the air removed. The tube was then cooled in liquid air and 0.12 mole of trifluoroacetonitrile was condensed therein. The tube was sealed and allowed to warm up to room temperature where it was maintained for 10 hours. A pale yellow solid formed at the bottom of the tube. After the tube was cooled in liquid air and opened to the vacuum system, it was found that 0.045 mole of trifluoroacetonitrile was unreacted, indicating a 1:1 reaction of the nitrile with hydrazine. The solid was removed from the tube and recrystallized from water to yield 9.0 g. (100% yield) of 2,5-bis-(trifluoromethyl)-1-N-amino-1,3,4-triazole, m.p. 118.5–120°. A mixed melting point taken with the compound prepared in (1) showed no depression. The infrared spectra of the two preparations were identical.

2,5-Bis-(pentafluoroethyl)-1-N-amino-1,3,4-triazole.—Method 2 (above) was used to carry out a reaction of 9.5 g. (0.065 mole) of pentafluoropropionitrile and 1.85 g. (0.058 mole) of anhydrous hydrazine. The reaction was allowed to continue for 48 hours at room temperature. Eleven grams (100% yield) of a tan solid was removed from the tube but on exposure to the atmosphere it became red and gummy. A small portion recrystallized from water showed a long melting range. The remainder of this product was dissolved in dry benzene and treated with dry hydrogen chloride to form the hydrochloride. The final solid product was filtered and washed thoroughly with dry benzene and ethyl ether to give 2,5 bis-(pentafluoroethyl)-1-N-amino-1,3,4-triazole hydrochloride, m.p. 80–85° dec.

Anal. Calcd. for $C_6F_{10}H_3N_4Cl$: C, 20.1; N, 15.6; F, 53.0; Cl, 9.92; neut. equiv., 365.5. Found: C, 20.4; N, 15.4; F, 52.9; Cl, 10.2; neut. equiv., 361.7.

Preparation and Titration of Hydrochlorides of the Hydrazidines and Triazoles.—The same procedure was used for the preparation of the hydrochlorides of each of the various hydrazidines and triazoles: the compound was dissolved in an inert solvent such as hexane, benzene or ether, and dry hydrogen chloride was bubbled through the solution until it was no longer absorbed. In every instance the hydrochloride separated out and was removed from the solvent by filtration and purified by thorough washing with a solvent known to dissolve the free base. No recrystallizations were attempted. The neutral equivalents were determined by dissolving the salts in an ethyl alcohol–water solution and titrating to a phenolphthalein end-point.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Hydroboration. VI. A Convenient Synthesis of the Alkane and Cycloalkane Boronic and Borinic Esters and Acids

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The addition of 1-pentene or cyclopentene to a solution of one-half the molar quantity of diborane in tetrahydrofuran solution at 0° results in the formation of 60 to 65% yields of di-*n*-pentylborane and dicyclopentylborane, readily converted to the corresponding borinic methyl esters by treatment with methanol. Equilibration of the initial reaction mixture with a deficiency of diborane (2 olefin/1 BH_3) leads to the preferred formation of di-*n*-pentylborane in the case of 1-pentene, but to the preferred formation of monocyclopentylborane (and tricyclopentylborane) in the case of the cyclic olefin, cyclopentene. Equilibration of the initial reaction mixtures at 25–50° with excess diborane leads to the formation of mono-*n*-pentylborane and monocyclopentylborane in yields of 65 and 73%, respectively. These boranes are readily converted to the methyl esters by treatment with methanol, and the esters are readily converted to the corresponding boronic acids by hydrolysis. Consequently, hydroboration of olefins provides a convenient synthetic route to the alkane and cycloalkane boronic and borinic acids and their derivatives.

The aliphatic boronic esters are generally synthesized by the reaction of the Grignard reagent with methyl borate at low temperatures.[3,4] The related borinic acids have been obtained from trialkylboranes by hydrolysis of the initial oxidation product[5] by the reaction with alcohols and aldehydes,[6] or by the hydrolysis of the dialkylboron chlorides[7] conveniently synthesized by the reaction of boron chloride with the trialkylboranes.[8] Diarylborinic acids have been synthesized by the reaction of the aryl Grignard reagent with alkyl borates in yields of 15–30%,[9] but this method does not appear to have been successfully utilized in the aliphatic series.

The observation that olefins rapidly undergo hydroboration to form the corresponding organoboranes in essentially quantitative yield[10] led to the investigation of this reaction as a possible route to the alkane and cycloalkane boronic and borinic acids. 1-Pentene and cyclopentene were selected as representative olefins for this study.

Results and Discussion

In the usual hydroboration procedure the diborane is either generated externally and introduced into a flask containing the olefin, or the diborane is generated *in situ*. In either case, the diborane is initially in the presence of an excess of olefin and the reaction generally proceeds to completion to the formation of the trialkylborane.[11] Accordingly, we examined the effect of introducing the olefin to a solution of diborane, in the hope that this procedure would permit the partial alkylation of the diborane.

In these studies the olefin was slowly added to a

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(1) American Cyanamid Co. Post-doctorate research assistant, 1958–1959.

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(3) H. R. Snyder, J. A. Kuck and J. R. Johnson, THIS JOURNAL, **60**, 105 (1938).

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(5) J. R. Johnson and M. G. Van Campen, Jr., *ibid.*, **60**, 121 (1938).

(6) H. Meerwein, G. Hinz, H. Majert and H. Sonke, *J. prakt. Chem.*, **147**, 226 (1937).

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(8) P. A. McCusker, G. F. Hennion and E. C. Ashby, *ibid.*, **79**, 5192 (1957).

(9) N. N. Mel'nikov, *J. Gen. Chem.* (*U.S.S.R.*), **6**, 636 (1936); *C. A.*, **30**, 5571 (1936); N. N. Mel'nikov and M. S. Rokitskaya, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1768 (1938); *C. A.*, **33**, 4969 (1939); W. Konig and W. Scharrnbeck, *J. prakt. Chem.*, **128**, 153 (1930). Better yields have been realized by the use of trimethoxyboroxine with aromatic Grignards: T. P. Povlock and W. T. Lippincott, THIS JOURNAL, **80**, 5409 (1958).

(10) H. C. Brown and B. C. Subba Rao, *ibid.*, **78**, 5694 (1956); *J. Org. Chem.*, **22**, 1137 (1957); THIS JOURNAL, **81**, 6423, 6428 (1959).

(11) In the case of a few highly substituted olefins, such as 2-methyl-2-butene, the reaction stops at the dialkylborane stage, whereas in more hindered cases, such as 2,3-dimethyl-2-butene, it stops at the monoalkylborane stage (ref. 10).

TABLE I

THE PARTIAL ALKYLATION OF DIBORANE IN TETRAHYDROFURAN[a]

Olefin	Olefin, mmoles	Borane,[b] mmoles	Time, hr.	Temp. °C.	Products, mmoles[c]			
					BH_3	RBH_2	R_2BH	R_3B
1-Pentene	300	150	1	0	47	14	9	77
Cyclopentene	300	150	1	0	26	12	45	47
Cyclopentene	300	150	1	−78 to 0[d]	27	20	79	39
1-Pentene	300	300	1	0	159	19	89	13
Cyclopentene	300	300	1	0	137	18	96	23

[a] 350 cc. of tetrahydrofuran. [b] Generated in 10% excess from sodium borohydride and boron trifluoride etherate, assuming a 90% yield. [c] Isolated as the methyl esters after solvolysis with methanol. [d] Olefin added at −78°, and the reaction mixture permitted to warm up to 0°.

solution of diborane[12] in tetrahydrofuran at 0°. After one hour at this temperature, excess methanol was added and the reaction mixture distilled. The residual borane in the reaction mixture was determined by titrating the methanol–methyl borate–tetrahydrofuran forerun for boric acid; the yields of monoalkylborane, dialkylborane and trialkylborane were established from the weights of the three fractions corresponding to the monoalkane boronic ester, the dialkane borinic ester and the trialkylborane. The analysis was facilitated by the fact that these individual fractions possess widely separated boiling points.

The addition of 300 mmoles of 1-pentene to 150 mmoles of borane in 200 cc. of tetrahydrofuran results in the predominant formation of tri-*n*-pentylborane, 77 mmoles, with only minor amounts of the mono-*n*-pentyl- and di-*n*-pentylborane. Under the same conditions, the reaction of cyclopentene produced less trialkylborane, 47 mmoles, with a higher yield of the dialkyl derivative, 45 mmoles. Addition of the cyclopentene at −78° with slow warming to 0° (1 hour) resulted in an increased yield of the dicyclopentylborane, 79 mmoles (53%).

The use of 300 mmoles of borane with 300 mmoles of olefin at 0° results in a further increase in the yield of dialkylborane. Thus, under these conditions 1-pentene gives 89 mmoles of the methyl ester of di-1-pentaneborinic acid, a yield of 59%, and cyclopentene gives 96 mmoles of the methyl ester of dicyclopentaneborinic acid, a yield of 64%, both yields based on the olefin introduced.

These results are summarized in Table I.

The isolated yields of borinic ester of 59–64% realized by this procedure must be considered quite satisfactory in view of the simplicity of the method. Consequently, the partial alkylation of diborane in tetrahydrofuran at 0° represents a new convenient route to the alkane and cycloalkane borinic acids and their derivatives.

Our failure to realize satisfactory yields of the boronic acids in these experiments led us to explore alternative procedures. Schlesinger and his coworkers have established the relatively rapid equilibration of diborane and the lower trialkylboranes (methyl, ethyl and *n*-propyl).[13,14] Accordingly, we undertook a study of the reaction of diborane with tri-*n*-pentylborane and with tricyclopentylborane under hydroboration conditions to learn whether an equilibration procedure might permit the synthesis in reasonable yield of monoalkylboranes, and consequently of boronic acids and esters.

The reaction between diborane and simple olefins, such as 1-pentene and cyclopentene, is complete in ether solvents in a very short time, less than a minute at room temperature. Consequently, the slow introduction of excess diborane into a solution of an olefin in tetrahydrofuran serves to produce a mixture of trialkylborane and diborane. Such mixtures were prepared, permitted to stand at room temperature or 50° for varying lengths of time, converted to the esters and fractionated.

The reaction of 2 moles of tri-*n*-pentylborane with 1 mole of borane in tetrahydrofuran solution was examined in sufficient detail to obtain an understanding both of the approximate rate of equilibration and the composition at equilibrium. In each experiment 300 mmoles of 1-pentene in 200 ml. of tetrahydrofuran was treated with 150 mmoles of borane at 20°. The reaction mixtures were allowed to stand at room temperature, 25°, for 1, 2, 6, 13.5, 24 and 48 hours. At the end of the appropriate time, the reaction mixture was treated with methanol and the products were isolated by fractional distillation.

The results are represented graphically in Fig. 1. It is evident that equilibrium was attained in approximately 12 hours. The same equilibrium mixture was realized in one hour at 50–55°. Under these conditions the major product (61% yield) is methyl di-1-pentaneborinate. By increasing the ratio of diborane to tri-*n*-pentylborane, the composition of the equilibrium mixture is shifted, and the monoalkylborane becomes the dominant species (54% yield).

The data are summarized in Table II.

The rate of equilibration between tricyclopentylborane and diborane is markedly slower than the tri-*n*-pentyl system, as indicated by Fig. 2. It is also of interest that under conditions where di-*n*-pentylborane is the dominant product in the equilibrated mixture from two moles of trialkylborane and one mole of borane (Fig. 1), the cyclopentyl system reveals the dominant products to be the monocyclopentylborane and tricyclopentylborane (Fig. 2).

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[12] The available evidence is that diborane exists in tetrahydrofuran largely in monomeric form: J. R. Elliot, W. L. Roth, G. F. Roedel and E. M. Boldebuck, THIS JOURNAL, **74**, 5211 (1952); B. Rice, J. A. Livasy and G. W. Schaeffer, *ibid.*, **77**, 2750 (1955); B. Rice and H. S. Uchida, *J. Phys. Chem.*, **59**, 650 (1955). Although there is no evidence as to the molecular state of the various alkyl diboranes in this solvent, it is convenient to discuss these reactions in terms of the concentrations and yields of monomeric borane and alkylboranes, and this practice will be utilized here.

[13] H. I. Schlesinger and A. O. Walker, THIS JOURNAL, **57**, 621 (1935); H. I. Schlesinger, L. Horwitz and A. B. Burg, *ibid.*, **58**, 407 (1936).

[14] For a recent study of the ethyldiborane system, see I. J. Solomon, M. J. Klein and K. Hattori, *ibid.*, **80**, 4520 (1958).

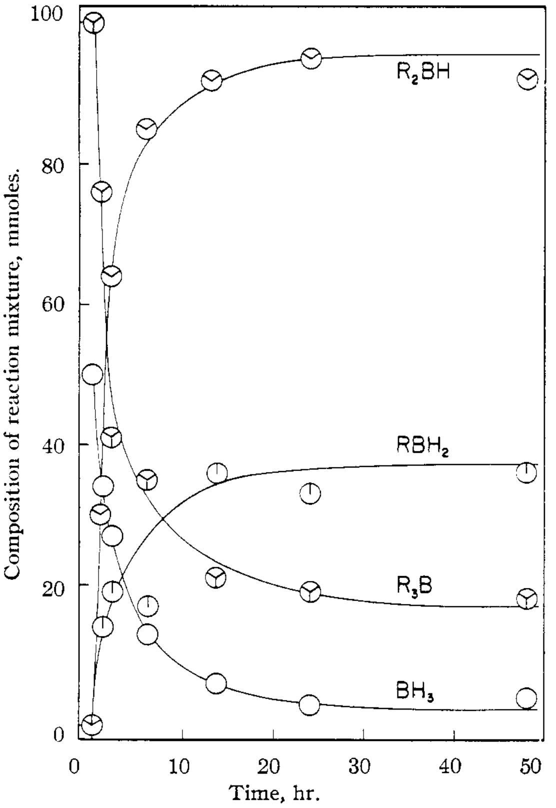

Fig. 1.—Equilibration of tri-*n*-pentylborane (100 mmoles) and diborane (25 mmoles) in tetrahydrofuran at room temperature.

This observation suggests that the dialkylboranes exist in tetrahydrofuran solution as the dimeric species, the tetralkyldiboranes. On this basis, it is not surprising that the large steric requirements of the four cyclopentyl groups should decrease the stability of this species relative to the two other reaction products, RBH_2 and R_3B. The lower steric requirements of the *n*-pentyl group would account for the absence of this effect in the *n*-pentyl system.

TABLE II

EQUILIBRATION OF TRI-*n*-PENTYLBORANE AND DIBORANE IN TETRAHYDROFURAN

Olefin,[a] mmoles	Borane,[c] mmoles	Temp., °C.	Time, hr.	Products,[d] mmoles			
				BH_3	BH_2R	R_2BH	R_3B
300	150	25–30	1	34	14	30	76
300	150	25–30	2	27	19	64	41
300	150	25–30	6	13	17	85	35
300	150	25–30	13.5	6	36	92	21
300	150	25–30	24	3	33	95	19
300	150	25–30	48	4	36	92	18
300	150	50–55	1	5	32	91	26
300	150	50–55	24	7	31	89	18
300	300	25–30	24	85	133	25	32
300	300	50–55	24	99	131	47	19
300	450	25–30	24	254	163	39	21
300[b]	550	50–55	6	328	198	8	31

[a] 200 cc. tetrahydrofuran, except in the last experiment. [b] 500 cc. of tetrahydrofuran. [c] Generated in 10% excess from sodium borohydride and boron trifluoride etherate, assuming a 90% yield. [d] Isolated as the methyl esters after solvolysis with methanol.

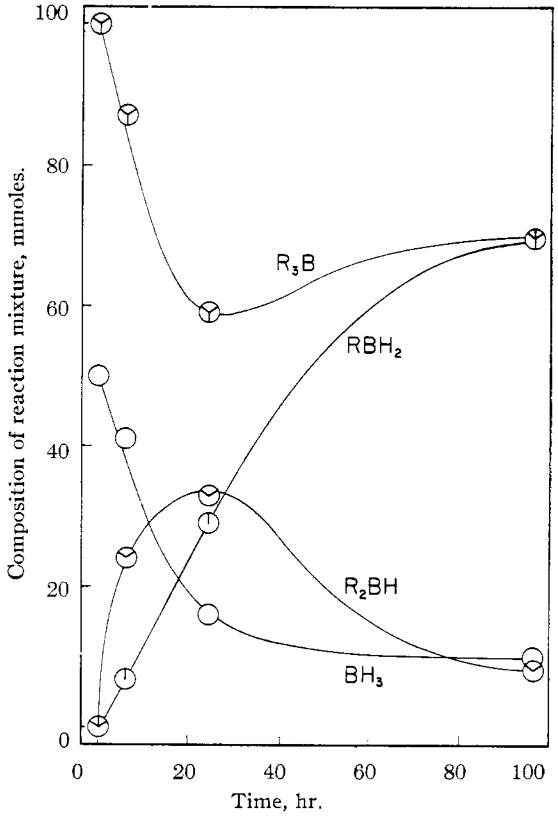

Fig. 2.—Equilibration of tricyclopentylborane (100 mmoles) and diborane (25 mmoles) in tetrahydrofuran at room temperature.

The slowness of the rate of equilibration of tricyclopentylborane with diborane introduces a practical difficulty in the utilization of this reaction for synthetic purposes. Thus, at 25–30° it apparently required most of the 96-hour reaction period for the system to approach equilibrium (Fig. 2). It is, of course, possible to go to somewhat elevated temperatures. Thus, after 24 hours at 50–55° the reaction mixture indicated the formation of 50 mmoles of RBH_2, 8 mmoles of R_2BH and 62 mmoles of R_3B, in reasonable agreement with the data for the 96-hour run at room temperature.

Alternatively, it is possible to take advantage of our observation that the addition of cyclopentene to diborane at 0° results in the predominant formation of the dicyclopentylborane (Table I). Since the latter is the least stable of the three possible cyclopentylboranes, it might be expected to react more readily with diborane than does tricyclopentylborane. This expectation was realized by repeating the 24-hour experiment at room temperature, with the sole change in the experimental procedure being the addition of the cyclopentene to the diborane. At the end of 24 hours, the composition of the reaction mixture corresponded closely to that realized previously in the 96-hour experiment. Similarly, the reaction of 450 mmoles of borane with 300 mmoles of cyclopentene resulted in the formation of 157 mmoles of the boronic ester in 24 hours at room temperature, whereas addition of the olefin to the diborane solution, all other conditions remaining constant, resulted in the formation of 190 mmoles (63% yield) of dimethyl cyclopentaneboronate.

The results are summarized in Table III.

TABLE III

EQUILIBRATION OF TRICYCLOPENTYLBORANE AND DIBORANE IN TETRAHYDROFURAN[a]

Olefin, mmoles	Mode of addition[e]	Borane,[c] mmoles	Time, hr.	Temp., °C.	Products,[d] mmoles			
					BH_3	RBH_2	R_2BH	R_3B
300	A	150	6	25–30	41	7	24	87
300	A	150	24	25–30	16	29	33	59
300	B	150	24	25–30	22	66	15	63
300	A	150	96	25–30	10	70	8	70
300	A	150	24	50–55	10	50	8	62
300	A	300	24	25–30	90	134	6	58
300	A	300	24	50–55	61	177	0	40
300	A	450	24	25–30	280	157	5	44
300	B	450	24	25–30	237	190	0	33
300[b]	B	550	6	25–30	342	219	0	20

[a] 200 cc. of tetrahydrofuran except the last experiment. [b] 500 cc. of tetrahydrofuran. [c] Generated in 10% excess from sodium borohydride and boron trifluoride, assuming a 90% yield. [d] Isolated as the methyl esters after solvolysis with methanol. [e] A: diborane passed into olefin solution; B: olefin added to diborane solution at 0°.

The data indicated that the reaction time could be decreased by running the equilibration at 50–55°, instead of 25°. It likewise appeared that the yields of the monoalkane boronate ester could be improved considerably by using a larger excess of diborane. Unfortunately, tests revealed that diborane is lost by volatilization from concentrated solutions in tetrahydrofuran at 50–55°. The highest concentration of diborane which can be tolerated at 50° without significant loss of the gas is approximately 0.7 *M* in borane.

Consequently, we adopted as a general preparative procedure the addition of 300 mmoles of olefin to 550 mmoles of borane in 500 ml. of tetrahydrofuran at 0°, followed by equilibration for 6 hours at 50°. By this procedure, 1-pentene is converted into dimethyl 1-pentaneboronate in a yield of 66%, and cyclopentene is converted into dimethyl cyclopentaneboronate in a yield of 73%.

Methyl di-1-pentaneborinate can be synthesized in yields of 60–65% either by the partial alkylation of diborane (Table I), or by the reaction of the olefin with one-half the molar amount of borane followed by equilibration (Table II). For the synthesis of methyl dicyclopentaneborinate, the partial alkylation procedure offers the preferred route (Table I).

These esters are readily converted to the acids by hydrolysis with water.[3] Alternatively, other esters are readily realized by treating the initial reaction product, the mono- or dialkylborane, with the appropriate alcohol.

Consequently, hydroboration provides a new, highly convenient synthetic route to the alkane and cycloalkane boronic and borinic acids and esters.

Experimental Part

Materials and Procedures.—Diglyme (diethylene glycol dimethyl ether) was dried over calcium hydride for 4 days, and then distilled under reduced pressure from a small quantity of lithium aluminum hydride, b.p. 72–73° at 25 mm. Tetrahydrofuran was dried over lithium aluminum hydride and distilled from it.[15] Boron trifluoride etherate was purified by distillation under reduced pressure from small amounts of calcium hydride, b.p. 67° at 43 mm.[16]

The 1-pentene and cyclopentene used were Phillips research grade (99%). The methanol was J. T. Baker analytical reagent, and the sodium borohydride was the product of Metal Hydrides, Inc., 98+% pure. These materials were utilized without further treatment.

All experiments were carried out in apparatus dried by heating for 5 hours at 150° and subsequently cooled in a stream of dry nitrogen. All experiments were carried out under an atmosphere of dry nitrogen. Refractive indexes were determined under a stream of dry nitrogen.

Diborane was generated by the addition of a solution of sodium borohydride in diglyme to a solution of boron trifluoride etherate in diglyme.[17] The gas was passed into the tetrahydrofuran, stirred magnetically, and contained in a reaction flask immersed in an appropriate cooling bath. The flask was fitted with an outlet containing acetone to absorb diborane (as diisopropoxyborane) not retained by the tetrahydrofuran. Titration of an aliquot of the acetone, after hydrolysis, for boric acid, in the presence of mannitol, revealed the presence of negligible quantities of boron. Nevertheless, the use of such a trap is a desirable precaution.

Control experiments demonstrated that a 1 *M* solution of diborane in tetrahydrofuran (2 *M* in borane) could be maintained at 25° without significant loss of diborane. However, at 50–55° such a solution lost diborane. A solution 0.35 *M* in diborane (0.7 *M* in borane) could be maintained at 50–55° without significant loss. Accordingly, this concentration was adopted as an upper limit for the diborane solutions used at elevated temperatures.

In handling diborane outside of a vacuum apparatus, some of the hydride is invariably lost in reacting with residual moisture in the solvents and on the apparatus. Tests revealed that the yield of active hydrogen in the tetrahydrofuran solution was 90 ± 3% of the sodium borohydride utilized in the generator. Consequently, we assumed a 90% yield and utilized 10% excess sodium borohydride and boron trifluoride etherate to achieve the presence of the desired quantity of diborane in the reaction flask.

Partial Alkylation of Diborane with 1-Pentene; Synthesis of Methyl Di-1-pentaneborinate.—Diborane, 150 mmoles, generated over a period of 2 hours, was passed into 350 ml. of stirred tetrahydrofuran, at 0°, contained in a 1-l. three-necked flask equipped with a gas dispersion tube (for the diborane), a pressure equalized dropping funnel, and a gas outlet connected *via* a cold finger condenser to an acetone trap. To this diborane solution there was added at 0°, during 1 hour, a solution of 21 g., 300 mmoles, of 1-pentene in 30 ml. of tetrahydrofuran. The reaction was allowed to proceed for one hour, and then methanol (100 ml.) was added slowly. Hydrogen was evolved.[18] The solvent, excess methanol and methyl borate were removed by distillation and an aliquot was analyzed for boric acid by titration with standard sodium hydroxide in the presence of mannitol (boric acid found, 167 mmoles). The residue, distilled *in vacuo*, yielded three fractions: 2.7 g., 19 mmoles, of dimethyl 1-pentaneboronate, b.p. 54–56° at 20 mm.; 16.3 g., 89 mmoles, of methyl di-1-pentaneborinate b.p. 101–104° at 20 mm., a yield of 59%; 3.0 g., 13 mmoles, of tri-*n*-amylborane, b.p. 88–90° at 1.5 mm.

The methyl di-1-pentaneborinate was redistilled, b.p. 91–93° at 10 mm., $n^{20}D$ 1.4238.

Anal. Calcd. for $C_{11}H_{25}BO$: C, 71.75; H, 13.69; B, 5.88. Found: C, 71.54; H, 13.64; B, 5.87.

Partial Alkylation of Diborane with Cyclopentene; Synthesis of Methyl Dicyclopentaneborinate.—The addition of 20.4 g., 300 mmoles, of cyclopentene in 50 cc. of tetrahydrofuran to a solution of 150 mmoles of diborane in 350 cc. of tetrahydrofuran was carried out as described above. After

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(15) Originally we subjected the tetrahydrofuran to a prior treatment with potassium hydroxide pellets. More recently, we have observed that this treatment no longer yields large amounts of colored materials and we have found it possible to dispense with it.

(16) The presence of the calcium hydride facilitates the easy distillation and appears to remove an impurity which forms by-product hydrogen in the reaction with sodium borohydride.

(17) H. C. Brown and P. A. Tierney, THIS JOURNAL, **80**, 1552 (1958); H. C. Brown and B. C. Subba Rao, *ibid.*, **82**, 681 (1960).

(18) Two-thirds of the hydrogen from borane is evolved rapidly at room temperature, the remainder slowly at room temperature, rapidly under reflux.

treatment with methanol and distillation, the following products were obtained: 137 mmoles of methyl borate (by titration as boric acid); 2.59 g., 18 mmoles, of dimethyl cyclopentaneboronate, b.p. 65–66° at 21 mm.; 17.4 g., 96 mmoles, of methyl dicyclopentaneborinate, b.p. 121–122° at 21 mm., a yield of 64%; and 5.0 g., 23 mmoles, of tricyclopentaneborane, b.p. 105–110° at 1.5 mm., solidified in the receiver.

The methyl dicyclopentylborinate was redistilled, b.p. 95–98° at 8 mm., $n^{20}\mathrm{D}$ 1.4717.

Anal. Calcd. for $C_{11}H_{21}BO$: C, 73.35; H, 11.75; B, 6.01. Found; C, 73.01; H, 11.55; B, 6.00.

Attempted Hydroboration at −78°.—Diborane, 150 mmoles, was dissolved in 200 ml. of tetrahydrofuran at 0°. The solution was cooled to −78° and 20.4 g., 300 mmoles, of cyclopentene was added to the solution over a period of 1 hour. After a second hour at −78°, 100 ml. of methanol was added. The hydrogen evolved was 94% of the theoretical amount for the diborane introduced. Distillation gave only small quantities of materials in the range of alkylated products. Evidently, hydroboration does not proceed at −80° in tetrahydrofuran.

The Equilibration of Tri-*n*-pentylborane and Diborane.—In a typical experiment, 150 mmoles of diborane was passed into a stirred solution of 21 g., 300 mmoles, of 1-pentene in 200 ml. of tetrahydrofuran at 0°, over a period of 1.5 hours. The reaction mixture was then permitted to stand at room temperature (25–30°) for 24 hours. Methanol was added and the reaction mixture distilled. The distillate contained the following: 85 mmoles of methyl borate (determined as boric acid); 19.1 g., 133 mmoles, of dimethyl 1-pentaneboronate, b.p. 57–65° at 19 mm., a yield of 44%; 4.56 g., 25 mmoles, of methyl di-1-pentaneborinate, b.p. 105–110° at 19 mm.; 7.1 g., 32 mmoles, of tri-*n*-pentylborane, b.p. 95–100° at 2 mm.

The dimethyl 1-pentaneboronate was redistilled; b.p. 55–57° at 20 mm., $n^{20}\mathrm{D}$ 1.4025.

Anal. Calcd. for $C_7H_{17}BO_2$: C, 58.37; H, 11.90; B, 7.51. Found: C, 58.34; H, 11.80; B, 7.50.

The rate of equilibration was followed by carrying out a number of identical experiments in which 75 mmoles of diborane was passed into a stirred solution of 21 g., 300 mmoles, of 1-pentene in 200 ml. of tetrahydrofuran at 25°, maintaining the temperature at that level with external cooling. After 1, 2, 6, 13.5, 24 and 48 hours at room temperature, the reaction mixture was treated with methanol and the reaction products isolated by distillation. The results are summarized in Table II and represented graphically in Fig. 1.

The Equilibration of Tricyclopentylborane and Diborane.—Since the rate of equilibration at room temperature was slow, it was more convenient to carry the reaction out at 50–55°. Diborane, 300 mmoles, was passed into a solution of 20.4 g., 300 mmoles, of cyclopentene in 200 ml. of tetrahydrofuran at 0°. The reaction mixture was heated to 50–55° and maintained at that temperature for 24 hours. After treatment with methanol, the product was distilled. There was obtained: 61 mmoles of methyl borate (determined as boric acid); 25.1 g., 177 mmoles, of dimethyl cyclopentaneboronate, b.p. 57–59° at 19 mm., a yield of 59%; and 8.5 g., 39 mmoles, of tricyclopentylborane, b.p. 100–110° at 1.5 mm.

The dimethyl cyclopentaneboronate was redistilled, b.p. 60–62° at 20 mm., $n^{20}\mathrm{D}$ 1.4300.

Anal. Calcd. for $C_7H_{15}BO_2$: C, 59.20; H, 10.65; B, 7.62. Found: C, 59.01; H, 10.81; B, 7.62.

Inverse addition provided a means of achieving equilibration in 24 hours at room temperature. To a stirred solution of 450 mmoles of diborane in 200 ml. of tetrahydrofuran at 0° there was added 20.4 g., 300 mmoles, of cyclopentene in 50 ml. of tetrahydrofuran. The reaction mixture was maintained at room temperature, 25–30°, for 24 hours. After treatment with methanol, distillation gave 27.0 g., 190 mmoles, of dimethyl cyclopentaneboronate and 7.3 g., 33 mmoles, of tricyclopentylborane.

The rates of equilibration was followed in the manner described for tri-*n*-pentylborane. Because of the slowness of the equilibration, the individual reactions were permitted to run for 6, 24 and 96 hours. The results are summarized in Table III and Fig. 2. It should be pointed out that the points do not completely define the lines shown in Fig. 2, but a number of other observations indicate that the system has reached final equilibrium in 96 hours (compare data for reaction at 50–55° for 24 hours).

Preparative Procedure for Dimethyl Cyclopentaneboronate.—To a magnetically stirred mixture of 110 ml. of freshly distilled boron trifluoride etherate and 20 ml. of diglyme in a 1-l. round-bottomed flask equipped with a side arm there was added from a pressure equalized dropping funnel 500 ml. of a 1.0 *M* solution of sodium borohydride in diglyme over a period of 1.5 hours, maintaining a slight stream of nitrogen. At the end of the addition, the flask was heated to 80–100° for 0.5 hr. to drive out residual diborane. The diborane thus generated was passed *via* a sintered glass dispersion tube into a 1-l. three-necked flask containing 500 ml. of tetrahydrofuran, magnetically stirred at 0°, and equipped with a thermometer and condenser. The top of the condenser was connected *via* a Dry Ice condenser to a wash bottle containing acetone with the inlet tube dipping beneath the surface of a layer of mercury. At the end of the generation of diborane, the sintered glass bubbler was removed from the reaction flask and was rapidly replaced by a pressure equalized dropping funnel containing a mixture of 20.4 g., 300 mmoles, of cyclopentene and 50 ml. of tetrahydrofuran. This mixture was added over 9.5 hour to the stirred solution of diborane at 0°. The reaction mixture was then heated to 50–55° and maintained thereat for 5 hours. The reaction mixture was then cooled to room temperature, and 100 ml. of methanol was placed in the dropping funnel, and added to the reaction mixture over 0.5 hour. Hydrogen was evolved.[18]

The dropping funnel was then replaced by a capillary through which a fine stream of nitrogen was introduced into the flask, the condenser replaced by a 12″ Vigreux column, and the materials volatile below 80° were removed by distillation at atmospheric pressure. There was obtained 31.0 g. of dimethyl cyclopentaneboronate, b.p. 57–59° at 19 mm., a yield of 73%.

Preparative Procedure for Dimethyl *n*-Pentaneboronate.—The procedure was identical to the above, with one exception. Because of the comparative rapidity of equilibration the diborane was passed directly into a solution of the 1-pentene in tetrahydrofuran at 0°. After 6 hours at 50–55°, and the usual work-up, there was obtained 28.8 g. of dimethyl 1-pentaneboronate, b. p. 55–57° at 70 mm., a yield of 66%.

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