benzene: Calcd. 213.2. Found: 214, 216. *MR*D: Calcd. 57.30. Found: 57.44.

This compound is a water-white liquid with a pleasant odor. Unlike other dialkyldichlorosilanes it does not fume in moist air and it does not titrate quantitatively with an excess of dilute alkali.

Attempted Preparation of Tri-*t*-butylchlorosilane.—In a 200-ml. three-necked flask, equipped with a reflux condenser, dropping funnel and thermometer, were placed 0.10 equivalent of *t*-butyllithium in 125 ml. of pentane and 21.3 g., 0.1 mole, of di-*t*-butyldichlorosilane. No reaction occurred at room temperature. Pentane was slowly distilled from the reaction mixture until the reaction temperature reached 75°. During twenty-four hours no formation of lithium chloride or other evidence of reaction was noted at this temperature.

Then, during forty-eight hours, pentane was slowly removed from the reaction mixture until the temperature reached 160°. The slow increase in the temperature was accompanied by the formation of a white deposit on the wall of the reaction flask. At the end of this time 125 ml. of pentane was added and a titration indicated that less than 5% of the *t*-butyllithium remained. The clear upper layer was decanted and, after removal of the solvent, fractionation gave 15.4 g. of unreacted di-*t*-butyldichlorosilane, a 72% recovery. Only 3.9 g. of a tarry high boiling residue remained.

Summary

1. The first tertiary alkylsilicon compound, *t*-butyltrichlorosilane (I) has been synthesized in good yield from *t*-butyllithium and silicon tetrachloride.

2. (I) has been found to react with an excess of methylmagnesium bromide to give *t*-butyltrimethylsilane.

3. The peroxide catalyzed chlorination of (I) with sulfuryl chloride proceeds smoothly to give chloro-*t*-butyltrichlorosilane. This latter compound undergoes a β-elimination reaction, evolving isobutylene, when treated with alkali.

4. At room temperature (I) does not react with *t*-butyllithium. At slightly higher temperatures a fair yield of di-*t*-butyldichlorosilane (II) was obtained. However, in an attempted reaction between (II) and *t*-butyllithium a third *t*-butyl group could not be introduced even under strenuous conditions.

STATE COLLEGE, PENNSYLVANIA

RECEIVED DECEMBER 22, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Dissociation of the Addition Compound of Trimethylboron with Quinuclidine; Further Evidence for the Steric Configuration of Triethylamine[1]

BY HERBERT C. BROWN[2] AND SEI SUJISHI[2,3]

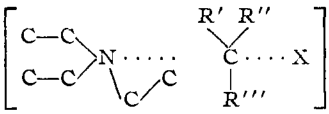
Despite the general similarity in structure, trimethylamine and triethylamine exhibit marked differences in their behavior. For example, in aqueous solution triethylamine is a considerably stronger base than trimethylamine.[4] Yet, in spite of its greater strength, triethylamine reacts at a considerably lower rate with alkyl halides[5] and forms a much less stable addition compound with trimethylboron.[6]

These differences in the behavior of the two amines have been attributed to the peculiar steric configuration of the triethylamine molecule.[7] The present investigation was undertaken to test the proposed explanation and to examine some of its consequences.

Discussion

It was originally proposed[7] that in triethylamine only two of the three ethyl groups can be removed to the "rear" of the nitrogen atom, away from the group adding or reacting at the vacant position of the nitrogen atom. For steric reasons the third ethyl group cannot be similarly accommodated, but is required to take up a position such that the group projects into the region usually assigned to the unshared electron pair (Fig. 1). With this arrangement, triethylamine resembles a typical hindered amine, such as 2-picoline (Fig. 2), much more closely than it does a relatively unhindered tertiary amine, such as trimethylamine (Fig. 3).

According to the interpretation advanced, formation of an addition compound by reaction of the amine with a bulky component, such as trimethylboron, introduces F-strain of high magnitude and leads to marked instability of the product (Fig. 4). Similarly, reaction of triethylamine with alkyl halides, particularly in cases where the steric requirements of the alkyl groups are large, should lead to an activated complex with large steric strains.



The rate of the reaction is thereby decreased relative to the corresponding reactions of less hindered amines. On the other hand, the ability of such hindered amines to react with aqueous acids is not noticeably affected because of the low steric requirements of the proton.

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(1) Acid–Base Studies in Gaseous Systems. V. Paper no. XIII in the series, Studies in Stereochemistry.

(2) Present address: Department of Chemistry, Purdue University.

(3) Ethyl Corporation Fellow at Wayne University, 1945–1947.

(4) Hall and Sprinkle, THIS JOURNAL, **54**, 3479 (1932), report values for the ionization constants of trimethyl- and triethylamine at 25° of 6.30×10^{-5} and 54.9×10^{-5}, respectively.

(5) For example, the reaction at 80° of trimethylamine with isopropyl iodide is 61 times faster than the corresponding reaction involving triethylamine; Perrin and Williams, *Proc. Roy. Soc.* (*London*), **A159**, 162 (1937).

(6) Brown, THIS JOURNAL, **67**, 1452 (1945).

(7) Brown and Taylor, *ibid.*, **69**, 1332 (1947).

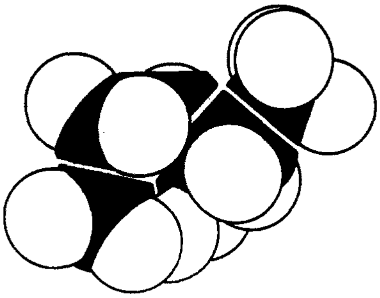


Fig. 1.—Molecular model of triethylamine.

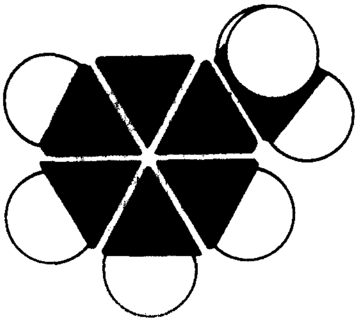


Fig. 2.—Molecular model of 2-picoline.

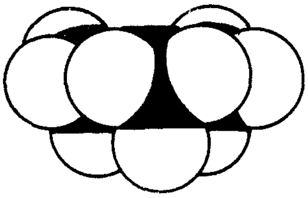


Fig. 3.—Molecular model of trimethylamine.

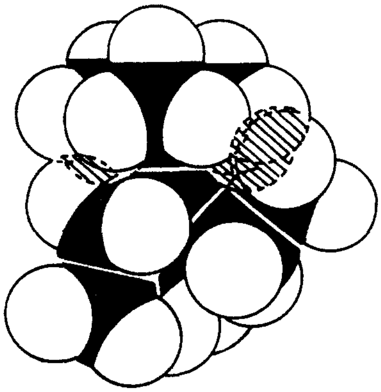


Fig. 4.—Molecular model of triethylamine-trimethylboron (cross-hatched area shows conflicting steric requirements).

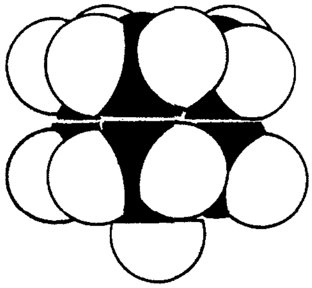
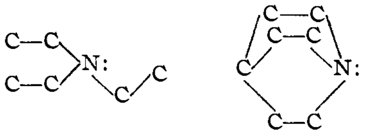
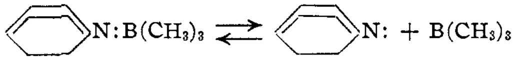


Fig. 5.—Molecular model of quinuclidine.

This interpretation suggests that removal of the ethyl group from its offending position should convert the triethylamine molecule from one which behaves as a sterically hindered amine into one which is sterically unhindered. The resulting base should not only form relatively stable addition compounds, but should be much more reactive toward alkyl halides than triethylamine itself. To test this conclusion, quinuclidine, a bicyclic analog of triethylamine, was synthesized, and its behavior compared with triethylamine (Figs. 1 and 5).



The present paper reports the results of an investigation of quinuclidine–trimethylboron in the vapor phase.[8]



The results of the dissociation study are summarized in Table I, along with previously obtained data for the dissociation of the corresponding addition compounds of trimethyl- and triethylamines.

The data clearly support the hypothesis advanced. Tying the third ethyl group to the other two groups in a position such that they cannot interfere with the approach to the nitrogen atom produces a tremendous change in the stability of the trimethylboron addition compound. Not only is the quinuclidine addition compound far more stable than that derived from triethylamine, but it is also markedly more stable than the corresponding trimethylamine compound.[9]

Results[10]

Quinuclidine was synthesized from 4-ethanolpyridine (from the Reilly Tar and Chemical Corporation) by a route adapted from that described

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[8] Comparison of the behavior of the two bases toward alkyl halides has been completed and will be reported shortly: Nelson R. Eldred, "The Relative Reactivity of Triethylamine and Quinuclidine towards Alkyl Iodides," M. S. Thesis, Wayne University, 1946.

[9] The increase in stability of the quinuclidine over the trimethylamine derivative may be in part ascribed to the increased inductive effect of the hydrocarbon portion of the cage amine and to the effect of the geometry of the cage in relaying the effect to the nitrogen atom. However, part of the effect may be due to a moderate decrease in F-strain in the addition compound resulting from the effect of the ring closure. Finally, there is the possibility that the cage may have a significant effect upon the magnitude of B-strain in the tertiary amine. However, detailed consideration of these points will be delayed until further investigations of the behavior of quinuclidine and related ring and cage amines have been completed.

[10] The experimental techniques have been described in earlier papers of this series: see especially, Brown, Taylor and Gerstein, THIS JOURNAL, **66**, 431 (1944).

TABLE I

SUMMARY OF DISSOCIATION DATA OF ADDITION COMPOUNDS OF TRIMETHYLBORON AND TERTIARY AMINES

Amine component	K_{100}	$\Delta F°_{100}$	ΔH	ΔS
Trimethylamine	0.472	557	17,620	45.7
Triethylamine[a]	Very large		(10,000)	
Quinuclidine	0.0196	2916	19,940	45.6

[a] Triethylamine–trimethylboron is too highly dissociated in the vapor phase to be studied by the present method. Within the limits of experimental error the vapor is dissociated 100% at all temperatures from 25 to 100°. The heat of dissociation has been estimated at 10 kcal.[7]

by Meisenheimer and his co-workers.[11] The base was introduced into the high vacuum apparatus and dried over a sodium mirror. The resulting product, a white crystalline solid, was tensiometrically homogeneous.

Quinuclidine is a representative of a group of highly symmetrical organic molecules such as hexamethylethane and bicyclo[2.2.2]octane, which melt at relatively high temperatures and possess boiling points in the neighborhood of their melting points. These substances are often reported to be exceedingly volatile and marked care is frequently urged in handling the compound even at room temperatures.[12]

It was therefore of interest to determine the sublimation pressures of quinuclidine. The results are listed in Table II and may be represented by the equation

$$\log P = -(2630/T) + 9.103$$

The heat of sublimation is 12.2 kcal., Trouton's constant is 28.8, and the extrapolated sublimation point is 150°.

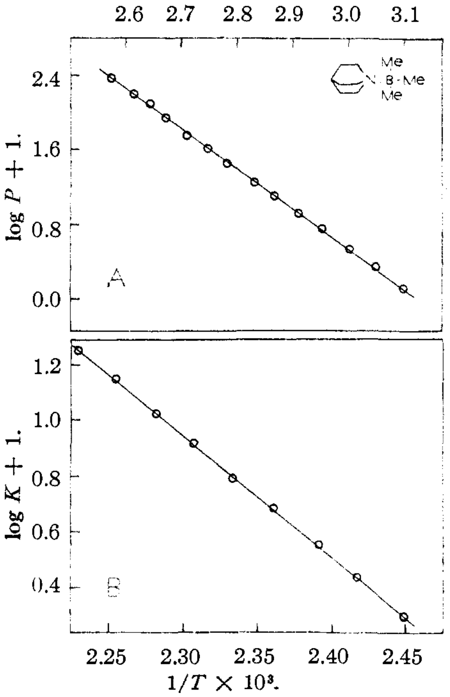

Fig. 6.—Quinuclidine–trimethylboron: A, saturation pressure data; B, dissociation data.

TABLE II

SUBLIMATION PRESSURES OF QUINUCLIDINE

Temp., °C.	0.0	9.1	20.5	29.9	39.9
Press., mm.	0.30	0.69	1.51	2.66	5.1
Temp., °C.	49.5	59.8	69.6	80.4	89.6
Press., mm.	9.1	16.1	26.7	44.8	68.0

It is evident that the high volatility frequently ascribed to quinuclidine (and, presumably, to similar substances) is not the result of an unusually high sublimation pressure at room temperature. Instead, it is more probable that the high volatility of these substances should be attributed to a relatively high rate of vaporization of the crystalline substance.

Quinuclidine was shown to combine with trimethylboron in a 1:1 ratio by treating a measured quantity of the base with an excess of the second component. The mixture was heated to 140° for a short period to ensure complete reaction, and then permitted to remain overnight at room temperature. The excess trimethylboron was recovered by distillation from the reaction mixture at −80°. The results showed that 0.421 millimole of quinuclidine combined with 0.421 millimole of trimethylboron. The product, quinuclidine–trimethylboron, was obtained as a white crystalline solid.

Saturation pressures for the addition compound were obtained from 0 to 115°. The values are listed in Table III and are represented graphically in Fig. 6-A. The data are represented by the equation

$$\log P = -(4155/T) + 12.015$$

The extrapolated sublimation point is 182°.

TABLE III

SATURATION PRESSURES OF QUINUCLIDINE–TRIMETHYLBORON

Temp., °C	45.4	59.2	70.5	80.1	91.0
Press., mm.	0.12	0.34	0.82	1.77	4.08
Temp., °C.	95.4	101.3	105.2	109.4	115.4
Press., mm.	5.7	8.8	12.5	15.4	23.0

The low volatility of the addition compound offered a number of difficulties. In order that van der Waals effects might not be so large as to affect the accuracy of the measurements, it was necessary to operate at much higher temperatures and with much smaller samples than customary. The small samples made it impractical to carry out the dissociation measurements by the usual procedure,[10] the "method of matched samples." Instead, a modification of this procedure, termed

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[11] Meisenheimer, Neresheimer and Schneider, *Ann.*, **420**, 190 (1920). See reference 8 for a complete description of the modified procedure.

[12] For example, Meisenheimer, *et al.*, state of quinuclidine: "It is extraordinarily volatile; the warmth of the hand alone will cause the sublimation of small amounts, which solidify in the cool part of the flask."

the "method of approximations," which had been developed previously for handling addition compounds of low volatility,[13] was utilized.

The results of a typical determination are given in Table IV and represented graphically in Fig. 6-B.

TABLE IV

DISSOCIATION DATA FOR QUINUCLIDINE–TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obsd.	Calcd.[a]	Degree of dissocn., α	Dissocn. constant, K (atm.)
135.2	35.08	18.454	0.9009	0.1988
140.5	35.96	18.694	.9236	.2745
145.0	36.64	18.816	.9390	.3592
150.1	37.34	19.127	.9522	.4775
155.1	37.97	19.353	.9620	.6197
160.3	38.60	19.588	.9706	.8263
165.1	39.14	19.805	.9763	1.049
170.2	39.71	20.036	.9819	1.403
175.2	40.23	20.262	.9855	1.784

[a] The pressure of quinuclidine–trimethylboron in the dissociation tensimeter was approximated to be 12.345 mm. (calculated to 0° as a perfect gas).

The values of the dissociation constants are reproduced by the equation

$$\log K_{P} = -(4360/T) + 9.975$$

The heat of dissociation is calculated to be 19.94 ± 1.0 kcal. and the value of the dissociation constant at 100° is 0.0196. At 100° the free energy of dissociation constant at 100° is 0.0196. At 100° the free energy of dissociation is 2.916 ± 0.05 kcal., and the entropy of dissociation is 45.6 ± 1.0 e. u. Several determinations yielded results which varied within the limits indicated.

The data clearly establish the high stability of the quinuclidine derivative relative to the triethylamine product.

Acknowledgment.—This investigation was made possible by Grants No. 710 and 776 from the Penrose Fund of the American Philosophical Society, and by the financial assistance afforded by two graduate fellowships supported by the Ethyl Corporation. This assistance is gratefully acknowledged.

Summary

1. Quinuclidine-trimethylboron has been prepared and characterized. The dissociation of the addition compound in the vapor phase has been studied, and the values of ΔH, $\Delta F^{\circ}_{100^{\circ}}$ and ΔS for the dissociation have been determined.

2. The addition compound is far more stable than the corresponding derivative formed by triethylamine. It is concluded that the results support the proposed steric configuration for triethylamine. Moreover, the results indicate that triethylamine should be considered a relatively hindered base with large steric requirements, while quinuclidine should be considered a relatively unhindered base with smaller steric requirements.

LAFAYETTE, INDIANA RECEIVED JANUARY 22, 1948

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[13] M. Gerstein, "The Dissociation of the Addition Compounds of Trimethylboron with Cyclic Imines," Ph.D. Dissertation, University of Chicago, 1945. In the method of matched samples the size of the sample of addition compound in the dissociation tensimeter is determined by combining carefully matched samples of each of the two components, measured as a gas. In the method of approximations the size of the sample of the addition compound in the tensimeter is not known. Instead, a small quantity of the carefully purified addition compound is introduced into the tensimeter and the pressures exhibited by the completely volatilized sample over a wide range of temperature are observed. The size of the sample is determined by utilizing the fact that for the relatively short temperature intervals under consideration, the heat of dissociation, ΔH, is constant. Thus, only the correct value of the sample size yields a linear relationship between log K and $1/T$ as required by the van't Hoff equation

$$\frac{\mathrm{d}\ln K}{\mathrm{d}\,1/T} = \frac{-\Delta H}{R}$$

A full description of the procedure will be published shortly.

[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES, A DIVISION OF SOCONY-VACUUM OIL COMPANY, INC., RESEARCH AND DEVELOPMENT DEPARTMENT]

Vapor Pressure Studies in the System, Aluminum Bromide–Hydrogen Bromide–Paraffin Hydrocarbon[1]

BY C. M. FONTANA AND R. J. HEROLD

In the recent literature pertaining to aluminum halide catalysis the hypothesis has frequently been put forward that the activity of these catalysts is due to the formation of the active complex "$HAlX_4$." Thomas[2] postulated the formation of the intermediate complex $HAlCl_4$, which was assumed to be highly reactive by virtue of its easily ionizable proton. Leighton and Heldman[3] and Heldman[4] have assumed the reaction of hydrogen bromide with aluminum bromide to form $HAlBr_4$ to be essentially complete in order to account for the kinetics of isomerization of normal butane in the presence of that catalyst system.

By analogy with the stability of such well known substances as the alkali metal halide–aluminum halide addition compounds[5] it might be expected that the corresponding acid, sometimes called "aluminic acid," should also be stable.

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[1] This work was part of a program of fundamental studies into the mechanism of Friedel–Crafts catalyzed reactions.

[2] C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, Chapter 4.

[3] P. A. Leighton and J. D. Heldman, THIS JOURNAL, **65**, 2276 (1943).

[4] J. D. Heldman, *ibid.*, **66**, 1786, 1789 (1944).

[5] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. V, Longmans, Green and Co., Ltd., New York, N. Y., 1929.