

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Studies in Stereochemistry. VIII. The Effect of F-Strain on the Relative Base Strengths of the Isopropyl- and *t*-Butylamines

BY HERBERT C. BROWN AND HOWARD PEARSALL

In previous papers of this series the effect of F-strain upon the sequence of base strengths shown by the methylamines¹ and by the ethylamines² has been described. In order further to test the hypothesis advanced, the investigation has been extended to include amines with bulkier alkyl groups, the isopropylamines and the *t*-butylamines. The results of this study are reported in the present paper.

Results

Isopropylamine-trimethylboron, $i\text{-C}_3\text{H}_7\text{NH}_2\cdot\text{B}(\text{CH}_3)_3$, was prepared by treating 22.4 cc. of the amine with 22.4 cc. of trimethylboron at -80° . The two components reacted readily to produce a white solid which melted sharply at 8.0 to 8.5° . The product was purified by sublimation from a U-tube maintained at 5° to another maintained at -15° . Saturation pressure measurements were made at a series of temperatures; representative values between 0 and 60° are listed in Table I.

It is significant that the values of the saturation pressure for the isopropylamine derivative are much higher than those previously reported for the corresponding derivative of ethylamine:² 1.0 and 6.5 mm. at 25 and 50° , respectively, for the latter, compared with 2.1 and 13.4 mm. at the same temperatures for the isopropyl derivative. Previous studies have shown that of two addition compounds of closely similar structure and molecular weight, the less stable exhibits the higher saturation pressure. It is therefore evident that isopropylamine is a weaker base than ethylamine with trimethylboron as the reference acid.

Diisopropylamine-trimethylboron, $(i\text{-C}_3\text{H}_7)_2\text{NH}\cdot\text{B}(\text{CH}_3)_3$, could not be synthesized by simply combining equimolar quantities of diisopropylamine and trimethylboron at -80° . At this temperature the product was solid and apparently trapped some unreacted diisopropylamine, leaving uncombined appreciable quantities of trimethylboron. Because of the marked instability of the addition compound at higher temperatures, it was deemed inadvisable to attempt to demonstrate the formation of a 1:1 addition compound above -80° . The difficulty was overcome by treating the diisopropylamine for several hours at -80° with an excess of trimethylboron sufficient to maintain a liquid phase which remained in intimate contact with the solid addition compound and, presumably, with the diisopropylamine which had previously escaped

reaction. In this way, 12.3 cc. of diisopropylamine was treated with a total of 25.5 cc. of trimethylboron; from the reaction mixture, 12.9 cc. of trimethylboron was recovered, demonstrating the existence of a 1:1 addition compound at -80° .

The product prepared in this way was highly unstable with respect to dissociation into its components. Not only did it melt over a considerable range, -28 to -24° , indicating marked dissociation at the melting point, but the saturation pressures exhibited by the compound were very high, 53 mm. at -20° and 165 mm. at 0° . At room temperature the compound was completely dissociated. Comparison of the relative values of the dissociation pressures leads to the conclusion that with trimethylboron as the reference acid, diisopropylamine is a far weaker base than either isopropylamine or ammonia, and is but slightly stronger than triethylamine.²

Since from these results there was little reason to doubt that triisopropylamine³ would not form an addition compound with trimethylboron, no attempt was made to include this tertiary amine in the investigation. However, it did appear desirable to compare the behavior of di-*n*-propylamine with that of its branched-chain isomer. Accordingly, the addition compound of di-*n*-propylamine and trimethylboron was synthesized and studied.

Di-*n*-propylamine-trimethylboron, $(n\text{-C}_3\text{H}_7)_2\text{NH}\cdot\text{B}(\text{CH}_3)_3$, was prepared by treating 10.2 cc. of di-*n*-propylamine with 10.2 cc. of trimethylboron at 0° . The two components combined to form a solid addition compound of low volatility. The crystals melted at 6.0 to 6.4° . Saturation pressure measurements were made from 0 to 80° ; representative values are listed in Table I. From this it is evident that di-*n*-propylamine forms a far more stable addition compound than does diisopropylamine. This marked difference in the behavior of the two isomers is in complete agreement with prediction based upon the F-strain hypothesis. Molecular models show that the steric strain introduced by the normal propyl group should not be significantly different than that introduced by the ethyl group. On the other hand, the bulkier isopropyl group requires considerably more space around the nitrogen atom and should, for that reason, be more effective in causing F-strain with a given reference acid.

***t*-Butylamine-trimethylboron**, $t\text{-C}_4\text{H}_9\text{NH}_2\cdot\text{B}(\text{CH}_3)_3$, was prepared by combining equimolar quantities, 24.6 cc. of the two components at 0° .

(1) Brown, *THIS JOURNAL*, **67**, 374, 378 (1945).(2) Brown, *ibid.*, **67**, 1452 (1945).(3) Reported to be formed in the reduction of acetone oxime: Sabatier and Mailhe, *Ann. chim. phys.*, [8] **16**, 104 (1909).

The product was a solid which melted from 18.5 to 19.5°. Purity of the product was established by the constancy of the observed saturation pressure at 0° as small portions of the compound were sublimed away. Representative values of the saturation pressures, listed in Table I, are considerably higher than the corresponding values for isopropylamine-trimethylboron. Indeed, the saturation pressure values are even higher than those previously reported for ammonia-trimethylboron: 14.5 and 80.1 mm. at 25 and 50° for the former, compared with the values, 7.0 and 44.7 mm. at the same temperatures, for the corresponding ammonia derivative. Thus, with trimethylboron as the reference acid, the strength of *t*-butylamine as a base is not only markedly below that of isopropylamine, but is even below that of ammonia itself.

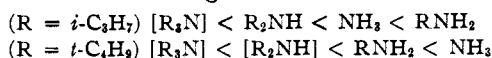
The high instability of the diisopropylamine addition compound, in conjunction with the great decrease in the stability of *t*-butylamine-trimethylboron as compared with the corresponding isopropylamine derivative, gave little reason to doubt the conclusion that di-*t*-butylamine⁴ would not combine with trimethylboron. For that reason, no attempt was made to include either this amine or the hitherto unreported tri-*t*-butylamine in the investigation.

TABLE I

SUMMARY OF SATURATION PRESSURE DATA IN MM.						
Compound	-20°	0.0°	25.0°	40.0°	50.0°	60.0°
NH ₃ :B(CH ₃) ₃ ^a		0.95	7.0	22.1	44.7	86.5
<i>i</i> -C ₃ H ₇ NH ₂ :B(CH ₃) ₃		0.26	2.1	6.6	13.4	26.0
(<i>i</i> -C ₃ H ₇) ₂ NH:B(CH ₃) ₃	53	>165	>700			
(<i>n</i> -C ₄ H ₉)NH ₂ :B(CH ₃) ₃		0.1	1.3	4.8	10.4	21.1
<i>t</i> -C ₄ H ₉ NH ₂ :B(CH ₃) ₃		1.3	14.5	41.0	80.1	

^a Calculated from equation given by Brown, Bartholomay and Taylor, *THIS JOURNAL*, **66**, 435 (1944). Included to facilitate comparison.

Summing up, it is apparent that with trimethylboron as the reference acid the isopropylamines and the *t*-butylamines show the following sequences of base strength



Discussion

Consideration of the polar effect of alkyl groups leads to the conclusion that the base strength of the aliphatic amines should increase with the number of alkyl groups (order A, Table II). Actually, in aqueous solution (that is, with the proton as the reference acid) an increase in strength is noted in going from ammonia to the aliphatic primary amines, a further increase is noted in the corresponding secondary amines, followed by a sharp decrease in the tertiary bases (order B, Table II). This surprising behavior has been ascribed to a steric effect (B-strain) of the three alkyl groups.⁵

(4) Klages, Nober, Kircher and Bock, *Ann.*, **547**, 1 (1941).

(5) Brown, Bartholomay and Taylor, *THIS JOURNAL*, **66**, 435 (1944).

TABLE II
EFFECT OF STERIC STRAIN UPON SEQUENCE OF BASE STRENGTH OF ALIPHATIC AMINES

Steric Strain Increasing ↓	Order	Relative strength
	A	NH ₃ < RNH ₂ < R ₂ NH < R ₃ N
B	NH ₃ < R ₃ N < RNH ₂ < R ₂ NH	
C	R ₃ N < NH ₃ < RNH ₂ < R ₂ NH	
D	R ₃ N < NH ₃ < R ₂ NH < RNH ₂	
E	R ₃ N < R ₂ NH < NH ₃ < RNH ₂	
F	R ₃ N < R ₂ NH < RNH ₂ < NH ₃	

Increasing F-strain should cause the observed sequence to shift from order B to orders C, D, E and F successively (Table II). The effect of increasing F-strain might be observed in two ways, either by operating with a given series of amines, *e. g.*, the methylamines, and successively using more and more bulky reference acids, or by maintaining the reference acid constant and successively substituting more and more bulky alkyl groups in the amines.

The first of these procedures was previously applied to the methylamines¹ and to the ethylamines.² In the case of the former, order B, observed with trimethylboron as the reference acid, shifts to order E with the more hindered reference acid, tri-*t*-butylboron. Similarly, the ethylamines yield order D with trimethylboron and order F with tri-*t*-butylboron.

The effect of steric strain, which is gradually increased by the second procedure, may now be noted. Thus, with trimethylboron as the reference acid, the methylamines yield order B, the ethylamines yield order D, the isopropylamines yield order E, and the *t*-butylamines yield order F (Table III).

TABLE III

SEQUENCES SHOWN BY AMINE SERIES WITH VARIOUS REFERENCE ACIDS

Amine series	H ⁺	Reference acid (CH ₃) ₃ B	Reference acid (<i>t</i> -C ₄ H ₉) ₃ B
Methyl	B	B	E
Ethyl	B	D	F
Isopropyl	B	E	
<i>t</i> -Butyl	B (?) ^a	F	

^a The strength of di-*t*-butylamine has not yet been determined. In this compound the large B-strain might be sufficient to reduce the strength of the amine to a point below that of the corresponding primary amine. The *t*-butylamines would then follow order D with the proton as the reference acid. This interesting problem is now under investigation.

From the relative stability of the addition compounds of the ethyl-, isopropyl- and *t*-butylamines, it is possible to draw some interesting deductions as to the preferred configurations of the free amines. However, discussion of this problem will be deferred until it becomes possible to report precise dissociation data⁶ for these substances.

Experimental

The preparation and purification of trimethylboron and

(6) Brown, Taylor and Gerstein, *ibid.*, **66**, 431 (1944).

the experimental techniques are described in previous publications in this series.

Isopropylamine (Eastman Kodak Company) was dried over anhydrous barium oxide for several days. It was then distilled over sodium and a middle fraction which boiled at 31.4° at 750 mm. was collected. This sample was introduced into the high vacuum apparatus and re-treated with sodium. The purified amine exhibited a constant vapor pressure of 194 mm. at 0°.

Diisopropylamine and **di-*n*-propylamine** were commercial samples obtained from Sharples Chemicals, Inc. The amines were treated with lead-sodium alloy for several days and then were distilled through a small column (15 plates) over sodium. Middle fractions which distilled at 82.6° at 750 mm. for diisopropylamine (n_{20}^D 1.3922) and 108.6° at 747 mm. for di-*n*-propylamine (n_{20}^D 1.4041) were collected and used. Diisopropylamine exhibited a vapor pressure of 23.5 mm. at 0°; di-*n*-propylamine, a pressure of 6.5 mm. at the same temperature.

***t*-Butylamine** was prepared by a Hofmann rearrangement of trimethylacetamide, prepared by standard procedures. The hydrochloride of the amine was recrystallized several times from absolute alcohol and the free amine then generated from the hydrochloride with potassium hydroxide and collected directly in the high vacuum apparatus. The amine was then treated with sodium to remove traces of water and fractionated in the high vacuum apparatus, discarding the first and last fractions. The product thus obtained exhibited a constant vapor pressure of 117 mm. at 0°.

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Summary

1. With trimethylboron as the reference acid, the sequence of base strength of the isopropylamines is $[(i-C_3H_7)_3N] < (i-C_3H_7)_2NH < NH_3 < i-C_3H_7NH_2$.

2. With the same reference acid, the sequence of base strength of the *t*-butylamines is $[(t-C_4H_9)_3N] < [(t-C_4H_9)_2NH] < t-C_4H_9NH_2 < NH_3$.

3. Diisopropylamine forms a highly unstable addition compound with trimethylboron; di-*n*-propylamine, a much stabler derivative.

4. The sequences observed and the relative stabilities of the addition compounds of the two isomeric dipropylamines are in excellent agreement with the predicted effect of F-strain on the behavior of the bases.

5. In the course of the investigation, the new addition compounds isopropylamine-trimethylboron, diisopropylamine-trimethylboron, di-*n*-propylamine-trimethylboron, and *t*-butylamine-trimethylboron were prepared and characterized.

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4-Allylthiosemicarbazide Derivatives and Some of their Analytical Properties¹

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Several compounds containing the 4-allylthiosemicarbazide grouping have been reported useful as organic precipitating agents.^{2,3} Compounds containing similar structures, such as allylthio-urea,⁴ thiosemicarbazide,⁵ and diphenylthiocarbazone,⁶ have been recommended as organic precipitating agents for certain metallic ions.

We have now prepared the allylthiosemicarbazones of some six hydroxy and methoxy benzaldehydes and have tested their usefulness as precipitants for the metallic ions of qualitative analysis. The properties of these new substances and their analytical behavior are listed in the table.

The carbazones were prepared by refluxing for about thirty minutes in ethanol a solution of equivalent molecular quantities of 4-allylthiosemicarbazide and the aldehyde. Upon cooling, minute white crystals were obtained (yellow crys-

tals with isatin) which were recrystallized from ethanol.

The carbazones were tested by adding 2–4 drops of an aqueous alcoholic solution to 3 ml. of a 0.1 *N* solution of the ions. Those ions which showed promise of giving a precipitate were then tested more fully, following the same procedure, in solutions of progressively increasing dilution.

4-Allylthiosemicarbazone of *p*-hydroxybenzaldehyde as a precipitating agent for Bi⁺⁺⁺ was the most promising. A comparison with sodium stannite gave the following results, respectively, at different concentrations of Bi⁺⁺⁺; at 10 to 0.1 g./liter a bright red *versus* a black precipitate; at 0.01 g./liter a slightly red *versus* a very slightly black precipitate, while at a ten times greater dilution neither reagent gave any precipitate. It would appear, therefore, that this carbazone can be used advantageously as a qualitative precipitant for bismuth. Its brilliant red color is very distinctive and it is sensitive enough for use in most qualitative procedures of analysis, being equal to the sensitivity of the test using sodium stannite. The use of the organic reagent eliminates the necessity of preparing fresh sodium stannite as usually required.

(1) Abstracted from a thesis submitted by Marvin A. McCall to the Graduate School of The University of Georgia in partial fulfillment of the requirements for the degree of Master of Science.

(2) Scott and Adams, *THIS JOURNAL*, **57**, 541 (1935).

(3) Scott and Andrews, *ibid.*, **64**, 2873–2874 (1942).

(4) C. J. van Nieuwenburg, "Tables of Reagents for Inorganic Analysis," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1938.

(5) Ibert Mellan, "Organic Reagents in Inorganic Analysis," The Blakiston Co., Philadelphia, Pa., 1941.