

## The Thermolysis and Photolysis of Ethyl Azidoformate in Acetic Acid. The Formation of Ethoxycarbonylnitrenium Ion Intermediate

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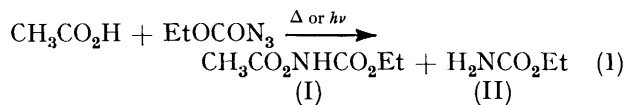
The thermolysis and photolysis of ethyl azidoformate in acetic acid afforded *O*-acetyl-*N*-hydroxyurethane (I) as the major product, together with a trace of ethyl carbamate (II). The formation of (I) was suppressed in the presence of cyclohexane-1,2-dione and cyclohexene which gave 3-(ethoxycarbonylimino)-2-hydroxycyclohexanone (III) and *trans*-1-acetoxy-2-(ethoxycarbonylamino)cyclohexane (IV), respectively. The yield of (I) levelled off at *ca.* 20%. The addition of the dione and the olefin also caused a remarkable increase in the yield of (II). The addition of 9,10-anthraquinone or 9,10-phenanthraquinone resulted both in a decrease in the yield of (II) and a slight increase in the yield of (I). The relative reactivity of the addition to cyclohexene [the formation of (IV)] with respect to C-H insertion of the nitrene into cyclohexane in acetic acid is greater than that of the addition of the nitrene with respect to insertion showing that the intermediate in acetic acid is more electrophilic than the nitrene. Further, the rate data obtained from thermolysis in acetic acid or toluene indicate that the nitrene is primarily formed in acetic acid. This suggests that the reaction in acetic acid proceeds *via* an ion pair intermediate,  $\text{CH}_3\text{CO}_2^- + \dot{\text{N}}\text{HCO}_2\text{Et}$ , which is formed as the result of the attack of the nitrene on acetic acid, and which either collapses to produce (I) or dissociates to form (I) on reaction with acetic acid. The ethoxycarbonylnitrenium ion which escapes from the solvent cage is trapped with cyclohexane-1,2-dione or cyclohexene to give (III) or the stereospecific isomer (IV), along with (II).

THE reactions of diazodiphenylmethane with carboxylic acids have been investigated systematically<sup>1-7</sup> since this system is suitable for studying the effects of temperature, solvent, and other variables. However, the analogous reactions between azides and carboxylic acids are little known other than the example quoted by Horner *et al.*<sup>8</sup> who reported the existence of benzoylnitrene as the primary cleavage species in the formation of the nitrene product,  $\text{CH}_3\text{CO}_2\text{NHCOPh}$ , during the photolysis of benzoyl azide in acetic acid.

In the course of the present work, we examined the thermal and photochemical reactions of ethyl azidoformate with acetic acid. We further report the novel, stereospecific, vicinal oxyamination of cyclohexene during the decomposition of ethyl azidoformate in the presence of cyclohexene in acetic acid.

### RESULTS AND DISCUSSION

*Thermolysis and Photolysis of Ethyl Azidoformate in Acetic Acid.*—Ethyl azidoformate was dissolved in acetic acid, and heated or irradiated (see Experimental section). *O*-Acetyl-*N*-hydroxyurethane (I) was formed in 72–75 or 62–70% yield along with a trace of ethyl carbamate (II) [equation (1)]. The procedure for



analysis and characterization of the products is described in the Experimental section.

*Effect of Cyclohexane-1,2-dione.*—The formation of (I) was suppressed by the addition of a small amount of cyclohexane-1,2-dione giving (II) and 3-(ethoxycarbonylimino)-2-hydroxycyclohexanone (III), and the yield of (I) levelled off at *ca.* 20% upon further addition (Tables 1 and 2 and Figure 1). The results suggest that

urethane (I) is not formed simply by a concerted reaction of ethoxycarbonylnitrene with acetic acid, but produced by either cage recombination of two species such as ion pairs or the reaction between acetic acid and species which have escaped from the cage (Scheme 1).

We have previously reported that cyclohexane-1,2-dione predominantly scavenges the triplet nitrene relative to the singlet giving a dramatic decrease in the yield of (II) upon thermolysis or photolysis of ethyl azidoformate in 1,4-dioxan-cyclohexane.<sup>9</sup> Thus, at first sight, the increase in the yield of (II) for the above addition appears to be contradictory. However, this can be explained by considering the pathway by which a triplet nitrenium ion escaped from cage abstracts hydrogen atoms from the dione as shown in Scheme 1. Such a hydrogen

TABLE 1

The effect of cyclohexane-1,2-dione on the photolysis of ethyl azidoformate (0.80M) in acetic acid

| [dione]<br>(M) | Yield (%)       |                  | Yield (%) of<br>decomposition<br>of azide |
|----------------|-----------------|------------------|---|
|                | (I)             | (II)             |   |
| 0              | 62 <sup>a</sup> | 1.6 <sup>a</sup> |   |
| 0.08           | 22              | 12               | 19.5                                      |
| 0.25           | 21              | 20.5             | 15.5                                      |
| 0.40           | 24              | 18.5             | 15  |

<sup>a</sup> The yield was obtained as the mean for 55.0, 60.0, and 86.5% decomposition of azide.

TABLE 2

The effect of cyclohexane-1,2-dione on the thermolysis of ethyl azidoformate (0.53M) in acetic acid

| [dione]<br>(M) | Yield (%) |      |       | Yield (%) of<br>decomposition<br>of azide |
|----------------|-----------|------|-------|---|
|                | (I)       | (II) | (III) |   |
| 0              | 71.5      | 4.6  |       | 92  |
| 0.16           | 40        | 17   |       | 94.5                                      |
| 0.25           | 29.5      | 22.5 | 17    | 80.5                                      |
| 0.53           | 18        | 24   |       | 92  |
| 0.74           | 19        | 23   |       | 92  |

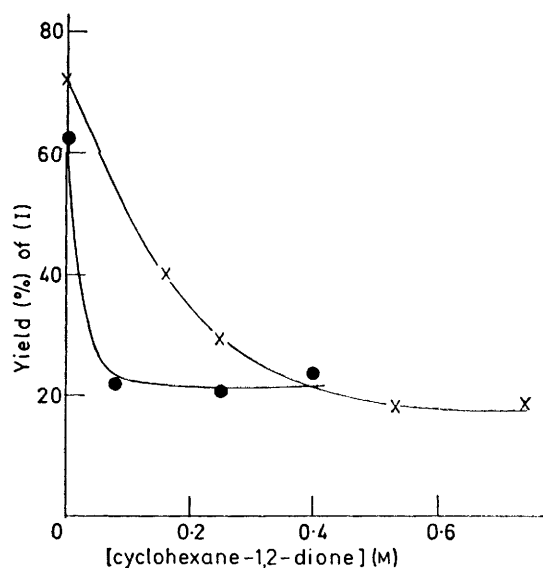


FIGURE 1 Effect of cyclohexane-1,2-dione on the decomposition of ethyl azidoformate in acetic acid: ●, photolysis; ×, thermolysis

abstraction by triplet nitrogen ion has been pointed out by Gassman and Cryberg.<sup>10</sup> The dione, which is almost in the enol form, also traps the nitrogen ion escaping from the cage to form a tertiary carbonium ion, yielding (III) after deprotonation (see Scheme 1).

*Effect of Cyclohexane-1,4-dione and Quinones.*—Cyclohexane-1,4-dione, 9,10-anthraquinone, or 9,10-phenanthraquinone was added instead of cyclohexane-1,2-dione (Table 3). Since cyclohexane-1,4-dione is completely in

TABLE 3

The effect of cyclohexane-1,4-dione (0.25M), 9,10-anthraquinone (0.07M), or 9,10-phenanthraquinone (0.07M) on the decomposition of ethyl azidoformate (0.80M) in acetic acid

| Additive                           | Yield (%) |      | Yield (%) of decomposition of azide |
|------------------------------------|-----------|------|-------------------------------------|
|                                    | (I)       | (II) |                                     |
| None <sup>a</sup>                  | 62        | 1.6  |                                     |
| Cyclohexane-1,4-dione <sup>a</sup> | 61.5      | 7.5  | 15                                  |
| None <sup>b</sup>                  | 75        | 4.4  | 94.5                                |
| Anthraquinone <sup>b</sup>         | 83        | 2.1  | 92.5                                |
| Phenanthraquinone <sup>b</sup>     | 80.5      | 2.5  | 92.5                                |

<sup>a</sup> Photolysis. <sup>b</sup> Thermolysis.

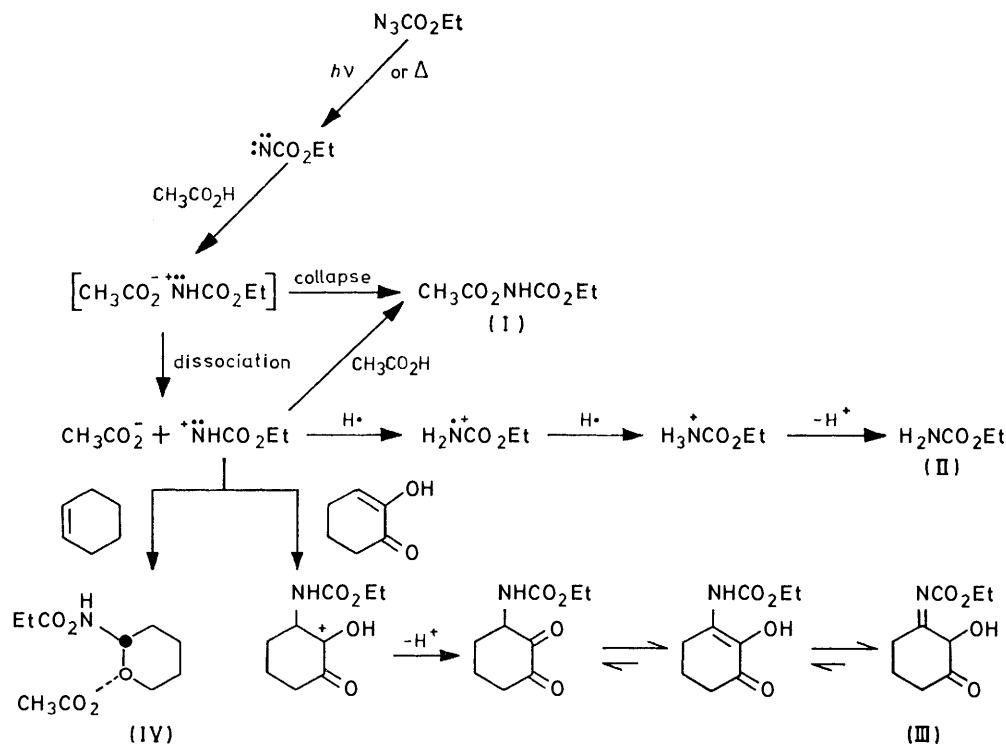
TABLE 4

The effect of cyclohexene on the photolysis of ethyl azidoformate (0.50M) in acetic acid

| [Cyclohexene] (M) | Yield (%) |      |      | Yield (%) of decomposition of azide |
|-------------------|-----------|------|------|-------------------------------------|
|                   | (I)       | (II) | (IV) |                                     |
| 0                 | 69.5      | 2.6  |      | 56                                  |
| 0.125             | 43        |      | 24   | 40                                  |
| 0.25              | 32.5      |      | 20   | 52                                  |
| 0.50              | 19.5      | 15.5 | 36   | 92.5                                |
| 1.0               | 20        |      | 40   | 42.5                                |

the keto form, it should not be as reactive towards nitrogen ion as cyclohexane-1,2-dione. The yield of (II) is decreased in the presence of the quinones which usually act as radical inhibitors,<sup>11</sup> but the yield of (I) is almost independent of their presence. This indicates that (I) is not formed *via* either radical species or the triplet nitrene.

*Effect of Cyclohexene.*—The effect of cyclohexene on the yield of (I) was nearly the same as that of cyclohexane-1,2-dione (Table 4 and Figure 2). The addition



SCHEME 1

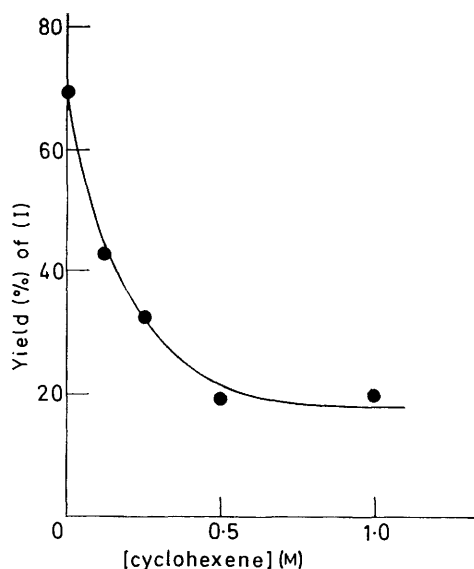


FIGURE 2 Effect of cyclohexene on the photolysis of ethyl azidoformate in acetic acid

of cyclohexene produced *trans*-1-acetoxy-2-ethoxycarbonylamino-cyclohexane (IV) stereospecifically in fairly good yield in spite of a very low concentration of cyclohexene (Table 4). As shown in Table 4, the yield of (II) also increased in the presence of cyclohexene, which efficiently traps triplet nitrenes or radicals.

Therefore these results support the idea that the reaction in acetic acid involves the ionic mechanism illustrated in Scheme 1. The nitrenium ion leaving the cage reacts with cyclohexene to give a cyclic ion. Acetic acid or acetate anion then attacks this ion to afford (IV) stereospecifically [see equation (2) in Scheme 2].

As indicated in the Experimental section, compound (IV) was quantitatively produced by the decomposition of 7-ethoxycarbonyl-7-azabicyclo[4.1.0]heptane (V), which was formed by the photolysis of ethyl azidoformate in cyclohexene, with acetic acid [equation (3)]. From consideration of the following results, we furthermore ascertained that (IV) is mainly formed through a pathway such as equation (2) and not (3) or (4) upon the decomposition of azide in the presence of cyclohexene in acetic acid. The observed relative reactivity of the addition to cyclohexene with respect to C-H insertion of

TABLE 5  
Relative reactivity of the addition to cyclohexene with respect to C-H insertion of ethoxycarbonylnitrene into cyclohexane

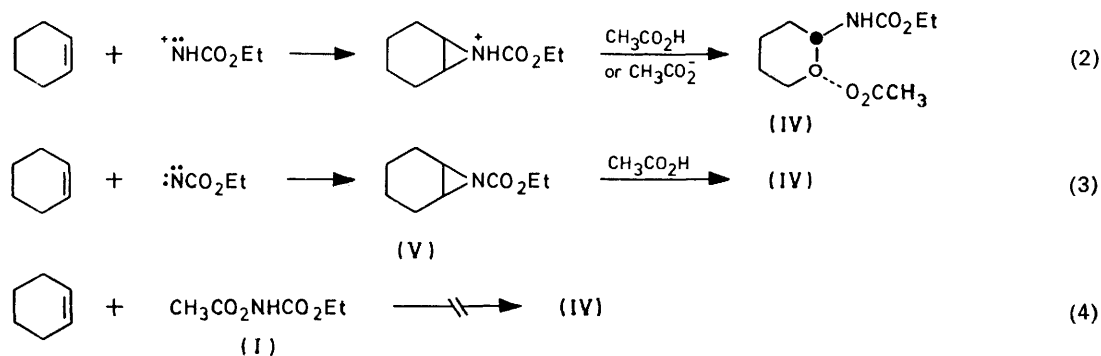
| Solvent                 | Relative reactivity |
|-------------------------|---------------------|
| Acetic acid             | 225                 |
| Cyclohexane-cyclohexene | 94.5                |

TABLE 6  
Rate constants and activation parameters for the decomposition of ethyl azidoformate

| Solvent     | Temperature (°C) | $10^5 k/s^{-1}$ | $E_a/kcal\ mol^{-1}$ | $\Delta S^\ddagger/cal\ mol^{-1}\ K^{-1}$ |
|-------------|------------------|-----------------|----------------------|---|
| Acetic acid | 109.4            | 13.0            |                      |   |
|             | 106.5            | 9.33            | 34.2                 | 10.6                                      |
|             | 99.2             | 3.79            |                      |   |
| Toluene     | 109.3            | 9.73            |                      |   |
|             | 106.5            | 6.73            | 32.2                 | 4.8                                       |
|             | 99.2             | 3.09            |                      |   |

the nitrene into cyclohexane was determined from the relative yield of (IV) or (V) to ethyl *N*-cyclohexylcarbamate. The value in acetic acid was more than twice that in cyclohexane-cyclohexene (Table 5). If the reaction in acetic acid proceeds *via* equation (3), the value in acetic acid should be nearly the same as that in the hydrocarbon mixture. The high reactivity in acetic acid probably depends upon the nature of the nitrenium ion which is more electrophilic than the nitrene. On the other hand, the treatment of (I) with acetic acid in the presence of cyclohexene did not produce (IV) under the reaction conditions for the formation of (I). Thus the process indicated in equation (4) was ruled out.

*Primary Formation of the Nitrene upon Decomposition of Ethyl Azidoformate in Acetic Acid.*—The rate of thermal decomposition of ethyl azidoformate in acetic acid or toluene was determined by measurement of the volume of nitrogen evolved as a function of time ( $V_t$ ). Linear plots of  $\ln V_\infty/(V_\infty - V_t)$  versus time were obtained, indicating the decompositions are first order in azide. Rate constants were determined from the slope of the plots, and the activation energies  $E_a$  and entropies of activation  $\Delta S^\ddagger$  were calculated from the equation derived from transition state theory. The results are summarized in Table 6. It is evident that  $E_a$  for acetic acid is somewhat greater than that for toluene, and that



SCHEME 2

compensation of  $E_a$  and  $\Delta S^\ddagger$  operates for both solvents. Since solvation of the azide in the initial state is greater in a polar than a non-polar solvent, the degree of desolvation in the transition state will be greater in acetic acid than in toluene. Therefore the small difference in activation parameters depends upon the ordinary solvent effect in which the transition state is solvated to a lesser extent than the initial state. If the decomposition in acetic acid proceeds through the conjugate acid of the azide,  $\text{EtO(OH)C=N-N}_2^+$  or  $\text{EtO(O=)C-NH-N}_2^+$ , the activation energy in acetic acid should be smaller than in toluene since the double-bond character of the  $\text{N-N}_2$  bond is decreased in acetic acid compared with toluene. Thus the result rules out acid-catalysed decomposition in acetic acid, and suggests the primary formation of nitrene. Though there is no direct connection with the reaction of ethyl azidoformate, Yukawa and Tsuno<sup>12</sup> have reported that the decomposition of *para*-substituted benzoyl azides in toluene or in acetic acid failed to give a Hammett plot: the rates for derivatives containing *para*-electron-releasing groups were nearly equal to that for the parent compound, but a linear Hammett correlation was observed in acetic acid containing 20%  $\text{H}_2\text{SO}_4$ . It is therefore assumed that acetic acid is not strong enough to allow acid-catalysed decomposition of carbonyl azides.

Although there is no clear evidence for primary nitrene formation during photolysis in acetic acid, this seems to be reasonable from the fact that photolysis provides enough energy to break the  $\text{N-N}_2$  bond whose double bond character is decreased by introducing an ester group in conjugation with the triazo group;<sup>13</sup> though acyl azides decompose thermally by a synchronous mechanism (Curtius rearrangement), the photochemical decomposition proceeds by an intermediate nitrene.

*Formation of Nitrenium Ion from Nitrene.*—On the basis of these results, we may conclude that the reaction of the nitrene with acetic acid gives the nitrenium-acetate ion pair as indicated in Scheme 1. Proton abstraction of carbene or nitrene from solvents is known. The results for photolysis of diazodiphenylmethane in methanolic solvent suggest the presence of a diphenyl-carbonium ion intermediate, arising by protonation of diphenylcarbene.<sup>14</sup> Reactions of benzenesulphonyl azide with *n*-butanol may or may not involve prior equilibration of the sulphonylnitrene and sulphonylnitrenium ion.<sup>15</sup> Recent work also indicates that only the singlet state of ethoxycarbonylnitrene<sup>16</sup> or phenylcarbene<sup>17</sup> can insert into alcoholic O-H bonds. However, we consider that experiments have not been performed to distinguish between direct insertion and various alternative mechanisms. In our case, we assume that the nitrenium ion is formed by proton abstraction by the electron pair of the singlet nitrene from acetic acid or through an O-N ylide intermediate which is generated by attack of the nitrene on the oxygen of acetic acid. The formation of nitrenium ion is perhaps assisted by the neighbouring acetate anion.

The stereospecific, vicinal *cis*-oxyamination of olefins by an alkylimido-osmium compound has been investigated by Patrick *et al.*<sup>18</sup> The study has stimulated us to examine the stereospecific *trans*-oxyamination of olefins.

#### EXPERIMENTAL

I.r. spectra were obtained on a Hitachi model EPI-G3 spectrometer. N.m.r. spectra were taken with a Nippon Denshi high resolution JNM 4H 100 spectrometer with tetramethylsilane as internal standard. Mass spectra were recorded on a Hitachi RMU-6E spectrometer. G.l.c. for quantitative analyses was carried out with Shimadzu GC-6A unit using glass columns (1 m  $\times$  3 mm) (column A, 10% polyethylene glycol 20M on 60–80 Chromosorb W; column B, 15% silicone SE-30 on 60–80 Uniport KS; column C, 10% polyethylene glycol 20M on 60–80 uniport KS). Photolyses were carried out externally in a quartz tube (25 cm  $\times$  1.8 cm) with a 300 W high pressure mercury lamp (Halos PIH-300) in the case not mentioned especially.

Acetic acid, 1,4-dioxan, cyclohexane, and toluene were purified by standard methods before use. Ethyl azidoformate,<sup>19</sup> *O*-acetyl-*N*-hydroxyurethane (I),<sup>20</sup> cyclohexane-1,2-dione,<sup>21</sup> 2-hydroxy-(3-ethoxycarbonylimino)cyclohexanone,<sup>9</sup> ethyl *N*-cyclohexylcarbamate (VI),<sup>19</sup> and cyclohexene<sup>22</sup> were prepared by methods described in the literature. Ethyl carbamate (II), m.p. 48–50° (from toluene), 9,10-anthraquinone, m.p. 278–279° (from ethanol), and 9,10-phenanthraquinone, m.p. 205–207° (from acetic acid), were purified by recrystallization from commercial materials (Wako). Cyclohexane-1,4-dione, m.p. 77–78° (lit.,<sup>23</sup> 78°), was a commercial material (Wako).

*Preparation of trans-1-Acetoxy-2-(ethoxycarbonylamino)cyclohexane (IV).*—Ethyl azidoformate (50.8 mmol) and cyclohexene (52.6 mmol) were dissolved in acetic acid (90 ml). After purging with dry nitrogen for 1 h, the solution was irradiated internally with a 100 W high pressure mercury lamp (Halos PIH-100) at room temperature for 17 h, resulting in *ca.* 100% decomposition of azide judging from the volume of evolved nitrogen. The mixture was distilled under reduced pressure, and the product (IV) (29%) was collected, b.p. 95–118° at 0.4 mmHg. It was recrystallized from light petroleum, m.p. 49.5–50°,  $\nu_{\text{max}}$  (neat) 3 320 (N-H), 2 920 (C-H), 1 725 (C=O), 1 530 (C-N), 1 260 (C-O), and 1 150  $\text{cm}^{-1}$  (C-O),  $\delta(\text{CCl}_4)$  4.6–4.9 (1 H, NH), 4.1–4.6 (1 H, m, 1-H), 3.8 (2 H, q,  $\text{OCH}_2$ ), 3.0–3.6 (1 H, m, 2-H), 1.9 (3 H, s,  $\text{O=CCH}_3$ ), 0.9–2.1 (8 H, m, 3-, 4-, 5-, and 6- $\text{H}_2$ ), and 1.1 (3 H, t,  $\text{CH}_3$ );  $m/e$  229 ( $M^+$ ), 186, 169, 140, 141, 128, and 123 (Found: C, 57.45; H, 8.5; N, 6.1.  $\text{C}_{11}\text{H}_{19}\text{NO}_4$  requires C, 57.6; H, 8.35; N, 6.1%).

Compound (IV) (3.13 mmol) and sodium hydroxide (62.6 mmol) were dissolved in 50% aqueous 1,4-dioxan (10 ml). The solution was refluxed for 3 h, and evaporated under reduced pressure. The residue was thoroughly extracted with ether-benzene (50 ml; 1:1), and the extract was dried ( $\text{MgSO}_4$ ). The solvent was removed, and *trans*-2-aminocyclohexanol was crystallized from ether (64%), m.p. 63–64° (lit.,<sup>24</sup> 65°).

*trans*-2-Aminocyclohexanol (0.94 mmol) was dissolved in absolute ether (5 ml), and anhydrous hydrogen chloride was slowly passed through. Crystalline *trans*-2-hydroxycyclohexylamine hydrochloride slowly precipitated (33%), m.p. 179–181° (lit.,<sup>19</sup> m.p. 175–178°).

Product (IV) was also obtained by the following pro-

cedure. A solution which consists of ethyl azidoformate (58.2 mmol) and cyclohexene (58.2 mmol) was purged with dry nitrogen for 1 h, and irradiated externally for 34.5 h, resulting in 76% decomposition of azide according to the volume of evolved nitrogen. Distillation of the mixture gave 7-ethoxycarbonyl-7-azabicyclo[4.1.0]heptane (V) (49%), b.p. 125–126° at 20–23 mmHg (lit.,<sup>16</sup> 67–68° at 1.25 mmHg),  $\delta(\text{CCl}_4)$  3.9 (2 H, q,  $\text{OCH}_2$ ), 2.3–2.9 (2 H, m, CH), 1.2 (3 H, s,  $\text{CH}_3$ ), and 0.6–2.3 (8 H, m,  $\text{CH}_2$ ) (Found: C, 63.7; H, 9.2; N, 8.2. Calc. for  $\text{C}_9\text{H}_{15}\text{NO}_2$ : C, 63.9; H, 8.95; N, 8.3%). Compound (V) (1.6 mmol) was dissolved in acetic acid (15 ml) at room temperature exothermically. The solution was allowed to stand at room temperature overnight. After the solution was evaporated under reduced pressure, crystalline (IV) was obtained (ca. 100%). G.l.c. analysis showed it to be at least 92% pure.

**Photochemical Reaction of Ethyl Azidoformate in Acetic Acid.**—Ethyl azidoformate (8.0 mmol) was dissolved in acetic acid to give a total volume of 10.0 ml. Dry nitrogen was bubbled through the solution for 1 h, and it was then irradiated at 25° for 5–10 h. Azide consumed (55, 60, or 87%) was determined by means of the i.r. bands at 2 185 and 2 137  $\text{cm}^{-1}$ . Products (I) and (II) were analysed by g.l.c. using column A, the amounts being calculated from the peak areas in the usual manner. The analyses of the yields agreed within < 3%. The reaction mixture was neutralized with aqueous sodium hydrogencarbonate at < 20° and extracted with ether. After evaporation of solvent, urethane (I) was isolated by preparative g.l.c. (Hitachi model 063-0012) on an aluminium column (2 m  $\times$  8 mm) packed with 15% silicone SE-30 on 60–80 Unipor KS,  $\nu_{\text{max}}$  (neat) 3 580 and 3 280 (NH), 2 990 (C–H), 1 800 and 1 750 (C=O), 1 480 (C–N), and 1 260, 1 190, and 1 110  $\text{cm}^{-1}$  (C–O);  $\delta(\text{CCl}_4)$  8.0–8.2 (1 H, NH), 4.2 (2 H, q,  $\text{OCH}_2$ ), 2.2 (3 H, s,  $\text{CH}_3$ ), and 1.3 (3 H, t,  $\text{CH}_3$ );  $m/e$  58, 43, and 28 (Found: C, 40.4; H, 6.1; N, 9.45. Calc. for  $\text{C}_5\text{H}_9\text{NO}_4$ : C, 40.8; H, 6.15; N, 9.5%). This had the same i.r. spectra as an authentic specimen.<sup>20</sup>

The experiments in the presence of cyclohexane-1,2-dione, cyclohexane-1,4-dione, and cyclohexene were carried out under conditions similar to those above. Azide consumed is indicated in Tables 1, 3, and 4, and the yields of products (I), (II), and (IV) were based on two or three runs with an error of  $\pm 4\%$ . In the presence of cyclohexene, azide (5 mmol) was dissolved in acetic acid to make a total volume of 10.0 ml, and the products were analysed by g.l.c. using column B.

Non-photolysed mixtures did not produce (I)–(IV). None of the g.l.c. peaks of the starting materials and products overlapped.

**Thermal Reactions of Ethyl Azidoformate in Acetic Acid.**—A solution (1.0 ml) containing the same components as for the photolysis was placed in a sealed tube and heated at 116° for 4 h, resulting in 92–95% decomposition of the azide. The yields of products (I)–(III) were determined by g.l.c. analysis using column A as described above. The experiments in the presence of cyclohexane-1,2-dione, 9,10-anthraquinone, and 9,10-phenanthraquinone were carried out as described above, and the determination of the yield of (I) and (II) was done by similar methods. In the presence of cyclohexane-1,2-dione, azide (ca. 5 mmol) was dissolved in acetic acid to give a total volume of 10.0 ml, the solution was heated at ca. 120° for 1.5 h, and products (I), (II), and (IV) were analysed by g.l.c. employing column

B. The experimental error was almost identical with that in the photochemical case.

**Treatment of (I) with Cyclohexene or Cyclohexane in Acetic Acid.**—Urethane (I) (5 mmol) and cyclohexene (5 mmol) or cyclohexane (5 mmol) were dissolved in acetic acid to give a total volume of 10.0 ml. The solution was heated at 116° for 2 or 4 h, or irradiated for 7 h as above. G.l.c. analysis using column B did not show the formation of (IV) or ethyl *N*-cyclohexylcarbamate. The amount of compound (I) was not decreased under the photochemical conditions, but ca. 7% of (I) was consumed under the thermal conditions during 2 h. However (I) was not consumed in the absence of cyclohexene under the thermal conditions.

**Relative Reactivity of the Addition to Cyclohexene versus the Insertion of the Nitrene into Cyclohexane.**—Cyclohexene (2.45 mmol), cyclohexane (7.3 mmol), and ethyl azidoformate (2.56 mmol) were dissolved in acetic acid to give a total volume of 10.0 ml. The solution was irradiated for 8 h as described above. A solution which contained cyclohexene (20.5 mmol), cyclohexane (61.1 mmol), and ethyl azidoformate (3.37 mmol) was also irradiated for 8 h. Both photolyses resulted in ca. 87% decomposition of azide. The yield of products (IV)–(VI) was determined by g.l.c. analysis using column C. The relative reactivity of addition to C–H insertion was calculated from the yields, the initial concentrations of cyclohexane and cyclohexene, and the reaction probabilities of the C–H and C=C bonds of cyclohexane and cyclohexene, respectively.

**Kinetic Measurements.**—Ethyl azidoformate (ca. 5.6 mmol) was dissolved in acetic acid or toluene (3 ml). The rates of decomposition of azide were determined at three temperatures by measurement of the volume of nitrogen evolved as a function of time.

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