

Photolyses of Ethoxalyl Azide in Alcohols and in Hydrocarbons Reactions of Ethoxalylnitrene

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The photolysis of ethoxalyl azide gives ethoxalylnitrene and ethoxycarbonyl isocyanate. The nitrene adds to C=C double bonds and is inserted into O—H and C—H bonds. At high ethanol concentrations, where the singlet nitrene predominates, the O—H insertion product is formed dominantly. At low ethanol concentrations, where much of the nitrene changes to the triplet state, the hydrogen-abstraction product is preferred. The reactivity of the nitrene toward the C—H bonds of 2-methylbutane is more selective than that of ethoxycarbonylnitrene.

In a preliminary communication,¹⁾ we reported that thermolysis of ethoxalyl azide in alcohols gave ethoxycarbonylurethanes *via* ethoxycarbonyl isocyanate, the Curtius rearrangement product, whereas the photolysis of the azide in alcohols or hydrocarbons yielded *N*-alkoxy- or *N*-alkyl-ethoxalamides, whose formation could be explained by the assumption of ethoxalylnitrene as an intermediate. This paper will deal chiefly with the reactions of ethoxalylnitrene with alcohols and hydrocarbons, and with the reactivities of the nitrene toward C—H bonds of hydrocarbons studied in further detail.

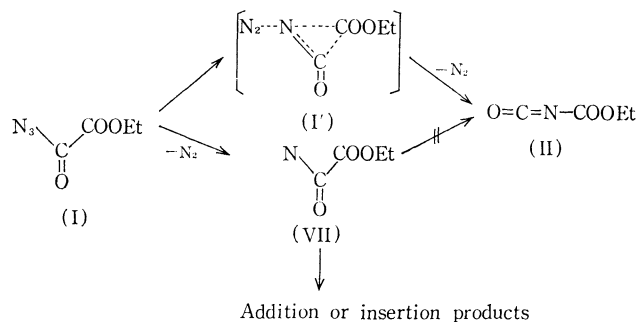
Results and Discussion

All experiments on the photolysis of ethoxalyl azide were carried out in dichloromethane, since the neat azide was explosive.

Photolysis of Ethoxalyl Azide in Alcohols and in Hydrocarbons. Ethoxalyl azide (I) was decomposed by the light (mainly 2537 Å) of a low-pressure mercury arc in a mixture of dichloromethane with alcohols at -78°C in an atmosphere of nitrogen. The reaction gave ethoxalamide (IV) and *N*-alkoxyethoxalamides (V), accompanied by *N*-alkoxycarbonylurethanes (III) and the dehydrogenation products of the alcohols employed.

Similarly, the photolysis of I with hydrocarbons yielded *N*-alkyl- or *N*-cycloalkyl-ethoxalamides (VI) and ethoxalamide (IV), in addition to ethoxycarbonyl isocyanate (II). The yields of the products are listed in Table 1.

As is shown in Table 1, the yields of isocyanate (II) were almost the same in all cases, while those of the amides (IV and V, IV and VI) varied with the substrate employed. The results suggest that the mechanism for the formation of isocyanate is different from that for the formation of amides; the rearrangement of I into II seems to proceed *via* a concerted mechanism, whose transition state is expressed by I', as has been



Scheme 1.

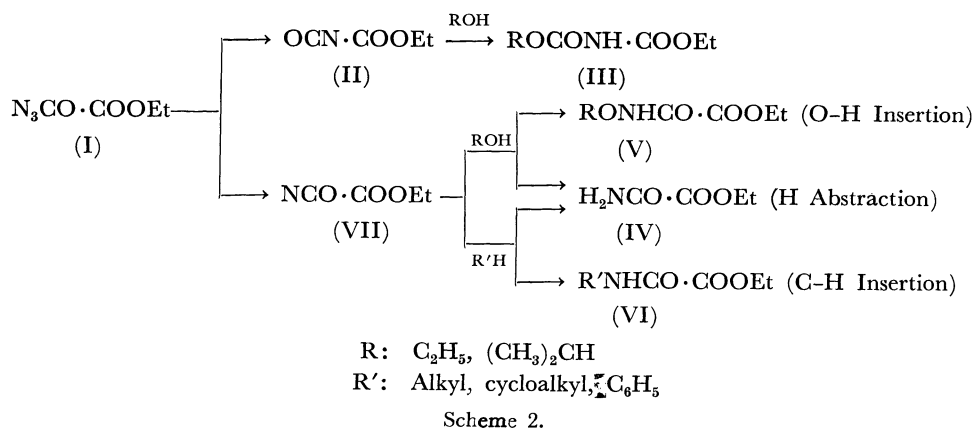
TABLE 1. PHOTOLYSIS OF ETHOXALYL AZIDE IN DICHLOROMETHANE

Substrate	Product (%) ^{a)}			
	OCN-COOEt (II)	H ₂ NCO-COOEt (IV)	RONHCO-COOEt ^{b)} (V)	R'NHCO-COOEt ^{c)} (VI)
None	47	2.8	—	—
Ethanol	45 ^{d)}	9.8	26	—
2-Propanol	45 ^{d)}	16.0	22	—
Cyclohexane	41	3.7	—	16
Cyclopentane	45	3.7	—	17
Cyclohexene	43	5.3	—	e)
Benzene	48	3.8	—	11
2-Methylbutane	47	9.3	—	21 ^{f)}

a) The yields are calculated based on the amount of azide. b) R indicates an alkyl group. c) R' indicates a hydrocarbon rest. d) Determined as urethanes. e) *N*-Ethoxalylcyclohexanonimine (20%). f) Total yields of different types of C—H insertion products.

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1) T. Shingaki, M. Inagaki, M. Takebayashi, R. Lebkücher, and W. Lwowski, This Bulletin, **43**, 1912 (1970).

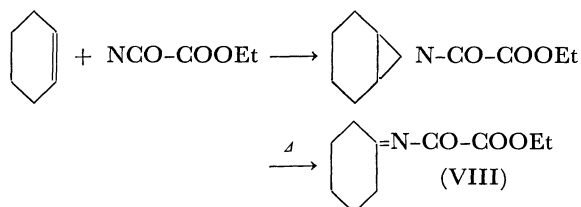


pointed out in the Curtius rearrangement of pivaloyl azide^{2,3}) (Scheme 1).

On the contrary, the formation of IV, V, and VI can be explained by assuming the intermediacy of a carbonylnitrene, ethoxalynitrene (VII), in a manner similar to that of the photolyses of ethyl azidoformate⁴) and pivaloyl azide³) in hydrocarbons (Scheme 2).

In the reaction with alcohols, no insertion products of ethoxalynitrene into C-H bonds of alcohols were recognized in the reaction products (Table 1). This shows that ethoxalynitrene is inserted preferentially into O-H bonds rather than C-H bonds, suggesting the electrophilic character of the nitrene, in analogy with ethoxycarbonylnitrene^{5,6}) and benzoylnitrene⁷).

In the reaction with hydrocarbons, however, products (VI) from the insertion of ethoxalynitrene into different types of C-H bonds were formed, excepting the case of cyclohexene (Table 1). The decomposition of I in cyclohexene gave a 20% yield of *N*-ethoxalylcyclohexanonimine (VIII) in place of insertion products. The product (VIII) may be formed by the addition of ethoxalynitrene to the double bond of cyclohexene, followed by isomerization during gas chromatography at a column temperature.



Dilution Effect. If it is assumed that the nitrene is formed in the singlet state and that part of the nitrene then changes into triplet nitrene before reacting with substrates, the lower the substrate concentration, the greater should be the quantity of triplet nitrene, leading to an increase in the formation of hydrogen-abstraction product (IV). This expectation led us to investigate the effect of the ethanol concentration on

TABLE 2. DISTRIBUTION OF IV AND Va IN THE PHOTOLYSIS OF ETHOXALYL AZIDE AT VARIOUS ETHANOL CONCENTRATION

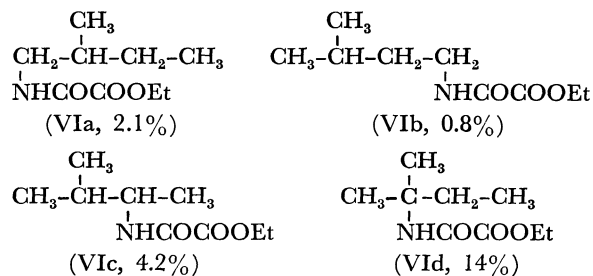
Mole % of ethanol in CH_2Cl_2	Yield of IV ^a) (%)	Yield of Va ^a) (%)	Ratio of IV:Va
64	9.8	26	0.38
15	7.6	8.1	0.94
12	7.8	6.4	1.2
10	13	4.0	3.3
7.9	14	3.8	3.7
5.4	13	3.5	3.7
4.1	14	3.3	4.2
0	2.8	—	—

a) The yields are calculated based on the amount of azide.

the distribution of ethoxamide (IV) and *N*-ethoxyethoxalamide (Va) in the product mixture. Table 2 shows the results of the photolyses of ethoxalyl azide in ethanol-dichloromethane mixtures, employing a 4 : 10 molar ratio of azide to ethanol. The ratio of the yield of IV to that of Va increased with the decrease in the ethanol concentration in dichloromethane. A similar tendency has been observed in the photolyses of ethyl azidoformate in isoprene-dichloromethane mixtures⁸) and of pivaloyl azide in cyclopentane-neopentane (solvent) mixtures.²)

The results indicate that the singlet ethoxalynitrene is inserted into the O-H bond of ethanol to give Va, while the triplet nitrene abstracts hydrogen atoms from ethanol to afford IV.

Reactivities of Ethoxalynitrene toward the C-H Bonds in 2-Methylbutane. When ethoxalyl azide was photolyzed in a dichloromethane solution of 2-methylbutane, four isomeric insertion products (VIa—VIId) were formed in a total yield of 21%.



8) A. Mishra, S. N. Rice, and W. Lwowski, *J. Org. Chem.*, **33**, 481 (1968).

2) G. T. Tisue, S. Linke, and W. Lwowski, *J. Amer. Chem. Soc.*, **89**, 6303 (1967).

3) W. Lwowski, *Angew. Chem.*, **79**, 922 (1967); *ibid. Int. Ed. Engl.*, **6**, 897 (1967).

4) W. Lwowski and T. W. Mattingly, Jr., *J. Amer. Chem. Soc.*, **87**, 1947 (1965).

5) W. Lwowski and R. DeMauriac, *Tetrahedron Lett.*, **1964**, 3285.

6) R. Kreher and G. H. Bockhorn, *Angew. Chem.*, **76**, 681 (1964).

7) L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963).

The division of their yields by the number of hydrogen atoms of each type available gives the relative reactivities of the various sites on 2-methylbutane. The two different sites of primary C-H bonds had nearly the same reactivity, within the limits of the accuracy of our measurements. The reactivities of ethoxalynitrene toward primary (1°), secondary (2°), and tertiary (3°) C-H bonds of 2-methylbutane are summarized in Table 3, those of ethoxycarbonylnitrene⁹ and pivaloylnitrene² toward the same C-H bonds are also cited there for the sake of comparison.

TABLE 3. REACTIVITIES OF ETHOXALYLNITRENE AND OTHER CARBOXYLNITRENES TOWARD THE C-H BONDS IN 2-METHYLBUTANE

Carboxyl nitrene (from photolysis of azide)	Type of C-H bond		
	1°	2°	3°
N-CO-COOEt	1	6.6(±11%) ^a	43(±14%)
N-CO-OEt	1	9 (±10%)	34(±5%)
N-CO-C(CH ₃) ₃	1	8.6(±10%)	160(±25%)

a) The relative errors appear in parentheses.

The results indicate that the reactivity of ethoxalynitrene is more selective than that of ethoxycarbonylnitrene, because of the larger resonance stabilization of the former.

Experimental

The IR spectra were recorded on a Hitachi EP-S spectrophotometer, and the NMR spectra were taken on a Hitachi R-20 instrument, using tetramethylsilane as the internal standard. Gas chromatography (vpc) was done on Yanagimoto GCG-3DH and GCG-5DH units, employing the following adsorbents: A, 10% Dioctyl phthalate on Neopak 1A (40~60 mesh); B, 15% Polyethylene glycol succinate on Neopak 1A (40~60 mesh). Quantitative analyses by vpc were carried out by calibrating the detector response for the compound in question by injecting known volumes of standard solutions and aliquots of the reaction mixture. Tests for the decomposition of samples during vpc analysis were made by collecting all the effluent in a dry ice-methanol trap, and by reinjecting. If no new vpc peaks appeared and no significant change was observed in the relative size and height of the peaks, decomposition was regarded as being absent.

Materials. Ethoxyl azide (I) has been described in the literature¹⁰, but the preparation of I from sodium azide and ethoxalyl chloride is much superior to the method reported in Ref. 10. Ethoxalyl chloride (29 g, 0.2 mol) dissolved in 60 g of dichloromethane was dropped, over a period of 0.5 hr, into a vigorously stirred solution of sodium azide (16 g, 0.24 mol) in 90 ml of water at -5~0°C. After the mixture had been stirred at 0°C for another 3 hr, the layers were separated, the aqueous layer was extracted with 20 ml of cold dichloromethane, and the combined

dichloromethane solution was washed twice with a 10% sodium carbonate solution and water as soon as possible. The dichloromethane solution was dried repeatedly over anhydrous sodium sulfate at the dry ice-methanol temperature until a clear solution was obtained. Since free ethoxalyl azide, like other carbonyl azides of a low molecular weight, was predicted to be explosive at room temperature, the formation of ethoxalyl azide in the solution was confirmed by the reaction with ethanol at 35°C to give *N*-ethoxycarbonylurethane (IIIa), the yield of azide was observed to be 50~60% by the measurement of nitrogen evolved during the reaction. The dichloromethane solution of azide may be preserved for a couple of days at the dry ice-methanol temperature.

The alcohols and hydrocarbons, except for cyclohexene, were purified according to published directions¹¹. Cyclohexene was prepared from cyclohexanol¹² and was then purified. The purities of the substrates and solvents were sufficiently proved by vpc.

Photolysis of I in Alcohols. About 50 g of a dichloromethane solution of I (about 0.04 mol), prepared by the reaction of 9.6 g (0.07 mol) of ethoxalyl chloride with 5.3 g (0.08 mol) of sodium azide, was placed in an irradiation vessel immersed in a dry ice-methanol mixture, and then 1.0 mol of an alcohol was added to the solution with stirring. After being flushed with dry nitrogen, the mixture was irradiated. When the evolution of nitrogen was over, the solvent was removed at room temperature under a 1-mmHg pressure, and the residue was distilled at 30~150°C under a 1×10⁻²-mmHg pressure. The distillate was analyzed by vpc using the A adsorbent, the structures of the products were determined by means of elemental analyses and by measurements of IR and NMR spectra.

In the photolysis of I (6 g, 0.042 mol) in ethanol, *N*-ethoxycarbonylurethane (IIIa), ethoxalamide (IV), and *N*-ethoxyethoxalamide (Va) were obtained in yields of 3.0 g (45%), 0.48 g (9.8%), and 1.8 g (26%) respectively. In the photolysis of I (5.6 g, 0.039 mol) in 2-propanol, *N*-isopropoxycarbonylurethane (IIIb), IV, and *N*-isopropoxyethoxalamide (Vb) were isolated in yields of 3.1 g (45%), 0.73 g (16%), and 1.5 g (22%) respectively. These products showed the following physical properties.

N-Ethoxycarbonylurethane (IIIa): mp: 49~50°C. IR (KBr, cm⁻¹): 3220 (NH); 1750 (C=O); 1210 (C-O). NMR (CCl₄, τ): 1.83 (NH, bs); 5.79 (C-CH₂, 4H, q); 8.70 (CH₃, 6H, t). Found: C, 44.71; H, 6.88; N, 8.69%. Calcd for C₆H₁₁O₄N: C, 44.90; H, 7.13; N, 8.60%.

N-Isopropoxycarbonylurethane (IIIb): IR (CCl₄, cm⁻¹): 3250 (NH); 1770, 1727 (C=O); 1380, 1360 (Me₂CH); 1215, 1200 (C-O).

NMR (CCl₄, τ): (CH₃)₂CH-OCO-NH-COO-CH₂-CH₃
8.73 5.06 1.98 5.84 8.70
(d) (h) (bs) (q) (t)

Found: C, 47.56; H, 7.29; N, 7.78%. Calcd for C₇H₁₃O₄N: C, 47.99; H, 7.48; N, 8.00%.

Ethoxalamide (IV): mp: 114°C. IR (KBr, cm⁻¹): 3350, 3200 (NH); 1735, 1685 (C=O); 1215 (C-O). NMR (CDCl₃, τ): 3.10 (NH₂, bs); 5.62 (O-CH₂, q); 8.60 (CH₃, t). Found: C, 41.31; H, 6.12; N, 11.91%. Calcd for C₄H₇O₃N: C, 41.99; H, 6.03; N, 11.96%.

N-Ethoxyethoxalamide (Va): IR (CCl₄, cm⁻¹): 3300 (NH); 1750, 1720 (C=O); 1215 (C-O).

9) W. Lwowski and T. J. Maricich, *J. Amer. Chem. Soc.*, **86**, 3164 (1964); cf. *ibid.*, **87**, 3630 (1965); M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *Tetrahedron Lett.*, **1964**, 2445; D. S. Breslow, T. J. Prosser, A. F. Marcantonio, and C. A. Genge, *J. Amer. Chem. Soc.*, **89**, 2384 (1967).

10) T. Curtius and K. Hochschowender, *J. Prakt. Chem.*, (2) **91**, 415 (1915).

11) A. Weissberger and W. S. Posokauer, "Organic Solvents," in "Technique of Organic Chemistry", Vol. VII, Interscience Publishers, Inc., New York, N. Y. (1935).

12) C. S. Marvel and A. B. Adams, "Organic Syntheses", Coll. Vol. I, (1956) p. 183.

NMR (CCl₄, τ): CH₃-CH₂-ONH-COCOO-CH₂-CH₃
 8.70 6.05 0.15 5.80 8.65
 (t) (q) (bs) (q) (t)

Found: C, 44.31; H, 6.72; N, 8.65%. Calcd for C₆H₁₁O₄N: C, 44.71; H, 6.88; N, 8.69%.

N-Isopropoxyethoxalamide (Vb): IR (CCl₄, cm⁻¹): 3200 (NH); 1770, 1750 (C=O); 1380, 1360 (Me₂CH); 1220 (C-O).

NMR (CCl₄, τ): (CH₃)₂CH-ONH-COCOO-CH₂-CH₃
 8.74 5.80 0.30 5.74 8.62
 (d) (h) (bs) (q) (t)

Found: C, 47.48; H, 7.45; N, 8.07%. Calcd for C₇H₁₃O₄N: C, 47.99; H, 7.48; N, 8.00%.

Photolysis of I in Cyclic Hydrocarbons. To about 50 g of a dichloromethane solution of I (about 0.04 mol), prepared from ethoxalyl chloride (9.6 g, 0.07 mol) with sodium azide (5.3 g, 0.08 mol), we added a mixture of a cyclic hydrocarbon (ten times the molar quantity of the I employed) and about 60 g of dichloromethane (the total amount of dichloromethane was adjusted to thirty times the molar quantity of the I), and then the photolysis was carried out as has previously been described. The isocyanate (II) thus produced was trapped at room temperature under a 1-mmHg pressure in a vessel, cooled by dry ice-methanol, and refluxed for two hr with an adequate amount of ethanol in order to convert it into *N*-ethoxycarbonylurethane (IIIa). The yield of II was estimated from that of IIIa, since the conversion of II into IIIa proceeded quantitatively.

The other products contained in the distillation residue were collected at 30–200°C under a 1 × 10⁻²-mmHg pressure and were analyzed by vpc using the B adsorbent and the corresponding urethanes as standard materials.

In the photolysis (I: 5.4 g, 0.0378 mol) in cyclohexane, *N*-cyclohexylethoxalamide (VI-1), IV, and II were obtained in yields of 1.2 g (16%), 0.17 g (3.7%), and 2.5 g (41%) respectively. In the photolysis (I: 5.7 g, 0.04 mol) in cyclopentane, *N*-cyclopentylethoxalamide (VI-2), IV, and

II were obtained in yields of 1.3 g (17%); 0.17 g (3.7%), and 2.9 g (45%) respectively. In the photolysis (I: 6.0 g, 0.042 mol) in benzene, *N*-phenylethoxalamide (VI-3), IV, and II were isolated in yields of 0.9 g (11%), 0.19 g (3.8%), and 3.3 g (48%) respectively. In the photolysis (I: 6.4 g, 0.045 mol) in cyclohexene, however, 1.8 g (20%) of *N*-ethoxalylcyclohexanonimine (VIII) was obtained, accompanied by 0.28 g (5.3%) of IV, 2.2 g (43%) of II, and 3 g of an unidentified tarry substance.

The physical properties of VI-1, VI-2, VI-3, and VIII are shown below.

N-Cyclohexylethoxalamide (VI-1): mp: 145°C. IR (KBr, cm⁻¹): 3300 (NH); 1735, 1655 (C=O); 1205 (C-O). NMR (CCl₄, τ): 2.81 (NH, bs); 5.80 (C-CH₂, q); 6.33 (N-CH, m); 8.65 (CH₃, t). Found: C, 60.01; H, 8.37; N, 7.01%. Calcd for C₁₀H₁₇O₃N: C, 60.28; H, 8.60; N, 7.03%.

N-Cyclopentylethoxalamide (VI-2): IR (CCl₄, cm⁻¹): 3250 (NH); 1730, 1675 (C=O); 1210 (C-O). NMR (CCl₄, τ): 2.65 (NH, bs); 5.3–6.0 (N-CH, m); 5.74 (O-CH₂, q); 7.7–8.8 (ring CH₂, 8H, m); 8.63 (CH₃, t). Found: C, 58.20; H, 8.20; N, 7.60%. Calcd for C₉H₁₅O₃N: C, 58.36; H, 8.10; N, 7.56%.

N-Phenylethoxalamide (VI-3): mp: 66°C. IR (KBr, cm⁻¹): 3325 (NH); 3100, 1595 (arom. CH); 1710, 1695 (C=O). NMR (CCl₄, τ): 0.74 (NH, bs); 2.2–2.4, 2.55–3.0 (ring CH, 5H, m); 5.76 (O-CH₂, q); 8.72 (CH₃, t). Found: C, 62.02; H, 5.68; N, 7.22%. Calcd for C₁₀H₁₁O₃N: C, 62.16; H, 5.74; N, 7.25%.

N-Ethoxalylcyclohexanonimine (VIII): IR (CCl₄, cm⁻¹): 1745, 1700 (C=O); 1670 (C=N); 1200 (C-O). No bands of NH and olefinic CH were observed. NMR (CCl₄, τ): 5.68 (O-CH₂, q); 8.60 (CH₃, t); 7.9–8.8 (ring CH₂, 10H, m). No signals expected at the aziridine⁴⁾ and oxazoline¹³⁾ rings were recognized. Found: C, 60.61; H, 7.78; N, 7.21%. Calcd for C₁₀H₁₅O₃N: C, 60.89; H,

TABLE 4. YIELDS OF ETHOXALAMIDES IN REACTION OF ETHOXALYLNITRENE WITH 2-METHYLBUTANE

Azide, mol	Product, g (mol %)				Relative ratio of product		
	VIa (1°)	VIb (1°)	VIc (2°)	VIId (3°)	1°	2°	3°
0.145	0.61 (2.3)	0.23 (0.9)	1.11 (4.1)	3.67 (13.5)	1	5.8	38
0.125	0.51 (2.2)	0.16 (0.7)	0.94 (4.0)	3.04 (13.0)	1	6.2	40
0.135	0.53 (2.1)	0.23 (0.9)	1.11 (4.4)	3.46 (13.7)	1	6.6	41
0.141	0.52 (2.0)	0.18 (0.7)	1.13 (4.3)	3.56 (13.5)	1	7.2	45
0.117	0.42 (1.9)	0.18 (0.8)	0.96 (4.4)	3.26 (14.9)	1	7.3	50
mean	(2.1 ± 9%)	(0.8 ± 12%)	(4.2 ± 5%)	(13.7 ± 9%)	1	6.6 (± 11%)	43 (± 14%)

TABLE 5. IR OF VIa–VIId (CCl₄, cm⁻¹)

	VIa	VIb	VIc	VIId
N-H	{ 3405 1510	3415 1520	3300 1530	3255 1520
C-H	2950	2935	2950	2950
C=O	{ 1712 }	1710	1735 1690	1725 1695
C-N	{ 1290 1270	1295 1275	1295 1275	1305 1287
C-O	{ 1208 1160	1208 1160	1208 1163	1203 1165

13) W. Lwowski and T. J. Maricich, *J. Amer. Chem. Soc.*, **87**, 3630 (1965); cf. M. A. Weinberger and R. Greenhalgh, *Can. J.*

Chem., **41**, 1938 (1963).

TABLE 6. NMR OF VIa—VIId (in CCl₄, τ)

9.03(d)CH ₃	} CH—CH ₂ —CH ₃ 9.01(t) (VIa)	8.2—8.7 (m)	NH—CO·CO·O—CH ₂ —CH ₃ 8.60(t)
6.83(d)CH ₂			
3.06(bs)			5.73(q)
9.08(d)	{ CH ₃ } CH—CH ₂ —CH ₂ 6.84(t) (VIb)	8.2—9.3 (m)	NH—CO·CO·O—CH ₂ —CH ₃ 8.64(t)
			2.53(bs) 5.75(q)
9.06(d)	{ CH ₃ } CH—CH—CH ₃ 8.88(d) (VIc)	8.28 (mc)	NH—CO·CO·O—CH ₂ —CH ₃ 8.64(t)
			2.93(bs) 5.79(q)
8.69(s)	{ CH ₃ } C—CH ₂ —CH ₃ 9.14(t) (VIId)	8.27(q)	NH—CO·CO·O—CH ₂ —CH ₃ 8.64(t)
			3.18(bs) 5.80(q)

TABLE 7. ANALYTICAL DATA OF VIa—VIId

		C	H	N
Found (%):	VIa	57.51	9.10	7.62
	VIb	57.29	9.10	7.52
	VIc	57.48	9.17	7.49
	VIId	57.65	9.20	7.60
Calcd (%) for C ₉ H ₁₇ O ₃ N:		57.73	9.15	7.48

7.67; N, 7.10%.

Dilution Effect. Dilution experiments were carried out, keeping the molar ratio of azide to ethanol at 4 : 10 (0.084 : 0.20 mol) and using dichloromethane as the diluent. For the quantitative determination of the products, the crude reaction mixture was injected into the vpc apparatus.

Photolysis of I in 2-Methylbutane (Reactivities of Ethoxalynitrene toward C—H Bonds). A solution of 2-methyl-

butane (72 g, 1.0 mol) in 85 g of dichloromethane was added to 115 g of a dichloromethane solution of I (about 0.12 mol) on cooling, after which the mixture was irradiated as has been described. The reaction products were fractionated into two portions, as has been described in the case of cyclic hydrocarbons. The one fraction obtained under a 1-mmHg pressure gave 9.1 g (47%) of II. The other fraction, obtained under a 1×10^{-2} -mmHg pressure, was analyzed by vpc on a column containing the B adsorbent at 160°C, using *N*-cyclohexylethoxalamide as the standard material.

Four isomeric ethoxalamides, VIa—VIId, were obtained in a total yield of 21%, besides 1.3 g (9.3%) of IV. The yields of the four isomers were determined by assuming that the detector response is nearly the same for VIa—VIId, and were taken as the bases for the calculation of the relative reactivities in Table 3. The results are arranged on Table 4, while the physical and analytical data of VIa—VIId are shown in Tables 5, 6, and 7.