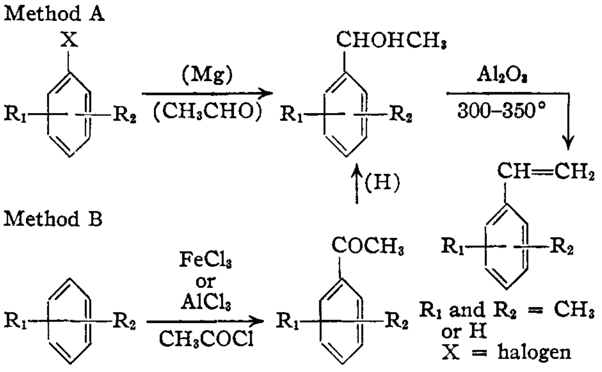
resonance effects of the methyl group becomes explicable.

Several workers have shown that benzyl halides with nucleophilic reagents in solvents of low dielectric constant can react by a bimolecular (SN2) mechanism and, moreover, that the *p*-methyl group increases the rate of this reaction over that of the unsubstituted compound.[10]

Franzen and Rosenberg[11] reported that benzyl chlorides, substituted in the aromatic ring, react with sodium ethoxide in absolute ethanol according to second-order kinetics and that the order of reactivity is *o*-CH_3 > *p*-CH_3 > *m*-CH_3 > H. This is the same order observed in this study.

Experimental

For most of the styrenes reported in this paper, two general methods of preparation were used.



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(10) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 327.

(11) H. Franzen and I. Rosenberg, *J. prakt. Chem.*, [2] **101**, 333 (1920).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITY OF MICHIGAN AND TULANE UNIVERSITY]

Acid-catalyzed Reactions of Aliphatic Azides[1]

BY J. H. BOYER, F. C. CANTER, J. HAMER AND R. K. PUTNEY

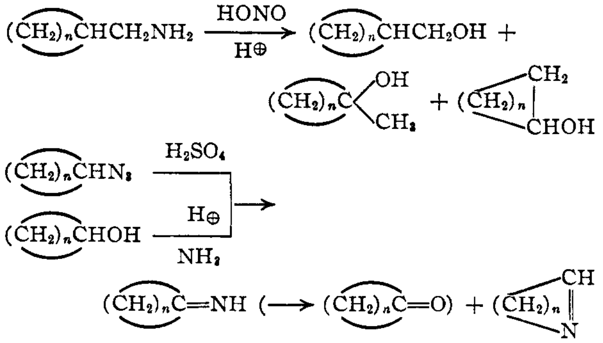
RECEIVED AUGUST 26, 1955

Ring expansion accounted for the major reaction of the alicyclic azides of the common rings in sulfuric acid. Migration of the *n*-propyl group from carbon to nitrogen as well as the formation of butyraldimine accounted for the products obtained from *n*-butyl azide. Similar treatment of *n*-hexyl and *n*-dodecyl azides in sulfuric acid, however, afforded nearly quantitative conversion to the corresponding aldimines. In contrast, triphenylmethyl azide underwent quantitative hydrolysis into triphenylcarbinol. Propylene and trimethylene azidohydrins with aromatic aldehydes in sulfuric acid were transformed into oxazolines and dihydroöxazines, respectively.

Whereas the normal action of strong acids upon aliphatic azides promotes the formation of imines, the presence of aldehydes was observed to bring about the formation of other products.[2] The work reported here was designed to obtain additional information on certain factors which control the formation of imines or Schiff bases and to learn more of the limitations of the reaction with aldehydes.

Benzyl,[3a] ethyl[3b] and now *n*-butyl azides have been observed to undergo acid-catalyzed transformation into aldimines by either hydrogen or alkyl migration. In agreement with the expected increased difficulty for larger alkyl groups to migrate from carbon to nitrogen, aldimines (isolated as corresponding aldehydes) were obtained from similar treatment of *n*-hexyl and *n*-dodecyl azides in which only hydrogen migration was involved. Quantitative conversion of triphenylmethyl azide in concentrated sulfuric acid into triphenylcarbinol provided one of the rare examples of acid hydrolysis of an alkyl azide.[4]

The predominance of ring expansion over ring-size retention for alicyclic azides of the common rings is reminiscent of the Demjanow ring expansion[5] of cycloalkylmethylamines on the one hand and parallels acid-catalyzed reactions of hydrogen azide upon alcohols[6] on the other. Similar results were obtained from the azides with stannic chloride and anhydrous hydrogen chloride in benzene; however, they were more resistant to attack by phosphoric acid.



Attempts to isolate and identify products resulting from possible reactions between benzaldehyde and either linear or cyclic aliphatic azides were unsuccessful. Apparently N-substituted benzamides failed to occur or did so in only trace amounts (compare the formation of N-β-phenylethylbenzamide from β-phenylethyl azide and benzaldehyde). The formation of hexahydro-1,3,5-triazine (isolated as the tribenzoyl derivative) in the treatment

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(2) J. H. Boyer and J. Hamer, THIS JOURNAL, **77**, 951 (1955).

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TABLE I

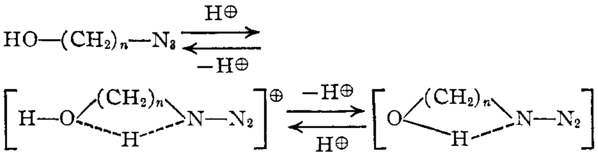
PREPARATION OF AZIDES

Azide[a]	Yield, %	B.p. °C.	Mm.	$n^{25}D$	d^{25}_{25}	Mol. formula	Carbon, % Calcd. Found	Hydrogen, % Calcd. Found	Nitrogen, % Calcd. Found	M_D Calcd. Found
Cyclopentyl	51	67–68	63	1.4615	0.9798	$C_5H_9N_3$	54.05	8.17	37.83	30.7
							54.17	8.40	37.76	31.2
Cyclohexyl[b]	68	68.5–69	21	1.4690	.9855	$C_6H_{11}N_3$	57.57	8.86	33.57	35.4
							57.62	8.84	33.55	35.9
Cycloheptyl[c]	55	83.4–83.8	19	1.4793	.9866	$C_7H_{13}N_3$	60.40	9.41	30.19	39.8
							60.35	9.24	30.50	41.3
n-Hexyl	93	80	3.5	1.4305	....	$C_6H_{13}N_3$	...	..	...	..
Triphenylmethyl	89	64–65 (m.p.)		....	....	$C_{16}H_{15}N_3$	...	..	...	..

[a] Each of these azides absorbed in the infrared at 2110 cm.$^{-1}$ (4.75 μ). [b] Reduction with lithium aluminum hydride (J. H. Boyer, THIS JOURNAL, **73**, 5865 (1951)) resulted in the formation of cyclohexylamine (83% yield) isolated as the hydrochloride, m.p. 205.5–206° (W. Markownikoff, *Ann.*, **302**, 1 (1898)). [c] Cycloheptyl bromide was very kindly supplied by Professor F. F. Blicke, College of Pharmacy, University of Michigan.

of *n*-butyl azide in benzaldehyde with sulfuric acid supported the absence of interaction between the aldehyde and the azide and established the intermediate formation of both formaldehyde and ammonia.

In combination with *m*- or *p*-nitrobenzaldehyde, propylene and trimethylene azidohydrins afforded good yields of oxazolines and dihydroöxazines, respectively. Neither oxazolines nor amides, however, resulted from acid-catalyzed reactions of cyclohexene azidohydrin, α-azido-α-phenylethanol, α-azido-α-phenylacetic acid, 1-azido-2-bromoethane or 1-azido-2-aminoethane in the presence of benzaldehyde. A possible explanation for the unique ability of azidohydrins to combine with aldehydes recognizes the increased stability of the azido group obtained through intramolecular hydrogen bonding. This presumably retards nitrogen elimination from the protonated azide and increases the opportunity for reaction with the conjugate acid of the aldehyde.



Experimental[7]

Preparation of the Azides.—*n*-Butyl, *n*-dodecyl azides, α-azido-α-phenylacetic acid, 1-azido-2-propanol and 1-azido-3-propanol were previously prepared.[2] β-Azido-β-phenylethanol,[8] 1-azido-3-bromoethane[9] and 1-azido-2-aminoethane[10] were obtained according to previously reported procedures of other workers. The procedure used for the preparation of *n*-hexyl azide,[11] the three alicyclic azides and triphenylmethyl azide was essentially that of Henkel and Weygand. Critical data are found in Table I.

Cyclohexene Azidohydrin.—The treatment of 35 g. (0.26 mole) of 2-chlorocyclohexanol with 19.5 g. (0.30 mole) of sodium azide in 100 ml. of 50% ethanol on a steam-bath for 24 hours did not bring about the formation of an azide. A solution of 10 g. of sodium hydroxide in 30 ml. of water was added to the mixture, which was then heated an additional 12 hours on the steam-bath. Alcohol was removed by distillation (40 mm.) and the azide was extracted with ether and fractionated. Cyclohexene azidohydrin, b.p. 68° (0.7 mm.), $n^{32}D$ 1.4902, d^{30} 1.1112, was obtained in 61% yield (22.4 g.).

Steric requirements of the displacement of halogen by azide ion were also revealed in the unsatisfactory results with menthyl and 2-methylcyclohexyl halides. The former halide with either sodium or silver azide was transformed into menthene in 30–35% yield. In each case organic azide was detected but the small amount present could not be isolated from unreacted halide and other products.

Acid Decomposition of the Azides.—To 12 ml. of concentrated sulfuric acid, externally cooled, as necessary, by an ice–salt-bath, was added dropwise 0.035 mole of azide. The solution was poured over cracked ice after gas evolution had ceased. From this acidic mixture (or solution) a DNP was prepared in the usual way. From *n*-hexyl azide the DNP of *n*-caproaldehyde, m.p. 106°,[12] was obtained in 73% yield. From *n*-dodecyl azide the DNP of lauraldehyde, m.p. 105–106°,[13] was obtained in 84% yield.

In one experiment with butyl azide the *p*H of the solution, after the reaction mixture was poured over cracked ice, was adjusted to 5.5 to 6.0 by the addition of sodium hydroxide. It was distilled until fresh distillate gave no aldehyde test. The residue was then made strongly basic from which a distillate containing ammonia and *n*-propylamine was obtained. Treating the distillate with mercuric oxide brought about the separation of ammonia.[14] *n*-Propylamine was then detected as its phenylthiourea derivative, m.p. 63°.[15]

In another experiment with butyl azide in benzene containing an excess of benzaldehyde, the aqueous acidic reaction mixture was treated with sodium hydroxide and benzoyl chloride. A small amount of 1,3,5-tribenzoylhexahydro-1,3,5-triazine, m.p. 225–226°[16] after recrystallization from ethanol, was obtained.

Anal. Calcd. for $C_{24}H_{21}N_3O_3$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.88; H, 5.33; N, 10.40.

With minor modifications, the same general conditions were used to bring about quantitative hydrolysis of triphenylmethyl azide by concentrated sulfuric acid at 150° to triphenylcarbinol, m.p. and mixed m.p. 162–162.5°.[17]

Upon refluxing a portion of the product from *n*-dodecyl azide and sulfuric acid in strong alkali, a solid product with m.p. near room temperature, b.p. 170–200° (0.2 mm.), $n^{25}D$ 1.4646, infrared absorption at 1675 cm.$^{-1}$ (5.97 μ) (conjugated carbonyl) was obtained. It was assumed to be 2-*n*-decyltetradecen-2-al, the expected aldol condensation product from lauraldehyde.

Anal. Calcd. for $C_{24}H_{46}O$: C, 82.23; H, 13.21. Found: C, 81.88; H, 13.68.

n-Dodecyl azide was reduced to *n*-dodecylamine, m.p.

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(7) Microanalyses by the Micro-tech Laboratories, Skokie, Illinois. Infrared analyses from Perkin-Elmer Spectrophotometers through the courtesy of the Perkin-Elmer Corporation, New Orleans, Louisiana. Melting points are corrected; boiling points uncorrected.

(8) W. E. McEwen, W. E. Conrad and C. A. VanderWerf, THIS JOURNAL, **74**, 1168 (1952).

(9) M. O. Forster and S. H. Newman, *J. Chem. Soc.*, **97**, 2570 (1910).

(10) M. O. Forster and S. H. Newman, *ibid.*, **99**, 1277 (1911).

(11) K. Henkel and F. Weygand, *Ber.*, **76**, 812 (1943).

(12) M. S. Newman, THIS JOURNAL, **57**, 734 (1935).

(13) C. F. H. Allen, *ibid.*, **52**, 2958 (1930).

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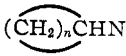
TABLE II

PREPARATION OF OXAZOLINES AND DIHYDROÖXAZINES

Azide	Substituted benzaldehyde	Product	Yield, %	M.p., °C.
1-Azido-2-propanol	*m*-Nitro	5-Methyl-2(3-nitrophenyl)-Δ^2-oxazoline	56	86[a,b]
1-Azido-2-propanol	*p*-Nitro	5-Methyl 2(4-nitrophenyl)-Δ^2-oxazoline	53	135–136[c,d]
1-Azido-3-propanol	*m*-Nitro	2-(*m*-Nitrophenyl)-Δ^2-dihydro-1,3-oxazine	82	94–95[a,e]
1-Azido-3-propanol	*p*-Nitro	2-(*p*-Nitrophenyl)-Δ^2-dihydro-1,3-oxazine	70	143.5–144.5[f,g]

[a] H. Elfeld, *Ber.*, **24**, 3220 (1891). [b] Picrate, m.p. 152°A. [c] A. Uedinck, *ibid.*, **32**, 978 (1899). [d] Picrate, m.p. 187°. [e] *Anal.* Calcd. for $C_{10}H_{10}N_2O_3$: C, 58.24; H, 4.89; N, 13.59. Found: C, 58.33; H, 4.92; N, 13.21. [f] *Anal.* Calcd. for $C_{10}H_{10}N_2O_3$: C, 58.24; H, 4.89; N, 13.59. Found: C, 58.47; H, 4.80; N, 13.13. [g] Picrate, m.p. 173–174°. *Anal.* Calcd. for $C_{16}H_{13}N_5O_{10}$: C, 44.16; H, 3.01; N, 16.09. Found: C, 43.96; H, 3.29; N, 16.21.

26–26.5°[18] with lithium aluminum hydride[19] in 84% yield.

Alicyclic Azides and Concentrated Sulfuric Acid.—A solution of about 0.15 mole of each of the three azides,  $(CH_2)_nCHN_3$ ($n = 4, 5, 6$) in 85–90 ml. of chloroform was cooled in an ice-bath to 15°. With stirring, 50 ml. of concentrated sulfuric acid was added at such a rate that the temperature was maintained between 15 and 20°. After all of the acid had been added (about 45 minutes), the ice-bath was removed and the reaction mixture was stirred until it came to room temperature. The acid layer was separated, the chloroform layer was washed with water, and the washings were added to the acid layer. Solid sodium carbonate was added to the acid layer until it was only slightly acidic. Undissolved sodium sulfate was removed by filtration. The filtrate was extracted with two 15-ml. portions of ether. Ten per cent. sodium hydroxide was then added to the slightly acidic aqueous layer until the solution was basic. The combined ether and chloroform solutions were dried over anhydrous magnesium sulfate and the solvents removed by distillation.

From 15.0 g. (0.135 mole) of cyclopentyl azide the residue from the organic layer was taken up in ethanol, filtered and treated with an ethanolic solution of 2,4-dinitrophenylhydrazine. A yellow precipitate of cyclopentanone-2,4-dinitrophenylhydrazone formed rapidly. After 15 minutes it was filtered and recrystallized from ethanol from which it separated in the form of yellow needles, m.p. and mixed m.p. 145–146°,[20] yield 0.59 g. (2.2%). Under similar conditions cyclohexanone, b.p. 70–73° (13 mm.), DNP m.p. 160–162°[21] was obtained from cyclohexyl azide in 19.5% yield. Cycloheptanone as its DNP, m.p. 147–149°,[22] was obtained in 4.6% from cycloheptyl azide.

The basic aqueous solution of material from 15.0 g. (0.35 mole) of cyclopentyl azide was allowed to stand for three hours after which time a yellow layer separated. This layer was removed and the aqueous layer was thoroughly extracted with ether. Upon removal of the dried ether a residue of 8.95 g. (79.8%) of piperideine was obtained. Polymerization commenced immediately, and after ten days at room temperature had transformed the product into a viscous oil. A portion was dissolved in a mixture of 5 ml. of acetone and 5 ml. of 95% ethanol. After two days the solvent had evaporated, leaving a yellowish solid residue. The solid was washed with a small amount of acetone and dried; m.p. 97.5–99.0°. A mixture of this material with authentic isotripiperideine (lit.[23] m.p. 97.5–98.5°) melted at 97.5–99.0°.

From the basic solution of material from 19.0 g. (0.152 mole) of cyclohexyl azide a gummy product (4.7 g.) separated which hardened upon standing in the solution. It had no definite melting point but softened and charred from approximately 75 to 250°. Because of the insolubility of the material, preparation of a sample for analysis involved washing it thoroughly with grinding in several solvents and drying *in vacuo*.

Anal. Calcd. for $C_{14}H_{24}N_2O_3$: C, 62.66; H, 9.01; N, 10.44. Found: C, 62.44; H, 9.21; N, 10.57.

A white, curdy, polymeric solid which resembled rubber was separated from the basic solution of material from 14.6 g. (0.104 mole) of cycloheptyl azide. It appeared to be a polymer of N-dehydroheptamethylenimine or the isomeric linear polymer of ω-aminoheptaldehyde, the hydrolysis product of the cyclic imine. After drying it weighed 5.4 g. (47%) and had no definite melting point but charred over the range 100–275°. Attempts to recrystallize the solid failed because of its extreme insolubility. The solid was ground twice under water, then ground twice under ethanol and twice under acetone and dried for three hours at approximately 64° (5 mm.).

Anal. Calcd. for $(C_7H_{13}N)_n$: C, 75.62; H, 11.78; N, 12.60. Found: C, 72.27; H, 10.96; N, 11.44; ash, 2.37. Corrected C, 74.02; H, 11.22; N, 11.72.

Oxazolines and Dihydroöxazines.—In accordance with the method previously described,[2] 1-azido-2-propanol and 1-azido-3-propanol were treated with *m*- and *p*-nitrobenzaldehyde in benzene to which sulfuric acid was added. The results are found in Table II.

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[18] F. Krafft, *Ber.*, **23**, 2363 (1890).

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