(J = 2.5), with relative areas 2:1, and (c) its mass spectrum where the most abundant peak is that of the parent ion, m/e 106.

As further confirmation, derivatives V, m.p. 226 dec., VI, m.p. 188°, and VII, m.p. 155°, were prepared from III by treating it with excess cyanogen chloride, benzoyl chloride, and acetic anhydride, respectively. In contrast to III, they are relatively stable in air. *Anal.* Calcd. for $C_8H_4N_4$ (V): C, 61.5; H, 2.58; N, 35.9; mol. wt., 156. Found: C, 61.7; H, 2.73; N, 35.8; mol. wt. (osmometric in chloroform), 163. Calcd. for $C_{20}H_{14}N_2O_2$ (VI): C, 76.4; H, 4.49; N, 8.90; mol. wt., 314. Found: C, 76.4; H, 4.59; N, 8.66; mol. wt. (osmometric in chloroform), 323. Calcd. for $C_{10}H_{10}N_2O_2$ (VII): C, 63.1; H, 5.30; N, 14.7. Found: C, 62.9; H, 5.29; N, 14.7.

The 1,3-location of substituents in the above derivatives follows from n.m.r. Thus, in VII, the 4,6 hydrogens appear as a doublet at τ 1.66 ($J_{4,5}$ = 2.8), the 2-hydrogen as a doublet at τ 2.60 ($J_{2,5}$ = 1.1), the 5-hydrogen as a triplet at τ 3.26 (J = 2.8) further split into doublets (J = 1.1), and the methyls as a singlet at τ 7.57, with relative intensities 2:1:1:6. In the n.m.r. spectrum of VI the 4,6-hydrogens appear as a doublet (J = 2.9) at τ 1.36; the 2-hydrogen is overlapped by the phenyl hydrogens (a multiplet in the τ 2.15–2.58 range). Nevertheless, the presence of a triplet (J = 2.9) further split into doublets (J = 1.1) at τ 3.12 is diagnostic of 1,3-disubstitution. The observed direction of electrophilic substitution in 3a,6a-diazapentalene is consistent with its charge distribution and the concentration of negative charge in the ring bearing an electron-delocalizing substituent.

2-Bromo-3a,6a-diazapentalene (IV) was obtained from II and identified by techniques employed for 3a,6a-diazapentalene.

The synthetic scheme employed in the present work is a versatile one and has led to diversely substituted 3a,6a-diazapentalenes. They will be reported along with the details of this work in a forthcoming publication.

S. Trofimenko

Contribution No. 1126, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington 98, Delaware
Received August 4, 1965

Carbonium Ion Rearrangements. VII. Protonated Cyclopropanes in the Nitrous Acid Deamination of *n*-Propylamine

Sir:

From n.m.r. studies we concluded[1] that 11.8% of the 1-propanol obtained from the deamination of 1-aminopropane-1,1,2,2-d_4 had resulted "mainly, if not exclusively," from 1,2-hydride shifts rather than successive 1,2 shifts. Protonated cyclopropanes were excluded by evidence[2] that the deamination of 1-aminopropane-1-^{14}C gave 1-propanol labeled exclusively at C-1 and C-3.

To clarify the discrepancy between the 11.8% isotopically rearranged 1-propanol and the 8% reported from the deamination[2,3] of 1-aminopropane-1-^{14}C and to identify the source of the small proton resonance detected[1] at τ 8.5, we have studied the reaction further by using mass spectrometry for isotopic analysis. We wish to present evidence supporting protonated cyclopropanes.[4]

The 1-propanol obtained from the deamination[5] of 1-aminopropane-1,1-d_2 (96.6%)[6] and 1-aminopropane-1-d_1 (3.4%) was converted with hexamethyldisilazane to the trimethylsilyl ether.[7] Isotopic composition of the silyl ether, estimated from the parent-less-methyl peaks, was 96.4% d_2 and 3.6% d_1. Good agreement of these values with isotopic composition of the diacetamide supports the view that methyl loss occurs solely from the trimethylsilyl group and that no deuterium–protium exchange occurred between substrate and solvent during the reaction. The parent-less-ethyl ion had the composition 3.5% d_0, 4.9% d_1, and 91.6% d_2. If this ion arose solely from primary loss of the ethyl group, then these values would correspond to the isotopic composition of the α-methylene group of 1-propanol. Mass spectral analysis of the trimethylsilyl ether of 1-propanol-1,1-d_2 that was prepared from reduction of propionic anhydride with lithium aluminum deuteride gave: parent-less-methyl, 98.8% d_2 and 1.2% d_1; parent-less-ethyl, 98.3% d_2, 1.6% d_1, and 0.1% d_0. From a second reduction the results were: parent-less-methyl, 99.0% d_2 and 1.0% d_1; parent-less-ethyl, 98.3% d_2, 1.6% d_1, and 0.1% d_0. The ether of a third sample of 1-propanol-1,1-d_2 that was prepared from reduction of propionyl chloride with a different batch of lithium aluminum deuteride gave: parent-less-methyl, 88.4% d_2, 11.5% d_1, and 0.1% d_0; parent-less-ethyl, 87.7% d_2, 12.0% d_1, and 0.3% d_0. After correction (0.5% d_1 and 0.1% d_0) the isotopic composition of the α-methylene group of 1-propanol obtained from the deamination becomes 3.4% d_0, 4.4% d_1, and 92.2% d_2. Since about 95% of the 1-propanol is isotopically unrearranged, the ether of the 1-propanol resulting from 1-aminopropane-1-d_1 (3.6%) contributes 0.2% d_0 and 3.4% d_1. The composition therefore of the methylene group of 1-propanol resulting solely from 1-aminopropane-1,1-d_2 (96.4%) should be 3.2% d_0, 1.0% d_1, and 92.2% d_2. The results are summarized.

$$\underset{100\%\ d_2}{CH_3CH_2CD_2NH_2} \xrightarrow{40^\circ} \underset{\text{I, 95.7\%}}{C_2H_5\text{–}CD_2OH} + \underset{\text{II, 1.0\%}}{C_2H_3D\text{–}CHDOH} + \underset{\text{III, 3.3\%}}{C_2H_3D_2\text{–}CH_2OH}$$

The trimethylsilyl ether of the 1-propanol obtained from the deamination of a new sample of 1-aminopropane-1,1-d_2 gave: parent-less-methyl, 98.0% d_2 and 2.0% d_1; parent-less-ethyl, 93.6% d_2, 3.2% d_1, and 3.2% d_0. Correcting as before gives 96.0% I, 0.8% II, and 3.2% III. When the reaction was run at 0° the results were 97.8% I, 0.6% II, and 1.6% III.

(1) G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **84**, 2838 (1962).
(2) O. A. Reutov and T. N. Shatkina, *Dokl. Akad. Nauk SSSR*, **133**, 606 (1960); *Tetrahedron*, **18**, 237 (1962).
(3) J. D. Roberts and M. Halman, *J. Am. Chem. Soc.*, **75**, 5759 (1953).
(4) R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252 (1964); A. A. Aboderin and R. L. Baird, *ibid.*, **86**, 2300 (1964).
(5) Reaction conditions were those described in ref. 3. The temperature in the reaction flask was about 40°.
(6) Isotopic composition was estimated from mass spectral analysis of the 1-propyldiacetamide. Uncertainties in these and other isotopic compositions reported here are about ±0.1.
(7) S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

Isotopic analysis of the trimethylsilyl ether of 1-propanol obtained from the deamination of 1-aminopropane-2,2-d_2 at 40° gave: parent-less-methyl, 98.0% d_2 and 2.0% d_1; parent-less-ethyl, 1.4% d_2, 1.1% d_1, and 97.5% d_0. The ether of authentic 1-propanol-2,2-d_2 gave the following reproducible results: parent-less methyl, 98.4% d_2 and 1.6% d_1; parent-less-ethyl, 0.2% d_2, 0.2% d_1, and 99.6% d_0. Correcting and summarizing, we have

$$\underset{100\%\ d_2}{CH_3CD_2CH_2NH_2} \xrightarrow{40^\circ} \underset{I',\ 1.2\%}{C_2H_5\text{–}CD_2OH} + \underset{II',\ 0.9\%}{C_2H_4D\text{–}CHDOH} + \underset{III',\ 97.9\%}{C_2H_3D_2\text{–}CH_2OH}$$

The data provide evidence that the 1-propanol arises mainly from a path leading to isotopically unrearranged alcohol and partly from a path leading to extensively rearranged alcohol. The higher concentration of I′ over II′ rules out reversible 1,2-hydride shifts as the rearrangement path. Since [II] = [II′], 1-aminopropane-1,1-d_2 and 1-aminopropane-2,2-d_2 must lead to the same isotope position intermediate, or its equivalent, prior to the formation of isotopically rearranged 1-propanol. This intermediate is best formulated as some protonated cyclopropane.

Mechanism I (Chart I) accommodates the results, provided the following are true: (a) From [II] = [II′], V ⇌ V′ is much faster than reaction of these ions with solvent to form 1-propanol. In terms of isotope position rearrangement this is indistinguishable from a symmetrical protonated cyclopropane. (b) From [I′] > [II′], V ⇌ VI is slower than V ⇌ V′ and competitive with reaction of the ions with solvent. Mechanism I is therefore ruled out, because it requires assumptions already excluded by solvolytic studies of cyclopropane in deuteriosulfuric acid.[4]

Mechanism II (Chart II), either A or B, is consistent with our results and those of Baird and Aboderin.[4] For path A to be correct, IV must go to V and V′ as fast or faster than it reacts with solvent to give 1-propanol. For path B (formation of V and V′ without the intervention of IV) to be correct, V and V′ must arise in the same ratio from either labeled species. Neither path requires the excluded[4] condition that V ⇌ VI be slower than V ⇌ V′.

From the results we conclude that at 40° about 5% (1.2% I, 0.9% II, and 3.2% III) of the 1-propanol arises from protonated cyclopropanes and 95% from an intermediate, or intermediates, leading to isotopically unrearranged alcohol. At 0° the contribution of the protonated cyclopropane path is about 3%.

The data disagree with the reported 8%[2,3] and 11.8%[1] isotopically rearranged 1-propanol. They require that in the case of 1-aminopropane-1-^{14}C over 96% of the label be at C-1 of 1-propanol and less then 4% be distributed between C-2 and C-3. The exact distribution of the rearranged label will depend on the relative rates of ion equilibration and ion capture by solvent. Probably more than one-half but less than two-thirds will be at C-2. In the case of 1-aminopropane-1,1,2,2-d_4 not more than 4% 1-propanol with protium at C-1 should have been obtained.

Mass spectral analysis of the trimethylsilyl ether of 1-propanol obtained from the deamination of 1-aminopropane-1-^{13}C at 40° gave parent-less-methyl 30.6% ^{13}C and parent-less-ethyl 29.8% ^{13}C. This corresponds to 2.6 ± 0.6% rearrangement (C-2 + C-3 labeled 1-propanol). The ether of authentic 1-propanol-1-^{13}C gave parent-less-methyl 30.6% ^{13}C and parent-less-ethyl 30.8% ^{13}C.

Mass spectral analysis of the acetate of 1-propanol obtained from the deamination of 1-propyl-1,1,2,2-d_4 ammonium perchlorate[1] gave 85% d_4, 12% d_3, and 3% d_2. Apparently the major source of 1-propanol labeled with protium at C-1 was 1-propyl-1,2,2-d_3 ammonium perchlorate that was undetected by n.m.r.[8]

Acknowledgment. We thank the Petroleum Research Fund (692-A4) and the National Science Foun-

Chart I

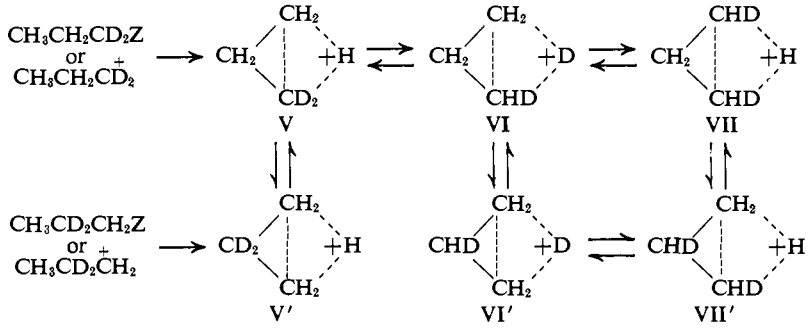
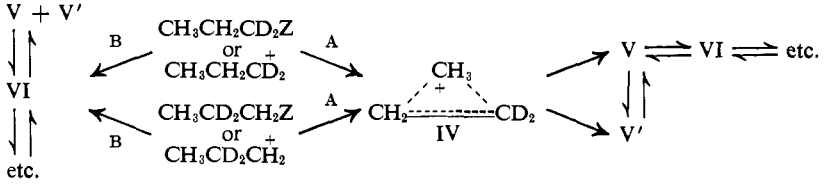


Chart II



(8) Our results are in good agreement with those of C. C. Lee, J. E. Kruger, and E. W. C. Wong, *J. Am. Chem. Soc.*, 87, 3985 (1965); C. C. Lee and J. E. Kruger, *ibid.*, 87, 3986 (1965).

dation (GP-3343) for financial support of the work performed at Michigan State University.

(9) Fellow of the Alfred P. Sloan Foundation.
(10) National Science Foundation Predoctoral Cooperative Fellow, 1962–1964.

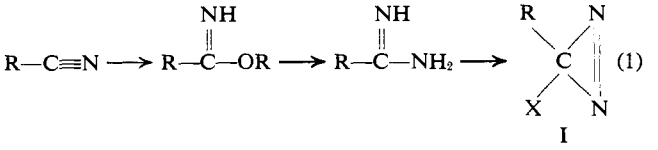
Gerasimos J. Karabatsos,[9] Chester E. Orzech, Jr.[10]
Department of Chemistry, Michigan State University
East Lansing, Michigan
Seymour Meyerson
Research and Development Department
American Oil Company, Whiting, Indiana
Received May 24, 1965

The Halogenation of Amidines. I. Synthesis of 3-Halo- and Other Negatively Substituted Diazirines[1]

Sir:

Syntheses of diazirine and a variety of its alkyl derivatives have been carried out successfully for several years.[2] However, the only reported 3-halodiazirine derivative is difluorodiazirine.[3]

We have found that halogenation of alkyl- or arylamidines and isoureas in aqueous dimethyl sulfoxide (DMSO) solution affords the corresponding alkyl-, aryl-, or alkoxy-3-halodiazirine (I) in practical yields. The method, which appears to be a general one, makes accessible the substituted 3-halodiazirine from the corresponding nitrile precursor (eq. 1).[4]



(1)

I

In the chlorination of acetamidine, addition of acetate ion produced a mixture of methylchlorodiazirine and methylacetoxydiazirine. Presumably, other nucleophiles which do not interfere with the halogenation of the amidine should compete with the halide ion to give the corresponding negatively substituted diazirine.

In a typical experiment aqueous sodium hypochlorite solution[5] (300 ml., 0.78 *M*) containing 60 g. of additional NaCl was dropped rapidly into a stirred 150-ml. DMSO solution of acetamidinium hydrochloride (0.025 mole) and 10 g. of LiCl. The volatile contents were removed continuously by means of a vacuum pump pulling through a train of four U-tube traps at −35, −80, −126 (methylcyclohexane slush bath), and −196°. The temperature of the reaction mixture rose from 25 to 55° during the addition. The product, methylchlorodiazirine, was retained principally in the −126° trap. Yields of 60% are typical. Less volatile diazirines were generally retained in the −80° trap. Methylbromodiazirine was prepared by a similar procedure using freshly prepared NaOBr. For less volatile diazirines it was convenient to add CCl_4 to the DMSO solution before addition of the NaOCl or NaOBr solution at atmospheric pressure. The product was extracted into the CCl_4 layer from which it was purified by the appropriate method, usually column chromatography through silica gel.

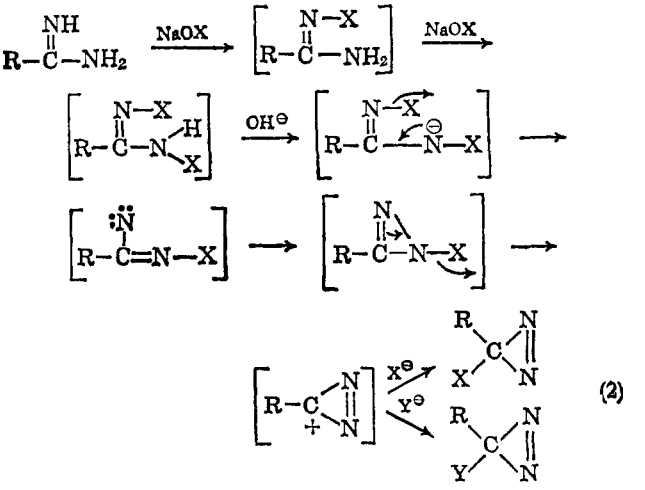
Table I. Diazirines (I) Prepared by Halogenation of Amidines in DMSO

Nitrile precursor	R	X	N=N stretch,[c] $cm.^{-1}$	Ultraviolet, $m\mu$
CH_3CN	CH_3	Cl	1585	354
CH_3CN	CH_3	Br	1570	355
CH_3CN	CH_3	CH_3COO	1575	349[d]
$(CH_3)_3CCN$	$(CH_3)_3C$	Cl	1565	358[d]
$c\text{-}C_3H_5CN$	$c\text{-}C_3H_5$	Cl	1565	357[d]
C_6H_5CN	C_6H_5	Cl	1560	388[d]
C_6H_5CN	C_6H_5	Br	1555	388[d]
$p\text{-}CH_3OC_6H_5CN$	$p\text{-}CH_3OC_6H_5$	Cl	1560	405[d]
CH_3OCN[a]	CH_3O	Cl	1545	365[d]
$CH_2{=}CHCN$[b]	$CH_2{=}CH$	Cl	1560	

[a] The actual starting material for this reaction was O-methylisourea hydrogen sulfate. [b] Preparation of this amidinium salt was not clean. By using the crude mixture a small amount of vinylchlorodiazirine was obtained. [c] Infrared spectra were recorded with a Perkin-Elmer Infracord instrument. [d] Broad peaks, position indicated is shoulder on long wave length side.

Product identification was substantiated by physical data such as proton n.m.r., ultraviolet, infrared, and mass spectra; molecular weights were obtained using a mass-spectral effusion method. Table I lists those diazirine derivatives which were prepared along with the infrared absorption frequency of the characteristic diazirine −N=N− stretch[3,6,7] and the wave length of their ultraviolet absorption.[6,8,9] In all cases the proton n.m.r. spectrum was consistent with the proposed structure. Mass spectra of the 3-halodiazirines were generally characterized by fragmentation to produce ions of *m/e* which result from loss of halide and both halide and a nitrogen molecule. The latter was usually the most intense peak. Satisfactory elemental analyses were obtained on several liquid diazirine products, but explosions in the combustion tube were frequent.

The reaction mechanism probably involves the sequence illustrated in eq. 2. Initial formation of the



(2)

(1) Presented before the Division of Organic Chemistry at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.
(2) For a survey of the field see E. Schmitz, *Angew. Chem. Intern. Ed. Engl.*, 3, 333 (1964); *Angew. Chem.*, 76, 197 (1964).
(3) R. A. Mitsch, *J. Heterocyclic Chem.*, 1, 59 (1964).
(4) The amidine salts used in this study were either purchased from Aldrich Chemical Company, Milwaukee, Wis., or prepared according to the method of Pinner as described by A. W. Dox, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 5.
(5) Commercial Clorox.
(6) W. H. Graham, *J. Am. Chem. Soc.*, 84, 1063 (1962).
(7) R. Ettinger, *J. Chem. Phys.*, 40, 1693 (1964).
(8) J. A. Merritt, *Can. J. Phys.*, 40, 1683 (1962).
(9) A. Lau, E. Schmitz, and R. Ohme, *Z. physik. Chem.*, 223, 417 (1963).