racemization data do not agree with those of Dwyer and Gyarfas,[3] and because for the immeasurably rapid isotopic-exchange reactions there is the ever-present possibility of complete separation-induced exchange. However, we did present evidence that the separation-induced exchanges were incomplete, and for the net chemical reactions, for which separations were not involved, there is no question but that the reaction between $Os(dipy)_3^{++}$ and $Fe(phen)_3^{+++}$ is much more rapid than the reaction between MnO_4^{--} and $Fe(CN)_6^{---}$ (specific rate, $\sim 10^4$ *M* sec.$^{-1}$ near 0°[5]).

It is of interest to speculate about the cause(s) for the apparent greater rate of electron exchange between the large complex cations than between the large anions. In addition to the difference in sign of the ionic charges, the complex cations differ from the anions in being larger and in having aromatic-type chelating groups. Although any or all of the factors may be significant, the apparent greater rate of electron exchange could be due entirely to the greater size of the cations. We estimate the radii of the cations to be 7 Å. from bond distances given by Pauling.[21] Marcus[22] estimated 2.8_6 Å. for the radii of MnO_4^{--} and MnO_4^{-} and 4.5 Å. for the radii of $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$. The greater the sizes of the reactants, the smaller will be both the coulombic repulsion between them and the Franck–Condon restrictions due to differences in their hydration spheres.[23] Using the radii given above we have calculated from the Marcus theory[22] of electron transfer that the rate of electron exchange should be $\sim 10^4$ greater between the complex cations than between the anions.

[21] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp. 158–176. Fe^{II} covalent radius, 1.23 Å.; Os^{II} covalent radius, 1.33 Å.; N radius, 0.70 Å.; N to C distance across the ring (taken equal to C to C distance across benzene), 2.78 Å.; C–H distance (taken same as in benzene) 1.08 Å.; H van der Waals radius 1.2 Å.

[22] R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); **26**, 867 (1957).

[23] W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE CHEMISTRY AND CHEMICAL ENGINEERING RESEARCH DEPARTMENT, ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Preparation of Tetraborane and Pentaborane-11[1]

BY MORTON J. KLEIN, BEN C. HARRISON AND IRVINE J. SOLOMON

RECEIVED FEBRUARY 21, 1958

A hot-cold tube technique has been devised which quantitatively converts diborane into a mixture of tetraborane and pentaborane-11. The yield of tetraborane under the reported conditions varies from 80–95%. Pentaborane-11 may be prepared from tetraborane in 70% yield by suitable adjustment of the operating conditions.

The chemistry of tetraborane and pentaborane-11 has received very little attention, primarily because the laboratory preparation of these two materials is exceedingly difficult.[2-9] Unless these compounds are prepared in a system which produces them in a relatively pure state, they are difficult to purify and the presence of impurities makes them highly unstable. Therefore, it was considered very desirable to devise a convenient laboratory method for the preparation of these two compounds.

Because of the instability of tetraborane and pentaborane-11, it was decided to use a hot-cold tube reactor as an approach to their syntheses. Koski, Maybury and Kaufman[10] have used this type of approach for the preparation of pentaborane-9, in that they pyrolyzed diborane in a glass vessel, one end of which was heated to 180°, while the other end was cooled to −80°. Their technique, while entirely satisfactory for a relatively stable compound such as pentaborane-9, was not useful for the preparations of tetraborane or pentaborane-11.

The method of preparation described below gives better yields than have ever been reported and employs a very simple apparatus that can be used repeatedly without frequent cleaning.

Experimental

Design of the Hot-Cold Tube Reactor.—The reactors consisted of two concentric test-tubes connected by a Dewar seal at the top. The outside of the reactor was surrounded by the cold bath. The temperature of the cold bath was determined by two factors. It had to be high enough so that the reactant or reactants would have a fair vapor pressure, and low enough so that the desired product would have a very low vapor pressure. The inner tube was then adjusted to the desired reaction (hot) temperature by placing a knife heater in a suitable heating liquid inside the inner tube. The annular space, 10 mm., was made very small so that the product could diffuse rapidly from the hot wall to the cold wall with minimum thermal decomposition. The reactor was made as long as was practical to give maximum heating and cooling surfaces. The dimensions of the two reactors in this study are given in Table I.

TABLE I

HOT-COLD TUBE REACTOR DIMENSIONS

	Height, cm.	Diameter, cm. Hot tube	Diameter, cm. Cold tube	Volume, cc.
Reactor I	30	6	8	337
Reactor II	27	8	10	550

Preparation of Tetraborane.—The diborane supply was obtained from the Callery Chemical Company, and was

---

[1] Presented before the Division of Physical and Inorganic Chemistry at the 131st meeting of the American Chemical Society, Miami, Florida, April, 1957.

[2] A. Stock and S. Wolfhart, *Ber.*, **57B**, 562 (1924).

[3] A. Stock, E. Wiberg and H. Martini, *ibid.*, **63B**, 2927 (1930).

[4] A. Stock and W. Mathing, *ibid.*, **69B**, 1456 (1936).

[5] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933.

[6] A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **55**, 4009 (1933).

[7] A. B. Burg and F. G. A. Stone, *ibid.*, **75**, 228 (1953).

[8] A. Stock and E. Pohland, *Ber.*, **59**, 2223 (1926).

[9] T. Wartik, M. Linevsky and H. Bowkley, "Thermodynamic Properties of Boron and Aluminum Compounds," Progress Report No. 3, March 1, 1955, Contract No. AF 18(600)-311.

[10] W. S. Koski, P. C. Maybury and J. J. Kaufman, *Anal. Chem.*, **26**, 1992 (1954).

purified by fractional condensation in a conventional high vacuum line[11] until it was tensiometrically homogeneous, exerting a vapor pressure of 61 mm. at −126°. The diborane was then distilled into the reactor by placing a liquid nitrogen bath on the reactor. The inner tube was filled with ethylene glycol and the temperature was adjusted to 120° by means of an immersion heater. This bath was stirred manually during the experiment. The liquid nitrogen bath surrounding the outer wall of the reactor was then replaced by a −78° bath. The vapor pressure of diborane is about 1400 mm. at this temperature, and the total pressure in the system rises to about 1700 mm. during the course of the reaction. A 2000-mm. blow-out manometer was attached to the system to observe the course of the reaction. At the conclusion of the experiment, the −78° bath was replaced with a liquid nitrogen bath and the hot glycol was siphoned out of the inner tube. The hydrogen was then removed by means of a Toepler pump and measured. The tetraborane was freed of the more volatile impurities by fractional condensation at −126°. The less volatile products were removed by repeatedly distilling the tetraborane through a −64° trap. The resulting material was tensiometrically homogeneous and exerted a vapor pressure of 388 mm. at 0°. The tetraborane was also identified by its infrared spectrum[12] and by analysis for active hydrogen and boron.

Preparation of Pentaborane-11.—The tetraborane used was obtained from the Callery Chemical Company or prepared from diborane. In either case, prior to each run, the material was purified as described above. The procedure for the preparation of pentaborane-11 was the same as that for tetraborane except that the cold tube was maintained at −30° with a boiling Freon 12 bath. The pressure generally increased from 110 to 200 mm. during a 15-min. run. As the tetraborane was consumed during a series of experiments, increments were added to make certain that the pressure of tetraborane did not drop below its vapor pressure. The more volatile products were removed from the pentaborane-11 by fractional condensation through a −78° bath and purified as described earlier. The last traces of tetraborane were removed by repeated fractional condensation through a −64° bath. The condensate was then freed of any less volatile material by repeated distillation through a −46° bath. The resulting pentaborane-11 was tensiometrically homogeneous and exerted a vapor pressure of 52.5 mm. at 0°. The pentaborane-11 also was identified by its infrared spectrum[12] and by boron and active hydrogen analyses.

Discussion of Results

Preparation of Tetraborane.—Some typical experiments in the preparation of tetraborane are given in Table II. The hydrogen in the last column was calculated from the amount of tetraborane and pentaborane-11 produced, using the stoichiometry of eq. 1 and 2. It is seen that the reaction

$$2B_2H_6 \longrightarrow B_4H_{10} + H_2 \qquad (1)$$

$$5B_4H_{10} \longrightarrow 4B_5H_{11} + 3H_2 \qquad (2)$$

is quite clean, *i.e.*, only very small quantities of higher boranes could have formed, or else higher hydrogen values would have been found. In addition, no solids were ever observed after evacuation of the reactor. In T-2 and T-3, a total of 69 cc. of diborane has been consumed, indicating 89% conversion to tetraborane and pentaborane-11. In T-4, this figure was 99%. Since the diborane measurement is a difference between fairly large numbers, the hydrogen measurement is a better criterion of the yield. The yield of tetraborane based on the diborane consumed in T-4 was 83%.

TABLE II

PREPARATION OF TETRABORANE

Expt.	Reactor	Time, min.	Products cc.[a] B_4H_{10}	B_5H_{11}	H_2	Calcd. H_2, cc.
T-1	II	60	39.0	1.5	43.0	42.0
T-2	I	30	5.5	0.94	8.5	7.4
T-3	I	90	18.6	4.2	27.4	27.1
T-4	I	180	23.7	3.7	31.2	31.1

[a] All quantities are given in cc. at S. T. P.

A comparison of the results from the two reactors can be obtained from the reaction times given in Table II. A 60-min. reaction time in Reactor II produced more tetraborane than a 90- or 180-min. reaction time in Reactor I. The ratio of the reaction rates appears to be greater than 2. The reaction pressure in both cases was the vapor pressure of diborane at −78°. The ratio of hot and cold surfaces of the two reactors was 1.17, while the ratio of their volumes was 1.63. Therefore, it appears that reaction does not occur exclusively on the hot surface, but takes place to a large extent in the vapor phase.

Preparation of Pentaborane-11.—A summary of some typical data obtained in the preparation of pentaborane-11 is given in Table III. These data were all obtained using Reactor II. The amount of hydrogen formed in P-1 was considerably greater than expected, based on the other products. This was also true in P-2 where the reaction was allowed to run 60 min. with the hydrogen being pumped out every 15 min. The formation of higher hydrides was confirmed by the presence of yellow oils and solids after evacuation of the reactor.

TABLE III

PREPARATION OF PENTABORANE-11

Expt.	Time, min.	Products, cc. B_2H_6	H_2	B_5H_{11}	B_5H_{11}/15 min.
P-1	15	1.6	60	23.6	23.6
P-2	60	14.6	250	84.5	21.1
P-3	75[a]	6.0	230	57.3	19.1
P-4	45[b]	..	..	86.4	28.8
P-5	60[b]	..	..	109.3	27.3
P-6	150[b]	..	..	336.0	33.6

[a] First 15 min. at 100°, second 15 min. at 110°, final 45 min. at 120°. [b] Only hydrogen and pentaborane-11 removed at 15-min. intervals.

The effect of allowing the pentaborane-11 to remain in the reactor for a longer time is seen in the last column of Table III. In P-3, an attempt was made to reduce the polymer formation by lowering the temperature of the hot tube to 100°. Only negligible amounts of hydrogen were obtained at this temperature and at 110°. The temperature of 120° appeared to be somewhat critical for this reaction. The detrimental effect of leaving pentaborane-11 in the reactor was observed again in this experiment.

Since the reaction used to prepare tetraborane has been reported to be reversible

$$2B_5H_{11} + 2H_2 \rightleftarrows 2B_4H_{10} + B_2H_6 \qquad (3)$$

it was believed that pentaborane-11 could be prepared most effectively by removing the hydrogen and pentaborane-11 from the reaction mixture every 15 min., while allowing the diborane to remain. In P-4, the amount of pentaborane-11 produced was 28.8 cc./15 min., compared to the value of 23.6 in P-1. This effect was confirmed in P-5. The total

---

[11] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[12] L. V. McCarty, G. C. Smith and R. S. McDonald, *Anal. Chem.*, **26**, 1027 (1954).

tetraborane consumed in Experiments P-1 through P-5 was 646.5 cc. The total pentaborane-11 produced was 361.1 cc., indicating a yield of 70%.

Since the first 15 min. of each of the latter two experiments was identical to P-1, it was believed that the actual effect of the diborane was probably greater than the figures indicated. A considerably longer series of experiments, P-6, in which the contribution of the first 15-min. segment is less significant and in which the diborane pressure was allowed to build up, illustrates this point. Therefore, it appears that the reaction given in eq. 3 is reversible and that P-6 represents the best conditions for the preparation of pentaborane-11.

Acknowledgment.—This work was supported by the Callery Chemical Company under a contract from the Bureau of Aeronautics, Department of the Navy, Contract NOa(s)52-1024(c).

CHICAGO, ILLINOIS

[CONTRIBUTION NO. 434 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Trialkyl- and Triaryl(iso)cyanosilanes[1]

BY T. A. BITHER, W. H. KNOTH, R. V. LINDSEY, JR., AND W. H. SHARKEY

RECEIVED DECEMBER 23, 1957

Several new syntheses for trialkyl- and triaryl(iso)cyanosilanes have been developed. Infrared studies suggest that these compounds may be equilibrium mixtures of the cyanide and isocyanide forms. The previously unreported antimony tricyanide and germanium tetracyanide have been prepared by exchange reactions between trimethyl(iso)cyanosilane and the corresponding metal chloride.

Organo(iso)cyanosilanes have been prepared from the corresponding halosilanes and silver cyanide.[2–7] Satisfactory yields usually are obtained from bromo and iodo compounds but not from the chlorosilanes. A brief study of the reaction of trimethylchlorosilane with silver cyanide demonstrated that a significant improvement in yield could be achieved by conducting the reaction in an autoclave at elevated temperatures. For example, at 125°, trimethyl(iso)cyanosilane was obtained in about 40% yield, compared to 14% reported[4] from runs in refluxing benzene.

In a search for alternative methods[8] for preparing the (iso)cyanosilanes, four new syntheses were found. These are (1) reaction of a chlorosilane with potassium mercuricyanide in dimethylformamide, (2) reaction of a hexaalkyldisilazane with hydrogen cyanide, (3) replacement of a methoxyl group on silicon by reaction with trimethylacetyl cyanide in the presence of aluminum chloride and (4) exchange between an (iso)cyanosilane and a chlorosilane.

$$2R_3SiCl \xrightarrow{K_2Hg(CN)_4} 2R_3Si(CN) + 2KCl + Hg(CN)_2 \quad (1)$$

$$R_3SiNHSiR_3 + 3HCN \longrightarrow 2R_3Si(CN) + NH_4CN \quad (2)$$

$$R_3SiOCH_3 + (CH_3)_3CCOCN \xrightarrow{AlCl_3} R_3Si(CN) + (CH_3)_3CCOOCH_3 \quad (3)$$

$$R_3SiCl + R'_3Si(CN) \longrightarrow R_3Si(CN) + R'_3SiCl \quad (4)$$

Methods 1 and 2 are probably general although they have been used only to prepare trimethyl(iso)cyanosilane. Yields are comparable to the best results obtained with silver cyanide. The third method, which should be applicable in all cases where the boiling point of the methoxysilane is above that of methyl trimethylacetate (b.p. 102°), was used to prepare triethyl(iso)cyanosilane in 64% yield. Triphenyl(iso)cyanosilane also was prepared by this method, although a pure product was not obtained. Triphenyl(iso)cyanosilane was obtained in 66% yield by the exchange reaction between trimethyl(iso)cyanosilane and triphenylchlorosilane (method 4).

The structure of the (iso)cyanosilanes has not been conclusively established. Most recently, McBride and Beachell[5] have reported that the isocyanide structure is favored on the basis of their chemical and infrared studies. The principal infrared evidence was the presence of a strong band at 6.28 μ for both *t*-butyl isocyanide and trimethyl(iso)cyanosilane, and the absence of such a band in normal cyanides. These authors do, however, point out that the infrared spectrum in the region characteristic of the cyanide and isocyanide groups could be interpreted as favoring the cyanide form or a mixture of the two forms.

In our work, new infrared data suggest that the trialkyl(iso)cyanosilanes exist as equilibrium mixtures of the cyanide and isocyanide isomers with the former predominating at room temperature. For both trimethyl- and triethyl(iso)cyanosilane, the existence of two forms is indicated by the presence of a CN band at 4.76 μ in addition to the one at 4.58 μ that was reported by McBride and Beachell. This is shown for triethyl(iso)cyano of silane in Fig. 1. It has been observed[9a] that the

---

(1) The nomenclature "(iso)cyanosilane" is used here in view of the uncertain structure of these compounds.

(2) H. Emeléus, A. G. Maddock and C. Reid, *J. Chem. Soc.*, 353 (1941).

(3) C. Eaborn, *ibid.*, 2755 (1949).

(4) C. Eaborn, *ibid.*, 3077 (1950).

(5) J. J. McBride and H. C. Beachell, THIS JOURNAL, **74**, 5247 (1952).

(6) H. Emeléus, M. Onyszchuk and W. Kuchen, *Z. anorg. allgem. Chem.*, **283**, 74 (1956).

(7) S. Sujishi, Paper 31P, Abstracts of the 119th A.C.S. Meeting, April, 1951.

(8) Trimethyl(iso)cyanosilane also has been obtained as a by-product in the reaction of trimethylchlorosilane, acetonitrile and sodium, M. Prober, THIS JOURNAL, **78**, 2274 (1956).

(9) (a) W. Gordy and D. Williams, *J. Chem. Phys.*, **4**, 85 (1936). (b) These authors, Gordy and Williams, also noted that the optical density of the CN band of an isocyanide is approximately double that of the corresponding cyanide. If this is true in the present case, then the equilibrium mixture contains 90% of the cyano form at room temperature because in the spectra of both trimethyl- and triethyl(iso)-cyanosilanes the optical density of the 4.58 μ band is 4.5 times as great as that of the 4.76 μ band.