Thermolysis of Ethyl Azidoformate in 2,3-Dimethyl-2-butene. An Example of a Simple Olefin Giving a Dominant 1,2,3-Δ^2-Triazoline Intermediate

Paul P. Nicholas

B. F. Goodrich Research and Development, Brecksville, Ohio 44141

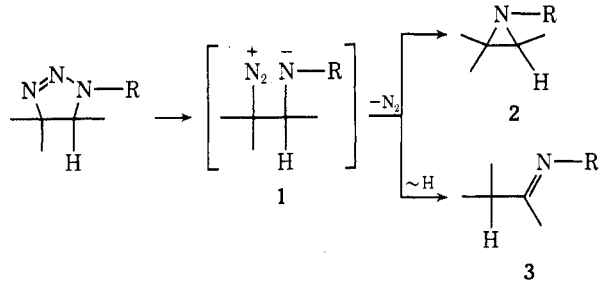
Received June 23, 1975

The thermolysis of ethyl azidoformate in refluxing 2,3-dimethyl-2-butene proceeds through competitive 1,2,3-Δ^2-triazoline and carbethoxynitrene routes. The triazoline route dominates by a factor of about 2–3. The main products are 3,3-dimethyl-2-butylidene ethyl carbamate (62%), 1-carbethoxy-2,2,3,3-tetramethylaziridine (36%), and *N*-1-(2,3-dimethyl-2-butenyl)ethyl carbamate (2.5%).

The thermolysis of alkyl azidoformates in many simple olefins proceeds by rate-determining loss of nitrogen to give carbalkoxynitrene intermediates.[1] The ultimate product is mainly the aziridine adduct of the olefin. However, the reaction can follow a different course with so-called activated olefins, that is olefins which are either strained[2-5] or contain strong electron-donating groups such as alkoxy[6] and amino[7] substituents. With such olefins, 1,3-dipolar cycloaddition becomes important, giving 1,2,3-Δ^2-triazoline intermediates. Similar trends have been observed with aryl azides.[8] A kinetic study of aryl azide cycloadditions to norbornene led Scheiner to propose a transition state for triazoline formation where some positive charge has developed at the olefinic carbon atom.[9]

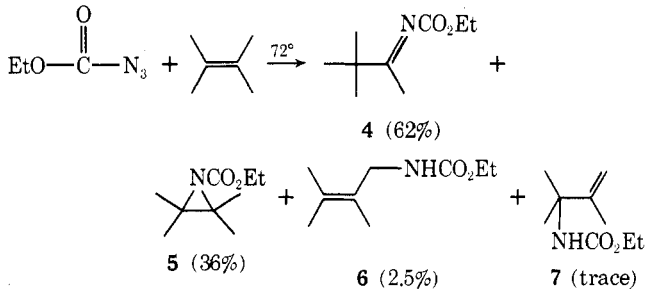
Differences in product distribution are among those features which distinguish between triazoline and nitrene intermediates. Like nitrenes, triazolines can give aziridines. However, unlike nitrenes, triazolines also produce anils, and these are usually the dominant products.[2,5,6,9-11] The often-proposed route to the anils involves a diazonium–betaine intermediate (**1**) which partitions between the aziridine **2** and the anil **3** on loss of nitrogen (Scheme I).

Scheme I



This paper describes the thermolysis of ethyl azidoformate in 2,3-dimethyl-2-butene. It appears to be the first report of a dominant 1,2,3-Δ^2-triazoline route for the thermolysis of an alkyl azidoformate in a simple olefin. The evidence further suggests that this is a borderline case of competitive nitrene and triazoline formation.

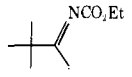
Thermolysis of ethyl azidoformate in refluxing 2,3-dimethyl-2-butene carried to about 90% conversion gives a quantitative yield of three carbamates. These are 3,3-dimethyl-2-butylidine ethyl carbamate (**4**), 1-carbethoxy-2,2,3,3-tetramethylaziridine (**5**), and *N*-1-(2,3-dimethyl-2-butenyl)ethyl carbamate (**6**). It is possible that a very small amount of *N*-3-(2,3-dimethyl-1-butenyl)ethyl carbamate (**7**) might also be present but is not completely resolved from the imide **4** under our VPC conditions. The imide **4** is not a product of the aziridine **5**. Repeating this reaction in the presence of labeled aziridine, 1-carbethoxy-2-methyl-d_1-2,3,3-trimethylaziridine (**8**) (Table I), gives negligible label in the imide **4**. Essentially all of the added label is accounted for as unconverted aziridine. Furthermore, forcing the thermal rearrangement of **5** at 150° (neat) gives only the carbamate **7** in a first-order reaction with $k_1 = 0.0207$ hr^{-1} ($\sigma = 2 \times 10^{-4}$), $t_{1/2} = 34$ hr.



The dominance of the imide **4** in the product distribution from the thermolysis of ethyl azidoformate in 2,3-dimethyl-2-butene suggests that the major route for this reaction is through 1-carbethoxy-4,4,5,5-tetramethyl-1,2,3-Δ^2-triazoline (**9**). This could decompose to the imide **4** through a methide shift analogous to the hydride shift in Scheme I. To confirm that the imide **4** does not result from an anomalous reaction of carbethoxynitrene, we generated authentic carbethoxynitrene in 2,3-dimethyl-2-butene by both α-elimination from *N*-*p*-nitrobenzenesulfonoxyurethane[12] (**10**) and photolysis of ethyl azidoformate.[13] The results show that the reaction of carbethoxynitrene with 2,3-dimethyl-2-butene is typical of carbethoxynitrene–olefin reactions. The expected aziridine **5** is, in fact, the dominant product with only small amounts of imide **4** being present.

There remains the question of whether any of the aziridine **5** from the thermolysis of ethyl azidoformate in 2,3-dimethyl-2-butene comes from a competing carbethoxynitrene route. The presence of carbamate **6** suggests that it does. Assuming that the mole ratio, **5/6**, from the α-elimination reaction (Table II) can serve as an approximate index of carbethoxynitrene-derived products, one can estimate that about 60% of the aziridine **5** from ethyl azidoformate thermolysis is produced in this way. This also means that triazoline formation is about three times faster than carbethoxynitrene formation. To test this prediction, a comparison was made between the observed first-order rate constant for ethyl azidoformate thermolysis in 2,3-dimethyl-2-butene and that in 2,3-dimethylbutane and cyclohexane (Table III). Only carbethoxynitrene formation can be rate determining in these two saturated C_6 hydrocarbons. Since the rate of azidoformate thermolysis is highly insensitive to solvent polarity,[1] such a comparison might serve as a useful test. From the above relative rate esti-

Table I
Thermolysis of 0.34 *M* Ethyl Azidoformate in 2,3-Dimethyl-2-butene with Added 1-Carbethoxy-2-methyl-d_1-2,3,3-trimethylaziridine

Reactants (mmol)	Products, mmol:  $-d_0$	$-d_1$	 $-d_0$	$-d_1$
1. EtO—C(=O)—N_3 (6.87)	3.84		2.24	
2. EtO—C(=O)—N_3 (6.87) 5 (0.22) 8 (1.87)	3.92	0.08 (σ = 0.07)	2.70	1.73

mate, thermolysis in 2,3-dimethyl-2-butene is expected to be about four times faster than in the saturated hydrocarbons. While there is a rate enhancement in 2,3-dimethyl-2-butene, it is only by a factor of 2.0–2.4 rather than 4. This is in better agreement with the 2.6-fold rate enhancement expected if all the aziridine **5** were produced through carbethoxynitrene. Thus, these two estimates of the carbethoxynitrene component in ethyl azidoformate thermolysis are not in good agreement. They bracket the nitrene contribution at between 60 and 100% of the aziridine **5** produced. The reason is unclear. Possibly the high sensitivity of the predicted relative rate to small errors in the analysis of a minor component, the carbamate **6**, is responsible. Nevertheless, both estimates support carbethoxynitrene as an important source of the aziridine **5**.

Therefore, it seems that four methyl substituents on a double bond provide sufficient charge stabilization in the triazoline-forming transition state[9] to make it the dominant reaction. This raises the interesting question of whether this chemistry of ethyl azidoformate is peculiar to 2,3-dimethyl-2-butene or fairly general for tetraalkyl-substituted olefins.

Experimental Section

Reagents. Ethyl azidoformate was prepared according to the method of Lwowski and Mattingly[14] and *N*-*p*-nitrobenzenesulfonoxyurethane (**10**) was prepared by the method of Lwowski and Maricich.[12] 2,3-Dimethyl-2-butene (99%) was purchased from Chemical Samples Co., Columbus, Ohio, and distilled from Na–K under nitrogen. A middle fraction was taken and shown by VPC to be >99.9% pure.

Thermolysis of Ethyl Azidoformate in 2,3-Dimethyl-2-butene. Preparative Scale. A 250-ml, three-neck flask was fitted with a water-cooled condenser, a gas dispersion tube, and a magnetic stirring bar. The opening at the top of the condenser was directed into a shallow mercury well with tubing. The apparatus was flame dried under nitrogen and charged with 5.94 g (0.0517 mol) of ethyl azidoformate and 150 ml of 2,3-dimethyl-2-butene. The stirred solution was purged with nitrogen, then heated, under nitrogen, at gentle reflux for 310 hr. This corresponds to about 90% conversion as measured by the disappearance of the 2140-cm^{-1} band in ethyl azidoformate. The product was distilled on a spinning band column, giving aziridine **5**: bp 59° (1.5 mm); ir (neat) no NH, 1705 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.26 ppm (t, 3, J = 7 Hz), 1.28 ppm (s, 12), 4.13 (q, 2, J = 7 Hz); mass spectrum parent ion m/e 171.

Anal. Calcd for $C_9H_{17}NO_2$: C, 63.12; H, 10.01; N, 8.18. Found: C, 63.32; H, 9.83; N, 8.28.

Imide **4**: bp 69–70° (1.8 mm); ir (neat) no NH, 1717 (C=O), 1660 cm^{-1} (C=N); NMR ($CDCl_3$) δ 1.16 (s, 9), 1.32 (t, 3, J = 7 Hz), 1.97 (s, 3), 4.24 ppm (q, 2, J = 7 Hz); mass spectrum parent ion m/e 171.

Anal. Calcd for $C_9H_{17}NO_2$: C, 63.12; H, 10.01; N, 8.18. Found: C, 62.20; H, 9.91; N, 8.10.

Table II
Product Distributions from the Reaction of Carbethoxynitrene with 2,3-Dimethyl-2-butene

Method	Products, % yield: 4	5	6	7
α-Elimination (10)[a]	0.5	59.	6.9	1.0
Photolysis (EtO—C(=O)—N_3)[b]	1.	54.	8.8	0.9

[a] Dichloromethane used as cosolvent (45% v/v); reaction carried out at 42°. [b] Reaction carried out at 0°.

Table III
Kinetics of Ethyl Azidoformate Decomposition at 70° in C_6 Hydrocarbon Solvents

Solvent	Concn, *M*	$k \times 10^3$, hr^{-1}	$\sigma \times 10^3$	$k(>=<)/k$
2,3-Dimethyl-2-butene	0.23	5.3	0.11	1.0
2,3-Dimethylbutane	0.18	2.7	0.01	2.0
Cyclohexane	0.23	2.2	0.06	2.4

The carbamate **6** was not isolated but identified by comparing its VPC retention time and normalized mass spectrometric fragmentation pattern with those of authentic material. Carbamate **6**: bp 81–82° (0.35 mm); ir (neat) 3340 (NH), 1695 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.23 (t, 3, J = 7 Hz), 1.68 (broad s, 9), 3.78 (d, 2, J = 6 Hz), 4.12 (q, 2, J = 7 Hz), 4.7 ppm (broad, 1).

Analytical Scale. A two-neck, 25-ml flask was fitted with a water-cooled condenser and a gas inlet tube. The opening at the top of the condenser was directed into a shallow mercury well with tubing. The apparatus was flame dried under nitrogen and charged with 0.790 g (0.00687 mol) of ethyl azidoformate and 20 ml of 2,3-dimethyl-2-butene. The system was purged with 600 ml of nitrogen, then heated at gentle reflux for 310 hr. The reaction mixture was cooled, transferred into a container having a known quantity of naphthalene (internal VPC standard), and analyzed by VPC. Quantitative analysis was performed on a calibrated 5 ft × 0.25 in. column packed with 20% Ucon 50 HB5100 on 70/80 mesh Anakrom U. A glass sleeve was used in the injection port, which was maintained at 190–200°.

Photolysis of Ethyl Azidoformate. A PCQ9G-1 photochemical immersion lamp, Ultraviolet Products, Inc., with a 2537-cm^{-1} peak intensity at 2.5 W was housed in a reaction vessel prepared from a 7.5-in. length of 18-mm Pyrex tubing. The reactor contained a gas inlet and outlet tube. It was charged with 0.88 g (7.6 mmol) of ethyl azidoformate and 21 ml of 2,3-dimethyl-2-butene. The solutions was purged with 400 ml of nitrogen through a 6-in. needle, cooled in an ice bath, and irradiated for 18 hr. Quantitative analysis was performed by VPC in the usual way. Distillation gave 0.53 g (41%) of aziridine **5**.

α-Elimination in *N*-*p*-Nitrobenzenesulfonoxyurethane (10). A three-neck, 50-ml flask was fitted with a nitrogen inlet, a rubber septum, a magnetic stirring bar, and a water-cooled condenser. The opening at the top of the condenser was directed to a shallow mercury well with tubing. The apparatus was flame dried under nitrogen, then charged with 0.770 g (2.65 mmol) of **10**, 11.7 ml of 2,3-dimethyl-2-butene, and 9.5 ml of dichloromethane. The system was purged with about 400 ml of nitrogen and heated to gentle reflux. Triethylamine (0.42 ml) was then added through a syringe over a 5-min period. Triethylammonium *p*-nitrobenzenesulfonate precipitates during the addition. After addition was complete, the mixture was stirred at gentle reflux for an additional 2 hr and cooled, and the solution was decanted from the precipitate into a bottle containing naphthalene, the VPC internal standard. The precipitate was rinsed twice with 2,3-dimethyl-2-butene and the rinse combined with the decanted solution. The mixture was then chilled and shaken with 15 ml of cold water. The organic phase was decanted off, chilled to −13° to crystallize residual water, and analyzed by VPC in the usual way. The purpose of this water extraction step is to remove small amounts of dissolved triethylammonium *p*-nitrobenzenesulfonate. This can catalyze some rearrange-

ment of the aziridine 5 to the carbamate 7 in the injection port of the gas chromatograph. For example, analysis of the chilled reaction mixture without the water extraction step gives 4 (0.8%), 5 (55%), 6 (7.0%), and 7 (2.8%).

1-Chloro-2,3-dimethyl-2-butene-4-d_1 (11). DCl was generated from 566 g (4.02 mol) of benzoyl chloride and 16.1 g (0.805 mol) of D_2O according to the method of Brown and Groot.[15] This was directed through a gas dispersion tube into a stirred, three-neck, 250-ml flask containing 120.1 g (1.46 mol) of 2,3-dimethyl-1,3-butadiene cooled to −80°.[16] After DCl generation was complete, the contents were purged with nitrogen and allowed to warm to room temperature and stand for 3 days. Distillation gave three fractions, 30.0 g (0.253 mol) of 3-chloro-2,3-dimethyl-1-butene-4-d_1 (12), bp 35° (45 mm) [lit.[16] bp 32° (45 mm)], 97 g of an unknown fraction, bp 37–53° (45 mm), and 48.6 g (0.410 mol) of the chloride 11, bp 53–55° (45 mm) [lit.[16] bp 57.7° (45 mm)]. Mass spectra: 11, 7% d_0, 88% d_1, 5% d_2; 12, 7% d_0, 89% d_1, 4% d_2.

2,3-Dimethyl-2-butene-d_1 (13). The chloride 11 was reduced using the method of Brown and Bell.[17] A three-neck 1-l. flask was fitted with an addition funnel, a magnetic stirring bar, a thermometer, and a water-cooled condenser. It was charged with 390 ml of glyme, 210 ml of water, and 24 g (0.60 mol) of sodium hydroxide. The mixture was stirred and heated to 55°. To this was added 90.6 g (2.40 mol) of sodium borohydride. When dissolved, 8.75 g (0.0739 mol) of the chloride 11 was added over a 15-min period. Some cooling was necessary to maintain the temperature at 50–55°. There was considerable gas evolution. The mixture was allowed to cool and stirred overnight. It was then extracted with two 400-ml aliquots of water. The organic phase was then dried over $CaSO_4$ and distilled on a spinning band column giving 11.6 g (46%) of 13, bp 71–72°, NMR ($CDCl_3$) 1.63 ppm (s).

1-Carbethoxy-2-methyl-d_1-2,3,3-trimethylaziridine (8). A solution of 1.57 g (13.6 mmol) of ethyl azidoformate in 21 ml of the butene 13 was photolyzed in the usual way. Distillation gave 1.14 g (49%) of aziridine 8: NMR ($CDCl_3$) same as that of aziridine 5; mass spectrum, 10% d_0 (σ 1.3), 85% d_1 (σ 1.4), 5% d_2 (σ 1.2).

Kinetics of 1-Carbethoxy-2,2,3,3-tetramethylaziridine (5) Thermolysis. This experiment was carried out by proton NMR using a sealed 30-μl Kontes microcell charged with aziridine 5. The cell was placed in a constant-temperature bath at 150° and periodically removed for analysis. The rate of carbamate 7 formation was followed by measuring the change in the combined area of the two vinylic protons in 7 relative to the total area of the methylene quartet of the ethoxy groups present. The final spectrum, at 88% conversion, was that of the carbamate 7.

Kinetics of Ethyl Azidoformate Thermolysis. Cyclohexane and 2,3-dimethylbutane were purchased and further purified by distillation from Na–K under nitrogen. Solutions of ethyl azidoformate were prepared, charged into several 7-mm glass tubes, evacuated, and sealed with a torch. These were placed in a constant-temperature bath and individual samples taken periodically for analysis. The rate of ethyl azidoformate decomposition was followed by infrared using the disappearance of the 2140-cm^{-1} band.

Acknowledgments. My thanks to Eugene Licursi for his technical assistance, to Kenneth Welch and Robert Lattimer for the mass spectrometric analyses, and to Jerry Westfahl for the NMR analyses.

Registry No.—4, 56488-01-8; 5, 56488-02-9; 6, 1611-51-4; 8, 56488-03-0; 10, 2955-74-0; 11, 56488-04-1; 12, 56488-05-2; 13, 56488-06-3; ethyl azidoformate, 817-87-8; 2,3-dimethyl-2-butene, 563-79-1; DCl, 7698-05-7; 2,3-dimethyl-1,3-butadiene, 513-81-5.

References and Notes

(1) W. Lwowski, "Nitrenes", Interscience, New York, N.Y., 1970, p 185.
(2) A. C. Oehlschlager, P. Tillman, and L. H. Zalkow, *Chem. Commun.*, 596 (1965).
(3) L. A. Paquette, R. J. Haluska, M. R. Short, K. L. Reed, and J. Clardy, *J. Am. Chem. Soc.*, **94**, 529 (1972).
(4) J. Oakland and F. Scheinmann, *J. Chem. Soc., Perkin Trans. 1*, 800 (1973).
(5) J. Bastable, J. Hobson, and W. Riddell, *J. Chem. Soc., Perkin Trans. 1*, 2205 (1972).
(6) I. Brown and O. E. Edwards, *Can. J. Chem.*, **43**, 1266 (1965).
(7) R. Fusco, G. Bianchetti, and D. Pocar, *Gazz. Chim. Ital.*, **91**, 933 (1961); *Chem. Abstr.*, **57**, 14020*h* (1962).
(8) G. L'Abbe, *Chem. Rev.*, **69**, 345 (1969).
(9) P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *J. Am. Chem. Soc.*, **87**, 306 (1965).
(10) P. Scheiner, *J. Org. Chem.*, **32**, 2022 (1967).
(11) P. Scheiner, *J. Org. Chem.*, **30**, 7 (1965).
(12) W. Lwowski and T. J. Maricich, *J. Am. Chem. Soc.*, **87**, 3630 (1965).
(13) W. Lwowski and T. W. Mattingly, Jr., *Tetrahedron Lett.*, 277 (1962).
(14) W. Lwowski and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **87** 1947 (1965).
(15) H. C. Brown and C. Groot, *J. Am. Chem. Soc.*, **64**, 2223 (1942).
(16) L. F. Hatch and G. E. Journey, *J. Am. Chem. Soc.*, **75**, 3712 (1953).
(17) H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962).

Dehydrogenation of Heterohelicenes by a Scholl Type Reaction. The Dehydrohelicenes[1]

J. H. Dopper, D. Oudman, and Hans Wynberg*

Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands

Received October 29, 1974

The reaction of seven heterohelicenes with $AlCl_3$ is described. The products are compounds in which the two helical termini of a helicene are connected by a σ bond. They are called dehydrohelicenes. The intramolecular ring closure is limited to hetero[5]- and -[6]helicenes. In addition to the synthesis, the spectral properties of dehydrohelicenes are discussed.

In our study of the synthesis, resolution, and chemistry of heterohelicenes,[2] the preparation of dehydrohelicenes by a Scholl reaction became of importance. The Scholl reaction has been defined by Balaban and Nenitzescu[3] as the elimination of two aryl-bound hydrogens accompanied by the formation of an aryl–aryl bond under the influence of Friedel–Crafts catalysts. Groen and Wynberg used this reaction in preparing 2 in low yield from the heterohexahelicene 1[4] (Scheme I). The conversion of 2 to the [7]heterocirculene 3[5] prompted us to undertake a more systematic study of the Scholl reaction of heterohelicenes. Compounds such as 2, in which the two helical termini of a helicene are connected by a σ bond, will be called dehydrohelicenes.[6]

Results

Most of the heterohelicenes used in this study (Schemes II and III) have been described previously.[4,7] The new compounds 4, 6, 7, 9, and 16 were prepared by standard methods.[1] In the original "Scholl" method employed by Groen,[4] 1 was dissolved in benzene at room temperature and to this solution an excess of $AlCl_3$ was added. The mixture was allowed to stand for 24 hr prior to isolating 2. This method is improved when a mixture of $AlCl_3$ and NaCl is used.[8] When 1, $AlCl_3$, and NaCl were mixed together and heated to 140°, a black melt was formed immediately. After hydrolysis of this melt 2 was obtained in 95% yield. The other dehydrohelicenes were obtained in a similar manner. A