 41%; (iii) $NH_2OH{\cdot}HCl$, NaOAc, MeOH, rt, 1 h, 89%; (iv) $CH{\equiv}C{-}CO_2^tBu$, Et_3N, rt, 2 h, 91%; (v) *o*-dichlorobenzene, Δ, 1 h, 35%; (vi) *m*-CPBA, CH_2Cl_2, 3 h, 100%.

Conclusion

In conclusion the conversion of alkyl *N*-(vinyloxy)-benzimidates to 2-alkyloxazoles proceeds through the 1-hydroxy-2-[[methylthio(phenyl)methylene]imino]maleic acid diester on the thermal reaction and takes place via a concerted [1,3] sigmatropic reaction on the photochemical reaction. The extension of this reaction to *N*-analogs of alkyl *N*-(vinyloxy)benzimidates was carried out. The present rearrangement was observed in the case of the *N*-analogs derived from *N*-alkyl-substi-

Table 4. Solvent Effect for Photochemical Reaction of **5a**

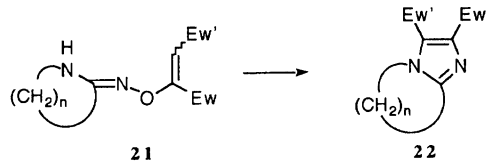
Solvent	Yield (%)
$C_6H_5CH_3$	10.5
C_6H_6	11.8
CH_2Cl_2	10.8



19 **20**

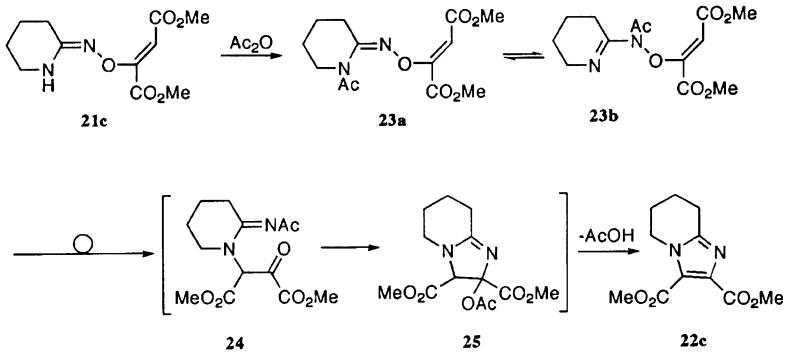
Scheme 6. Thermal reaction of **19**.

Table 5. Thermal Reaction of **21**



21 **22**

	Starting compound **21**				Product **22**	
	n	E_w	$E_{w'}$	E or Z	Yield	(%)
21a	3	H	CO_2Et	E	**22a**	59
21b	3	CO_2Me	CO_2Me	E, Z	**22b**	19
21c	4	CO_2Me	CO_2Me	Z	**22c**	59
21d	5	CO_2Me	CO_2Me	E, Z	**22d**	46



21c **23a** **23b**

24 **25** **22c**

Scheme 7. Thermal reaction mechanism of **21**.

tuted lactam, while the [3,3] sigmatropic reaction occurred in the case of the *N*-analogs derived from the *N*-non-substituted lactam.

Experimental

Microanalyses were performed with a Perkin–Elmer 240 element analyser at the Chemical Analysis Center of Chiba University. IR spectra were recorded on a Hitachi 215 spectrometer. Mass spectra were obtained on a JEOL JMS-HX 110A for FAB and on a Hitachi M-60 for EI. ^{1}H NMR spectra, for $CDCl_3$ solution were recorded on JEOL MH-100, JNM-FX-270, JNM-GSX-400, and JNM-GSX-500 spectrometers. J values are given in Hz. Wakogel C-200 was used for low-pressure liquid chromatography (LPLC) and Wakogel B-5F was used for preparative TLC (PLC).

Ethyl *N*-[1,2-Bis(methoxy-d_3-carbonyl)vinyloxy]-benzimidate-d_5 [*E*,*Z*(3 : 2)-Mixture] 1a-*D*. To the magnesium (0.75 g, 30 mmol) dipped in dry ether (10 mL), was added two drops of diiodoethane for the activation of magnesium. A mixture of bromobenzene-d_5 (4.86 g, 30 mmol) and ether (20 mL) was added dropwise to the ether solution obtained above under gentle refluxing. The mixture was further refluxed for 1.5 h. The phenyl-d_5-magnesium bromide solution was dropped to diethyl carbonate (5.31 g, 45 mmol) in dry ether (20 mL) while keeping the solution boiling. After stirring for 0.5 h, the reaction mixture was allowed to stand overnight. Then the reaction mixture was treated with ice and with 4 M HCl (30 mL) (1 M=1 mol dm^{-3}). The ether layer was separated and the aqueous layer was extracted with ether (40 mL). The combined ether solution was dried over Na_2SO_4, and then concentrated under reduced pressure. The residue was purified by a low-pressure liquid chromatography (LPLC) on silica gel [AcOEt–hexane (1 : 6)] to give ethyl benzoate-d_5 (2.1 g, 45% yield).

A mixture of ethyl benzoate-d_5 (0.95 g, 6.1 mmol), Lawesson's reagent (1.33 g, 3.3 mmol) and *o*-xylene (10 mL) was refluxed for 5 h under nitrogen. The resulting mixture was concentrated under reduced pressure to give a yellow oil, which was purified by LPLC on silica gel with hexane as eluent. The obtained ethyl thiobenzoate-d_5 (0.76 g, 72% yield) was dissolved in ethanol (20 mL). The resultant solution was stirred at room temperature for 5 h with the hydroxylamine prepared from hydroxylamine hydrochloride (0.62 g, 8.9 mmol) and 28% sodium methoxide (1.7 g, 8.9 mmol). The reaction mixture was concentrated under reduced pressure to give an oil. Purification by LPLC on silica gel [AcOEt–hexane (1 : 2)] gave ethyl *N*-hydroxybenzimidate-d_5 as an oil in 91% yield.

On the other hand, dimethyl acetylenedicarboxylate (1.7 g, 12 mmol) was stirred with excess methanol-d_4 (10 mL) and two drops of conc. sulfuric acid at 50 °C for 2 d. The reaction mixture was concentrated to give an oil, which was then purified by LPLC on silica gel with chloroform as eluent to give dimethyl-d_6 acetylenedicarboxylate in 91% yield.

A mixture of ethyl *N*-hydroxybenzimidate-d_5 (0.68 g, 4 mmol) and dimethyl-d_6 acetylenedicarboxylate (0.56 mL, 4 mmol) was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure to give a brown oil, which was then purified by preparative TLC (PLC) on silica gel [AcOEt–chloroform (1 : 40)] to afford **1a-*D*** [*E*,*Z*(3 : 2)-mixture] in 98% yield: IR (neat) 2920 (CH), 2250, 2180 (CD), and 1700 (CO) cm^{-1}. ^{1}H NMR ($CDCl_3$,

270 MHz) δ=1.37, 1.43 (3H, t×2, J=7.1, 6.2 Hz, $OCH_2\underline{Me}$), 4.18, 4.64 (2H, q×2, J=7.1, 6.2 Hz, $O\underline{CH_2}Me$), and 5.92, 6.05 (1H, s×2, 2′-H). FABMS Found: m/z 318.1748. Calcd for $C_{15}H_6D_{11}NO_6$: M, 318.1746.

Crossover Experiment for Thermal Reaction. A mixture of ethyl *N*-[1,2-bis(methoxycarbonyl)vinyloxy]-benzimidate **1a** (170 mg, 0.55 mmol) and its deutrated **1a-*D*** (175 mg, 0.55 mmol) was refluxed in *o*-xylene (5 mL) for 2 h. The reaction mixture was concentrated to give a brown oil, which was purified by PLC on silica gel [AcOEt–hexane (1:3)] affording a mixture of an oxazole derivative **5a** and **5a-*D*** in 53% yield. The mass spectrum (EI) of the reaction mixture did not show the presence of any crossover products (m/z 266 and 267).

Mesurement of Solvent Effect for Thermal Reaction. Six sealed tubes containing 0.33 M solution (0.6 mL) of different solvents were heated at 95±1°C for 4 h. The isolated yields were calculated in the usual way.

Measurement of Reaction Rate. Eight sealed tubes (6 mm ϕ×50 mm) containing 1 M toluene solution (0.2 mL) of **1a** were heated in the oil bath by changing the reaction temperature (91±1°C, 100±1°C, and 119±1°C). After 5, 30, 60, and 240 min, two sealed tubes were cooled in the ice bath successively and the reaction mixture were treated by the usual PLC. The weights of thus obtained oxazoles were measured. The results calculated from the values are summarized in Table 2.

Subsutituent Effect. Compounds **1b**, **1c**, **1d**, and **1e** were prepared by the same method as preparation of **1a**.[1b] Ten sealed tubes containing 1 M toluene solution of **1** (**1a**—**1e**) were heated at 95±1°C for 4 h. Thus obtained **5** (**5a**—**5e**) were weighed.

Ethyl *N*-[1,2-Bis(methoxycarbonyl)vinyloxy]-*p*-methoxybenzimidate (*Z*-Form) 1b. Oil; 64% yield based on ethyl *p*-methoxybenzoate. IR (neat) 3040 (Ar, CH), 2920 (CH), and 1715 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.37 (3H, t, J=7.1 Hz, $OCH_2\underline{Me}$), 3.73 (3H, s, $CO_2\underline{Me}$), 3.84 (3H, s, $CO_2\underline{Me}$), 3.85 (3H, s, $O\underline{Me}$), 4.13 (2H, q, J=7.1 Hz, $O\underline{CH_2}Me$), 5.88 (1H, s, 2′-H), 6.95 (2H, d, J=8.8 Hz, arom), and 7.94 (2H, d, J=8.8 Hz, arom). Anal. Calcd for $C_{16}H_{19}NO_7$: C, 57.0; H, 5.7; N, 4.2%. Found: C, 57.1; H, 5.4; N, 4.5%.

Ethyl *N*-[1,2-Bis(methoxycarbonyl)vinyloxy]-*p*-methylbenzimidate (*Z*-Form) 1c. Oil; 59% yield based on ethyl *p*-methylbenzoate. IR (neat) 3040 (Ar, CH), 2920 (CH), and 1715 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.37 (3H, t, J=7.0 Hz, $OCH_2\underline{Me}$), 2.39 (3H, s, $\underline{Me}$), 3.73 (3H, s, $CO_2\underline{Me}$), 3.83 (3H, s, $CO_2\underline{Me}$), 4.14 (2H, q, J=7.1 Hz, $O\underline{CH_2}Me$), 5.89 (1H, s, 2′-H), 7.25 (2H, d, J=8.1 Hz, arom), and 7.80 (2H, d, J=8.1 Hz, arom). Anal. Calcd for $C_{16}H_{19}NO_6$: C, 59.8; H, 6.0; N, 4.6%. Found: C, 59.7; H, 5.7; N, 4.8%.

Ethyl *N*-[1,2-Bis(methoxycarbonyl)vinyloxy]-*p*-chlorobenzimidate [*E*,*Z*(4:1)-Mixture] 1d. Crystals; mp 56—57 °C; 46% yield based on ethyl *p*-chlorobenzoate. IR (KBr) 3040 (Ar, CH), 2940 (CH), and 1715 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.35, 1.44 (3H, t, J=7.1 Hz, $OCH_2\underline{Me}$), 3.68, 3.73, 3.84, 3.87 (6H, s×4, $CO_2\underline{Me}$), 4.15, 4.67 (2H, q×2, J=7.1 Hz, $O\underline{CH_2}Me$), 5.93, 6.05 (1H, s×2, 2′-H), 7.34, 7.65 (4H×4/7, d, J=8.8 Hz, arom), and 7.42, 7.88 (4H×3/7, d, J=9.0 Hz, arom). Anal. Calcd for $C_{15}H_{16}NO_6Cl$: C, 52.7; H, 4.7; N, 4.1%. Found: C, 52.6; H, 4.5; N, 4.4%.

Ethyl *N*-[1,2-Bis(methoxycarbonyl)vinyloxy]-*p*-cyanobenzimidate [*E*,*Z*(1:1)-Mixture] 1e. Oil; 18% yield based on ethyl *p*-cyanobenzoate. IR (neat) 3040 (Ar, CH), 2920 (CH), and 1700 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ=1.39, 1.46 (3H, t, J=7.1 Hz, $OCH_2\underline{Me}$), 3.69, 3.73, 3.85, 3.88 (3H, s×4, $CO_2\underline{Me}$), 4.13, 4.77 (2H, q, J=7.1 Hz, $O\underline{CH_2}Me$), 5.99, 6.10 (1H, s×2, 2′-H), 7.66, 7.85 (4H×1/2, d, J=8.3 Hz, arom), and 7.75, 8.05 (4H×1/2, d, J=8.3 Hz, arom). Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.8; H, 4.8; N, 8.4%. Found: C, 57.5; H, 4.7; N, 8.2%.

Compounds **5b**, **5c**, **5d**, and **5e** were prepared by the same method as used for the preparation of **5a**.[1b]

Dimethyl 2-(*p*-Methoxyphenyl)-4,5-oxazoledicarboxylate 5b. Crystals; mp 106 °C. IR (KBr) 3040 (Ar, CH), and 1725 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=3.88 (3H, s, $O\underline{Me}$), 4.00 (6H, s, $CO_2\underline{Me}$×2), 6.99 (2H, dt, J=9.1, 2.5 Hz, arom), and 8.12 (2H, dt, J=9.1, 2.5 Hz, arom). Anal. Calcd for $C_{14}H_{13}NO_6$: C, 57.7, H, 4.5, N, 4.8%. Found: C, 57.4; H, 4.6; N, 4.8%.

Dimethyl 2-(*p*-Methylphenyl)-4,5-oxazoledicarboxylate 5c. Crystals; mp 86 °C. IR (KBr) 3050 (Ar, CH), and 1720 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=2.43 (3H, s, $\underline{Me}$), 4.00 (6H, s, $CO_2\underline{Me}$×2), 7.30 (2H, d, J=8.4 Hz, arom), and 8.06 (2H, d, J=8.4 Hz, arom). Anal. Calcd for $C_{14}H_{13}NO_5$: C, 61.1, H, 4.8, N, 5.1%. Found: C, 61.4; H, 4.9; N, 5.3%.

Dimethyl 2-(*p*-Chlorophenyl)-4,5-oxazoledicarboxylate 5d. Crystals; mp 102—103 °C. IR (KBr) 3000 (Ar, CH), and 1720 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ=4.01 (6H, s, $CO_2\underline{Me}$×2), 7.49 (2H, dt, J=8.6, 2.2 Hz, arom), 8.11 (2H, dt, J=8.6, 2.2 Hz, arom). Anal. Calcd for $C_{14}H_{10}N_2O_5$: C, 58.7; H, 3.5; N, 9.8%. Found: C, 58.5; H, 3.6; N, 9.7%.

Dimethyl 2-(*p*-Cyanophenyl)-4,5-oxazoledicarboxylate 5e. Crystals; mp 174—175 °C. IR (KBr) 3040 (Ar, CH), and 1745 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ=4.02 (6H, s, $CO_2\underline{Me}$×2), 7.82 (2H, d, J=8.8 Hz, arom), and 8.30 (2H, d, J=8.8 Hz, arom). Anal. Calcd for $C_{14}H_{10}N_2O_5$: C, 58.7; H, 3.5; N, 9.8%. Found: C, 58.5; H, 3.6; N, 9.7%.

Photolysis. The 0.2 M solutions (1 mL) of different solvents were irradiated in quartz tubes (15 mm ϕ×250 mm) by a high-pressure Hg lamp for 8 h. The measurement was carried out in the same way as mentioned above. This reaction did not occur in the dark.

Crossover Experiment for Photochemical Reaction. A mixture of **1a** (157 mg, 0.51 mmol), **1a-*D*** (160 mg, 0.51 mmol), and dichloromethane (5 mL) was irradiated with a high-pressure Hg lamp at room temperature for 9 h. The reaction mixture was concentrated under reduced pressure to give an oil, which was then purified by PLC on silica gel [AcOEt–hexane (1:3)], affording a mixture of **5a** and **5a-*D*** in 8% yield (61% of **1a** and **1a-*D*** were recoverd). The crossover products could not be detected in thus obtained oxazoles from the mass measurements.

***N*-(Thiobenzoyl)glycine Ethyl Ester 7.** To a mixture of glycine ethyl ester hydrochloride (1.40 g, 10.0 mmol), triethylamine (2.02 g, 20.0 mg), and dichloromethane (30 mL) was added benzoyl chloride (1.55 g, 1.10 mmol) slowly under stirring at 0 °C. After stirring for 1 h, the reaction mixture was washed with water and then extracted with dichloromethane. The organic layer was dried over Na_2SO_4

and then concentrated. The residue was purified by PLC [AcOEt–hexane (1 : 1)] to give *N*-benzoylglycine ethyl ester as colorless crystals in 99.4% yield.

A mixture of *N*-benzoylglycine ethyl ester obtained above, Lawesson's reagent (2.49 g, 5.96 mmol), and THF (30 mL) was refluxed for 30 min under argon. The resulting solution was concentrated under reduced pressure to give a brown oil, which was purified by column chromatography on silica gel with benzene as eluent, affording a yellow solid **7** in 99.7% yield: IR (neat) 3300 (NH), 2950 (CH), 1720 (CO), and 1210 (CS) cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ=1.34 (3H, t, J=7.25 Hz, $OCH_2\underline{Me}$), 4.31 (2H, q, J=7.25 Hz, $O\underline{CH_2}Me$), 4.57 (2H, d, J=4.28 Hz, $\underline{CH_2}$), 7.41—7.59 (3H, m, Ph), 7.80—7.84 (2H, m, Ph), and 8.1 (1H, br, $\underline{NH}$). FABMS Found: m/z 224.0749. Calcd for $C_{11}H_{14}NO_2S$: M, 224.0744.

***N*-[Methylthio(phenyl)methylene]glycine Ethyl Ester [*E*,*Z*(1 : 1)-Mixture] 8.** To the dichloromethane solution (15 mL) of **7** (1.12 g, 50.0 mmol) was added trimethyloxonium tetrafluoroborate (0.784 g, 53.0 mmol) at −78 °C with stirring under argon. The reaction temperature was raised to 0 °C for 2 h. The reaction mixture was washed with aq. $NaHCO_3$ solution and then extracted with dichloromethane. The extract was dried over Na_2SO_4 and concentrated under reduced pressure to give **8** (1.19 g, 100%) as a pale yellow oil. Thus obtained **8** could be used without further purification. IR (neat) 2950 (CH), 1730 (CO), and 1600 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ=1.26, 1.31 (3H, t×2, J=7.25 Hz, $OCH_2\underline{Me}$), 2.13, 2.47 (3H, s×2, $S\underline{Me}$), 4.17, 4.26 (2H, q×2, J=7.25 Hz, $O\underline{CH_2}Me$), 4.13, 4.45 (2H, s×2, $\underline{CH_2}$), and 7.25—7.55 (5H, m, Ph). FABMS Found: m/z 238.0906. Calcd for $C_{12}H_{14}NO_2S$: M, 238.0901.

Diethyl 2-Phenyl-4,5-oxazoledicarboxylate 10. A mixture of **10** (0.300 g, 1.26 mmol), DBU (1.15 g, 7.56 mmol), diethyl oxalate (1.10 g, 7.56 mmol), and THF (3.8 mL) was stirred at room temperature for 4 h under argon. The reaction mixture was washed with water three times and then extracted with ether. The ether extract was dried over Na_2SO_4, and then concentrated to give a yellow oil, which was purified by PLC [AcOEt : hexane (1 : 5)], affording **10** as colorless crystals in 98.5% yield. IR (KBr) 2940 (CH), and 1700 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ=1.43 (3H, t, J=7.25 Hz, $OCH_2\underline{Me}$), 1.44 (3H, t, J=7.25 Hz, $OCH_2\underline{Me}$), 4.46 (2H, q, J=7.25 Hz, $O\underline{CH_2}Me$), 4.48 (2H, q, J=7.25 Hz, $O\underline{CH_2}Me$), 7.46—7.58 (3H, m, Ph), and 8.16—8.17 (1H, m, Ph). FABMS Found: m/z 290.1030. Calcd for $C_{15}H_{16}NO_5$: M, 290.1027.

***O*-Ethyl (Phenylthio)thioacetate 14.** Ethyl (phenylthio)acetate **13** was prepared by the reaction of ethyl bromoacetate **12** with thiophenol in the presence of pyridine in quantitative yield. A mixture of **13** (2.74 g, 14 mmol), Lawesson's reagent (2.83 g, 7 mmol), and *o*-xylene (10 mL) was refluxed for 5 h under nitrogen. The resulting mixture was concentrated to give a yellow oil, which was purified by column chromatography on silica gel with hexane as eluent to give **14** in 41% yield. ^1H NMR ($CDCl_3$, 100 MHz) δ=1.28 (3H, t, J=6.0 Hz, $OCH_2\underline{Me}$), and 7.28 (5H, br s, Ph).

Ethyl (Phenylthio)acetohydroximate 15. A mixture of **14** (6.36 g, 30 mmol), hydroxylamine hydrochloride (2.08 g, 30 mmol), sodium acetate (2.46 g, 30 mmol), and methanol (40 mL) was stirred at room temperature for 4 h and then filtered. The filtrate was concentrated under reduced pressure to give a yellow oil. Purification by the column chromatography on silica gel [AcOEt–hexane (1 : 2)] gave **15** as an oil in 89% yield. IR (neat) 3100 (OH), 2850 (CH), and 1630 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$, 100 MHz) δ=1.16 (3H, t, J=6.0 Hz, $OCH_2\underline{Me}$), 3.76 (2H, s, $\underline{CH_2}$), 3.90 (2H, q, J=6.0 Hz, $O\underline{CH_2}Me$), 7.16, 7.36 (5H, br s, Ph), and 7.80 (1H, br, $\underline{OH}$).

Ethyl *N*-[2-(*t*-Butoxycarbonyl)vinyloxy](phenylthio)acetimidate 16. A mixture of **15** (0.23 g, 1.1 mmol), *t*-butyl propiolate (0.13 g, 1.3 mmol), and triethylamine (0.04 g, 0.4 mmol) was stirred at room temperature for 10 min. The resulting mixture was concentrated under reduced pressure to give a brown oil, which was purified by column chromatography on silica gel [AcOEt–hexane (1 : 2)], affording **16** in 91% yield. IR (neat) 2950 and 2890 (CH), and 1700 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ=1.22 (3H, t, J=7.0 Hz, $OCH_2\underline{Me}$), 1.46 (9H, s, $C\underline{Me_3}$), 3.71 (2H, s, $\underline{CH_2}$), 4.07 (2H, q, J=7.0 Hz, $O\underline{CH_2}Me$), 5.41 (1H, d, J=12.2 Hz, 2′-$\underline{H}$), 7.28—7.41 (5H, m, Ph), and 7.52 (1H, d, J=12.2 Hz, 1′-$\underline{H}$). FABMS Found: m/z 338.4379. Calcd for $C_{17}H_{24}NO_4S$: M, 338.4380.

***t*-Butyl 2-(Phenylthio)methyl-4-oxazolecarboxylate 17.** Compound **16** (0.67 g, 2 mmol) was heated in a glass tube oven at 170 °C for 10 min to give a black oil, then it was then purified by PLC on silica gel [AcOEt–hexane (1 : 2)], affording **17** in 35% yield. IR (KBr) 2970 and 2940 (CH), and 1750 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ=1.53 (9H, s, $C\underline{Me_3}$), 4.19 (2H, s, $\underline{CH_2}$), 7.28—7.39 (5H, m, Ph), and 8.03 (1H, s, 5-$\underline{H}$). FABMS Found: m/z 292.1008. Calcd for $C_{15}H_{18}NO_3S$: M, 292.1007.

***t*-Butyl 2-(Phenylsulfonylmethyl)-4-oxazolecarboxylate 18.** A mixture of **17** (0.58 g, 2 mmol) and *m*-CPBA (0.35 g, 2 mmol) was stirred in dichloromethane (5 mL) at room temperature for 3 h. The resulting mixture was concentrated under reduced pressure, then it was purified by column chromatography on silica gel [AcOEt–hexane (1 : 1)] to give **18** in quantitative yield. IR (KBr) 2980, 2940 (CH), 1725 (CO), and 1450, 1330 (SO_2) cm^{-1}. ^1H NMR ($CDCl_3$, 100 MHz) δ=1.56 (9H, s, $C\underline{Me_3}$), 4.61 (2H, s, $\underline{CH_2}$), 7.07, 7.19, 7.30 (5H, m, Ph), and 8.12 (1H, s, 5-H). FABMS Found: m/z 324.0905. Calcd for $C_{15}H_{18}NO_5S$: M, 324.0906.

1-Methyl-2-[1,2-bis(methoxycarbonyl)vinyloxy]-iminopyrrolidine 19. This compound was prepared by the same method as described in **21a** using *N*-methyl-2-pyrrolidone instead of 2-pyrrolidone. IR (KBr) 3040 (Ar), 2950 (CH), 1730 (CO), and 1620 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ=1.95 (2H, quint, J=7.0 Hz, 4-$\underline{CH_2}$), 2.70 (3H, s, $N\underline{Me}$), 2.84 (2H, t, J=7.0 Hz, 5-$\underline{CH_2}$), 3.30 (2H, t, J=7.0 Hz, 3-$\underline{CH_2}$), 3.70 (3H, s, $CO_2\underline{Me}$), 3.80 (3H, s, $CO_2\underline{Me}$), and 5.70 (1H, s, $\underline{CH}$). FABMS Found: m/z 257.2670. Calcd for $C_{11}H_{17}N_2O_5$: M, 257.2670.

Dimethyl 2-[3-(*N*-Methylbenzoylamino)propyl]-4,5-oxazoledicarboxylate 20. Compound **19** was heated with benzoyl chloride at 140 °C for 3 h by the same way as described in the crossover experiment for thermal reaction. Usual work-up gave **20** in 39% yield. IR (KBr) 3040 (Ar), 2940 (CH), and 1730 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 100 MHz) δ=2.10 (2H, m, 2′-$\underline{CH_2}$), 2.75—3.00 (2H, br, 1′-$\underline{CH_2}$), 2.95, 3.10 (3/2H×2, s×2, $N\underline{Me}$), 3.35—3.65 (2H, br, 3′-$C\underline{H_2}$), 3.90 (3H, s, $CO_2\underline{Me}$), 4.00 (3H, s, $CO_2\underline{Me}$), and 7.40 (5H, m, Ph). FABMS Found: m/z 361.3779. Calcd for $C_{18}H_{21}N_2O_6$: M, 361.3777.

2-[[2-(Ethoxycarbonyl)vinyloxy]imino]pyrrolidine (*E*-Form) 21a. A mixture of 2-pyrrolidinone (5.1 g, 60 mmol), Lawesson's reagent (12.1 g, 30 mmol), and toluene (50 mL) was refluxed for 1.5 h under nitrogen. The resulting mixture was concentrated under reduced pressure and purified by column chromatography on silica gel [AcOEt–chloroform (1:20)] to give 2-pyrrolidethione (3 g, 30 mmol), which was then stirred at 50 °C for 10 h with the hydroxylamine prepared by the treatment of hydroxylamine hydrochloride (2.98 g, 43 mmol) with 5% sodium methoxide methanolic solution (4.64 g, 43 mmol). The reaction mixture was concentrated under reduced pressure. Purification by recrystallization from ethanol gave *N*-hydroxy-2-pyrrolidinethione in 83% yield. Next, a mixture of *N*-hydroxy-2-pyrrolidinethione (0.76 g, 7.6 mmol), ethyl propiolate (0.75 g, 7.6 mmol), and triethylamine (0.78 g, 7.6 mmol) was stirred at room temperature for 10 min. The resulting mixture was concentrated under reduced pressure to give a brown oil, which was purified by column chromatography on silica gel [AcOEt–hexane (1:2)] to afford **21a** in 83% as colorless crystals. Mp 32—33 °C. IR (KBr) 3280 (NH), 2920, 2860 (CH), and 1650 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.26 (3H, t, J=7.4 Hz, $OCH_2\underline{Me}$), 2.08 (2H, m, 4-$\underline{H_2}$), 2.56 (2H, t, J=7.7 Hz, 3-$\underline{H_2}$), 3.44 (2H, t, J=6.9 Hz, 5-$\underline{H_2}$), 4.15 (2H, q, J=7.1 Hz, $O\underline{CH_2}Me$), 5.31 (1H, br s, $\underline{NH}$), 5.55 (1H, d, J=12.1 Hz, 2′-$\underline{H}$), and 7.80 (1H, d, J=12.1 Hz, 1′-$\underline{H}$). FABMS Found: m/z 199.1077. Calcd for $C_9H_{15}N_2O_3$: M, 199.1083.

2-[[1,2-Bis(methoxycarbonyl)vinyloxy]imino]pyrrolidine [*E*,*Z*(1:1)-Mixture] 21b. This compound was prepared from 2-pyrrolidinone in the same way as mentioned for **21a**: 77% (*O*/*S* exchange), 97% (amidoxime), 90% (vinylation). Mp 85—86 °C. IR (KBr) 3350 (NH), 2920, 2880 (CH), and 1750 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=2.09 (2H, m, 4-$\underline{H_2}$), 2.59 (2H, t, J=10.7 Hz, 3-$\underline{H_2}$), 3.44 (2H, t, J=10.0 Hz, 5-$\underline{H_2}$), 3.68 (3H, s, $CO_2\underline{Me}$), 3.89 (3H, s, $CO_2\underline{Me}$), 5.39 (1H, br s, $\underline{NH}$), and 5.79 (1H, s, 2′-$\underline{H_2}$). FABMS Found: m/z 243.0981. Calcd for $C_{10}H_{15}N_2O_5$: M, 243.0981.

2-[[1,2-Bis(methoxycarbonyl)vinyloxy]imino]piperidine (*Z*-Form) 21c. This compound was prepared from δ-valerolactam in the same way as mentioned for **21a**: 88% (*O*/*S* exchange), 58% (amidoxime), 99% (vinylation). Mp 64—65 °C. IR (KBr) 3290 (NH), 2920, 2860 (CH), and 1710 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.76 (4H, m, 4,5-$\underline{H_2}$), 2.27 (2H, t, J=6.3 Hz, 3-$\underline{H_2}$), 3.27 (2H, m, 6-H_2), 3.72 (3H, s, $CO_2\underline{Me}$), 3.86 (3H, s, $CO_2\underline{Me}$), 5.72 (1H, s, 2′-$\underline{H}$), and 6.23 (1H, br s, $\underline{NH}$). NOE 1′-CO_2Me↔2′-H, 2′-CO_2Me↔3-H_2. FABMS Found: m/z 257.1137. Calcd for $C_{11}H_{17}N_2O_5$: M, 257.1137.

2-[[1,2-Bis(methoxycarbonyl)vinyloxy]imino]perhydroazepine [*E*,*Z*(1:1)-Mixture] 21d. This compound was prepared by the same method as described in the preparation of **21a**: 73% (*O*/*S* exchange), 70% (amidoxime), 100% (vinylation). IR (KBr) 3340 (NH), 2890, 2830 (CH), and 1715, 1700 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.72 (6H, m, 4,5,6-$\underline{H_2}$), 2.34 (2H, m, 3-$\underline{H_2}$), 3.22 (3H, m, 7-H_2, $\underline{NH}$), 3.60, 3.68, 3.89, 3.92 (6H, s×4, $\underline{Me}$×2), and 5.66, 5.82 (1H, s×2, 2′-$\underline{H}$). FABMS Found m/z 271.2936. Calcd for $C_{12}H_{19}N_2O_5$: M, 271.2937.

Ethyl 6,7-Dihydro-5*H*-pyrrolo[1,2-*a*]-imidazole-3-carboxylate 22a. Compound **21a** (0.11 g, 0.56 mmol) was reacted with acetic anhydride (0.28 g, 2.78 mmol) in toluene (5 mL) at 110 °C for 5 h. The reaction mixture was concentrated under reduced pressure to give a black oil, which was purified by PLC on silica gel [AcOEt–hexane (1:1)] to afford **22a** in 59% yield. IR (KBr) 2940, 2880 (CH), and 1710 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.36 (3H, t, J=7.1 Hz, $OCH_2\underline{Me}$), 2.64 (2H, m, 3-$\underline{H_2}$), 2.91 (2H, t, J=7.5 Hz, 4-$\underline{H_2}$), 4.22 (2H, t, J=7.3 Hz, 2-$\underline{H_2}$), 4.30 (2H, q, J=7.1 Hz, $O\underline{CH_2}Me$), and 7.68 (1H, s, 7-$\underline{H}$). FABMS Found: m/z 181.0975. Calcd for $C_9H_{13}N_2O_2$: M, 181.0977.

Dimethyl 6,7-Dihydro-5*H*-pyrrolo[1,2-*a*]-imidazole-2,3-dicarboxylate 22b. Compound **21b** was reacted in the same way as mentioned for **22a** to give **22b** in 19% yield. IR (KBr) 2940, 2870 (CH), and 1730 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=2.63 (2H, m, 3-$\underline{H_2}$), 2.91 (2H, t, J=8.0 Hz, 4-$\underline{H_2}$), 3.91 (6H, s, $CO_2\underline{Me}$×2), and 4.28 (2H, t, J=7.4 Hz, 2-$\underline{H_2}$). FABMS Found: m/z 225.0878. Calcd for $C_{10}H_{13}N_2O_4$: M, 225.0875.

Dimethyl 5,6,7,8-Tetrahydroimidazo[1,2-*a*]-2,3-pyridinedicarboxylate 22c. Compound **21c** was reacted in the same way as mentioned for **22a** to give **22c** in 59% yield. IR (KBr) 2925, 2860 (CH), and 1705 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.97 (4H, m, 3,4-$\underline{H_2}$), 2.91 (2H, t, J=6.2 Hz, 5-$\underline{H_2}$), 3.89 (6H, s, $CO_2\underline{Me}$×2), and 4.19 (2H, t, J=5.9 Hz, 2-$\underline{H_2}$). FABMS Found: m/z 239.1030. Calcd for $C_{11}H_{15}N_2O_4$: M, 239.1032.

Dimethyl 6,7,8,9-Tetrahydro-5*H*-imidazo[1,2-*a*]-2,3-azepinedicarboxylate 22d. Compound **21d** was reacted in the same way as mentioned in the preparation of **22a** to give **22d** in 45% yield. Mp 71—72 °C. IR (KBr) 2910, 2850 (CH), and 1710 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ=1.72, 1.81, 1.87 (2H×3, m, 3,4,5-$\underline{H_2}$), 2.97 (2H, m, 6-$\underline{H_2}$), 3.90 (3H, s, $CO_2\underline{Me}$), 3.92 (3H, s, $CO_2\underline{Me}$), and 4.25 (2H, t, J=4.77 Hz, 2-$\underline{H_2}$). FABMS Found: m/z 253.1185. Calcd for $C_{12}H_{17}N_2O_4$: M, 253.1188.

***N*-Acetyl-2-[1,2-bis(methoxycarbonyl)vinyloxy]-imino]piperidine 23a.** Compound **21c** was reacted in the same way as described for **22c**. The reaction was stopped after 30 min. Usual work-up gave **23a** (yield 20%) and **23b** (yield 30%), together with a small amount of **22c**. IR (KBr) 2900 (CH) and ca. 1750 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 100 MHz) δ=1.85 (4H, m, 4,5-$\underline{H_2}$), 2.07 (3H, s, $CO\underline{Me}$), 2.66 (2H, t, J=6.9 Hz, 3-$\underline{H_2}$), 3.51 (2H, t, J=5.0 Hz, 6-$\underline{H_2}$), 3.74 (3H, s, $CO_2\underline{Me}$), 3.83 (3H, s, $CO_2\underline{Me}$), and 6.23 (1H, s, 2′-$\underline{H}$). FABMS Found: m/z 299.1243. Calcd for $C_{13}H_{19}N_2O_6$: M, 299.1243.

[*N*-Acetyl-[1,2-bis(methoxycarbonyl)vinyloxy]amino]-3,4,5,6-tetrahydropyridine. 23b. IR (KBr) 2900 (CH) and 1760, 1735, 1705 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 100 MHz) δ=1.87 (4H, m, 4,5-$\underline{H_2}$), 1.93 (3H, s, $CO\underline{Me}$), 2.55 (2H, m, 3-$\underline{H_2}$), 3.18 (2H, t, J=5.8 Hz, 6-$\underline{H}$), 3.79, 3.83 (3H×2, s, $CO_2\underline{Me}$×2), and 6.42 (1H, s, 2′-$\underline{H}$). NOE 2′-H↔1′-CO_2Me, COMe↔2′-CO_2Me. FABMS Found: m/z 299.1241. Calcd for $C_{13}H_{19}N_2O_6$: M, 299.1243.

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