was obtained and substantial amounts of triphenylphosphine borane were isolated. There thus appears to be a correlation between the strength of the ligand bond in XB_3H_7 compounds and the mode of reaction toward a stronger nucleophile: the stronger the initial ligand bond the greater the extent of degradation of the triborane.

CONTRIBUTION FROM
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A DIRECT METHOD OF PREPARATION OF DIAZIRINE

Sir:

Recent reports in the German literature[1,2] have described the preparation of several substituted diazirines, a class of compound previously unknown. Although some early workers had incorrectly assigned the cyclic, three-membered ring structure to aliphatic diazo compounds, modern physical methods have been used to prove the linear arrangement of this class of compound.[3] We now wish to report a direct one-step method of preparation of diazirine (I), the parent member of the diazirine series and the cyclic isomer of diazomethane. The preparation of diazirine by another method[4] has been reported since the inception of this work.


I

The preparation was carried out in a vacuum system by the reaction of difluoramine[5] with *t*-butylazomethine or *t*-octylazomethine[6] in carbon tetrachloride solution. In the latter case diazirine was obtained in 62% yield. The product was purified by fractionation through a series of traps, the diazirine being retained in the −128° trap. The small amount of difluoramine contaminant was removed easily by an aqueous potassium iodide solution. In the reaction with *t*-butylazomethine, isobutylene and *t*-butyl fluoride were identified as major volatile by-products. Because of the preliminary nature of these results, a mechanistic interpretation of the reaction will be deferred until later.

The identity of diazirine was established by several observations. It is a colorless gas, b.p. −14°, of molecular weight 42, which produced the mass-spectral cracking pattern in Table I; the gas-phase ultraviolet spectrum (Fig. 1) exhibits a number of sharp, regularly spaced peaks between 282 and 324 mμ ($\epsilon_{308.5\ m\mu}$, 176 liter/mole-cm.); the similarity in shape of the spectrum with that of 2,3-diazabicyclo[2,2,1]-2-heptene,[7] a strained aliphatic azo compound, is rather striking; the proton n.m.r. spectrum, run in CCl_4 solution at 0° with a 40 megacycle probe, is a singlet at +241 cps. (relative to external benzene). This relatively high-field absorption for methylene protons is consistent with a strained three-membered ring structure. The methylene protons of sterculic acid, a cyclopropene derivative, absorb at +271 cps.[8] The gas-phase infrared spectrum (Fig. 2) is characterized by the expected C–H absorptions and multiple peaks in the range 1610–1660 cm.$^{-1}$. This absorption probably derives from the nitrogen–nitrogen double bond stretching vibration.[9]

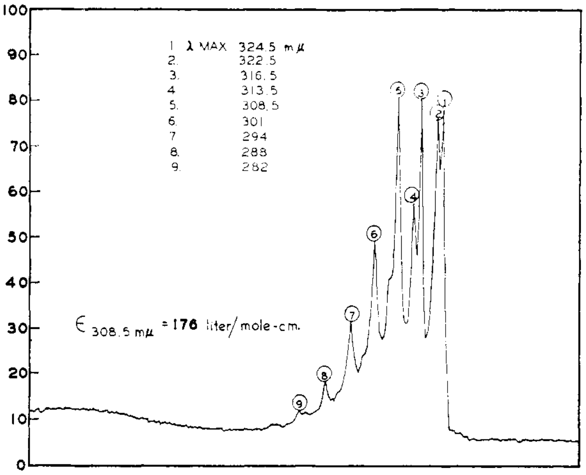
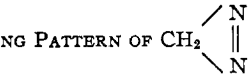


Fig. 1.—Ultraviolet spectrum of diazirine.

Chemically, diazirine appears to be less reactive than diazomethane. It is decomposed relatively slowly by sulfuric acid with liberation of a molecule of nitrogen. It is stable to *t*-butoxide ion in *t*-butyl alcohol and, although storable in glass, is decomposed by ultraviolet radiation.

TABLE I

MASS SPECTRAL CRACKING PATTERN OF 

m/e	Pat.	Ion
12	10.8	C^+
13	22.9	CH^+
14	100.0	CH_2^+
15	2.2	?
26	1.8	CN^+
27	5.8	CHN^+
28	17.8	CH_2N^+, N_2^+
29	2.3	HN_2^+
40	1.8	CN_2^+
41	10.8	CHN_2^+
42	43.1	$CH_2N_2^+$
43	0.8	C^{13+} and N^{15+} of parent

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[1] S. R. Paulsen, *Angew. Chem.*, **72**, 781 (1960).

[2] E. Schmitz and R. Ohme, *Chem. Ber.*, **94**, 2166 (1961).

[3] For a summary of the evidence with pertinent literature references, see H. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 42–44.

[4] E. Schmitz and R. Ohme, *Tetrahedron Letters*, 612 (1961).

[5] J. P. Freeman, A. Kennedy and C. B. Colburn, *J. Am. Chem. Soc.*, **82**, 5304 (1960).

[6] W. D. Emmons, *ibid.*, **79**, 5739 (1957).

[7] S. G. Cohen, R. Zand and C. Steel, *ibid.*, **83**, 2895 (1961).

[8] K. L. Rinehart, Jr., W. A. Nilsson, and H. A. Whaley, *ibid.*, **80**, 503 (1958).

[9] For a discussion of the spectra of *azo* compounds, see L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Edition, John Wiley and Sons, New York, N. Y., 1958, p. 271.

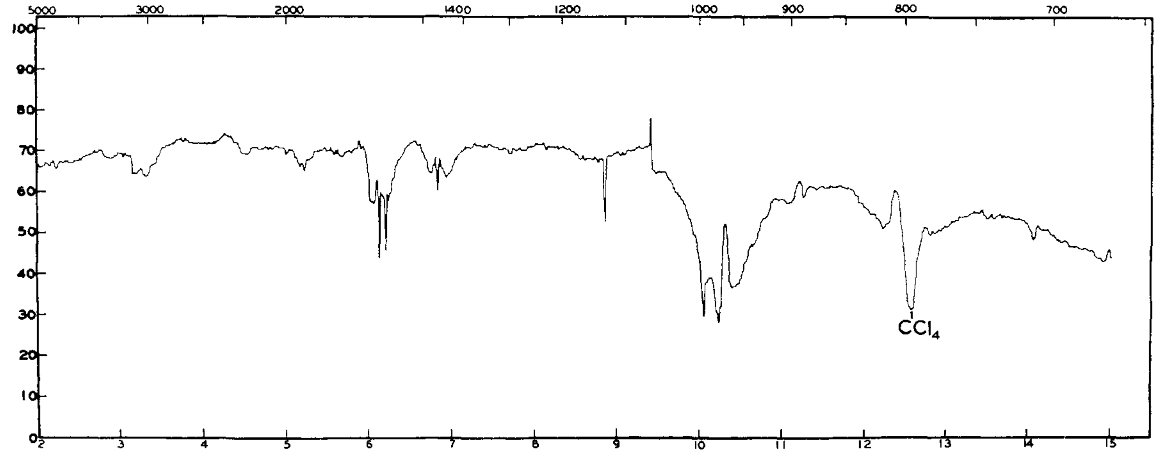

Fig. 2.—Infrared spectrum of diazirine.

Diazirine has been handled routinely as a gas and neat liquid[10] although it exploded once upon warming after being frozen in a liquid nitrogen trap; several times gaseous samples exploded when air was admitted.

Acknowledgment.—This investigation was supported by Army Ordnance Contract DA-01-021-ORD-11909.

[10] This contrasts with the observation in reference (4) that diazirine is explosive at −40°.

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RECEIVED FEBRUARY 1, 1962

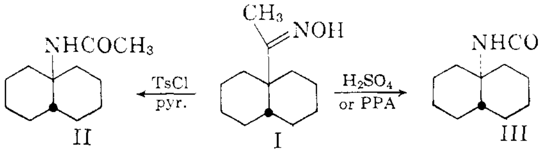
STEREOISOMERIZATION OF MIGRATING GROUP DURING BECKMANN REARRANGEMENT

Sir:

It is a cardinal principle of rearrangements to electron-deficient nitrogen that the reaction occurs with retention of configuration of the migrating group. Previous work[1] has established the validity of this conclusion for a variety of rearrangements including that under consideration here, the Beckmann rearrangement.[2]

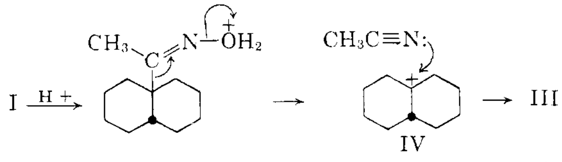
We wish to report the first violation of this rule of retention of configuration, and the consequent demonstration of an alternate mechanism for Beckmann rearrangements in strong acid, in the rearrangement of 9-acetyl-*cis*-decalin oxime (I). The oxime, m.p. 107.5–108.5° (calcd. for $C_{12}H_{21}NO$: C, 73.79; H, 10.84; N, 7.17. Found: C, 73.72; H, 10.81; N, 7.35) was prepared from the ketone, b.p. 84° (1 mm.) (calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.13; H, 11.41), which was synthesized by treatment of the acid chloride of *cis*-decalin-9-carboxylic acid[3] with dimethylcadmium. Reaction of I with *p*-toluenesulfonyl chloride in pyridine at room temperature afforded, in 92% yield, N-(*cis*-9-decalyl)-acetamide (II),[4] m.p. 126°, shown identical by mixed m.p. determination and comparison of infrared spectra with an authentic sample.[5]

On the other hand, treatment of oxime I with concentrated sulfuric acid or polyphosphoric acid overnight at room temperature yielded N-(*trans*-9-decalyl)-acetamide (III),[4] m.p. 183°, again identified by comparison with an authentic sample. The *cis* amide (II) was recovered unchanged under these conditions.



The stereoisomerization which occurs in the decalyl moiety during the conversion of I to III requires the existence of an alternate mechanism for the Beckmann rearrangement, in addition to the well-known stereospecific process.[2] We propose the pathway shown in Chart I for the rearrangement in acid: (1) fragmentation of the protonated oxime into acetonitrile and the 9-decalyl carbonium ion (IV), a step which finds ample analogy in the cleavage of α-trisubstituted oximes,[6] and (2) recombination of these fragments in a Ritter[7] reaction.

CHART I



In support of this postulate, we find, first, that acetonitrile can be identified as a product of the reaction of I with phosphorus pentachloride and, second, that the addition of acetonitrile to ion IV can be verified by treating the nitrile separately

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[1] Summarized by G. W. Wheland, in "Advanced Organic Chemistry," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 597–610.

[2] J. Kenyon and D. P. Young, *J. Chem. Soc.*, 263 (1941); A. Campbell and J. Kenyon, *ibid.*, 25 (1946).

[3] R. E. Pincock, E. Grigat and P. D. Bartlett, *J. Am. Chem. Soc.*, **81**, 6332 (1959).

[4] W. Hückel and M. Blohm, *Ann.*, **502**, 114 (1933); W. G. Dauben, R. C. Tweit and R. L. MacLean, *J. Am. Chem. Soc.*, **77**, 48 (1955).

[5] Authentic samples of the *cis* and *trans* amides were kindly furnished by Prof. W. G. Dauben, University of California, to whom we express our gratitude.

[6] See R. K. Hill and R. T. Conley, *J. Am. Chem. Soc.*, **82**, 645 (1960), for examples and additional references.

[7] J. J. Ritter and P. P. Minieri, *ibid.*, **70**, 4045 (1948).