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Photolysis of Ethyl Azidoformate in Ethers and in Alcohols

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Ethoxycarbonyl nitrene, generated by the photolysis of ethyl azidoformate (I), was inserted preferentially into the α C–H bonds of acyclic ethers. Each of the reactions with acyclic ethers gave *N*-alkoxyurethane *via* a cleavage of the C–O bond, indicating that an O–N ylide is an intermediate of the nitrene reaction. Comparing sensitized photolysis with direct photolysis of I in ethers and in alcohols, it was found that the nitrene insertion into the α C–H bonds of ethers proceeds for both singlet and triplet and that the insertion into the β and γ C–H bonds of ethers and the O–H bonds of alcohols proceeds only for the singlet.

In a previous paper,[1] the photolysis of ethyl azidoformate (I) in cyclic ethers was reported. The ethoxycarbonyl nitrene, generated by the photolysis of I, was inserted preferentially into the α C–H bonds of cyclic ethers. The reactions with cyclic ethers bearing an alkyl group at the α-position gave unsaturated alkoxyurethane *via* a cleavage of the ring C–O bond. In addition, the nitrene insertion into the α C–H bonds of *cis*- and *trans*-2,5-dimethyltetrahydrofurans proceeded non-stereospecifically. From these results, a mechanism which included an O–N ylide intermediate for the insertion reaction was proposed, although the hydrogen abstraction-recombination mechanism was not ruled out.

The present paper reports further information about the mechanism based on a study of the photolyses of I carried out in acyclic ethers and in alcohols. Furthermore, the sensitized photolysis of I was examined and compared with direct photolysis in the ethers and alcohols.

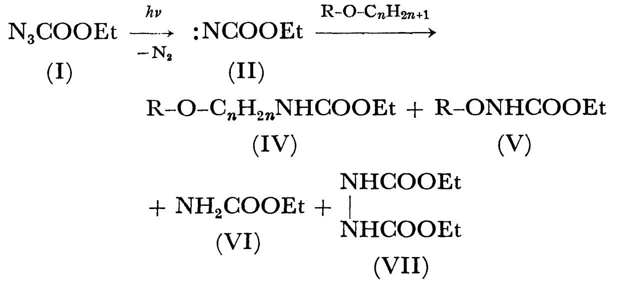
Results and Discussion

Direct Photolysis of Ethyl Azidoformate in Acyclic Ethers. Ethyl azidoformate (I) in acyclic ether (III) was irradiated by the light (mainly of 2537 Å) from a low-pressure mercury arc at 0 °C with stirring in an atmosphere of nitrogen. Insertion products (IV) of ethoxycarbonyl nitrene (II) into the C–H bonds of the acyclic ethers were obtained, accompanied by the hydrogen abstraction product, urethane (VI), and small amounts (0.3—1.3%) of diethyl hydrazodiformate (VII). In addition, *N*-alkoxyurethanes (V) were obtained for each reaction.

Table 1. Direct photolysis of ethyl azidoformate in acyclic ethers

Ether (III)	Product (%)[a]				
	Insertion (IV)		C–O Cleavage (V)		Abstraction (VI)
(a) Diethyl	(a) $CH_3\underset{NHR}{C}HOC_2H_5$	31.2	(a) CH_3CH_2ONHR[b]	3.9	17.6
(b) Dipropyl	(b₁) $CH_3CH_2\underset{NHR}{C}HOC_3H_7$ (b₂) $CH_3\underset{NHR}{C}HCH_2OC_3H_7$	32.3 3.1	(b) $CH_3CH_2CH_2ONHR$	5.6	20.5
(c) Dibutyl	(c₁) $CH_3CH_2CH_2\underset{NHR}{C}HOC_4H_9$ (c₂) $CH_3CH_2\underset{NHR}{C}HCH_2OC_4H_9$ (c₃) $CH_3\underset{NHR}{C}HCH_2CH_2OC_4H_9$	25.0 3.8 3.9	(c) $CH_3CH_2CH_2CH_2ONHR$	4.1	17.4
(d) Diisopentyl	(d₁) $(CH_3)_2CHCH_2\underset{NHR}{C}HOC_5H_{11}$ (d₂) $(CH_3)_2\underset{NHR}{C}CH_2CH_2OC_5H_{11}$	17.1 5.7	(d) $(CH_3)_2CHCH_2CH_2ONHR$	2.4	15.1
(e) Isobutyl methyl	(e₁) $(CH_3)_2CH\underset{NHR}{C}HOCH_3$ (e₂) $(CH_3)_2CHCH_2O\underset{NHR}{CH_2}$	16.5 5.7	(e₁) $(CH_3)_2CHCH_2ONHR$ (e₂) CH_3ONHR	2.6 trace	20.3
(f) 2-Methoxy-ethanol	ND[c]		(f) $CH_3OCH_2CH_2ONHR$[d]	37.8	21.2

a) Calculated on the basis of the azide used. b) R: COOEt. c) ND: not detected. d) This compound is the O–H insertion product.



$$\underset{(I)}{N_3COOEt} \xrightarrow[-N_2]{h\nu} \underset{(II)}{:NCOOEt} \xrightarrow{R\text{-}O\text{-}C_nH_{2n+1}} \underset{(IV)}{R\text{-}O\text{-}C_nH_{2n}NHCOOEt} + \underset{(V)}{R\text{-}ONHCOOEt} + \underset{(VI)}{NH_2COOEt} + \underset{(VII)}{\begin{array}{l}NHCOOEt\\ |\\ NHCOOEt\end{array}}$$

The yields of the products mentioned above are listed in Table 1.

The insertion occurred preferentially at the C–H bonds of the α-position. In the reaction with an unsymmetrical ether, isobutyl methyl ether, insertion into the secondary α C–H bond predominated over insertion into the primary α C–H bond. In the reaction with 2-methoxyethanol (methylcellosolve), however, the product of O–H insertion was isolated instead of that of C–H insertion. The formation of *N*-alkoxyurethane (V) shows that cleavage of the C–O bonds occurs during the reactions. Olefins, although not detected, might be formed concomittantly by V, in analogy to the formation of an unsaturated product of the cleavage of the ring C–O bonds of cyclic ethers.[1,2]

Relative Reactivities. As mentioned above, the α C–H bonds of the acyclic ethers were more reactive for nitrene insertion than the other C–H bonds. In order to compare the insertion reactivities of the α C–H bonds with those of the cyclohexane C–H bonds, direct photolysis of I was carried out in a mixture of equimolar amounts of an acyclic ether and cyclohexane. The yields of the products and the reactivities are summarized in Table 2, with the reactivities of primary (1°), secondary (2°), and tertiary (3°) C–H bonds in 2-methylbutane.[3]

TABLE 2. DIRECT PHOTOLYSIS OF I IN A MIXTURE OF AN ACYCLIC ETHER AND CYCLOHEXANE

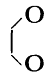
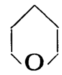
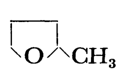
	Product (%)[a)		Type of C–H bond	Relative reactivity[b)	2-Methylbutane		
	Insertion (IV)	Cyclohexylurethane			1°	2°	3°
(c_1)	17.8	12.0	2°(α)	4.5			
(c_2)	2.8		2°(β)	0.7			
(c_3)	3.0		2°(γ)	0.8			
(d_1)	13.2	9.2	2°(α)	4.4			
(d_2)	4.5		3°(γ)	2.9			
					0.09	0.8	3.0

a) Calculated on the basis of the azide used.
b) Relative reactivity: per C–H bond of cyclohexane.

The secondary C–H bonds at the α-position of the acyclic ethers were much more reactive for nitrene insertion than the corresponding C–H bonds of hydrocarbons. Such unusually high reactivities and the formation of *N*-alkoxyurethanes (V) are very similar to reactions with cyclic ether.[1)] Thus the reaction of nitrene with acyclic ethers may involve the O–N ylide, which has been proposed for the reaction with cyclic ethers.[1)]

Sensitized Photolysis in Ethers. As has been pointed out in a previous paper,[1)] the abstraction-recombination mechanism due to the triplet nitrene was not ruled out for insertion into the α C–H bonds of the ethers. Thus, the decomposition of I was carried out under conditions involving no singlet nitrene. Ethyl azidoformate (I) in ether was irradiated with the light from a high-pressure mercury lamp in the presence of a sensitizer, acetophenone, in an atmosphere of nitrogen. A 1.5 M-$CuSO_4$ aqueous solution was circulated as a filter. The filter completely inhibited the direct excitation of I. The yields of the products are listed in Table 3, in which they are compared with those for reactions using a low-pressure mercury lamp (direct photolysis).

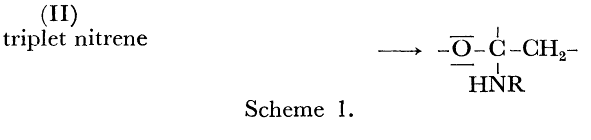
TABLE 3. SENSITIZED PHOTOLYSIS OF I IN ETHERS

Ether	Product (%)[a): Insertion into α C–H bond (IV)	Abstraction (VI)	Ratio VI/IV
	27.0(32.8)	44.6(22.2)	1.7(0.7)
	27.8(25.0)[b)	72.5(16.0)	2.6(0.6)
	16.5[c) (12.0)[b,c)	65.2(34.0)	4.0(2.8)
$(CH_3CH_2CH_2\text{-}CH_2)_2O$	8.4(25.0)	50.5(17.4)	6.0(0.7)

( ) Indicates the values for direct photolysis.
a) Calculated on the basis of the azide used.
b) From Ref. 1.
c) Insertion into the tertiary C–H bond.

The nitrene species involved in these sensitized photolysis reactions must be in the triplet state.[4)] The molar ratios of VI/IV for sensitized photolysis are larger than those for direct photolysis. The findings for dioxane are similar to those reported by Nozaki *et al.*[5)] In the sensitized photolysis with dibutyl ether, neither the products of insertion into the β and γ C–H bonds nor *N*-butoxyurethane were detected in contrast to direct photolysis, as is shown in Table 1. Furthermore, neither the product of insertion into the β C–H bonds of tetrahydropyran nor the C–O cleavage product in 2-methyltetrahydropyran was detected, although both were isolated for direct photolysis.[1)] It is noteworthy that both singlet and triplet ethoxycarbonyl nitrenes are inserted into the C–H bonds adjacent to the oxygen atom, in contrast to insertion by only the singlet into the C–H bonds of hydrocarbons.[6–8)]

The insertion of the triplet nitrene is initiated by hydrogen abstraction from the etheral α-position, followed by the radical recombination, as shown in Scheme 1.

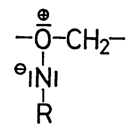


(II)
triplet nitrene

Scheme 1.

Concerning hydrocarbons, such a radical recombination mechanism has been ruled out because of no insertion by the triplet.[6–8] For ethers, however, the α-carbon radical is stabilized by the adjacent oxygen atom, permitting recombination with the $H\dot{N}R$ radical. As is seen in Table 3, the molar ratios of VI/IV for direct photolysis are much smaller than those for sensitized photolysis. This means that the singlet nitrene participates in the insertion into the α C–H bonds. Judging from the view point of non-stereospecific insertion,[1] the singlet nitrene is not inserted into the α C–H bonds by a one-step mechanism.

The insertion of the singlet nitrene, which results only from direct photolysis, is initiated by the formation of an O–N ylide (VIII) with the ethereal oxygen. The ylide VIII abstracts a proton from the α C–H bond, followed by homolytic cleavage of the O–N bond giving



(VIII)

the radical species, the α-carbon radical, and $H\dot{N}R$. The recombination of these two radicals results in the α-insertion product as has been reported in a preceding paper.[1] On the other hand, VIII leads to V *via* hydrogen abstraction and cleavage of the C–O bond.[1]

Insertion into the β and γ- C–H bonds, however, may proceed by the one-step mechanism proposed for the reaction with hydrocarbons,[6–8] since the β- and γ-carbon radicals, whose resonances with the oxygen lone pair are insulated by the methylenes, are not as stable as the α-carbon radical. These two distinct mechanisms can explain the difference in reactivity between the α C–H bond and the β or γ C–H bond shown in Table 2.

In the reaction with isobutyl methyl ether, as shown in Table 1, preferential insertion into the α-methylene group may be due to the difference between the radical stabilities of $-\dot{C}HOCH_3$ and $-CH_2O\dot{C}H_2$.

Direct and Sensitized Photolysis in Alcohols. To obtain further information about the behavior of the nitrene for other oxygen compounds, direct and sensitized photolysis of I were carried out in alcohols. The results are shown in Table 4. Direct photolysis gave products for nitrene insertion into the O–H bonds, while sensitized photolysis gave no such insertion products. Therefore, it is concluded that the O–H insertion products are formed only by the singlet nitrene as shown in Scheme 2.[9] The O–H insertion can be considered to proceed by a one-step of the singlet nitrene.

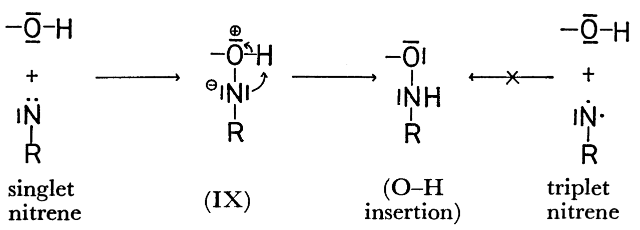
Table 4. Photolysis of I in alcohols

Alcohol	Product (%)[a,b] Insertion into O–H bond		Abstraction (VI)	
	Direct	Sensitized	Direct	Sensitized
CH_3CH_2OH	11.0	ND[c]	71.0	64.6
$CH_3CH_2CH_2OH$	15.0	ND	46.0	80.5
$CH_3CH_2CH_2CH_2OH$	27.0	ND	47.0	74.9

a) Calculated on the basis of the azide used.

b) Photolysis gave the corresponding aldehydes in addition to the insertion and abstraction products.

c) ND: not detected.



Scheme 2.

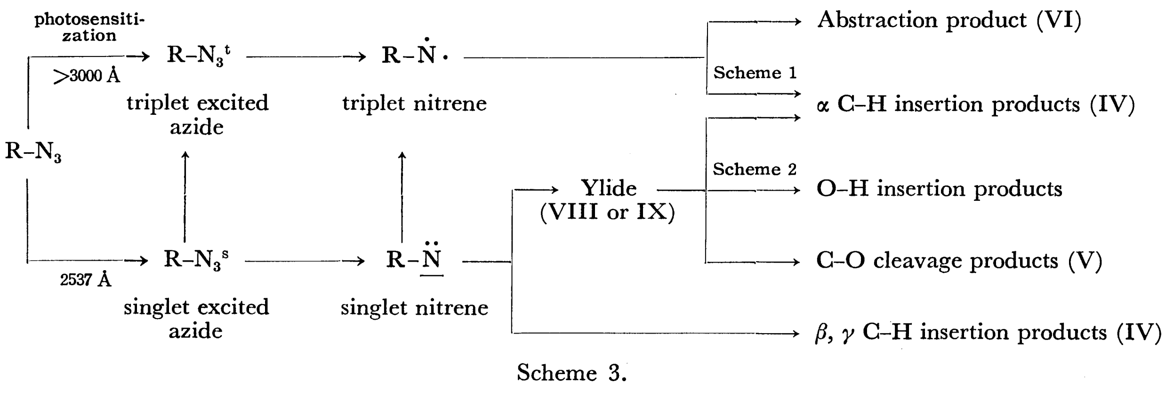
However, it is more reasonable that O–H inserion proceeds *via* an O–N ylide intermediate (IX), in analogy to reactions of ethers with the singlet nitrene, as mentioned above.

Reaction Course. The facts observed for the reactions of nitrene with ethers and alcohols can be accommodated into Scheme 3.

Experimental

Most of the equipment and techniques have been described in preceding papers.[1,10] In addition, a Nippon Bunko (JASCO) Model A-3 photometer was used for the IR measurements and a 20% mixture Apiezone Grease L on Neosorb NC (60—80 mesh) was employed as the absorbent for VPC.

Materials. Ethyl azidoformate (I) was prepared by the method of Lwowski and Mattingly.[4] Cyclohexane, dioxane, alcohols, and most of the ethers were used after the



Scheme 3.

commercial reagents had been purified according to published directions.[11] All the acyclic ethers were purified by boiling with sodium and by distillation. The absence of alcohols in the ethers was confirmed by VPC. Isobutyl methyl ether was prepared from sodium isopropoxide and methyl iodide using the Williamson procedure; bp 58.5 °C (lit,[12] 59 °C); yield, 73%. Diisobutyl ether was prepared from isobutyl alcohol and concentrated sulfuric acid. A mixture of 100 ml of concentrated sulfuric acid and 400 ml of isobutyl alcohol was refluxed in a flask equipped with a distillation column. A fraction, bp 82—91 °C, was collected and dried over anhydrous calcium chloride. After the solid part had been removed by filtration, the filtrate was washed with water, dried over anhydrous calcium chloride, and distilled; bp 120—123 °C (lit, 122—124 °C). To prepare the authentic IVc_2, amino ether was prepared from 2-amino-1-butanol and butyl iodide using the Williamson procedure; bp 96 °C/25 Torr; yield, 76%. A solution of 10 g of the amino ether in diethyl ether was cooled and 7 g of ethyl chloroformate was added dropwise to the solution. The solution was washed with 10% sodium carbonate and with water. The ether layer was dried over anhydrous sodium sulfate, the solvent was evaporated, and the residue was distilled; bp 124 °C/3 Torr; yield, 56%.

Direct Photolysis of I in Acylic Ethers. A solution of 5.0 g (0.043 mol) of ethyl azidoformate in 0.5 mol of acyclic ether was irradiated using a low-pressure mercury lamp, with stirring and cooling at 0 °C, until the evolution of nitrogen was no longer observed. The nitrogen evolved then gave almost the theoretical amount based on the azide used. The excess substrate was removed by distillation at 25—85 °C and 20—30 Torr. The residue was analyzed by VPC on columns. The IR and NMR spectra and VPC retention time of urethane (VI) were identical to those of an authentic sample, and a mixed melting point test with the authentic sample was undepressed. Diethyl hydrazodiformate (VII) was obtained in yields of 0.01—0.05 g for each experiment. The IR and NMR spectral, and elemental analysis data of VII have been described previously.[1] The insertion products (IV) and *N*-alkoxyurethanes (V) displayed strong absorptions in the 3260—3360 and 1700—1730 cm^{-1} regions due to the NH groups and the ester C=O groups, respectively. The NMR spectra of IV and V were measured in carbon tetrachloride and the chemical shifts were given in τ values. The IR and NMR spectral data, and the VPC retention times of V are identical to those of the products obtained by nitrene insertion into the O–H bonds when I was photolyzed in alcohols.[13]

(a) In Diethyl Ether (IIIa): *N*-(1-ethoxyethyl)urethane (IVa, 2.16 g) and *N*-ethoxyurethane (Va, 0.22 g) were isolated. IVa: NMR: 4.25 (NH, 1H, bs), 5.00 (CH, 1H, m), 5.94 (ester-CH_2, 2H, q), 6.50 (OCH_2, 2H, m), 8.70 (CH_3, 3H, d), 8.76 (ester-CH_3, 3H, t), 8.86 (CH_3, 3H, t). Found: C, 52.58; H, 9.51; N, 8.46%. Calcd for $C_7H_{15}O_3N$: C, 52.15; H, 9.38; N, 8.69%. Va: NMR: 1.97 (NH, 1H, bs), 5.85 (ester-CH_2, 2H, q), 6.14 (CH_2, 2H, q), 8.70 (CH_3, 3H, t), 8.73 (ester-CH_3, 3H, t). Found: C, 45.62; H, 8.08; N, 10.91%. Calcd for $C_5H_{11}O_3N$: C, 45.10; H, 8.33; N, 10.52%.

(b) In Dipropyl Ether (IIIb): *N*-(1-propoxypropyl)urethane (IVb_1, 2.62 g), *N*-[1-(propoxymethyl)ethyl]urethane (IVb_2, 0.25 g), and *N*-propoxyurethane (Vb, 0.35 g) were isolated. IVb_1: NMR: 4.65 (NH, 1H, bs), 5.25 (CH, 1H, m), 5.93 (ester-CH_2, 2H, q), 6.57 (OCH_2, 2H, m), 8.40 (CH_2, 4H, m), 8.76 (ester-CH_3, 3H, t), 9.08 (CH_3, 6H, t). Found: C, 56.98; H, 10.01; N, 7.62%. Calcd for $C_9H_{19}O_3N$: C, 57.11; H, 10.12; N, 7.40%. IVb_2: NMR: 5.29 (NH, 1H, bs), 5.97 (ester-CH_2, 2H, q), 6.06 (CH, 1H, m), 6.64 (OCH_2, 2H, bt), 6.68 (CH_2, 2H, d), 8.40 (CH_2, 2H, m), 8.84 (CH_3, 3H, d), 8.78 (ester-CH_3, 3H, t), 9.07 (CH_3, 3H, t). Found: C, 57.37; H, 10.28; N, 7.15%. Calcd for $C_9H_{19}O_3N$: C, 57.11; H, 10.12; N, 7.40%. Vb: NMR: 2.00 (NH, 1H, bs), 5.86 (ester-CH_2, 2H, q), 6.25 (OCH_2, 2H, t), 8.37 (CH_2, 2H, six), 8.71 (ester-CH_3, 3H, t), 9.03 (CH_3, 3H, t). Found: C, 49.15; H, 9.12; N, 9.81%. Calcd for $C_6H_{13}O_3N$: C, 48.96; H, 8.90; N, 9.52%.

(c) In Dibutyl Ether (IVc): *N*-(1-butoxybutyl)urethane (IVc_1, 2.33 g), *N*-[1-(butoxymethyl)propyl]urethane (IVc_2, 0.35 g), *N*-(3-butoxy-1-methylpropyl)urethane (IVc_3, 0.36 g), and *N*-butoxyurethane (Vc, 0.28 g) were isolated. IVc_1: NMR: 5.15 (NH, 1H, bs), 5.16 (CH, 1H, m), 5.94 (ester-CH_2, 2H, q), 6.56 (OCH_2, 2H, t), 8.53 (CH_2, 8H, m), 8.74 (ester-CH_3, 3H, t), 9.05 (CH_3, 6H, t). Found: C, 61.08; H, 10.35; N, 6.18%. Calcd for $C_{11}H_{23}O_3N$: C, 60.80; H, 10.67; N, 6.45%. IVc_2: NMR: 5.30 (NH, 1H, bs), 5.96 (ester-CH_2, 2H, q), 6.40 (CH, 1H, m), 6.62 (OCH_2, 4H, bt), 8.25 ($CHCH_2$, 2H, m), 8.52 (CH_2, 4H, m), 8.77 (ester-CH_3, 3H, t), 9.06 (CH_3, 6H, t). Found: C, 61.18; H, 10.42; N, 6.08%. Calcd for $C_{11}H_{23}O_3N$: C, 60.80; H, 10.67; N, 6.45%. IVc_3: NMR: 4.85 (NH, 1H, bs), 5.98 (ester-CH_2, 2H, q), 6.33 (CH, 1H, m), 6.56 and 6.65 (OCH_2, 4H, t), 8.50 (CH_2, 6H, m), 8.58 (CH_3, 3H, d), 8.79 (ester-CH_3, 3H, t), 9.07 (CH_3, 3H, t). Found: C, 60.98; H, 10.38; N, 6.11%. Calcd for $C_{11}H_{23}O_3N$: C, 60.80; H, 10.67; N, 6.45%. Vc: NMR: 1.97 (NH, 1H, bs), 5.86 (ester-CH_2, 2H, q), 6.22 (OCH_2, 2H, t), 8.2—8.9 (CH_2, 4H, m), 8.71 (ester-CH_3, 3H, t), 9.05 (CH_3, 3H, t). Found: C, 52.51; H, 9.19; N, 8.44%. Calcd for $C_7H_{15}O_3N$: C, 52.15; H, 9.38; N, 8.69%. The insertion product, IVc_2, exhibited IR and NMR spectra and a VPC retention time identical with those of an authentic sample.

(d) In Diisopentyl Ether (IIId): *N*-(3-methyl-1-isopentyloxybutyl)urethane (IVd_1, 1.80 g), *N*-(1,1-dimethyl-3-isopentyloxypropyl)urethane (IVd_2, 0.60 g), and *N*-isopentyloxy urethane (Vd, 0.18 g) were isolated. IVd_1: NMR: 5.14 (NH, 1H, bs), 5.14 (OCH, 1H, t), 5.94 (ester-CH_2, 2H, q), 6.57 (OCH_2, 2H, t), 8.15 and 8.30 (CH, 2H, m), 8.70 (CH_2, 4H, m), 8.75 (ester-CH_3, 3H, t), 9.06 and 9.10 (CH_3, 12H, d). Found: C, 63.69; H, 10.92; N, 5.58%. Calcd for $C_{13}H_{27}O_3N$: C, 63.64; H, 11.09; N, 5.71%. IVd_2: NMR: 4.55 (NH, 1H, bs), 6.04 (ester-CH_2, 2H, q), 6.50 and 6.60 (OCH_2, 4H, t), 8.39 (two CH_2 and CH, 5H, m), 8.66 (CH_3, 6H, s), 8.80 (ester-CH_3, 3H, t), 9.08 (CH_3, 6H, d). Found: C, 63.23; H, 10.98; N, 5.95%. Calcd for $C_{13}H_{27}O_3N$: C, 63.64; H, 11.09; N, 5.71%. Vd: NMR: 2.08 (NH, 1H, bs), 5.85 (ester-CH_2, 2H, q), 6.18 (OCH_2, 2H, t), 8.1—8.6 (CH_2 and CH, 3H, m), 8.71 (ester-CH_3, 3H, t), 9.06 (CH_3, 6H, d). Found: C, 54.52; H, 9.54; N, 8.27%. Calcd for $C_8H_{17}O_3N$: C, 54.83; H, 9.78; N, 7.99%.

(e) In Isobutyl Methyl Ether (IIIe): *N*-(1-methoxy-2-methylpropyl)urethane (IVe_1, 1.24 g), *N*-(isobutoxymethyl)-urethane (IVe_2, 0.43 g), and *N*-isobutoxyurethane (Ve_1, 0.18 g) were isolated. IVe_1: NMR: 4.68 (NH, 1H, bs), 5.45 (OCH, 1H, m), 5.90 (ester-CH_2, 2H, q), 6.71 (OCH_3, 3H, s), 8.26 (CH, 1H, m), 8.75 (ester-CH_3, 3H, t), 9.08 (CH_3, 6H, d). Found: C, 55.12; H, 9.92; N, 7.69%. Calcd for $C_8H_{17}O_3N$: C, 54.83; H, 9.78; N, 7.99%. IVe_2: NMR: 4.19 (NH, 1H, bs), 5.14 (NCH_2, 2H, d), 5.87 (ester-CH_2, 2H, q), 6.77 (OCH_2, 2H, d), 8.10 (CH, 1H, m), 8.74 (ester-CH_3, 3H, t), 9.10 (CH_3, 6H, d). Found: C, 55.05; H, 9.98; N, 7.70%. Calcd for $C_8H_{17}O_3N$: C, 54.83; H, 9.78; N, 7.99%. Ve_1: NMR: 2.04 (NH, 1H, bs), 5.85 (ester-CH_2, 2H, q), 6.42 (OCH_2, 2H, d), 7.63—8.57 (CH, 1H, m), 8.71 (ester-CH_3, 3H, t), 9.05 (CH_3, 6H, d). Found: C, 52.51; H, 9.12; N, 8.81%. Calcd for $C_7H_{15}O_3N$: C, 52.15; H, 9.38; N, 8.69%.

The VPC retention time for methoxyurethane (Ve_2) was identical with that of an authentic sample.

(f) In 2-Methoxyethanol (IIIf): *N*-(2-methoxyethoxy)-urethane (Vf, 2.39 g) was isolated. Vf: NMR: 1.37 (NH, 1H, bs), 5.84 (ester-CH_2, 2H, q), 5.81—6.21 (CH_2ON, 2H, m), 6.26—6.58 (CH_2, 2H, m), 6.62 (CH_3, 3H, s), 8.72 (ester-CH_3, 3H, t). Found: C, 49.25; H, 9.12; N, 9.28%. Calcd for $C_6H_{13}O_3N$: C, 48.96; H, 8.90; N, 9.52%.

Direct Photolysis of I in Dioxane and Alcohols. In dioxane, ethyl 1,4-dioxan-2-ylcarbamate was obtained in yield of 2.47 g. NMR: 4.37 (NH, 1H, bs), 4.87—5.27 (CH, 1H, m), 5.82 (ester-CH_2, 2H, q), 5.97—6.77 (CH_2, 6H, m), 8.74 (ester-CH_3, 3H, t). Found: C, 47.46; H, 7.62; N, 8.21%. Calcd for $C_7H_{13}O_4N$: C, 47.99; H, 7.48; N, 8.00%. The NMR spectrum was in good agreement with that reported in Ref. 8. In the alcohols, Va, Vb, and Vc were obtained in yields of 0.63, 0.95, and 1.87 g, respectively.

Sensitized Photolysis of I in Ethers and Alcohols. A solution of 2.3 g (0.02 mol) of ethyl azidoformate (I) and 3.12 g (0.026 mol) of acetophenone in 0.5 mol of a substrate was irradiated, with stirring at 25 °C, using a high-pressure mercury lamp until the evolution of nitrogen was no longer observed. The reaction mixture was treated as in the case of direct photolysis. In addition, for each of the reactions with alcohols, the excess substrate and a volatile product, aldehyde, were trapped in a flask immersed in a Dry Ice–methanol bath under reduced pressure. The trapped solution was added to a 2,4-dinitrophenylhydrazine solution and the aldehyde was converted to hydrazone. For ethanol, 1-propanol, and 1-butanol, acetaldehyde, propionaldehyde, and butyraldehyde were isolated as hydrazones in yields of 0.43, 0.58, and 0.53 g, respectively. For the reactions with IIIc, dioxane, tetrahydropyran, and 2-methyltetrahydrofuran, IVc_1, ethyl 1,4-dioxan-2-ylcarbamate, ethyl 2-tetrahydropyranylcarbamate, and ethyl 2-methyl-2-tetrahydrofurylcarbamate were isolated in yields of 0.36, 0.95, 0.96, and 0.57 g, respectively. The identification procedure for the third and fourth products has been reported elsewhere.[1)]

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

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