

# The Decomposition of Ethyl Azidoformate in Cyclohexene and in Cyclohexane<sup>1</sup>

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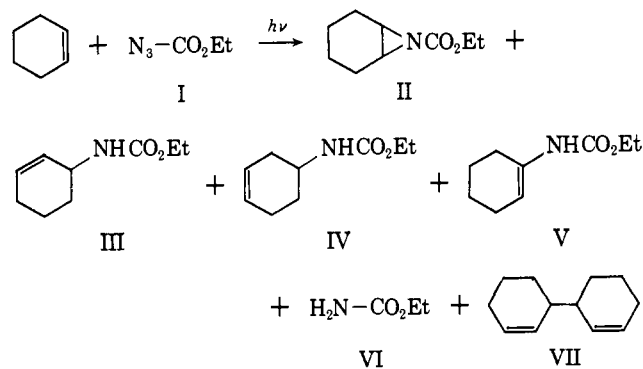
The photolytic and thermal decomposition of ethyl azidoformate in cyclohexene and cyclohexane has been studied. Carboethoxy nitrene, *N*-COOEt, seems to be the reactive intermediate. Products from its addition to the double bond and its insertion into the different types of C-H bonds are formed in good yield, and their distribution has been measured. Identical products are formed in the direct photolysis and the thermolysis. Photosensitized decomposition in cyclohexene gives urethane and 3,3'-bicyclohexenyl, rather than addition or insertion products.

## Introduction

The decomposition of organic azides has often been discussed in terms of an electron-deficient, monovalent, nitrogen intermediate, often called a nitrene.<sup>3</sup> We are studying the decomposition of ethyl azidoformate in various solvents as part of a program designed to elucidate the mechanism of such reactions and to separate intermolecular nitrene reactions from intermolecular reactions involving all three nitrogens of the azide group (azide reactions). This paper deals with the decomposition of ethyl azidoformate in cyclohexene and cyclohexane.

## Results and Discussion

*1. Direct Photolysis.* When a dilute solution of ethyl azidoformate in cyclohexene was irradiated at room temperature, using a low-pressure mercury arc source,<sup>4</sup> nitrogen was smoothly evolved in 80 to 90% yield. Analysis of the reaction mixture, using both fractional distillation and gas-liquid partition chromatographic (g.l.p.c.) techniques, showed the anticipated addition product, the 7-carboethoxy-7-azabicyclo[4.1.0]heptane (II), to be present in about a 50% yield.



(1) Communicated in part: W. Lwowski and T. W. Mattingly, Jr., *Tetrahedron Letters*, 277 (1962).

(2) National Institutes of Health Predoctoral Fellow, 1962-1964.

(3) For a review see R. A. Abramovitch and B. A. Davies, *Chem. Rev.*, **64**, 149 (1964).

(4) The source employed had its maximum (84%) emission at the 2537 Å. resonance line of mercury. At 2540 Å. ethyl azidoformate absorbs with an  $\epsilon$  79.6 (hexane).

The structure of this aziridine (II) was proven by its basic hydrolysis to the known 2-aminocyclohexanol and by the complete identity of its infrared and nuclear magnetic resonance (n.m.r.) spectra, as well as its g.l.p.c. retention time on two different columns, with those of the authentic material.

The two isomeric urethans, 3-cyclohexenylurethan (III) and 4-cyclohexenylurethan (IV), were present in a total yield of about 12%. A third isomer, 1-cyclohexenylurethan (V), was found in trace amounts. The relative ratios and yields of the products under varying reaction conditions are found in Table I. The relative ratios are almost constant; no significant change occurred when oxygen was carefully excluded during the reaction or when the irradiation was carried out at  $-75^\circ$ .

Table I. Photodecomposition of Ethyl Azidoformate in Cyclohexene

Condi- tions	Relative ratios and yields (%) of isomeric urethans					
	II	III	IV	V	VI	VII
A <sup>a</sup>	18.8 (49)	3.2 (8.4)	1.0 (2.6)	0.5 (1)	(3)	(1-6)
B <sup>a</sup>	17.2 (56)	3.2 (9.1)	1.0 (2.9)	0.5 (1)	(<1)	(4)
C <sup>a</sup>	20.7 (75)	3.6 (14.1)	1.0 (3.9)	0.5 (2)	(0)	(7)

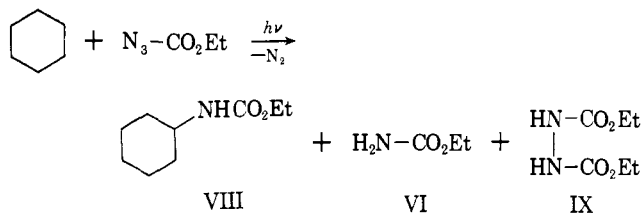
<sup>a</sup> Conditions: A, (38°) peroxide impurities in cyclohexene, oxygen present; B, (38°) under nitrogen in absence of oxygen; and C, ( $-75^\circ$ ) under nitrogen in absence of oxygen; maximum relative error, 9%.

A small amount, about 3%, of urethan VI was found. This yield could be greatly reduced by carrying out the irradiation in the absence of oxygen and totally eliminated by also reducing the temperature to  $-75^\circ$ . Also present was a small but variable yield (1-7%) of 3,3'-bicyclohexenyl (VII) which, contrary to expectations, was apparently unaffected by lowering of the reaction temperature or the removal of oxygen. Often minor amounts (0.5%) of 3-aminocyclohexene were isolated, probably resulting from the decomposition or hydrolysis of II or III. Structure assignments for all products are based on a comparison of their infrared spectra and g.l.p.c. retention times with those of the authentic compounds.

The reaction appears to be truly photolytic. A dilute solution of ethyl azidoformate in cyclohexene after standing for 3 months in the dark still showed strong azide absorption at 2137  $\text{cm}^{-1}$  in the infrared and was found to contain no significant amount of the aziridine II or the isomeric cyclohexenylurethans III, IV, and V when analyzed by g.l.p.c. Any possibility that some or all of the 3- and 1-cyclohexenylurethan arose from rearrangement of the aziridine, rather than from a direct reaction at a carbon-hydrogen bond, was greatly reduced by the observation that no significant

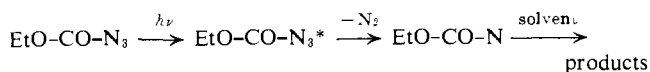
rearrangement of the pure aziridine upon irradiation in cyclohexene occurred. Nor was there any change in the relative amounts of these isomeric urethans upon continued irradiation of the reaction mixture. Control experiments excluded any appreciable rearrangement of this kind on the hot injector block or on the polar column during g.l.p.c. analysis.

When a dilute cyclohexane solution of ethyl azidoformate was irradiated in the absence of oxygen an almost quantitative yield of nitrogen was evolved. Cyclohexylurethan (VIII) was isolated in 51% yield by chromatography of the concentrated reaction mixture on neutral alumina. A 12% yield of urethan VI was also found. In addition, trace amounts of diethyl hydrazodiformate (IX) were present among the products resulting from irradiation of more concentrated solutions of the azide. The products were identified by comparison of their infrared spectra and g.l.p.c. retention times with those of the authentic material.



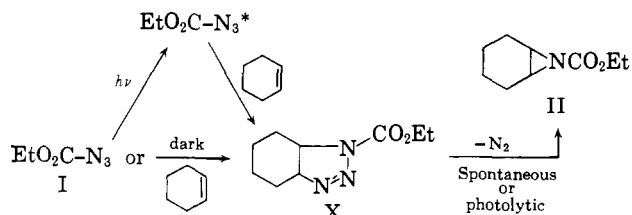
Neither the irradiation in cyclohexene nor that in cyclohexane appears to proceed by a radical chain process. When the light source was shut off, nitrogen evolution ceased immediately, and started rapidly when the irradiation was begun anew. Attempts to initiate the reaction of I with cyclohexane by the addition of the radical initiator diethyl peroxydicarbonate failed. Even when amounts in excess of 1 mole of this peroxide per mole of azide present were added, at most 9% of cyclohexylurethan (VIII) and 6% of urethan VI were obtained. A value of approximately 0.2 was found for the quantum yield of the photolysis of I in cyclohexane.<sup>5</sup>

The formation of the observed products in the photolysis of ethyl azidoformate in the two solvents can formally be explained by a variety of mechanisms which fall into two general groups, depending upon whether the loss of nitrogen occurs before or after the attack upon the solvent. Loss of nitrogen from the azide before reaction with the substrate would generate a nitrene. The nitrene could then react with solvent

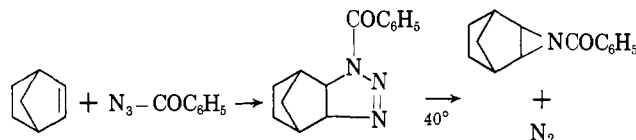


(or rearrange). The other class of mechanisms involves attack of azide, possibly excited azide, on the substrate. This would lead to a transition state or intermediate containing all three azide nitrogens. In particular, triazoline intermediates must be considered for the decomposition in olefins, like cyclohexene. The decomposition of the initially formed triazoline X to the aziridine II might be thermal, photolytic, or possibly due to excess vibrational energy remaining from its formation from the excited azide. Numerous analogies in the literature support such an intermediate triazoline formation. Methyl azidoformate is reported

(5) W. Lwowski and E. Scheiffle, unpublished results.



to add to acetylenedicarboxylate, forming a triazole.<sup>6</sup> Though there is no reported addition of an azidoformate to a double bond, benzoyl azide has been observed to add to the double bond in the strained norbornene ring system to give a triazoline in 87% yield.<sup>7</sup> This triazoline decomposes at temperatures as low as 40°, losing nitrogen to give an aziridine.

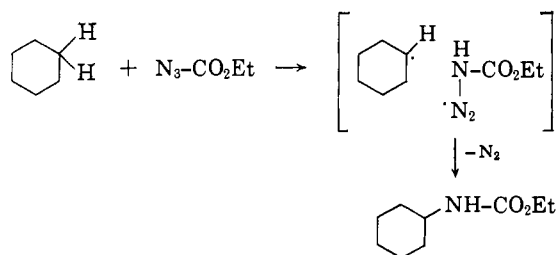


Phenyl azide is known to add to a large number of acetylenes to form triazoles, and to strained or activated double bonds to yield triazolines.<sup>8-12</sup> Most of these triazolines decompose with loss of nitrogen, forming the corresponding aziridine, when heated above 100°. When phenyl azide and styrene, for example, are heated at 100° the major product is 1,5-diphenyl-4,5-dihydrotriazole, which decomposes very rapidly at 130° to the aziridine. Walker and Waters,<sup>13</sup> from their kinetic study of the thermal decomposition of aryl azides in cumene, toluene, styrene, and indene, have calculated that, in the case of the latter two olefins, the activation energy for triazoline formation followed by elimination of nitrogen to yield the aziridine is 15 to 20 kcal./mole lower than that for the aziridine formation by way of an intermediate nitrene.

However, no triazoline was formed prior to irradiation when ethyl azidoformate was added to cyclohexene. The ultraviolet spectrum of the azide was the same whether taken in cyclohexene, hexane, or methanol, and remained so over a long period of time. Therefore, any triazoline formed must result from addition of excited ethyl azidoformate to the olefin. However, no trace of triazoline was found when an irradiation of the azide in cyclohexene at -15° was stopped well before the theoretical amount of nitrogen had been produced. A plot of the volume of nitrogen evolved vs. the infrared absorbance of the azide in the reaction mixture gave a straight line up to about 75% reaction. Thus, if a triazoline intermediate is present, its decomposition must be fast compared to the rate of its formation. Otherwise, nitrogen evolution should lag behind the decrease in azide concentration.

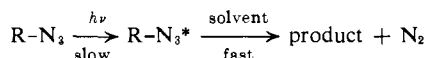
An azide mechanism for the formation of cyclohexylurethan would involve an intermediate ion or radical pair, of a type for which there is no supporting analogy.

- (6) T. Curtius and W. Klavehn, *J. prakt. Chem.*, **125**, 498 (1930).
- (7) R. Huisgen, *Angew. Chem.*, **72**, 359 (1960).
- (8) L. Wolf, *Ann.*, **394**, 30 (1912).
- (9) K. Alder and G. Stein, *ibid.*, **501**, 1 (1933); **515**, 165, 185 (1935).
- (10) K. Alder and R. Rühmann, *ibid.*, **566**, 1 (1950).
- (11) S. J. Davis and C. S. Rondestvedt, Jr., *Chem. Ind.* (London), 845 (1956).
- (12) J. H. Boyer and F. C. Canter, *Chem. Rev.*, **54**, 41 (1954), and references cited therein.
- (13) R. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962).



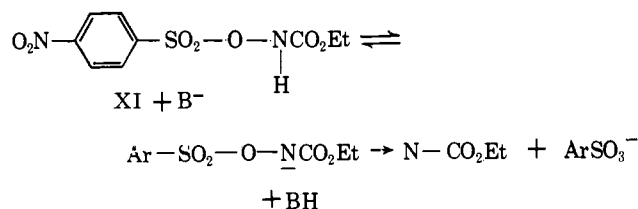
The nitrene mechanism, on the other hand, explains the products as well as, if not better than, any of the other plausible mechanisms and has strong analogy in the reactions of carbenes. In particular, there is an exceptional parallel between the behavior of ethyl azidoformate upon photolysis and that of ethyl diazoacetate.<sup>14-18</sup> This diazo compound, upon irradiation, loses nitrogen to yield carbethoxycarbene which, rather than rearranging to the ethoxyketene, undergoes intermolecular reaction with the solvent. In hydrocarbon solvents carbon-hydrogen bond insertion occurs; with olefins cyclopropane formation is observed; in aromatic solvents addition reactions take place leading to ring expansion to the cycloheptatriene system.

The nitrene mechanism for the reactions discussed above is further supported by a number of other observations. The rate of nitrogen evolution is the same in cyclohexane and cyclohexene, demonstrating that the solvent does not assist in the rate-determining step of the decomposition. This does not exclude a photolytic azide mechanism of the type



However, the rate of thermal decomposition of *n*-octadecyl azidoformate also is independent of the type of solvent<sup>19</sup> supporting a primary formation of a carbalkoxy nitrene.

Even stronger support for the nitrene mechanism is found in the study of the base-induced decomposition, in various solvents, of *N-p*-nitrobenzenesulfonyurethane (XI). All evidence indicates that this reaction yields the carbethoxynitrene by an  $\alpha$ -elimination mechanism such as the following.<sup>20,21</sup>

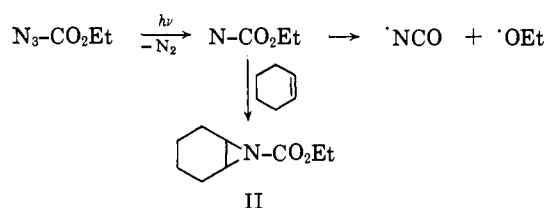


Such decomposition of XI in cyclohexene and cyclohexane, employing triethylamine as a base, led to the same products previously described as resulting from

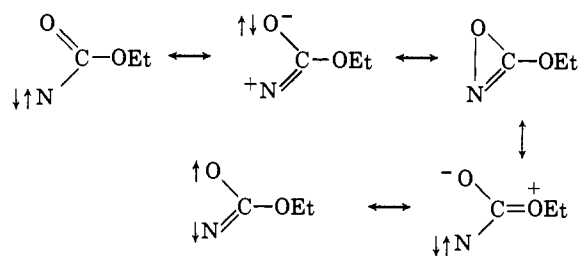
- (14) W. Kirmse, *Angew. Chem.*, **67**, 439 (1955); **73**, 161 (1961).  
 (15) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1963, pp. 82, 110.  
 (16) E. Chinoperos, *Chem. Rev.*, **63**, 247 (1963).  
 (17) W. Doering and L. Knox, *J. Am. Chem. Soc.*, **78**, 4947 (1956); **83**, 1989 (1961).  
 (18) P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961).  
 (19) T. J. Prosser, A. F. Marcantonio, C. A. Genge, and D. S. Breslow, *Tetrahedron Letters*, 2483 (1964).  
 (20) W. Lwowski, T. Maricich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **85**, 1200 (1963).  
 (21) W. Lwowski and T. J. Maricich, *ibid.*, **86**, 3164 (1964).

the photodecomposition of ethyl azidoformate in these solvents. *N*-Carbethoxyazepin is the major product formed when either decomposition is carried out in benzene<sup>20,22</sup>; when acetonitrile is the solvent both reactions yield 2-ethoxy-5-methyl-1,3,4-oxadiazole.<sup>23</sup> Not only are the products identical, but significantly, the ratios of the isomeric urethans obtained by using either nitrene source in cyclohexene<sup>20</sup> and isopentane<sup>21</sup> are quite similar.

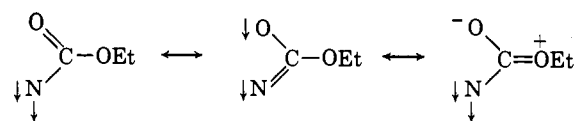
Further support for the intermediacy of this species is found in the study of the flash photolytic decomposition of ethyl azidoformate.<sup>24</sup> When a mixture of the azide and carbon dioxide was flash photolyzed the principal, ultraviolet-absorbing, transient decomposition product was found to be the NCO radical. When the azide was photolyzed in the presence of cyclohexene vapor none of the NCO radical was observed and 7-carbethoxy-7-azabicyclo[4.1.0]heptane (II) was isolated. The authors conclude that the azide loses a molecule of nitrogen to give the unstable and reactive carbethoxy nitrene; this may be trapped if a suitable substrate is present; otherwise its carbon-oxygen single bond breaks yielding the NCO radical.



Accepting a nitrene-type intermediate the question arises as to its electronic state. Is the reacting species a singlet having no unpaired electrons



or is it in a triplet state with two unpaired electrons?



Quantum theory predicts that upon absorption of a photon of irradiation the azide is most probably promoted to an excited singlet state. As the lowest triplet state of elemental nitrogen lies about 140 kcal. above its ground state, nitrogen should be lost from the excited singlet azide in the singlet state, leaving behind a singlet carbethoxy nitrene. In agreement with this conclusion, Berry and Cornell<sup>25</sup> did not observe spectroscopically the formation of any triplet nitrogen upon flash photolysis of ethyl azidoformate. How-

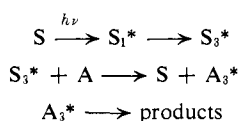
- (22) K. Hafner and C. König, *Angew. Chem.*, **75**, 89 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 96 (1963).  
 (23) W. Lwowski, A. Hartenstein, C. deVita, and R. I. Smick, *Tetrahedron Letters*, 2497 (1964).  
 (24) R. S. Berry, D. Cornell, and W. Lwowski, *J. Am. Chem. Soc.*, **85**, 1199 (1963).  
 (25) D. Cornell, Thesis, Yale University, 1964.

ever, spin conservation rules are less stringent for excited singlet states and, in cases where it is energetically feasible, there is a high probability that the excited nitrene will undergo spin inversion forming a triplet species. Spectroscopic evidence indicates,<sup>26</sup> in agreement with theoretical calculations,<sup>27</sup> that unsubstituted nitrene (N-H) has a triplet ground state, but at the present time there is no compelling reason for preferring a triplet over a singlet ground state for carbethoxy nitrene. It is possible that carbethoxy nitrene could react either in its initially formed singlet state or first decay to a triplet species.

The photolysis, at 77° K. in a glass, of alkyl, aryl, and sulfonyl azides led to the detection of triplet nitrenes by electron spin resonance spectrometry.<sup>28-31</sup> E.s.r. signals were not, however, obtained from azidoformates.

In the reactions of alkyl azidoformates, some dehydrogenation products are always formed.<sup>19, 32-36</sup> A triplet nitrene would be expected to exhibit diradical character and give rise to such dehydrogenation products. Singlet nitrene, however, might also be able to dehydrogenate, and might lead to a triplet radical pair on reactive collision. Thus, no decision as to the electronic multiplicity of the nitrene can be made on the basis of the nature of the reaction products alone.

**2. Photosensitized Decomposition.** An outgrowth of Hammond's study of the mechanism of photosensitization has been the suggestion that in suitable systems the excited triplet state of a species may be obtained directly by use of photosensitizers such as benzophenone.<sup>37-42</sup> A molecule of sensitizer (S) upon



absorption of a quantum of radiation is promoted to an excited singlet state (S<sub>1</sub><sup>\*</sup>) from which it rapidly decays (intersystem crossing) to a long-lived triplet state (S<sub>3</sub><sup>\*</sup>). Such a triplet sensitizer molecule, upon collision with an acceptor molecule (A), may bring about excitation of the acceptor molecule to its triplet

(26) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Co., Inc., Princeton, N. J., 1950, p. 369.

(27) R. A. Abramovitch and V. A. Davies, *Chem. Rev.*, **64**, 178 (1964).

(28) E. Wasserman, G. Smolinsky, and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 3166 (1964).

(29) G. Smolinsky, L. C. Snyder, and E. Wasserman, *Rev. Mod. Phys.*, **35**, 576 (1963).

(30) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3220 (1962).

(31) A. M. Trozolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *ibid.*, **85**, 2526 (1963).

(32) W. Lwowski and L. H. Selman, unpublished results.

(33) M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *Tetrahedron Letters*, 2945 (1964).

(34) J. Prosser, A. F. Marcantonio, and D. S. Breslow, *ibid.*, 2479 (1964).

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

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

(37) G. S. Hammond, Abstracts of the 17th Organic Chemistry Symposium of the American Chemical Society, June 1961, p. 48.

(38) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

(39) D. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Am. Chem. Soc.*, **83**, 2397 (1961); **84**, 1015 (1962), and references quoted therein.

(40) G. S. Hammond and J. Saltiel, *ibid.*, **84**, 4983 (1962); **85**, 2516 (1963).

(41) G. S. Hammond and N. J. Turro, *ibid.*, **85**, 2516 (1963).

(42) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

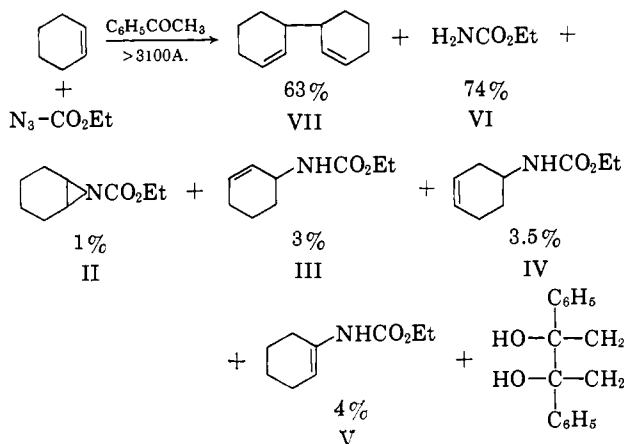
state, the sensitizer itself being reduced to its singlet ground state.

If ethyl azidoformate were to be made the acceptor molecule in such a scheme the excited azide in a triplet state might be produced. This triplet species, if it were to decompose, should lose singlet nitrogen and form carbethoxy nitrene in the triplet state. Ethyl azidoformate is well suited to such a photosensitization reaction. Its ultraviolet absorption has an  $\epsilon$  of only 0.01 at 3200 Å. Benzophenone and similar sensitizers have strong absorption in the region 3200 to 3600 Å.

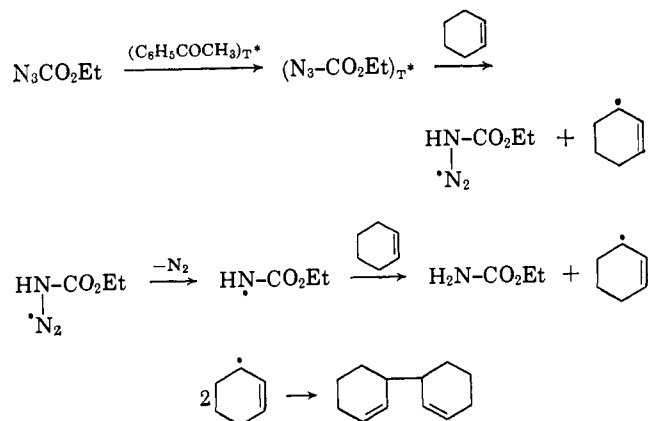
When a solution of ethyl azidoformate and benzophenone in cyclohexene was irradiated in a Pyrex vessel with light of 3100-4100 Å., no significant azide decomposition was observed. The benzophenone was rapidly consumed and benzpinacol and 3,3'-biscyclohexenyl were the only products isolated. Under identical photolytic conditions benzophenone in *t*-butyl alcohol was shown to be rapidly reduced to the pinacol.

Since this lack of photosensitized decomposition might be due to an inefficient sensitization process unable to compete favorably with the rapid photo-reduction of the sensitizer, rather than due to insufficient triplet energy<sup>42</sup> of the sensitizer, phenanthrene was tried as a sensitizer. Even though phenanthrene has a slightly lower triplet energy ( $E_T = 62.2$  kcal./mole as compared with benzophenone,  $E_T = 68.5$  kcal./mole) it has the advantage of forming a much longer lived triplet species which is chemically inert toward cyclohexene. However, phenanthrene also failed to sensitize the azide's decomposition.

Sensitized decomposition was obtained when a cyclohexene solution of the azide and acetophenone (which has a triplet energy of 73.6 kcal./mole) was irradiated under the same conditions. The main products, determined by comparison of infrared spectra and g.l.p.c. retention times with those of the authentic materials, were urethan in 74% and 3,3'-biscyclohexene in 63% yield. The maximum yields of the isomeric cyclohexenylurethans found previously to result from the direct photodecomposition were 1% of 7-carbethoxy-7-azabicyclo[4.1.0]heptane (II), 3% of 3-cyclohexenylurethan (III), 3.5% of 4-cyclohexenylurethan (IV), and 4% of 1-cyclohexenylurethan (V). Some of the sensitizer was consumed as indicated by isolation of some acetpinacol; only 87% of the acetophenone could be recovered.



However, the conclusion that this photosensitized decomposition involves triplet carbethoxy nitrene, and the resulting inference that the direct photodecomposition involves a singlet nitrene, must be qualified. Accepting that the sensitization process does indeed produce an excited azide in the triplet state, the triplet azide itself could react with the solvent to give the observed urethan without first decomposing to a triplet nitrene species.



This sensitized decomposition of ethyl azidoformate seems to be in contrast to the other such photosensitized decomposition of a carbonyl azide reported in the literature. When ApSimon and Edwards<sup>43</sup> decomposed dihydropimaric acid azide, using benzophenone as a photosensitizer, they obtained the same products in identical yields as from the direct irradiation, namely the isocyanate from rearrangement in 58% yield and the cyclic amide from an intramolecular insertion reaction of the proposed nitrene in a sterically favorable methylene group in 26% yield. However, as no experimental or further details were given, it is difficult to judge how authentic a photosensitized reaction this represents.

**3. Thermal Decomposition.** Carbethoxy nitrene can also be generated by thermal decomposition of ethyl azidoformate. When a dilute solution of the azide was decomposed in refluxing cyclohexene (b.p. 83°) nitrogen was smoothly evolved and the same products as found in the photodecomposition were isolated. However, the ratios of the isomeric urethans varied with reaction conditions, the amount of 1-cyclohexenylurethan increasing, apparently at the expense of the aziridine, with increasing reflux time. Thus after a reaction time of 42 hr., at which point no azide absorption was present in the infrared, the ratio of V to II was 1.0 to 7.7. Yet when the reaction time for the same amount of starting material was increased to 118 hr., this ratio was found to be 1.0 to 0.6. It is interesting that there is no corresponding change in the ratio of III to IV, this value remaining constant and, within experimental error, the same as the ratio found previously for the photodecomposition of the azide. This would suggest a slow rearrangement of the aziridine to the 1-cyclohexenylurethan under the reaction conditions. Rearrangements of this type have been reported previously.<sup>44-46</sup> Our rearrangement, how-

ever, cannot be purely thermal in nature. When a solution of the pure aziridine II in cyclohexene was refluxed for 114 hr. not more than 5% rearrangement to III and V was observed. Even neat pyrolysis at 230° for 2 hr. gave a maximum rearrangement of only 16%. Some other compound present in the product mixture of the thermal decomposition must catalyze the isomerization.

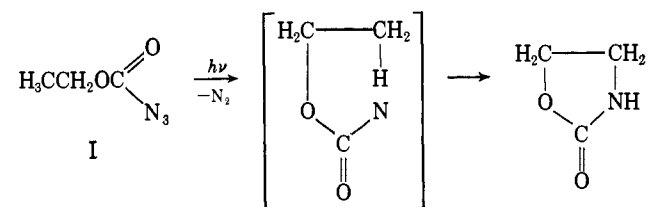
As is apparent from Table II, the presence of oxygen affects the relative product composition. In a system open to the atmosphere, the total products resulting from addition of the carbethoxy nitrene to the solvent were formed in only 33% yield. A minimum of 16% urethan and about a 24% yield of 3,3'-biscyclohexenyl were also formed. When the reaction was repeated under oxygen-free conditions, using cyclohexene from which all peroxides had been carefully removed, the amount of urethan formed was reduced to a maximum of 2% and no 3,3'-biscyclohexenyl was found. Under these conditions the total amount of products resulting from a nitrene reaction with the solvent rose to 72%. In a control experiment, refluxing pure cyclohexene in the presence of atmospheric oxygen resulted in the rapid formation of cyclohexene peroxides and some 3,3'-biscyclohexenyl. In the presence of oxygen, the urethans, R-NH-COOEt (III, IV, and V), are destroyed much faster than the aziridine II.

**Table II.** Thermal Decomposition of Ethyl Azidoformate in Cyclohexene

Condi- tions <sup>a</sup>	Product ratio and yield (%)					
	II	III	IV	V	VI	VII
A	36.2 (26)	3.7 (2.7)	1.0 (0.7)	4.7 (3)	22 (16)	33 (24)
B	10.2 (24)	3.1 (7)	1.0 (2)	16.8 (39)	..	(0)

<sup>a</sup> Conditions: A, refluxed (83°) with oxygen present for 41.5 hr.; B, refluxed (83°) in the absence of oxygen under nitrogen for 118 hr

One might anticipate that some 2-oxazolidone would be formed as a result of an intramolecular insertion reaction of the nitrene in a methyl carbon-hydrogen bond. Certainly, such an intramolecular reaction



should be able to compete kinetically with any intermolecular attack upon the solvent, and the many analogies found in various other azide decompositions would seem to indicate that the necessary cyclic transition state is not unfavorable. Such cyclizations of azidoformates have been reported recently. Smolinsky studied the cyclization of isopentyl azidoformate to the oxazolidone.<sup>47</sup> This thermolysis was carried out

(43) J. W. ApSimon and O. E. Edwards, *Can. J. Chem.*, **40**, 986 (1962).

(44) D. V. Kshelbar and P. E. Fanta, *J. Am. Chem. Soc.*, **82**, 4930 (1960); *J. Org. Chem.*, **26**, 1841 (1961).

(45) P. E. Fanta and A. S. Deutsch, *ibid.*, **23**, 72 (1958).

(46) H. W. Heine, M. E. Fetter, and E. M. Nicholson, *J. Am. Chem. Soc.*, **81**, 2202 (1959).

(47) G. Smolinsky and B. I. Feuer, *ibid.*, **86**, 3085 (1964).

in the vapor phase where the alternative of an intermolecular reaction is far less probable. Cotter and Beach<sup>48</sup> have isolated benzoxazolone-2 in about 1% yield from the products of the pyrolysis of phenyl azidoformate in benzene, and suggest an intramolecular insertion of carbophenoxy nitrene into an aromatic carbon-hydrogen bond. Photolysis of *t*-butyl azidoformate gives high yields of 5-dimethyl oxazolidone-2.<sup>35,36</sup> *n*-Octadecyl azidoformate also cyclized to an oxazolidone.<sup>19</sup>

No 2-oxazolidone, however, was ever found among the products resulting from the various decompositions of ethyl azidoformate whether thermal or photolytic, neat or in a dilute solution (cyclohexene, cyclohexane, or benzene). Furthermore, this compound was conclusively demonstrated, using g.l.p.c. techniques, not to be present in any significant amount in the reaction mixture resulting from the azide's photodecomposition in cyclohexene. Under conditions where a quantity equivalent to a 1% yield was easily detected, none could be found.

### Conclusions

Our results can be explained most easily by assuming that, in the reactions studied here, photolysis and thermolysis of the azidoformate first induces loss of nitrogen, followed by intermolecular reactions of the carbethoxy nitrene produced. The products obtained by photosensitized decomposition are different, excluding the triplet excited azide as a transient intermediate in the main path of the reaction. It seems possible, however, that triplet-excited azide (or triplet nitrene) cause the observed formation of small amounts of dehydrogenation products.

The ratio of the yields of products from insertion into the 3- and 4-positions of cyclohexene is the same in the photolytic and the thermolytic process. With isopentane as the substrate, almost identical product ratios were found for the photolytic<sup>21</sup> and the thermolytic<sup>33</sup> process, as well as for carbethoxy nitrene generated by  $\alpha$ -elimination.<sup>21</sup> This indicates a common intermediate, in energetic equilibrium with its environment. The observed facts can be accommodated by

Scheme I. It is hoped that the abundance of question marks will be reduced by work now in progress.

### Experimental

**General Equipment and Techniques.** Infrared spectra were obtained with a Perkin-Elmer Model 221 or Model 421 spectrophotometer. Absorption band positions are reported in frequency units of  $\text{cm}^{-1}$ .

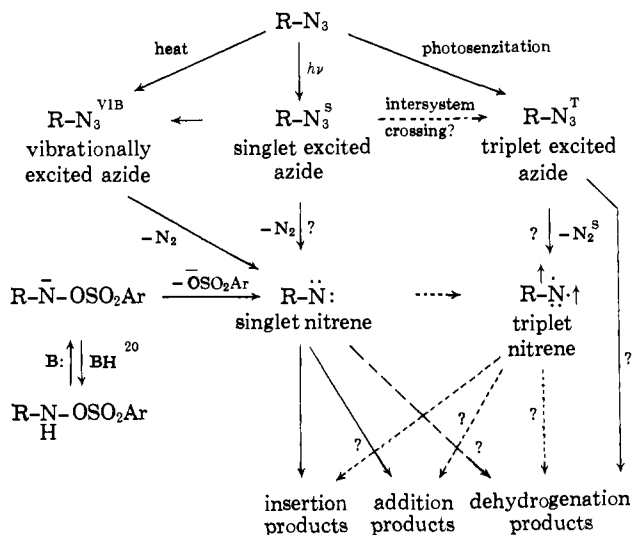
Nuclear magnetic resonance (n.m.r.) spectra were taken on either a Varian Associates high resolution HR-60 (V4300 B) or Varian Associates A-60 spectrometer. Positions are reported in  $\tau$ -units, that is, p.p.m. from tetramethylsilane which is defined as  $\tau$  10. Peak shapes are denoted by the following symbols: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m).

Ultraviolet spectra were obtained with a Model 14 Cary recording spectrophotometer. Commercial Spectrograde solvents were used without further purification.

Melting points were obtained on a Fisher-Johns (block) or a Hershberg (capillary) melting point apparatus, and like the boiling points are reported uncorrected.

For gas-liquid partition chromatography (g.l.p.c.) Wilkens Aerograph Model A-90-P-2 and Model A-90-P gas chromatography units were used. A planimeter was employed for measuring the peak areas of the g.l.p.c. tracing. These measurements were easily reproduced within  $\pm 2\%$ . Over half the measurements made were also checked by comparing the products of their peak height and their peak width at one-half peak height or the peaks were traced on unruled index cards (found to be quite uniform in weight), the peaks carefully were cut out and weighed, the weight taken to be proportional to the area. Although the reproducibility of these last two methods was less, they always agreed with the planimeter measurements within  $\pm 2\%$ . To obtain absolute yields, a calibration curve (weight injected vs. peak area) was first made using a standard solution of the pure material or a substance, often an isomer, of similar peak shape and retention time. The use of the latter for calibration required the assumption that the response of the detector was the same for both compounds. Whenever it was suspected that some component of a mixture was decomposing during g.l.p.c. analysis (possibly on the hot injector block or on a polar column substrate) a large volume of the mixture was injected for analysis and all of the material exiting from the g.l.p.c. unit was collected at Dry Ice temperatures. The infrared spectrum of this collected material was compared with that taken of the mixture previous to its injection. If no new peaks appeared or no significant change occurred in the relative size of the peaks, it was concluded that no decomposition had taken place. The following columns were used: column A, 5 ft.  $\times$  0.25 in., containing 20% 50 HB 2000 Ucon Polar oil stationary phase on 40-60 mesh crushed firebrick support; column D, 5 ft.  $\times$  0.25 in., containing 20% XF 1150 Cyano Silicon oil stationary phase on 45-50 mesh Chromosorb W support; column F, 5 ft.  $\times$  0.25 in., containing 20% XF 1150 Cyano Silicon oil stationary phase on 45-50 mesh Chromosorb W support; Column G, 5 ft.  $\times$  0.25 in., containing

Scheme I



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

20% GE-SF-96 Silicon oil stationary phase on mesh 60-80 crushed firebrick support; Column H, 5 ft.  $\times$  0.25 in., containing 20% Apiezon N stationary phase on mesh 60-80 crushed firebrick support; Column I, 10 ft.  $\times$  0.5 in., containing 20% GE-SF-96 Silicon oil stationary phase on mesh 40-60 crushed firebrick support.

Photochemical reactions were carried out using vessels of Vycor 7912 or quartz glass. For runs at room temperature, the Rayonet photochemical reactor<sup>49</sup> was used most often. It consists essentially of sixteen tubular ultraviolet sources mounted around the inner surface of a polished cylindrical reflector, air cooled by a fan. The vessel to be irradiated is suspended in the center of the cylinder along its axis. This unit uses either low-pressure mercury lamps (No. RPR-2537A), 84% of whose emission is at 2537-Å., or longer wave length black light lamps (No. RPR-3500-A), 90% of whose emission is in the 3100- to 4100-Å. region (maximum at 3500 Å.). When the reactor is fitted with its normal complement of sixteen RPR-2537A lamps the intensity of 2537-Å. ultraviolet irradiation at the center of the chamber is 12,800  $\mu\text{w./cm.}^2$ , equivalent to about  $1.65 \times 10^{16}$  photons/sec.  $\text{cm.}^{-3}$ ; when fitted with the longer wave length lamps the intensity at the chamber's center of radiation in the 3100-4100-Å. range is approximately 9200  $\mu\text{w./cm.}^2$ , equivalent to approximately  $1.5 \times 10^{16}$  photons/sec.  $\text{cm.}^{-3}$ . For irradiations below room temperature, the reaction vessel was immersed in a cooling bath and a low-pressure mercury lamp, Westinghouse G 10T5 1/2H, was placed in a vacuum-jacketed well in the center of the vessel. The lamp emits a total of 5.3 w. of ultraviolet energy.

Gas evolution was measured using a Fisher precision model gas measuring unit (No. 10-600-32) or an equivalent noncommercial apparatus of larger capacity attached directly to the irradiation system. Mercury was used as the leveling liquid in all cases.

*Preparation of Ethyl Azidoformate (I).* Ethyl azidoformate was prepared by a modification of the method of Forster and Fierz.<sup>50</sup> To an ice-cooled solution of 35 g. (0.54 mole) of sodium azide in 190 ml. of distilled water was added a solution of 50 g. (0.45 mole) of ethyl chloroformate in 50 ml. of pure ether. The mixture was vigorously stirred with constant cooling (ice bath) for 2.5 hr., by which time the infrared spectrum of the ether layer no longer showed any acid chloride absorption at 1798  $\text{cm.}^{-1}$ . The ether layer was separated, the aqueous layer was washed once with ether, and the combined ether solutions were dried thoroughly over anhydrous sodium sulfate. The ether was removed by distillation at atmospheric pressure and the residue was then distilled at reduced pressure through a 5-in. Vigreux microcolumn yielding 40.5 g. of crude ethyl azidoformate, b.p. 39-41° (ca. 30 mm.), 87.4% yield. Before using, this material was redistilled giving 31.1 g. (60% yield) of I, b.p. 40° (30.5 mm.);  $n_D^{24}$  1.4180. This material was shown by g.l.p.c. analysis on column G (injector 60°, column 45°) to be at least 99% pure.

The infrared spectrum of I (in  $\text{CCl}_4$ ) showed<sup>51</sup>  $\text{N}_3$

(49) A product of the Southern New England Ultraviolet Co. of Middletown, Conn.

(50) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93**, 81 (1908).

at 2416 (w), 2185 (s), and 2137 (s);  $\text{C}=\text{O}$  at 1759 (s) and 1730 (vs); and  $\text{C}-\text{O}$  at 1242  $\text{cm.}^{-1}$  (vs). The ultraviolet spectrum of I (in hexane, methanol, and cyclohexene)<sup>52</sup> is shown in Table III.

Table III. The Ultraviolet Spectrum of I

Wave length, Å.	Solvents		
	Hexane	Methanol	Cyclohexene <sup>a</sup>
2500	88.1	85.1	...
2600	66.9	63.1	...
2700	40.6	36.9	41.9
2800	17.4	15.3	19.0
2900	6.9	6.0	8.1
3000	2.7	2.1	3.6
3100	1.2		
3200	[0.1] <sup>b</sup>		
3300	[0.04]		
3400	[0.02]		

<sup>a</sup> Cyclohexene carefully purified. <sup>b</sup> Obtained using extremely concentrated solution.

Although the azide was far more stable to heat than had been expected, care should be taken when distilling. Ethyl azidoformate was heated neat at temperatures of around 100° for prolonged periods without difficulty; a test sample upon slow heating did not detonate until 160°. The azide's vapors are toxic producing vertigo, severe headaches, and sometimes vomiting.

The pure azide was stored for a period of 3 months in the cold (4°), protected from light, without apparent deterioration (no change in infrared spectrum); however, it rapidly turned yellow when stored at room temperature in the presence of light.

*Preparation of 7-Carboethoxy-7-azabicyclo[4.1.0]heptane (II).* To a mixture of 0.409 g. ( $1.02 \times 10^{-2}$  mole) of sodium hydroxide, 15 ml. of benzene, 1.015 g. ( $1.04 \times 10^{-2}$  mole) of cyclohexenimine,<sup>53</sup> and about 20 ml. of ice flakes, was slowly added under constant stirring and cooling 1.1120 g. ( $1.02 \times 10^{-2}$  mole) of ethyl chloroformate. The mixture was vigorously stirred for 2 hr., the temperature never rising above 5°. The organic layer was separated; the aqueous layer was extracted twice with small portions of ether and the combined organic layer was dried over anhydrous magnesium sulfate and three-quarters of the solvent was removed on a rotary evaporator. 7-Carboethoxy-7-azabicyclo[4.1.0]heptane (II) was the only major product found by g.l.p.c. on column H (injector ca. 200°, column 155°).

The infrared spectrum of II (in  $\text{CCl}_4$ ) showed no band above 3000 (no  $\text{N}-\text{H}$  or olefinic  $\text{C}-\text{H}$ );  $\text{C}=\text{O}$  at 1720 (s); and no  $\text{C}=\text{C}$  band at 1680-1620; ester at 1220 (s) and 1268 (s)  $\text{cm.}^{-1}$ . The n.m.r. spectrum of II (in  $\text{CCl}_4$ ) showed ethyl  $\text{CH}_3$ ,  $\tau$  8.80 (T); ring  $\text{CH}_2$  at 3 and 4, 8.6-8.9 (m); ring  $\text{CH}_2$  at 2 and 5, 8.22 (m); ring  $\text{CH}$  at 1 and 6, 7.47 (m); and ethyl  $\text{CH}_2$ , 5.95 (q).

*N-(3-Cyclohexenyl)phthalimide.* To a solution of 31.14 g. (0.173 mole) of 3-bromocyclohexene<sup>54</sup> in 300 ml.

(51) See also Yu. N. Sheinker and Ya K. Syrkin, *Izv. Akad. Nauk SSR, Ser. Fiz.*, **14**, 478 (1950); *Chem. Abstr.*, **45**, 3246g (1951).

(52) See also Yu. N. Sheinker, *Dokl. Akad. Nauk SSSR*, **79**, 1043 (1951); *Chem. Abstr.*, **45**, 6927c (1951).

(53) E. Paris and P. Fanta, *J. Am. Chem. Soc.*, **74**, 3009 (1952).

(54) K. Ziegler, A. Späth, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann.*, **551**, 110 (1942).

of dried, redistilled dimethylformamide was added 33.0 g. (ca. 0.17 mole) of potassium phthalimide. The mixture was heated overnight at 50° and then for 2 hr. at 90°, by which time the reaction mixture had assumed a dark brown color and a white solid had precipitated. After diluting with 300 ml. of chloroform the reaction mixture was poured into 200 ml. of water. The chloroform phase was separated and the aqueous phase was thoroughly extracted with chloroform. The combined chloroform extracts were washed with 200 ml. of 0.2 *N* sodium hydroxide solution and then with 200 ml. of water. After drying over anhydrous sodium sulfate, most of the chloroform was removed at reduced pressure, leaving a dark brown liquid which deposited 6.2 g. of buff crystals upon standing overnight in a refrigerator. Recrystallization from cyclohexane gave *N*-(3-cyclohexenyl)phthalimide, m.p. 110–112.5° (capillary). The filtrate yielded additional product, total yield 21.3 g. (54%).

The infrared spectrum (CCl<sub>4</sub>) showed olefinic C—H at 3035 (m); phthalimide C=O at 1778 and 1720 (s), C=C at 1670 (sh), and phenyl at 1610 (w) cm.<sup>-1</sup>.

*3-Aminocyclohexene*. A mixture of 4.51 g. (2 × 10<sup>-2</sup> mole) of recrystallized *N*-(3-cyclohexenyl)phthalimide, 50 ml. of methanol, and 2.0 ml. (3.3 × 10<sup>-2</sup> mole) of 85% aqueous hydrazine hydrate was heated under reflux for 1 hr. After cooling, 25 ml. of water was added and the pH was adjusted to 2; 4.5 ml. of hydrochloric acid was required. The solution was allowed to stand for 2.5 hr., the phthalyl hydrazide was removed by filtration and washed with methanol, and the filtrate was concentrated under reduced pressure. This concentrate was made basic with 17 ml. of approximately 6 *N* sodium hydroxide solution and extracted with a total of 200 ml. of ether, and the ether extract was dried over anhydrous sodium sulfate and cooled in a Dry Ice-acetone bath, and anhydrous hydrochloric gas was slowly passed through. White crystalline 3-aminocyclohexene hydrochloride (0.4 g.) slowly precipitated. Removal of the ether under reduced pressure gave an additional 1.82 g., total yield of 85%, m.p. 156.5–159 (capillary).<sup>55</sup>

The free 3-aminocyclohexene was obtained by dissolving about 2 g. of the hydrochloride in a small quantity of warm water, adding about 50 ml. of 3 *N* sodium hydroxide solution, and extracting with ether. Fractional distillation through a 4-in. Vigreux column gave amine, b.p. 58–60° (42 mm.).

*3-Cyclohexenylurethan (III)*. To an ice-cold solution of 0.484 g. (5.0 × 10<sup>-3</sup> mole) of 3-aminocyclohexene and 0.390 g. (4.9 × 10<sup>-3</sup> mole) of dried pyridine (redistilled from barium oxide) in 8 ml. of anhydrous ether was added, dropwise with constant stirring and cooling (ice bath), a solution of 0.539 g. (5.0 × 10<sup>-3</sup> mole) of ethyl chloroformate in 4 ml. of ether. A white precipitate rapidly formed, slowly turning yellow-green upon standing. The solution was withdrawn from the precipitate with a filter pipet. The precipitate was washed repeatedly with small portions of anhydrous ether. The dried ether solutions were concentrated to about one-fourth of the original volume and analyzed by g.l.p.c. on column

G (injector 190°, column 160°). 3-Cyclohexenylurethan was the only major product present. This material was isolated in quantity by preparative g.l.p.c. on columns I and A (injector 190°; column temperature 160°).

*Anal.* Calcd. for C<sub>9</sub>H<sub>15</sub>NO<sub>2</sub>: C, 63.88; H, 8.94; N, 8.28. Found: C, 63.70; H, 8.83; N, 3.33.

The infrared spectrum (in CCl<sub>4</sub>) showed N—H at 3454 (m) (sharp) and 3348 (w) (broad); olefinic C—H at 3030 (m), C=O at 1720 (vs), C=C at 1653 (w) and 1497 (s), and C—O at 1213 (s) cm.<sup>-1</sup>. The n.m.r. spectrum (in CCl<sub>4</sub>) showed ethyl CH<sub>3</sub>, τ 8.78 (q); ring CH<sub>2</sub> at 4, 5, and 6, 8.28 (m), 8.05 (m); ethyl CH<sub>2</sub>, 5.95 (q); ring CH at 3, 5.95; NH, 5.28; and ring CH at 1 and 2, 4.28.

*Ethyl Cyclohexene-4-carboxylate*.<sup>56</sup> Butadiene-1,3 (62 ml., 40.3 g., 0.75 mole) was condensed into a bomb containing ethyl acrylate (60 g., 0.6 mole) and 4.5 g. of hydroquinone. The bomb was heated in a shaker for 2 hr. to 160–180°, giving 41 g. of ethyl cyclohexene-4-carboxylate, b.p. 99–100 (33 mm.) (67.8% yield).

The infrared spectrum (in CCl<sub>4</sub>) showed olefinic C—H at 3030 (m); C=O at 1722 (s); and C=C at 1650 (w); ester at 1220 (s) and 1167 (s) cm.<sup>-1</sup>. The n.m.r. spectrum (in CCl<sub>4</sub>) showed ethyl CH<sub>3</sub>, τ 8.80 (t); ring CH<sub>2</sub> at 3, 5, and 6, 7.3–8.6 (m); ring CH at 4, 4.36; and ethyl CH<sub>2</sub>, 5.92 (m).

*Cyclohexene-4-carboxylic Acid*. A mixture of 60 g. (0.4 mole) of ethyl cyclohexene-4-carboxylate and 600 ml. (1.2 mole) of a 10% methanolic (50–50) potassium hydroxide solution was refluxed for 2 hr. by which time the mixture had become homogeneous. Most of the methanol was removed by evaporation at reduced pressure, the base concentration being kept low by addition of water. The reaction mixture was then extracted with a total of 250 ml. of ether and the aqueous phase was acidified by slow addition of concentrated hydrochloric acid with rapid stirring and cooling to pH 2. The oil which separated was taken up in ether and the aqueous solution was extracted with a total of 400 ml. of ether. The combined ether extracts were dried and concentrated. Fractional distillation gave 42 g. of cyclohexene-4-carboxylic acid, b.p. 109–110 (3.0 mm.), 83% yield.

The infrared spectrum (in CCl<sub>4</sub>) gave bonded O—H 3500 to 2500; C=O at 1705 (s); C=C at 1650 (w); also bands at 1305 (s) and 1240 (s) cm.<sup>-1</sup>. The n.m.r. spectrum (in CCl<sub>4</sub>) showed ring CH<sub>2</sub> at τ 3, 5, and 6, 9.2–8.7 (m); ring CH at 4, 9.2–8.7 (m); ring CH at 1 and 2, olefinic, 4.37; and OH, -2.15.

*Cyclohexene-4-carboxylic Acid Chloride*. To 119 g. (1 mole) of thionyl chloride was added 60 g. (0.5 mole) of cyclohexene-4-carboxylic acid, and the mixture was heated to reflux for 12 hr. Fractional distillation through an 8-in. Vigreux column yielded crude cyclohexene-4-carboxylic acid chloride, b.p. 52–57° (1.8 mm.); g.l.p.c. analysis on column G (injector 160°; column 140°) indicated no trace of the acid.

The infrared spectrum (in CCl<sub>4</sub>) showed olefinic C—H at 3036 (m), C=O at 1796 (vs), and C=C at 1652 (w) cm.<sup>-1</sup>.

*4-Cyclohexenylurethan (IV)*. To a solution of 9 g. (1.4 × 10<sup>-1</sup> mole) of sodium azide in about 50 ml. of

(55) A. Hoffmann, O. Damm, *Mitt. Kohlenforsch. Breslau*, **2**, 111 (1926).

(56) K. Toki, *Bull. Chem. Soc. Japan*, **32**, 233 (1959).



distilled water was added a solution of 10 g. ( $0.7 \times 10^{-1}$  mole) of redistilled cyclohexene-4-carboxylic acid chloride in about 50 ml. of ether. After vigorous stirring for 8 hr. at room temperature the light pink ethereal solution was separated from the aqueous layer, the latter was extracted twice with ether, and the combined ether solutions were dried briefly over anhydrous magnesium sulfate. Some gas was slowly evolved while solution was drying. An infrared spectrum indicated mainly the desired acid azide ( $2137 \text{ cm.}^{-1}$ ) and the isocyanate resulting from its decomposition ( $2260 \text{ cm.}^{-1}$ ) in nearly equal amounts together with traces of the acid.

About 100 ml. of absolute ethanol was added to this ether solution, the ether was removed on a rotary evaporator, and another 100 ml. of absolute ethanol was added. The solution was placed in a quartz vessel and the remaining azide was decomposed by irradiation with RPR-2537 A lamps until the evolution of nitrogen ceased. The ethanol was then removed by distillation, leaving a light yellow viscous residue of crude 4-cyclohexenylurethan. Distillation at reduced pressures ( $<1 \text{ mm.}$ ) led to much decomposition; purification was accomplished by chromatography on alumina and by preparative g.l.p.c. using columns I and D (injector  $180^\circ$ , column  $150^\circ$ ).

*Anal.* Calcd. for  $\text{C}_9\text{H}_{15}\text{NO}_2$ : C, 63.88; H, 8.94; N, 8.28. Found: C, 64.09; H, 9.02; N, 8.29.

The infrared spectrum (in  $\text{CCl}_4$ ) showed NH at 3448 (m) (sharp) and 3338 (m) (broad), olefinic C—H at 3030 (m); C=O at 1720 (vs); and C=C at 1648 (w); other bands at 1505 (s), 1215 (s), and 1230 (s)  $\text{cm.}^{-1}$ . The n.m.r. spectrum (in  $\text{CCl}_4$ ) gave ethyl  $\text{CH}_3$ ,  $\tau$  8.80 (t); ring  $\text{CH}_2$  at 3, 5, 6, 8.6–7.2 (m); ring CH at 4, 6.33, ethyl  $\text{CH}_2$ , 5.95 (q); N—H, 4.58; and ring CH at 1 and 2, olefinic, 4.38.

*1-Cyclohexenylurethan (V) by Isomerization of 7-Carboethoxy-7-azabicyclo[4.1.0]heptane.* A mixture of 1.05 g. ( $6 \times 10^{-3}$  mole) of 7-carboethoxy-7-azabicyclo[4.1.0]heptane (II) and 6.4 g. ( $4.2 \times 10^{-3}$  mole) of anhydrous sodium iodide<sup>57</sup> in 150 ml. of very dry acetone was refluxed for 4 days. The acetone was evaporated at reduced pressures and the concentrate was extracted with carbon tetrachloride leaving a quantity of insoluble residue. After the carbon tetrachloride was evaporated from the extract at reduced pressure, the resulting mush of solid and oil was recrystallized from a hexane-carbon tetrachloride mixture (90–10) yielding as its major component 2-iodocyclohexylurethan, m.p.  $118\text{--}119^\circ$  (block).<sup>58</sup> 1-Cyclohexenylurethan was separated by preparative g.l.p.c. on column F; elemental analysis was obtained on a sample twice further purified by g.l.p.c. on column D (injector  $175^\circ$ , column  $155^\circ$ ).

*Anal.* Calcd. for  $\text{C}_9\text{H}_{15}\text{NO}_2$ : C, 63.88; H, 8.94; N, 8.28. Found: C, 63.77; H, 8.81; N, 8.14.

The infrared spectrum (in  $\text{CCl}_4$ ) showed N—H at 3415 (m) (sharp) and 3359 (w) (broad), olefinic C—H at 3002, C=O at 1736 (s), C=C at 1670 (m); other bands

(57) The amount of 2-iodocyclohexylurethan formed was observed to decrease when the acetone and sodium iodide were thoroughly dried before use. The acetone was dried by first shaking with potassium carbonate and then distilling from phosphorus pentoxide; commercial "anhydrous" sodium iodide was found to contain much water; it was dried overnight in a vacuum at  $100^\circ$ .

(58) L. Birckenbach and M. Linhard, *Ber.*, **64B**, 961 (1931), report m.p.  $120^\circ$ .

at 1520 (s), and C—O at 1210 (s)  $\text{cm.}^{-1}$ . The n.m.r. spectrum (in  $\text{CCl}_4$ ) gave ethyl  $\text{CH}_3$ ,  $\tau$  8.80 (t); ring  $\text{CH}_2$  at 3, 4, 5, and 6, 8.41 (m) and 7.92 (m); ethyl  $\text{CH}_2$ , 5.92 (q); ring C—H at 1 (olefinic), 4.25; and N—H, 3.31.

*3,3'-Biscyclohexenyl (VIII).* To a mixture of 2.4 g. (0.1 g.-atom) of magnesium in ether, activated by the presence of a small amount of methyl bromide, was added with constant stirring 11.65 g. (0.1 mole) of 3-chlorocyclohexene<sup>59</sup> in 100 ml. of ether at such a rate as to maintain refluxing; the mixture was then stirred at room temperature for 10 hr. Dilute (approximately 1 *N*) hydrochloric acid was slowly added to the rapidly stirred mixture until no further reaction occurred and the solution was acidic; the ether layer was separated and the aqueous layer was extracted with ether. The combined ether solutions were dried over anhydrous sodium sulfate and the solvent was removed. The crude 3,3'-biscyclohexenyl was purified by distillation through a 5-in. Vigreux microcolumn. About 2.8 g. (35%) of a clear, colorless fragrant oil, b.p.  $85\text{--}89^\circ$  (3.7–4 mm.),<sup>60</sup> was obtained.

The infrared spectrum (in  $\text{CCl}_4$ ) showed olefinic C—H at 3024 (m); aliphatic C—H at 2934 (s), 2863 (m), and 2814 (m); C=C at 1645 (m); also 1446 (m); 1435 (m).

*Irradiation of Ethyl Azidoformate in Cyclohexene.* A dilute solution (ca. 0.01 *M*) of redistilled ethyl azidoformate in cyclohexene was irradiated until the evolution of nitrogen ceased and infrared analysis of the solution showed no presence of azide. Most of the cyclohexene and any possible low-boiling reaction products present were removed by distillation at room temperature (maximum  $30^\circ$ ) and reduced pressure (minimum ca. 1 mm.), the distillate being collected in a Dry Ice trap. The residue was analyzed by g.l.p.c. on column A (typical temperatures; injector  $180^\circ$ , column  $150^\circ$ ) and column D (injector  $144^\circ$ , column  $128^\circ$ ). The components had infrared spectra (as well as n.m.r. spectra in the case of II and V) identical with those of the authentic materials.

Both columns gave good separation of II from its isomers; however, only column D achieved any separation of the 3-cyclohexenylurethan from the 4-isomer and even this resolution was not clear to the base line. Peak area measurements were made using a planimeter and checked by the "cut out and weigh" method; agreement was always within 2%. Because of the great disparity between the amount of II and that of III or IV present in the reaction mixtures, the error in these cases was large; the maximum deviation for six analyses of the same reaction residues was 9%; the error is smaller for the comparison of III to IV, being reproducible within  $\pm 6\%$ . The amount of V in the product mixtures could only be approximated. Pure II was used as a calibration standard for absolute yield measurements. The cyclohexene used in all reactions had previously been dried and redistilled. For the runs under condition A no attempt had been made to remove peroxides and the system was open to the atmosphere during irradiation. Often a film of buff-colored solid material was found on the walls of the irradiation vessel.

(59) C. Grob, H. Kny, and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

(60) A. Hoffman and O. Damm, *Mitt. Kohlenforsch. Breslau*, **2**, 131 (1926), and *Chem. Zent.* **I**, 2343 (1926), report b.p.  $103^\circ$  (8 mm.) for VIII

The cyclohexene used in reactions B and C was purified; commercial cyclohexene was thoroughly shaken with concentrated sodium hydroxide solution and then dried with molecular sieves (Linde type 4A), then fractionally distilled under nitrogen<sup>61</sup> through a 15-in. column packed with glass helices onto dried sodium hydroxide pellets; the center cut, boiling at 83° (760 mm.), was collected and stored under nitrogen over dried sodium hydroxide pellets. Cyclohexene so treated gave a negative test for peroxides. Before use, this cyclohexene was thoroughly degassed and saturated with nitrogen. In both reactions the irradiation itself was carried out under a nitrogen atmosphere. Total irradiation time for reaction B was *ca.* 21.5 hr. and for reaction C *ca.* 117 hr. To prepare II in quantity no attempt was made to exclude atmospheric oxygen. A 10% solution of ethyl azidoformate in cyclohexene was irradiated until nitrogen evolution ceased. Two distillations (first through a 10-in. Vigreux column, then through a 10-in. microcolumn packed with nichrome helices) gave a 50% yield of II, b.p. 76–77 (*ca.* 35 mm.), shown by g.l.p.c. analysis to be 95% pure; a further distillation through the helices-packed column gave essentially pure II, b.p. 67–68° (1.25 mm.).

A mixture of 0.617 g. ( $3.65 \times 10^{-3}$  mole) of II and 20 ml. of 20% methanolic potassium hydroxide solution was refluxed for 8 hr. and the solution was concentrated and thoroughly extracted with ether. The dried ether extract was cooled in a Dry Ice–acetone bath and anhydrous hydrogen chloride gas was slowly passed through the solution. The white crystalline product was washed with dry ether and dried under vacuum for a short period, yielding 0.275 g. of a compound shown by comparison of its infrared spectrum with that of the authentic material to be impure *trans*-2-hydroxycyclohexylamine hydrochloride. A sample was further purified by sublimation, m.p. 175–178° (not sharp because of sublimation).<sup>62</sup>

A solution of 20 ml. of dioxane and 15 ml. of water was saturated with hydrogen chloride, 2.22 g.  $1.3 \times 10^{-2}$  mole) of II was added, and the mixture was heated to reflux for 40 hr. Most of the solvent was removed at 15 mm. leaving a mixture of a white, crystalline material in a brown oil. This residue was extracted with ether and the combined extracts were evaporated to dryness giving a total of 1.09 g. of crystalline product; recrystallization from hexane yielded fine white crystals, m.p. 97–98°. Its infrared spectrum identified it as *trans*-2-chlorocyclohexylurethan, showing (in CHCl<sub>3</sub>) N—H at 3442 (w) (sharp); C—H at 2982 (w), 2946 (m), and 2865 (w); and C=O at 1712 (s); also 1510 (s) cm.<sup>-1</sup>; in general the spectrum was almost identical with that of *trans*-2-iodocyclohexylurethan.

Elemental analyses were obtained on samples of the reaction products II and VII purified by g.l.p.c. on column A (injector 160°, column 135°).

*Anal.* Calcd. for C<sub>9</sub>H<sub>10</sub>NO<sub>2</sub> (II): C, 63.88; H, 8.94; N, 8.28. Found: C, 64.03; H, 8.91; N, 8.22.

*Anal.* Calcd. for C<sub>12</sub>H<sub>18</sub> (VII): C, 88.82; H, 11.18. Found: C, 88.50; H, 11.13.

(61) Purified nitrogen from which water and oxygen had been carefully removed. For procedure see L. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, p. 299.

(62) G. E. McCasland, R. K. Clark, and H. E. Carter, *J. Am. Chem. Soc.*, **71**, 637 (1949), report m.p. 175°.

The low-boiling distillate removed from a typical irradiation reaction mixture was thoroughly extracted with 6 *N* hydrochloric acid and the acid extract was washed with ether and then evaporated to dryness at reduced pressure leaving a very small residue of unidentified solid material.

*Irradiation of 7-Carboethoxy-7-azabicyclo[4.1.0]heptane.* A solution of 0.51 g. of 7-carboethoxy-7-azabicyclo[4.1.0]heptane (II), shown to be at least 99% pure by g.l.p.c. analysis on column A, in 100 ml. of purified cyclohexene was irradiated in a quartz vessel under nitrogen using RPR-2537A lamps for 10 hr. The solvent was then removed by distillation at room temperature and reduced pressure and the residue was analyzed by g.l.p.c. on column A (injector 175°, column 130°). A maximum of 0.5% rearrangement to 3-cyclohexenylurethan could have occurred.

*Thermal Isomerization of 7-Carboethoxy-7-azabicyclo[4.1.0]heptane.* A sample of 7-carboethoxy-7-azabicyclo[4.1.0]heptane (II), which when analyzed by g.l.p.c. on column D (injector 148°, column 130°) was shown to contain 13.6% 3-cyclohexenylurethan (III) and 7.8% 1-cyclohexenylurethan (V) as impurities, was dissolved in purified cyclohexene and refluxed (system open to the atmosphere) for 114 hr. The cyclohexene was removed by distillation at reduced pressure and the residue was again analyzed by g.l.p.c. as before, the composition being 82.3% II, 12% III, and 5.8% V. Product identification was by comparison of retention times with those of the authentic materials.

A sample of 7-carboethoxy-7-azabicyclo[4.1.0]heptane, shown by g.l.p.c. analysis to be at least 98% pure, was heated in a small tube filled with nichrome helices to 230°. After 2 hr. the material was analyzed by g.l.p.c. as before; a maximum of 16% of a compound with a retention time the same as III had been formed.

*2-Oxazolidone* was prepared by a modification of the procedure of Frankel and Cornelius.<sup>63</sup> Ethanolamine (3 g.,  $4.9 \times 10^{-2}$  mole) was dissolved in about 200 ml. of chloroform from which all traces of alcohol had been removed by passage through a column of alumina. Phosgene gas was passed through this solution with constant stirring for 3 hr.; a white crystalline precipitate formed. Nitrogen was bubbled through the reaction mixture for an additional 6 hr. to remove any remaining phosgene. Lead carbonate (5.2 g.,  $6.7 \times 10^{-2}$  mole) was added and the mixture was stirred for 24 hr. It became warm and carbon dioxide was slowly evolved. The filtrate from reaction mixture was evaporated to dryness, yielding 2.06 g. of fine white crystals of 2-oxazolidone, yield 51%. Recrystallization from chloroform–pentane yielded white crystals, m.p. 89–90.5°.

The infrared spectrum (in CHCl<sub>3</sub>) showed N—H at 3475 (m) (sharp) and 3280 (m) (broad), C=O at 1755 (s), C—O at 1291 (sh) (m), and C—N at 1205 (m) cm.<sup>-1</sup>.

*Demonstration of the Absence of 2-Oxazolidone Formation in the Photolysis of Ethyl Azidoformate in Cyclohexene.* Mixtures containing 2-oxazolidone could be analyzed by g.l.p.c. without decomposition on column G (injector 205°, column 164°). Analysis of the concentrated reaction mixture resulting from the irradiation of ethyl azidoformate in cyclohexene showed

(63) S. Frankel and M. Cornelius, *Ber.*, **51**, 1662 (1918).

no component with a retention time of 2-oxazolidone. The one unidentified minor component present with a similar retention time had a different infrared spectrum.

A mixture of 2-oxazolidone and the reaction residue was made with a ratio to aziridine II of about 1:100. When this mixture was analyzed as before the 2-oxazolidone was easily detected.

*Thermal Decomposition of Ethyl Azidoformate in Cyclohexene.* A. A dilute solution of 4.4 g. ( $4 \times 10^{-2}$  mole) of redistilled ethyl azidoformate in 333 g. ( $400 \times 10^{-2}$  mole) of dry, redistilled cyclohexene was refluxed ( $83^\circ$ ) until infrared analysis showed no azide absorption at  $2137 \text{ cm.}^{-1}$ ; total reaction time was 41.5 hr. The system was open to the atmosphere throughout the reaction. The reaction mixture was then concentrated by distillation at room temperature ( $30^\circ$ ) and reduced pressure (minimum 10 mm.), the distillate being collected in a Dry Ice trap.

The resulting residue (11.7 g.) was separated by g.l.p.c. on column A (injector  $190^\circ$ , column  $150^\circ$ ) and column D (injector  $144^\circ$ , column  $128^\circ$ ). The identity of the components was established by comparison of g.l.p.c. retention times and infrared spectra with those of the authentic materials. The treatment and analysis of this reaction mixture was identical with that employed previously in the photolysis of the azide in cyclohexene.

The low-boiling distillate was thoroughly extracted with 6 *N* hydrochloric acid and the acid extract was made basic with sodium hydroxide solution and then extracted with ether. The dried (sodium sulfate) extract was carefully distilled; no residue remained after removal of the ether.

B. A similar thermal decomposition of the azide was carried out under an atmosphere of purified nitrogen using dried, purified cyclohexene from which all oxygen and peroxides had been carefully removed, and a reflux time of 118 hr. Treatment and analysis of the reaction mixture was identical with that in A above.

The relative ratios and yields of the identified products for both of these reactions are found in Table II.

*Acetophenone-Sensitized Photodecomposition of Ethyl Azidoformate in Cyclohexene.* A solution of 4.371 g. ( $3.8 \times 10^{-2}$  mole) of redistilled ethyl azidoformate and 6.16 g. ( $5.1 \times 10^{-2}$  mole) of acetophenone in 200 ml. (1.97 mole) of purified cyclohexene from which oxygen and peroxides had been removed was irradiated in a 3-mm. wall Pyrex vessel under a nitrogen atmosphere in the Rayonet reactor fitted with RPR-3500A lamps. Nitrogen was smoothly evolved at a rate of about 9–10 ml./hr. When the rate of evolution began to decrease an additional 2.05 g. ( $1.7 \times 10^{-2}$  mole) of acetophenone was added and the irradiation was finally stopped when the rate of nitrogen evolution had decreased to about 3 ml./hr. Total irradiation time was *ca.* 104 hr.; total yield of nitrogen evolved at this point was about 43%.

Solvent and unreacted azide were removed from the reaction solution by distillation at room temperature ( $30^\circ$ ) and reduced pressure (minimum 1 mm.). The residue was separated by g.l.p.c. on columns A and D. Treatment and analysis of this reaction mixture were identical with that previously employed in the photolysis of the azide in cyclohexene. Product identification was by comparison of retention time and infrared

spectra with those of the authentic material. The two main products found were urethan (73.5%)<sup>64</sup> and 3,3'-biscyclohexenyl (62.7%); 87% of the acetophenone added was still present. The maximum yields of the isomeric urethans formed were (identification by g.l.p.c. retention times only) *ca.* 1% 7-carbethoxy-7-azabicyclo[4.1.0]heptane (II), 3% 3-cyclohexenylurethan (III), 3.5% 4-cyclohexenylurethan, and 4% 1-cyclohexenylurethan. A small quantity of acetpinacol, m.p.  $118\text{--}120^\circ \text{ dec.}$ ,<sup>65</sup> crystallized out of the reaction residue.

*Preparation of Cyclohexylurethan (VIII).* To a solution of 9.9 g. ( $1 \times 10^{-1}$  mole) of cyclohexylamine in 75 ml. of anhydrous ether was added dropwise with constant stirring and cooling (ice bath) 5.4 g. ( $0.5 \times 10^{-1}$  mole) of ethyl chloroformate in 50 ml. of anhydrous ether. The white precipitate (amine hydrochloride) was filtered out and washed with anhydrous ether, and the combined filtrates were evaporated to dryness on a rotary evaporator giving 8.1 g. (95% yield) of cyclohexylurethan, m.p.  $55.5\text{--}56.6^\circ$ .<sup>66</sup>

The infrared spectrum (in  $\text{CCl}_4$ ) gave NH at 3455 (m) (sharp) and 3359 (w) (broad), C=O at 1724 (s) and 1500 (s), and C—O at 1214 (s)  $\text{cm.}^{-1}$ . The n.m.r. spectrum (in  $\text{CCl}_4$ ) showed ethyl  $\text{CH}_3$ ,  $\tau$  8.80 (t); ring  $\text{CH}_2$  at 2, 3, 4, 5, and 6, 7.4–8.6 (m); ring CH at 1, 6.58 (m); ethyl  $\text{CH}_2$ , 5.93 (q); and NH, 5.83 (d).

*Irradiation of Ethyl Azidoformate in Cyclohexene.* A dilute solution of redistilled ethyl azidoformate (6.650 g.,  $5.8 \times 10^{-2}$  mole) in cyclohexane (800 ml., 7.4 mole), thoroughly flushed with nitrogen to remove all oxygen, was irradiated under nitrogen until nitrogen evolution ceased and infrared analysis of the solution showed no azide ( $2137 \text{ cm.}^{-1}$ ) remaining. The nitrogen evolution was greater than 90% of theory; total time of irradiation was 33 hr.

The solvent and other low-boiling materials were removed by distillation at room temperature ( $30^\circ$  maximum) and reduced pressure (1 mm. minimum). The resulting yellow oil upon standing gave a crystalline mush; filtration and two recrystallizations from pentane yielded white crystalline cyclohexylurethan, m.p.  $56\text{--}57.3^\circ$  (block). This material had infrared and n.m.r. spectra and a g.l.p.c. retention time (on column H) identical with that of authentic VIII; a mixture melting point with authentic VIII was undepressed. Chromatography of the concentrated filtrate on neutral alumina yielded urethan VI (12.1%), identified by comparison of infrared spectra to that of the authentic material, in addition to more VIII; total yield of cyclohexylurethan was 51%.

An elemental analysis was obtained on a sample of VIII from this irradiation which had been purified by distillation, b.p.  $94\text{--}96^\circ$  (1.7 mm.), followed by sublimation.

*Anal.* Calcd. for  $\text{C}_9\text{H}_{17}\text{NO}_2$ : C, 63.13; H, 10.02; N, 8.02. Found: C, 63.40; H, 10.00; N, 8.18.

The original distillate containing solvent and possible low-boiling product was cooled to  $5^\circ$  and dry hydrogen chloride gas was passed through the solution; no precipitate was formed. This distillate was then

(64) Per cent yields were calculated assuming that the moles of nitrogen evolved represented the moles of azide decomposed.

(65) A. Emmerlung and C. Engler, *Ber.*, **4**, 179 (1871), report m.p.  $120^\circ$ .

(66) A. Skita and H. Rolfes, *ibid.*, **54**, 1242 (1920), report m.p.  $52^\circ$ .

thoroughly extracted with 6 *N* hydrochloric acid, the acidic extract was made strongly alkaline by addition of potassium carbonate, and this basic solution was extracted with ether. After drying with anhydrous magnesium sulfate the ether was carefully distilled off leaving a small quantity (*ca.* 200 mg.) of a white crystalline material with an infrared spectrum identical with that of urethan.

In a similar irradiation of a more concentrated solution of I in cyclohexane (1:10 *M* ratio) a small amount of diethyl hydrazodiformate (IX) was found.

*Attempted Radical-Initiated Decomposition of Ethyl Azidoformate in Cyclohexane.* In a water bath of  $49 \pm 1^\circ$ , a solution of 1.060 g. ( $9 \times 10^{-3}$  mole) of redistilled ethyl azidoformate in 125 ml. of purified cyclohexane was placed in the flask, and the system was flushed with purified nitrogen and then sealed. A total of about  $1.8 \times 10^{-2}$  moles of diethyl peroxydicarbonate<sup>67</sup> was injected in portions over a 4-day period producing a slow evolution of an unidentified gas; the volume evolved at various intervals is recorded in Table IV.

The solvent and other low-boiling material were distilled from the reaction mixture at reduced pressure (minimum 2 mm.) and room temperature. The resulting residue was analyzed by g.l.p.c. on column A (injector  $185^\circ$ , column  $145^\circ$ ) and column D (injector  $148^\circ$ , column  $132^\circ$ ) and was found to contain not

(67) H. C. McBay and O. Tucker, *J. Org. Chem.*, **19**, 869, 1003 (1954).

Table IV

Total reaction time, hr.	Total vol. evolved (uncorr.), ml.
2.7	2
2.5 $\times 10^{-3}$ mole of peroxide added	
3.6	4
5.1 $\times 10^{-3}$ mole of peroxide added	
6.1	39
9.0	100
20.8	202
26.3	216
5.1 $\times 10^{-3}$ mole of peroxide added	
29.6	289
79.0	428
5.1 $\times 10^{-3}$ mole of peroxide added	
100.0	482

more than a 8.7% yield of cyclohexylurethan and a 5.8% yield of urethan; identification was by comparison of g.l.p.c. retention times with those of the authentic materials.

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## Absolute Configuration and Optical Rotatory Power of Sulfoxides and Sulfinates Esters<sup>1,2</sup>

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*Evidence is presented which firmly establishes the absolute configuration of a number of sulfinates esters and sulfoxides. Previous speculations which bear on the problem of the absolute configuration of optically active sulfoxides and sulfinates esters are critically examined. The optical rotatory dispersion of sulfoxides and sulfinates esters has been investigated. The observed Cotton effects are for the most part conveniently categorized*

*according to the previously adopted viewpoint of inherently dissymmetric and asymmetrically perturbed symmetric chromophores.*

It has been known for decades that suitably substituted tricoordinate sulfur compounds such as sulfonium salts ( $R_1R_2R_3S^+X^-$ ), sulfoxides ( $R_1R_2SO$ ), and sulfinates esters ( $RSOOR$ ) are dissymmetric, configurationally stable under ordinary conditions, and thus, in principle, resolvable into optically active enantiomeric forms.<sup>4</sup> In this paper we shall demonstrate that a correlation exists between the absolute configuration of sulfoxides and sulfinates and their optical activity, expressed in terms of the signs and rotational strengths of appropriate Cotton effects.

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(2) Portions of this work have been reported in preliminary form at the 18th National Organic Symposium, Columbus, Ohio, June 19, 1963, and in the following communications: (a) K. Mislow, A. L. Ternay, Jr., and J. T. Melillo, *J. Am. Chem. Soc.*, **85**, 2329 (1963); (b) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *ibid.*, **86**, 1452 (1964); (c) E. B. Fleischer, M. Axelrod, M. Green, and K. Mislow, *ibid.*, **86**, 3395 (1964); (d) K. Mislow, M. M. Green, P. Laur, and D. R. Chisholm, *ibid.*, **87**, 665 (1965).

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(4) R. L. Shriner, R. Adams, and C. S. Marvel, "Organic Chemistry," Vol. 1, H. Gilman, Ed., 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 419 ff.