Photolyses of Ethyl Azidoformate in Cyclic Ethers

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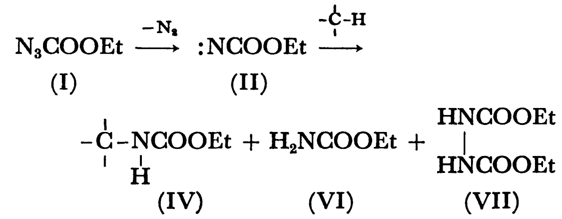
Ethoxycarbonyl nitrene, generated by the photolysis of ethyl azidoformate (I), were inserted preferentially into the α C–H bonds of cyclic ethers. The α C–H bonds of cyclic ethers were much more reactive than the corresponding C–H bonds of hydrocarbons for the insertion of the nitrene. In addition, the reactions in cyclic ethers with an alkyl group at the α-position gave unsaturated alkoxyurethanes *via* a cleavage of the ring C–O bond. It was found that the nitrene insertion into the α C–H bonds of *cis*- and *trans*-2,5-dimethyltetrahydrofurans proceeded non-stereospecifically, while the insertion into the C–H bonds of hydrocarbons proceeded stereospecifically. The formation of the alkoxyurethanes can be explained by a mechanism in which an O–N ylide is included as an intermediate of the nitrene reaction; the non-stereospecific insertion of the nitrene give support to this mechanism.

The relative reactivities for the insertion of nitrenes toward C–H bonds have been reported for primary: secondary:tertiary,[1,2] exo:endo, bridge:bridgehead,[3,4] and axial: equatorial[5] C–H bonds, and in those earlier experiments hydrocarbons have been employed as the substrates. In the reaction of ethoxycarbonyl nitrene, which was generated by the photolysis of ethyl azidoformate, with cyclic ethers, was found that the α C–H bonds showed unusually large reactivities compared with the corresponding C–H bonds of hydrocarbons in the insertion of the nitrene, and observed that cyclic ethers with an α-methyl (or ethyl) group gave unsaturated alkoxyurethanes as a result of the ring C–O bond cleavage. According to Nozaki's report, ethoxycarbonyl nitrene is inserted into the α C–H bonds of five- and six-membered cyclic ethers[6] and into the α-methylene C–H bonds of cyclohexanone ethylene acetal; this is, in a radical sense, a hydrogen abstraction-recombination process.[7] On the other hand, the nitrene insertion into the cyclohexane ring C–H bonds of the acetal was explained in terms of the intermediacy of the oxygen-imine or the direct attack of the singlet nitrene on the C–H bonds. In the present paper, we wish to report that the reaction of the nitrene with cyclic ethers includes an O–N ylide (oxygen-imine) as an intermediate and that the nitrene insertion into the α C–H bonds of the ethers proceeds by means of a mechanism different from that advanced in the insertion into the hydrocarbon C–H bonds.[8]

Results and Discussion

Photolyses of Ethyl Azidoformate in Cyclic Ethers. Ethyl azidoformate (I) in cyclic ether (III) was irradiated by the light (mainly 2537 Å) of a low-pressure mercury arc at 0 °C with stirring under an atmosphere of nitrogen. The insertion products (IV) of ethoxycarbonyl nitrene (II) into the C–H bonds of the cyclic ethers, except for the three- and four-membered cyclic ethers, were obtained accompanied by the hydrogen abstraction product, urethane (VI), and small amounts (0.5—2%) of diethyl hydrazoformate (VII). In addition, the reactions of I with α-alkyl cyclic ethers gave unsaturated alkoxyurethanes (V). No insertion products into the ring C–H bonds were recognized in the reactions with the three- and four-membered cyclic ethers. In the reactions with the five- and six-membered cyclic ethers, the insertion took place preferentially at the ring C–H bonds of the α-position. The yields of the products mentioned above are listed in Table 1.



$$\underset{\text{(I)}}{N_3COOEt} \xrightarrow{-N_2} \underset{\text{(II)}}{:NCOOEt} \xrightarrow{-\overset{|}{\underset{|}{C}}-H} \underset{\text{(IV)}}{-\overset{|}{\underset{|}{C}}-\underset{\displaystyle H}{N}COOEt} + \underset{\text{(VI)}}{H_2NCOOEt} + \underset{\text{(VII)}}{\begin{array}{c}HNCOOEt\\|\\HNCOOEt\end{array}}$$

The reaction in 2-methyltetrahydrofuran, which bears a tertiary hydrogen atom, gave an increased yield of urethanes (VI) compared with the reactions in tetrahydrofuran and in tetrahydropyran. This can be understood in terms of hydrogen abstraction by the triplet nitrene.[9] The reactions with the small ring ethers gave comparatively low yields of VI. It seems that some of the triplet nitrene and/or some of the amido radical, $H\dot{N}COOEt$, has been consumed in the ring-opening polymerization of the small-ring ethers employed.

Relative Reactivities. As has been mentioned above, the α C–H bonds of the cyclic ethers are more reactive than the others for the nitrene insertion; the reactivities of the α C–H bonds are greatly enhanced. Therefore, in order to compare the insertion reactivities of the C–H bonds of the cyclic ethers with those of cyclohexane, the photolysis of I was carried out in a mixture of equimolar amounts of a cyclic ether and cyclohexane. The product distributions and the relative reactivities are summarized in Table 2. These relative reactivities are displayed in Fig. 1, where they are compared with

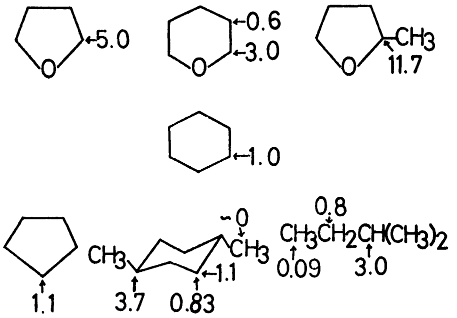
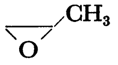
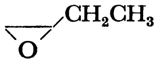
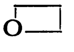
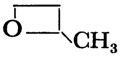
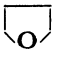
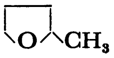
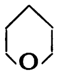
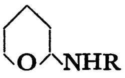
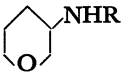


Fig. 1. Relative reactivities of various C–H bonds.

Table 1. Photolyses of I in cyclic ethers

Ether (III)	Product (%)[a]		
	Insertion (IV)	Ring-opening (V)	Abstraction (VI)
(a) 		(a) $CH_2{=}CHCH_2ONHR$[b] 21	12
(b) 		(b) $CH_3CH{=}CHCH_2ONHR$ 13	10
(c) 		ND[c]	9
(d) 		(d) $CH_2{=}CHCH_2CH_2ONHR$ 28	23
(e) 	(e)  25		21
(f) 	(f)  12	(f) $CH_2{=}CHCH_2CH_2CH_2ONHR$ 7	34
(g) 	(g_1)  25 (g_2)  5		16

a) Calculated on the basis of the azide used. b) R: COOEt. c) ND: not detected.

Table 2. Photolysis of I in a mixture of a cyclic ether and cyclohexane

Product (%)[a]				
	Insertion (IV)	Cyclohexylurethane	Type of C–H bond	Relative reactivity[b]
(e)	18.1	10.8	2°(Ring-α)	5.0(±0.1)[c]
(f)	6.9	7.0	3°(Ring-α)	11.7(±1.1)
(g_1)	13.3	13.5	2°(Ring-α)	3.0(±0.2)
(g_2)	2.6		2°(Ring-β)	0.6(±0.1)

a) Calculated on the basis of the azide used. b) Relative reactivities: per C–H bond of cyclohexane. c) The relative errors appear in parentheses.

those of some hydrocarbons,[10] obtained in experiments carried out under the same conditions as the present work.

The relative reactivities of primary, secondary, and tertiary C–H bonds of the cyclic hydrocarbons toward ethoxycarbonyl nitrene are as follows: $1^\circ \ll 2^\circ < 3^\circ$; these values are about the same as those of the corresponding C–H bonds of the acylic hydrocarbons. On the other hand, it was found that the α C–H bonds of the cyclic ethers were much more reactive than the corresponding C–H bonds of hydrocarbons in the nitrene insertion. Such unusual reactivities suggest that the insertion in question must proceed by a mechanism other than that proposed in the reaction with hydrocarbons.[3,8,11] Therefore, the reaction of I with cyclic ethers was studied from the stereochemical point of view as one approach to the problem.

Stereochemistry of the Insertion Reaction. Ethyl azidoformate (I) was irradiated in *cis*- and *trans*-2,5-dimethyltetrahydrofurans (IIIh and IIIi). Two insertion products (stereoisomers) into the α C–H bonds and the abstraction product were well separated from the reaction mixture by the use of gas chromatography. The IR and NMR spectral data of neither of these stereoisomers, however, led to a decision between the two alternative conformations because of the extreme similarity of their IR and NMR spectra. Methyl azidoformate (VII) was then employed instead of I, since the structures of the insertion product into IIIh were more simple than those formed in the reaction of I. The reaction of VII gave two insertion products (stereoisomers, XI and XII) and an abstraction product (methyl carbamate) in yields of 19% and 53% respectively. A comparison between the reactions of VII and I showed that the interrelationships of the yields, the VPC retention times, and the IR and NMR spectra between XI and XII were very similar to those between IVh_1 and IVh_2. Such information may lead to the consideration that the conformations of XI and XII correspond to those of IVh_1 and IVh_2 respectively. The NMR spectrum of a mixture of the insertion products, XI and XII, is shown in Fig. 2-i. Each of the peaks in Fig. 2 was due to XI or XII, judging from a comparison of the peak areas. After a shift reagent, $Eu(fod)_3$, had been added to the solution, the NMR spectrum was measured (Fig. 2-ii). The singlet peak (XIIb) of the 2-methyl protons of XII was shifted to a field lower than that (XIb) of XI. Their peaks were far separated by the further addition of the shift reagent (Fig. 2-iii), while the induced downfield shift for the NH proton

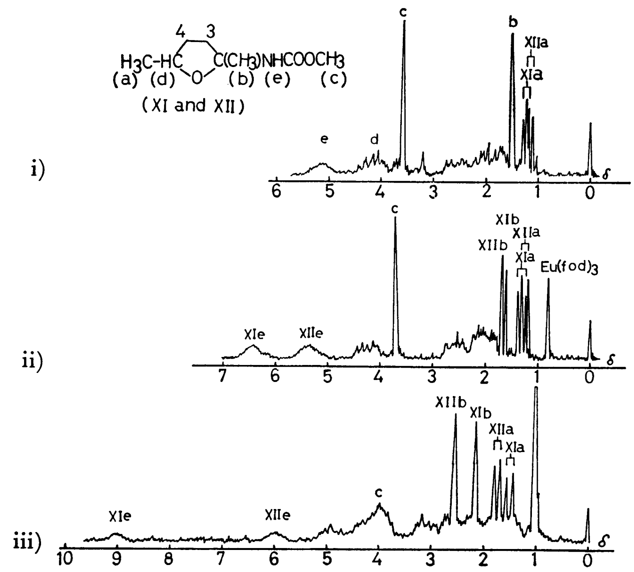
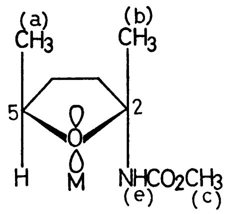
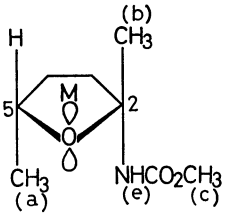


Fig. 2. NMR spectra of a mixture of XI and XII in ratio of 45:55.
i) A 0.2 ml of CCl_4 contains 20 mg of a mixture of XI and XII.
ii) The solution contains 3 mg of $Eu(fod)_3$.
iii) The solution contains 9 mg of $Eu(fod)_3$.

(XIIe) of XII was smaller than that (XIe) of XI. The addition of the shift reagent caused a downfield shift of XII larger than that of XI also with regard to the two doublet peaks (XIIa and XIa) of the 5-methyl protons. These findings can be explained as follows: the bulky shift reagent approaches the ethereal oxygen atom through an opening in the crowded environment of two methyl and one NHR groups. The *cis*-isomer (with regard to two methyl groups), one of the stereoisomers, coordinates to the shift reagent at the side on which the NHR group in the isomer is located, thus giving XIII. The other, the *trans*-isomer, coordinates to the shift reagent at the opposite side of the NH group, thus giving XIV.



(XIII)



(XIV)

M: $Eu(fod)_3$

The singlet peak of the 2-methyl protons of XIV should then be shifted to a field lower than that of XIII. The peaks of XI and XII in Fig. 2 were thus assigned to the protons of XIII and XIV respectively. The difference between the induced shifts of the XIa and XIIa peaks, in spite of the relationship between the 5-methyl group and the shift reagent being the same at both XIII and XIV, shows that XIV might be formed more rapidly than XIII. That is, a coordination equilibrium in the *trans*-isomer lies further toward XIV compared with an equilibrium in the *cis*-isomer. The great downfield shift of the XIe peak compared with that of the XIIe peak means that the difference in the distances between the shift reagent and the NH proton affects the shift more strongly than that in the concentrations of the adducts (XIII and XIV).

In the case of I, one insertion product, IVh_1, has the same conformation as XI, while the other, IVh_2, has the same conformation as XII since XI and XII correspond to IVh_1 and IVh_2 respectively, as has been described above. Table 3 shows the product yields in the reactions of I.

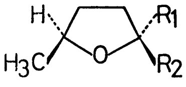
The coordination compound between the shift reagent and the NH or the $COOCH_3$ group is not formed. If the coordination compound between the shift reagent and the NH group were formed, the peak (XIIe) of the NH proton must be shifted downfield as well as the XIe peak. If the coordination compound between the shift reagent and the $COOCH_3$ group were formed, the induced downfield shifts for the ester methyl protons (Peak c) must have larger magnitudes than those for the 2-methyl protons (Peak b) (Fig. 2-i—ii).

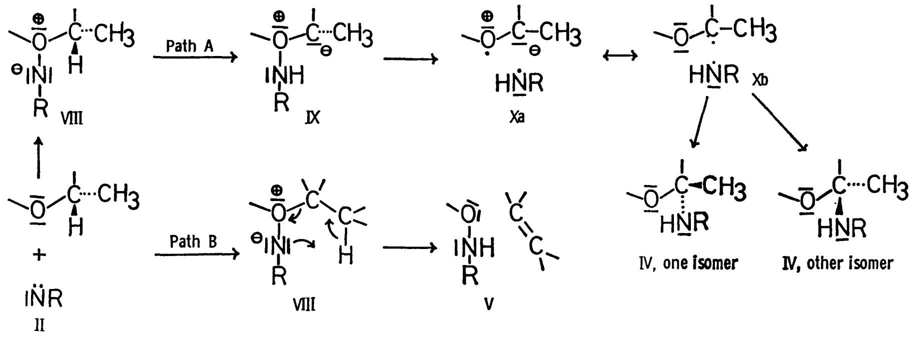
It may be concluded that the insertion reactions of the nitrene (II) into α C–H bonds of the cyclic ethers proceed non-stereospecifically, in contrast to the stereospecific insertion of II into the C–H bonds of hydrocarbons.[3,8,11]

The nitrene (II) is able to coordinate, by means of its nitrogen atom, to an ethereal oxygen atom as the nitrene does to the sulfur atoms of thioethers[12,13] and sulfoxides[13,14] to give the nitrogen-sulfur ylides. Therefore, the reaction of the nitrene with ethers is initiated by an electrophilic attack of the nitrene on the ethereal

Table 3. Photolyses of I in *cis*- and *trans*-2,5-dimethyltetrahydrofurans

Ether (III)	Product (%)[a]			
	Insertion (IV)		Ring-opening (V)	Abstraction (VI)
	IVh_1	IVh_2	(h) $CH_2{=}CH(CH_2)_2CH(CH_3)ONHR$[b]	
(h) R_1[d]: H R_2 : CH_3	8	13	ND[c]	54
(i) R_1 : CH_3 R_2 : H	8	11	12	53
Mixture of h and i[e]	11	15	8	34

a) b) c) See Table 1, footnotes. d)  e) A mixture of h and i in a ratio of 45:55 was used.



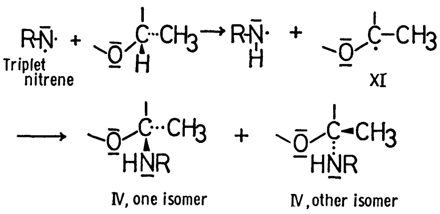
Scheme 1.
R: COOEt
Path A　Insertion into α C–H bond
Path B　Cleavage of ring C–O bond

oxygen atom to give an O–N ylide (oxygen-imine intermediate, Scheme 1).

The ylide (VIII) abstracts a proton from the α C–H bond to give IX, followed by the homolytic cleavage of the O–N bond to give a radical species (X). The radical, $\dot{N}HR$, combines with the α-carbon radical to give IV (Path A). On the other hand, VIII leads to V *via* hydrogen abstraction from the α-methyl or α-methylene group and the cleavage of the C–O bond in a concerted pericyclic manner (Path B).

The non-stereospecific insertion by ethoxycarbonyl nitrene into C–H bonds of cyclic ethers does not exclude a hydrogen abstraction-recombination mechanism.

The triplet nitrene is able to abstract a hydrogen atom from the α-position of ethers, giving an amido radical and XI, whose recombination leads to the insertion products (IV isomers).



Scheme 2.

The mechanism of Scheme 2 has been ruled out for the nitrene insertion into C–H bonds of hydrocarbons.[8,11] The XI radical, however, is stabilized by the adjacent oxygen atom in comparison with a hydrocarbon radical. Consequently, IV may be formed by the radical recombination.

In the isomerization from the O–N ylide (VIII) to the insertion product (IV), the distance between the nitrogen atom and one C–H bond, to which the nitrene would be inserted, seems to be an important factor. In the case of tetrahydropyran, the insertion product (IVg_1) into the α C–H bond, which is located nearly at the nitrogen atom of the ylide, is derived from the ylide intermediate. On the other hand, the insertion product (IVg_2) into the β C–H bond is formed by the one-step mechanism[8] proposed in the reaction of nitrene with hydrocarbons, since the β C–H bond is too far from the ylide nitrogen atom. These two distinct mechanisms can explain the difference between the reactivities of the α and β C–H bonds shown in Table 2.

Experimental

The IR spectra were recorded on a Hitachi EP-S photometer and a Nippon Bunko (JASCO) Model IR-E photometer, while the NMR spectra were taken on Hitachi R-20 and Hitachi R-24 instruments, using tetramethylsilane as the internal standard. Gas chromatography (VPC) was done on Shimadzu GC-2C and Nippon Denshi (JEOL) JGC 20K units, employing as absorbents: A, 20% Ucon Oil 5 HB 2000 on Celite (60—80 mesh); B, 10% polyethylene glycol succinate on Neopak 1A (60—80 mesh). The products were separated by VPC, and the structures of the products were determined by means of elemental analyses and by measurements of the IR and NMR spectra. The quantitative analyses of the products by VPC and test for the stability of each product during VPC analysis have been described in a previous paper.[15]

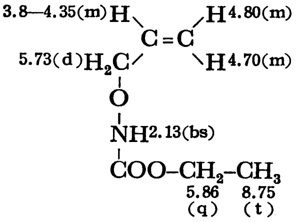
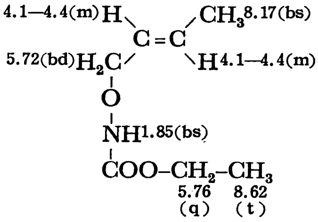
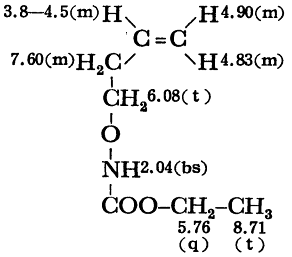
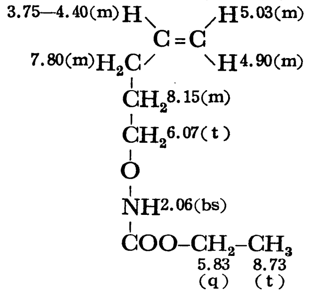
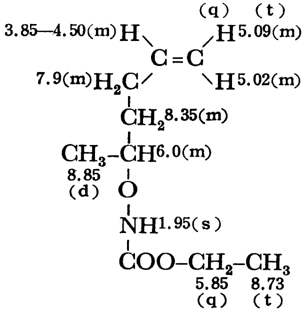
Materials. The ethyl azidoformate (I) was prepared by the method of Lwowski and Mattingly.[16] The methyl azidoformate (VII) was prepared from methyl chloroformate and sodium azide in the manner used for the preparation of ethyl azidoformate; bp 24 °C/40 mmHg; yield, 83%. All the cyclic ethers, except for oxetanes (IIIc and IIId), dichloromethane, and cyclohexane were used after the commercial reagents had been purified according to the published directions.[17] The oxetane was prepared by the ring closure of 3-chloropropyl acetate,[18] which had been obtained by the chlorination of 1,3-propanediol[19] followed by the acetylation.[20] The 2-methyloxetane was prepared in a way similar to the synthesis of oxetane. The introduction of dry hydrogen chloride into 500 g (5.6 mol) of 1,3-butanediol gave 314 g (3 mol) of the chlorohydrin;[21] bp 63—65 °C/11 mmHg; yield, 54%. A reaction of the chlorohydrin (314 g) and acetic acid (240 g, 4 mol) gave 260 g (1.7 mol) of the ester;[22] bp 70—74 °C/13 mmHg; yield, 57%. The ester (260 g) was cyclized by potassium hydroxide into 42 g (0.6 mol) of 2-methyloxetane; bp 60 °C,[23-25] yield; 35%. NMR (CCl_4, τ): 4.8—5.4 (CH, m), 5.5 (ring γ-CH_2, m), 7.0—8.0 (ring β-CH_2, m), 8.65 (CH_3, d). The cyclohexylurethane was prepared from cyclohexylamine and ethyl chloroformate.[16] The data of mp, IR, and NMR were in good agreement with those reported in the literature. The *cis*-2,5-dimethyltetrahydrofuran (IIIh) (bp 90 °C (lit, 90—91 °C)) was prepared by the ring closure of *dl*-2,5-hexanediol[26] (*dl*-diol), which had itself been obtained by the separation of a mixture of *dl*- and *meso*-diols.[27] The *trans*-2,5-dimethyltetrahydrofuran (IIIi), bp 93 °C (lit, 92—

94 °C) was also prepared from *meso*-diol separated from the mixture. Their IR and NMR spectra were in good agreement with those reported in the literature.[28] In the same manner, a mixture of *cis*- and *trans*-2,5-dimethyltetrahydrofurans was prepared by the ring closure of a mixture of *dl*- and *meso*-diols; bp 92—94 °C; yield, 86%. No photochemical isomerization between *cis*- and *trans*-2,5-dimethyltetrahydrofurans was observed under the conditions of these experiments.

Photolyses of I in Cyclic Ethers. A solution of 5.0 g (0.043 mol) of ethyl azidoformate in 0.5 mol of a cyclic ether was irradiated, with stirring and cooling at 0 °C, by a low-pressure mercury lamp (internal-irradiation type) until the evolution of nitrogen was not observed. The nitrogen evolved then gave almost the theoretical amount based on the azide used. The excess substrate was removed by distillation at 25—75 °C under 25—30 mmHg pressure. The residue was analyzed by VPC on Columns A and B. Urethane (VI) had IR and NMR spectra and a VPC retention time identical with those of authentic VI, and a mixed melting point with the authentic sample was undepressed. Ethyl hydrazoformate (VII) was obtained in the yields of 0.02—0.08 g from every experiment; mp 132 °C,[29] IR (Nujol, cm^{-1}): 3240 (NH), 1754 and 1693 (C=O), 1260 (C–O). NMR ($CDCl_3$, τ): 3.24 (NH, 2H, s), 5.80 (CH_2, 4H, q), 8.73 (CH_3, 6H, t). Found: C, 40.96; H, 6.73; N, 15.98%. Calcd for $C_6H_{12}O_4N_2$: C, 40.90; H, 6.87; N, 15.90%. The spectral data of IR and NMR, and elemental analyses of unsaturated *N*-alkoxyurethanes (V) are presented in Table 4.

(a) In Propylene Oxide (IIIa), 1,2-Epoxybutane (IIIb), and 2-Methyloxetane (IIId): *N*-Allyloxyurethane (Va, 1.3 g), *N*-2-

Table 4. NMR and IR data, and analyses of V

V	NMR (τ) in CCl_4	IR (neat, cm^{-1})			Formula		Analyses		
		NH	C=O	C–O			C%	H%	N%
(Va)[31]		3250	1718	1260	$C_6H_{11}O_3N$	Found Calcd	50.03 49.64	7.29 7.64	9.60 9.65
(Vb)		3260	1720	1266	$C_7H_{13}O_3N$	Found Calcd	52.56 52.81	8.20 8.23	8.95 8.80
(Vd)		3260	1716	1262	$C_7H_{13}O_3N$	Found Calcd	53.05 52.81	8.39 8.23	8.38 8.80
(Vf)		3260	1720	1260	$C_8H_{15}O_3N$	Found Calcd	55.14 55.47	8.99 8.73	8.10 8.09
(Vh)		3230	1720	1260	$C_9H_{17}O_3N$	Found Calcd	57.72 57.73	9.42 9.15	7.39 7.48

butenyloxyurethane (Vb, 0.9 g), and *N*-3-butenyloxyurethane (Vd, 1.9 g) were isolated.

(b) In Tetrahydrofuran (IIIe): Ethyl 2-tetrahydrofurylcarbamate (IVe, 1.7 g) was isolated. IVe: IR (neat, cm^{-1}): 3300 (NH), 1705 (C=O), 1260 (C–O). NMR (CCl_4, τ): 4.00 (NH, bs), 4.4—4.8 (ring-CH, m), 5.94 (ester-CH_2, q), 6.0—6.5 (ring δ-CH_2, m), 7.7—8.5 (ring β- and γ-CH_2, 4H, m), 8.83 (ester-CH_3, t).[30] Found: C, 52.63; H, 8.45; N, 8.70%. Calcd for $C_7H_{13}O_3N$: C, 52.81; H, 8.23; N, 8.80%.

(c) In 2-Methyltetrahydrofuran (IIIf): Ethyl 2-methyl-2-tetrahydrofurylcarbamate (IVf, 0.29 g) and *N*-4-pentenyloxyurethane (Vf, 0.52 g) were isolated. IVf: IR (neat, cm^{-1}): 3310 (NH), 1760 (C=O), 1258 (C–O). NMR (CCl_4, τ): 4.50 (NH, bs), 5.6-6.2 (ring δ-CH_2, m), 5.87 (ester-CH_2, q), 7.5—8.5 (ring β- and γ-CH_2, 4H, m), 8.76 (ester-CH_3, t), 8.80 (α-CH_3, s). Found: C, 55.03; H, 9.04; N, 8.21%. Calcd for $C_8H_{15}O_3N$: C, 55.47; H, 8.73; N, 8.09%.

(d) In Tetrahydropyran (IIIg): Ethyl 2-tetrahydropyranylcarbamate (IVg_1, 1.9 g) and ethyl 3-tetrahydropyranylcarbamate (IVg_2, 0.37 g) were isolated. IVg_1: IR (neat, cm^{-1}): 3300 (NH), 1710 (C=O), 1250 (C–O). NMR (CCl_4, τ): 4.00 (NH, bs), 5.16 (C_2-methine, 1H, bt), 5.86 (ester-CH_2, q), 6.0—6.6 (C_6-methylene, 2H, m), 8.0—8.9 (C_3-, C_4-, and C_5-methylene, 6H, m), 8.76 (ester-CH_3, t).[30] Found: C, 55.01; H, 9.15; N, 8.06%. Calcd for $C_8H_{15}O_3N$: C, 55.47; H, 8.73; N, 8.09%. IVg_2: IR (neat, cm^{-1}): 3300 (NH), 1700 (C=O), 1250 (C–O). NMR (CCl_4, τ): 4.65 (NH, bs), 5.88 (ester-CH_2, q), 6.0—6.6 (C_2- and C_6-methylene, 4H, m), 6.7—6.9 (C_3-methine, m), 8.0—8.9 (C_4- and C_5-methylene, 4H, m), 8.77 (ester-CH_3, t). Found: C, 54.92; H, 9.16; N, 8.19%. Calcd for $C_8H_{15}O_3N$: C, 55.47; H, 8.73; N, 8.09%.

(e) In cis-*2,5-Dimethyltetrahydrofuran (IIIh)*: Ethyl *cis*-2,5-dimethyl-2-tetrahydrofurylcarbamate (IVh_1, 0.64 g) and ethyl *trans*-2,5-dimethyl-2-tetrahydrofurylcarbamate (IVh_2, 1.0 g) were isolated. IVh_1: IR (neat, cm^{-1}): 3300 (NH), 1710 (C=O), 1265 (C–O). NMR (CCl_4, τ): 5.25 (NH, bs), 6.00 (ester-CH_2, q), 5.55—6.25 (ring α-CH, m), 7.22—8.42 (ring β- and γ-CH_2, 4H, m), 8.50 (δ-CH_3, s), 8.75 (α-CH_3, d), 8.85 (ester-CH_3, t). Found: C, 57.50; H, 9.27; N, 7.60%. Calcd for $C_9H_{17}O_3N$: C, 57.73; H, 9.15; N, 7.48%. IVh_2: IR (neat, cm^{-1}): 3290 (NH), 1705 (C=O), 1260 (C–O). NMR (CCl_4, τ): 5.05 (NH, bs), 6.00 (ester-CH_2, q), 5.5—6.2 (ring α-CH, m), 7.22—8.38 (ring β- and γ-CH_2, 4H, m), 8.50 (δ-CH_3, s), 8.85 (α-CH_3, d), 8.77 (ester-CH_3, t). Found: C, 57.57; H, 9.10; N, 7.56%. Calcd for $C_9H_{17}O_3N$: C, 57.73; H, 9.15; N, 7.48%.

(f) In trans-*2,5-Dimethyltetrahydrofuran (IIIi)*: IVh_1 (0.64 g), IVh_2 (0.88 g), and *N*-(1-methyl-4-pentenyloxy)urethane (Vh, 0.96 g) were isolated.

(g) In a Mixture of IIIh and IIIi: IVh_1 (0.88 g), IVh_2 (1.2 g), and Vh (0.64 g) were isolated.

Photolysis of Methyl Azidoformate. A solution of 4.4 g (0.043 mol) of methyl azidoformate in 0.5 mol of *cis*-2,5-dimethyltetrahydrofuran (IIIh) was irradiated in the same manner as in the case of ethyl azidoformate. Methyl *cis*-2,5-dimethyl-2-tetrahydrofurylcarbamate (IVj_1), methyl *trans*-2,5-dimethyl-2-tetrahydrofurylcarbamate (IVj_2), and methyl carbamate were thus isolated in the yields of 0.52 g, 0.90 g, and 1.7 g respectively. IVj_1: IR (neat, cm^{-1}): 3290 (NH), 1710 (C=O), 1265 (C–O). NMR (CCl_4, τ): 4.90 (NH, bs), 5.55—6.12 (ring α-CH, m), 6.42 (ester-CH_3, s), 7.20—8.60 (ring β- and γ-CH_2, 4H, m), 8.51 (δ-CH_3, s), 8.74 (α-CH_3, d). Found: C, 55.52; H, 8.66; N, 8.10%. Calcd for $C_8H_{15}O_3N$: C, 55.47; H, 8.73; N, 8.09%. IVj_2: IR (neat, cm^{-1}): 3300 (NH), 1715 (C=O), 1270 (C–O). NMR (CCl_4, τ): 4.90 (NH, bs), 5.55—6.12 (ring α-CH, m), 6.42 (ester-CH_3, s), 7.20—8.60 (ring β- and γ-CH_2, m), 8.51 (δ-CH_3, s), 8.83 (α-CH_3, d). Found: C, 55.58; H, 8.66; N, 8.18%. Calcd for $C_8H_{15}O_3N$: C, 55.47; H, 8.73; N, 8.09%. Methyl carbamate was identified by comparing its VPC retention time and IR and NMR spectra with those of the authentic sample. No photochemical mutual isomerization between *cis* and *trans* isomers of the insertion products was observed under the conditions of these experiments.

Photolysis of I in a Mixture of a Cyclic Ether and Cyclohexane. A solution of I (5.0 g, 0.043 mol) in III (0.25 mol) and a cyclohexane (21 g, 0.25 mol) mixture was irradiated internally as has been described above. The excess of the substrate was removed by distillation, and the residue was analyzed by VPC. The *N*-cyclohexylurethane was identified by comparison with the authentic sample. The yields of the insertion products and urethane are displayed in Table 2.

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