Experimental Part

n-Butyldimethylamine.—N,N-Dimethylbutyramide b.p. 185–189°, was prepared in 84% yield by adding an excess of gaseous dimethylamine to a solution of 134 g. of butyryl chloride[8] in 200 cc. of ether. A solution of 117 g. of this amide in an equal volume of ether was added during two hours to a stirred solution of 38 g. of lithium aluminum hydride.[9] After standing overnight, an excess of acetone was slowly added to destroy excess lithium aluminum hydride, followed by 100 ml. of water. The reaction mixture was then placed in a 1-l. distilling flask, 200 ml. of water added, and the ether removed by distillation. Sodium hydroxide, 80 g., was added and a mixture of water and amine was collected until the distillate no longer reacted basic. The distillate was neutralized with hydrochloric acid and evaporated to a sirupy consistency. The concentrated solution of the amine hydrochloride was dropped onto solid pellets of potassium hydroxide and the free amine collected over pellets of potassium hydroxide. The amine was separated and distilled through a Todd micro column from phosphorus pentoxide. The pure amine, b.p. 94.7–95.2° at 749 mm., $n^{20}D$ 1.3970, was obtained in yields of 50%.

Neopentyldimethylamine.—Pivalic acid was converted into the acid chloride[8] in yield of 88%. The acid chloride was transformed into N,N-dimethylpivalamide, b.p. 180–183°, in 76% yield by the procedure described above. The amide was reduced[9] to dimethylneopentylamine, b.p. 97.5–97.8° at 754 mm., $n^{20}D$ 1.3972, in 50% yield.

Procedure for Kinetic Studies.—Technical nitrobenzene (du Pont) was used as the solvent. Standard solutions of the amine and alkyl iodide in this solvent were made by weighing. The concentrations were verified by analyzing the amine solutions by acid–base titration and the halide solution by the Volhard procedure, after converting the halogen into ionic form with an excess of piperidine. The change of concentration with change in temperature was corrected by applying a factor for the change in density of nitrobenzene with temperature. Equal volumes of equimolar (approximately 0.2 *N* each) solutions were mixed in a flask and 8 samples (10 ml.) were pipetted into small thin-walled ampules. These were sealed and placed in a constant temperature bath. At appropriate intervals an ampule was removed, rinsed with acetone, and smashed in a flask containing 10 ml. of 0.15 *N* hydrochloric acid in 40 ml. of water. The free base was determined by titration of the excess acid with standard (0.1 *N*) barium hydroxide solution, using methyl red as the indicator.

The reaction of methyl iodide with *n*-butyldimethylamine was too rapid to permit utilization of this procedure. In this case the concentration of the iodide and of the amine in the reacting mixture was reduced by a factor of five. Standardized solutions of the two reagents were brought to the reaction temperature, rapidly mixed and 25-ml. aliquots removed by pipet at suitable intervals. The extent of reaction was then determined as in the case of the sealed ampules.

The data for each determination were corrected by the method of least squares to give the best straight line through the points. The energies of activation were calculated from the reaction constants at three temperatures, again using the method of least squares in the calculation.

LAFAYETTE, INDIANA

(8) H. C. Brown, THIS JOURNAL, **60**, 1325 (1938).

(9) A. Uffer and E. Schlittler, *Helv. Chim. Acta*, **31**, 1397 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Dissociation of the Addition Compounds of Trimethylboron with *n*-Butyl- and Neopentyldimethylamines; Interaction of Trimethylboron and Boron Trifluoride with Highly Hindered Bases[1,2]

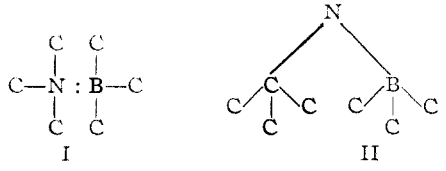
BY HERBERT C. BROWN AND ROLF B. JOHANNESEN[3]

RECEIVED FEBRUARY 28, 1952

The conclusion that neopentyldimethylamine is a highly hindered base is verified by a study of the relative stabilities of the addition compounds of this base and of *n*-butyldimethylamine with trimethylboron. Whereas the latter base forms a stable addition compound with ΔH 15.3 kcal., ΔF°_{100} − 1720 cal. and ΔS° 45.6 e.u., the compound with neopentyldimethylamine is at least 98.5% dissociated at 50° and is too unstable to allow thermodynamic constants for its dissociation to be obtained. Neither 2-*t*-butylpyridine nor 2,6-lutidine add trimethylboron at temperatures as low as −80°. The Henry's law constants at 0°, 3060 and 4100 mm., respectively, are much larger than the value for an ideal solution, 1546 mm., indicating the absence of any attractive forces between the two bases and trimethylboron. From these observations, strains in the homomorphs of *o*-di-*t*-butylbenzene and 2,6-dimethyl-*t*-butylbenzene of at least 17 kcal. are estimated. Boron trifluoride does not add to *o*-*t*-butyl-N,N-dimethylaniline, leading to an increased estimate of 25 kcal. for the strains in homomorphs of *o*-di-*t*-butylbenzene. Boron trifluoride adds to 2,6,N,N-tetramethylaniline to form an unstable addition compound with a high dissociation pressure at room temperature.

Introduction

The estimated heat of dissociation for the addition compound, trimethylamine-trimethylboron (I) is 25.4 kcal.; the experimental value is 17.6



I II

kcal.[4] The discrepancy of 8 kcal. is attributed to steric strain.[4,5] It has long been recognized that the accumulation of alkyl groups about a reaction center may markedly decrease the reactivity of the molecule.[6] There is, therefore, no great surprise in the observation that the attachment of six

(1) Acid–Base Studies in Gaseous Systems. X. Strained Homomorphs. V.

(2) Based upon a thesis submitted by Rolf B. Johannesen to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) A.E.C. Fellow at Purdue University (1949–1951).

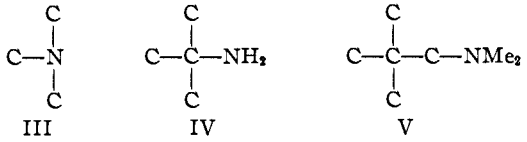
(4) H. C. Brown, H. Bartholomay and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944).

(5) The strain is considered to be of two types: F-strain, which is dependent upon the steric requirements of the reference acid (*e.g.*, trimethylboron), and B-strain, which is independent of the reference acid. R. Spitzer and K. S. Pitzer [*ibid.*, **70**, 1261 (1948)] have carried out a calculation of B-strain from spectroscopic data and concluded that it is too small to be considered significant in trimethylamine itself. We have recently completed a number of similar calculations, using methods that in our opinion represent a less approximate approach, and have by these methods obtained values for B-strain that are some 10 times greater than that previously calculated by Spitzer and Pitzer. Moreover, we now have considerable new experimental data which strongly point to the presence of considerable strain in trimethylamine and related molecules. This work with E. A. Fletcher, E. Lawton and S. Sujishi will be reported shortly.

(6) For a review of the older literature dealing with steric hindrance see J. Cohen, "Organic Chemistry," Vol. 1, Edward Arnold and Co., London, 1928, 5th Ed., Chapt. V.

methyl groups to adjacent boron and nitrogen atoms (or to adjacent carbon atoms, as in hexamethylethane[7]) produces a highly strained system. It is more surprising to observe that *t*-butylamine-trimethylboron (II) is also highly strained.[8] Here the six methyl groups are separated by an additional atom.

In following up the consequences of the concept of homomorphic systems,[7] it was predicted that neopentyldimethylamine should also be a highly hindered amine in reactions with methyl iodide or other molecules with appreciable steric requirements.[9] Here the substituents are located at a position two atoms removed from the reaction center (III–V). On the basis of classical considerations,

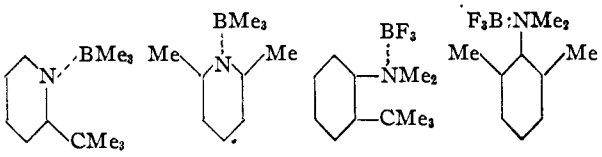


III IV V

an unusual inertness would not have been anticipated.

This prediction was verified for the reaction of methyl iodide with neopentyldimethylamine.[9] It was of interest to test further the conclusion that neopentyldimethylamine is a highly hindered base. Accordingly the addition compounds of trimethylboron with neopentyl- and *n*-butyldimethylamines were prepared and their dissociation in the gas phase studied.

In order to estimate the strains present in homomorphs of *o*-di-*t*-butylbenzene[7,10] and 2,6-dimethyl-*t*-butylbenzene,[7,11] we also investigated the interaction of trimethylboron with 2-*t*-butylpyridine (VI) and 2,6-lutidine (VII) and of boron trifluoride with *o*-*t*-butyl-N,N-dimethylaniline (VIII) and 2,6-N,N-tetramethylaniline (IX).



VI VII VIII IX

Results and Discussion

n-Butyldimethylamine-trimethylboron.—The addition compound was synthesized by treating *n*-butyldimethylamine in the high vacuum apparatus with an excess of trimethylboron. The product, a white crystalline solid, was purified by sublimation. The center fraction, which exhibited a constant sublimation pressure of 0.24 mm. at 0° and melted from 16.4–19.0°, was utilized for vapor pressure measurements and dissociation studies. The saturation pressure data for the solid and liquid compound are reported in Table I and Fig. 1A.

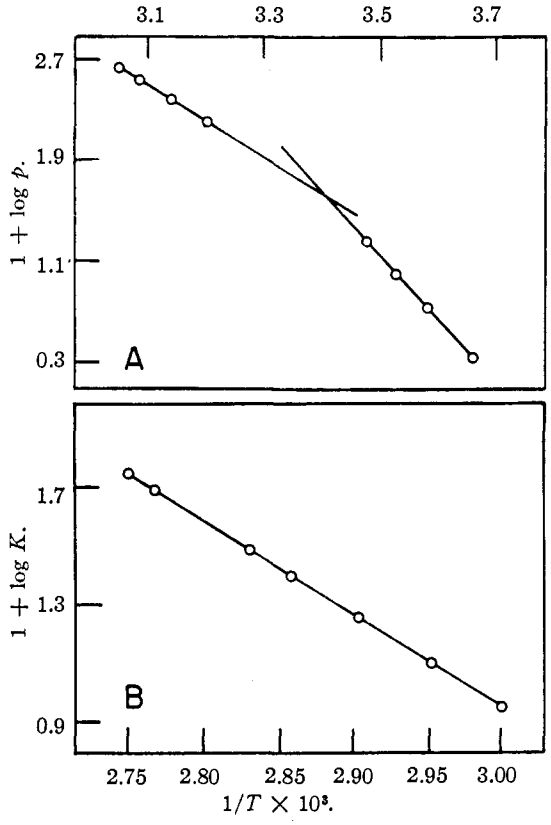


Fig. 1.—*n*-Butyldimethylamine–trimethylboron: A, saturation pressure data; B, dissociation data.

The data were fitted to the equations

$$\log P_s = -4192/T + 14.806$$
$$\log P_l = -3140/T + 11.252$$

These lines intersect at 22.8°, slightly above the observed melting point. This phenomenon together with the wide melting point range indicate appreciable dissociation of the addition compound at the melting point.

Dissociation pressures were measured and the data handled by the method of approximations.[12]

TABLE I

SATURATION PRESSURES OF *n*-BUTYLDIMETHYLAMINE-TRIMETHYLBORON

Solid				
Temp., °C.	0.0	5.0	10.1	14.6
Press., mm.	0.24	0.55	1.01	1.75
Liquid				
Temp., °C.	39.3	44.8	50.4	54.1
Press., mm.	15.8	24.0	35.5	45.7

TABLE II

DISSOCIATION DATA FOR *n*-BUTYLDIMETHYLAMINE-TRIMETHYLBORON

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.[a]	Degree of dissociation, α	Dissociation constant, K (atm.)
60.0	48.698	24.752	0.9674	0.935
65.2	49.672	24.767	.9760	1.31
70.0	50.555	25.495	.9830	1.91
75.1	51.407	25.874	.9868	2.51
80.1	52.207	26.245	.9892	3.13
85.1	53.036	26.617	.9926	4.66
90.0	53.790	26.981	.9936	5.48

[a] The pressure of *n*-butyldimethylamine and of trimethylboron calculated by the method of approximations was 20.295 mm. at 0.0°.

(7) H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson and K. L. Nelson, THIS JOURNAL, **75**, 1 (1953).

(8) H. C. Brown and G. K. Barbaras, *ibid.*, **75**, 6 (1953).

(9) H. C. Brown and W. H. Bonner, *ibid.*, **75**, 14 (1953).

(10) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 24 (1953).

(11) H. C. Brown and M. Grayson, *ibid.*, **75**, 20 (1953).

(12) H. C. Brown and M. Gerstein, *ibid.*, **72**, 2923 (1950).

Results of a typical study are summarized in Table II and represented graphically in Fig. 1-B.

Presumably because of the high dissociation of the compound, the precision was not as good as that obtained in previous studies by these methods. The results of three different determinations are reported in Table III. The mean of these three determinations give ΔH = 15.3 kcal., ΔF°_{100} = −1720 cal., ΔS° = 45.6 e.u., K_{100} = 10.2 atm., with the variation in the dissociation constant with temperature represented by the equation, log $K_p = -3346/T + 9.973$.

TABLE III

SUMMARY OF THERMODYNAMIC CONSTANT FOR DISSOCIATION OF *n*-BUTYLDIMETHYLAMINE-TRIMETHYLBORON

Detmn.	K_{100}, atm.	ΔF°_{100}, cal.	ΔH, kcal.	ΔS°, e.u.
1	9.18	−1640	15.6	46.2
2[a]	11.07	−1780	15.4	46.0
3	10.35	−1730	15.0	44.8
Mean values	10.2	−1720	15.3	45.6

[a] Experimental data in Table II.

Neopentyldimethylamine - trimethylboron.—A purified sample of neopentyldimethylamine was treated at 0° with a slight excess of trimethylboron in the high vacuum apparatus. The product, a white crystalline solid, was sublimed to free it from the excess trimethylboron. The addition compound was obviously highly unstable. It had a saturation pressure of well over 100 mm. at its melting point, 13–16.5°. Saturation pressures for the solid are reported in Table IV and are satisfactorily reproduced by the equation log $P_s = -3947/T + 15.942$.

TABLE IV

SATURATION PRESSURES OF NEOPENTYLDIMETHYLAMINE-TRIMETHYLBORON

Temp., °C.	−4.1	−2.0	0.0	2.9	5.3	7.9	10.0
Press., mm.	19.2	24.4	31.3	43.9	58.0	79.8	103

A number of attempts were made to measure the dissociation of the compound. However, when the usual samples of the two components were introduced into the tensimeter, the total pressure observed corresponded to a minimum dissociation at 50° of 98.5%. We attempted to repress the dissociation by using trimethylboron in considerable excess. This procedure was tested with trimethylamine and in this case yielded both satisfactory data and decreased values of the degree of dissociation under comparable conditions. However, even with this modification, the dissociation of neopentyldimethylamine-trimethylboron was so high that the thermodynamic constants could not be obtained. It follows that neopentyldimethylamine is indeed a highly hindered amine relative to typical aliphatic tertiary amines, such as the *n*-butyl derivative.

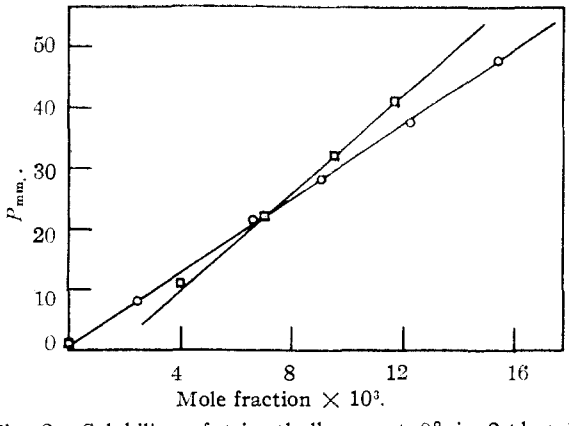


Fig. 2.—Solubility of trimethylboron at 0° in 2-*t*-butylpyridine (○) and 2,6-lutidine (□).

2-*t*-Butylpyridine and Trimethylboron.—No evidence of compound formation was observed when 2-*t*-butylpyridine was treated with trimethylboron at temperatures down to −80°. This is in marked contrast to the behavior of pyridine itself which reacts readily to form pyridine-trimethylboron with a heat of dissociation of 17.0 kcal.[13]

In an attempt to learn whether there was even a weak interaction between the two components, the solubility of trimethylboron in liquid 2-*t*-butylpyridine was determined at 0°. The data are given in Table V and Fig. 2.

TABLE V

SOLUBILITY OF TRIMETHYLBORON IN 2-*t*-BUTYLPYRIDINE AT 0°

2-*t*-Butylpyridine, g.	Trimethylboron: Mmole. n	Trimethylboron: Mole fraction, $N \times 10^3$	Trimethylboron: Pressure, mm.	Henry's law constant,[a] mm.
4.662	0.0	0.0	1.3	3060
	.0892	2.58	8.2	
	.236	6.79	21.8	
	.319	9.17	28.5	
	.433	12.4	37.5	
	.540	15.4	47.6	

[a] $P_{mm} = kN$. The value of the constant was determined graphically (Fig. 2).

If the solution of trimethylboron in 2-*t*-butylpyridine were ideal, the solubility of the gas at 0° would be expected to obey the equation P_{mm} = 1546 N where N is the mole fraction and P is the pressure of the gas. If there were any tendency for trimethylboron and 2-*t*-butylpyridine to interact, the solubility should be greater than that given by this equation. However, the observed constant, 3060 mm., shows that the solubility of trimethylboron in the pyridine base is even less than the ideal value. It follows that trimethylboron and 2-*t*-butylpyridine exhibit no attraction for each other. The heat of dissociation of pyridine-trimethylboron is 17.0 kcal. Since 2-*t*-butylpyridine is a slightly stronger base than pyridine, the steric strain involved in structures such as the unknown 2-*t*-butylpyridine-trimethylboron molecule and its homomorph, *o*-di-*t*-butylbenzene, must be at least 17 kcal.

2,6-Lutidine and Trimethylboron.—The m.p. of 2,6-lutidine is −6°. When liquid trimethylboron is placed in contact with solid 2,6-lutidine at −80°, the vapor pressure of the mixture is 30 mm., identical with that for pure trimethylboron. No reaction between the two components was observed over the entire temperature range examined, −80 to 25°. The solubility of trimethylboron in liquid 2,6-lutidine at 0° was determined. The data are given in Table VI and Fig. 2.

TABLE VI

SOLUBILITY OF TRIMETHYLBORON IN 2,6-LUTIDINE AT 0°

2,6-Lutidine, g.	Trimethylboron: Mmole., n	Trimethylboron: Mole fraction, $N \times 10^3$	Trimethylboron: Pressure, mm.	Henry's law constant,[a] mm.
4.282	0.0	0.0	1.3	4100
	.168	4.17	11.2	
	.286	7.10	22.0	
	.387	9.59	32.3	
	.477	11.8	41.4	

[a] $P_{mm} = kN$. The value of the constant was determined graphically (Fig. 2).

(13) H. C. Brown and G. K. Barbaras, THIS JOURNAL, **69**, 1137 (1947).

In this case the line representing the data (Fig. 2) does not pass through the origin but intersects the abscissa at 0.0017 mole fraction. This is interpreted to mean that the 2,6-lutidine must contain 0.17 mole % of other pyridine bases as impurities, pyridine bases which combine with trimethylboron to form relatively stable addition compounds. Since both 3- and 4-picoline have boiling points that are practically identical with that of 2,6-lutidine, it is probable that these picolines are responsible for the deviation.

The Henry's law constant, 4100 mm., shows that trimethylboron is even less soluble in 2,6-lutidine than in 2-*t*-butylpyridine. Accordingly, a minimum strain of 17 kcal. can be assigned to the hypothetical molecule 2,6-lutidine-trimethylboron and the other homomorphs of 2,6-dimethyl-*t*-butylbenzene.

o-t-Butyl-N,N-dimethylaniline and Boron Trifluoride.—Neither at 0° nor at −80° is there any evidence of reaction of boron trifluoride with *o-t*-butyl-N,N-dimethylaniline. In one case the amine was treated with boron trifluoride at a pressure of approximately 4 atmospheres at room temperature, but no absorption of the gas was observed. From the heats of reaction of the methylboron fluorides with trimethylamine,[14] the heat of dissociation of trimethylamine-boron trifluoride may be estimated as 28 kcal. and that of dimethylaniline as 25 kcal. It follows that steric strain in the hypothetical addition compound, *o-t*-butyl-N,N-dimethylaniline-boron trifluoride, must be at least 25 kcal. Tentatively, then, a strain of this magnitude is assigned to homomorphs of *o*-di-*t*-butylbenzene. However, it should be pointed out that the steric requirements of boron trifluoride are somewhat greater than those of borine. Unfortunately, data for the latter are not now available: The experiment previously described with 2-*t*-butylpyridine and trimethylboron fixes a lower limit to the strain of 17 kcal. It follows that the value of 25 kcal. assigned to homomorphs of *o*-di-*t*-butylbenzene on the basis of the present experiment cannot be seriously in error, although some modification may be required in the future.

2,6,N,N-Tetramethylaniline and Boron Trifluoride.—At −80° 2,6,N,N-tetramethylaniline absorbs approximately 1 mole of boron trifluoride to form an unstable addition with a dissociation pressure of 10 mm. at 0°. The compound is unstable not only with respect to dissociation into its components, but an irreversible decomposition into green substances was also observed. Accordingly, accurate dissociation pressures could not be obtained. The dissociation pressures observed, 10.5 mm. at 0.0°, 29.9 mm. at 10.0°, and 90.1 mm. at 20.0°, lead to the equation

$$\log P = -3959/T + 15.455$$

This is the first amine we have observed which liberates boron trifluoride at ordinary temperatures. Although a precise determination of the heat of dissociation must await completion of experimental work now in progress, the value must be quite low, certainly less than 10 kcal. The experiment points to steric strain in the addition compound in the neighborhood of 15 kcal.

Experimental Part

Materials.—The *n*-butyl- and neopentyldimethylamines were products prepared and purified by Bonner.[9] 2,6,N,N-Tetramethylaniline was provided by Grayson[11] and *o-t*-butyl-N,N-dimethylaniline by Nelson.[10] The 2-*t*-butylpyridine was a sample prepared by Murphey.[15] The 2,6-lutidine was a commercial product (Reilly Chemical Co.). It was distilled through an efficient fractionating column and the center fractions utilized. However, preliminary experiments indicated the presence of approximately 3% of material capable of absorbing trimethylboron strongly, presumably 3- and 4-picolines. The material was therefore purified by twice cooling the liquid until it was partially crystallized and then separating the liquid from the crystals. The freezing point was determined to be −6.05° (reported[16] −5.9°). From the cooling curve the purity was estimated to be 99.6%. The solubility experiments with trimethylboron indicated the presence of 0.17% of less hindered pyridine bases.

Boron trifluoride was purified through the benzonitrile addition compound.[17] Trimethylboron was prepared by the Grignard reaction in di-*n*-butyl ether.[18] The original procedure was modified to avoid isolation of the gas. Instead, the crude trimethylboron, distilled out of the reaction mixture, was passed into liquid ammonia at −80° to form ammonia-trimethylboron. The addition compound was purified by sublimation and trimethylboron liberated by treating with a deficiency of hydrogen chloride. The trimethylboron prepared in this way is at least 99% pure, but proved not to be satisfactory for the dissociation measurements. The gas apparently contained a small amount of a volatile impurity (possibly carbon dioxide arising from ammonium carbonate present in the addition compound). A pure product was obtained by converting the material into the trimethylamine addition compound, which was purified by sublimation and then converted into free trimethylboron with hydrogen chloride. (Carbon dioxide does not combine with trimethylamine.[19]) If it is desired to avoid the prior isolation and handling of the crude trimethylboron, the direct conversion of the gas into the addition compound with trimethylamine would probably eliminate these difficulties.

The Method of Excess.—The use of trimethylboron in excess offers promise as a means of depressing the degree of dissociation of relatively unstable addition compounds and improving the precision of the data. The method was tested on trimethylamine-trimethylboron. The results, ΔH = 17.67 (17.66) kcal., ΔF°_{100} = 533 (512) cal., ΔS 45.9 (45.9) e.u., agree satisfactorily with the values (in parentheses) obtained previously by the method of approximations.[12] The equilibrium constant at each temperature can be readily calculated from the observed pressure, P, and the previously measured pressures for the two components, P_A and P_B (corrected to the temperature in question) with the aid of the equation

$$K = \frac{(P - P_B)(P - P_A)}{(P_A + P_B - P)}$$

Determination of Solubilities of Trimethylboron.—The apparatus used is shown in Fig. 3. The trimethylboron was maintained in the bulb SB, whose volume was accurately known to the point Z. The pressure in this bulb could be followed on the combination manometer and valve. The weighed pyridine base was introduced (by distillation) into the tube containing the magnetically operated stirrer. The tube was immersed in an ice-bath and the pressure noted on the second combination valve-manometer. Trimethylboron was introduced and the pressure again noted after

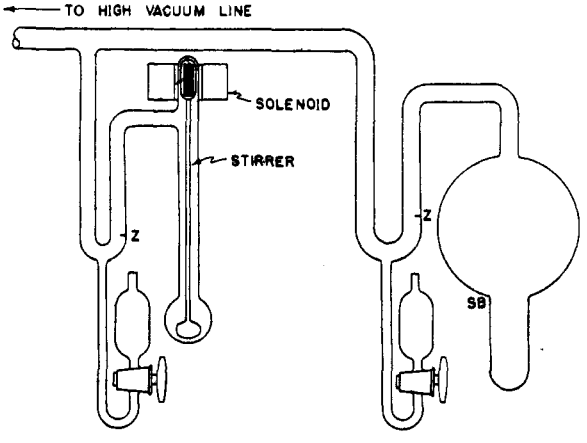


Fig. 3.—Apparatus for solubility determinations.

(14) A. B. Burg and A. A. Green, THIS JOURNAL, **65**, 1838 (1943).

(15) H. C. Brown and W. A. Murphey, *ibid.*, **73**, 3308 (1951).

(16) E. A. Coulson and J. I. Jones, *J. Soc. Chem. Ind.*, **65**, 169 (1946).

(17) H. C. Brown and R. B. Johannesen, THIS JOURNAL, **72**, 2934 (1950).

(18) H. C. Brown, *ibid.*, **67**, 374 (1945).

(19) H. C. Brown and R. H. Harris, *ibid.*, **71**, 2751 (1949).

equilibrium had been reached. The decrease in pressure in SB gave the amount of trimethylboron introduced. After a correction for the quantity in the gas phase, the trimethylboron in solution was accurately known together with the equilibrium pressure. Additional quantities of trimethylboron could then be introduced to obtain a series of points for a pressure versus mole fraction graph.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Homomorphs of 2,6-Dimethyl-*t*-butylbenzene[1,2]

BY HERBERT C. BROWN AND MARTIN GRAYSON[3]

RECEIVED FEBRUARY 28, 1952

2,6,N,N-Tetramethylaniline does not react with methyl iodide to form the quaternary ammonium salt, a homomorph of 2,6-dimethyl-*t*-butylbenzene. Similarly, mesitylene could not be *t*-butylated under conditions which result in the ready *t*-butylation of *m*-xylene to form 1,3-dimethyl-5-*t*-butylbenzene. Treatment of mesityldimethylcarbinol with hydrogen chloride results in the formation of α,2,4,6-tetramethylstyrene. The olefin does not add hydrogen chloride to form the tertiary chloride under a wide variety of conditions. At −30° considerable hydrogen chloride is absorbed with the formation of a red solid; the gas is evolved at higher temperatures. It is considered that the absorption is the result of the formation of a carbonium ion salt: $[2,4,6\text{-}Me_3C_6H_2CMe_2]^+Cl^-$. It is concluded that the high strain present in homomorphs of 2,6-dimethyl-*t*-butylbenzene accounts for the observations. Methyl 2,6-xylate could not be converted into 2,6-dimethylphenyldimethylcarbinol. No reaction occurred between the ester and methylmagnesium iodide; methyllithium yielded 2,6-dimethylacetophenone. The tertiary alcohol was prepared from 2,6-dimethylphenylmagnesium bromide and acetone in a yield of 4.5%. Mesityldimethylcarbinol was prepared from mesitylmagnesium bromide and acetone in 9% yield and from mesityllithium and acetone in 5.6% yield.

Introduction

Trimethylboron does not react with 2,6-lutidine.[4] Since pyridine, a somewhat weaker base,[5] readily reacts with trimethylboron to form a stable addition compound with a heat of dissociation of 17.0 kcal.,[6] steric strains of at least 17.0 kcal. are assigned to homomorphs[7] of 2,6-lutidine-trimethylboron (I) and 2,6-dimethyl-*t*-butylbenzene (II) (Fig. 1).

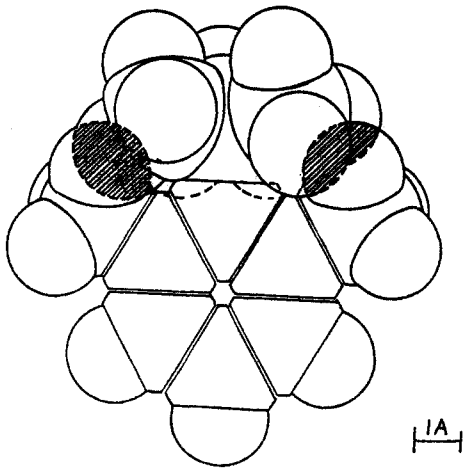
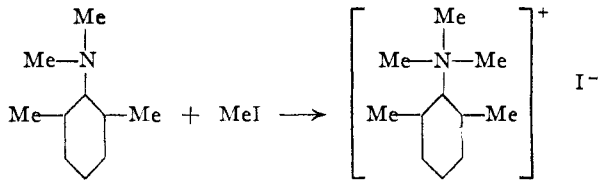


Fig. 1.—Molecular model of 2,6-dimethyl-*t*-butylbenzene.

I II

With one exception no homomorphs of 2,6-dimethyl-*t*-butylbenzene have been reported. Rate constants for the reaction of 2,6,N,N-tetramethylaniline (III) with methyl iodide at 35 and 45° in methanol have been reported.[8] From the data the reaction should proceed to the extent of 25% in



III IV

nine days at 45°. However, the quaternary salt (IV) which is presumably formed in the course of the reaction has not been isolated. The situation is confused by the earlier report that treatment of the amine (II) with methyl iodide in anhydrous ether for two months led to the formation of only "a trace of a crystalline substance."[9] Accordingly it was decided to reinvestigate this reaction and to attempt the isolation of the homomorph (IV).

In the course of this study we also examined the reactions of 2,6-dimethylphenyldimethylcarbinol and mesityldimethylcarbinol with hydrogen chloride in an attempt to prepare the homomorphic tertiary chloride (V).

(1) Studies in Stereochemistry. XX. Strained Homomorphs. VI.

(2) Based upon a thesis submitted by Martin Grayson to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Standard Oil Company (Indiana) Fellow (1949-1950); A.E.C. Fellow (1950-1952).

(4) H. C. Brown and R. B. Johannesen, THIS JOURNAL, **75**, 16 (1953).

(5) Pyridine: pK_A 5.17 at 25°; 2,6-lutidine: pK_A 6.75 at 25°. Unpublished work with F. X. Mihm, Ph.D. Thesis, Purdue University, 1951.

(6) H. C. Brown and G. K. Barbaras, THIS JOURNAL, **69**, 1137 (1947).

(7) H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson and K. L. Nelson, *ibid.*, **75**, 1 (1953).

(8) W. G. Brown and S. Fried, *ibid.*, **65**, 1841 (1943).

(9) W. C. Davies and H. W. Addis, *J. Chem. Soc.*, 1622 (1937).