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The Decomposition of *N,N*-Dichlorourethane by Copper: A Comparison with the Photolysis of Ethyl Azidoformate

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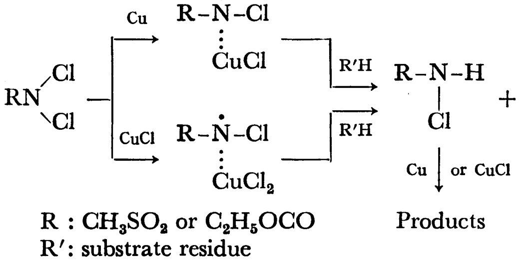
The reactions of *N,N*-dichlorourethane (**1**) with substrates, such as hydrocarbons and ethers, gave *N*-substituted urethanes (**3**) and urethane (**4**) in the presence of copper or copper(I) chloride. The reactions with aromatic hydrocarbons and cyclic ethers possessing an alkyl group at the α-position, however, gave no azepine and no alkoxyurethane respectively, in contrast to those of ethoxycarbonylnitrene generated from the azide. The reactions with the tertiary C–H bonds of *cis*- and *trans*-1,4-dimethylcyclohexanes proceeded non-stereospecifically, contrary to those of the nitrene. The reactions with alcohols led to high yields of **4**, accompanied by the corresponding aldehydes, but afforded no O–H insertion product. The addition of a radical inhibitor, nitrobenzene, reduced the yield of **3**, while it had no appreciable effect on the yield of **4**. Furthermore, the reactions of *N*-chlorourethane with hydrocarbons also gave **3** and **4**. These results suggest that the reaction of **1** with substrates proceeds not by a nitrene mechanism, but by a metal-radical mechanism.

The α-elimination of certain compounds has been reported as a method of generating a nitrene intermediate other than by the photolysis or thermolysis of azides. For example, *N*-(*p*-nitrophenylsulfonyloxy)-urethane[1] was thermolyzed to give ethoxycarbonylnitrene. The decomposition of chloramine-T[2] and dichloramine-T[3] in the presence of zinc dust has also been advanced as a method of generating the sufonylnitrene. These α-eliminations afforded the same products as those produced by the photolyses or thermolyses of the corresponding azides.

On the other hand, the thermolysis of *N,N*-dichloromethanesulfonamide in benzene afforded methanesulfonamide (82% yield), but not mesylaniline.[4] This finding suggests that the reaction involves no nitrene. We reported, prior to Ref. 4, the thermolysis of *N,N*-dichloromethanesulfonamide in the presence of copper.[5,6] Therefore, we tentatively advanced the idea that the reaction proceeded by means of a radical mechanism involving no sulfonylnitrene. In that mechanism, although an intervention of *N*-chloromethanesulfonamide was postulated (Scheme 1), further experimental evidence for the postulate was not yet found because of the difficulty of preparing the monochloramide.



Scheme 1.

In this study, *N,N*-dichlorourethane was employed instead of *N,N*-dichloromethanesulfonamide to obtain further corroborating evidence about the radical mechanism in the dihaloamide–metal system. When the urethane is employed, *N*-chlorourethane, whose intervention is assumed in the dichlorourethane–metal system, is easy to prepare and can be utilized for the present investigation.

Results and Discussion

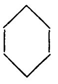
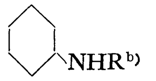
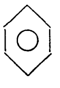
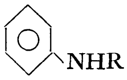
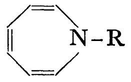
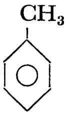
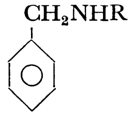
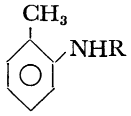
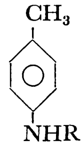
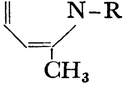
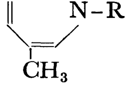
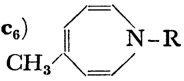
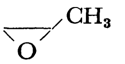
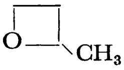
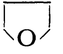
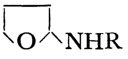
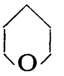
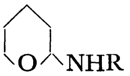
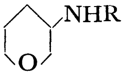
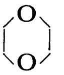
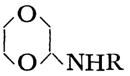
Reaction of N,N*-Dichlorourethane (1) with Hydrocarbons and Cyclic Ethers in the Presence of Copper.* Copper powder was suspended in a substrate (**5**), and **1** was added, drop by drop, into the suspension in a stream of nitrogen. The yields of the products are listed in Table 1 and compared with those of the photolyses of ethyl azidoformate (**2**).[7,8]

Each of the reactions of **1** with substrates gave the *N*-substituted urethane (**3**) and urethane (**4**).

$$\underset{(\mathbf{1})}{\mathrm{Cl_2NCOOEt}} + \underset{(\mathbf{5})}{\mathrm{R'H}} \xrightarrow{\mathrm{Cu}} \underset{(\mathbf{3})}{\mathrm{R'NHCOOEt}} + \underset{(\mathbf{4})}{\mathrm{NH_2COOEt}}$$

The products, **3** and **4**, correspond formally to those resulting from insertion into the C–H bonds and from the abstraction of the hydrogen atoms respectively by ethoxycarbonylnitrene. In the reactions with cyclic ethers, **5f**, **5g**, and **5h**, the α-substituted derivatives were isolated. The preferential formation of the α-substituted derivatives in these reactions paralles that in the direct[7] and sensitized[8] photolyses of **2**. The reactions of **1** with small-membered cyclic ethers, **5d** and **5e**, gave large quantities of colorless, viscous substances whose IR spectra showed the respective strong O–H stretching absorptions. Contrary to the reactions of **1**, the reactions of **2** with **5d** and **5e** gave two ring-opening products, **3d** and **3e** respectively. In the reactions of **1** with aromatic hydrocarbons, azepines, whose formation is a typical nitrene reaction, were not detected, although they were obtained in the photolyses of **2**. In the reaction with **5c**, the product with a side-chain C–H bond was preferentially obtained. The ring-opening products (**3d** and **3e**) in **5d** and **5e** are formed by only singlet ethoxycarbonylnitrene *via* an O–N ylide mechanism.[6] In addition, singlet ethoxycarbonylnitrene adds to aromatic double bonds to give the aziridines, followed by the cleavage of C–C bonds to give the azepines.[9] Therefore, the generation of the singlet nitrene from **1** must be ruled out.

TABLE 1. REACTION OF **1** AND **2** WITH HYDROCARBONS AND ETHERS

Substrate (**5**)	Product (%)[a]			
	3			**4**
(**a**) 	(**a**)  1.4 (32.0)			57.2(15.0)
(**b**) 	(**b**$_1$)  5.5 (1.7)	(**b**$_2$)  ND[c] (20.8)		38.0(7.6)
(**c**) 	(**c**$_1$)  21.6 (1.8)	(**c**$_2$)  1.4 (2.9)	(**c**$_3$)  ND (1.1)	
	(**c**$_4$)  ND (6.7)	(**c**$_5$)  ND (9.0)	(**c**$_6$)  ND (6.2)	31.5(5.0)
(**d**) 	(**d**) CH_2=$CHCH_2ONHR$ ND (21.0)			34.3(12.0)
(**e**) 	(**e**) CH_2=$CHCH_2CH_2ONHR$ ND (28.0)			85.9(23.0)
(**f**) 	(**f**)  12.3 (25.0)			32.7(21.0)
(**g**) 	(**g**$_1$)  27.1 (25.0)	(**g**$_2$)  ND (4.8)		32.0(16.0)
(**h**) 	(**h**)  30.2 (32.8)			68.7(22.2)

( ) Indicates the values resulting from the photolyses of **2**.[8,9] a) Calculated on the basis of the **1** used. b) R: $COOC_2H_5$. c) ND: not detected.

Stereochemistry. In order to compare the reaction of **1** with that of **2** in stereochemical behavior, the reactions of **1** were carried out in *cis*- and *trans*-1,4-dimethylcyclohexanes (*cis*-**5** and *trans*-**5**).

As can be seen in Table 2, the reaction of **1** with either *cis*-**5** or *trans*-**5** gave a mixture of *cis*-**3** and *trans*-**3** (stereoisomer), though the yield was low. Such non-stereospecific formation has also been observed in the reaction of *N*,*N*-dichloromethanesulfonamide with *cis*-**5** or *trans*-**5**, where the tertiary sulfonamides are isolated in moderate yields.[5,6]

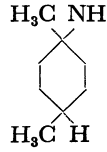
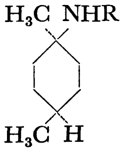
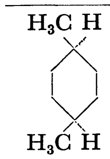
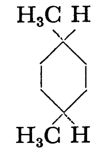
The stereospecific formation of *cis*-**3** or *trans*-**3** in the photolyses of **2**, as shown in Table 2, indicates that triplet ethoxycarbonylnitrene does not lead to the formation of **3**. Thus, the non-stereospecific formation in the reaction of **1** means that neither the singlet nor the triplet nitrene takes part in the formation of **3**.

Reaction of **1** *with Alcohols.* The reaction of **1** with ethanol and 1-butanol gave urethane in yields of 84 and 86% respectively, accompanied by the corresponding aldehydes. None of the O–H insertion products was detected in these reactions. On the other hand, the photolyses of **2** in ethanol and 1-butanol gave O–H insertion products in yields of 11 and 27% respectively, accompanied by urethane.[8] The O–H insertion products have been formed by a singlet nitrene *via* an O–N ylide intermediate, but not by a triplet nitrene *via* a radical mechanism.[8]

Reaction of **1** *in the Addition of Radical Inhibitors.* The above-mentioned results suggest that some radical species is involved in the reaction of **1**. Therefore, the reactions of **1** with toluene and tetrahydropyran were carried out in the presence of a radical inhibitor, nitrobenzene. The results are displayed in Table 3.

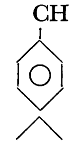
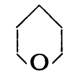
Breslow and Edwards reported the effect of radical inhibitors, such as nitrobenzene, *m*-dinitrobenzene, and sulfur, on the decomposition of **2** in cyclohexane.[12] That is, decompositions in the presence of these inhibitors

Table 2. Reaction of **1** and **2** with *cis*- and *trans*-1,4-dimethylcyclohexanes

Substrate (5)	Product (%)[a]		
	 (*cis*-**3**)	 (*trans*-**3**)	**4**
 (*cis*)	1.0(14.0)	2.0(ND[c])	50.8(18.0)
 (*trans*)	1.2(ND)	2.3(11.0)	56.6(16.0)

( ) Indicates the values resulting from the photolyses of **2**.[10] a) b) c) See Table 1, footnotes.

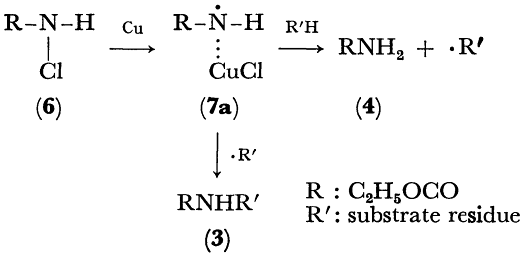
Table 3. Reaction of **1** with substrate in the presence of nitrobenzene

Substrate (5)	Radical inhibitor	Product (%)[a]				
		3				**4**
	presence	c_1	8.4	c_2	1.3	31.1
	absence		21.6		1.4	31.5
	presence	g_1	13.8			30.0
	absence		27.1			32.0

a) See Table 1, footnotes.

gave *N*-cyclohexylurethane and urethane in yields of 56—76 and 12—21% respectively, while those in their absence gave *N*-cyclohexylurethane and urethane in yields of 52 and 25% respectively. These additives led to increased yields of the insertion, but to decreased yields of the abstraction. They gave the following interpretation of the findings. A radical, $H\dot{N}COOEt$, produced by the hydrogen abstraction of the triplet nitrene can catalyze the singlet-triplet intersystem crossing. The reaction of the radical with the additive decreases its radical concentration, resulting in a slow singlet-to-triplet conversion and, therefore, in a high yield of the product from the singlet. Contrary to the decomposition of **2**, in the reaction of **1** the addition of nitrobenzene led to decreased yields of the *N*-substituted urethanes, while it had no appreciable effect on the yield of urethane.

Reaction of N-*Chlorourethane.* The reaction of *N*-chlorourethane (**6**) with dioxane in the presence of copper gave the expected *N*-substituted urethane, **3h**, and urethane in yields of 18.1 and 71.2% respectively.



Scheme 2.

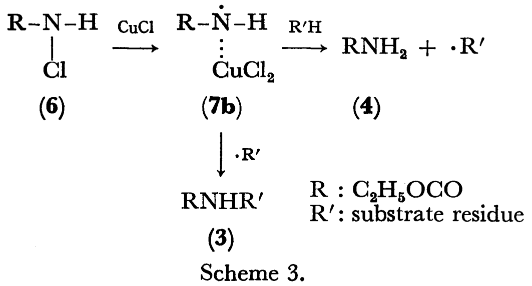
The reactions of **6** with either *cis*-**5** or *trans*-**5** gave a mixture of *cis*-**3** and *trans*-**3** non-stereospecifically, as in the case of **1**.

The decomposition of *N,N*-dichlorourethane (**1**) in the presence of copper leads to the formation of *N*-chlorourethane (**6**), as has been shown in Scheme 1. The chlorine atom of **6** is eliminated by copper to give a metal-radical complex (**7a**), as is shown in Scheme 2, followed by a hydrogen abstraction to give urethane (**4**). On the other hand, **7a** recombines with a substrate radical, ·R', to afford the *N*-substituted urethane (**3**).

In the decomposition of the azide in hydrocarbons, the free $H\dot{N}COOEt$ radical which resulted from triplet nitrene was not able to recombine with the substrate radical (·R'), but exclusively abstracted a hydrogen atom from the substrate. However, the $H\dot{N}COOEt$ radical in the dichloramide- or chloramide-system may recombine with the substrate radical because of the stabilization produced by forming the metal-radical complex represented as **7a**.[6] In addition, a difference between the characteristics of the metal-radical and the free radical was shown also by the addition of the radical inhibitor, nitrobenzene. That is, the addition of the radical inhibitor caused a decreased yields of **3**, but had appreciable effect on the yield of **4** (Table 3). The substrate radical would be trapped by the inhibitor, while the metal-radical complex is not affected by the inhibitor, though the free radical can be captured by it.[12,13]

*Reaction of **1** and **6** in the Presence of Copper(I) Chloride.* As has been shown in Scheme 1, the copper-initiated decomposition of dichloramide should produce copper(I) chloride. This copper(I) chloride is expected to take part in the present reactions. The reaction of **1** with dioxane in the presence of copper(I) chloride gave the *N*-(1,4-dioxan-2-yl)urethane (**3h**) and urethane in yields of 6 and 64.4% respectively. The reactions with both *cis*-**5** and *trans*-**5** gave the *N*-substituted urethane isomer mixtures. The reaction of **6** with dioxane gave **3h** and urethane in yields of 9.6 and 65.4% respectively.

The reaction of **6** with a substrate in the presence



Scheme 3.

of copper(I) chloride is also outlined in Scheme 3. The metal-radical complex (**7b**) resulting from chlorine abstraction by copper(I) chloride abstracts a hydrogen atom from the substrate to give urethane. On the other hand, **7b** recombines with a substrate radical to afford **3**.

In Conclusion. In the absence of metals, the reactions of **1** with toluene and dioxane gave urethane in yields of 68 and 36% respectively, but not the C–H insertion products (**3**).

The formation of the insertion products from the chloramides is shown in Schemes 1—3, under the indispensable condition of the presence of copper or copper(I) chloride.

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. The gas chromatography (VPC) was done on Shimadzu GC-2C and Nippon Denshi (JEOL) JGC 20K units, employing as absorbents: A, 20% Apiezon Grease M on Neopak 1A (60—80 mesh); B, 20% Ucon Oil 5HB 2000 on Celite (60—80 mesh); C, 10% Polyethylene Glycol Succinate on Neopak 1A (60—80 mesh). The quantitative analyses of the products by VPC and the test for the stability of each product during VPC analysis have been done in the ways described in a previous paper.[14)]

Materials. The *N*,*N*-dichlorourethane (**1**),[15)] *N*-chlorourethane (**6**),[16)] 2-methyloxetane,[7)] and *cis*- or *trans*-1,4-dimethylcyclohexane (*cis*-**5** or *trans*-**5**)[17)] were prepared by the methods already described. The propylene oxide, tetrahydrofuran, tetrahydropyran, 1,4-dioxane, cyclohexane, benzene, toluene, ethanol, and 1-butanol were used after purification by the methods recommended in the literature.[18)]

Authentic Samples. The *N*-cyclohexylurethane (**3a**) was prepared by the method of Lwowski and Mattingly.[19)] The *N*-phenylurethane (**3b$_1$**), *N*-benzylurethane (**3c$_1$**), *N*-(2-tolyl)urethane (**3c$_2$**), and *N*-(4-tolyl)urethane (**3c$_3$**) were prepared from ethyl chloroformate and the corresponding amines in a way similar to that used in the preparation of *N*-cyclohexylurethane. **3a**: IR (Nujol, cm^{-1}): 3350, 1680, 1220. NMR (CCl_4, δ): 4.52 (NH, 1H, bs), 4.01 (2H, q), 3.40 (1H, m), 2.42—1.40 (ring-CH_2, 10H, m), 1.21 (3H, t). **3b$_1$**: IR (Nujol, cm^{-1}): 3350, 1700, 1240. NMR (CCl_4, δ): 7.80 (NH, 1H, bs), 7.64—6.75 (5H, m), 4.20 (2H, q), 1.21 (3H, t). **3c$_1$**: IR (Nujol, cm^{-1}): 3360, 1690, 1285. NMR (CCl_4, δ): 7.22 (5H, s), 5.36 (NH, 1H, bs), 4.21 (2H, d), 4.01 (2H, q), 1.67 (3H, t). **3c$_2$**: IR (Nujol, cm^{-1}): 3355, 1700, 1230. NMR (CCl_4, δ): 7.96—6.92 (4H, m), 6.68 (NH, 1H, bs), 4.20 (2H, q), 2.21 (3H, s), 8.71 (3H, t). **3c$_3$**: IR (Nujol, cm^{-1}): 3320, 1710, 1230. NMR (CCl_4, δ): 7.48—6.64 (5H, m), 4.10 (2H, q), 2.22 (3H, s), 1.19 (3H, t). The *cis* and *trans* isomers of *N*-(1,4-dimethylcyclohexyl)urethane (*cis*-**3** and *trans*-**3**) were prepared as follows. A mixture of the stereoisomers (*cis*-**3** and *trans*-**3**) was prepared from ethyl chloroformate and 1,4-dimethylcyclohexylamine (*cis*-*trans* mixture), which had been prepared in a way similar to that used in the preparation of 1-methylcyclohexylamine.[20)] The urethanes were well separated into *cis* and *trans* isomers by using column B. The assignment of each stereoisomer was done by comparison with the products obtained from the stereospecific insertions of singlet ethoxycarbonylnitrene into the tertiary C–H bond of *cis*- and *trans*-1, 4-dimethylcyclohexanes.[10)] *cis*-**3**: IR (neat, cm^{-1}): 3340, 1710, 1230, NMR (CCl_4, δ): 4.80 (NH, 1H, bs), 4.22 (2H, q), 2.11—1.45 (ring-CH and CH_2, 9H, m), 1.38 (3H, s), 1.27 (3H, t), 0.98 (3H, d). *trans*-**3**: IR (neat, cm^{-1}): 3360, 1710, 1235. NMR (CCl_4, δ): 4.44 (NH, 1H, bs), 4.06 (2H, q), 2.50—1.40 (ring-CH and CH_2, 9H, m) 1.31 (3H, s), 1.22 (3H, t), 0.92 (3H, d). The IR and NMR spectral data of *N*-(2-tetrahydrofuryl)urethane (**3f**), *N*-(2-tetrahydropyranyl)urethane (**3g$_1$**), and *N*-(1,4-dioxan-2-yl)urethane (**3h**) have been described previously.[6,7)]

Reaction of N,N-*Dichlorourethane (1) with Hydrocarbons and Ethers in the Presence of Copper.* Copper powder (4.8 g, 0.075 mol) was suspended in a substrate (0.5 mol of ethers and hydrocarbons), and *N*,*N*-dichlorourethane (**1**, 4 g, 0.025 mol) was added, drop by drop, into the suspension in a stream of nitrogen. The reactions with ethers and hydrocarbons were carried out at 20 and 50 °C respectively. After **1** had been added, the stirring was continued for about another 5 h, Then, the suspension was filtered, and the filtrate was concentrated under reduced pressure. The residue was analyzed by VPC on Columns B and C.

In Cyclohexane (5a), Benzene (5b), and Toluene (5c): **3a** (0.06 g), **3b$_1$** (0.22 g), **3c$_1$** (0.97 g), and **3c$_2$** (0.06 g) were isolated.

In tetrahydrofuran (5f), Tetrahydropyran (5g), and 1,4-Dioxane (5h): **3f** (0.49 g), **3g$_1$** (1.17 g), and **3h** (1.32 g) were isolated.

In cis-*1,4-Dimethylcyclohexane* (cis-*5*): *cis*-**3** (0.05 g) and *trans*-**3** (0.1 g) were isolated.

In trans-*1,4-Dimethylcyclohexane* (trans-*5*): *cis*-**3** (0.06 g) and *trans*-**3** (0.11 g) were isolated.

Reaction of 1 with Alcohols in the Presence of Copper. Copper powder (0.075 mol) was suspended in ethanol (0.5 mol) or 1-butanol (0.5 mol), and then **1** (4 g, 0.025 mol) was added, drop by drop, to the suspension kept at 5—7 °C in a stream of nitrogen. After the **1** had been added, the stirring was continued for about 5 h. Then, the suspension was filtered, and the excess substrate and the 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 hydrazone was isolated.

Reaction of 1 with 5c and 5g in the Addition of Nitrobenzene. Copper powder (0.075 mol) was suspended in a mixture of substrate (0.5 mol) and nitrobenzene (0.025 mol), and then **1** (4 g, 0.025 mol) was added, drop by drop, into the suspension in a stream of nitrogen. The reactions with **5c** and **5g** were carried out at 50 and 20 °C respectively. Then, the reaction mixture was treated as has been described above. **3c$_1$** (0.38 g) and **3c$_2$** (0.06 g) were isolated in the reaction with **5c**, and **3g$_1$** (0.6 g) was isolated in the reaction with **5g**.

Reaction of N-*Chlorourethane (6) with 5h and Hydrocarbons in the Presence of Copper.* Copper powder (0.075 mol) was suspended in a substrate (0.5 mol), and *N*-chlorourethane (**6**, 3.1 g, 0.025 mol) was added, drop by drop, into the stirred suspension at 20 °C (case of **5h**) or 50 °C (case of hydrocarbons) in a stream of nitrogen. Then, the reaction mixture was treated as has been described above.

In 5h: **3h** (0.8 g) was isolated.

In 5a: **3a** (0.08 g, 1.8%) and urethane (**4**, 50.0%) were isolated.

In cis-*5*: *cis*-**3** (0.06 g, 1.2%), *trans*-**3** (0.1 g, 2.1%), and **4** (50.4%) were isolated.

In trans-*5*: *cis*-**3** (0.05 g, 1.0%), *trans*-**3** (0.08 g, 1.6%), and **4** (63.7%) were isolated.

Reaction of 1 and 6 with 5h and Hydrocarbons in the Presence of Copper(I) Chloride. Copper(I) chloride (7.5 g, 0.075 mol) was suspended in a substrate (0.5 mol), and **1** or **6** (0.25 mol) was added to the suspension at 20 °C (case of **5h**) or 50 °C (case of hydrocarbons) in a stream of nitrogen. Then, the reaction mixture was treated as has been described above.

*In the Reaction of **1** with **5h**:* **3h** (0.26 g) was isolated.

*In the Reaction of **1** with* cis-**5**: *cis*-**3** (0.06 g, 1.2%), *trans*-**3** (0.09 g, 1.8%), and **4** (62.0%) were isolated.

*In the Reaction of **1** with* trans-**5**: *cis*-**3** (0.09 g, 1.8%), *trans*-**3** (0.15 g, 3.0%), and **4** (54.8%) were isolated.

*In the Reaction of **6** with **5h**:* **3h** (0.42 g) was isolated.

*Reaction of **1** in the Absence of Copper.* The chloramide (**1**, 0.025 mol) was added, drop by drop, to **5h** (0.5 mol) kept at 20 °C or to **5c** (0.5 mol) kept at 50 °C in a stream of nitrogen. Then, the reaction mixture was treated as has been described above. Urethane was isolated in yields of 0.8 g and 1.51 g in **5h** and **5c** respectively.

Photolyses of Ethyl Azidoformate in Hydrocarbons. A solution of ethylazidoformate (0.02 mol) in hydrocarbon (0.5 mol) 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 excess substrate was then removed under reduced pressure. The residue was analyzed by VPC on Colums B and C.

*In **5a**:* **3a** (1.36 g) was isolated.

*In **5b**:* $\mathbf{3b_1}$ (0.07 g) and *N*-(ethoxycarbonyl)azepine ($\mathbf{3b_2}$, 0.86 g) were isolated. $\mathbf{3b_2}$: IR (neat, $\mathrm{cm^{-1}}$): 1715 (C=O), 1655 and 1630 (C=C). NMR ($\mathrm{CDCl_3}$, δ): 6.12—5.18 (6H, m), 4.17 (2H, q), 1.25 (3H, t) (Found: C, 65.32; H, 6.62; N, 8.51%).

*In **5c**:* $\mathbf{3c_1}$ (0.08 g), $\mathbf{3c_2}$ (0.13 g), $\mathbf{3c_3}$ (0.05 g), 2-methyl-*N*-(ethoxycarbonyl)azepine ($\mathbf{3c_4}$, 0.3 g), 3-methyl-*N*-(ethoxycarbonyl)azepine ($\mathbf{3c_5}$, 0.4 g), and 4-methyl-*N*-(ethoxycarbonyl)-azepine ($\mathbf{3c_6}$, 0.28 g) were isolated. $\mathbf{3c_4}$: IR (neat, $\mathrm{cm^{-1}}$): 1710 (C=O), 1650 and 1630 (C=C). NMR ($\mathrm{CDCl_3}$, δ): 6.35—5.63 (5H, m), 4.17 (2H, q), 2.07 (3H, s), 1.29 (3H, t) (Found: C, 67.21; H, 7.25; N, 7.76%). $\mathbf{3c_5}$: IR (neat, $\mathrm{cm^{-1}}$): 1715 (C=O), 1660 and 1630 (C=C). NMR ($\mathrm{CDCl_3}$, δ): 6.10—5.30 (5H, m), 4.22 (2H, q), 1.78 (3H, d, J=1.5 Hz), 1.32 (3H, t) (Found: C, 66.92; H, 7.41; N, 7.94%). $\mathbf{3c_6}$: IR (neat, $\mathrm{cm^{-1}}$): 1720 (C=O), 1660 and 1630 (C=C). NMR ($\mathrm{CDCl_3}$, δ): 6.10—5.14 (5H, m), 4.20 (2H, q), 1.80 (3H, s), 1.30 (3H, t) (Found: C, 67.30; H, 7.21; N, 7.95%). The IR and NMR data of $\mathbf{3c_4}$, $\mathbf{3c_5}$, and $\mathbf{3c_6}$ were assigned on the basis of those of 2-, 3-, and 4-methyl-*N*-(methoxycarbonyl)azepines.[21]

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