fur compounds are converted to their alternate valence states, and are in effect regenerated and may be effective repeatedly, not being consumed. The percentage of inhibition depends on the concentration of inhibitor; the period of inhibition does not, providing a new mechanism of inhibition. In classical inhibition of chain reactions the inhibitor is consumed and the inhibition period is related to the rate of initiation and the quantity of inhibitor.[7]

The ^{60}Co γ-ray irradiation of benzophenone in 2-propanol leads to benzopinacol and acetone in a non-chain process,[8] apparently *via* radicals I and II. We find that under conditions of ^{60}Co radiation which otherwise lead to 0.19 mmole of benzopinacol, the presence of 0.025 mmole of mesityl disulfide or 0.050 mmole of 2-mercaptomesitylene leads to complete inhibition of formation of this product. In both light and high energy radiation induced reactions the mercaptan–disulfide system inhibits non-chain processes, each molecule countering the action of many quanta. The radiation converts compounds into radicals by removal or addition of hydrogen atoms. The sulfur compounds, in rapid hydrogen transfer processes, convert the free radicals to stable molecules, and may do this repeatedly. Such reactions may describe a chemical mechanism by which mercaptans protect biological systems against damage by high energy radiation.[9a,b] In other circumstances the hydrogen transfer reactivity of the mercaptan–thiyl system leads to catalysis.[6,10a,b,c]

[7] S. G. Cohen, *J. Am. Chem. Soc.*, **69**, 1057 (1947).

[8] J. G. Burr and J. D. Strong, *J. Phys. Chem.*, **63**, 873 (1959).

[9] (a) E. S. G. Barron, S. Dickman, J. A. Muntz and T. P. Singer, *J. Gen. Physiol.*, **32**, 537 (1949); (b) B. Smaller and E. C. Avery, *Nature*, **83**, 539 (1959).

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CLEAVAGE OF TRIMETHYLAMINE TRIBORANE[1]

Sir:

We wish to report a unique degradation reaction of a triborane Lewis base adduct. The reaction of trimethylamine triborane with triphenylphosphine resulted in cleavage of the triborane to triphenylphosphine borane and a triphenylphosphine adduct of a new boron hydride, I. The yield of I increased as the ratio of triphenylphosphine to the triborane complex was increased. Based on the reaction

$$3(C_6H_5)_3P + (CH_3)_3NB_3H_7 \xrightarrow[50°]{C_6H_5H} \underset{I}{((C_6H_5)_3PBH_2)_2\downarrow} + (C_6H_5)_3PBH_3 + N(CH_3)_3\uparrow$$

a 93% yield of the insoluble I was obtained, m.p. 185° (*Anal.* Calcd. for $(C_6H_5)_3PBH_2$: B, 3.94; C, 78.60; H, 6.19; P, 11.27. Found: B, 3.79; C, 78.61; H, 6.27; P, 13.2). Triphenylphosphine borane (m.p. 187–188°) was isolated in 67% yield and a 98% recovery of the trimethylamine liberated was achieved. It was demonstrated that I was different from either triphenylphosphine borane or triphenylphosphine triborane, by mixed melting points and a comparison of their solubilities and infrared spectra. The B^{11} n.m.r. spectrum (at 12.8 megacycles) of a saturated solution of I in methylene chloride showed a single unresolved band at 53.1 p.p.m. relative to methyl borate.[2]

An ebullioscopic molecular determination in methylene chloride indicated that I was dimeric (Calcd. 550. Found: 570, 566, 580). This suggests that I is the bis-triphenylphosphine adduct of the hitherto unknown diborane (4); $((C_6H_5)_3P)_2B_2H_4$. Hydrolysis experiments supported this formulation. Treatment of I with trifluoroacetic acid–ethanol (1:3) at 100° for 24 hours resulted in an active hydrogen to boron ratio of 1.97, while reaction of I with ethanolic potassium hydroxide under the same conditions yielded a H/B ratio of 2.46. The difference in the active hydrogen boron ratios of the two hydrolysis experiments is attributed to cleavage of the boron–boron bond by the basic ethanolic mixture. Apparently, the boron–boron bond was stable in the trifluoroacetic acid solution. The relative stability of the boron–boron bond toward hydrolysis in acid media as opposed to its facile hydrolysis in base was demonstrated by Brotherton, *et al.*, for several alkoxy and dialkylamino diboron derivatives.[3]

The formulation of I as a diboron derivative would make it isoelectronic with the unstable boron hydride ion, $B_2H_6^{=}$, proposed by Hough and coworkers,[4] and similar to the reported diadducts formed between diboron tetrachloride and phosphines or sulfides.[5] The alternate formulation of I as the salt $(C_6H_5)_3P)_2BH_2^+BH_4^-$ is not completely eliminated although the observed hydrolytic stability is in contrast with that expected from the borohydride group.

Although displacement of trimethylamine from trimethylamine triborane upon treatment with triphenylphosphine occurred, no evidence for the formation of triphenylphosphine triborane was found.

Triphenylphosphine triborane was therefore prepared from triphenylphosphine and the tetrahydrofuran adduct of triborane in a manner analogous to that reported by Parry for the preparation of ammonia triborane.[6] A yield of 54% of $(C_6H_5)_3PB_3H_7$ was obtained, m.p. 161° (*Anal.* Calcd. for $(C_6H_5)_3PB_3H_7$: B, 10.77; C, 71.66; H, 7.30; P, 10.27. Found: B, 10.80; C, 71.42; H, 7.11, P, 9.20). However, if dimethylsulfide triborane was employed instead of the tetrahydrofuranate only a small yield of triphenylphosphine triborane

[1] This work was supported by the U. S. Army Ordnance Corps, Contract No DA-01-021-ORD-11878.

[2] The B^{11} n.m.r. spectrum of $(C_6H_5)_3PBH_3$ in methylene chloride was practically identical to that of I. It showed a broad band (centered at 52.8 p.p.m. relative to methyl borate) which was not completely resolved. The spectrum was complicated due to P–B coupling as well as B–H coupling.

[3] R. J. Brotherton, *et al.*, *J. Am. Chem. Soc.*, **82**, 6245 (1960).

[4] W. V. Hough, L. J. Edwards and A. D. McElroy, *ibid.*, **80**, 1828 (1958).

[5] T. Wartik and E. F. Apple, *ibid.*, **80**, 6155 (1958).

[6] G. Kodama, R. W. Parry and J. C. Carter, *ibid.*, **81**, 3534 (1959).

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.

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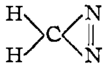
A DIRECT METHOD OF PREPARATION OF DIAZIRINE

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]

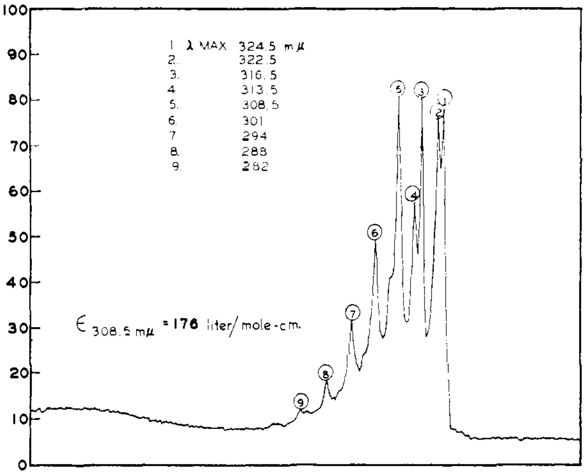
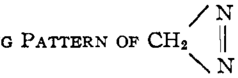


Fig. 1.—Ultraviolet spectrum of diazirine.

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.