lene.[3] Assumption of this proportionality factor also for linear polyethylene converts eq. 7 into

$$[\eta]_{\alpha\text{-ClN},\ 125°} = 1.84 \times 10^{-4}\ \bar{M}_w^{0.78}\text{dl./g.} \qquad (8)$$

Equation 1 is probably more accurate than 8 in view of the uncertainties in Duch and Kuchler's light scattering measurement.[25]

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(25) Equation 1 was later supported by the relation

$$[\eta]_{\text{decalin},\ 135°} = 6.77 \times 10^{-4}\ \bar{M}_w^{0.67}\text{dl./g.} \qquad (9)$$

suggested for linear polyethylene by Francis, *et al.*[26]

For branched polyethylene, the intrinsic viscosity in decalin is 1.48 times that in α-chloronaphthalene.[3] Equation 9 converts into

$$[\eta]_{\alpha\text{-ClN},125°} = 4.6 \times 10^{-4}\ \bar{M}_w^{0.67}\text{dl./g.} \qquad (10)$$

in excellent agreement with (1).[27]

(26) P. S. Francis, R. C. Cooke, Jr., and J. H. Elliott, presented at the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September 19, 1956.

(27) Note added in proof (May 27, 1957). Recently, Tung[28] proposed the following relation based on osmotic data on fractions of linear polyethylene

$$[\eta]_{\text{tetralin},\ 130°} = 5.10 \times 10^{-4}\ \bar{M}_n^{0.725} \qquad (11)$$

Conversion to α-chloronaphthalene at 125° gives

$$[\eta]_{\alpha\text{-ClN},\ 125°} = 4.0 \times 10^{-4}\ \bar{M}_n^{0.725} \qquad (12)$$

For molecular weights in the range 20,000–100,000, eq. 2 leads to results about half those from eq. 1. The discrepancy probably reflects heterogeneity of Tung's fractions ($\bar{M}_w/\bar{M}_n \sim 2$).

(28) L. H. Tung, *J. Polymer Sci.*, **24**, 333 (1957).

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Alkenylboranes. I. Preparation and Properties of Some Vinyl- and Propenylboranes[1,2]

BY T. D. PARSONS, M. B. SILVERMAN AND D. M. RITTER

RECEIVED MARCH 18, 1957

Dimethylvinyl-, methyldivinyl- and trivinylborane, dimethylpropenyl- and methyldipropenylborane were prepared from dimethylbromoborane and vinylsodium or propenyllithium, respectively. The products in each case were separated by fractional condensation and the vinyl derivatives were separated more effectively by gas partition fractometry. The structures were demonstrated to be as claimed through identity of the hydrocarbons formed in the reaction with silver ammonium ion. Acidity of the vinylboranes toward ammonia was diminished as would be expected if the vacant boron orbital participated in the pi-electron system belonging to the alkenyl substituents. Relative acidity was found to account for the several products obtained in the preparative reaction, for absence of reaction of trivinylborane with oxygen and the slow autoöxidation of methyldivinylborane.

Compounds such as dimethoxyborane, dimethylaminoborane and borazole are stable as monomers, presumably because dimerization is prevented through internal dative bonding, which serves as an alternative to formation of three-center bonds in the dimers. This inspires the question concerning other sources from which electrons might be drawn into the vacant orbital of boron, and there comes to mind the intriguing possibility that in such structurally favorable cases as the alkenylboranes the phenomenon might cause the vacant boron orbital to participate in the carbon pi-electron system. The resulting mesomerism would be depicted by canonical forms involving a shift in the unsaturation from $\Delta^{\text{C}-\text{C}}$ to $\Delta^{\text{C}-\text{B}}$. Synthesis of suitable compounds becomes even more interesting when the vinylboranes are seen to be isoelectronic with allyl carbonium ion, and the possibility arises of observing with stable substances the properties attributed to unstable species.

The acidity of vinylboranes and the behavior of related hydrogen compounds with respect to dimerization should test the validity of the structural hypothesis; while observations of spectra and their comparison with predictions of molecular orbital computations should serve to evaluate any similarity with allyl carbonium ion. The latter program is outside the scope of the work reported here, and observations from this and other studies[3] makes improbable the existence of the vinyldiboranes. Accordingly this paper presents the syntheses of some completely substituted alkenylboranes, an efficient method for their separation, a chemical proof of their structure, a preliminary measure of their acidity, and some related chemical reactions.

The preparative method selected to involve the fewest unknown reactions was that in which a suitable carbanion displaced halide ion from a boron halide. Two such reagents were available, vinylsodium[4] and propenyllithium.[5] A weakly acidic boron halide was needed to avoid polymerization of the olefins, and for this purpose dimethylbromoborane[6] was chosen. Though a single product might have been expected from each organoalkali compound, there was obtained in addition to the dimethylalkenylboranes both the methyldialkenylboranes, and the trialkenylboranes.

The products were separated by fractional condensation and in the case of the vinylboranes also by gas partition fractometry, a method so superior as to be greatly preferred.

Experimental

Analytical Methods.—The bomb combustion method used for elementary analysis of organoboron compounds was essentially that described by McKennon. The sample

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(1) A portion of this research (M. B. S.) was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF18(600)-1541. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) Based on doctoral theses submitted to the Graduate School, University of Washington by Theran D. Parsons, 1953, and Morris Bernard Silverman, 1956.

(3) F. G. A. Stone and H. J. Emeleus, *J. Chem. Soc.*, 2755 (1950).

(4) A. A. Morton, *et al.*, THIS JOURNAL, **72**, 3785 (1950).

(5) E. A. Baude, J. A. Coles and C. J. Timmons, *J. Chem. Soc.*, 2000 (1950); *Nature*, **166**, 58 (1950).

(6) F. L. McKennon, Dissertation, University of Chicago Libraries, 1936.

Table I

Data on Alkenylboranes

Borane	Carbon, % Found	Carbon, % Calcd.	Boron, % Found	Boron, % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.	Mol. wt. Found	Mol. wt. Calcd.	Vap. p., mm. at 0°
Dimethylvinyl	..	...	..	...	...	...	73	68	126
Methyldivinyl	73.4	75.12	13.6	13.54	...	...	83.5	80	109.5
Trivinyl	77.7	78.40	11.9	11.79	9.76	9.86	93.2	92	67
Bis-(dimethylboro)-ethylene	66.2	66.85	21.5	20.08	...	...	114	108	21
Dimethylpropenyl	73.8	73.30	13.1	13.21	13.3	13.52	85	82	76.5
Methyldipropenyl	78.0	77.84	10.2	10.02	12.0	12.13	109	108	12.5

(15–20 mg.) was weighed in a small sample tube fitted with a stopcock and ₮ joint for attachment to the vacuum apparatus, where it was transferred to a breakoff-closure-fitted bomb tube. The charge and manipulation of the bomb tube depended upon whether hydrogen was to be determined or not.

In the former case the charge was oxygen (607 mmoles) and nitric oxide (0.5 mmole) generated by heating potassium permanganate and silver nitrite, respectively.

To ensure dryness these gases were introduced through a trap cooled to −80°. The bomb tube was heated 8–12 hours depending upon the sample.

The tube was opened by impact and the contents was fractionated through a trap cooled to −80°. The bomb tube was flamed lightly to decompose any boric acid to boric oxide and water. Each fraction, *i.e.*, that stopping at −80° and that passing through, was passed over a catalytic copper–gauze surface heated to 600° until the water and carbon dioxide were tensiometrically pure. Carbon dioxide was measured by gas volume and water was weighed. Boron was determined by titration of boric acid.

Where determination of hydrogen was to be omitted the bomb-tube charge was fuming nitric acid (one drop per mg. of sample). The heating was carried out at 280–290° for four hours. In other respects the procedure for carbon dioxide was the same.

Molecular weights were computed without correction for gas imperfection from gas densities of samples measured in the vacuum apparatus with respect to volume and pressure within 0.5–1.0% with temperature ±0.1° and weighed within ±0.01 mg. on a semi-microbalance with a compensating counterpoise.

Vinylsodium.—The method developed by Morton[4] was followed with a few modifications. A 3 to 1 ratio of amylsodium to sodium isopropoxide was used in the step involving exchange between amylsodium and ethylene, instead of the 1 to 1 ratio used by Morton. *n*-Hexane was used as a solvent in place of *n*-pentane. The ethylene needed rigorous scrubbing, and a too rapid flow of ethylene during the exchange had as a result poor purification and greatly diminished exchange.

Yields were determined by assay of a vacuum-dried aliquot with deuterium oxide or aniline. The monodeuteroethylene slightly contaminated with dideuteroethylene, was observed with the mass spectrometer. In one case 600 ml. of suspension was prepared from 1.12 g. atom sodium, 0.5 mole of amyl chloride and 0.13 mole of isopropyl alcohol. An aliquot of 50 ml. gave 225 cc. of deuteroethylene corresponding to a yield of 45% vinylsodium. Another preparation from the same amounts of reactants assayed by reaction with aniline gave for a 45/600 aliquot 12.4 mmoles of ethylene, v.p. −146°, 38 mm. corresponding to a yield of 43%.

Reaction of Vinylsodium with Dimethylbromoborane.—A suspension (310 ml.) containing 0.17 mmole per ml. of vinylsodium and a total of 0.64 mmole per ml. of sodium-containing compounds was dried *in vacuo*.

Dimethylbromoborane was prepared from tribromoborane and trimethylborane as described by McKennon[6] and stored in liquid nitrogen.

Dimethylbromoborane (90 mmoles) was condensed in three portions on the vinylsodium powder by means of liquid nitrogen. Each time the mixture was warmed slowly to room temperature, and the crude product was removed. The boron compound was expected to react with any of the numerous sodium compounds present. The amount used was therefore in excess of the vinylsodium present but in deficiency compared with the total of sodium compounds. In this way an undesirable excess of acid was avoided; however, as the last-formed substance in a heterogeneous system, the vinylsodium was thought to be most accessible and thus most efficient in its reaction with dimethylbromoborane.

Next, the solid was similarly treated with 309 mmoles of dry hydrogen chloride in three approximately equal portions. Non-condensable gas thought to be methane was formed.

Fractional condensation was applied to separation of a homogeneous portion of the crude product. Slow passage through U-tubes cooled to −40, −112 and −196° gave condensates of which that found at −196° contained ethylene and excess hydrogen chloride. From the −40° condensate the only boron-containing material obtained had the analysis B 4.05%, C 80.7% with a simplest formula B $C_{18}H_{38}$; subsequently all of the material was similarly fractionated, and the condensate collected at −40° was discarded.

Repeated rapid fractionation of the condensate at −112° was carried out through a U-tube cooled to −55°, and the material passing through was caught in a tube cooled with liquid nitrogen. Finally the condensate at −55° was passed slowly through the U-tubes cooled to −55, −80 and −196°. The condensate at −80° was bis-dimethylboroethylene. The condensates caught at the temperature of liquid nitrogen were retained for further processing.

The material remaining from the separation of bis-dimethylboroethylene was treated with a small excess of water to hydrolyze the borate esters. A fractionation with the bath temperature at −65° sufficed to remove the water and hydrolysis products, the most volatile of which was dimethylboronic acid.

The mixture of substances was next treated with dry ammonia at −80°, and any non-acidic material was removed by long pumping on the ammoniates. Treatment with dry hydrogen chloride regenerated the acids.

The final steps in purification were repeated fractionations with U-tubes cooled to −80, −90, −112 and −196°. No one of the substances sought condensed separately in the appropriate U-tube, but many repetitions of the sequence with frequent mixing and recycling of fractions gave roughly trivinylborane at −80°, methyldivinylborane at −90°, dimethylvinylborane at −112° and the residual trimethylborane was condensed at liquid nitrogen temperature. Analytical data, molecular weights and some vapor pressure data for these compounds are given in Table I.

Reaction of Propenyllithium with Dimethylbromoborane.—An ether solution of propenyllithium[5] (15.4 mmoles) was evaporated to dryness under vacuum. Dimethylbromoborane (10 mmoles) was condensed on the dry powder by means of liquid nitrogen. The reaction bulb was allowed to warm to 0° and after one hour the products were removed to the vacuum apparatus. The mixture was treated with water to remove any oxygen-containing substances introduced by reaction of propenyllithium with ether. Fractionation followed through a U-tube cooled to −35° to remove water. The ammonia complexes of boron-containing substances were made and the non-acidic residue was removed by pumping while the ammoniates were kept at −35°. Treatment with excess hydrogen chloride released the boranes. Repeated fractionation through U-tubes cooled to −35, −45, −65, −80, −112 and −196° yielded methyldipropenylborane condensed at −45 and −65°, and dimethylpropenylborane condensed at −112°. Analytical data, molecular weights and some vapor pressures for these compounds are given in Tables I and II. The constants in the vapor pressure equation were determined from the best straight line drawn through points for the observed values. Equations in Tables IV and V were constructed similarly.

Reaction of Propenyllithium with Trimethylborane.—Propenyllithium (13.4 mmoles) dissolved in 20 ml. of di-

TABLE II

VAPOR PRESSURES OF DIMETHYLPROPENYLBORANE

t, °C.	Pressure mm. Obsd.	Pressure mm. Calcd.[a]
−29.0	14.5	14.8
−19.9	26.5	25.9
−11.2	41.0	42.3
0	76.5	75.9
6.2	104	103.5
10.8	129	129.2
17.4	178	173

[a] From $\log P_{\text{mm}} = -1637/T + 7.875$.

ethyl ether was treated with trimethylborane (25.6 mmoles) at room temperature for 64 hours. The volatile portion was removed and separated by fractional condensation through U-tubes cooled to −80 and −112°. Only ether and trimethylborane (12.5 mmoles) were found. The proportions (13.4 mmoles propenyllithium:13.1 mmoles trimethylborane) were close to those required for formation of $Li^+[B(CH_3)_3CH{=}CH\text{-}CH_3]^-$.

Hydrolysis of the salt gave: ether (apparently held in the salt), propene 1.70 mmoles (v.p. at −111.8° (9 mm.), calcd. 9.3 mm.), trimethylborane 5.4 mmoles (v.p. −80° (29 mm.), calcd. 28 mm.), methane 5.8 mmoles; dimethylpropenylborane and methyldipropenylborane, approximately 0.5 mmole.

Formation of Dimethylethylborane and Dimethylpropylborane.—Dimethylbromoborane (11.05 mmoles) and diethylzinc (5.52 mmoles) were placed in an evacuated bulb and allowed to react at room temperature for 20 minutes. The products were passed through traps cooled to −48, −80 and −196°. Vapor pressure values for the fraction condensed at −80° were determined by slowly raising the temperature of the cooling bath and measuring the pressure at intervals. Between −9 and 0° rapid decomposition occurred. Below that point the vapor pressures obeyed the Clapeyron–Clausius equation as seen in Fig. 1 and differed from those for trimethylborane and triethylborane. Presumably the product is dimethylethylborane. *n*-Propyllithium (10.7 mmoles) was prepared in petroleum ether[7] and the solvent was removed. Dimethylbromoborane (8.5 mmoles) was condensed on the dry powder, and the mixture was warmed slowly to room temperature. The products were fractionated immediately through traps cooled to −40, −80 and −196°. The vapor pressure values for the material collected at −80° obeyed the Clapeyron–Clausius equation at temperatures below −18° as shown in Fig. 1. Above that temperature rapid disproportionation occurred. Presumably the substance is dimethylpropylborane.

Fractometric Separation of Methylvinylboranes. A. Apparatus.—Except for the use of a captive atmosphere, the fractometer was essentially the same as many other such devices depicted and described in the literature.[8] It consisted of a U-tube for loading the sample to be analyzed; a column packed with silicone oil on firebrick; a thermal conductivity cell for sample detection; several U-tubes in series for condensing the fractionated products; a glass spiral to warm the helium that had passed through the cold traps; a second thermal conductivity cell located in the Wheatstone bridge, opposite to the first cell; a Urry-type Toepler pump with automatic operation to circulate the helium; and a manostat to start the pump when the gas pressure at the input to the column dropped too low. Two three-liter bulbs in series with the gas stream, one at the high pressure side and the other at the low pressure side of the apparatus, served to damp pressure fluctuation caused by the stroke of the Toepler pump. A large bulb of purified helium, attached to the apparatus through a stopcock, made possible continual use of the fractometer with only occasional need to purify tank helium and introduce it into the system.

B. Column.—Dow-Corning "Silicone" 702 fluid was supported on Johns-Manville firebrick (crushed and sieved to 32–65 Taylor mesh) in a weight ratio of 1:2, respectively.

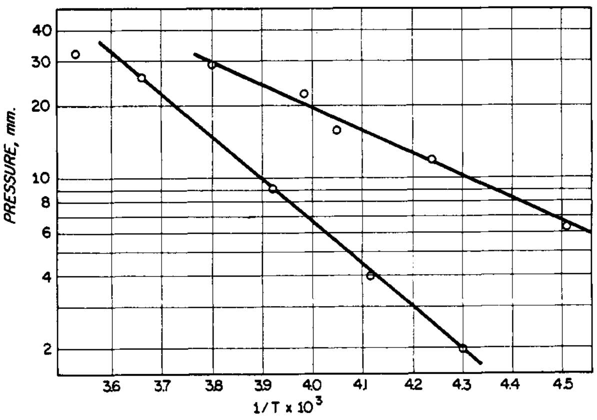

Fig. 1.—Vapor pressures of dimethylethylborane (upper curve) and dimethylpropylborane (lower curve).

Two columns were used: the one, "A," was constructed of 10 mm. i.d. glass tubing filled with 82.3 g. of packing over a length of 180 cm.

Later, when it appeared that a shorter length would be satisfactory, a second column, "B," was made containing 45.2 g. of packing; the tube measured 100 cm. in length and 10 mm. i.d. It is to this latter column that all reference will be made unless otherwise stated.

C. Captive Atmosphere.—Since the preparation of unsaturated boranes involved considerable expenditure of time and because of the inflammable nature of boranes in general, it was decided to protect these compounds by employing a closed helium atmosphere of ensured purity; the water-pumped helium was purified by passage through a calcium chloride column to remove the water and then through closely packed, degassed silica gel at −196° to adsorb oxygen.

The circulating system restricted the operation of the apparatus to pressures lower than atmospheric, an unimportant limitation except where columns of long dimensions make a high pressure drop necessary. Of course, the pressure could be higher than atmospheric with this system if compressed air were used to lift the mercury in the Toepler pump.

D. Sensing Device.—The thermal conductivity cells were constructed from Pyrex glass tubes of 1 cm. diameter and 10 cm. length. The two parallel tungsten wire leads (0.025 inch diameter) were sealed through a uranium glass junction at the half-length of the tube. The sensitive element was a thermistor[9] with leads welded to hang from adjacent ends of the tungsten wires. The inlet and outlet were 4 mm. Pyrex tubes, the former sealed to the bottom of the 1 cm. tube about 0.5 cm. below the thermistor and the latter sealed just below the graded seal. The inlet and outlet tubes were bent parallel to the larger tube to permit immersion of the cell in a water-filled Dewar flask to within 1 cm. of the open end. This design permitted the cell to be immersed in the Dewar at sufficient depth for good temperature stability while keeping the actual cell volume small to minimize the mixing of components of the fractionated sample.

E. Wheatstone Bridge.—The Wheatstone bridge arrangement did not depart greatly from the conventional design. By means of a 10,000 ohm multiturn helical potentiometer (Helipot) operated as a potential divider, the bridge voltage (as read on a 100 ohm per volt meter) from the 12 volt storage cell might be controlled to within one per cent. of the desired value. This arrangement was designed to give a high sensitivity without heating the thermistors more than necessary, a desirable precaution owing to the unstable nature of the compounds being studied. When it is permissible to heat the sample the resistance of the load resistors may be lowered with the result that a lower bridge voltage may be used without a decrease in sensitivity. The output of the bridge was fed to a bank of resistors from which a portion of the load was drawn to actuate a 10 millivolt recording potentiometer.

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(7) H. Gilman, F. W. Moore and O. Baine, THIS JOURNAL, **63**, 2479 (1941).

(8) A. B. Littlewood, C. S. G. Phillips and D. T. Price, *J. Chem. Soc.*, 1480 (1955).

(9) No. 26A2 purchased from Victory Engineering Company, Springfield Road, Union, N. J.

F. **Recovery of Samples.**—At liquid nitrogen temperature about 30% of a sample passed through the ordinary U-type trap at high flow rate. At a low flow rate, the problem was a lesser one and at about ten ml. per minute one unpacked trap was sufficient. Since highly volatile compounds such as trimethylborane were lost as much as those of lower vapor pressure, *e.g.*, trivinylborane, the problem appeared to be one of entrainment of mist rather than failure to condense owing to poor heat transfer. As a remedy a loose Pyrex glass wool plug was packed into 2–4 cm. of the posterior arm of the U-tube. This gave sufficient trapping efficiency to prevent escape of material into the next U-tube. Stainless steel wool was equally effective, but stainless steel gauze (80 mesh) allowed a small loss.

The necessity for such a device is somewhat unfortunate since the wool is bound to cause turbulence in the gas stream, which in the case of two compounds consecutively eluted, might cause some mixing to occur. However, the advantage greatly outweighs the disadvantage and, at least in this work, the separation was obtained without complication.

G. **Operation of the Fractometer.**—The material for analysis was condensed into the fractometer sample tube at −196° directly from the adjoining vacuum line. The helium pressure before and after the silicone column was adjusted to within a millimeter of 330 and 120 mm., respectively, and the temperature in the column and thermal conductivity cells was adjusted at 25°.

A bath of liquid nitrogen was placed around that member of the U-tube series furthest removed from the column and, by turning the appropriate stopcocks and closing the electrical switches, the fractionation was begun. The pattern made by the recording potentiometer was used as a guide, and when a component was seen to be eluted another cold bath was placed around the second U-tube. Each portion was condensed successively in the same manner in the remaining traps until the fractionation was completed.

Figure 2 is a fractometer pattern from column A, representing all the volatile products resulting from the reaction between vinylsodium and dimethylbromoborane and subsequent treatment of the products with water. To separate trivinylborane from the substances immediately preceding, two refractionations of an enriched portion were performed with the result shown in Fig. 3. Dimethylvinylborane presented a similar problem although the inflection in its curve was barely discernible. This compound was purified in the same manner as trivinylborane except that the desired compound was seen in the first portion of its fractometer pattern. Both trimethylborane and methyldivinylborane were obtained pure in a single pass. The molecular weights of the substances separated are given in Table III. Vapor pressures are given in Tables IV and V for trivinylborane and methyldivinylborane, respectively.

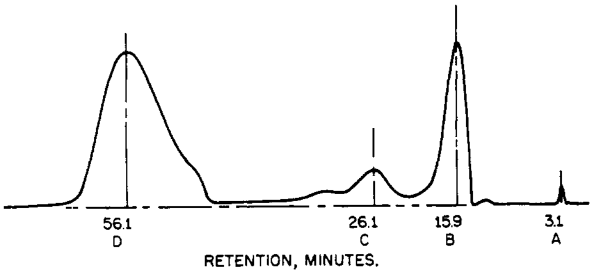

Fig. 2.—Fractometer pattern for trimethylborane A; dimethylvinylborane B; methyldivinylborane C; trivinylborane D.

Calibration of the Fractometer.—Figure 4 shows a calibration curve for the fractometer using column B at 25 ± 0.1° with a flow rate of 73 cc. per minute of gas at S. C. Of several parameters[10] such as peak height, product of peak height and half width, and area under the curve, the last was most consistently proportional to the amount of substance. The others have proved useful for certain substances, but apparently not all, depending upon the shape of the elution curve and the loading procedure. The precision of the measurements, estimated to be about ±2%, was fixed by 1% error in the voltmeter for measuring the bridge voltage, ±0.1° temperature fluctuation in the cooling bath for the column, 0.3% uncertainty in the recording millivoltmeter, and up to 1% error in the planimeter. The calibration curve departs slightly from linearity, a result at variance with those obtained for shorter ranges of sample size.[8,10] The reason for this is not understood in detail, but it is the combined effect of the response time of the thermistors, lag in the recording millivoltmeter and non-linearity of the Wheatstone bridge as it departs from balance. Each calibration curve is characteristic of a particular experimental arrangement, including the column, for substances of similar thermal conductivity or other influence upon the sensing device. Some combination of factors may give linearity fortuitously, but not necessarily.

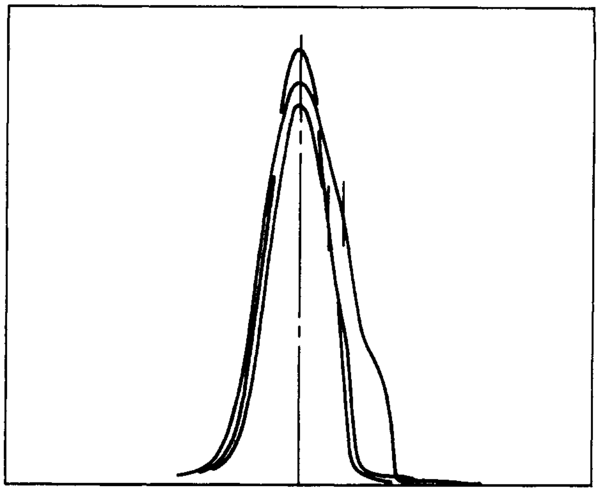

Fig. 3.—Patterns showing successive steps in fractometric purification of trivinylborane.

TABLE III

MOLECULAR WEIGHTS OF ALKENYLBORANES

Borane	Mol. wt. Found	Calcd.
Dimethylvinyl	67.5, 69.0	68
Methyldivinyl	80.9, 80.0	80
Trivinyl	92.8, 93.2	92

TABLE IV

VAPOR PRESSURE OF TRIVINYLBORANE

Temp., °C.	Pressure, mm. Obs.	Calcd.[a]
−45.4	2.9	2.8
−30.6	9.2	8.9
−22.6	15.5	15.6
0.0	63.1	63.1
14.5	131	140

Extrapolated b.p. 55°
Trouton's constant 24.4 e.u.

[a] From log $P_{mm} = -1848/T + 8.570$.

TABLE V

VAPOR PRESSURE OF METHYLDIVINYLBORANE

Temp., °C.	Pressure, mm.[a] Obsd.	Calcd.[b]
−46.0	7.7	7.7
−31.0	20.7	20.5
−23.2	33.5	32.8
0	113	113.6

[a] 0.35 mmole in 58 ml. [b] From log $P_{mm} = -1574/T + 7.816$.

H. **Partition Coefficients.**—With reference to one particular column the retention time is a distinctive physical

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[10] W. C. Percival, *Anal. Chem.*, **29**, 20 (1957); L. C. Browning and J. O. Watts, *ibid.*, **29**, 24 (1957).

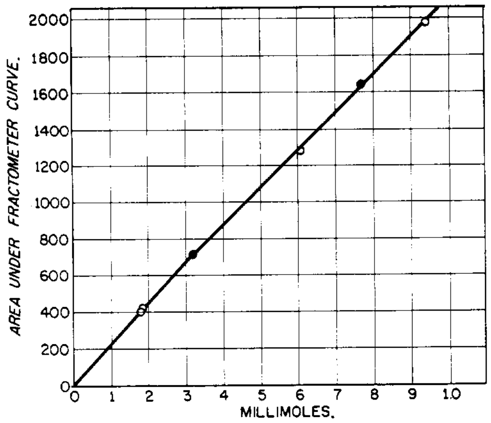

Fig. 4.—Calibration curve for fractometer column B based on triethylborane (dark circles) and trivinylborane (open circles).

property suitable for identification. When retention time values are very close, the characteristic slopes for the linear relation R *vs.* $1/T$ can be used to differentiate. For application to columns with various dimensions but the same packing an expression has been derived[11] for the partition coefficient,[12] H^0, and for the temperature coefficient of that quantity $\partial \ln H^0/\partial (1/T)$. Values for H^0 are given in Fig. 5.

Some Chemical Reactions of Alkenylboranes. A. Proof of Structure, Reactions with Silver Ammonium Hydroxide.[13]—Well-washed silver oxide (3–4 mmoles) was transferred to a reaction tube where it was treated with sufficient 15 *M* ammonium hydroxide for solution to occur. The tube was evacuated while the contents was frozen in liquid nitrogen and a measured sample (0.05–0.7 mmole) of a borane was added by condensation. At room temperature rapid reaction gave a silver mirror. After several hours the noncondensable gas was removed with a Toepler pump; the remaining products were separated by fractional condensation and identified tensiometrically. The data are given in Table VI.

Ammonia Complexes of Methyldivinylborane and Trivinylborane.—To 0.128 mmole of pure methyldivinylborane was added 0.251 mmole of ammonia at −196°. The mixture was warmed to room temperature, cooled to −80°, and then free ammonia was removed. Several times more, the reaction mixture was warmed and condensed in the same manner until, finally, no more ammonia could be removed. The amount of ammonia remaining with the borane was 0.129 mmole, equivalent, within experimental error, to the quantity of methyldivinylborane.

In Table VII are given saturation pressures of the addition compound as observed for 0.13 mmole in 147 ml.; for the purpose of comparison, the corresponding pressures of the triethylborane ammonia complex have been included.

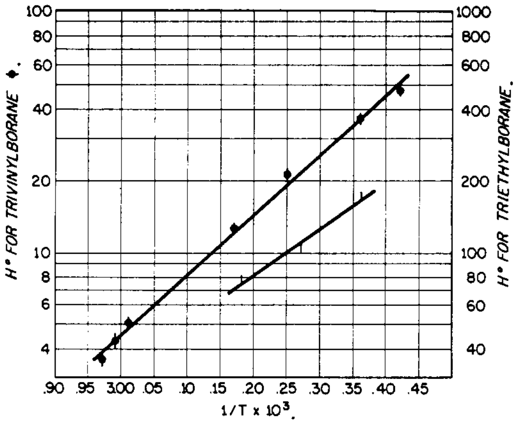

Fig. 5.—Temperature dependence of partition coefficients, *H*.

They were calculated from the equation $\log P = -3094/T + 10.538$.[14]

To 0.219 mmole of trivinylborane frozen at −196°, was added 0.344 mmole of purified ammonia. The mixture was warmed to −78° and allowed to stand for five minutes. The ammonia removed by pumping the mixture at −78° measured only two thirds of the calculated excess, but after pumping for 1.5 hours, more material was removed than could be expected assuming the formation of a monoammoniate.

TABLE VI

PRODUCTS OF REACTION OF ALKENYLBORANES WITH SILVER AMMONIUM HYDROXIDE

Borane	Used, mmole	CH_4	C_2H_4	Products, mmole C_2H_6	other	Total[a] recovered
Trimethyl	0.67	0.42		0.52[b]		1.46
Methyldipropenyl	.29	.22		.09[c]	C_6H_{10} 0.05[e]	0.36
Trivinyl	.048		0.022[h]		C_4H_6[f] 0.008	.038
Bis-dimethylboroethylene[j]	.156	.10	.009[i]	.044[d]	C_3H_6[g] 0.030	.173

[a] Calculated as mmoles of substituent groups. [b] V.p. −111.8° (167 mm.). [c] 165 mm. [d] 164 mm., calcd. 168 mm. [e] Δ-2,4-Hexadiene extrapolated b.p. 82–84°, calcd. 82°. [f] Δ-1,3-Butadiene v.p. −80° 9 mm., calcd. 9.7 mm. [g] Propene v.p. −111.8° 9 mm., calcd. 9.3 mm. [h] V.p. −145° 28 mm. [i] 27 mm., calcd. 28 mm. [j] Not named as a borane.

TABLE VII

SATURATION PRESSURES, MM.

Temp., °C.	$CH_3(C_2H_3)_2B{-}NH_3$	$(C_2H_5)_3B{-}NH_3$
0	0.6 ± 0.2	0.17
24	2.8 ± 0.2	1.3

The gases were recombined at −195° and warmed to −90°. After pumping for three hours, all but 2.5% of the excess ammonia had been removed. The mixture was warmed to somewhat below room temperature, cooled to −90° and ammonia was again pumped away. Following another repetition of that procedure, no more gas could be removed. The resulting compound was composed of 0.217 mmole of ammonia and 0.219 mmole of trivinylborane.

At 26.7°, the complex was expanded into a 257-ml. volume to give a pressure of 31.0 mm. The number of millimoles calculated (0.427) was 98% of the expected value for complete dissociation.

Decomposition of Methylvinylboranes.—A mixture of dimethylvinylborane (0.012 mmole) and methyldivinylborane (0.028 mmole) was stored at room temperature for 5.5 days. A fractometer pattern showed that the resulting mixture contained 0.002 mmole of trimethylborane, 0.03 mmole of methyldivinylborane and 0.008 mmole of dimethylvinyl-

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(11) P. E. Porter, C. H. Deal and F. H. Stross, THIS JOURNAL, **78**, 2999 (1956).

(12) $H^0 = M_sRT/\gamma P^0$; $V^0_R = V_m + H^0V_S$ and

$$V^0_R = \frac{V_R}{\frac{2}{3}\,\frac{(P_i/P_0)^3 - 1}{(P_i/P_0)^2 - 1}}$$

where

V_m = vol. of mobile vapor phase in the column
V_S = vol. of stationary solvent phase
H^0 = solute partition coefficient
$= \frac{\text{solute per vol. of solvent phase}}{\text{solute per vol. of gas phase at S.C.}}$
V_R = apparent retention vol.
P_i = pressure at column inlet
P_0 = pressure at column outlet
M_S = moles of stationary liquid phase per unit vol.
γ = activity coefficient of the solute in the solvent phase
P^0 = vapor pressure of the solute.

(13) H. R. Snyder, J. A. Kuck and J. R. Johnson, THIS JOURNAL, **60**, 105 (1938); R. L. Letsinger and I. H. Skoog, *J. Org. Chem.*, **18**, 895 (1953).

(14) H. C. Brown, THIS JOURNAL, **67**, 374 (1945).

borane. Some gas that did not condense at −196°, probably methane, was also produced but was not measured quantitatively. Thus dimethylvinylborane disproportionated about 33%.

Methyldivinylborane (0.356 mmole) was heated for one hour at 100°. Thereafter a barely discernible manometer pressure was observed at −80° and the amount of gas had increased about 0.9%. After removing the gas not condensable at −196°, 98.5% of the original sample remained unchanged. The fractometer pattern of the products showed that two rapidly eluted substances were produced; the one appearing first was a compound of unknown composition with a retention time of 0.9 minute and the other, trimethylborane. These two compounds, appearing in approximately equal amounts, represented slightly less than one per cent. of the total sample. The decomposition was not appreciably more after 70 hours at 100°.

After a storage period of 2.5 hours at 0°, the vapor pressure of 1.35 mmoles of trivinylborane dropped from 63.1 to 62.3 mm. in a 215-ml. volume. Whereas the original compound was pure, the 0° vapor pressure of the aged product dropped a few millimeters when moved from a 2.5-ml. to a 10-ml. vessel. A decomposition product showed an inflection situated just before the apex of the trivinylborane fractometer pattern; this irregularity in the curve was estimated to account for 1 to 3% of the total sample. The product appears to be identical with an impurity which was eliminated from the original mixture obtained from the reaction of vinylsodium and dimethylbromoborane.

Another sample of trivinylborane (0.09 mmole) was stored at room temperature for ten days. Two substances were discernible in the fractometer pattern, but the compound found in the previous experiment did not appear. Most of the mixture was trivinylborane. The other product issuing from the column a few minutes before trivinylborane gave an ill-defined fractometer pattern, since it was eluted from the silicone column over an extended period of time. The vapor pressure of the daughter compound was about 37 mm. at 0°; it was not further purified.

Treatment of Trivinylborane and Methyldivinylborane with Air.—From a 260-ml. container equipped with a manometer, 3.32 mmoles of dry air at 25° was allowed to expand into a 56-ml. volume containing 0.131 mmole of pure trivinylborane frozen in liquid nitrogen.

Two minutes after mixing (*i.e.*, as soon as the gases had warmed to room temperature), the pressure in the combined volumes was 195 mm. at 24°, and did not change. The calculated pressure should have been 199 mm., assuming no reaction.

Two hours from the time of mixing, the gases were passed through a U-tube at liquid nitrogen temperature to remove air and all other non-condensable products; 0.127 mmole of gas was recovered. This represents 97% of the original amount of trivinylborane. The vapor pressure of this substance was 63 ± 0.5 mm. at 0° and 128.5 ± 0.5 mm. at 14.3°, both readings taken in a 10-ml. volume; the vapor pressure of pure trivinylborane at these temperatures is 63.1 and 132 mm., respectively. A fractometer pattern of the product had only one discernible peak with a retention time of 15.2 minutes, a correct value for trivinylborane.

Methyldivinylborane (0.12 mmole; retention time 24 min.) was cooled with liquid nitrogen in a volume of 150 cc., and dry air was admitted until the pressure was 200 mm. (an excess of oxygen). The mixture was sealed-off, warmed to room temperature, and kept for 1.5 hours. No smoking or other visible change was detected. The condensable material was collected in liquid nitrogen and later passed through fractometer column "B."

The elution curve shown in Fig. 6 was analyzed approximately by counting squares. Material which appeared in the first three peaks was separated by fractional condensation. The portion passing through a bath cooled to −145° had a vapor pressure at −112° of 13 mm. (calcd. for propylene 11 mm.). The infrared spectrum of the same material was identical with that of propylene, and an authentic sample had the same retention time. The elution curve was analyzed after making some assumptions: (1) the companion peaks near propylene were ethane and butadiene; (2) the residual methyldivinylborane was to be seen with a retention time of 24 minutes at the leading edge of the curve envelope which resulted from incomplete resolution of that substance and one more; (3) all the boron appeared in the last three components as compounds containing one boron atom per molecule. The results are summarized in Table VIII.

TABLE VIII

FRACTOMETER DATA ON METHYLDIVINYLBORANE OXIDATION

Retention time, min.	Identity	Amount, mmole
1.7	Ethane	0.0012
3.3	Propylene	.043
5.7	Butadiene	.012
24	Methyldivinylborane	.036
30	Unknown	.057
44	Unknown	.027

Discussion of Results

Proof of structure depended upon the appearance in the products of oxidation by silver ion of the groups present in the boranes. These were detached as free radicals in the reaction with silver ions and transformed into hydrocarbons by radical combination or abstraction of hydrogen atoms from other substances present (*e.g.*, solvent, etc.). Though the methane recorded in Table VI probably contained some hydrogen, the finding of ethane made that unimportant. While a quantitative reaction would have been more elegant the substances found were those expected from the structures assigned, and no unexpected substances were found. Particularly significant was the appearance of Δ-2,4-hexadiene confirming location of the unsaturation along the three carbon chain in the propenyl derivatives.

Organoboranes decompose at elevated temperature, in the case of tri-*n*-butylborane to give diborane derivatives and alkenes,[15,16] and this or similar decomposition can be observed with triethylborane and tributylborane even at room temperature where equilibrium or a point of inappreciable reaction is reached after a very little decomposition. Dimethylpropenylborane and methyldivinylborane appeared to undergo this same type of decomposition very slightly and to be stable in other respects up to 100°.

Unsymmetrical alkylboranes disproportionated very rapidly at temperatures above −10 to −20°. Dimethylvinylborane exhibited this instability to a much lesser degree, being about one third disproportionated in a few days at room temperature. Concurrently the first type of decomposition was observed to a slight extent. The disproportionation proceeded rapidly enough to vitiate all effort to obtain a useful series of vapor pressures. Nevertheless, the behavior of this least stable of the methylalkenylboranes examined is that of a substance much less readily disproportionated than the mixed alkylboranes. The differences in reactivity can possibly be ascribed to the expected mesomerism which restrains the alkenylborane in a planar configuration. If the activated complex for disproportionation be considered a bridge-bonded dimer with tetrahedral configuration about the boron atoms, the activation energy for the alkenyl derivatives should be higher than for the saturated compounds.

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(15) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 100.

(16) L. Rosenblum, THIS JOURNAL, **77**, 5016 (1955).

Though the data are too few for better than an approximate evaluation, enough is known to see that trivinylborane is weakly acidic as expected, but methyldivinylborane must be considered about as strong as triethylborane. A difference between the two alkenylboranes would be predicted since formation of the ammonia complex with trivinylborane destroys mesomerism describable by three canonical structures, while for methyldivinylborane only two canonical structures are involved,[17] and a difference in resonance energy is made manifest by a difference in acidity.

A crude estimate of the resonance energy can be made. From the measurement on the trivinylborane–ammine is obtained the value for K dissoc. $= 30 \pm 15$; the corresponding constant for methyldivinylborane can be estimated indirectly. The acidity of methyldivinylborane appears close to that of triethylborane. The latter in turn has an acidity toward ammonia about that of trimethylborane toward trimethylamine, and for this case a value for K^{298} dissoc. $= 8.8 \times 10^{-5}$ can be calculated from existing data.[14] This makes $\Delta\ pK_a = 5.5 \pm 0.2$, and assuming $\Delta S = 0$, the resonance energy difference becomes about 7.5 kcal. through the relation $\Delta F = -2.302\, RT\, \Delta\, pK_a$.

Similar cases have been observed where acids describable by several canonical structures give conjugate bases having fewer. Oppositely ordered cases are known when the reverse is true. Some examples are given in Table IX.

TABLE IX

EFFECT OF RESONANCE ON ACID STRENGTH

	Pairs	pK_a	ΔpK_a
I	Guanidinium ion	13.6[a]	
	Acetamidinium ion	12.4[b]	1.2
II	Triacetylmethane	5.81[b]	2.4[c]
	Acetylacetone	8.24[b]	
III	Crystal violet cation		2.9[d]
	Malachite green cation		
IV	Nitric acid	−1	4.35[e,c]
	Nitrous acid	3.35	
V	Trivinylborane		
	Methyldivinylborane		5.5

[a] H. N. Hall, THIS JOURNAL, **52**, 5115 (1930). S. J. Angyal and W. K. Warburton, *J. Chem. Soc.*, 2492 (1951). [b] Reference 17. [c] Reference 18. [d] Reference 19. [e] R. P. Bell, "Acids and Bases," Methuen and Co., Ltd., London, 1952, p. 59.

Defects can be found in the analogies based on pairs II and IV,[18] but the comparisons within pairs I and III are unambiguous. Pair III[19] is a particularly elegant example where spectroscopic resonance energies and heats of carbinol formation give a $\Delta\ pK_a$ value in good agreement with that for the alkenylboranes, considering the way in which the latter value was obtained.

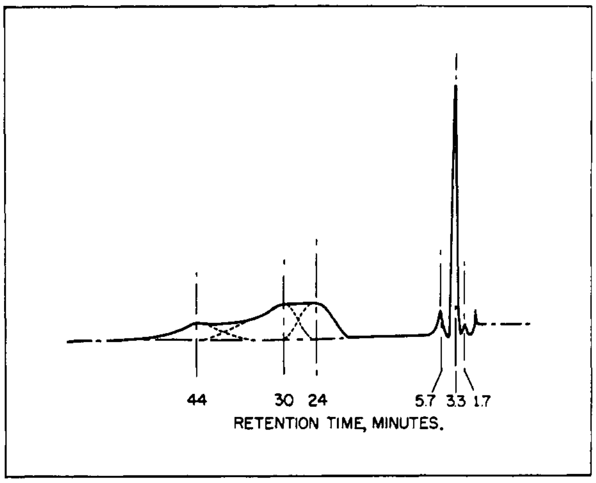

Fig. 6.—Fractometer pattern for oxidation products from trivinylborane; *cf.* Table VIII.

In what follows two other very interesting results can be understood on the basis of the relative acid strength. One of these is the distribution of products obtained in the preparative reaction; the other is the behavior of trivinylborane and methyldivinylborane toward oxygen.

Observations on decomposition of methyldivinylborane and dimethylvinylborane show accumulation of trivinylborane through disproportionation to be very unlikely. On the other hand a reaction mixture including vinylsodium, in which the other substances have acid strengths in the order $(CH_3)_2BBr > (CH_3)_2B(C_2H_3) > (CH_3)B(C_2H_3)_2 > B(C_2H_3)_3$, should reach a state of enrichment with respect to the weakest acid. The process would be a series of displacement reactions involving formation and decomposition of quaternary borate anions of the same type as lithium trimethylpropenylborate.

The absence of reaction at room temperature between trivinylborane and oxygen must be interpreted as indicative of a slow rate of reaction which would doubtless become greater at a higher temperature. Obviously the reaction rates are proportional to the acid strengths, and the more reactive methyldivinylborane is much less so than either triethylborane which, smoking and fuming in air, is quickly consumed or trimethylborane which similarly is oxidized rapidly and sometimes explodes. In methyldivinylborane oxidation there appeared in the products hydrocarbons which could have been formed only by combination of methyl and vinyl radicals. If the intermediates were peroxides such as that found in the oxidation of trimethylborane,[20] the radicals could originate from decomposition of the peroxides, though not necessarily, because alternatively, radicals are formed in oxidations involving direct attack, as where silver

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(17) G. Schwartzenbach and K. Lutz, *Helv. Chim. Acta*, **23**, 1147 (1940).

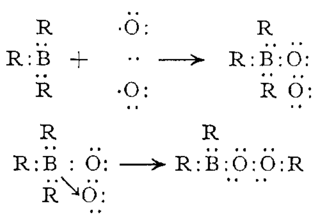
(18) Direct comparison with pair II is complicated by the contribution to the total resonance energy from the cyclic hydrogen-bonded enol. The effect is to diminish the difference in resonance energy between the undissociated enol and the enolate ion thus diminishing the acidity. Estimated spectroscopically the contribution amounts to about 3 pK units (M. Tsuboi, *Bull. Chem. Soc. Japan*, **25**, 385 (1952)) which is consistent with $\Delta pK_a = 3.0$ for acetylacetone compared with 1,3-cyclohexanedione (ref. 13). However, the substances in pair II should be affected about equally, which validates the comparison attempted here.

For pair IV contributions to ΔpK_a come from the mesomeric difference but in addition a variation of inductive effect arising from nitrogen of oxidation No. 3 + as distinct from that of oxidation No. 5 + makes a contribution which cannot be assessed.

(19) C. W. Looney and W. T. Simpson, THIS JOURNAL, **76**, 6293 (1954).

(20) R. C. Petry and F. H. Verhoek, *ibid.*, **78**, 6416 (1956).

ion is the oxidizing agent.[11] Possibly the oxidation of organoboranes can be considered to proceed as indicated.[21]



Acknowledgment.—The authors wish to thank Professor W. T. Simpson for many stimulating discussions, Professor B. S. Rabinovitch and his students for deuterium assays of vinylsodium, and Mr. Daniel B. Ritter for assistance with the figures.

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[21] C. H. Bamford and D. M. Newitt, *J. Chem. Soc.*, 695 (1946).

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The Infrared Spectra of Some Amino Acids

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RECEIVED MARCH 21, 1957

The infrared spectra of some optically inactive amino acids including α- and β-alanine, α-, β- and γ-aminobutyric acids, and N-methylated glycines were obtained using the KBr technique in the region 5000-667 cm.$^{-1}$. The functional group frequencies have been correlated with the molecular structure of these compounds. The spectrum of betaine hydrate indicates that it is a dipolar ion in the form of a water complex.

Introduction

The infrared spectra of solids can be conveniently obtained from KBr pellets in which finely ground samples have been dispersed.[2] Koegel, *et al.*,[3] using this technique, obtained the spectra of a large number of optically active amino acids. This paper presents some further work on optically inactive amino acids.

The object of this study was (1) to correlate the spectra of optically inactive amino acids including the N-methyl substituted glycines, (2) to see the effect on the spectra of amino acids when the position of the amino group is varied along the chain, and finally (3) to evaluate the structure of betaine hydrate.

Experimental

The spectra were obtained from a Perkin–Elmer Model 112, single beam, double pass infrared spectrometer equipped with a sodium chloride prism. Pellets were prepared by first mixing the amino acid with KBr (J. T. Bakers Analytical Grade) in a Wig-L-Bug Amalgamator for 30 seconds. The resulting mixtures were used to make clear pellets 10 mm. in diameter and approximately 0.5 mm. thick. The procedure for pressing the pellets was essentially the same as described by Kirkland.[4] In this technique it was found that there was a finite concentration of an amino acid below which a clear pellet could be obtained. However above this concentration the pressed pellet became cloudy, as though excess amino acid had crystallized out. This may mean that the amino acid forms a solid solution in KBr.

The following substances were obtained from Nutritional Biochemical Co.: glycine, DL-α-amino-*n*-butyric acid, β-alanine, DL-norvaline, DL-norleucine, DL-valine, DL-isoleucine, DL-β-aminobutyric acid, γ-aminobutyric acid, sarcosine hydrochloride, N,N-dimethylglycine hydrochloride and betaine hydrochloride. The substances DL-alanine, α-amino-isobutyric acid and betaine hydrate were obtained from Eastman Kodak Company.

Results

The amino acids are divided into two groups: I—the straight and branched-chained amino acids and compounds in which the amino group is varied along the chain and II—glycine and N-methyl substituted glycines.

The Region 3500-2000 Cm.$^{-1}$.—Amino acids exhibit a great deal of hydrogen bonding as evidenced by the presence of many broad bands in their spectra, especially in the region 3000–2000 cm.$^{-1}$. This makes it difficult to differentiate between the C–H and N–H bands. Nevertheless there are a few generalizations which can be made in this region. α-Amino-*n*-butyric acid and α-alanine of group I both have broad bands at 2300 and 2262 cm.$^{-1}$, respectively, which do not appear in the β- and γ-acids. The same is true for the medium bands 3050 and 3042 cm.$^{-1}$ for the above two acids, respectively.

There is a characteristic band at 2130 cm.$^{-1}$ which has been tentatively assigned to the N–H stretching in the group NH_3^+.[3,5] Table I also confirms that this band is related to the NH_3^+ group; however, a closer inspection of the data indicates that it may be related to an N–H bending mode rather than an N–H stretching mode. Evidence for this is that in the β-amino acids the absorption peaks are shifted to higher frequencies while the α-amino acids absorb at the normal frequency. This shift may be interpreted on the basis of hydrogen bonding which leads to ring formation. The α-, β- and γ-amino acids could form, respectively, 5-, 6- and 7-membered hydrogen bonded rings. The β-compound would be more stable since it could conceivably form a six-membered ring and as a result the N–H bending mode would have a higher absorption frequency in comparison to the other two types. If this were an N–H stretching mode the reverse would be true and the β-amino acid would absorb at a lower frequency in compari-

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[1] National Institute of Health Fellow, 1955–1956.

[2] (a) U. Scheidt and H. Reinwein, *Z. Naturforsch.*, **7b**, 270 (1950). (b) M. M. Stimson and M. J. O'Donnel, THIS JOURNAL, **74**, 1805 (1952).

[3] R. J. Koegel, J. P. Greenstein, M. Winitz, S. M. Birnbaum and R. A. McCallum, *ibid.*, **77**, 5708 (1955).

[4] J. J. Kirkland, *Anal. Chem.*, **27**, 1537 (1955).

[5] L. A. Duncanson, *J. Chem. Soc.*, 1753 (1953).