An acidic and a neutral fraction were recovered from this solution. Infrared examination indicated the former to be a mixture of organophosphorus acids and benzoic acid. The neutral fraction contained benzaldehyde and possibly benzyl alcohol. A 2,4-dinitrophenylhydrazone derivative of the aldehyde component had m.p. 235–236° alone and mixed with an authentic specimen of this derivative of benzaldehyde.

Reaction of Phosphine with *p*-Tolualdehyde.—This reaction was conducted as described for the preparation of VIIb, method C. A solution of 48 g. (0.4 mole) of *p*-tolualdehyde, 100 ml. of concentrated hydrochloric acid and 50 ml. of tetrahydrofuran was allowed to react with an excess of phosphine. The reaction was completed after 45 minutes. A temperature rise from 25 to 53° was observed and 0.14 mole of phosphine was taken up. Water (150 ml.) was added to the mixture and, after cooling to 0°, the supernatant liquid was decanted. The residual gum was thoroughly washed with water and triturated with 100 ml. of ethanol. The solid which formed was collected to give 24.6 g. of *p*-methylbenzylbis-(*p*-methyl-α-hydroxybenzyl)-phosphine oxide (XIII), m.p. 165–166°. An additional 4.5 g. was obtained from the aqueous and ethanolic filtrates (total yield 55%). The analytical sample was prepared by recrystallization from ethanol, m.p. 167–168°.

Anal. Calcd. for $C_{24}H_{27}O_3P$: C, 73.08; H, 6.90; P, 7.85. Found: C, 72.82; H, 6.94; P, 8.01.

Reaction of Phosphine with *p*-Chlorobenzaldehyde.—This reaction also was carried out by method C. A solution of 42 g. (0.3 mole) of *p*-chlorobenzaldehyde, 150 ml. of tetrahydrofuran and 40 ml. of concentrated hydrochloric acid was treated with phosphine. The reaction was completed in 50 minutes and a rise in temperature from 25 to 32° was noted. The resulting solution was concentrated *in vacuo* and the residue was washed thoroughly with water and recrystallized from ethanol to give 19.5 g. of (XIV) *p*-chlorobenzyl-bis-(*p*-chloro-α-hydroxybenzyl)-phosphine oxide, m.p. 163–165°. An additional 9.5 g. m.p. 162–164°, was obtained from the filtrates (total yield 64%). The analytical sample prepared by further recrystallization from ethanol had m.p. 165–166°.

Anal. Calcd. for $C_{21}H_{18}Cl_3O_3P$: Cl, 23.34; P, 6.80. Found: Cl, 23.06; P, 6.92.

Reaction of Dibutylphosphine with Benzaldehyde.—Dibutylphosphine (14.6 g., 0.1 mole) was added in a nitrogen atmosphere to a solution of 21.2 g. (0.2 mole) of benzaldehyde, 11 ml. of concentrated hydrochloric acid and 40 ml. of tetrahydrofuran in the course of 20 minutes. The solution then was heated under reflux for 1.5 hours. Most of the tetrahydrofuran now was distilled, and the residual liquid was added to a mixture of 100 ml. of water and 150 ml. of ether in a separatory funnel. A three-phase system resulted. The middle phase was separated and solidified when dried *in vacuo*. After washing with ether, 18.2 g. (46%) of dibutylbis-(α-hydroxybenzyl)-phosphonium chloride was obtained, m.p. 88–91°. Repeated recrystallization from ethyl acetate gave a sample of m.p. 96–98°.

Anal. Calcd. for $C_{22}H_{32}ClO_2P$: C, 66.90; H, 8.17; Cl, 8.98; P, 7.84. Found: C, 66.66; H, 8.29; Cl, 8.81; P, 7.99.

Acid-catalyzed Reaction of Dibenzylphosphine Oxide with Benzaldehyde.—A solution of 4.6 g. (0.02 mole) of dibenzylphosphine oxide (prepared by the method of Miller, Bradley and Hamilton[22]), 2.1 g. (0.02 mole) of benzaldehyde, 25 ml. of tetrahydrofuran and 5 drops of concentrated hydrochloric acid was allowed to stand at room temperature for 16 hours. The solution then was evaporated to dryness and the residue washed with ether and filtered to give 6.6 g. (98%) of dibenzyl-α-hydroxybenzylphosphine oxide (VIII), m.p. 161–163°. There was no depression of this melting point upon admixture with a specimen prepared by the base-catalyzed procedure[11] (reported yield, 85%).

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[22] R. C. Miller, J. S. Bradley and L. A. Hamilton, THIS JOURNAL, **78**, 5299 (1956).

STAMFORD, CONN.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, N. Y.]

Reactions of Active Nitrogen with Silane and Methylsilanes

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The reactions of silane and the methylsilanes with active nitrogen have been investigated at 28 and 250°. Hydrogen was the only volatile product obtained from silane, while the methylsilanes yielded hydrogen cyanide and ammonia, in addition to hydrogen. At 250° one mole of hydrogen cyanide was produced for each carbon atom in the silane consumed, but at 28° only approximately one-half the carbon was recovered as hydrogen cyanide. The ratio of ammonia to hydrogen cyanide was independent of temperature but increased with increasing methyl substitution. The results of this study indicate that the imine (NH) radical is not an important intermediate in ammonia formation. It is suggested that ammonia is formed directly by some sort of molecular process or that the amine (NH_2) radical is the intermediate.

The chemical reactions of active nitrogen with hydrocarbons and their derivatives have been studied extensively by a number of workers.[1,2] At the time this work was initiated, the only published work on silicon-containing molecules was a spectroscopic study of the reaction flame with $SiCl_4$.[3] In a recent note the results of a survey study of the reactions of active nitrogen with tetramethylsilane and some hydrocarbons were presented.[4] In all cases it was found that significant amounts of ammonia were formed.

The failure of other workers to observe ammonia has been cited as evidence that nitrogen atoms, alone of the electronegative atoms, do not attack hydrocarbons by hydrogen atom abstraction.[2] The fact that ammonia *is* formed raises the question of the importance of hydrogen abstraction by nitrogen atoms. In this connection it was of interest to examine the reactions of active nitrogen with compounds containing the Si–H bond since the low dissociation energy of this bond compared with the C–H bond should favor hydrogen atom abstraction. Accordingly, the reactions of active nitrogen with silane, SiH_4, and the methylsilanes CH_3SiH_3, $(CH_3)_2SiH_2$, $(CH_3)_3SiH$ and $(CH_3)_4Si$ have been investigated.

Experimental

The apparatus and procedure used in carrying out the reactions was similar to that described by Gartaganis and Winkler,[5] except that the discharge tube and reaction bulb

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[1] H. G. V. Evans, G. R. Freeman and C. A. Winkler, *Can. J. Chem.*, **34**, 1271 (1956).

[2] K. R. Jennings and J. W. Linnett, *Quart. Rev.*, **12**, 116 (1958).

[3] S. C. Jevons, *Proc. Royal Soc. (London)*, **A89**, 187 (1914).

[4] H. A. Dewhurst, *J. Phys. Chem.*, **63**, 1976 (1959).

[5] P. A. Gartaganis and C. A. Winkler, *Can. J. Chem.*, **34**, 1457 (1956).

were not poisoned. The nitrogen (Linde, prepurified)[6] was passed through a liquid nitrogen trap and then directly to the discharge tube. The nitrogen flow rate was maintained constant at 1.2×10^{-5} mole/sec. which corresponded to a pressure of 1.2 mm. in the reaction bulb. The active nitrogen was produced by a condensed discharge using a 5000 ohm resistance and three condensers in series (each 10 μf., 2500 v. d.c.). The applied voltage and therefore flash rate was maintained constant. The intensity of the afterflow was monitored continuously with a 931A photomultiplier tube placed midway between the discharge tube and the reaction bulb. All experiments were made at approximately the same value of the photomultiplier current. Under these conditions the nitrogen atom flow rate was approximately 5×10^{-7} mole/sec. as measured by the amount of HCN formed from ethylene at 250°.[7,8]

The silanes were introduced into the spherical reaction bulb (approximately 300 ml. volume) through a fine jet. The reactant flow rate was calculated from the pressure drop in a calibrated volume. The condensable reaction products were collected in a liquid nitrogen trap and were then distillled into an infrared cell having a volume of 75 ml. and a path length of 5 cm. In a few cases gas samples were collected while a reaction was in progress, by allowing the gas stream from the reactor to enter a previously evacuated bulb.

Materials.—Tetramethylsilane was a commercially available product (Dow Corning, purified grade) and was used without further purification. Silane, methylsilane, dimethylsilane and trimethylsilane were prepared by the reaction of the corresponding chlorosilanes with lithium aluminum hydride in di-*n*-butyl ether[9] and were purified by fractional distillation through a low temperature Podbielniak column rated at 100 theoretical plates. Methyltrideuteriosilane was prepared in the same way by the reaction of methyltrichlorosilane with lithium aluminum deuteride. The infrared spectrum of this material showed, in addition to the band at 1586 cm.$^{-1}$ due to Si–D, a weak absorption band at 2180 cm.$^{-1}$ due to Si–H. From the infrared and mass spectra of the deuterated material the ratio of Si–H to Si–D was estimated to be approximately 0.06.

Analysis.—Ammonia was identified by its characteristic infrared spectrum and determined quantitatively by its absorbance at 968 cm.$^{-1}$. In the presence of large amounts of methylsilane or dimethylsilane, accurate determination of the ammonia was not possible, because the silanes also absorb in this region. In these cases ammonia was determined only at low reactant flow rates where the silanes were almost completely destroyed. Hydrogen cyanide was determined from the absorbance at 714 cm.$^{-1}$ and by gas chromatography using a two-meter didecyl phthalate column at room temperature. The unreacted silanes also were measured by gas chromatography and by infrared spectrophotometry using these bands: CH_3SiH_3, 2180 and 930 cm.$^{-1}$; $(CH_3)_2SiH_2$, 2180 and 930 cm.$^{-1}$; $(CH_3)_3SiH$, 1260 cm.$^{-1}$; $(CH_3)_4Si$, 1258 cm.$^{-1}$. Results obtained by the two methods showed good agreement.

Results

Silane.—The reaction of active nitrogen with silane produced a lilac-colored reaction flame at room temperature and at 250°. When the silane flow was stopped and the active nitrogen reached the liquid nitrogen product trap an intense blue glow was observed. The blue glow also was observed with methylsilane, but was not observed with any of the other methylsilanes nor with any of a large number of hydrocarbons and other compounds which have been studied. This glow also was observed when active nitrogen was allowed to enter a liquid nitrogen trap in which methylsilane or silane previously had been condensed and appeared to be a low temperature reaction flame of active nitrogen with the silane. A preliminary examination of the emission spectra of these flames showed the presence of silicon atoms; a detailed analysis of the spectra will be reported separately.

No ammonia, hydrazine or other liquid nitrogen condensable products were formed either at room temperature or 250°. Under the conditions used, the unreacted silane largely escaped the liquid nitrogen product trap so that it was not possible to determine the amount of silane reacted in the usual manner. An estimate of the amount of silane reacted and of the hydrogen produced was obtained by mass spectrometric analysis of gas samples taken while a reaction was in progress. The results of these measurements are shown in Table I.[10]

TABLE I

REACTION OF SILANE WITH ACTIVE NITROGEN AT 250°

Silane flow rate, moles/sec. $\times 10^7$	Silane reacted, moles/sec. $\times 10^7$	H_2, moles/sec. $\times 10^7$
2.0	..[a]	2.6
2.1	1.65	2.8
14.3	..[a]	3.2

[a] Silane was not determined in these runs.

Methyl Substituted Silanes.—Methylsilane, dimethylsilane, trimethylsilane and tetramethylsilane were allowed to react at varying temperatures and flow rates with the results shown in Table II. At 250° all of the methylsilanes gave hydrogen cyanide as the only carbon-containing product, except for a trace of acetylene. One molecule of hydrogen cyanide was obtained for each carbon atom in the silane consumed. At 28° only about one-half of the carbon in the silane consumed was recovered as hydrogen cyanide. Gas chromatography of the condensable products obtained at 28° did not show any carbon-containing products other than hydrogen cyanide. Analysis of a gas sample collected by the evacuated bulb technique from the methylsilane reaction showed that methane was not formed and that hydrogen was the only volatile product. However, the infrared spectrum of the solid deposited on the walls of the reaction vessel indicated the presence of Si-C bonds and probably accounts for the carbon deficiency. It is extremely interesting that there was no significant difference in the fraction of carbon recovered as hydrogen cyanide as the number of methyl groups per molecule was increased from one to four.

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[6] Mass spectrometric analysis showed that it contained 0.09% hydrogen and 0.01% methane. In control experiments (reactant absent) ammonia never was observed.

[7] D. M. Wiles and C. A. Winkler, *Can. J. Chem.*, **35**, 1298 (1957).

[8] This is a much lower nitrogen atom concentration than that used by Winkler (ref. 1), and may account for the fact that we observed ammonia in the reaction of active nitrogen with hydrocarbons, while previous workers did not. It seems likely that at high active nitrogen concentrations most of the ammonia formed might be destroyed. It has been suggested that the destruction of ammonia by active nitogen is due to reaction with excited nitrogen molecules, rather than nitrogen atoms (R. Kelly and C. A. Winkler, *ibid.*, **37**, 76 (1959)). The concentration of excited molecules would be expected to vary as the square of the nitrogen atom concentration.

An alternative, though less probable, explanation for the failure of previous workers to observe ammonia is that it reacted with the phosphoric acid used as a wall poison.

[9] R. W. Shade and G. D. Cooper, *J. Phys. Chem.*, **62**, 1467 (1958).

[10] Approximately 2.8 moles of hydrogen was observed for 1.65 moles of silane consumed, while complete decomposition to silicon and hydrogen would produce 3.3 moles of hydrogen. It is believed that the difference represents the experimental error in this analysis. A solid deposit was formed on the walls of the reaction vessel. This appeared to be principally metallic silicon, although there was a broad band of low intensity at approximately 900 cm.$^{-1}$ which may indicate some silicon–nitrogen bonds. There was no detectable absorption due to silicon–hydrogen bonds.

TABLE II

REACTION OF METHYLSILANES WITH ACTIVE NITROGEN

T, °C.	Flow rate, moles/sec. × 10^7	Silane reacted, moles/sec. × 10^7	HCN, moles/sec. × 10^7	NH_3, moles/sec. × 10^7	$\frac{NH_3}{HCN}$	$\frac{HCN}{\Delta C}$
			Methylsilane			
28	1.07	0.70	0.34	..	..	0.49
28	2.06	.81	.41	..	..	.51
28	5.9	1.28	.44	..	..	.35
28	16.7	..	.92	..	..	..
28	20.9	..	.68	..	..	..
250	1.13	0.90	.92	0.24	0.26	1.02
250	1.72	1.42	1.52	.30	.20	1.07
250	14.3	..	1.80	..	..	..
250	46.5	..	1.77	..	..	..
350	10.0	..	1.97	..	..	..
			Dimethylsilane			
28	1.15	0.735	0.665	.20	.31	0.45
250	1.44	.97	2.03	.48	.24	.99
250	12.6	..	2.8	..	..	..
250	13.8	..	3.0	..	..	..
			Trimethylsilane			
28	1.32	.49	0.88	.29	.33	.59
28	19	..	1.39	..	..	..
250	1.32	.80	2.44	.94	.39	1.03
250	36.8	..	3.1	..	..	..
			Tetramethylsilane			
28	11	..	0.7	.35	.50	..
28	40	..	0.8	.35	.44	..
250	10	..	2.5	1.2	.48	..
250	40	..	3.2	1.3	.41	..
320	30	..	4.0	..	..	..

In addition to hydrogen cyanide, all of the methylsilanes yielded significant quantities of ammonia, both at 28° and at 250°. The ratio of ammonia to hydrogen cyanide was the same, within the precision of the measurements, at both temperatures. There was a definite trend to higher proportions of ammonia with increasing methyl substitution, from approximately 23% with methylsilane to 40% with tetramethylsilane.

Methyltrideuteriosilane.—Active nitrogen was reacted with methyltrideuteriosilane at 250° at a silane flow rate of 1.14×10^{-7} mole/sec. Mass spectrometric analysis of the condensable products showed that the principal ammonia product was NH_2D, with possibly small amounts of NH_3 and no more than a trace of ND_3 and NHD_2. The hydrogen cyanide product contained only small amounts of DCN. However, the possibility of hydrogen–deuterium exchange between ammonia and hydrogen cyanide, or between either of these and traces of absorbed water on the glass surface cannot be excluded.

In a separate experiment the only non-condensable product observed was hydrogen; no methane was present. The hydrogen consisted of 39.5% H_2, 43.5% HD and 17% D_2.

From this distribution the quantity $(HD)^2/(H_2)(D_2)$ is calculated to be 2.85, which is appreciably lower than the equilibrium constant of 3.63 for the hydrogen–deuterium system at 250°.[11]

Discussion

On the basis of bond energy data it would be expected that nitrogen atoms, which are believed to be the principal reactive constituent of active nitrogen, would readily abstract hydrogen atoms from silane to give imine radicals.

$$SiH_4 + N \longrightarrow SiH_3 + NH$$

With a reasonable value of 80 kcal. for the bond dissociation energy of silane[12] and 92 kcal. for the imine radical[13] the above reaction is exothermic by 12 kcal., whereas the analogous reaction with methane is endothermic by 12 kcal. The present study shows that hydrogen is the only volatile product from the reaction of nitrogen atoms with silane. If hydrogen abstraction occurs the imine radicals must either disproportionate to nitrogen and hydrogen or react with nitrogen atoms

$$NH + N \longrightarrow N_2 + H$$

This is a highly exothermic reaction which would rapidly destroy the imine radicals.[14,15]

In Table III are summarized the limiting rates of hydrogen cyanide formation at 250° for the silanes investigated. In addition to hydrogen cyanide, significant amounts of ammonia were formed from the methylsilanes. Since ammonia could not be determined at high reactant flow rates in all cases, limiting values for ammonia formation were estimated from the limiting hydrogen cyanide rate, assuming that the ratio of ammonia to hydrogen cyanide was independent of the flow rate, as was found in the case of tetramethylsilane. The sum of the limiting values for ammonia and hydrogen cyanide is shown in Table III as "observed nitrogen atoms." It is of interest to compare the observed nitrogen atom values obtained from the silanes with the value from ethylene at 250° since Winkler[7] has suggested that the limiting value of the rate of hydrogen cyanide formation from ethylene is equal to the nitrogen atom flow rate. The observed nitrogen atom values for the silanes increased with increasing methyl substitution, from 2.2×10^{-7}

TABLE III

LIMITING RATES OF HYDROGEN CYANIDE AND AMMONIA FORMATION AT 250°

Reactant	Limiting HCN, moles/sec. × 10^7	$\frac{NH_3}{HCN}$	Limiting NH_3,[a] moles/sec. × 10^7	Observed N-atoms, moles/sec. × 10^7
SiH_4	0	..	0	0
CH_3SiH_3	1.8	0.23	0.4	2.2
$(CH_3)_2SiH_2$	3.0	.24	0.7	3.7
$(CH_3)_3SiH$	3.1	.39	1.2	4.3
$(CH_3)_4Si$	3.2	.41	1.3[b]	4.5
C_2H_4	4.9	..		4.9

[a] Inferred from NH_3/HCN ratio at low flow rates. [b] Measured directly at high flow rates.

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(11) H. C. Urey, *J. Chem. Soc.*, 562 (1947).

(12) The bond dissociation energy of silane is not known, but the bond energy has been reported as 76 kcal. [T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 2nd edition, 1958, p. 238].

(13) H. Guenebaut, *Bull. soc. chim. France*, **962** (1959).

(14) G. B. Kistiakowsky and G. G. Volpi, *J. Chem. Phys.*, **28**, 665 (1958).

(15) It has been pointed out by one of the referees that the formation of hydrogen and of silicon atoms may be due, at least in part, to a "catalyzed recombination of nitrogen atoms by SiH_4: $SiH_4 + N + N \rightarrow Si + N_2 + 2H_2$.

mole/sec. for methylsilane to 4.5 × 10^{-7} for tetramethylsilane. Such a trend would be expected if some of the nitrogen atoms abstract hydrogen atoms from silicon to form imine radicals which then disproportionate to nitrogen and hydrogen, since this reaction should become less important as the number of Si–H bonds in the molecule decreases.

The formation of ammonia from the methylsilanes does not prove, of course, that hydrogen abstraction occurs. The results of the present study indicate that ammonia is not produced by way of imine radicals resulting from hydrogen atom abstraction. This conclusion is based on the fact that ammonia was not formed in the reaction of active nitrogen with silane. The fact that ammonia was not formed from silane itself but was formed from the methylsilanes in increasing amount with increasing methyl substitution shows that it is the hydrogens attached to carbon rather than to silicon which are involved in ammonia formation. Since it seems likely that the imine radical is not an important intermediate in ammonia formation, it is suggested that the nitrogen atom must remove either two or three hydrogen atoms from the methyl group in one step. This implies that ammonia is formed directly by some sort of molecular process or that the amine radical, NH_2, is the intermediate. Some support for this view is provided by the observation that the ammonia obtained from CH_3SiD_3 was principally NH_2D.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

Boron–Nitrogen Compounds. III.[1,2] Aminoboranes, Part 2: The B–N Bond Character in Substituted Aminoboranes

BY KURT NIEDENZU AND JOHN W. DAWSON

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The preparation of (amino)-monochlorophenylboranes, $R_2N-B(Cl)(C_6H_5)$, and of unsymmetrical tetrasubstituted aminoboranes is reported. The special feature of the B–N bond of aminoboranes has been investigated. Data have been collected and analyzed in order to ascertain the double bond character of this linkage. A theoretical study of electron delocalization in the aminoborane system is presented.

Aminoboranes are conventionally illustrated by the basic structure =N—B=. To understand the chemical and physical behavior of these compounds, the fundamental character of the B—N bond must be considered. To date little work has been done to elucidate the character of this linkage.

Primarily, there exists only one normal covalent bond (I), providing an electron deficiency on the boron. Naturally, this presents a very reactive state, which can explain most of the chemical reactions of aminoboranes. Participation of the free electron-pair of the nitrogen in the B–N linkage, however, promotes double bond character (II) as the electrons then residue in π-orbitals.

$$\begin{array}{ccc} =\ddot{N}\cdot\cdot B= & \longleftrightarrow & =\overset{(+)}{N}::\overset{(-)}{B}= \\ \text{I} & & \text{II} \end{array}$$

A special kind of double bond, where one partner is responsible for the contribution of three electrons to the bond, is highly important in such situations. A convincing experimental proof of the double bond in most cases depends upon recognition of the parts played by bond distances, bond forces and the mechanism of chemical reactions, in consonance with certain empirical rules.

Planar arrangement of its three bonds, according a sp^2-hybridization, enables the free electron-pair of the nitrogen to participate as π-electrons in the double bond of aminoboranes. Such a planar arrangement of the nitrogen bonds in boron compounds has been established for aminoboranes[3] as well as for borazine[4] and boron nitride.[5] Furthermore, spectroscopic investigations of aminoboranes[6] provide convincing evidence for the double bond character of the B–N linkage.

In reference to the bond moment,[7] however, three electronic structures are necessary to describe the B–N bond of aminoboranes according to Pauling's theory.

$$\begin{array}{ccccc} =\ddot{N}\cdot\cdot B= & \longleftrightarrow & =\overset{(+)}{N}::\overset{(-)}{B}= & \longleftrightarrow & =\overset{(-)}{N}:\overset{(+)}{B}= \\ \text{I} & & \text{II} & & \text{III} \end{array}$$

Which of these structures predominates should depend on the nature of the substituents bonded to the basic structure.

Since a boron–nitrogen grouping is isosteric and isoelectronic with a carbon–carbon grouping,[8] aminoboranes have been compared with analogous ethylene compounds. More than a quarter of a century ago Langmuir[9] suggested the correspondence of melting and boiling points as a sensitive criterion for the similarity of molecules. Indeed,

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[1] Boron–Nitrogen Compounds, II, THIS JOURNAL, **81**, 5553 (1959).

[2] Supported by the Office of Ordnance Research, U. S. Army.

[3] J. Goubeau and H. J. Becher, *Z. anorg. allgem. Chem.*, **268**, 133 (1952).

[4] S. H. Bauer, THIS JOURNAL, **60**, 524 (1938).

[5] A. Brager and H. Shdanow, *C. R. (Doklady) Acad. Sci. SSSR*, **29**, NS 8, 629 (1940).

[6] Compare for instance: H. J. Becher, *Z. anorg. allgem. Chem.*, **289**, 262 (1957).

[7] H. J. Becher, *ibid.*, **270**, 273 (1952).

[8] J. Goubeau, *Naturw.*, **35**, 246 (1948).

[9] I. Langmuir, THIS JOURNAL, **41**, 1543 (1919); **42**, 274 (1920).