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 Britton[25] to data from a titration curve. In order to avoid precipitation of the acid 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 calculated[25] 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 (ϵ_{283} 1.77×10^4, ϵ_{300} 1.26×10^4), in 0.1 *M* aqueous sodium hydroxide (ϵ_{283} 2.53×10^4, ϵ_{300} 2.13×10^4), and in aqueous buffer solutions at pH 3.80 (ϵ_{283} 2.08×10^4, ϵ_{300} 1.62×10^4) and pH 4.00 (ϵ_{283} 2.16×10^4, ϵ_{300} 1.74×10^4), 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}.

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

(26) E. Grunwald 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 Azides[1]

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Experimental Station, E. I. du Pont de Nemours and Company,
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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 decomposition[2] 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 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

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(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).

(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).

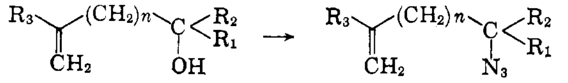
(5) W. L. Meyer and A. S. Levinson, *J. Org. Chem.*, **28**, 2859 (1963).

Table I. Decomposition of Azides

Azide	Temp., °C.	Solvent	Time,[a] hr.	Yield,[b] %	Products	Ratio of products[c]
$CH_2{=}CH{-}(CH_2)_2{-}\underset{\underset{N_3}{\mid}}{C}{-}(CH_3)_2$, IIa	80[d]	Cyclohexane[e,j]	8	70	IIIa + IVa	2.2:1
	80–120	*o*-Dichlorobenzene[f]	1	35	IIIa + IVa	3.5:1
	320	Vapor phase[g]		15[h]	IIIa + IVa[i]	12:1
$CH_2{=}CH{-}(CH_2)_2{-}\underset{\underset{N_3}{\mid}}{C}HCH_3$, IIb	111[d]	Toluene[j]	4	50	IIIb + IVb	2.5:1
	138[d]	Xylene[j]	0.5	50	IIIb + IVb	8:1
	25, *hν*[l]	Petroleum ether[j]	2	~10[m]	IIIb + IVb	
$CH_2{=}CH{-}(CH_2)_3{-}N_3$, IIc	120–130	*o*-Dichlorobenzene[n]	2	72	IIIc + IVc	7:1
$CH_2{=}\overset{\overset{CH_3}{\mid}}{C}{-}(CH_2)_2{-}\underset{\underset{N_3}{\mid}}{C}HCH_3$, IId	138[d]	Xylene[j]	18	55	IIId + IVd + VI	5:4:1
	25, *hν*[l]	Petroleum ether[j]	2	Trace[m]	IIId + IVd	
$CH_2{=}CH{-}(CH_2)_4{-}N_3$, IIe	160	*o*-Dichlorobenzene[f]	2	40	IIIe[o]	
$CH_2{=}CH{-}CH_2N_3$	75[d]	Cyclohexane[e]	24	10[p]	$(CH_2{=}CH{-}CH_2N_3)_2$[q]	
	320	Gas phase			Starting material	
	500	Gas phase			$CH_2{=}CH_2$, $CH_3C{\equiv}CH$, $HC{\equiv}CH$, etc.[r]	
	hν[s]	Cyclohexane		52[s]	$CH_2{=}CH{-}CH{=}NH$[s]	
$CH_2{=}CH{-}CH_2{-}\underset{\underset{N_3}{\mid}}{C}HCH_3$, IIf	179[d]	*o*-Dichlorobenzene[e]	18	[k]	[t]	

[a] Time required for completion of nitrogen evolution. [b] Total yield of distilled products. [c] Estimated by gas chromatography. [d] Heated by means of a sun lamp. [e] 15% solution. [f] 30% solution. [g] The apparatus used has been described by G. Smolinsky, *J. Org. Chem.*, **26**, 4108 (1961). [h] The rest of the product resinified in the pyrolysis tube. [i] Small amounts of unidentified product were present. [j] 5% solution. [k] No yield was estimated. [l] Irradiated by means of a high-pressure mercury lamp, G.E. A-H6. [m] The rest of the product was high boiling amines. [n] 50% solution. [o] An isomeric amine was also present in 5% but was not separated and identified. [p] The rest of the product was starting allyl azide. [q] The allyl azide dimer, m.p. 192°, $\lambda_{\max}^{\mathrm{EtOH}}$ 241 mμ (ε 5350), 271 mμ (ε 7200), was first reported in ref. 7. [r] Small explosions were noticed in the pyrolysis tube and only degradation products were obtained. [s] This experiment was taken from the paper of D. H. R. Barton and L. R. Morgan, Jr., *J. Chem. Soc.*, 206 (1961). [t] No volatile compounds were obtained, the products being resinous materials.

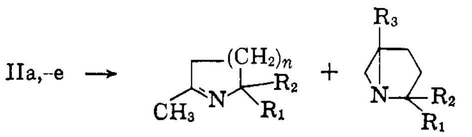
chloroform at about −5°.[6] That no intramolecular rearrangement had taken place during the synthesis of the above olefinic azides was established by n.m.r. and infrared spectra.



I II

a, $n = 2$, $R_3 = H$, $R_1 = R_2 = CH_3$
b, $n = 2$, $R_2 = R_3 = H$, $R_1 = CH_3$
c, $n = 2$, $R_1 = R_2 = R_3 = H$
d, $n = 2$, $R_1 = H$, $R_2 = R_3 = CH_3$
e, $n = 3$, $R_1 = R_2 = R_3 = H$
f, $n = 1$, $R_1 = R_3 = H$, $R_2 = CH_3$

The azides were decomposed under a variety of conditions as shown in Table I. Allyl azide, when heated at 75° in a solvent, gave slowly a dimer of unknown structure identical with the dimer isolated by Forster and Fierz.[7] Fragmentation products were obtained when allyl azide was pyrolyzed in the vapor phase at 500°. Similarly, 4-azido-1-pentene (IIf) decomposed very slowly in refluxing *o*-dichlorobenzene (b.p. 179°) to give resinous products. The other olefinic azides, IIa–e, however, decomposed smoothly in hydrocarbon solvents, the temperature depending on the azide (80–160°). The nitrogen evolution followed first-order kinetics. The products of these decompositions were a mixture of the cyclic imines IIIa–e and the 1-azabicyclo[3.1.0]hexanes IVa–d in various ratios. The two isomeric amines were separated by gas chromatography and the imines IIIa–e were identified by comparison of their physical and spectral properties and the melting points of their picrates with those reported in the literature or with synthesized authentic samples.



III IV

IIIa, $n = 1$, $R_1 = R_2 = CH_3$
b, $n = 1$, $R_1 = H$, $R_2 = CH_3$
c, $n = 1$, $R_1 = R_2 = H$
d, $n = 2$, $R_1 = H$, $R_2 = CH_3$
e, $n = 2$, $R_1 = R_2 = H$

IVa, $R_3 = H$, $R_1 = R_2 = CH_3$
b, $R_2 = R_3 = H$, $R_1 = CH_3$
c, $R_1 = R_2 = R_3 = H$
d, $R_1 = H$, $R_2 = R_3 = CH_3$

The structures of the 1-azabicyclo[3.1.0]hexanes (IV)[8,9] isomeric with the cyclic imines III were assigned on the bases of their infrared (absence of unsaturation) and proton n.m.r. spectra. In the case of 2,2-dimethyl-1-azabicyclo[3.1.0]hexane (IVa), the two methyl groups appeared in the n.m.r. spectrum as two distinct peaks at τ 8.97 and 8.84, one for the *endo*- and the other for the *exo*-methyl. The 1-azabicyclo[3.1.0]hexanes are not stable to heat; for example, attempts to distill IVa at atmospheric pressure slowly caused resinification. They yield crystalline picrates and oily perchlorates and hydrochlorides, while with excess methyl iodide they form ring-opened products.[10] The n.m.r. spectra

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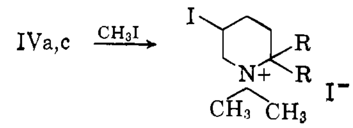
(6) C. L. Arcus and R. J. Mesley, *J. Chem. Soc.*, 178 (1953), has prepared azidotriphenylmethane from the corresponding carbinol by this procedure.

(7) M. O. Forster and H. E. Fierz, *ibid.*, **93**, 1174 (1908).

(8) The only previously described 1-azabicyclo[3.1.0]hexane is the carbethoxy compound reported by C. Schöpf, German Patent 1,054,088 (1959); *Chem. Abstr.*, **55**, 8439g (1961).

(9) N. J. Leonard, K. Jann, J. V. Paukstelis, and C. K. Steinhardt, *J. Org. Chem.*, **28**, 1499 (1963), recently reported the synthesis of 1-azabicyclo[4.1.0]heptane perchlorates by the addition of diazomethane to the appropriate cyclic iminium perchlorates.

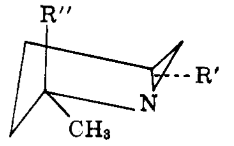
(10) Ethylenimine reacts with methyl iodide to give the ring-opened product, $ICH_2{-}CH_2N^{+}(CH_3)_3I^{-}$: J. S. Fruton in "Heterocyclic Compounds," R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York,



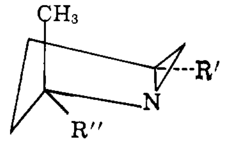
Va, R = CH_3
b, R = H

of these ring-opened salts (Va,c) showed two different N-CH_3 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 (IId) gave, besides 2,6-dimethyl-3,4,5,6-tetrahydropyridine (IIId) 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.

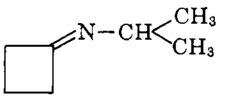


exo



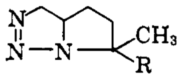
endo

IVa, R' = H, R'' = CH_3
b, R' = H, R'' = H
d, R' = CH_3, R'' = H



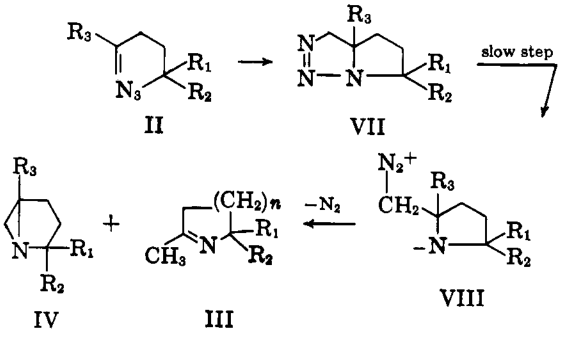
VI

When 4-azido-5-methyl-1-hexane (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_3 and $CH{=}CH_2$ 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 (IIf) 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.



VIIa, R = CH_3
b, R = H

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



n = 1; when R_3 = H, migration of R_3
n = 2; when R_3 = CH_3, migration of ring methylene

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 R_3 = H) to give IIIa–c,e and of methylene (when R_3 = CH_3) to give IIId 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 IIId is compared to the migratory aptitudes of *n*-alkyl group which is about 17 times faster than a methyl in the pinacol–pinacolone[15] rearrangement and Bayer–Villiger[16] 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

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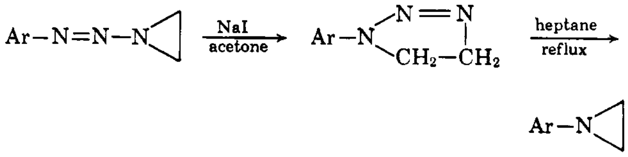
N. Y., 1950, p. 76. N-Ethylethylenimine reacts explosively with the same reagent: P. A. Lasselle and S. A. Sundet, *J. Am. Chem. Soc.*, **63**, 2374 (1941).

(11) Δ^2-1,2,3-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) Δ^2-1,2,3-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-arylazoaziridines isomerize to 1-aryl-Δ^2-1,2,3-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 adduct[18] and in the addition of cyanogen azide to olefins.[19]

A nitrene[20] 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 IId 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 IId) to give as the major products high-boiling amines (presumably *via* nitrene intermediates).

Experimental[21]

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 (*IIf*) 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 (N_3), 6.1 (C=C), and 10.8 μ (=CH_2); 50% yield.

Anal. Calcd. for $C_5H_9N_3$: 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 (N_3), 6.11 (C=C), and 10.97 μ (=CH_2).

Anal. Calcd. for $C_6H_{11}N_3$: 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 N_3 and CH=CH_2), proton n.m.r. (neat) τ-values at 8.9 (doublet, $J \sim 7$ c.p.s., CH_3), 8.5 (multiplet, 2CH_2), 6.0 (multiplet, NCH_2, 2N–C*H*<). The mass spectrum has the same peaks as 5-azido-1-hexene except in different intensities.

Anal. Calcd. for $C_6H_{11}N_3$: 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 (*IId*) 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 (N_3), 6.05 (C=C), and 11.25 μ (=CH_2).

Anal. Calcd. for $C_7H_{13}N_3$: 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 (N_3), 6.1 (C=C), and 10.90 μ (=CH_2) 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 (N_3), 6.1 (C=C), and 10.97 μ (=CH_2).

Anal. Calcd. for $C_6H_{11}N_3$: 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 (N_3), 6.1 (C=C), and 10.9 μ (=CH_2).

Anal. Calcd. for $C_7H_{13}N_3$: C, 60.44; H, 9.41; N, 30.19. Found: C, 60.94; H, 9.50; N, 28.68.

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[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 preformed 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.

[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^{25}D 1.4265; infrared absorption (neat) at 2.98, 3.05 (NH$_2$), 3.24 (=C—H), 60.7 (C=C), 6.25 (broad, -NH$_2$), 7.27 and 7.31 (*gem*-dimethyl), and 11.00 μ (=CH$_2$); the proton n.m.r. spectrum is in complete agreement with the proposed structure.

Anal. Calcd. for $C_7H_{15}N$: 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 $C_{14}H_{19}NO$: 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^{24}D 1.4808, transparent in the infrared at 4.75, 6.1, and 10.9 μ (absence of N$_3$ and CH=CH$_2$), proton n.m.r. (neat) in τ-values: 8.84, 8.48 (singlets, 2CH_3), 8.5 (multiplet, 2CH_2), 6.0 (multiplet, N-CH_2, 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^{26}D 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-(CH_3)$_2$, 8.62 (unsym. triplet, ⋗-CH_2—), 8.59 (singlet, =C—CH_3), 7.75 (unsym. triplet, =C—CH_2).

Anal. Calcd. for $C_7H_{13}N$: 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 $C_7H_{14}ClNO_4$: 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 $C_{13}H_{16}N_4O_7$: 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 $C_8H_{16}IN$: 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^{25}D 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, CH_3), 8.94 (singlet, CH_3), 8.77–9.0 (poorly resolved triplets, 2CH_2), and 8.0 (multiplet, aziridine protons).

Anal. Calcd. for $C_7H_{13}N$: 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., λ_{max}^{Nujol} transparent at 5.8–6.1 μ.

Anal. Calcd. for $C_{13}H_{16}N_4O_7$: 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 (CF$_3$COOH): 8.82 and 8.66 (singlets, >C—(CH_3)$_2$, 7.33 and 7.10 (singlets, N—(CH_3)$_2$), and 8.0 (multiplet, ring protons).

Anal. Calcd. for $C_9H_{19}I_2N$: 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-hexanone[23] (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^{25}D 1.4488, transparent in the infrared at 6.0 μ region.

Anal. Calcd. for $C_9H_{17}NO_4$: 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^{26}D 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^{25}D 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-CH_3), 8.45 (doublet, J = 2.0 c.p.s., =C-CH_3), 7.1–9.1 (multiplet, 2CH_2), and 6.5 (broad, N-CH-CH$_3$).

Anal. Calcd. for $C_6H_{11}N$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.46; H, 11.49; N, 14.06.

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(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°, $\nu_{\max}^{\mathrm{KBr}}$ 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 $C_7H_{14}IN$: 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^{25}D 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–CH_3, $J_{\mathrm{CH_3-H}}$ = 6.5 c.p.s.), 7.9–9.05 (multiple peaks, ring protons), and 7.0 multiplet, C*H*–CH$_3$).

Anal. Calcd. for $C_6H_{11}N$: 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 $C_{14}H_{14}N_4O_7$: 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^{25}D 1.4390, infrared absorption (neat) at 6.09 μ (C=N) (lit.[24,26] b.p. 99–101°, n^{20}D 1.4296, $\lambda_{\max}^{\mathrm{liquid}}$ 6.11 μ).

Anal. Calcd. for C_5H_9N: 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 $C_{15}H_{17}N_5O_5$: 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 C_5H_9N: 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 (CF_3COOH) at: 7.8–8.4 (broad unresolved peak, ring protons), 7.05 (doublet, N–CH_3), and 6.7 (multiplet, N–CH_2–).

Anal. Calcd. for $C_7H_{15}NI_2$: 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–CH_3, $J_{\mathrm{CH_3-H}}$ = 6.7 c.p.s.), 8.84 (>C–CH_3), 8.0–8.9 (multiplets, 2CH_2), and 7.0 (broad sextet, N–C*H*–CH$_3$). It was characterized as its picrate which after recrystallization from ethanol had a m.p. of 156–157° dec.

Anal. Calcd. for $C_{13}H_{16}N_4O_7$: 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–CH_3, $J_{\mathrm{CH_3-H}}$ = 6.2 c.p.s.), 8.89 ([illegible]C–CH_3), 8.0–9.0 (multiplets, 2CH_3), and 6.8 (broad sextet, N–C*H*–CH$_3$). It was characterized as its picrate, m.p. 162.5–164.0° dec. after recrystallization from ethanol.

Anal. Calcd. for $C_{13}H_{16}N_4O_7$: 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–$(CH_3)_2$, $J_{\mathrm{CH_3-H}}$ = 7.1 c.p.s.), 6.4 (ill-defined septet split into broad triplets, =N—*CH*—(CH$_3$)$_2$), 7.6–8.5 (multiplets, 3CH_2). It was characterized as its picrate which was recrystallized from ethanol–ethyl acetate, m.p. 119–120° dec.

Anal. Calcd. for $C_{13}H_{16}N_4O_7$: 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^{25}D 1.4530, infrared absorption (neat) at 6.0 μ (C=N), n.m.r. τ-values (neat) at: 9.17 (doublet, CH–CH_3, $J_{\mathrm{CH_3-H}}$ = 6.5 c.p.s.), 8.5 (doublet, =C—CH_3, $J_{\mathrm{CH_3-H}}$ = 2 c.p.s.), 8.1–9.0 (multiplets, 3CH_2), and 7.0 (broad multiplet, C*H*–CH$_3$).

Anal. Calcd. for $C_7H_{13}N$: 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 $C_{13}H_{16}N_4O_7$: 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 $C_{12}H_{14}N_4O_7$: C, 44.17; H, 4.33; N, 17.18. Found: C, 44.23; H, 4.50; N, 17.01.

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