Photolyses of *S,S*-Dimethyl-*N*-(ethoxycarbonyl)sulfimide in Hydrocarbons and in Oxygen Compounds

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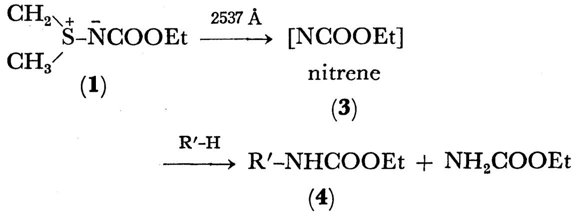
The behavior of ethoxycarbonylnitrene (**3**), generated photochemically from *S,S*-dimethyl-*N*-(ethoxycarbonyl)-sulfimide (**1**), upon insertion into the C–H bonds and the O–H bonds was compared with that of **3** generated from ethyl azidoformate (**2**). Ethoxycarbonylnitrene generated from **1** was inserted preferentially into the α C–H bonds of cyclic ethers. The relative reactivity toward **3** of the primary, secondary, and tertiary C–H bonds in 2,4-dimethylpentane is in the ratio of 1: 9: 35. The insertion of **3** into the tertiary C–H bonds of *cis*- and *trans*-1,4-dimethylcyclohexanes proceeded stereospecifically. The reaction of **3** with alcohols gave the O–H insertion products. These results show that the insertion of **3** generated from **1**, as well as that of the nitrene from **2**, into the hydrocarbon C–H bonds and the O–H bonds proceeds only for the singlet.

The decomposition of some amidates or sulfimides is known to be a method of generating a nitrene intermediate. For example, *N*-trimethylammoniododecanesulfonamidate was thermolyzed to give a sulfonylnitrene,[1] *S,S*-dimethyl-*N*-benzoylsulfimide was photolyzed to give benzoylnitrene,[2] and *S,S*-dimethyl-*N*-(ethoxycarbonyl)-sulfimide was photolyzed to give ethoxycarbonylnitrene.[3] Ethoxycarbonylnitrene, generated by the photolysis of *S,S*-dimethyl-*N*-(ethoxycarbonyl)sulfimide (**1**),[3] gave a product distribution similar to that resulting photochemically from the azide[4] in the reaction with cyclohexene. On the other hand, the nitrene from **1** was produced largely (more than 50%) in triplet form,[3] although the photodecomposition of the azide showed that one-fourth of the nitrene formed was in the triplet state,[4] in addition to *cis*- and *trans*-4-methyl-2-pentenes. As for C–H insertion, ethoxycarbonylnitrenes, generated by the photochemical[5] and thermal[6] decompositions of ethyl azidoformate or by the α-elimination of *N*-(*p*-nitrophenylsulfonyloxy)urethane,[5] showed nearly the same regioselectivities. It has not been reported, however, whether or not the ethoxycarbonylnitrene generated from the ylide shows, on insertion into C–H bonds, behavior similar to that of the nitrene generated from the other precursors.

In this paper, the regioselectivity and the stereospecificity of **3** derived from the precursors **1** and ethyl azidoformate (**2**) in the insertion into C–H bonds will be described.

Results and Discussion

Photolysis of 1 in Hydrocarbons and in Ethers. A solution of *N*-carbethoxyiminodimethylsulfurane (**1**) in cyclic ether or in a mixture of hydrocarbon and 1,2-dichloroethane 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 (**4**) of **3** into the C–H bonds were obtained, accompanied by an abstraction product, urethane. The yields are listed in Table 1.



$$\mathrm{CH_2 \diagdown \overset{+}{S}{-}\overset{-}{N}COOEt,\ CH_3 \diagup}\ (\mathbf{1}) \xrightarrow{2537\ \text{Å}} \underset{(\mathbf{3})}{\underset{\text{nitrene}}{[\mathrm{NCOOEt}]}} \xrightarrow{\mathrm{R'{-}H}} \underset{(\mathbf{4})}{\mathrm{R'{-}NHCOOEt}} + \mathrm{NH_2COOEt}$$

(R′: hydrocarbon residue or ether residue)

The insertion took place preferentially at the C–H bonds of the α-position of the ethers. The preferential formation of the α C–H insertion products in the ethers was also observed in the photolyses of **2**.[7–9] The reaction with 2,4-dimethylpentane gave three isomeric insertion products, resulting from an attack on all the primary (1°), secondary (2°), and tertiary (3°) C–H bonds.

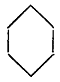
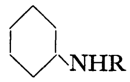
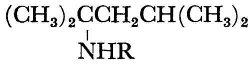
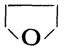
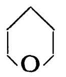
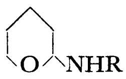
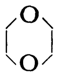
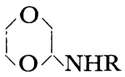
Relative Reactivity. From the yields of the insertion products of **1** with 2,4-dimethylpentane, the relative reactivities of the 1, 2, and 3° C–H bonds toward **3** was calculated to be in the ratio of 1: 9: 35. On the other hand, **3**, generated by the photolysis of **2**, reacted with the 1, 2, and 3° C–H bonds of 2-methylbutane in the ratio of 1: 9: 34.[4] The values resulting from these two experiments are in remarkably good agreement, though the substrate hydrocarbons employed are not the same.

Stereochemistry. In order to investigate the stereospecificity in the C–H insertion of **3**, generated from **1**, **1** was photolyzed in *cis*- and *trans*-1,4-dimethylcyclohexanes. The results are displayed in Table 2, compared with those of **3** generated from **2**.[10]

The reaction of **3** generated from **1** with either *cis*- or *trans*-1,4-dimethylcyclohexane gave only one tertiary urethane, accompanied by urethane and two kinds of secondary urethanes; the reaction was virtually completely stereospecific. In this respect, it has the same tendency as the reaction of **3** generated from **2**.[10] Therefore, the results show that the ethoxycarbonylnitrene generated from **1** is inserted into the C–H bonds of hydrocarbon only in the singlet state, like the nitrene from the azide.

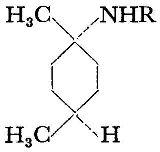
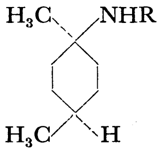
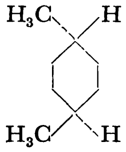
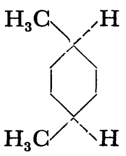
Dilution Effect. It is well known that, in the nitrene reaction, dilution with such inert solvents as dichloromethane and dibromomethane promotes the singlet-triplet intersystem crossing of nitrenes. For example, cyanonitrene, generated thermally from cyanogen azide, was inserted stereospecifically into the C–H bonds of *cis*- and *trans*-1,2-dimethylcyclohexanes in

TABLE 1. PHOTOLYSIS OF **1** IN HYDROCARBONS AND IN ETHERS

Substrate		Product (%)[a)]			H$_2$NR[b)]
		4			
(**a**)		(**a**)		18.1	27.0
(**b**)	$(CH_3)_2CHCH_2CH(CH_3)_2$	(**b$_1$**)	 $(CH_3)_2\underset{NHR}{C}CH_2CH(CH_3)_2$	14.1	71.4
		(**b$_2$**)	 $(CH_3)_2CH\underset{NHR}{CH}CH(CH_3)_2$	3.6	
		(**b$_3$**)	 $(CH_3)_2CHCH_2\underset{CH_2NHR}{CH}CH_3$	2.4	
(**c**)		(**c**)		23.8	27.6
(**d**)		(**d**)		20.0	39.5
(**e**)		(**e**)		24.1	7.5

a) Calculated on the basis of the ylide used. b) R: $COOC_2H_5$

TABLE 2. PHOTOLYSIS OF **1** IN 1,4-DIMETHYLCYCLOHEXANES

Mole ratio	Product (%)[a)]			
	 (*cis*-**4**)	 (*trans*-**4**)	*cis*-**5**[c)] or *trans*-**5**[c)]	H$_2$NR[b)]
 $C_2H_4Cl_2$ *trans*				
1 : 2	ND[d)] (ND)	13.1 (11.0)	16.3 (11.7)	34.5 (16.0)
 *cis*				
1 : 2	8.4	ND	8.7	27.7
1 : 4	5.2	ND	5.0	37.3
1 : 20	3.9 (14.0)	ND (ND)	4.8 (12.8)	80.4 (18.0)

( ) Indicates the values resulting from the photolysis of **2** without dilution.[10)] a) b) See Table 1, footnotes. c) Total yields of the secondary urethanes. d) ND: not detected.

the absence of the inert solvents. However, the insertion of the nitrene with the cyclohexanes diluted with the inert solvents proceeded non-stereospecifically, giving a mixture of *cis* and *trans* isomeric products.[11] That is, triplet cyanonitrene, produced from the decay of a singlet, is also inserted into the C–H bonds of hydrocarbons. On the other hand, the insertion of ethoxycarbonylnitrene, generated by the photochemical and the thermal decompositions of the azide or by the α-elimination of *N*-(*p*-nitrophenylsulfonyloxy)urethane, proceeded completely stereospecifically toward the C–H bond of optically active 3-methylhexane diluted with dichloromethane.[12]

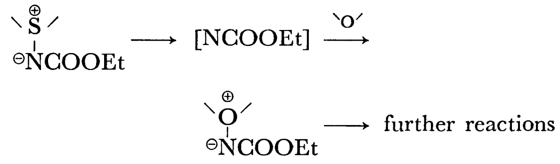
As can be seen in Table 2, the insertion of **3** into the tertiary C–H bond proceeded completely stereospecifically, even at about a 5 mol % dilution with 1,2-dichloroethane. Therefore, it may be concluded that the ethoxycarbonylnitrene generated from *S*,*S*-dimethyl-*N*-(ethoxycarbonyl)sulfimide behaves just like those generated from the other precursors in stereochemistry as well as in the selectivity of the insertion into the C–H bonds of hydrocarbons, and that triplet ethoxycarbonylnitrene, unlike triplet cyanonitrene, can not be inserted into C–H bonds. The difference in behavior between the triplet ethoxycarbonyl and cyano-nitrenes may be explained as follows: the $H\dot{N}CN$ radical, produced through hydrogen abstraction by the triplet nitrene, is much more resonance-stabilized than the $H\dot{N}COOEt$ radical, permitting combination with the radicals derived from substrates.

Table 3. Photolysis of **1** and **2** in alcohols

Alcohol	Product (%)[a]					
	Insertion into O–H bond			Abstraction (H_2NR[b])		
	1	**2**		**1**	**2**	
		Direct	Sensitized		Direct	Sensitized
C_2H_5OH	9.1	11.0	ND[c]	63.0	71.0	64.6
n-C_3H_7OH	11.0	15.0	ND	61.8	46.0	80.5
n-C_4H_9OH	6.2	27.0	ND	52.4	47.0	74.9

a) b) See Table 1, footnotes. c) ND: not detected.

Photolysis of 1 in Alcohols. The behavior toward alcohols of the **3** generated from **1** was similar to that of the **3** derived by the direct photolysis of **2**, although the insertion-abstraction ratio decreased in the present precursor (**1**) compared with that in the **2** precursor, as is shown in Table 3. The photolyses of **1**, as well as the direct photolyses of **2**, gave products for nitrene insertion into the O–H bonds, while the sensitized photolyses gave no such insertion products.[8] The insertion in the direct photolyses has been concluded to proceed *via* the formation of O–N ylide intermediate resulting from the singlet nitrene.[8] Consequently, the O–H insertion in the photolyses of **1** is also thought to involve O–N ylide formation, as is shown in the following scheme:



Scheme 1.

Experimental

The equipment and techniques have been described previously.[7]

Materials. The preparation of *cis*- and *trans*-1,4-dimethylcyclohexanes has been described previously.[13] The *S*,*S*-dimethyl-*N*-(ethoxycarbonyl)sulfimide (**1**) was prepared by the method of Whitfield *et al.*[14] The tetrahydrofuran, tetrahydropyran, 1,4-dioxane, cyclohexane, 2,4-dimethylpentane, 1,2-dichloroethane, ethanol, 1-propanol, and 1-butanol were used after the commercial reagents had been purified according to the published directions.[16]

Authentic Samples. The preparation of authentic samples of *N*-cyclohexylurethane (**4a**), *N*-(*cis*-1,4-dimethylcyclohexyl)urethane (*cis*-**4**), and *N*-(*trans*-1,4-dimethylcyclohexyl)urethane (*trans*-**4**) has been described previously.[13] The authentic samples of *N*-(1-isopropyl-2-methylpropyl)urethane (**4b$_2$**) and *N*-(2,4-dimethylpentyl)urethane (**4b$_3$**) were prepared from ethyl chloroformate and the corresponding amines, which was themselves previously been prepared by the method of Breslow.[15] **4b$_2$**: IR (neat, cm^{-1}): 3350 (NH), 1710 (C=O), 1250 (C–O). NMR (CCl_4, τ): 5.42 (NH, 1H, bs), 5.95 (OCH_2, 2H, q), 6.51—7.02 (NCH, 1H, m), 7.93—8.60 (2CH, 2H, m), 8.78 (ester-CH_3, 3H, t), 9.09 ($2CH_3$, 6H, d), 9.14 ($2CH_3$, 6H, d). **4b$_3$**: IR (neat, cm^{-1}): 3350 (NH), 1710 (C=O), 1255 (C–O). NMR (CCl_4, τ): 5.10 (NH, 1H, bs), 6.00 (OCH_2, 2H, q), 6.92—7.27 (NCH_2, 2H, m), 8.04—9.02 (2CH and CH_2, 4H, m), 8.81 (ester-CH_3, 3H, t), 9.13 (CH_3, 3H, d), 9.16 ($2CH_3$, 6H, d).

Photolyses of 1 in Hydrocarbons and in Ethers. A solution of **1** (450 mg, 3 mmol) in ethre (0.6 mol) or in a mixture of hydrocarbon (0.4 mol) and 1,2-dichloroethane (19.8 g, 0.2 mol) was irradiated by the light (mainly 2537 Å) of a low-pressure mercury arc at 0 °C with stirring under an atmosphere of nitrogen untill the NMR signal at τ 7.30 due to the *gem*-dimethyl group of **1** has disappeared. Then, the excess substrate was evaporated under reduced pressure and the residue was analyzed by VPC.

In Hydrocarbons: In cyclohexane, **4a** (95 mg) was isolated. In 2,4-dimethylpentane, *N*-(1,1,3-trimethylbutyl)urethane (**4b$_1$**, 79 mg), **4b$_2$** (20 mg), and **4b$_3$** (13 mg) were isolated. **4b$_1$**: IR (neat, cm^{-1}): 3350 (NH), 1710 (C=O), 1260 (C–O). NMR (CCl_4, τ): 5.49 (NH, 1H, bs), 6.05 (OCH_2, 2H, q), 8.02—8.60 (CH and CH_2, 3H, m), 8.77 ($2CH_3$, 6H, s), 8.83 (ester-CH_3, 3H, t), 9.10 ($2CH_3$, 6H, d). Found: C, 63.98; H, 11.26; N, 7.35%. Calcd for $C_{10}H_{21}O_2N$: C, 64.13; H, 11.30; N, 7.48%. The IR and the NMR spectral data and VPC retention times of **4a**, **4b$_2$**, and **4b$_3$** were identical with those of the authentic samples. In *cis*-1, 4-dimethylcyclohexane, *cis*-**4** (50 mg) and a mixture of two kinds of secondary urethanes (*cis*-**5**, 52 mg) were isolated. The mixture of the secondary urethanes did not separate into two parts on the columns employed. The IR and the NMR spectral data and the VPC retention time of *cis*-**4** were identical with those of the authentic sample. *N*-(*cis*-2,5-Dimethylcyclohexyl)urethane (*cis*-**5**, a mixture of the isomers): IR (neat, cm^{-1}): 3320 (NH), 1700 (C=O), 1240 (C–O). NMR (CCl_4, τ): 5.2 (NH), 5.76 (OCH_2), 7.50—9.23 (ring-CH and

CH_2, ring-side CH_3, ester-CH_3). Found: C, 65.99; H, 10.48; N, 6.98%. Calcd for $C_{11}H_{21}O_2N$: C, 66.29; H, 10.62; N, 7.03%. In *trans*-1,4-dimethylcyclohexane, *trans*-**4** (66 mg) and two kinds of secondary urethane (*trans*-$\mathbf{5}_1$ and *trans*-$\mathbf{5}_2$, 70 mg), which were subsequently cleanly separated into individual isomers by VPC, were isolated. The analytical data of *trans*-**4** were identical with those of the authentic sample. One isomer of *N*-(*trans*-2,5-dimethylcyclohexyl)urethanes (*trans*-$\mathbf{5}_1$): IR (neat, cm^{-1}): 3350 (NH), 1700 (C=O), 1240 (C–O). NMR (CCl_4, τ): 5.22 (NH, 1H, bs), 5.86 (OCH_2, 2H, q), 7.93—9.30 (ring-CH and CH_2, 9H, m), 8.73 (ester-CH_3, 3H, t), 9.07 ($2CH_3$, 6H, d). Found: C, 66.11; H, 10.49; N, 7.10%. The other (*trans*-$\mathbf{5}_2$): IR (neat, cm^{-1}): 3320 (NH), 1690 (C=O), 1270 (C–O). NMR (CCl_4, τ): 5.20 (NH, 1H, bs), 5.86 (OCH_2, 2H, q), 7.60—9.36 (ring-CH and CH_2, 9H, m), 8.74 (ester-CH_3, 3H, t), 9.05 ($2CH_3$, 6H, d). Found: C, 66.41; H, 10.58; N, 6.09%.

In Ethers: In tetrahydrofuran, tetrahydropyran, and 1,4-dioxane, *N*-(2-tetrahydrofuryl)urethane (**4c**, 113 mg), *N*-(2-tetrahydropyranyl)urethane (**4d**, 104 mg), and *N*-(1,4-dioxan-2-yl)urethane (**4e**, 126 mg) were isolated respectively. The IR and the NMR spectral data of **4c**, **4d**, and **4e** have been given in previous papers.[7,8]

In cis-*1,4-Dimethylcyclohexane Diluted with Dichloroethane*: The reaction of **1** (450 mg, 3 mmol) in a solation of *cis*-1, 4-dimethylcyclohexane (14 g, 0.12 mol) and 1,2-dichloroethane (48 g, 0.48 mol) gave 31 mg of *cis*-**4** and 30 mg of *cis*-**5**. When a solution of 0.03 mol of *cis*-1,4-dimethylcyclohexane and 0.6 mol of 1,2-dichlroethane were used, the reaction gave 23 mg of *cis*-**4** and 29 mg of *cis*-**5**.

Photolyses of 1 in Alcohols. A solution of **1** (3 mmol) in alcohol (0.6 mol) was irradiated by the light (mainly 2537 Å) of a low-pressure mercury arc at 0 °C with stirring in an atmosphere of nitrogen. The reaction mixture was treated by the procedures described for the reaction in hydrocarbons and in ethers.

In ethanol, 1-propanol, and 1-butanol, *N*-ethoxyurethane (36 mg), *N*-propoxyurethane (48 mg), and *N*-butoxyurethane (30 mg) were isolated respectively. The IR and the NMR spectral data and elemental analyses of these products have been given in a previous paper.[8]

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References

1) P. Robson and P. R. H. Speakman, *J, Chem. Soc.*, *B*, **1968**, 463.

2) U. Lerch and J. G. Moffatt, *J. Org. Chem.*, **36**, 3391 (1971).

3) Y. Hayashi and D. Swern, *Tetrahedron Lett.*, **1972**, 1921.

4) W. Lwowski and F. W. Mattingly, *J. Am. Chem. Soc.*, **87**, 1947 (1965).

5) W. Lwowski and T. J. Maricich, *J. Am. Chem. Soc.*, **87**, 3630 (1965).

6) D. S. Breslow, T. J. Prosser, A. F. Marcantonio, and C. A. Genge, *J. Am. Chem. Soc.*, **89**, 2384 (1967).

7) N. Torimoto, T. Shingaki, and T. Nagai, *Bull. Chem. Soc. Jpn.*, **49**, 2572 (1976).

8) N. Torimoto, T. Shingaki, and T. Nagai, *Bull. Chem. Soc. Jpn.*, **50**, 1517 (1977).

9) H. Nozaki, S. Fujita, H. Takaya, and R. Noyori, *Tetrahedron*, **23**, 45 (1967).

10) T. Shingaki, M. Inagaki, N. Torimoto, and M. Takebayashi, *Chem. Lett.*, **1972**, 155.

11) A. G. Anastassiou, *J. Am. Chem. Soc.*, **89**, 3184 (1967).

12) J. M. Simon and W. Lwowski, *J. Am. Chem. Soc.*, **91**, 5107 (1969).

13) N. Torimoto, T. Shingaki, and T. Nagai, *J. Org. Chem.*, in press.

14) G. F. Whitfield, H. S. Beilan, D. Saika, and D. Swern, *Tetrahedron Lett.*, **1970**, 3543.

15) D. S. Breslow, E. I. Edwards, E. C. Linsay, and H. Omura, *J. Am. Chem. Soc.*, **98**, 4268 (1976).

16) J. A. Riddic and W. B. Bunger, "Organic Solvents," in "Techniques of Chemistry," Vol. VII, ed by A. Weissberger, Wiley-Interscience, New York, N. Y. (1970).