

completion or from standard solutions prepared with compounds known to comprise the reaction products. Extinction coefficients used for IV, IX, X, and XI in ethanol were ($\times 10^{-4}$): 1.73, 1.55, 0.845, and 2.20, respectively. Plots of $\log(A_{\infty} - A)$ vs. time yielded straight lines for reactions carried out in the alcohols, water, and alcohol-water mixtures. Individual runs in acetonitrile were approximately zero order with respect to the tolan substrate. A few experiments carried out in dimethylformamide gave results similar to those for acetonitrile.

Aqueous buffer solutions ranging in pH from 3.4 to 6.0 were prepared by mixing appropriate volumes of 0.01 *M* aqueous sodium acetate solution with a solution 0.01 *M* in acetic acid and 0.01 *M* in sodium chloride. More acidic solutions were prepared with hydrochloric acid and sufficient sodium chloride to maintain an ionic strength of 0.01. For use in the experiments with 2,4'-tolandicarboxylic acid, buffers in aqueous ethanol were prepared by mixing a solution 0.05 *M* in disodium hydrogen phosphate with one 0.025 *M* in citric acid. The solvent for each of these solutions was 16.3% ethanol by weight.

Titration Data. Values for K_1 and K_2 for 2,2'-tolandicarboxylic acid were obtained by application of the equations of Britton²⁵ to data from a titration curve. In order to avoid precipitation of the acid

(25) H. T. S. Britton, *J. Chem. Soc.*, 1903 (1925).

in the course of the titration some alcohol was added to the aqueous solvent. Thus, a 15 ml. solution of the disodium salt of 2,2'-tolandicarboxylic acid (from 0.9849 g. of acid) was added to 50 ml. of 0.15 *M* KCl in water and 20 ml. of 95% ethanol. The solution was titrated with aqueous hydrochloric acid at 30°, the pH change being followed with a Beckman Model G pH meter. The values of pK_1 and pK_2 calculated²⁵ from these data were 4.08 and 4.88. To correct to values for water, it was assumed that the effect of solvent change on the K values for 2,2'-tolandicarboxylic acid was the same as the effect of the ionization constant of benzoic acid.²⁶ With this correction $K_1 = 2.63 \times 10^{-4}$ and $K_2 = 4.17 \times 10^{-5}$ for 2,2'-tolandicarboxylic acid.

K_a for 2-tolancarboxylic acid was obtained from extinction coefficients for the acid in 0.1 *M* hydrochloric acid ($\epsilon_{283} 1.77 \times 10^4$, $\epsilon_{300} 1.26 \times 10^4$), in 0.1 *M* aqueous sodium hydroxide ($\epsilon_{283} 2.53 \times 10^4$, $\epsilon_{300} 2.13 \times 10^4$), and in aqueous buffer solutions at pH 3.80 ($\epsilon_{283} 2.08 \times 10^4$, $\epsilon_{300} 1.62 \times 10^4$) and pH 4.00 ($\epsilon_{283} 2.16 \times 10^4$, $\epsilon_{300} 1.74 \times 10^4$), using the equations of Brown and Mihm.²⁷ Measurements were made at 23°. The value of K_a found by this procedure was 1.12×10^{-4} .

(26) E. Grunwold and B. J. Berkowitz, *J. Am. Chem. Soc.*, 73, 4939 (1951).

(27) H. C. Brown and R. Mihm, *ibid.*, 77, 1723 (1955).

The Decomposition of Olefinic Azides¹

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Contribution No. 931 from the Central Research Department,
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The synthesis of olefinic azides and their thermal decomposition in a solvent to give 1-azabicyclo[3.1.0]hexanes and cyclic imines is described. Evidence is presented to show that the azide functionality adds intramolecularly to the double bond to give an isolable triazoline VII, which opens up in the rate-determining step to a diazonium ion type intermediate VIII, followed by evolution of nitrogen and formation of products.

The finding that the thermal decomposition² of 2-biphenyl azides gives carbazoles in good yields has prompted many investigations of the synthetic utility of the decomposition of organic azides. For example, vapor phase pyrolysis of aromatic azides having an alkyl chain in the *ortho* position gives indanes and tetrahydroquinolines^{3a-d} while pyrolysis of vinyl azides

(1) A preliminary account of this work was presented before the Organic Division, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 3, 1964.

(2) P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, 73, 2435 (1951); P. A. S. Smith and J. H. Boyer, *ibid.*, 73, 2626 (1951); P. A. S. Smith, J. M. Glegg, and J. H. Hall, *J. Org. Chem.*, 23, 524 (1958).

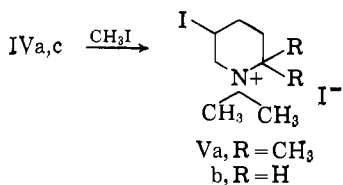
gives azirines.^{3e} Similarly, ultraviolet irradiation of steroidal acyl azides gives bicyclic lactams.^{4,5} In this paper, the synthesis and decomposition of olefinic azides containing unsaturation two, three, four, and five bonds away from the azide group is described. The assumption was made that the π -electrons four and five bonds away would assist anchimerically in the decomposition of these azides to give cyclic and bicyclic amines as products.

The primary and secondary azides IIb-f were prepared by converting the corresponding alcohols to the *p*-toluenesulfonate esters and treating the crude esters with sodium azide in aqueous ethanol or pyridine at room temperature. The tertiary azide IIa was prepared by adding the corresponding alcohol to a mixture of hydrazoic acid and concentrated sulfuric acid in

(3) (a) G. Smolinsky, *J. Am. Chem. Soc.*, 83, 2489 (1961); (b) G. Smolinsky, *J. Org. Chem.*, 26, 4108 (1961); (c) G. Smolinsky and B. J. Feuer, *J. Am. Chem. Soc.*, 86, 3085 (1964); (d) G. Smolinsky and B. J. Feuer, *J. Org. Chem.*, 29, 3097 (1964); (e) G. Smolinsky, *J. Am. Chem. Soc.*, 83, 4483 (1961); *J. Org. Chem.*, 27, 3557 (1962).

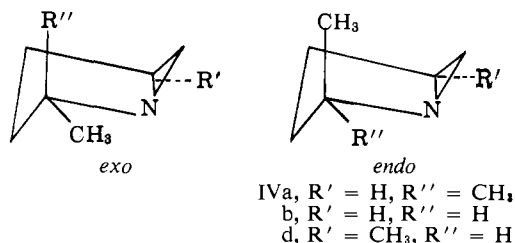
(4) J. W. Apsimon and O. E. Edwards, *Can. J. Chem.*, 40, 896 (1962).

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

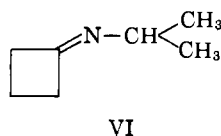


of these ring-opened salts (Va,c) showed two different N-CH₃ peaks, one for the *cis*- and the other for the *trans*-methyl group with respect to the iodine in the 5-position.

From conformational analysis one would expect two stereoisomers for each IVb and IVd, one isomer where the methyl group is *exo* and the other where it is *endo*. Although gas chromatography showed only one



peak for 2-methyl-1-azabicyclo[3.1.0]hexane IVb (it is possible that the two isomers are not resolved), it showed two peaks for IVd. The two isomers of IVd were separated as pure liquids and were found to possess very similar but definitely different infrared and n.m.r. spectra. They were characterized by their crystalline picrates, m.p. 156–157° and 162.5–164°, respectively (mixture melting point depressed). Decomposition of 5-azido-2-methyl-1-hexene (IIc) gave, besides 2,6-dimethyl-3,4,5,6-tetrahydropyridine (IIIc) and the two isomers of 2,5-dimethyl-1-azabicyclo[3.1.0]hexane (IVd), a fourth component assigned tentatively the structure VI on the basis of elemental analysis and infrared and n.m.r. spectra. How this last product was formed is not yet understood.



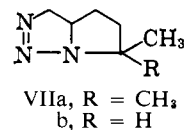
When 4-azido-5-methyl-1-hexene (IIa) and 4-azido-1-hexene (IIb) were heated to 50° or allowed to stand at 25° for 2 months, the isomeric triazolines^{11–13} VIIa,b, respectively, are formed in quantitative yield. The structure of VIIa,b is supported by infrared (absence of

N. Y., 1950, p. 76. N-Ethylethylenimine reacts explosively with the same reagent: P. A. Lasselle and S. A. Sundet, *J. Am. Chem. Soc.*, **63**, 2374 (1941).

(11) Δ²-1,2,3-Triazolines are formed by addition of aryl azide to N-arylmaleimides: A. Mustafa, S. M. A. D. Zayed, and S. Khattab, *ibid.*, **78**, 145 (1956); aryl azide to benzoquinone: L. Wolff, *Ann.*, **394**, 23, 59 (1912); **399**, 274 (1913); F. D. Chattaway and G. D. Parker, *J. Chem. Soc.*, 127, 1307 (1925); aryl azide on styrenes: G. D. Buckley, *ibid.*, 1850 (1954); aryl azide to dicyclopentadienes: α,β-unsaturated ketones, cyclopentenes: K. Alder, G. Stein, and W. Friedrichsen, *Ann.*, **501**, 1 (1933); aryl azide on acrylonitrile: S. M. Gurvich and A. P. Terentev, *Chem. Abstr.*, **49**, 1048 (1955).

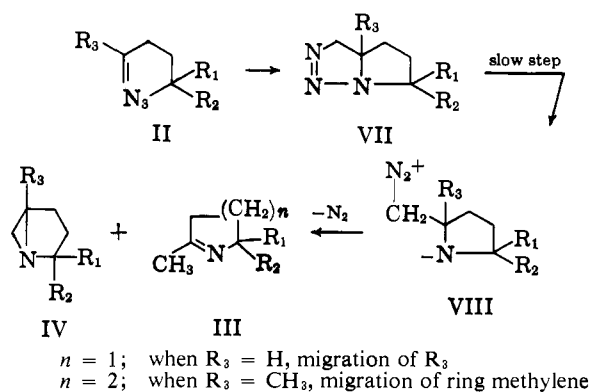
(12) Δ²-1,2,3-Triazolines are also formed by addition of diazomethane to anils: A. Mustafa, *J. Chem. Soc.*, 234 (1949); H. J. Backer, *Rec. trav. chim.*, **69**, 1127 (1950); G. D. Buckley, *J. Chem. Soc.*, 1850 (1954); P. K. Kataba and J. I. Edwards, *J. Org. Chem.*, **26**, 2331 (1961).

(13) It is reported by H. W. Heine and D. A. Tomalia, *J. Am. Chem. Soc.*, **84**, 993 (1962), that 1-aryloaziridines isomerize to 1-aryl-Δ²-



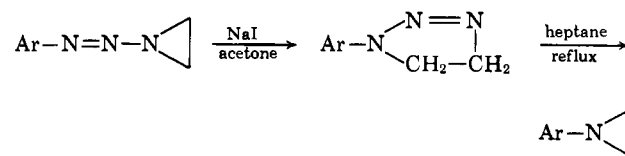
N₃ and CH=CH₂ functionalities) and proton n.m.r. spectroscopy. Decomposition of these two triazolines under conditions identical with the decomposition of the corresponding azides gave identical results in the rate of nitrogen evolution and products. By analogy it is assumed that triazolines are intermediates in the decomposition of all the other olefinic azides (IIc–e). Allyl azide and 4-azido-1-pentene (IIc) cannot form an internal triazoline similar to VII because of too much strain in such a structure. As a result, their decomposition is very sluggish and no products analogous to III and IV are isolated.

The mechanism proposed which satisfactorily explains the formation of the products is



The formation of the dipolar intermediate VIII in the rate-determining step is supported (a) by the fact that the rate of nitrogen evolution increases about 10-fold when nitromethane and 20-fold when aqueous diglyme are substituted for toluene as solvents, and (b) migration of proton (when R₃ = H) to give IIIa–c,e and of methylene (when R₃ = CH₃) to give IIIc takes place, very analogous to the rearrangements observed in the decomposition of alkyldiazonium ions.¹⁴ The exclusive migration of a methylene group over a methyl in IIIc is compared to the migratory aptitudes of *n*-alkyl group which is about 17 times faster than a methyl in the pinacol–pinacolone¹⁵ rearrangement and Bayer–Villiger¹⁶ reaction, and about the same as a methyl group in the reaction of diazomethane with ketones.¹⁷ A dipolar intermediate analogous to VIII has been recently postulated in the decomposition of

1,2,3-triazolines which in turn evolve nitrogen with production of 1-arylaziridines when refluxed in heptane.



(14) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957), and references therein.

(15) M. Stiles and R. P. Mayer, *J. Am. Chem. Soc.*, **81**, 1497 (1959).

(16) M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *ibid.*, **80**, 6393 (1958).

(17) H. O. House, E. J. Grubbs, and W. F. Gannon, *ibid.*, **32**, 4099 (1960).

the norbornene-phenyl azide adduct¹⁸ and in the addition of cyanogen azide to olefins.¹⁹

A nitrene²⁰ intermediate is completely excluded in the reaction. Nitrenes are usually formed by thermal and photolytic decompositions of organic azides, and may isomerize to imines by 1,2-hydrogen shift, when primary or secondary; otherwise they abstract hydrogen from the solvent to give amines or couple to give azo compounds or, when structure permits, undergo intramolecular 1,5-hydrogen shifts followed by cyclization to pyrrolidines. In the decomposition of the olefinic azides reported here, none of the compounds obtained can be interpreted as a nitrene reaction product. Moreover, when the azides IIb and IIc were photolyzed in petroleum ether using a high-pressure mercury lamp at room temperature, the rates of decomposition were practically identical (thermally IIb decomposes about 50 times faster than IIc) to give as the major products high-boiling amines (presumably *via* nitrene intermediates).

Experimental²¹

Preparation of Olefinic Azides. A solution of 1 equiv. of *p*-toluenesulfonyl chloride in dry pyridine was cooled in an ice bath and treated with 1 mole of the olefinic alcohol. **Method A.** After standing for 18 hr. at 0° the solution was diluted with water, and the precipitated oil was taken up in benzene and washed with water and cold 5% hydrochloric acid solution. The solvent was evaporated *in vacuo*, the oily tosylate was dissolved in ethanol, 1.2 equiv. of sodium azide in water was added, and the mixture was stirred at 25° for 50–96 hr. After dilution with water, the organic products were taken up in petroleum ether, washed well with water, dried, and evaporated *in vacuo* to give the azides in better than 90% purity. **Method B.** After standing for 18 hr. at 0°, the solution was treated with a 20% aqueous solution of 1.2 equiv. of sodium azide and the mixture was stirred 18–40 hr. at 25°. After dilution with water, the organic products were taken up in petroleum ether, washed with cold 5% hydrochloric acid solution until neutral, dried, and evaporated *in vacuo* to give the corresponding azide in better than 90% purity. All azides crude or purified were stored in the cold at –30°.

A. 4-Azido-1-pentene (IIc) was prepared by method A and was purified by distillation, b.p. 70–71° (140 mm.), *n*²⁵_D 1.4352, infrared absorption (neat) at 4.7 (N₃), 6.1 (C=C), and 10.8 μ (=CH₂); 50% yield.

(18) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963); *ibid.*, **2**, 633 (1963), and references cited therein, although some of the explanations and results of the "1,3-dipolar cycloadditions" are being questioned by J. E. Baldwin, G. V. Kaiser, and J. A. Ramersberger, *J. Am. Chem. Soc.*, **86**, 4509 (1964).

(19) F. D. Marsh and M. E. Hermes, *ibid.*, **86**, 4506 (1964).

(20) The chemistry of nitrenes is reviewed in articles by L. Horner and A. Christman, *Angew. Chem.*, **75**, 707 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 599 (1963), and R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 147 (1964).

(21) All melting points were taken on a Fisher-Johns block and are corrected. Infrared spectra were measured on a Perkin-Elmer Model 21 recording spectrophotometer with sodium chloride prisms. The listings of infrared bands include only those which are relevant to the structural arguments. Gas chromatographic analyses were performed on a 1-m. column packed with 20% Dow-Corning silicone oil 200 on 40–60 mesh chromosorb W at 50°, helium flow of 120 ml. per min. The n.m.r. spectra were determined with a Varian Associates Model A-60 spectrometer. In all cases magnesium sulfate was used as a drying agent, unless otherwise stated.

Anal. Calcd. for C₅H₉N₃: C, 54.03; H, 8.16; N, 37.82. Found: C, 54.46; H, 8.01; N, 38.10.

B. 5-Azido-1-hexene (IIb) was prepared by method B (crude product in 80% yield) and was purified by dissolving the crude azide in petroleum ether (b.p. 30–60°), passing it through Woelm neutral alumina (activity grade 1),²² and distilling at 59–60° (40 mm.), *n*²⁴_D 1.4400 (40% yield), infrared absorption (neat) at 4.78 (N₃), 6.11 (C=C), and 10.97 μ (=CH₂).

Anal. Calcd. for C₆H₁₁N₃: C, 57.56; H, 8.86; N, 33.57. Found: C, 57.70; H, 8.81; N, 33.36.

3,3a,4,5-Tetrahydro-6-methyl-6H-pyrrolo[1,2-c]-v-triazole (VIIb). 5-Azido-1-hexene (IIb) was heated at 50° for 18 hr. or allowed to stand at 25° for 2 months. Distillation of the product gave 3,3a,4,5-tetrahydro-6-methyl-6H-pyrrolo[1,2-c]-v-triazole in quantitative yield, b.p. 43–44° (0.3 mm.), *n*²⁴_D 1.4823, transparent in the infrared at 4.78, 6.11, and 10.97 μ (absence of N₃ and CH=CH₂), proton n.m.r. (neat) τ-values at 8.9 (doublet, *J* ~ 7 c.p.s., CH₃), 8.5 (multiplet, 2CH₂), 6.0 (multiplet, NCH₂, 2N-CH<). The mass spectrum has the same peaks as 5-azido-1-hexene except in different intensities.

Anal. Calcd. for C₆H₁₁N₃: C, 57.56; H, 8.86; N, 33.57. Found: C, 57.89; H, 8.90; N, 33.28.

C. 5-Azido-2-methyl-1-hexene (IIc) was prepared by method B and was purified by passing a petroleum ether solution through a column of Woelm neutral alumina (activity grade 1) to give the pure azide in 90% yield, b.p. 64° (25 mm.), *n*²⁶_D 1.4460, infrared absorption (neat) at 4.75 (N₃), 6.05 (C=C), and 11.25 μ (=CH₂).

Anal. Calcd. for C₇H₁₃N₃: C, 60.39; H, 9.41; N, 30.19. Found: C, 60.63; H, 9.49; N, 30.08.

D. 5-Azido-1-pentene (IIc) was prepared by method A in 10–25% yield but was not further purified. The crude material was more than 90% pure as shown by its infrared absorption peaks at 4.78 (N₃), 6.1 (C=C), and 10.90 μ (=CH₂) and n.m.r. spectra.

E. 6-Azido-1-hexene (IIe) was prepared by method A in 45% yield, b.p. 73–74° (38 mm.), infrared absorption (neat) at 4.78 (N₃), 6.1 (C=C), and 10.97 μ (=CH₂).

Anal. Calcd. for C₆H₁₁N₃: C, 57.56; H, 8.86; N, 33.57. Found: C, 57.94; H, 8.94; N, 33.39.

F. 5-Azido-5-methyl-1-hexene (IIa). A hydrazoic acid solution was prepared by adding slowly 45 ml. of concentrated sulfuric acid to an ice-cold suspension of 25 g. of sodium azide in 250 ml. of chloroform. While the temperature was kept at 0° to –5°, 33 g. (0.3 mole) of 2-methyl-5-hexen-2-ol was added slowly (2.5 hr.), and the mixture was stirred in the cold for 1 more hr. It was then diluted with ice-water, the chloroform solution was separated, washed well with water, dried over anhydrous sodium carbonate, and evaporated under aspirator vacuum at 25° to give crude 5-azido-5-methyl-1-hexene. It was purified by passing a petroleum ether solution through Woelm neutral alumina (activity grade 1) to give 17–19 g. (41–46%) of azide, b.p. 57–58° (20 mm.), *n*²⁴_D 1.4386, infrared absorption (neat) at 4.75 (N₃), 6.1 (C=C), and 10.9 μ (=CH₂).

Anal. Calcd. for C₇H₁₃N₃: C, 60.44; H, 9.41; N, 30.19. Found: C, 60.94; H, 9.50; N, 28.68.

(22) This method of purification of organic azides has been described by G. Smolinsky.^{2b,3}

5-Amino-5-methyl-1-hexene was obtained as the only product from the lithium aluminum hydride reduction of 5-azido-5-methyl-1-hexene (IIa) in ethyl ether as judged by a gas chromatographic analysis, b.p. 124–125°; n_D^{25} 1.4265; infrared absorption (neat) at 2.98, 3.05 (NH₂), 3.24 (=C—H), 60.7 (C=C), 6.25 (broad, —NH₂), 7.27 and 7.31 (*gem*-dimethyl), and 11.00 μ (=CH₂); the proton n.m.r. spectrum is in complete agreement with the proposed structure.

Anal. Calcd. for C₇H₁₅N: C, 74.27; H, 13.36; N, 12.38. Found: C, 74.56; H, 13.76; N, 12.48.

A benzamide was formed which after crystallization from hexane had m.p. 96–97°.

Anal. Calcd. for C₁₄H₁₉NO: C, 77.38; H, 8.82; N, 6.45. Found: C, 77.43; H, 8.63; N, 6.43.

3,3a,4,5-Tetrahydro-6,6-dimethyl-6H-pyrrole[1,2-*c*]-*v*-triazole (VIIa). 5-Azido-5-methyl-1-hexene (IIa) was heated at 50° for 18 hr. or allowed to stand at 25° for 2 months. Distillation of the product gave 3,3a,4,5-tetrahydro-6,6-dimethyl-6H-pyrrole[1,2-*c*]-*v*-triazole in quantitative yield, b.p. 63–64° (1.5 mm.), n_D^{24} 1.4808, transparent in the infrared at 4.75, 6.1, and 10.9 μ (absence of N₃ and CH=CH₂), proton n.m.r. (neat) in τ-values: 8.84, 8.48 (singlets, 2CH₃), 8.5 (multiplet, 2CH₂), 6.0 (multiplet, N—CH₂, N—CH<). The mass spectrum has the same peaks as 5-azido-5-methyl-1-hexene except in different intensities.

Azide Decompositions. The azides were decomposed in various solvents (see Table I for details), and the reaction was followed by the evolution of nitrogen. The basic products were extracted from the solvent with a 10% hydrochloric acid solution; the aqueous solution was then basified, extracted with ethyl ether, dried, and distilled.

A. 5-Azido-5-methyl-1-hexene (IIa) on decomposition gave only two isomeric products which were separated by preparative gas chromatography to give as a first eluent (retention time, 4.7 min.) 1,5,5-trimethyl-1-pyrroline (IIIa), b.p. 56° (50 mm.), n_D^{26} 1.4290, infrared absorption (neat) at 6.05 (C=N), 7.27 and 7.34 μ (*gem*-dimethyl), n.m.r. τ-values (neat) at: 9.13 (singlet C—(CH₃)₂), 8.62 (unsym. triplet, >—CH₂—), 8.59 (singlet, =C—CH₃), 7.75 (unsym. triplet, =C—CH₂).

Anal. Calcd. for C₇H₁₃N: C, 75.62; H, 11.80; N, 12.60. Found: C, 75.43; H, 12.05; N, 12.77.

A perchlorate was prepared which after recrystallization from ethyl acetate gave colorless crystals, m.p. 149–150°, infrared absorption (KBr) at 5.96 μ (C=N).

Anal. Calcd. for C₇H₁₄ClNO₄: C, 39.72; H, 6.67; Cl, 16.75; N, 6.62. Found: C, 39.45; H, 6.91; Cl, 16.54; N, 6.71.

A picrate was formed which was recrystallized from ethanol, m.p. 168–169° dec., infrared absorption (KBr) at 5.90 μ (C=N).

Anal. Calcd. for C₁₃H₁₆N₄O₇: C, 45.83; H, 4.74; N, 16.46. Found: C, 45.98; H, 4.70; N, 16.66.

A methiodide was formed which was recrystallized from ethyl acetate, m.p. 262–264° dec. (sealed tube), infrared absorption (KBr) at 5.98 μ (C=N).

Anal. Calcd. for C₈H₁₆IN: C, 37.96; H, 6.37; I, 50.15; N, 5.54. Found: C, 37.76; H, 6.23; I, 50.34; N, 5.40.

The second eluent (retention time 7.4 min.) was 2,2-dimethyl-1-azabicyclo[3.1.0]hexane (IVa), b.p. 62° (50

mm.), n_D^{26} 1.4432, transparent in the infrared (neat) in the 6.0 μ region (no unsaturation), absorption at 7.24 and 7.32 μ (*gem*-dimethyl), n.m.r. τ-values (neat): 8.97 (singlet, CH₃), 8.94 (singlet, CH₃), 8.77–9.0 (poorly resolved triplets, 2CH₂), and 8.0 (multiplet, aziridine protons).

Anal. Calcd. for C₇H₁₃N: C, 75.62; H, 11.80; N, 12.60. Found: C, 75.77; H, 11.76; N, 12.71.

A picrate was formed which was recrystallized from ethanol, m.p. 187.5–189° dec., $\lambda_{\max}^{\text{Nujol}}$ transparent at 5.8–6.1 μ.

Anal. Calcd. for C₁₃H₁₆N₄O₇: C, 45.83; H, 4.74; N, 16.46. Found: C, 46.09; H, 5.21; N, 16.33.

Treatment of the 1-azabicyclohexane (IVa) in ethyl ether with excess methyl iodide at 25° for 18 hr. gave 1,1,2,2-tetramethyl-5-iodopiperidinium iodide (Va) quantitatively as colorless crystals, which were recrystallized from ethanol, m.p. 248–249° (dec.), n.m.r. τ-values (CF₃COOH): 8.82 and 8.66 (singlets, >C—(CH₃)₂), 7.33 and 7.10 (singlets, N—(CH₃)₂), and 8.0 (multiplet, ring protons).

Anal. Calcd. for C₉H₁₉I₂N: C, 27.36; H, 4.85; I, 64.26; N, 3.55. Found: C, 27.77; H, 4.87; I, 64.72; N, 3.58.

2,5,5-Trimethyl-1-pyrroline (IIIa). 5-Methyl-5-nitro-2-hexanone²³ (0.705 mole) was added to a mixture of 300 ml. of benzene, 50 ml. of ethylene glycol, and 1.0 g. of *p*-toluenesulfonic acid, and the solution was refluxed in a Dean–Stark apparatus for 4 hr. The benzene solution was washed well with water, dried, and distilled to give 102 g. (64%) of 5-methyl-5-nitro-2-hexanone ethylene ketal as a colorless liquid, b.p. 78° (0.35 mm.), n_D^{26} 1.4488, transparent in the infrared at 6.0 μ region.

Anal. Calcd. for C₉H₁₇NO₄: C, 53.18; H, 8.43; N, 6.89. Found: C, 53.16; H, 8.42; N, 7.06.

A mixture of 97 g. (0.48 mole) of 5-methyl-5-nitro-2-hexanone ethylene ketal and 250 ml. of methanol was hydrogenated over 8.0 g. of Raney nickel catalyst at 25°. The filtered solution was added to 500 ml. of water and 50 ml. of concentrated sulfuric acid and stirred at 25° for 2 hr. The aqueous layer was washed with ethyl ether, basified with sodium carbonate, and extracted with ethyl ether. The ether extracts were dried and distilled to give 11.5 g. (22%) of 2,5,5-trimethyl-1-pyrroline as a colorless liquid, b.p. 118°, n_D^{26} 1.4288, homogeneous to a gas chromatographic analysis, identical with a sample prepared above by comparison of the infrared and n.m.r. spectra, retention times in gas chromatography, and melting point of its picrate and perchlorate.

B. 5-Azido-1-hexene (IIb) on decomposition gave two isomeric amines separated by preparative gas chromatography. The major component that eluted first (retention time 5.0 min.) was 2,5-dimethyl-1-pyrroline (IIIb), b.p. 60° (120 mm.), n_D^{26} 1.4330, infrared absorption (neat) at 6.05 μ (C=N), n.m.r. τ-values (neat): 9.18 (doublet, *J* = 6.5 c.p.s., CH—CH₃), 8.45 (doublet, *J* = 2.0 c.p.s., =C—CH₃), 7.1–9.1 (multiplet, 2CH₂), and 6.5 (broad, N—CH—CH₃).

Anal. Calcd. for C₈H₁₁N: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.46; H, 11.49; N, 14.06.

(23) R. B. Moffet and J. L. White, *J. Org. Chem.*, 17, 407 (1952); H. Schechter, D. E. Ley, and L. Zeldin, *J. Am. Chem. Soc.*, 74, 3664 (1952).

A *picrate* was formed which was recrystallized from ethanol, m.p. 135–136°, infrared absorption (KBr) at 5.95 μ (C=N) (lit.^{24,25} m.p. 135°, ν_{\max}^{KBr} 1673 cm^{-1}).

A *methiodide* was formed which was recrystallized from ethanol–ethyl acetate, m.p. 262–263° dec. It slowly resinified on standing in air.

Anal. Calcd. for $\text{C}_7\text{H}_{14}\text{IN}$: C, 35.17; H, 5.90; N, 5.86. Found: C, 35.36; H, 5.96; N, 5.52.

The minor component that eluted second (retention time 6.4 min.) was 2-methyl-1-azabicyclo[3.1.0]hexane (IVb), b.p. 60° (120 mm.), n_D^{25} 1.4518, transparent in the infrared at the 6.0 μ region (no saturation), n.m.r. τ -values (neat) at: 9.2 (doublet, CH–CH₃, $J_{\text{CH}_3-\text{H}} = 6.5$ c.p.s.), 7.9–9.0 (multiple peaks, ring protons), and 7.0 multiplet, CH–CH₃).

Anal. Calcd. for $\text{C}_8\text{H}_{11}\text{N}$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.40; H, 11.50; N, 14.12.

A *picrate* was formed which was recrystallized from ethanol–acetonitrile (a few drops) avoiding a long heating period, m.p. 149–150° dec.

Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_7$: C, 44.18; H, 4.33; N, 17.18. Found: C, 44.35; H, 4.37; N, 17.09.

C. 5-Azido-1-pentene (IIc) was decomposed to give two isomeric compounds which were separated by preparative gas chromatography. The major component, eluted first (retention time 2.5 min.), was 2-methyl-1-pyrroline (IIIc), b.p. 51° (105 mm.), n_D^{25} 1.4390, infrared absorption (neat) at 6.09 μ (C=N) (lit.^{24,26} b.p. 99–101°, n_D^{20} 1.4296, $\lambda_{\max}^{\text{liquid}}$ 6.11 μ).

Anal. Calcd. for $\text{C}_8\text{H}_9\text{N}$: C, 72.24; H, 10.91; N, 16.85. Found: C, 72.37; H, 11.24; N, 16.89.

A *picrate* was formed which after recrystallization from ethanol had m.p. 124–125° (lit. m.p. 123–124°,²³ 121°²²).

A *picrolonate* was made and was recrystallized from ethanol, m.p. 212–214°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{17}\text{N}_5\text{O}_6$: C, 51.87; H, 4.93; N, 20.16. Found: C, 52.06; H, 5.04; N, 20.54.

The minor component that eluted last (retention time 3.2 min.) was 1-azabicyclo[3.1.0]hexane (IVc), transparent in the infrared at 6.0 μ (no unsaturation), n.m.r. τ -values (neat) showed *no* vinyl protons present but showed a number of peaks between 8.97 and 6.1.

Anal. Calcd. for $\text{C}_8\text{H}_9\text{N}$: C, 72.24; H, 10.91. Found: C, 72.17; H, 11.29.

Treatment of the amine with excess methyl iodide in ethyl ether gave 1,1-dimethyl-3-iodopiperidinium iodide (Vc), m.p. 210–215° dec., n.m.r. τ -values (CF₃COOH) at: 7.8–8.4 (broad unresolved peak, ring protons), 7.05 (doublet, N–CH₃), and 6.7 (multiplet, N–CH₂–).

Anal. Calcd. for $\text{C}_7\text{H}_{15}\text{NI}_2$: I, 69.17; N, 3.82. Found: I, 69.07; N, 3.93.

D. 5-Azido-2-methyl-1-hexene (IID) was decomposed to give a mixture of four isomeric amines in a 2:2:1:5 ratio which were separated by gas chromatography. The first component to elute (retention time 5.0 min.) was one of the stereoisomers of 2,5-dimethyl-1-azabicyclo[3.1.0]hexane (IVd), transparent in the infrared in the 6.0 μ region (no unsaturation), n.m.r. τ -values (neat) at: 9.07 (doublet, CH–CH₃, $J_{\text{CH}_3-\text{H}} = 6.7$ c.p.s.), 8.84 (>C–CH₃), 8.0–8.9 (multiplets, 2CH₂),

(24) G. C. Evans, *J. Am. Chem. Soc.*, **73**, 5230 (1951).

(25) R. Bonnett, V. M. Clark, A. Giddey, and A. Todd, *J. Chem. Soc.*, 2087 (1959).

(26) J. H. Burckhalter and J. H. Short, *J. Org. Chem.*, **23**, 1281 (1958); **23**, 1278 (1958).

and 7.0 (broad sextet, N–CH–CH₃). It was characterized as its *picrate* which after recrystallization from ethanol had a m.p. of 156–157° dec.

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_7$: C, 45.83; H, 4.74; N, 16.46. Found: C, 45.79; H, 4.62; N, 16.65.

The second component in order of elution (retention time, 5.7 min.) was the other stereoisomer of 2,5-dimethyl-1-azabicyclo[3.1.0]hexane (IVd), transparent in the infrared in the 6.0 μ region (no unsaturation), n.m.r. τ -values (neat) at: 9.05 (doublet, CH–CH₃, $J_{\text{CH}_3-\text{H}} = 6.2$ c.p.s.), 8.89 (>C–CH₃), 8.0–9.0 (multiplets, 2CH₂), and 6.8 (broad sextet, N–CH–CH₃). It was characterized as its *picrate*, m.p. 162.5–164.0° dec. after recrystallization from ethanol.

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_7$: C, 45.83; H, 4.74; N, 16.46. Found: C, 45.66; H, 4.82; N, 16.57.

The third and least abundant component (retention time 7.1 min.) was N-isopropylcyclobutylimine (VI), infrared absorption (neat) at 6.1 μ (C=N), n.m.r. τ -values (neat) at: 9.15 (doublet, CH–(CH₃)₂, $J_{\text{CH}_3-\text{H}} = 7.1$ c.p.s.), 6.4 (ill-defined septet split into broad triplets, =N–CH–(CH₃)₂), 7.6–8.5 (multiplets, 3CH₂). It was characterized as its *picrate* which was recrystallized from ethanol–ethyl acetate, m.p. 119–120° dec.

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_7$: C, 45.83; H, 4.74; N, 16.46. Found: C, 45.64; H, 4.88; N, 16.79.

The last and most abundant component (retention time 9.6 min.) was 2,6-dimethyl-3,4,5,6-tetrahydropyridine (IIId), b.p. 83° (160 mm.), n_D^{25} 1.4530, infrared absorption (neat) at 6.0 μ (C=N), n.m.r. τ -values (neat) at: 9.17 (doublet, CH–CH₃, $J_{\text{CH}_3-\text{H}} = 6.5$ c.p.s.), 8.5 (doublet, =C–CH₃, $J_{\text{CH}_3-\text{H}} = 2$ c.p.s.), 8.1–9.0 (multiplets, 3CH₂), and 7.0 (broad multiplet, CH–CH₃).

Anal. Calcd. for $\text{C}_7\text{H}_{13}\text{N}$: C, 75.62; H, 11.79; N, 12.60. Found: C, 75.93; H, 11.86; N, 12.36.

A *picrate* was formed which was recrystallized from ethanol, m.p. 138–139° dec., infrared absorption (KBr) at 5.9 μ (C=N).

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_7$: C, 45.83; H, 4.74; N, 16.46. Found: C, 45.57; H, 4.83; N, 16.63.

An authentic sample of 2,6-dimethyl-3,4,5,6-tetrahydropyridine (IIId) was prepared by the method of Grundon and Reynolds,²⁷ and it was identical with the sample prepared above.

E. 6-Azido-1-hexene (IIe) gave on decomposition 2-methyl-3,4,5,6-tetrahydropyridine (IIIe), b.p. 55–56° (40 mm.), which was contaminated with ~5% of an isomer (very likely 1-azabicyclo[4.1.0]heptane) as shown by gas chromatography. The *picrate* of IIIe was formed from the mixture which, after recrystallization from ethanol, melted at 120–122°, infrared absorption (KBr) at 5.90 μ (C=N) (lit. m.p. 120–121°,²⁸ 120.5–121.0°,²⁹ 120.4–121.4°,³⁰ 119–120°³¹).

Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_7$: C, 44.17; H, 4.33; N, 17.18. Found: C, 44.23; H, 4.50; N, 17.01.

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(28) I. Mukarowski, *Yakugaku Zasshi*, **79**, 72 (1959); *Chem. Abstr.*, **53**, 10217e (1959).

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(31) A. Lipp, *Ann.*, **289**, 173 (1896).