mixture was cooled and transferred to a 40 theoretical plate spinning-band distillation column. Distillation in a nitrogen atmosphere and at reduced pressures afforded a small forerun of starting materials followed by the desired product. In every case a distillation residue was obtained which could not be fractionated successfully at lower pressures. Table I reports the yields and characterization data obtained.

General Procedure for the Preparation of Trialkylthioborates.—This procedure was essentially that described above except that 0.10 mole of trimethylamine borane was employed with 0.30 mole of the desired alkanethiol. Table I records yields and characterization data.

Reaction of Mercuric Chloride with Di-n-pentyl-n-butylthioboronate.—To a well-stirred slurry of 27.3 g. (0.10 mole) of dry, powdered mercuric chloride in 30 ml. of dry toluene contained in a three-necked flask which carried a reflux condenser, stirrer and dropping funnel, was added 15.0 g. (0.05 mole) of di-n-pentyl-n-butylthioboronate. The addition was carried out in a dropwise fashion under nitrogen and over the course of 1 hour. The reaction mixture was maintained at 80° during the addition and for 1 hour thereafter. After the addition of the first few drops of thioester, a voluminous precipitate formed. The reaction mixture was cooled, filtered in the absence of air and the product separated by distillation in a nitrogen atmosphere. A small spinning-band distillation column was employed. The distillate weighed 4.2 g. (60%) and boiled at 104–106°.[9] The infrared and H^1 n.m.r. spectra were identical with an authentic sample of n-butyldichloroborane.

Reaction of Mercuric Chloride with Di-n-pentyl-t-butyl-thioboronate.—The same procedure described above for the similar reaction of di-n-pentyl-n-butylthioboronate was employed. This reaction proceeded much more slowly than that described above. Distillation of the reaction mixture afforded 4.2 g. (60%) of pure t-butyl dichloroborane boiling at 86–88°.[10] The product was identical to an authentic specimen in its infrared and H^1 n.m.r. spectra.

Nuclear Magnetic Resonance Spectra.—All n.m.r. spectra were determined with neat samples and a 40 mc. H^1 probe or 12.8 m. B^{11} probe. Boron spectra were measured with a trimethylborate reference contained in a capillary tube.

Infrared Spectra.—All infrared spectra were obtained with a model 21 Perkin–Elmer infrared spectrophotometer. Samples were examined as capillary layers prepared in an efficient dry-box.

(9) P. A. McCusker, E. C. Ashby and H. S. Makowski, *J. Am. Chem. Soc.*, **79**, 5182 (1957), reported a boiling point of 106°.

(10) Ref. 9 reported a boiling point of 88°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE, NEWARK, DEL.]

The Reaction of Decaborane with Aromatic Amines[1,2]

BY HAROLD C. BEACHELL AND BRUCE F. DIETRICH

Decaborane reacts with p-anisidine, p-toluidine, p-chloroaniline, aniline, N-methylaniline and N,N-dimethylaniline to yield a product possessing the formula $B_{10}H_{12}(amine)_n$, where $n = 2$ or 3. The rates of reaction for these amines vary from 0.02 to 23.8 × 10^{-3} liter mole^{-1} sec.$^{-1}$ at 25.0° in benzene solution. Rate constants have also been obtained for the reactions occurring at 20.0°, 30.3° and 35.9°. An activation energy of 11.9 ± 0.3 kcal. was calculated for aniline and the p-substituted anilines. Evidence is presented for the formation of a reaction intermediate.

Introduction

The reactions of decaborane with nitrogen-containing compounds have been known since the work of Stock.[3] He noted that decaborane reacts with ammonia to form a diammonia compound. Since then investigations have been made involving other nitrogen compounds including the amines and nitrogen heterocycles.

The reactions involving amines were investigated mainly with the aliphatic series. Fitch[4] reported obtaining amine adducts of decaborane from the reaction of the hydride with dimethylamine. He observed compounds with decaborane:dimethylamine ratios of 1:1, 1:2 and 1:3 with indications for 1:4 and 1:5 products. The formation of a salt was noted by Hawthorne[5] when he added diethylamine to decaborane. The composition of the product was represented by the formula $B_{10}\overset{-}{H}_{13}\overset{+}{N}H_2(C_2H_5)_2$. Upon adding decaborane to ex-

cess amine this same investigator obtained a product which corresponded to $B_{10}H_{14}(NH(C_2H_5)_2)_2$.

An investigation of the reaction of decaborane with aniline and its N-methyl homologs was conducted recently by Terpko.[6] His results indicated that the products formed were condensation type compounds and were represented by the formula $B_{10}H_{14-x}(amine)_x$.

Discussion

The addition of decaborane to a benzene solution of p-toluidine produces a white solid which precipitates from the reaction medium. Elemental analysis of the product indicates that it has a decaborane:amine ratio of 1:2. Stoichiometry studies show that the reaction is essentially quantitative and that one mole of hydrogen is evolved for each mole of decaborane reacted. Other amines which undergo the same type of reaction include p-anisidine, p-chloroaniline, N-methylaniline and N,N-dimethylaniline.

The product of the decaborane–aniline reaction has a decaborane:amine ratio of 1:3 as indicated by the results of an elemental analysis. Though three moles of amine are observed for each mole of decaborane, the reaction, nevertheless, releases only one mole of hydrogen. Since, as it will be shown

(3) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(4) S. J. Fitch and A. W. Laubengayer, *J. Am. Chem. Soc.*, **80**, 5911 (1958).

(5) M. F. Hawthorne, A. R. Pitochelli, R. D. Strahn and J. J. Miller, *ibid.*, **82**, 1825 (1960).

(6) S. P. Terpko, *Dissert. Abs.*, **20**, 1572 (1959).

later, the kinetics for the aniline reaction are similar to those for the reaction of decaborane with the substituted anilines, it is suspected that the aniline product is merely a hydrogen bonded complex of $B_{10}H_{12}$(aniline)$_2$ and aniline. This formation of a 1:3 decaborane:aniline product was likewise observed by Terpko.[6] From the reaction of the N-methyl homologs of aniline with decaborane, this same investigator obtained decaborane:amine products with 1:2 ratios.

The product of the decaborane–p-toluidine reaction is independent of the order of addition of the reactants and the ratio of reactants used. In all cases the product has an empirical formula which corresponds to $B_{10}H_{12}(NH_2C_6H_5CH_3)_2$. This is unlike that observed by Hawthorne[5] for the reaction of decaborane with the aliphatic amine diethylamine. In his investigations he obtained either an amine salt, $(C_2H_5)_2 NH_2 B_{10}H_{13}$, or an adduct, $B_{10}H_{14}\cdot2(C_2H_5)_2NH$, depending upon which reactant was in excess and upon the order in which the reactants were mixed.

All of the above decaborane–aromatic amine reactions exhibit the same phenomena. Upon adding the two reactants to the reaction medium there is an immediate formation of a yellow solution and the evolution of hydrogen. As the reaction proceeds the intensity of the yellow color decreases and the white powder precipitates from the solution.

The products of all the decaborane–aromatic amine reactions investigated are insoluble in or react with most of the common solvents. Dry acetone is the only solvent investigated in which there is no reaction. However, the nature of the solution is such that the solute can be reclaimed only upon evaporation to dryness.

The white powders obtained from these reactions do not possess melting points. These products all decompose above 150° to viscous amber liquids.

The evolution of gas from the reaction of decaborane with the tertiary amine N,N-dimethylaniline, similar to the reactions of the primary and secondary amines, indicates that the decaborane portion of the product loses the hydrogen. This evidence along with the previously mentioned observations concerning the stoichiometry indicate that—the reaction can be written as
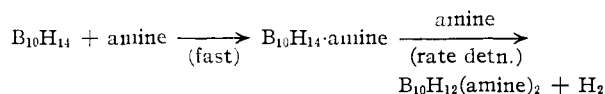
$$B_{10}H_{14} + 2\text{amine} \longrightarrow B_{10}H_{12}(\text{amine})_2 + H_2$$
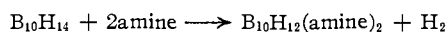
These results suggest the formation of compounds with the general formula $B_{10}H_{12}R_2$. Several products of this type have been reported earlier[7,8] and have been the result of the reaction of decaborane with compounds containing available electrons. These latter materials possess basic character and since decaborane has been shown to be an acid[9] the reaction conceivably can be considered as belonging to the acid–base group.

A kinetic study of these decaborane–aromatic amine reactions yielded data which were used to formulate a more detailed picture of the nature of the reactions. These studies were carried out by measuring the rate of gas evolution from the reac-

tion. Since one mole of gas was evolved for each mole of decaborane used as reactant, it was assumed that each mole of gas evolved represented the reaction of one mole of decaborane.

The results of these investigations indicate that the reaction is second order, first order with respect to each reactant. It was noted that the reactions are best expressed if the effective amine concentration is taken as the original concentration of the amine minus a concentration equivalent to that of the decaborane. This indicates a mechanism analogous to that proposed by Fetter[10] for the reaction of decaborane with pyridine. That is to say, a complex composed of one molecule of decaborane and one molecule of amine forms and in turn reacts in a rate-determining step with another molecule of amine to produce the solid product and hydrogen gas. The reaction can be written as

$$B_{10}H_{14} + \text{amine} \xrightarrow[\text{(fast)}]{} B_{10}H_{14}\cdot\text{amine} \xrightarrow[\text{(rate detn.)}]{\text{amine}} B_{10}H_{12}(\text{amine})_2 + H_2$$

The rate equation which describes this equation is

$$v = k(B_{10}H_{14}\cdot\text{amine})(\text{amine})$$

The specific rate constants for a number of amine reactions were calculated using the above kinetic expression. The values obtained are listed in Table I. Data collected from a typical rate experiment and from which the specific rate constants were calculated are given in Table II.

TABLE I

SPECIFIC RATE CONSTANTS FOR THE REACTION OF DECABORANE WITH VARIOUS AROMATIC AMINES IN BENZENE SOLUTION AT VARIOUS TEMPERATURES

	Specific rate constant $k \times 10^3$, liters mole^{-1} sec.$^{-1}$			
Amine	20.0°	25.0°	30.3°	35.9°
p-Anisidine	15.7	23.8	32.6	46.7
p-Toluidine	5.42	8.30	11.9	15.4
Aniline	2.04	2.88	4.22	5.61
p-Chloroaniline	0.49	0.69	0.97	1.37
N-Methylaniline		3.6		
N,N-Dimethylaniline		0.02		

TABLE II

TYPICAL EXPERIMENT FOR DETERMINING RATE OF REACTION OF DECABORANE WITH AROMATIC AMINES

Experiment number	2-16-60D
Reaction temp., °C.	20.0 ± 0.03
Solvent	Benzene
Amine	p-Toluidine
Amine concn. (a), mole l.$^{-1}$	14.84 × 10^{-3}
$B_{10}H_{14}$ concn. (b), mole l.$^{-1}$	2.79 × 10^{-3}
Vol. of reacn. soln., ml.	20.50
Vol. of gas (S.T.P.). ml.	12.83
Slope $d \ln \dfrac{b(a - b - x)}{(a - b)(b - x)} \Big/ dt$, sec.$^{-1}$	5.02 × 10^{-5}
Rate constant, l. mole^{-1} sec.$^{-1}$	5.42 × 10^{-3}

Further evidence for the formation of an intermediate complex was obtained from an ultraviolet absorption study of the decaborane–p-toluidine reaction solution. It was observed that immediately after mixing the two reactants an absorption

(7) R. Schaeffer, J. Am. Chem. Soc., 79, 1006 (1957).

(8) M. F. Hawthorne and A. R. Pitochelli, ibid., 80, 6685 (1958).

(9) G. A. Guter and G. A. Schaeffer, ibid., 78, 3456 (1956).

(10) N. Fetter and L. A. Burkardt, Abstr. 135th Meeting, Am. Chem. Soc., Boston, Mass., p. 45M (1959).

band occurs at 355 mμ. This band reaches its maximum intensity in a short time and as the reaction proceeds the intensity of the band slowly decreases. Hawthorne[5] noticed the presence of an absorption band at 335 mμ in his studies of the reaction of decaborane with aliphatic amines. His reactions were also accompanied by the formation of a yellow solution in a manner similar to that previously described for the reactions of decaborane with aromatic amines. This band observed by Hawthorne was attributed to the formation of the $B_{10}H_{13}^-$ species. In light of this, it is conceivable that an intermediate complex is formed when decaborane reacts with an aromatic amine and that this complex is an ion pair. Such an intermediate could be expressed by the formula

$$[B_{10}H_{13}\overset{\ominus}{}\cdot\overset{\oplus}{N}H_3C_6H_5R]$$
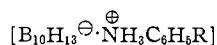
The specific rate constants obtained for the reactions involving partially deuterated decaborane and partially deuterated p-toluidine can be explained in terms of an intermediate complex composed of one decaborane and one amine unit. The values calculated for these constants are given in Table III. It is noted that the rate constants

TABLE III

SPECIFIC RATE CONSTANTS FOR REACTIONS INVOLVING
DEUTERATED REACTIONS IN BENZENE AT 25°

Reactants	Specific rate constants $k \times 10^3$ l. mole^{-1} sec.$^{-1}$
$B_{10}H_{14} + p\text{-}NH_2C_6H_5CH_3$	8.30
$B_{10}H_{14} + p\text{-}NH_{2-y}D_yC_6H_5CH_3{}^a$	6.86
$B_{10}H_{14-x}D_x{}^b + p\text{-}NH_2C_6H_5CH_3$	6.74
$B_{10}H_{14-x}D_x{}^b + p\text{-}NH_{2-y}D_yC_6H_5CH_3{}^a$	5.86

^{a} Estimated y-value = 1.5. ^{b} Estimated x-value = 3.

for the reactions involving only one deuterated reactant are the same regardless of which species is tagged. Such a similarity would occur if the formation of an ion pair intermediate was a rapid reversible reaction. In such a case there would be an equilibration of protons and deuteriums and the resulting ion pair intermediate for the reaction of deuterated decaborane with an amine would be identical to that obtained in the reaction of decaborane with a deuterated amine.

Further support for the formation of these equivalent intermediates is given by the results of gas analysis of the reaction and by infrared spectral data. In the results given for the gas analysis in Table IV it is noted that the percentages of the various types of gas evolved are similar for the two reactions involving one deuterated reactant. It is also observed that D_2 is evolved from these reactions. Since the work with tertiary amines indicated that the gas is released from the decaborane portion of the molecule, D_2 can be obtained from the reaction of decaborane with deuterated p-toluidine only if there is an equilibration of the hydrogens and deuteriums between the two portions of the complex. This also explains the low D_2 yield obtained from the reaction of the deuterated decaborane with p-toluidine. The infrared spectrum of the product from the reaction of deuterated p-toluidine with decaborane shows the presence of a B–D absorption band. thereby indi-
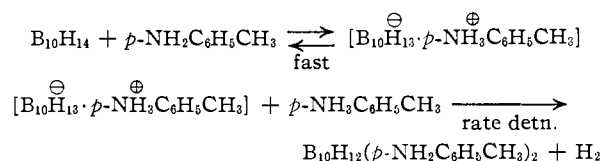
cating the occurrence of an exchange. Such an exchange is not at all unexpected since a previous investigation[11] has demonstrated the ease with which such a deuterium exchange occurs under base-catalyzed conditions.

TABLE IV

GAS ANALYSES FOR REACTIONS INVOLVING DEUTERATED
REACTANTS

Reactants	H_2, %	HD, %	D_2, %
$B_{10}H_{14} + p\text{-}NH_{2-y}D_yC_6H_5CH_3{}^a$	84.6	14.7	0.7
$B_{10}H_{14-x}D_x{}^b + p\text{-}NH_2C_6H_5CH_3$	83.8	15.3	0.9
$B_{10}H_{14-x}D_x{}^b + p\text{-}NH_{2-y}D_yC_6H_5CH_3{}^a$	60.5	33.7	5.8

^{a} Estimated y-value = 1.5. ^{b} Estimated x-value = 3.

Consideration of all the evidence obtained in the investigation leads to the conclusion that the reaction of decaborane with p-toluidine proceeds through a two-step process. The first step involves the rapid reversible formation of a complex composed of a molecule of decaborane and a molecule of p-toluidine. In the second step, the rate-determining step, the complex reacts with another molecule of p-toluidine releasing a molecule of hydrogen and forming the decaborane–diamine compound. The reaction can thus be written as

$$B_{10}H_{14} + p\text{-}NH_2C_6H_5CH_3 \underset{\text{fast}}{\overset{}{\rightleftarrows}} [B_{10}\overset{\ominus}{H}_{13}\cdot p\text{-}N\overset{\oplus}{H}_3C_6H_5CH_3]$$

$$[B_{10}\overset{\ominus}{H}_{13}\cdot p\text{-}N\overset{\oplus}{H}_3C_6H_5CH_3] + p\text{-}NH_2C_6H_5CH_3 \xrightarrow[\text{rate detn.}]{}$$

$$B_{10}H_{12}(p\text{-}NH_2C_6H_5CH_3)_2 + H_2$$

This path is proposed for the reaction of decaborane with all of the aromatic amines investigated because of the similarity of the reactions as indicated by the relative rates of reaction and the activation energies. The latter values were calculated for the reactions involving p-anisidine, p-toluidine, aniline and p-chloroaniline and are given in Table V. It is noted that the values for the activation energies all fall within the limit of experimental error of the value 11.9 kcal.

TABLE V

ACTIVATION ENERGIES FOR THE REACTION OF DECABORANE
WITH AROMATIC AMINES IN BENZENE SOLUTION

Amine	E, kcal.
p-Anisidine	12.2 ± 0.3
p-Toluidine	11.8 ± .3
Aniline	11.6 ± .3
p-Chloroaniline	11.6 ± .3

The rate constants for aniline and the p-substituted anilines follow the structural considerations proposed by Hammett. This is seen in Fig. 1 where the logarithmic values of the rate constants for the decaborane–amine reactions in benzene at 25° are plotted against Hammett's σ-values.[12] The ρ-value of -2.75 obtained from this graph suggests that the proposed mechanism is correct since a negative ρ-value indicates an increase in reaction rate with an increase in electron density.

(11) J. J. Miller and M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 4501 (1959).

(12) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 188.
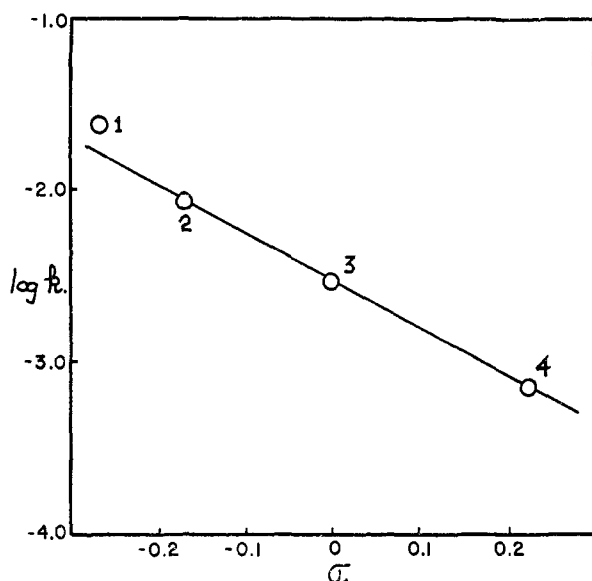
Fig. 1.—Comparison of decaborane–amine reaction rates with σ: 1, p-anisidine; 2, p-toluidine; 3, aniline; 4, p-chloroaniline.

This is to be expected when one considers that the reaction is essentially an acid–base-type reaction.

Experimental

Materials.—Decaborane was purified by sublimation and stored in an evacuated desiccator until used. The amines were dried with sodium hydroxide and purified by distillation and recrystallization. The solvents were thoroughly dried with anhydrous magnesium sulfate, metallic sodium or lithium aluminum hydride and purified by distillation.

Apparatus.—Infrared spectra were obtained through the use of a Baird Associates, Inc., model B recording infrared spectrophotometer equipped with sodium chloride optics. The samples were prepared as potassium bromide pellets. Ultraviolet absorption spectra were obtained with a Perkin–Elmer Spectracord model 400 recording ultraviolet spectrophotometer. A Barcroft–Warburg apparatus was used to observed the rate of gas evolution from the decaborane-amine reactions. This was equipped with a manometer containing Brodie solution. The bath temperature was regulated to $\pm 0.03°$ and read to the nearest $0.1°$.

Preparation of Reagents.—Partially deuterated decaborane was prepared by the procedure described by Hillman[13]; 3.16 g. of decaborane was dissolved in 50 ml. of anhydrous diethyl ether. To this solution was added 40 ml. of 99.5% deuterium oxide (obtained from Stuart Oxygen Co.). The mixture was agitated for 10 minutes after which time the aqueous phase was removed. The ether solution was then dried with anhydrous magnesium sulfate and evaporated to dryness. Sublimation of the residue yielded 2.4 g. of the presumed μ,μ',μ'',μ''' - tetradeuteriodecaborane. An infrared spectral analysis of the sublimate indicated the presence of bridge hydrogen and bridge deuteriums.

N,N-Dideuterio-p-toluidine was obtained from the deuterium oxide hydrolysis of the magnesylamine prepared by the method of Petyunin.[14] The synthesis consisted of the addition of 10.3 g. of p-toluidine dissolved in diethyl ether to a diethyl ether solution of ethylmagnesium bromide. The reaction produced 3.2 l. of gas which corresponded to the replacement of magnesium bromide of 67% of the replaceable hydrogens. Addition of deuterium oxide to the solution resulted in the hydrolysis of the magnesylamine and in the formation of the N,N-dideuterio-p-toluidine with 67% of the hydrogens having been replaced by deuterium. The presence of both hydrogen and deuterium on the nitrogen atom was verified from an infrared spectrum of the purified product.

(13) M. Hillman, *J. Am. Chem. Soc.*, **82**, 1096 (1960).

(14) P. A. Petyunin and I. J. Berdinsky, *J. Gen. Chem. U.S.S.R.*, **27**, 3028 (1957).

Preparation of Decaborane–Amine Products.—The decaborane–aromatic amine products were prepared by adding a benzene solution of the hydride to a benzene solution of the amine. Decaborane–amine reactant ratios between 1:2 and 1:10 have been used. In a typical preparation 0.04 g. (3×10^{-4} mole) of decaborane dissolved in 3 ml. of benzene was added to 0.30 g. (28×10^{-4} mole) of p-toluidine dissolved in 7 ml. of benzene. The resulting precipitate was filtered and washed several times with benzene. Analysis of this white solid indicated that the composition was $B_{10}H_{12}$ $(NH_2C_6H_5CH_3)_2$.

Anal. Calcd. for $B_{10}H_{12}(NH_2C_6H_5CH_3)_2$: B, 28.43; C, 49.67; H, 9.18; N, 8.08. Found: B, 32.34; C, 50.25; H, 9.04; N, 8.37.

Analyses of the products from reactions of decaborane with p-chloroaniline and aniline indicate products with the compositions $B_{10}H_{12}(NH_2C_6H_5Cl)_2$ and $B_{10}H_{12}(NH_2C_6H_5)_3$, respectively.

Anal. Calcd. for $B_{10}H_{12}(NH_2C_6H_5Cl)_2$: B, 28.82; C, 38.39; H, 6.44; N, 7.46; Cl, 18.89. Found: B, 29.97; C, 38.44; H, 6.60; N, 7.90; Cl, 17.69. Calcd. for $B_{10}H_{12}$-$(NH_2C_6H_5)_3$: B, 27.14; C, 54.23; H, 8.09; N, 10.54. Found: B, 25.72; C, 57.28; H, 7.85; N, 9.63.

Rate of Reaction.—The procedure used in following the rate of reaction consisted of mixing a solution of decaborane with a solution of amine and noting the increase in pressure in a closed system. The solutions used were made by weighing samples of the reactants and preparing standard solutions. Known volumes of the decaborane and amine solutions were placed in a reaction vessel and a sample tube, respectively. The latter was a small vial placed upright in the reaction flask. This was used to prevent the solutions from mixing prematurely. Pure solvent was added to the solutions. This decreased both the concentrations of the reactants and the gas volume of the system. After the reactants were thus prepared, the flasks were attached to the manometers and immersed in the water-bath. A period of 20 minutes was allowed for the attainment of thermal equilibrium. The reaction system was then opened to the atmosphere, the manometer fluid adjusted to a reference point, and the system again closed. Next, the solutions were mixed by shaking the flask, thereby upsetting the sample vial. At the same time, a stop watch was started so that the manometer readings could be associated with the reaction time. The reaction solutions were constantly agitated by the Warburg apparatus except during the time the pressure readings were taken. Before each reading was made the manometer fluid was adjusted to the reference point, thereby keeping the volume constant. The concentrations of the solution and the volume of the system were such that approximately 30 minutes was necessary for a manometer reading of 100 mm. to be observed. This corresponded to about 15% reaction.

The number of moles of gas evolved was calculated from the volume of the system, the temperature of the bath and the manometer readings. The following equation was used.

$$n = \frac{h}{22,400} \times \frac{V}{P} \times \frac{p}{13.56} \times \frac{273.2}{T}$$

where

n = number of moles of gas
h = height of manometer fluid (mm.)
p = density of manometer fluid (g. ml.$^{-1}$)
V = effective volume of system (ml.)
T = temperature of water bath (°K.)

The effect volume of the system was determined by adding the volumes of the manometer and reaction vessel used and subtracting from this the sum of the displacement volume of the sample vial and the volume of the reaction solution.

The number of moles of gas evolved was related to the number of moles of decaborane reacted according to the equation

$$B_{10}H_{14} + n \text{ amine} \longrightarrow B_{10}H_{12}(\text{amine})_n + H_2$$
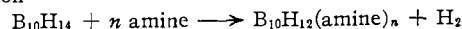
The kinetic order was determined by plotting the linear relationships of concentration with time for the various reaction orders and noting which results yielded the best plot. The data indicated that the gas evolution was first order with respect to both decaborane and amine concentrations. The following equation was used for the calculation of the rate constant

$$k = \frac{1}{(A - 2B)t} \qquad \ln \frac{b(a - b - x)}{(a - b)(b - x)}$$

where

k = rate constant (1. mole^{-1} sec.$^{-1}$)
A = concentration of amine (mole 1.$^{-1}$)
B = concentration of decaborane (mole 1.$^{-1}$)
a = initial number of moles of amine in reaction
b = initial number of moles of decaborane in reaction
x = moles of hydrogen evolved in time, t

The reactions of decaborane with p-toluidine, p-anisidine, p-chloroaniline and aniline were run at 20.0°, 25.0°, 30.3° and 35.9°. From the rate constants obtained for these reactions the activation energies were calculated. Rate constants were also calculated for the reaction of decaborane with N-methylaniline and N,N-dimethylaniline in benzene solution at 25°.

The Addition of Silicon Hydrides to Olefinic Double Bonds. Part VI. Addition to Branched Olefins
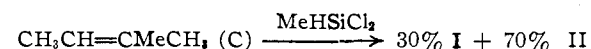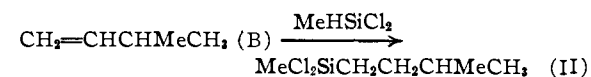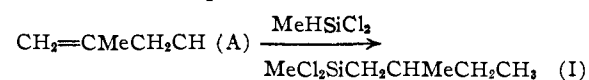
BY JOHN SAAM AND JOHN SPEIER

After the addition of methyldichlorosilane to an excess of an olefin in the presence of chloroplatinic acid, the excess olefin is recovered as a mixture of isomers. The process was studied with each of the methylbutenes, 1- and 4-methylcyclohexene and methylenecyclohexane. The distribution of the isomeric adducts obtainable under various conditions and the factors involved in the formation of isomeric olefins were studied.

Normal alkylsilanes result from the addition of silicon hydrides to linear olefins in the presence of chloroplatinic acid. This was found to be true even with non-terminal olefins. Pentene-2[1] gave n-pentylsilanes, and heptene-3[2] gave n-heptylsilanes. In these examples the silicon atom became attached exclusively to the terminal position on the alkyl chain.

To extend these observations, a study was undertaken to determine the positions favored by silicon during the addition of methyldichlorosilane to the methylbutenes in which there are distinguishably different terminal positions and to methylenecyclohexene and to 1- and 4-methylcyclohexenes in which there is only one terminal position.

An excess of each olefin, methyldichlorosilane and chloroplatinic acid were heated together. In each case one or more adducts formed and the excess olefin was recovered as a mixture of isomers.

The methylbutenes formed good yields of adducts outlined in the equations

$$CH_2{=}CMeCH_2CH \text{ (A)} \xrightarrow{\text{MeHSiCl}_2} MeCl_2SiCH_2CHMeCH_2CH_3 \text{ (I)}$$

$$CH_2{=}CHCHMeCH_3 \text{ (B)} \xrightarrow{\text{MeHSiCl}_2} MeCl_2SiCH_2CH_2CHMeCH_3 \text{ (II)}$$

$$CH_3CH{=}CMeCH_3 \text{ (C)} \xrightarrow{\text{MeHSiCl}_2} 30\% \text{ I} + 70\% \text{ II}$$

The adducts I and II were treated with methylmagnesium bromide to make the corresponding (methylbutyl)-trimethylsilanes. Authentic samples of these were synthesized as standards so that the identity of I and II could be established and their purity estimated by gas chromatography. In this way I and II were found to be quite pure. No trace of one was to be found in the other despite the fact that the olefins A and B were largely recovered as C. The purity of I and II seemed to require that either C was not made from A and B while the bulk of I and II were forming or else C was so unreactive that even if it were present
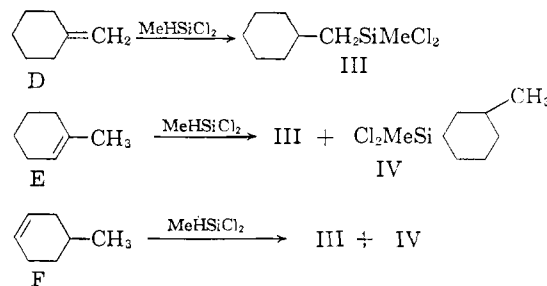
it did not compete detectably in forming adducts in the presence of A or B.

One equivalent of A and one equivalent of B were made to compete for one equivalent of methyldichlorosilane. The same was done with A and C, and with A and methallyl chloride. The products were analyzed by gas chromatography and the relative reactivities of the olefins were then calculated to be B/methallyl chloride/A/C = 1/0.8/0.07/0.02.

Branching as in A impedes the reaction, but a negative substituent accelerates the reaction. The rates of addition of both A and C differ only by a factor of about 3. The formation of essentially pure I from A cannot, therefore, be ascribed to the inability of C to compete with A, but indicates that C forms from A only after all or almost all of the I has been made.

Two experiments were run with an excess of methyldichlorosilane and A. In one case the two were mixed and sealed into a glass tube with the catalyst. A quantitative yield of pure I resulted. In the second case, the methyldichlorosilane was added slowly during three hours to the olefin at reflux. Again a quantitative yield was obtained, but the adduct was a mixture of 82% I with 18% II.

Methylenecyclohexane (D) gave an excellent yield of (cyclohexylmethyl)-methyldichlorosilane (III) free of isomers, but excess olefin was largely converted to 1-methylcyclohexene (E). 1-Methyl-

[Chemical structure scheme]

D: cyclohexane=CH$_2$ $\xrightarrow{\text{MeHSiCl}_2}$ cyclohexane–CH$_2$SiMeCl$_2$ (III)

E: (methyl)cyclohexene–CH$_3$ $\xrightarrow{\text{MeHSiCl}_2}$ III + Cl$_2$MeSi–(cyclohexane)–CH$_3$ (IV)

F: (methyl)cyclohexene–CH$_3$ $\xrightarrow{\text{MeHSiCl}_2}$ III + IV

(1) J. L. Speier, J. A. Webster and G. H. Barnes, J. Am. Chem. Soc., 79, 974 (1957).
(2) J. C. Saam and J. L. Speier, ibid., 80, 4104 (1958).

cyclohexene (E) or 4-methylcyclohexene (F) each formed both III and IV and excess olefin was re-