interval in the dark and the reaction allowed to proceed to completion.

The resulting solutions of toluene and chlorotoluene in acetic acid were then transferred to a continuous liquid-liquid extractor, 1500 ml. of water added, and the mixture subjected to extraction for 16–20 hours with carbon disulfide. The resulting extract was concentrated by the distillation of the carbon disulfide in a small column, and the residual carbon disulfide and toluene were removed by fractionation in a Todd micro column. Yields of monochlorotoluene of 78–81% were realized. The column was washed down with carbon disulfide and the combined washings and product were utilized for infrared analysis of the *o*- and *p*-chlorotoluenes in dilute (0.25 *M*) carbon disulfide solution, using the wave lengths 9.48 μ for *o*- and 12.44 μ for *p*-.

Small quantities of benzyl chloride interfered with the analysis for the *meta* isomer. To ensure the absence of benzyl chloride, 2,4,6-collidine (b.p. 169° at 750 mm.) was added to the reaction product and the material distilled through the Todd micro column. The fraction collected included a trace of toluene and an excess of the collidine. The base was extracted with hydrochloric acid and the chlorotoluene fraction was dried over calcium hydride.

The resulting product was analyzed for *ortho* and *para* isomers as before. No significant change in the isomer distribution was observed as a consequence of these manipulations. The product was analyzed for the *meta* isomer using the wave length of 12.98 μ and a differential infrared technique with *o*- and *p*-chlorotoluene in the reference cell.

The characteristic bands for the dichlorinated toluenes were absent from spectra obtained in concentrated carbon disulfide solutions and as the pure chlorotoluenes. Consequently, the reaction had proceeded to the monochlorotoluene stage and no further.

These procedures were extensively tested through the recovery of synthetic mixtures of the chlorotoluenes and toluene from acetic acid solutions. In these experiments we realized average recoveries of 95% and analyses for *o*- and *p*-chlorotoluene which agree with the synthetic composition with an average error of 1–1.5%. The precision of the analyses for the much smaller content of the *meta* isomer was considerably lower, with a mean error of 15% indicated. The results of these analyses are summarized in Table VIII.

TABLE VIII

THE ANALYSIS OF SYNTHETIC MIXTURES OF THE CHLOROTOLUENES ISOLATED FROM ACETIC ACID SOLUTIONS

Run	Mole % chlorotoluene Known *ortho*	 *meta*	 *para*	 Found *ortho*	 *meta*	 *para*	Recovery,[a] %
1^b	63.93	1.21	34.86	64.30	1.45	34.25	95.5
2^b	64.18	0.72	35.10	64.57	0.66	34.77	95.2
3^b	64.02	.83	35.15	64.45	.75	34.80	95.8
4^b	61.55	.53	37.92	62.20	.45	37.35	100.5
5^b	60.13	..	39.87	61.49	..	38.51	93.5
4^{a,c,d}	...	..	...	62.25	0.36	37.39	...
6^c	60.23	1.12	38.65	59.50	1.28	39.22	90.1
7^c	59.65	0.52	39.83	59.17	0.41	40.42	...
8^c	58.59	0.71	40.70	60.22	0.69	39.09	...

[a] Chlorotoluenes recovered from solutions of acetic acid based on analysis of pot composition. [b] Analysis performed on pot residues. [c] Analyses performed on isolated chlorotoluene fraction after distillation from 2,4,6-collidine. [d] The results of the subsequent distillation of run 4 from 2,4,6-collidine.

Isomer Distribution in *m*-Xylene.—Two chlorinations were carried out under the conditions of procedure B and the isolation and extraction were achieved in a manner similar to that utilized for the *o*- and *p*-chlorotoluenes. Since *m*-xylene possesses a very strong band at 13.07 μ, the only suitable wave length for 2-chloro-1,3-dimethylbenzene, it was necessary to remove the *m*-xylene by fractionation from the reaction product prior to the infrared analysis. Analysis for 4-chloro-1,3-dimethylbenzene was based on the absorption band at 12.45 μ. The procedure was tested on a synthetic mixture containing 5 ml. of *m*-xylene, 7.48 g. (74.7%) of 4- and 2.53 (25.3%) of 2-chloro-1,3-dimethylbenzene. After recovery from acetic acid, the analysis indicated 7.24 g. (72.0%) 4- and 2.81 g. (28.0%) 2-chloro-1,3-dimethylbenzene. The isomer distribution and recoveries in the actual chlorination experiments are summarized in Table III.

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LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Organoboron Compounds. II. Preparation and Properties of Some Trialkylboroxines[1–3]

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An azeotropic distillation process has been found to be convenient for the quantitative dehydration of large laboratory quantities of organoboronic acids. A number of new or heretofore unpurified trialkylboroxines have been prepared, purified and characterized. The trialkylboroxines have been found to undergo disproportionation to a very slight extent above 200° into boric oxide and trialkylboranes but to be completely stable on distillation at lower temperatures.

For the preparation of a series of alkyldichloroboranes a variety of trialkylboroxines was required. The preparation, purification and characterization of a number of trialkylboroxines from the corresponding alkylboronic acids are reported in the present paper. A direct procedure for the preparation of trialkylboroxines without isolation of the boronic acids is also described.

Experimental

***n*-Butyl-, *sec*-Butyl-, *t*-Butyl-, *n*-Amyl-, Cyclohexyl- and *n*-Hexylboronic Acids.**—These were prepared in three- or four-mole quantities by the method of Snyder, Kuck and Johnson,[4] as previously described.[1]

Methylboronic Acid.—Some modifications of the standard procedure[4] were required for the preparation of methylboronic acid. This preparation is therefore described in detail. A 3-liter, 3-neck flask was equipped with a condenser, high speed Tru-bore stirrer, a 2-liter dropping funnel with delivery tube bent to deliver solution to the center of the flask and a bridge-bubbler system to supply and maintain a nitrogen atmosphere. A solid carbon dioxide trap to

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[1] Paper I, P. A. McCusker and L. J. Glunz, THIS JOURNAL, **77**, 4253 (1955).

[2] The authors acknowledge with thanks helpful discussions with Professor G. F. Hennion.

[3] Trialkylboroxines are also known as trialkylboroxols, alkylboron oxides and alkylboronic acid anhydrides.

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

catch any trimethylborane also was provided. The flask was flushed out with dry nitrogen and 264 g. (3.5 moles) of methyl borate in one liter of ether was added. The solution was cooled to solid carbon dioxide temperature and three moles of methylmagnesium bromide in one liter of ether was added with vigorous stirring, over a period of 4 hr. The mixture was then allowed to warm to room temperature (overnight) with stirring. It was next refluxed for 2 hr. during which 10 ml. of trimethylborane was collected in the solid carbon dioxide trap. An ice-bath was then placed around the reaction flask, and 15% sulfuric acid (150 ml.) was added until layer separation occurred. The lower layer consisted of a suspension of magnesium salts. The upper layer was forced over by nitrogen pressure into a 2-liter separatory funnel and was shaken with 50 ml. of water. The excess water was removed and the ether solution was dried over calcium chloride. The dried ether solution was fractionated at a 5-1 reflux ratio through a 60-cm. glass-helix packed column. Slow distillation was required to prevent carry-over of the volatile methylboronic acid. When the head temperature reached 40°, 50 ml. of water was added. Distillation was continued to remove methanol until the head temperature passed 65°; 100 ml. of benzene was then added and distillation continued until the head temperature reached 75°. The two-layer solution was then allowed to cool until crystals separated. The crystals were filtered and recrystallized from a benzene–ligroin mixture. The aqueous layer was separated, saturated with calcium chloride and extracted with ether. Benzene was added to the dried ether and the ether was removed by distillation. The benzene was allowed to cool until solid separated. The combined yield of crystals was 60 g. (33%).

Dehydration of Alkylboronic Acids.—The preparation of tri-*n*-butylboroxine from *n*-butylboronic acid will be described as typical of the procedure found satisfactory for the dehydration of alkylboronic acids, butyl and higher. Three moles of *n*-butylboronic acid was dissolved in 150 ml. of benzene, and the solution was refluxed with a Stark–Dean apparatus. Over a period of 24 hr. the calculated amount of water was separated and no more water distilled over. The excess benzene was then removed by distillation through a 60-cm. column and the residue distilled under vacuum. Product was collected at 134° at 16 mm. (yield 90%). Replacement of the benzene by toluene or xylene gave more rapid dehydration. The higher boiling solvents were used where there was sufficient difference in the boiling points of the product and solvent to permit easy separation by fractional distillation.

Triethyl-, Tri-*n*-propyl- and Triisopropylboroxines.—The preparation of these compounds was conveniently carried out without isolation of the intermediate boronic acids. The apparatus was the same as that used for the preparation of methylboronic acid and the same procedure was followed through the addition of benzene. At this point the solution was refluxed with the Stark–Dean apparatus and water and methanol removed. Excess benzene was removed by distillation and the residues were fractionated through a 60-cm., glass-helix packed column to give products with boiling ranges less than 0.1°. The physical constants for these and other alkylboroxines obtained are listed in Table II.

Trimethylboroxine.—This compound could not be prepared from the boronic acid by the azeotropic distillation process because its boiling point is too close to that of benzene. The great volatility of methylboronic acid also increases the difficulty of dehydration. A fairly satisfactory dehydration was effected according to the following procedure. Crude methylboronic acid (83 g., 1.4 moles) was placed in a 500-ml., round-bottom flask, fitted with a distilling head, condenser and receiver; 200 ml. of concentrated sulfuric acid was added and the mixture heated immediately to cause distillation. Within ten minutes all the crude methylboroxine distilled between 78 and 82°, to give 21 g. (36% yield) of product. Refractionation of this liquid gave 20 g. of product boiling at 79.5–80.0° at 732 mm.

Attempts to dehydrate methylboronic acid by the use of phosphoric anhydride in ether and 85% phosphoric acid were unsuccessful. Heating of the mixtures caused sudden evolution of gas, and polymeric residues were obtained.

Ethyl-, *n*-Propyl- and Isopropylboronic Acids.—These were most conveniently prepared by the addition of the calculated amount of water to the purified alkylboroxines. Hydrolysis to white crystalline solids occurred immediately. The acids were then recrystallized from benzene–ligroin mixtures. Previously unreported melting points for the alkylboronic acids prepared are listed in Table I.

Physical Properties and Analyses.—Densities were obtained using a 5-ml. Lipkin pycnometer flushed out with dry nitrogen and filled by nitrogen pressure. Refractive indexes were measured with an Abbé refractometer by forcing samples by nitrogen pressure between the prisms of the refractometer which had been previously flushed with nitrogen. The trialkylboroxines were analyzed for boron by a potentiometric titration with sodium hydroxide in the presence of mannitol.

Disproportionation Studies.—The resistance of the trialkylboroxines to disproportionation was studied by subjecting the compounds to repeated fractional distillation in a 60-cm., glass-helix packed column at a variety of pressures to control the distillation temperatures. Series of fractions were collected and their refractive indexes and densities measured. When fractions of constant index of refraction and density were obtained and no residue of boric acid was observed, it was concluded that no disproportionation occurred. In cases where residues of boric oxide were observed, fractions of varying index of refraction and density also were obtained.

Results and Discussion

The method of Snyder, Kuck and Johnson[4] is capable of giving high yields of the alkylboronic acids, propyl- and above. In large runs of several moles efficient stirring is necessary to avoid incomplete reaction, but under favorable conditions yields of 70% readily are obtained. For the preparation of ethyl- or methylboronic acid, however, care must be taken to avoid losses due to water solubility and volatility. Particularly in the case of the methylboronic acid, salting out of the aqueous layers and careful fractionation of ether from the solution are necessary to obtain satisfactory yields. Methylboronic acid is sufficiently volatile to be largely carried over with ether on a simple distillation. Previously unreported melting points of some alkylboronic acids are listed in Table I.

TABLE I

MELTING POINTS OF ALKYLBORONIC ACIDS

R–	M.p., °C.
CH_3–	96–100
C_2H_5–	166–167
i-C_3H_7–	160–162
s-C_4H_9–	87–88
Cyclo-C_6H_{11}–	119–120

Dehydration of alkylboronic acids may be accomplished in a number of ways.[4] As a general procedure, however, the azeotropic distillation process offers several advantages. It is applicable to any acid whose anhydride boils above the boiling point of benzene, can be used for large or small quantities and gives practically quantitative yields. Its use also makes unnecessary the isolation of the intermediate acid. All the alkylboronic acids dehydrated in our work have sufficiently high dissociation pressures that the water is readily removed on azeotropic distillation. Recently Mattraw, Erickson and Laubengayer[5] made an extensive study of *n*-butylboronic acid and its anhydride and reported that about 6% of the acid was dissociated into water and boroxine at 68°, with the percentage dissociation increasing as the temperature increased. This partial dissociation is

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(5) H. C. Mattraw, C. E. Erickson and A. W. Laubengayer, THIS JOURNAL, **78**, 4901 (1956).

sufficient to permit complete removal of the water with benzene and similar solvents.

Of the trialkylboroxines prepared in this work only the methyl-,[6] *n*-butyl-[4,5] and *t*-butyl- have been characterized previously. *n*-Propyl- and isobutyl-[7] have been mentioned as products of the oxidation of the corresponding trialkylboranes but were not isolated. The physical properties of the trialkylboroxines prepared in this work are listed in Table II.

TABLE II

PHYSICAL PROPERTIES OF SOME TRIALKYLBOROXINES

Trialkyl boroxine	B.p. °C.	Mm.	d^{25}	$n^{25}\text{D}$	Boron, % Calcd.	Obsd.
Methyl	80	742				
Ethyl	153	736	0.8963	1.3958	19.3	19.2
n-Propyl	109.5	25	.8746	1.4080	15.4	15.3
i-Propyl	184.3	748	.8558	1.4305	15.4	15.5
n-Butyl	134	16	.8718	1.4175	..	..
i-Butyl	96	5	.8540	1.4127	12.8	12.6
t-Butyl	89	17	....	....	(M.p. 30–31°)	
n-Amyl	121	1	.8675	1.4275	..	..
n-Hexyl	211	23	.8654	1.4337	..	..

The liquid trialkylboroxines absorb oxygen only slowly from the air and can be handled easily by maintaining an atmosphere of nitrogen in the containers used. Repeated fractional distillations in packed columns gave products of constant refractive index and density as long as the distillation was carried out below about 200°. This behavior establishes the fact that under these conditions of relatively low temperatures the cyclic trialkylboroxines are completely resistant to disproportionation.

An attempted purification of tri-*n*-amylboroxine, by fractional distillation at atmospheric pressure, however, resulted in appreciable disproportionation. Five fractions were collected whose boiling points ranged from 241 to 273°, and a large residue of boric oxide remained. The densities of the five fractions increased steadily from 0.80743 to 0.84329 while the refractive indexes showed only a small and insignificant change from fraction to fraction. The densities of the trialkylboranes are about 10% lower[8] than the densities of the trialkylboroxines, but the refractive indexes differ by about only 1%. Thus the densities were much more sensitive to the presence of trialkylborane with trialkylboroxine in the fractions. The density of the highest boiling fraction is significantly lower than the density of tri-*n*-amylboroxine, 0.8675. It is concluded from these data that the distillation of tri-*n*-amylboroxine at atmospheric pressure (240–270°) results in appreciable disproportionation into boric oxide, which remains as a residue, and tri-*n*-alkylborane which appears in the distillate with undecomposed tri-*n*-amylboroxine. An entirely similar result was observed on the fractional distillation of tri-*n*-hexylboroxine at atmospheric pressure.

The formation of boric oxide and the indications of the formation of trialkylborane in the disproportionation reaction lead to the following equation for the disproportionation. $(RBO)_3 \rightarrow R_3B + B_2O_3$. The equilibrium point for the disproportionation reaction is apparently so far to the left at temperatures below 200° that effectively no disproportionation occurs. At higher temperatures the equilibrium shifts more to the right, and, even though only a small proportion of disproportionation products is present in the equilibrium mixture, the lower boiling trialkylborane is removed from the equilibrium mixture by volatilization, and the reaction proceeds appreciably in the forward direction. That this equilibrium disproportionation does occur with trialkylboroxines is further suggested by the observation of Goubeau and Keller[9] that quantitative conversion to trimethylboroxine was effected by heating trimethylborane and boric oxide in a bomb[10] at 300–330°. Mattraw, Erickson and Laubengayer[5] also observed in their measurements that an irreversible decomposition took place when the system was heated above 284°, and low vapor density values were obtained. If disproportionation into alkylborane and boric oxide occurred, reformation of trialkylboroxine would be slow and trialkylborane may have been present.

In all cases the anhydrides were obtained in the trimeric form as indicated by boiling point. There is apparently little tendency for the trialkylboroxines to form higher cyclic polymers or linear polymers. This is in contrast to the dialkylsilicon oxides which form a number of cyclic molecules which are convertible to one another and to linear polymers.

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(6) A. Burg, THIS JOURNAL, **62**, 2228 (1940).

(7) E. Krause and R. Nitsche, *Ber.*, **54**, 2784 (1921).

(8) Unpublished work by the authors.

(9) J. Goubeau and H. Keller, *Z. anorg. allgem. Chem.*, **267**, 1 (1951).

(10) While Goubeau and Keller found that no reaction occurred between trimethylborane and boric oxide *at atmospheric pressure* even at high temperature, we found recently that all higher trialkylboranes can be made to react almost quantitatively with boric oxide to produce the trialkylboroxines, merely by refluxing at atmospheric pressure.