

Fig. 2.—Solvent salts: (A) sodium acetate; (B) ammonium acetate; (C) lithium nitrate.

in Fig. 2, where solubility isotherms at 40°, obtained by interpolation from the data of Davidson and his co-workers,¹ may be compared with the corresponding curve from the present work. Thus, for example, in a 1 molal solution of lithium nitrate the solubility of zinc acetate is only about 0.08 molal, whereas its solubility in 1 molal ammonium acetate solution amounts to 0.28 molal. At higher concentrations of solvent salt the difference becomes even more pronounced.

This rather large difference in solvent action lends support to the belief, mentioned above, that specific chemical interaction is involved in the behavior of zinc acetate toward the other acetates. It suggests that the action of lithium nitrate, on the other hand, may perhaps be at-

tributed largely to "salt effect." It does not seem possible at present, however, to subject such a conclusion to a quantitative theoretical test, and the possibility that specific chemical effects may be involved, even here, cannot be excluded.

A brief comment seems called for concerning the solubility of lithium nitrate. Davidson and Geer⁵ report the solubility of lithium nitrate at 30° to be 1.49 moles per 1000 g. of acetic acid. This would correspond to a value of *R* of about 8.2. It will be seen in Table II that three of the binary solutions used had values of *R* higher than 8.2, the highest being 10.51. These more concentrated solutions were prepared hot, the zinc acetate was added to the hot solution, and equilibrium was then approached from above 30°. It is possible that the solutions may have remained supersaturated with respect to lithium nitrate, but it seems more likely that the solubility of lithium nitrate is simply increased by the presence of zinc acetate in the solution. Similar mutual solvent action has been demonstrated in other cases.^{4,5}

Summary

1. The solubility of zinc acetate in solutions of lithium nitrate in acetic acid has been determined over a wide range of temperatures and concentrations, and has been found to increase with increasing concentrations of the latter salt.

2. Comparison with results of previous investigators using other solvent salts has been made. The solvent effect of lithium nitrate is found to be distinctly weaker than those of sodium and ammonium acetates on zinc acetate.

3. It is suggested that the solvent action of lithium nitrate may perhaps be attributed largely to salt effect.

(5) Davidson and Geer, *THIS JOURNAL*, **60**, 1211 (1938).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Studies in Stereochemistry. V. The Effect of F-Strain on the Relative Base Strengths of Ammonia and Trimethylamine¹

BY HERBERT C. BROWN

In previous articles of this series evidence has been advanced that steric strain is an important factor in the strength of generalized acids and bases.² It has recently been suggested that steric strain is of two kinds, "F-strain" and "B-strain".³ F-strain is that strain which is caused by steric interference of the atoms or groups which are attached to different atoms,

resulting in a force which tends to separate the two atoms. On the other hand, B-strain is that strain which is introduced into a molecule as a result of changes in the normal bond angles of an atom in a molecule, brought about by the steric requirements of bulky groups attached to that atom.

The need for both types of strain may be demonstrated by considering how each affects the strength of a base such as trimethylamine. In this base, the three methyl groups can easily satisfy their steric requirements by a slight spread-

(1) Presented before the Division of Organic Chemistry at the Cleveland meeting of the American Chemical Society, April 6, 1944.

(2) (a) Brown, Schlesinger and Cardon, *THIS JOURNAL*, **64**, 325 (1942); (b) Brown and Adams, *ibid.*, **64**, 2557 (1942).

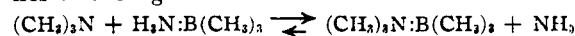
(3) Brown, Bartholomay and Taylor, *ibid.*, **66**, 435 (1944).

ing of the C-N-C bond angle to a value greater than the tetrahedral value. Addition of a fourth group (a proton, trimethylboron, or any generalized acid) to the free electron pair of the amine, forces the nitrogen atom toward a tetrahedral configuration and results in a reduction of the expanded angles. The methyl groups are, therefore, crowded toward each other, setting up a strain which increases the tendency toward dissociation of the addition compound and thereby reduces the measured strength of the base. Since the effect is independent of the steric requirements of the reference acid, B-strain results in a permanent decrease in the strength of trimethylamine and other tertiary amines.

On the other hand, F-strain is markedly dependent upon the steric requirements of the reference acid. Thus F-strain in the trimethylammonium ion, $(\text{CH}_3)_3\text{N}:\text{H}^+$ (the strain resulting from steric interference between the three methyl groups and the proton), is considerably less than the corresponding strain in the trimethylamine-trimethylboron molecule, $(\text{CH}_3)_3\text{N}:\text{B}(\text{CH}_3)_3$ (the strain in this case resulting from steric interference between the three methyl groups attached to nitrogen and the three attached to boron). Accordingly, the strength of trimethylamine relative to other bases with smaller steric requirements, such as ammonia, will vary with the steric requirements of the reference acids used. Thus, it will appear much weaker (relative to these other bases) if a comparatively bulky acid, such as trimethylboron, is used than if the reference acid is one with small steric requirements, such as the proton.

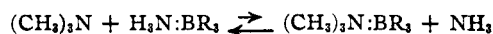
The present paper is the first of a series of studies of some of the more important consequences of the F- and B-strain hypothesis outlined above. It reports the results of an investigation of the effect of increasing F-strain on the relative base strength of ammonia and trimethylamine.

Trimethylamine is a stronger base than ammonia with trimethylboron as the reference acid.³ That is, in the following equation, the equilibrium lies to the right



In accordance with the steric strain hypothesis, as the methyl groups in the trimethylboron molecule are replaced by increasingly bulkier alkyl groups (as in triethyl-, trisopropyl- and tri-*t*-butylboron), F-strain becomes larger, thus increasing the dissociation of the amine addition compounds and diminishing the apparent strength of the amines. The greater steric requirements of the trimethylamine as compared to the ammonia molecule should cause a relatively greater decrease in the measured strength of the methylated base. A sufficiently large F-strain should then result in a reversal of the apparent strength of the two bases. That is to say, for a sufficiently bulky alkyl group R in the acid BR_3 , the equilib-

rium involving the two amines should be shifted to the left



To test this deduction of the effect of F-strain on the relative base strength of ammonia and trimethylamine, the addition compounds of these amines with trimethyl-, triethyl-, trisopropyl- and tri-*t*-butylboron were prepared and their relative stability determined.

Experimental Part

Apparatus.—The high vacuum apparatus used to prepare and handle the addition compounds is described in previous papers of this series.² Measurements of temperatures above 0° were made with thermometers calibrated to 0.1° and compared with Bureau of Standards thermometers. Below 0° the temperatures were measured with vapor tension thermometers. The pressures were measured with a student-type cathetometer (the only instrument available for the purpose), and these measurements are probably not accurate to more than 0.2 mm.

Preparation and Purification of Materials.—The preparation of the methylamines in pure form has been described previously.³

Trimethylboron was prepared by the action of magnesium bromide on boron trifluoride in *n*-butyl ether. This procedure offers many advantages over previously described methods for preparing trimethylboron in quantities of more than a few grams. A representative preparation follows.

In a 1-liter three-necked flask, fitted by means of ground glass joints to a mercury-sealed stirrer, a reflux condenser, and a dropping funnel containing an opening for introducing nitrogen, were placed 72 g. (3.0 gram atoms) of magnesium turnings and 250 cc. of dry *n*-butyl ether. A solution was prepared of 285 g. (3.0 moles) of methyl bromide (from a tank) in 500 cc. of *n*-butyl ether at 0°, and this solution was added slowly with stirring to the magnesium in the flask. The initial reaction was quite vigorous. The flask was then immersed in a cooling bath of cold water and the rate of addition of the methyl bromide solution adjusted so that the temperature of the reaction mixture did not rise above 50°. The formation of the Grignard reagent required six hours. Two traps, equipped with stopcocks, were then connected to the condenser in series by means of ground glass joints and the entire apparatus was thoroughly flushed out with nitrogen introduced through the opening in the dropping funnel. A slow stream of the gas was maintained throughout the remainder of the reaction. The two traps were then immersed in Dry Ice baths. Meanwhile a solution of 61 g. (0.9 mole) of boron trifluoride in 400 cc. of *n*-butyl ether was prepared and this solution was then added to the Grignard reagent over a period of four hours. The flask was then heated at 70° for two hours to complete the reaction and to distill the residual trimethylboron out of the reaction mixture and into the traps. The stopcocks on the traps were then closed. Practically the entire yield of trimethylboron was in the first trap. The crude product thus obtained weighed 44 g. (70 cc. at -80°), a yield of 87% of that calculated.⁴

The trimethylboron was introduced into the high vacuum apparatus in portions of approximately 10-20 cc. and sealed in glass tubes containing a slight excess (calculated on a molar basis) of triethylamine. Trimethylboron forms an addition compound with triethylamine from which the volatile boron compound may easily be recovered. The procedure described thus offers a convenient way of storing appreciable quantities of trimethylboron in small glass tubes at below atmospheric pressures.

The purification of trimethylboron is carried out with

(4) Although less desirable, it is possible to carry out the preparation with simpler equipment, using rubber tubing and stoppers to connect the different parts of the apparatus.

the aid of the addition compound by taking advantage of the fact that the addition compound is a stable non-volatile solid at -80° , but is largely dissociated into its components at room temperature. The procedure consists of distilling all volatile impurities from the solid addition compound at -80° . The purified addition compound is then permitted to attain room temperature and the trimethylboron is separated from the amine by a rapid distillation through a U-tube at -80° . A single distillation leads to the recovery of only part of the trimethylboron, but nearly all of the trimethylboron can be obtained by repeating the process several times. Distillation of the trimethylboron thus obtained through a U-tube at -120° (partially solid diethyl ether bath) yields an exceedingly pure product.⁵

Triethylboron was prepared in a similar manner by the action of boron trifluoride in *n*-butyl ether on ethylmagnesium bromide in *n*-butyl ether. The quantities of the reagents used were the same as in the above preparation of trimethylboron. When the reaction was over, the condenser was replaced by a ground-glass stopper and the mercury-sealed stirrer by a short fractionation column, the changes being made quickly in a rapid stream of nitrogen to avoid exposure of the reaction mixture to the atmosphere. The triethylboron was then distilled directly out of the reaction mixture; the fraction which distilled at $94-97^{\circ}$ was collected. The yield of crude triethylboron was 65 g., 74% of the calculated value.

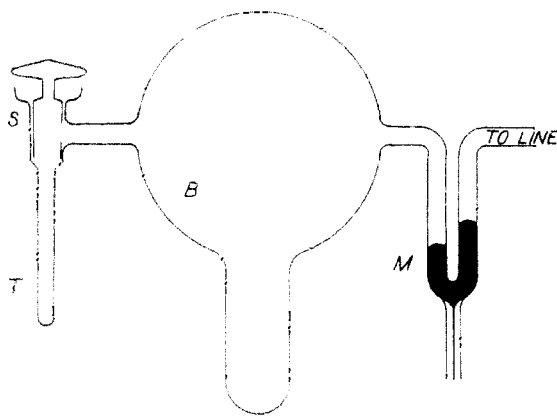


Fig. 1.

The purification of the triethylboron was carried out by means of its ammonia addition compound as follows. Approximately 5 g. of triethylboron was distilled into an evacuated flask and treated with a slight excess of ammonia. The ammonia was absorbed with considerable liberation of heat to form an addition compound of low volatility. This compound was purified by distillation in the high vacuum apparatus. It was trapped at 0° and the fore and hind fractions—approximately 10% of the whole—were discarded. The remaining material was distilled into a flask where it was treated with a slight deficiency of dry hydrogen chloride. The triethylboron set free was distilled out of the flask and subjected to a further distillation, trapping the substance at -40° and discarding the fore and hind fractions. The vapor pressure at 0° was 12.4 mm.⁶

Triisopropylboron and tri-*t*-butylboron were prepared in yields of 60-65% by the action of ethyl ether-boron trifluoride on the corresponding alkylmagnesium chloride in ethyl ether.⁷ The compounds were purified by distillation under reduced pressure through a short column attached to the high vacuum apparatus. Triisopropylboron melts at -54 to -53° . Tri-*t*-butylboron is liquid at

-80° and solidifies to a glass in liquid nitrogen. The vapor pressures at 50.0° are 25.8 mm. and 3.5 mm. for triisopropylboron and tri-*t*-butylboron, respectively.

Comparison of Base Strength.—The relative strengths of two amines were compared by competition of the amines for the reference acid: $B:A + B' = B':A + B$. Equimolar quantities (1-2 millimoles) of each of the amines under study and of the reference acid were placed in a small vessel (100-cc. capacity) and left at 0° for two to four hours. (Test experiments showed that it required but a few minutes for equilibrium to be reached.) The vessel was then opened to the vacuum apparatus and the volatile amine distilled out of the tube (maintained at 0°) away from the slightly volatile mixture of addition compounds, through a U-tube at -80° (to remove traces of the addition compound which may have distilled), and into a calibrated bulb. The gas volume of the mixture of the two amines was measured and the average molecular weight determined. In this way the composition of the uncombined amine could be fixed to 1-2% and the relative strength of the two amines established.

A source of uncertainty in this simple procedure lies in the possibility that the equilibrium in the reaction tube shifts as two amines of different volatility are distilled away for analysis. To avoid this difficulty, the apparatus shown in Fig. 1 was constructed. The volume of the bulb B was 1 liter, and that of the tube T, 20 cc. The two amines and the trialkylboron were condensed in the lower part of the tube T which was then immersed in an ice-bath while the stopcock S remained closed until the addition compound had been formed and equilibrium approached (two to four hours). The stopcock was then opened and the amine allowed to expand into the bulb. Twenty-four hours were allowed for equilibrium to be reached, which was facilitated by the low pressure (15-20 mm.). The stopcock was then closed and the amine thus cut off in the flask was removed through M for analysis. The results obtained by this procedure did not differ appreciably from those obtained by the simpler method first described, so that in subsequent studies the latter was utilized.

The conclusions thus reached as to the relative strength of two amines with a given reference acid may be further tested by comparing the saturation pressures of the individual addition compounds formed by the two amines with that reference acid. From previous studies it appears that of two related addition compounds of approximately equal molecular weight, the less stable will exhibit the higher saturation pressure. Where the two methods mentioned yield identical information as to the strength of two amines, it is probably safe to conclude that the result may be accepted without undue reservation.

Results

Trimethylboron as the Reference Acid.—Study of the dissociation of ammonia-trimethylboron and trimethylamine-trimethylboron in the gas phase has established that trimethylamine is a considerably stronger base than ammonia with this reference acid.³ It was desirable, however, to compare this conclusion with the result obtained by use of the competition method. In the vessel were placed 31.8 cc. each of trimethylboron, ammonia and trimethylamine. The uncombined amine recovered by distillation measured 31.7 cc. The molecular weight of the mixture was found to be 23.4, indicating a composition of 85% ammonia and 15% trimethylamine. The value predicted from the dissociation data is 89% ammonia and 11% trimethylamine.

These values were calculated from the expression

$$\frac{[\text{NH}_3][(\text{CH}_3)_3\text{B}(\text{CH}_3)_3]}{[(\text{CH}_3)_3\text{BN}][\text{NH}_3\text{B}(\text{CH}_3)_3]} = \frac{K_{\text{NH}_3}}{K_{\text{N(CH}_3)_3}} = 67$$

⁵ The preliminary development of this method of purifying triethylboron is due to Dr. Moddie D. Taylor.

⁶ Compare Stock and Zeidler, *Ber.*, **54**, 531 (1921).

⁷ Kraus and Naldu, *ibid.*, **64**, 2422 (1931).

The ratio $K_{\text{NH}_3}/K_{\text{N}(\text{CH}_3)_3}$ was estimated on the assumption that the equations representing the change of K_p with temperature⁸ could be extrapolated to 0° and the ratio of the two dissociation constants would not be greatly altered by the change of the addition compounds from the gaseous to the solid state. In view of the approximations thus introduced, no great importance can be given to the value obtained for $K_{\text{NH}_3}/K_{\text{N}(\text{CH}_3)_3}$ and to the good agreement of the experimentally determined composition of the uncombined amine with the calculated value. It is of interest, however, that the competition method yields results of the order of magnitude to be expected.

Triethylboron as the Reference Acid.—**Ammonia-triethylboron**, $\text{H}_3\text{N}:\text{B}(\text{C}_2\text{H}_5)_3$, was prepared by Frankland,⁸ who described it as a somewhat oily liquid with an aromatic odor and an alkaline reaction. No physical constants were reported. In the present study the addition compound was prepared by treating triethylboron with an excess of ammonia, the excess being removed by distillation from the reaction product at 0°. In this way 224 cc. of triethylboron absorbed 225 cc. of ammonia to form a slightly volatile liquid, which solidified at low temperature to a white crystalline solid, melting from -11 to -10°. Saturation pressures were studied from 0 to 80°; the data may be represented by the equation

$$\log P = -(3094/T) + 10.538$$

with an average deviation of 0.2 mm. The extrapolated "boiling point" is 131°.

The preparation of **trimethylamine-triethylboron** has not been reported previously. Triethylboron, 165 cc., was treated with an excess of trimethylamine at 0° and the excess removed by distillation from the reaction mixture at -20°. Exactly 165 cc. of the amine was absorbed, indicating that the addition compound has the expected composition, $(\text{CH}_3)_3\text{N}:\text{B}(\text{C}_2\text{H}_5)_3$. At -80° the substance solidified to white crystals which melted at -46 to -45°. The compound is considerably more volatile than the corresponding ammonia derivative. The saturation pressures were measured from 0 to 50°; the data may be represented by the equation

$$\log P = -(3164/T) + 11.698$$

with an average deviation of 0.2 mm. The extrapolated "boiling point" is 86°.

The comparison of the base strength of the two amines was carried out in the usual manner using 28.1 cc. each of ammonia, trimethylamine and triethylboron. The uncombined amine, 27.4 cc., had a molecular weight of 55.1, indicating a composition of 91% trimethylamine and 9% ammonia.

Triisopropylboron as the Reference Acid.—**Ammonia-triisopropylboron**⁹ was prepared by

(8) Frankland, *Ann.*, **124**, 129 (1852).

(9) Krause and Nobbe, *Ber.*, **64**, 2112 (1931), report that triisopropylboron and tri-*t*-butylboron react with ammonia to form ammonia(es) which readily lose ammonia. No other descriptive data are given.

combining equal volumes of the two components. The compound solidified at -80° and melted at -27 to -26°. Saturation pressures for the addition compound were measured from 0 to 65°. The observed pressure is 0.4 mm. at 0° and 2.3 mm. at 25°. Above 30° the data are represented by the equation

$$\log P = -(3040/T) + 10.518$$

with an average deviation of 0.3 mm. The extrapolated "boiling point" is 125°.

Trimethylamine and triisopropylboron do not combine at temperatures as low as -80°. An equimolar mixture of the two components was liquid at -80°, and exerted a pressure at that temperature of 4 mm. A partial pressure of this magnitude is to be expected from a solution consisting of mole fractions of 0.5 trimethylamine and 0.5 inert solvent of negligible volatility. Moreover, the trimethylamine could be recovered by distillation out of the mixture maintained at -80°, and at 0° the pressure of trimethylamine above the triisopropylboron corresponded to complete dissociation.

From equimolar samples (13.1 cc.) of ammonia, trimethylamine and triisopropylboron was obtained a mixture of amines (12.7 cc.) which analyzed for 96% trimethylamine and 4% ammonia.

Tri-*t*-butylboron as the Reference Acid.—**Ammonia-tri-*t*-butylboron** was prepared by combining equimolar quantities of the base with tri-*t*-butylboron.¹⁰ The compound was liquid at 0° and solidified to a glass at -80°. The saturation pressures of this compound are considerably higher than those of the compounds previously described, and exhibit a dependence upon the proportion of the substance which is in the vapor phase, decreasing with increasing proportion of the compound vaporized. This inconstancy of the saturation pressures has not been observed previously in our studies and is probably to be ascribed to the high dissociation pressure of the complex as compared to the low volatility of the acidic component. (In all of the cases previously studied, the pressures exerted by the addition compound were considerably less than the vapor tensions of the less volatile component.) Observed pressures for ammonia-tri-*t*-butylboron are 1.5, 13.3 and 35.1 mm. at 0, 25.0 and 40.0°, respectively. (The measurements were made under conditions such that the observed pressure accounted for less than 10% of the amine present. Under these conditions, the observed pressures at a given temperature are easily reproducible and are probably close approximations of the maximum values possible.)

Trimethylamine and tri-*t*-butylboron do not combine. At -80° an equimolar mixture of the

(10) The low volatility of tri-*t*-butylboron made it more convenient to weigh out samples of the substance than to measure it as a gas. These samples were introduced into the vacuum apparatus and handled in the usual manner.

two components exhibits a pressure of 4 mm.; at 0° the pressure corresponds to complete dissociation.

Competition reactions were run between ammonia and trimethylamine with tri-*t*-butylboron as the reference acid. From 56.4 cc. of ammonia, trimethylamine and the boron acid was obtained 53.2 cc. of amine which analyzed for 98% trimethylamine. It should be pointed out that in these last experiments involving triisopropylboron and tri-*t*-butylboron, the quantitative recovery of excess amine is a slow process—apparently the addition compounds formed have a marked affinity for excess amine.

Discussion

The data on the relative strength of the bases ammonia and trimethylamine are summarized in Table I. The letters W and S are used to indicate the weaker and stronger of the two amines. The first of the two figures in the parentheses following each letter gives the mole fraction of the amine which combined with the reference acid; the second gives the saturation pressure of the addition compound at 25° in mm. It should be noted that the order of base strength established by the competition experiments is fully confirmed by the saturation pressure data.

TABLE I

RELATIVE BASE STRENGTH OF AMMONIA AND TRIMETHYLAMINE

Reference acid	Ammonia	Trimethylamine
Trimethylboron	W (0.15, 6.4)	S (0.85, 2.1)
Triethylboron	S (.91, 1.4)	W (.09, 12.1)
Triisopropylboron	S (.96, 2.3)	W (.04, N. C. ^a)
Tri- <i>t</i> -butylboron	S (.98, 13.3)	W (.02, N. C. ^a)

^a No compound formed.

It is evident that the order of base strength observed with the reference acid trimethylboron, $\text{NH}_3 < (\text{CH}_3)_3\text{N}$, is reversed with triethylboron. Moreover, trimethylamine exhibits no basic

properties with the highly hindered acids, triisopropyl- and tri-*t*-butylboron. The predictions of the steric strain hypothesis on the effect of F-strain on the relative strength of ammonia and trimethylamine are thus in complete accord with experiment.

Before closing, one further point may be mentioned. There has been considerable discussion as to whether a monotonic series of generalized acids and bases exists.¹¹ The present investigation offers a clear-cut illustration of the dependence of base strength upon the reference acid and supports the viewpoint that such a monotonic series cannot be set up.¹²

Acknowledgment.—The purchase and construction of the apparatus used in this investigation was made possible by a grant from the Penrose Fund of the American Philosophical Society. This assistance is gratefully acknowledged.

Summary

1. The relative strength of the bases ammonia and trimethylamine was determined using trimethyl-, triethyl-, triisopropyl- and tri-*t*-butylboron as the reference acids.

2. The order $\text{NH}_3 < \text{N}(\text{CH}_3)_3$, observed with the hydrogen acids and with trimethylboron, is reversed with triethylboron and the more hindered acids. These observations are in accord with the predicted effect of F-strain on the relative strength of the two bases.

3. In the course of this study improved procedures for the preparation and purification of trimethylboron and triethylboron were developed; and saturation pressures were measured for the addition compounds of triethyl-, triisopropyl-, and tri-*t*-butylboron with ammonia and trimethylamine.

(11) Luder, *Chem. Rev.*, **27**, 547 (1940).

(12) Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Studies in Stereochemistry. VI. The Effect of F-Strain on the Relative Base Strengths of Ammonia and the Methylamines

BY HERBERT C. BROWN

In the absence of steric complications, the strength of ammonia and the methylamines should increase regularly with the number of methyl groups as a result of the inductive effect (+I) of alkyl groups. However, this predicted order, $\text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N}$ (Fig. 1, curve A), is not observed. B-Strain¹ slightly reduces the strength of dimethylamine and markedly reduces the strength of trimethylamine, so that the order of base strength estab-

lished by acids with a comparatively low F-strain factor is that represented by curve B, $\text{NH}_3 < (\text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}$.

It is the object of the present investigation to examine the effect of F-strain on the order shown by these amines. The order represented by curve B is observed both with hydrogen ion and with trimethylboron as the reference acid.¹ Replacement of the methyl groups in trimethylboron by larger, bulkier alkyl groups should lead to an increase in F-strain and thus result in a decrease in the apparent strength of the bases. The higher

(1) Brown, Bartholomay and Taylor, *This Journal*, **66**, 435 (1944).