Table II. Partial Mass Spectrum of 1,2-Di(2-isobutyl-4,5-diphenylimidazoyl)ethane (**24**) at 70 ev

m/e	% of largest peak	*m/e*	% of largest peak	Metastable peaks and transition assignments *m/e*	Transition
579	44.7	269	20.8	550	578 → 563
578	100.0	261	49.0	505–506	563 → 535
523	20.4	260	51.2	495–496	578 → 535
304	26.0	259	83.0	158.5	578 → 303
303	81.0	247	23.4		
302	39.5	246	38.2		
301	20.4	245	37.4		
289	33.6	244	24.6		
288	20.0	234	76.7		
287	24.2	233	81.0		
276	22.9	232	34.0		

crystallized from acetone to give colorless rectangles, mp 269–271°. The nmr (multiplet at δ 7.26, Ar*H*, singlet at 3.78, N–CH_2–, multiplets at 1.80–2.30, C*H*CH_2, doublet at 0.90, CH(CH_3)$_2$), infrared (KBr disk, strong absorptions at 2970, 1600, 760, and 690 cm^{-1}), and ultraviolet (λ_{max} 257.5 mμ (ϵ 23,400), λ shoulder 268 mμ (ϵ 21,100)) spectra were consistent with a 1-substituted 4,5-diphenylimidazole dimer, assigned the structure 1,2-di(2-isobutyl-4,5-diphenylimidazoyl)ethane (**24**). The mass spectrum (Table II) at 70 ev was consistent with the structure assigned.

Anal. Calcd for $C_{42}H_{42}N_4$: C, 83.06; H, 7.37; N, 9.68; mol wt, 578. Found: C, 82.93; H, 7.31; N, 9.81; mol wt, 523 (chloroform).

Photolysis of 2,3-Diphenyl-5,5,6,6-tetramethylpyrazine (39). A solution of 915 mg of 2,3-diphenyl-5,5,6,6-tetramethylpyrazine (**39**) in 420 ml of absolute ethanol was photolyzed using a Pyrex-filtered high-pressure lamp for 2.5 hr. The residue remaining after solvent evaporation was chromatographed on 15 g of silica gel.

Elution with 2% ether–benzene gave 71 mg (9% recovery) of **39**.

Elution with 5% ether–benzene gave 474 mg (60% yield) of crystalline solid which was recrystallized from Skelly B and sublimed at 80° (0.15 mm) to give colorless needles, mp 86.5–88.5°. The nmr (multiplet at δ 7.40 (relative area 10), Ar*H*, singlet at 5.48 (relative area 1), C*H*, broad singlet (removed by shaking with D_2O) at 3.14 (relative area 1), NH, singlet at 1.62 (relative area 3), CH_3, and singlet at 1.48 (relative area 3), CH_3), infrared (strong absorptions at 2980, 1635, 1500, and 1450 cm^{-1}), and ultraviolet (λ_{max} 245 mμ (ϵ 12,500)) spectra of the photoproduct are consistent with the assigned structure, 2,2-dimethyl-4,5-diphenyl-3-imidazoline (**40**). The mass spectrum (Table III) was consistent with the assigned imidazoline structure.

Table III. Partial Mass Spectrum of 2,2-Dimethyl-4,5-diphenyl-3-imidazoline at 13 ev

m/e	% of largest peak
250	2.8
248	3.1
235	4.7
148	12.7
147	100.0
145	10.0

Anal. Calcd for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19; mol wt, 250. Found: C, 81.70; H, 7.38; N, 11.06; mol wt, 271.

The presence of *ca.* 9% 2,2-dimethyl-4,5-diphenylisoimidazole was shown by nmr analysis of the crude reaction mixture.

Dehydrogenation of 2,2-Dimethyl-4,5-diphenyl-3-imidazoline (40). A sample of 120 mg of purified 2,2-dimethyl-4,5-diphenyl-3-imidazoline was heated with an equimolar quantity of elemental sulfur for 3 hr at 95° and 1 hr at 125°.[66] The sample was dissolved in ether, the unreacted sulfur was removed by filtration, and the solvent was removed under reduced pressure to leave 100 mg (83% yield) of pinkish crystals. The nmr, infrared, and ultraviolet spectra were identical with those of 2,2-dimethyl-4,5-diphenylisoimidazole (**41**). The compound was sublimed to give colorless needles, mp 78–79.5° (lit.[62] 78–79°). A mixture melting point with authentic **41** was undepressed.

Acid Hydrolysis of 2,2-Dimethyl-4,5-diphenyl-3-imidazoline (40). A sample of 220 mg of 2,2-dimethyl-4,5-diphenyl-3-imidazoline was hydrolyzed by heating for 1 hr in a few milliliters of 2 *N* hydrochloric acid. The solution was neutralized with sodium carbonate and the impure desylamine was collected by filtration; mp 85–90° (lit.[66] 109°).

A sample of the hydrolysis product was dissolved in warm dilute hydrochloric acid and aqueous picric acid was added. The precipitate was recrystallized from water to give yellow needles, mp 185–186° dec. A mixture melting point with authentic desylamine picrate was undepressed.[67] The infrared spectrum of this picrate was identical with that of the authentic sample.

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[66] F. Asinger, M. Thiel, and R. Sowada, *Monatsh. Chem.*, 90, 402 (1959).

[67] R. Pschorr and F. Bruggemann, *Ber.*, 35, 2740 (1902).

Thermal Reactions of Azidoformates

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Abstract: Kinetic studies have shown that azidoformates decompose thermally in a variety of solvents in a clean first-order reaction, the rate-determining step being evolution of nitrogen and formation of a nitrene. The nitrene reacts with saturated hydrocarbons by insertion into a C–H bond and by abstraction of two hydrogen atoms from adjacent carbons. The insertion reaction is highly selective, the primary:secondary:tertiary reactivity being in the ratio of 1:10:32. The mechanisms of these reactions are discussed.

In a search for new reactions of saturated hydrocarbons, our attention was focused on the reactions of several of Curtius's "starre" or nonrearranging azides: azidoformates, sulfonyl azides, and aryl azides.[1] It was felt that, if these compounds decompose by loss of nitrogen and formation of an electron-deficient nitrene species, the nitrene might insert into a carbon–hydrogen bond, in analogy to the well-known carbene reaction. If the reaction followed this course, monofunctional compounds could be used to introduce polar groups into saturated hydrocarbon polymers, such as polyethylene and polypropylene, while difunctional derivatives could be used as cross-linking agents for these polymers as

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[1] A. Bertho, *J. Prakt. Chem.*, [2] 120, 89 (1929).

well as for saturated hydrocarbon elastomers, such as ethylene–propylene copolymers and polyisobutylene. Although peroxides can be used to cross-link polyethylene and ethylene–propylene copolymers, free radical reagents are known to degrade polypropylene and polyisobutylene when used in small quantities.[2]

This paper describes our experience with azidoformates.[3] When this work was initiated, the literature was devoid of any pertinent references. Methyl,[4,5] ethyl,[5,6] and *t*-butyl[7] azidoformates had been described, but, except for the work of Curtius and Klavehn[8] on 1,3-dipolar cycloaddition of the azide group to acetylenic compounds, the references described essentially only nucleophilic displacement of the azide group from the azidoformate.[9]

Results

When preliminary experiments showed that the thermal decomposition of an alkyl azidoformate in cyclohexane did indeed give an N-cyclohexylcarbamate as one of the products of the reaction, a study of the kinetics of azidoformate decomposition in a variety of solvents was initiated. The kinetic runs were carried out by determining the increase in pressure at constant volume by means of a transducer connected to a recorder; a read-out device enabled one to take individual points.[10] *n*-Octadecyl azidoformate was chosen because it could be purified by recrystallization, it is safe,[11] and its low volatility simplified the kinetics; tetramethylene bis(azidoformate) was chosen as a difunctional compound.[11]

A representative run with *n*-octadecyl azidoformate in diphenyl ether is illustrated in Figure 1. The reaction is cleanly first order to 95% reaction; at 120°, *n*-octadecyl azidoformate has a half-life of 48.1 min. Table I shows that the rate constant is independent of concentration at two different temperatures and that gas evolution is essentially quantitative. Tetramethylene bis(azidoformate), in which the two azidoformate groups are separated by only four carbon atoms, gives practically the same rate. The aromatic bis(azidoformate), 2,2-bis(4-azidocarbonyloxyphenyl)propane, is slightly less stable; at 120° it has a half-life of 33.4 min. For the decomposition of both the *n*-octadecyl and the tetramethylene azidoformates $\Delta H^{\ddagger}$ is 29.9 kcal/mole and $\Delta S^{\ddagger}$ is +4.7 eu.

The first-order decomposition of azidoformates is unaffected by a wide variety of reagents. Potassium *t*-butoxide, *p*-toluenesulfonic acid, fatty acid salts of divalent calcium, zinc, cadmium, copper, lead, manganese, cobalt, and nickel, titanium(IV) naphthenate, and aluminum and magnesium acetylacetonates at the 10 mole % level, as well as equal weights of carbon black and calcium carbonate, had no effect on the rate of thermal decomposition of *n*-octadecyl azidoformate in diphenyl ether.

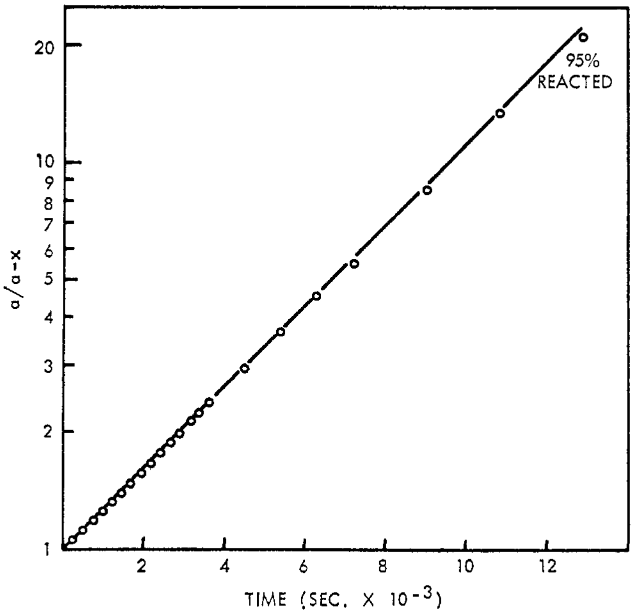

Figure 1. Decomposition of 0.1 *M* *n*-octadecyl azidoformate in diphenyl ether at 120°.

Table I. Decomposition of Azidoformates in Diphenyl Ether

Azido-formate	Concn, *M*	Temp, °C	$k_1 \times 10^4$ sec^{-1}	N_2 evolved, % of theory
ODAF[a]	0.02	133.3	8.70	98.5
	0.10	133.3	9.00	99.5
	0.02	120.0	2.44	97.4
	0.10	120.0	2.40	100
	0.10	100.0	0.267	102.7
TBAF[b]	0.02	133.3	8.48	
	0.10	133.3	9.00	97.0
	0.02	120.0	2.26	98.2
	0.10	120.0	2.34	
	0.10	100.0	0.261	101
BPAF[c]	0.02	120.0	3.46	97.5

[a] *n*-Octadecyl azidoformate. [b] Tetramethylene bis(azidoformate). [c] 2,2-Bis(4-azidocarbonyloxyphenyl)propane.

Table II lists the first-order rate constants for the decomposition of *n*-octadecyl azidoformate in a variety of solvents. Good first-order plots were obtained to better than 75% reaction in most of these solvents; deviations from first order were observed in the fatty acid after 50% and in 2-heptanone after 65%. Since the excess gas in the fatty acid run was identified as carbon dioxide, apparently a concurrent reaction disturbed the normal first-order kinetics; the reason for the low gas yield and the poor kinetics in 2-heptanone has not been explained. The less than fourfold variations in rate can undoubtedly be attributed to the widely varied nature of the solvents rather than to different mechanisms.[13]

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(2) G. D. Jones in "Chemical Reactions of Polymers," E. M. Fettes, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 250.

(3) A portion of this work was described in a preliminary communication: T. J. Prosser, A. F. Marcantonio, C. A. Genge, and D. S. Breslow, *Tetrahedron Letters*, 2483 (1964).

(4) T. Curtius and K. Heidenreich, *J. Prakt. Chem.*, [2] **52**, 454 (1895).

(5) A. Bertho, *ibid.*, [2] **116**, 101 (1927).

(6) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93**, 72 (1908).

(7) L. A. Carpino, *J. Am. Chem. Soc.*, **79**, 4427 (1957).

(8) T. Curtius and W. Klavehn, *J. Prakt. Chem.*, [2] **125**, 498 (1930).

(9) See, for example, L. A. Carpino, C. A. Giza, and B. A. Carpino, *J. Am. Chem. Soc.*, **81**, 955 (1959).

(10) We are indebted to Dr. F. A. Fritz for the design and construction of this apparatus.

(11) Ethyl azidoformate and tetramethylene bis(azidoformate) were found to be somewhat shock sensitive. Explosions during distillation of the former have since been reported.[12]

(12) R. J. Cotter and W. F. Beach, *J. Org. Chem.*, **29**, 751 (1964).

(13) Huisgen and Blaschke[14] have recently reported similar results for the thermal decomposition of *n*-propyl azidoformate in anethole,

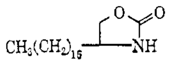
Table II. Decomposition of *n*-Octadecyl Azidoformate in Various Solvents at 120.0°[a]

Solvent	$k_1 \times 10^4$ sec^{-1}	Relative rate	Gas evolved, % of theory
Diphenyl ether	2.40	1	100
Mineral oil	2.15	0.90	103
1-Octadecene	3.76	1.57	97.7
Indene	5.88	2.45	100.8
Bis(2-methoxyethyl) ether	3.32	1.39	101.2
1-Octanol	7.40	3.18	107.2
2-(*n*-Butoxyethoxy)-ethanol	4.04	1.68	91.7
Phenol	3.74	1.56	97.4
C_8–C_{10} fatty acid	2.02	0.84	119
Diethyl sebacate	2.52	1.05	101
2-Heptanone	2.96	1.23	93.8

[a] 0.10 *M* in *n*-octadecyl azidoformate.

To determine the products of the reaction, an attempt was made to obtain a complete material balance in the reaction of *n*-octadecyl azidoformate with cyclohexane. Separations were made using a "Scanalyzer," a liquid–solid chromatographic apparatus in which the polarity of the eluting solvent is increased automatically; the previously described apparatus[15] was modified to monitor fractions by infrared rather than by ultraviolet, as described in the Experimental Section. The results obtained by heating a 1.25% solution of the azidoformate in cyclohexane at 130° are given in Table III; it was gratifying to be able to account for 95% of the initial azide. Fraction I was identified as *n*-octadecyl carbonate, an impurity present in this sample of azidoformate. The major product of the reaction, *n*-octadecyl N-cyclohexylcarbamate (fraction II), is formed by insertion of the nitrene moiety into a C–H bond of cyclohexane. However, there is also a considerable amount of the hydrogen abstraction product, *n*-octadecyl carbamate (fraction III).[16] Fractions I–III were identified by comparison with authentic specimens. Fractions IV and V, which accounted for 12.7% of the initial azide, are isomeric materials which analysis showed to be $C_{19}H_{37}O_2N$; they are therefore intramolecular condensation products of the nitrene. Fraction IV was shown to be 4-*n*-hexadecyl-2-oxazolidinone by comparison of its infrared and nmr spectra with those of an authentic sample of the 4-ethyl derivative. Thus, both compounds showed carbonyl absorption at 1760 cm^{-1}. In very similar nmr spectra, both compounds showed four hydrogens in addition to those in the alkyl side chain, a multiplet (2 H) centered at about τ 6.4 for the two hydrogens adjacent to oxygen, a multiplet (1 H) centered at about τ 5.9 for the one hydrogen adjacent to nitrogen, and a broad line (1 H) for the amide hydrogen at about τ 2.4.

Table III. Reaction of *n*-Octadecyl Azidoformate with Cyclohexane at 130°

		Mole % of initial azide	
Fraction	Product	*m*-C_6H_4-$(NO_2)_2$ absent	*m*-C_6H_4-$(NO_2)_2$ present
I	$[CH_3(CH_2)_{17}O]_2CO$		
II	$CH_3(CH_2)_{17}OCONHC_6H_{11}$	59.8	72.6
III	$CH_3(CH_2)_{17}OCONH_2$	22.6	14.7
IV		5.0	5.0
V	$C_{19}H_{37}O_2N$	7.7	8.1
		95.1	100.4

Although fraction V would be expected to be the corresponding six-membered ring compound, 4-*n*-pentadecyltetrahydro-2H-1,3-oxazin-2-one, comparison with the analogous 4-methyl derivative probably excludes this structure. Thus, the 4-methyl derivative showed carbonyl absorption at 1704 cm^{-1}, while fraction V in various samples absorbed in the 1725-cm^{-1} region. The presence of an absorption band at 3250 cm^{-1} typical of N–H in a secondary amide together with the complete absence of an amide II band indicates a cyclic amide structure. In the nmr spectrum, the 4-methyl derivative showed the expected pattern: a multiplet (2 H) centered at τ 8.14 for the middle methylene hydrogens, a multiplet (2 H) centered at τ 6.64 for the two hydrogens adjacent to oxygen, a multiplet (1 H) centered at τ 5.58 for the one hydrogen adjacent to nitrogen, and a broad line (1 H) for the amide hydrogen at τ 2.76. Fraction V showed only three types of hydrogen in addition to those in the side chain: a broad line (1 H) at τ 6.86, a broad line (2 H) at τ 5.90, and a broad line (1 H) at τ 2.06. The absence of the expected middle methylene peak is not significant, since, if present, it would have been buried under the large side-chain peak. The difficulty arises from the peak for the two hydrogens being downfield from that for the one hydrogen, the direct inverse of the pattern for the 4-methyl derivative. Unfortunately, lack of material precluded further investigation.

On the basis of the assumption that hydrogen abstraction might be a radical reaction, the decomposition of *n*-octadecyl azidoformate in cyclohexane was carried out in the presence of a small amount (0.25% based on cyclohexane) of a potential radical trap, *m*-dinitrobenzene. The results, shown in Table III, were quite surprising. Although the yield of hydrogen-abstraction product was indeed decreased, the yield of insertion product was increased. There was no reaction with the *m*-dinitrobenzene; all the azidoformate added could be accounted for by reaction with cyclohexane or with itself.

That the results with *m*-dinitrobenzene are well outside of experimental error was demonstrated by carrying out the decomposition in methylcyclohexane, without added nitro compound. Although the various insertion isomers were not separated from each other, the yields of the different types of products were prac-

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ethyl 10-undecenoate, benzonitrile, phenylacetylene, diphenylacetylene, diphenyl ether, mesitylene, and paraffin. Although their rates seemed to be about one-third slower than ours and their result in paraffin was abnormal, their rate constants varied by only a factor of 4 in the different solvents.

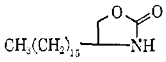
(14) R. Huisgen and H. Blaschke, *Chem. Ber.*, **98**, 2985 (1965).

(15) W. C. Kenyon, J. E. McCarley, E. G. Boucher, A. E. Robinson, and A. K. Wiebe, *Anal. Chem.*, **27**, 1888 (1955).

(16) Lwowski and Mattingly[17] have recently reported a 51% yield of N-cyclohexylurethan and a 12% yield of urethan from the photolysis of ethyl azidoformate in cyclohexane. Huisgen and Blaschke[14] reported a 78% yield of N-cyclohexylurethan in the same experiment, but details are lacking.

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

Table IV. Reaction of *n*-Octadecyl Azidoformate with Cyclohexane and with Methylcyclohexane

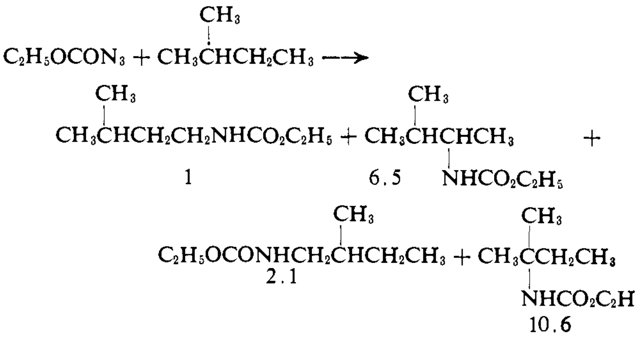
	Mole % of initial azide	
Product	Cyclohexane	Methyl-cyclohexane
$CH_3(CH_2)_{17}OCONHC_6H_{11}$	59.8	. . .
$CH_3(CH_2)_{17}OCONHC_7H_{13}$	. . .	60.4
$CH_3(CH_2)_{17}OCONH_2$	22.6	24.4
	5.0	4.5
$C_{19}H_{37}O_2N$	7.7	7.9

tically identical with those obtained in cyclohexane (Table IV).

Comparable results were obtained in the decomposition of tetramethylene bis(azidoformate) in cyclohexane. Thus, a 32% yield of tetramethylene bis(N-cyclohexylcarbamate), from C–H insertion at both ends, 36% of tetramethylene N-cyclohexyldicarbamate, from insertion at one end and hydrogen abstraction at the other, and 8.6% of tetramethylene dicarbamate, from abstraction at both ends, were isolated. Based on the number of azidoformate groups, 50% of the reaction involved C–H insertion and 27% hydrogen abstraction, in reasonable agreement with the *n*-octadecyl azidoformate results, considering that only 77% of the material was accounted for.

To determine the source of the hydrogen in the unsubstituted carbamate, the decomposition of an 11% solution of *n*-octadecyl azidoformate in cyclohexane was investigated. Cyclohexene was identified in the volatile fraction by mass spectrographic analysis; assuming the same amount of unsubstituted carbamate was formed as in the more dilute reaction, the cyclohexene yield, based on the amount of *n*-octadecyl carbamate formed, was 42%. The low yield is not surprising, in view of the finding by Lwowski and Mattingly[17] that the double bond in cyclohexene reacts with thermally generated ethoxycarbonylnitrene 36 times faster than do the nonallylic methylene groups; in our work no attempt was made to isolate the expected aziridine. No trace of bicyclohexyl could be found by either gas chromatographic or mass spectrographic analysis.

To determine the relative reactivities of different C–H bonds toward insertion, ethyl azidoformate was decomposed in 2-methylbutane, the products being separated by gas chromatography. After correction for the number of hydrogens, the relative reactivities



$$C_2H_5OCON_3 + CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_3 \longrightarrow$$

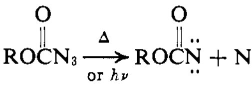
$$\underset{1}{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_2NHCO_2C_2H_5} + \underset{6.5}{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}H\underset{\displaystyle NHCO_2C_2H_5}{\underset{|}{C}}HCH_3} +$$

$$\underset{2.1}{C_2H_5OCONHCH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_3} + \underset{10.6}{CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle NHCO_2C_2H_5}{\underset{|}{C}}}}CH_2CH_3}$$

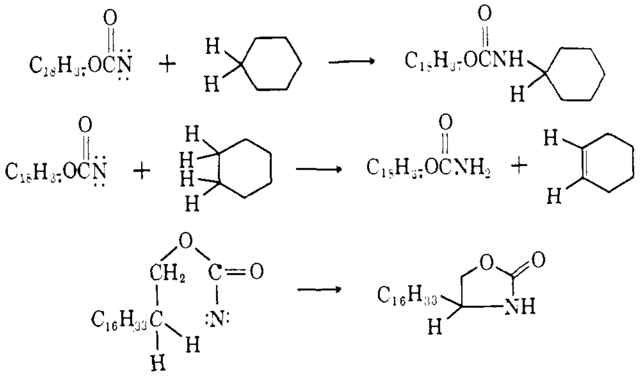
of primary:secondary:tertiary C–H bonds were found to be 1:10:32.

Discussion

There would appear to be little doubt from the kinetic results that the rate-determining step in the thermal decomposition of azidoformates is the loss of nitrogen and the formation of an electron-deficient nitrene species, in complete agreement with the elegant work of Lwowski and his co-workers on the photochemical decomposition. The reaction of *n*-octadecyl azidoformate with cyclohexane can then be pictured as follows·



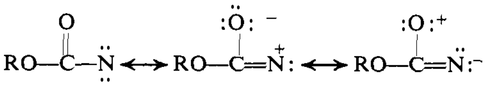
$$RO\overset{\displaystyle O}{\overset{\|}{C}}N_3 \xrightarrow[\text{or } h\nu]{\Delta} RO\overset{\displaystyle O}{\overset{\|}{C}}\ddot{\underset{\cdot\cdot}{N}} + N_2$$



About 65% of the azidoformate undergoes insertion, either intra- or intermolecularly, and about 20% undergoes hydrogen abstraction by a process of removing two hydrogen atoms from adjacent carbons.

Several examples of 2-oxazolidinone formation have been reported recently. Thus, Smolinsky and Feuer[18] obtained a 68% yield of the 4-methyl-4-ethyl derivative by vapor-phase decomposition of 2-methylbutyl azidoformate, conditions under which intermolecular reactions would be minimized. The fact that *t*-butyl azidoformate, upon irradiation in the reactive solvent, *t*-butyl alcohol, cyclizes to the 4,4-dimethyl derivative in 60–75% yield[19,20] is probably a reflection of the well-known *gem*-dimethyl effect, while the complete absence of 2-oxazolidinone in the decomposition of ethyl azidoformate under a variety of conditions[17] is probably a result of the lower activity of a primary as compared to a secondary C–H bond. Although it appears rather unlikely that the unknown isomer in the reaction is the six-membered cyclic carbamate, intramolecular nitrene insertion to give a six-membered ring is not without precedent; several examples of δ-lactam formation by photolysis of carbonyl azides have been reported.[21,22]

The reactivity of a formylnitrene toward insertion into a C–H bond is remarkably independent of its modes of formation. As shown in Table V, essentially identical results are obtained by azide thermolysis, by azide photolysis, and by α elimination. In view of the quite high selectivity found, there must be considerable resonance stabilization of the nitrene, *e.g.*



$$RO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\ddot{\underset{\cdot\cdot}{N}} \longleftrightarrow RO{-}\overset{\displaystyle :\ddot{O}:^{-}}{\overset{|}{C}}{=}\overset{+}{N}: \longleftrightarrow RO{-}\overset{\displaystyle :O:^{+}}{\overset{|}{C}}{=}\ddot{N}:^{-}$$

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(18) G. Smolinsky and B. I. Feuer, *J. Am. Chem. Soc.*, **86**, 3085 (1964).

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

(20) R. Puttner and K. Hafner, *Tetrahedron Letters*, 3119 (1964).

(21) J. W. ApSimon and O. E. Edwards, *Can. J. Chem.*, **40**, 896 (1962).

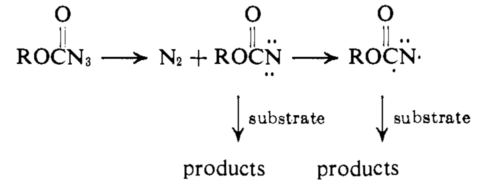
(22) W. L. Meyer and A. S. Levinson, *J. Org. Chem.*, **28**, 2859 (1963).

Table V. Insertion of Carbethoxynitrene into the C–H Bonds of 2-Methylbutane

Method of formation	Type of bond Primary	 Secondary	 Tertiary
Azide thermolysis	1	10	32
Azide photolysis[a]	1	9	34
α elimination[a]	1	11	27

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

Some progress is being made in determining the nature of the nitrene, singlet or triplet, responsible for its different reactions. Considering the relatively low temperature at which nitrene can be formed from azide, it is highly likely that nitrene is formed initially as a singlet.[23] This can then react with substrate to give products, or it can decay to ground-state triplet[25]



$$\mathrm{RO\overset{O}{\overset{\|}{C}}N_3 \longrightarrow N_2 + RO\overset{O}{\overset{\|}{C}}\underset{\cdot\cdot}{\ddot{N}} \longrightarrow RO\overset{O}{\overset{\|}{C}}\underset{\cdot}{\ddot{N}}\cdot}$$

which in turn can react with substrate. The facts that tetramethylene bis(azidoformate) cross-links polyisobutylene,[30] whereas radicals are known to lead to degradation,[2] and that the insertion reaction can be highly stereospecific,[18,31] argues for singlet nitrene being involved in C–H insertion. However, recent work with cyanogen azide[32] indicates that a triplet nitrene can insert nonstereospecifically. Thus, the spin multiplicities involved in C–H insertion seem to parallel quite closely those involved in addition to a carbon–carbon double bond. Here, too, Lwowski and McConaghy[33] concluded that both singlet an triplet nitrene add, the former stereospecifically and the latter nonstereospecifically.

There is much less evidence available at present regarding hydrogen abstraction. It seems to be fairly certain from our results that two hydrogen atoms are abstracted from adjacent carbon atoms in a concerted fashion,[34] or at least in rapid consecutive reactions, since the formation of free cyclohexyl radicals would have been expected to lead to the formation of at least some bicyclohexyl. Although there is no *a priori* reason for eliminating the possibility of this being a singlet reaction, it is easier to explain our results with *m*-dinitrobenzene on the basis of hydrogen abstraction involving a triplet nitrene. Although the mechanism of action of nitroaromatics as inhibitors of free-radical reactions may be uncertain, they appear to inhibit by reacting with free radicals.[35] Although the yield of hydrogen abstraction product was indeed reduced by the addition of *m*-dinitrobenzene, all of the azidoformate was accounted for as reaction products with cyclohexane or with itself. If the same nitrene species (singlet or triplet) were responsible for both insertion and abstraction, one would have expected *m*-dinitrobenzene to decrease the insertion yield as well, whereas in actual fact the yield of insertion product in the presence of *m*-dinitrobenzene actually increased over that obtained in its absence. If one assumes that C–H insertion under these conditions involves a singlet nitrene, then hydrogen abstraction probably involves a triplet.

Experimental Section

Preparation of Chloroformates. Several different procedures were used to prepare the chloroformates. *n*-Octadecyl chloroformate was prepared as follows. To 198 g (2 moles) of phosgene in a flask connected to a Dry Ice condenser was added 270.5 g (1 mole) of molten 1-octadecanol over a period of 90 min, the reaction being kept at 5–10° by external cooling. The cooling bath was then removed and the reaction stirred for 5 hr. The Dry Ice condenser was removed and the excess phosgene was allowed to evaporate overnight, the last traces being removed *in vacuo*. A quantitative yield of chloroformate was obtained as a clear yellow oil; the absence of a hydroxyl band in the infrared spectrum indicated the completeness of the reaction.

To 70 ml of carbon tetrachloride in a flask attached to a Dry Ice condenser was added 45 g (0.5 mole) of tetramethylene glycol while 114 g (1.15 moles) of phosgene was passed in. The reaction was kept at 10–15° during the addition, which took 45 min. The reaction mixture was stirred at 15° for an additional 4.5 hr, the Dry Ice condenser was removed, and the solution was refluxed to remove excess phosgene. Stripping the solvent *in vacuo* left 106 g of tetramethylene bis(chloroformate), an essentially quantitative yield. Although pure enough for subsequent reaction, the material could be further purified by distillation, bp 126° (5–6 mm).

A solution of 46 g (0.2 mole) of 2,2-bis(4-hydroxyphenyl)propane in 300 ml of ether was added to 49 g (0.5 mole) of phosgene cooled below 0° in an ice–salt bath. To the stirred and cooled resulting white slurry was then added dropwise 60.5 g (0.5 mole) of dimethylaniline. The mixture was stirred in the cooling bath for an additional hour and allowed to warm to room temperature overnight, and the solvent and excess phosgene were removed *in vacuo*. The residual solid was suspended in 400 ml of ether and poured onto ice, and the organic layer was separated. After being washed once with 5% hydrochloric acid and then with water, the solution was dried over sodium sulfate and the solvent evaporated. There was thus obtained 60 g (85%) of 2,2-bis(4-chlorocarbonyloxyphenyl)propane, mp 93–96°. Recrystallization from heptane gave a 77% yield of product melting at 96.5–98.5°.

Preparation of Azidoformates. A solution of 16.7 g (0.05 mole) of *n*-octadecyl chloroformate in 100 ml of chloroform was added dropwise to a vigorously stirred solution of 6.5 g (0.10 mole) of sodium azide in 15 ml of water at room temperature. The reaction mixture was stirred vigorously at room temperature for 3 days, and the organic layer was separated, washed several times with water, and dried over a mixture of magnesium and sodium sulfates. Removal of the solvent yielded 16.5 g (97%) of crystalline *n*-octadecyl azidoformate, mp 37.8–38.8°.

Anal. Calcd for $C_{19}H_{37}N_3O_2$: C, 67.21; H, 10.99; N, 12.38; O, 9.43. Found: C, 67.54; H, 11.07; N, 12.16; O, 9.07. For the kinetic runs, a sample was recrystallized several times from methanol, mp 41.0–41.5°.

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(23) If the law of spin conservation is to be obeyed, a nitrene triplet can be the initial product if singlet azide decomposes into triplet nitrene and triplet nitrogen, or if singlet azide is first converted into triplet azide, which then decomposes into triplet nitrene and singlet nitrogen. Neither path seems very likely at decomposition temperatures in the vicinity of 100°.[24]

(24) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 64, 178 (1964).

(25) Evidence is accumulating that all nitrenes have triplet ground states. This has been demonstrated for HN,[26] NCN,[27] alkyl azides,[28] aryl azides,[29] and sulfonyl azides.[29]

(26) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Co., New York, N. Y., 1950, p 369.

(27) A. G. Anastassiou, *J. Am. Chem. Soc.*, **87**, 5512 (1965).

(28) E. Wasserman, G. Smolinsky, and W. A. Yager, *ibid.*, **86**, 3166 (1964).

(29) G. Smolinsky, E. Wasserman, and W. A. Yager, *ibid.*, **84**, 3220 (1962).

(30) D. S. Breslow, U. S. Patent 3,284,421 (1966).

(31) S. Yamada, S. Terashima, and K. Achiwa, *Chem. Pharm. Bull.* (Tokyo), 13, 751 (1965).

(32) A. G. Anastassiou, *J. Am. Chem. Soc.*, **88**, 2322 (1966).

(33) W. Lwowski and J. S. McConaghy, Jr., *ibid.*, **87**, 5490 (1965).

(34) A referee has suggested that a concerted reaction is unlikely because the two C–H bonds are skew. In view of the rapid interconversion of cyclohexane structures, we do not consider this a valid objection.

(35) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 169.

By the same procedure, tetramethylene bis(chloroformate) was converted into tetramethylene bis(azidoformate) in 96% yield, mp 33° after recrystallization from ethanol–hexane.

Anal. Calcd for $C_6H_8N_6O_4$: C, 31.58; H, 3.53; N, 36.84; O, 28.05. Found: C, 31.57; H, 3.27; N, 37.05; O, 28.19.

2,2-Bis(4-azidocarbonyloxyphenyl)propane was obtained in 92% yield, mp 69–70.5° after recrystallization from ethanol.

Anal. Calcd for $C_{17}H_{14}O_4N_6$: C, 55.74; H, 3.86; N, 22.93. Found: C, 56.29; H, 3.72; N, 23.16.

Kinetic Runs. The reactor consisted of a 200-ml creased flask with a long neck ending in a 29/42 standard-taper female joint. Just below the joint was a side arm closed off by a pressure stopcock, and below this was a glass-enclosed magnet on which the sample cup was set. The entire apparatus was immersed in an oil bath controlled to ±0.01°; the reaction was stirred by a magnetic stirring bar, the stirring magnet drive being placed just below the oil bath. A pressure transducer built into a stainless-steel 29/42 standard-taper male joint was used to determine pressure changes. The flask was connected through the side arm to a thermostated gas buret and also to a 100-cm, closed-end manometer to determine absolute pressure; the entire system could be evacuated or filled with an inert gas.

In operation, the desired volume of solvent was placed in the reactor, and the azidoformate, in a small glass sample cup, was set on the bar magnet. After the transducer was inserted and clamped, the entire apparatus was alternately evacuated to about 2 mm and filled with an inert gas, nitrogen or argon, to a pressure of about 800 mm. Finally, the apparatus was filled with inert gas to a pressure slightly in excess of 1 atm, and the reactor was lowered into the constant-temperature bath. During equilibration, the reactor was vented, as required, to maintain the pressure at about 780 mm. When the pressure had become constant (usually 0.5–1 hr), the bar magnet was retracted, and the sample cup was dropped into the hot solvent. Pressure was recorded automatically on a strip chart recorder set at 2 in./hr. For rapid reactions, the pressure was read manually from a digital read-out system. At the end of the run, the gas formed in the reaction was bled to the thermostated gas buret. After equilibration, the pressure in the system was adjusted to the initial pressure by manipulating the mercury level in the gas buret and the volume was read. The theoretical reaction gas volume was calculated in the usual way from the known sample weight, pressure, and temperature data.

Chromatographic Separations. The products from reaction of the azidoformate with cyclohexane or methylcyclohexane were separated on adsorbent columns 17 cm long and 1.8 cm i.d., consisting of 100 parts by weight of Woelm neutral alumina and 6 parts of water. The two-bottle gradient solvent system comprised about 1500 ml of a relatively nonpolar solvent in a 9.6-cm i.d. bottle and about 550 ml of a more polar solvent in a 5.2-cm i.d. bottle.

The chromatographic separations were made in an automated apparatus which used an infrared spectrophotometer (Perkin-Elmer Infracord Model 237-B) as the detector. This was set to scan over the carbonyl region, 1850–1650 cm^{-1}. This apparatus is similar to the "Scanalyzer" previously described[15] which used an ultraviolet spectrophotometer as the detector. A typical run produced about 250 cuts which were stored in a fraction collector. A strip chart recorded the carbonyl absorbance of each chromatographic cut. Each of the several components of a sample was isolated by appropriately combining the pertinent cuts and evaporating solvents. A weight per cent analysis was obtained; typical recoveries for a 200-mg sample were 95–98 wt %.

Two different solvent systems were used in these chromatographic separations. One system used 0.4 vol % ethanol in chloroform in the larger bottle and 1.6 vol % ethanol in chloroform in the smaller bottle (ethanol-free chloroform was obtained by passing Mallinckrodt's analytical reagent chloroform through an alumina column). This system gave good separation of fractions I–III but did not resolve fractions IV and V (Table III); the presence of these two materials in a combined elution band was readily apparent because of the difference in carbonyl frequencies, 1760 *vs.* 1730 cm^{-1}.

In the early work, this mixture of fractions IV and V was separated by rechromatographing, again on the alumina and 6% water column, using *n*-heptane as the nonpolar solvent and 10 vol % of *t*-butyl alcohol in *n*-heptane as the polar solvent. In later work, however, complete resolution of all five components in the monoazidoformate–hydrocarbon reaction mixture was achieved using a solvent mixture consisting of 1 vol % of acetonitrile in carbon tetrachloride in the larger bottle and 20 vol % of acetonitrile in carbon tetrachloride in the smaller bottle.

Reaction of *n*-Octadecyl Azidoformate with Cyclohexane. *n*-Octadecyl carbamate was prepared by passing ammonia into a cold solution of 1 g of *n*-octadecyl chloroformate in 250 ml of ether. Filtration to remove ammonium chloride, evaporation of the solvent, and recrystallization of the residue from aqueous acetone yielded 1.2 g (82% of theory) of product, mp 101.5–103°.

Anal. Calcd for $C_{19}H_{39}O_2N$: C, 72.78; H, 12.54; N, 4.47. Found: C, 72.68; H, 12.54; N, 4.56.

n-Octadecyl N-cyclohexylcarbamate was prepared by refluxing a solution of 2.71 g (10 mmoles) of 1-octadecanol, 1.38 g (11 mmoles) of cyclohexyl isocyanate,[36] and 0.27 g of triethylamine in 25 ml of chloroform. Removal of solvent and recrystallization from acetone yielded 3.26 g (83% of theory) of white solid, mp 68.5–69.5°.

Anal. Calcd for $C_{25}H_{49}O_2N$: C, 75.88; H, 12.48; N, 3.54. Found: C, 75.98; H, 12.87; N, 2.94.

4-Ethyl-2-oxazolidinone was prepared in 47% yield from 2-amino-1-butanol and ethyl carbonate according to the procedure of Homeyer,[37] bp 129–131° (0.5 mm), $n^{20}D$ 1.4637, mp 17° (lit.[37] $n^{20}D$ 1.4631, mp 16.0–16.5°).

Anal. Calcd for $C_5H_9O_2N$: N, 12.17. Found N, 12.20.

4-Methyltetrahydro-2H-1,3-oxazin-2-one was prepared in the same fashion from 3-amino-1-butanol. Recrystallization from acetone gave a 39% yield of product, mp 98.5–99.5° (lit.[38] mp 91°).

Anal. Calcd for $C_5H_9O_2N$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.13; H, 7.89; N, 12.14.

Solutions of 1.00 g (2.95 mmoles) of *n*-octadecyl azidoformate in 100 ml of cyclohexane (Eastman Kodak Spectro Grade) were heated at 130° under nitrogen in capped pressure bottles for 16 hr. Eight such runs were combined, using chloroform to rinse the bottles. Removal of the solvent *in vacuo* left 8.745 g of solid.

The acetonitrile–carbon tetrachloride solvent system gave five fractions (Table III). Fraction I (1.9 wt %) had an infrared spectrum very similar to that of decyl carbonate; it is presumably octadecyl carbonate, present as a minor impurity in the azidoformate, and the yield calculations were corrected accordingly. Fraction II (62.6 wt %) analyzed correctly for *n*-octadecyl N-cyclohexylcarbamate, and its melting point and infrared spectrum agreed with those of an authentic sample. In the same way fraction III (18.7 wt %) was identified as *n*-octadecyl carbamate. Fraction IV (4.1 wt %) was identified as 4-*n*-hexadecyl-2-oxazolidinone, mp 60.5–62° after recrystallization from aqueous acetone.

Anal. Calcd for $C_{19}H_{37}O_2N$: C, 73.25; H, 11.97; N, 4.50; mol wt, 311. Found: C, 72.94; H, 12.10; N, 4.36; mol wt (Rast), 295.

The infrared and nmr spectra of fraction IV were very similar to those of 4-ethyl-2-oxazolidinone. Fraction V (6.7 wt %), mp 75.5–77° after recrystallization from aqueous acetone, was an isomer of fraction IV.

Anal. Calcd for $C_{19}H_{37}O_2N$: C, 73.25; H, 11.97; N, 4.50; mol wt, 311. Found: C, 73.45; H, 12.25; N, 4.43; mol wt (Rast), 309.

To determine the source of the hydrogen in the unsubstituted carbamate, 1.00 g of *n*-octadecyl azidoformate was decomposed in 10 ml of cyclohexane as described above. Mass spectral analysis showed the presence of 0.30 ± 0.05 mole % of cyclohexene.[39] This corresponds to a 42% yield of cyclohexene, if a 22% yield of unsubstituted carbamate is assumed.

Reaction of *n*-Octadecyl Azidoformate with Cyclohexane in the Presence of *m*-Dinitrobenzene. A solution of 2.00 g of *n*-octadecyl azidoformate and 0.50 g of *m*-dinitrobenzene in 200 ml of cyclohexane was heated for 17 hr at 130° as described above. Removal of solvent left 2.750 g of residue.

Chromatographic separation of the product gave fractions II–V; *n*-octadecyl carbonate, previously separated as fraction I, was apparently absent from this sample of azidoformate. Fraction II, *n*-octadecyl N-cyclohexylcarbamate, did contain a yellow contaminant which did not shown carbonyl absorbance. Rechromatographing on a similar column, using carbon tetrachloride and 5 vol % of diethyl ether in carbon tetrachloride in the 9.6- and 5.2-cm

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(36) A. Skita and H. Rolfes, *Ber.*, **53B**, 1248 (1920).

(37) A. H. Homeyer, U. S. Patent 2,399,118 (1946).

(38) A. M. Paquin, *Z. Naturforsch.*, 1, 518 (1946).

(39) We are indebted to P. W. Shearer of this laboratory for this determination. Since cyclohexane has a small peak contribution at M − 2 (*m/e* 82, the parent ion for cyclohexene), a fresh calibration sample of cyclohexane (Eastman Kodak Spectral Grade) was run immediately preceding the questioned samples. This calibration pattern was then used to apply the proper correction on the M − 2 (*m/e* 82) peak, leaving the residual *m/e* 82 free for calculating cyclohexene. Relative sensitivities for constituents reported were based on our instrumental parameters.

bottles, respectively, separated the yellow contaminant from fraction II. Infrared indicated that most of this contaminant was *m*-dinitrobenzene, but unidentified material was present also. Fractions II–V were identical by infrared with the analogous components discussed above and accounted for 100.4 mole % of the initial azidoformate. Thus, the contaminants, 14.2 wt % of the sample, apparently were not derived from the azidoformate.

Reaction of *n*-Octadecyl Azidoformate with Methylcyclohexane. Solutions of 1.00 g of azidoformate in 100 ml of methylcyclohexane were treated as described above. From eight runs, 8.20 g of yellow-white solid was obtained.

Chromatographic separative analysis of the reaction product also produced five fractions (Table IV). Fraction I was *n*-octadecyl carbonate (2.5 wt %). Fraction II was a mixture of isomeric *n*-octadecyl N-methylcyclohexylcarbamates (66.1 wt %).

Anal. Calcd for $C_{26}H_{51}O_2N$: C, 76.22; H, 12.55; N, 3.42; mol wt, 410. Found: C, 75.74; H, 12.30; N, 3.28; mol wt (Rast), 400.

Rechromatographing fraction II on neutral alumina and 6% water with 2.0 vol % of diethyl ether in petroleum ether (bp 45–70°) in the 9.6-cm solvent bottle and 8.0 vol % of diethyl ether in petroleum ether in the 5.2-cm bottle showed the presence of at least three components. One component (25%) was resolved from the mixed elution band containing the other two. The latter were approximately in the ratio of 2:3 in order of elution. Infrared spectra of these three components showed differences, but these were not readily interpreted in terms of structure. Fractions III (20.4 wt %), IV (3.8 wt %), and V (6.6 wt %) were identical with those described above.

Reaction of Tetramethylene Bis(azidoformate) with Cyclohexane. Tetramethylene bis(carbamate) was prepared from the chloroformate and ammonia in 92% yield according to Rabjohn,[40] mp 197–198°.

Tetramethylene bis(N-cyclohexylcarbamate) was prepared from 1.00 g (11 mmoles) of 1,4-butanediol, 3.20 g (26 mmoles) of cyclohexyl isocyanate,[36] and 2 drops of triethylamine. The resulting white solid was filtered and recrystallized several times from aqueous acetone, yielding 2.66 g of product (71% of theory), mp 178.5–180.5°).

Anal. Calcd for $C_{18}H_{32}O_4N_2$: C, 63.49; H, 9.47; N, 8.23. Found: C, 63.48; H, 9.62; N, 8.94.

Solutions of 1.00 g of azidoformate in 100 ml of cyclohexane were treated as described above. From eight runs there was obtained 9.95 g of yellow-white solid. This material was incompletely soluble in chloroform; 1.00 g gave 53 mg of crystalline solid whose analysis, melting point, and infrared spectrum identified it as tetramethylene bis(carbamate).

Oils and other extraneous matter in the soluble portion of the sample were removed by passage through a chromatographic column of activated charcoal (Darco G60) 10 cm high and 1.8 cm in diameter; 87% of the sample was recovered by chloroform elution. This material was chromatographed on the alumina and 6% water column in the "Scanalyzer" with the ethanol–chloroform solvent system. The first fraction eluted accounted for 38.9 wt % of the original sample. Comparison of analysis, melting point, and infrared spectrum with those of a synthetic sample showed this fraction, recrystallized from acetone–*n*-heptane, was tetramethylene bis(N-cyclohexylcarbamate). It accounted for 32.3 mole % of the initial azidoformate.

The second fraction eluted in the "Scanalyzer" run, 35.9 wt %, was indicated by its infrared spectrum to be tetramethylene N-cyclohexylcarbamate.

Anal. Calcd for $C_{12}H_{22}O_4N_2$: C, 55.79; H, 8.58; N, 10.85. Found: C, 55.98; H, 8.73; N, 10.79.

The infrared spectrum indicated the presence of both $-CONH_2$ and $-CONHC_6H_{11}$. The same four N–H bands shown by tetramethylene bis(carbamate) at 3410, 3300, 3245, and 3200 cm^{-1} were present, indicating NH_2. Except for the 3300-cm^{-1} band, these bands were in the correct ratios of intensities. The more intense 3300 cm^{-1}, which was exhibited also by the tetramethylene bis(N-cyclohexylcarbamate), indicated the presence of $-NHC_6H_{11}$ in this second fraction. Corroborating evidence for the $-CONH_2$ grouping was the amide II band at 1615 cm^{-1}. The presence of a $-CONHC_6H_{11}$ grouping was indicated by the amide II band at 1530 cm^{-1}.

An additional elution band containing at least two components (two carbonyl bands at 1760 and 1700 cm^{-1}) was isolated. Limited work on rechromatographing this mixed fraction was unsuccessful in attaining adequate separation.

Reaction of Ethyl Azidoformate with 2-Methylbutane. Isoamylamine, 2-methylbutylamine, and *t*-amylamine were commercial materials (K & K Laboratories). 2-Amino-3-methylbutane was prepared by the reductive amination of 3-methyl-2-butanone according to the procedure of Schwoegler and Adkins,[41] bp 86.5–86.8°, $n^{25}D$ 1.4032. The amines were then converted to the corresponding urethans by reaction with ethyl chloroformate according to the procedure of Hartman and Brethen.[42] Gas chromatography indicated the compounds to be 94–98% pure without distillation. One sample was purified by preparative-scale gas chromatography and was shown to have an infrared spectrum identical with that of the crude material, indicating that no decomposition had taken place on the chromatographic column.

To determine reactivities, a solution of approximately 1.5 g of ethyl azidoformate in 40 ml of 2-methylbutane was heated for 4 hr at 120° under nitrogen in a 110-ml stainless-steel bomb. The solvent was then stripped and the residue was analyzed by gas chromatography. The results shown in Table V are averages of two runs. The gas chromatographic analyses were carried out on an F & M Model 500 temperature-programmed instrument. A 12-ft stainless steel column packed with UCON 75H on Chromosorb W was used. The initial column temperature was 100°, and this was raised to 200° at a rate of 11°/min. The fact that the two primary isomers were obtained in the expected 2:1 ratio was a good check on the analytical procedure.

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(40) N. Rabjohn, *J. Am. Chem. Soc.*, 70, 1181 (1948).

(41) E. J. Schwoegler and H. Adkins, *ibid.*, **61**, 3499 (1939).

(42) W. W. Hartman and M. R. Brethen, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p 278.