ORGANOBORON COMPOUNDS

COMMUNICATION 56.* SYNTHESIS OF TRIALKYLBORINES FROM METABORIC ESTERS AND THEIR CONVERSION INTO DIALKYLBORINIC ESTERS

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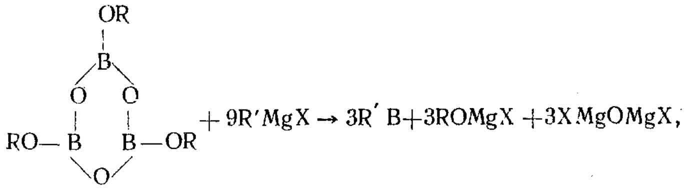
Metaboric esters react with arylmagnesium halides with formation of diarylborinic acids [1]. It may be supposed that the analogous reaction between metaborates and aliphatic organomagnesium compounds will provide a simple route to the relatively difficultly accessible dialkylborinic acids or their esters. The first experiments in this direction appeared to confirm that reaction proceeded in this way. In fact, when a mixture of reactants (6-6.5 moles of Grignard reagent per mole of trimeric metaboric ester [2]) was heated for two hours, followed by hydrolysis with dilute hydrochloric acid and removal of solvents and excess of alcohols at atmospheric pressure, dialkylborinic esters were isolated in 60-65% yield from the residue.

A more detailed study of the process showed, however, that the primary products are not dialkylborinic esters, but trialkylborines. This was shown by a series of experiments in which after the hydrolysis of the reaction mixture solvents and alcohol were removed in a vacuum at low pressure in presence of an excess of water. Under these conditions, even with a ratio of Grignard reagent to metaborate of 6 : 1, the main reaction products were trialkylborines (40-45%,) the yield of dialkylborinic anhydrides did not exceed 10%, and 30-35% of the metaboric ester remained unchanged. With increase in the amount of Grignard reagent to 9-9.5 moles per mole of trimeric metaboric ester, the yield of trialkylborine rose to 70-80% with almost complete utilization of the metaborate



$+ 9R'MgX \rightarrow 3R'B + 3ROMgX + 3XMgOMgX,$

where $R' = i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_5H_{11}$; $R = i\text{-}C_4H_9$, $\text{cyclo-}C_6H_{11}$; $X = Cl$, Br

In this way we prepared triisopropyl-, tributyl-, and triisopentyl-borines. It should be noted that the synthesis of trialkylborines from metaboric esters is very simple and convenient and can be recommended equally with the synthesis from boron trifluoride for the preparation of organoboron compounds of this class.

It was natural to assume that the formation of dialkylborinic esters in our first experiments was to be explained by reaction between the primarily formed trialkylborines and alcohol during the distillation of the alcohol

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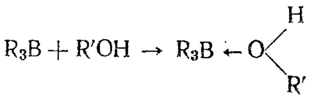
*For Communication 52 see Doklady Akad. Nauk SSSR 130, 782 (1960); for Communications 53 and 54 see Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 368, 370 (1960); for Communication 55 see Doklady Akad. Nauk SSSR 131, 843 (1960) [see C. B. translations].

at atmospheric pressure. The next stage of the work therefore appeared to be the study of the action of alcohols on individual trialkyl borines. These experiments showed, on the one hand, the correctness of this assumption and, on the other, the possibility of passing smoothly from various trialkylborines to dialkylborinic esters.

The reaction between trialkylborines and alcohols was first observed by Meerwein and co-workers [3]. By heating triethylborine with 2,2,2-trichloro- or 2,2,2-tribromo-ethanol, they obtained the corresponding diethylborinic ester. According to the authors, the reaction was accompanied by the liberation of ethane. Ulmschneider and Goubeau [4] found that, when heated for a long time with ethylene glycol or pinacol at 340°, trimethylborine is converted into the corresponding cyclic methaneboronic ester with elimination of two molecules of methane. By heating trimethylborine with pyrocatechol at 290°, the same authors obtained the cyclic pyrocatechol ester of methaneboronic acid [4].

We investigated the action of cyclohexyl, benzyl, 1-methylheptyl, and isopentyl alcohols on triisopropyl-, tributyl-, and triisopentyl-borines and found that in all cases the corresponding dialkylborinic esters were formed smoothly. Reaction proceeded at 140-160° and was complete in 1.5-2 hours. It was accompanied by the liberation not only of saturated hydrocarbons, but also of the corresponding unsaturated hydrocarbons and hydrogen.

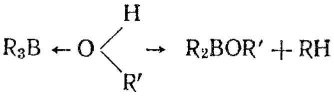
The reaction between trialkylborines and alcohols evidently proceeds through the intermediate stage of the formation of the formation of the complex compound (I)



$$R_3B + R'OH \rightarrow R_3B \leftarrow O\begin{matrix}H\\R'\end{matrix}$$

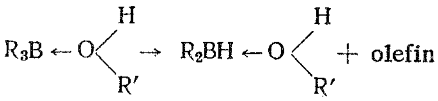
(I)

which may then break down in accordance with (1) with formation of a dialkylborinic acid and a saturated hydrocarbon



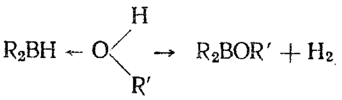
$$R_3B \leftarrow O\begin{matrix}H\\R'\end{matrix} \rightarrow R_2BOR' + RH \tag{1}$$

or may eliminate an olefin and be converted into an unstable complex compound of alcohol and dialkylborine



$$R_3B \leftarrow O\begin{matrix}H\\R'\end{matrix} \rightarrow R_2BH \leftarrow O\begin{matrix}H\\R'\end{matrix} + \text{olefin} \tag{2}$$

The complex (II) is then converted into a dialkylborinic ester with liberation of hydrogen



$$R_2BH \leftarrow O\begin{matrix}H\\R'\end{matrix} \rightarrow R_2BOR' + H_2 \tag{3}$$

It was recently shown that, when heated, triethylborine is slowly converted into dibutylborine and butene [5]. The value that we observed for the rate of reaction between trialkylborines and alcohols with liberation of olefin indicates that the complexes (I) rapidly break down in accordance with (2), whereas trialkylborines are converted only extremely slowly into dialkylborines.

The relative rates of the two reactions, i.e., that proceeding according to Equation (1) and that proceeding according to Equations (2) and (3), are determined by the natures of the trialkylborines and the alcohols. From the relative amounts of saturated and unsaturated hydrocarbons formed in the reaction it follows that in the reaction of 2-octanol with triisopropylborine the ratio of the rates of the above two processes is 1 : 2.5, whereas in the reaction of triisopropylborine with cyclohexanol the formation of cyclohexyl diisopropylborinate proceeds mainly by the second mechanism [Equations (2) and (3).] The reaction between tributylborine and isopentyl alcohol proceeds by both mechanisms, which operate at equal rates.

The reaction between trialkylborines and alcohols is a very convenient preparative method for the synthesis of dialkylborinic esters. The synthesis can be carried out in one stage, without isolating the pure trialkylborines (obtained from a metaboric ester or boron trifluoride), by direct treatment of the reaction mixture with the appropriate alcohol.

Substance	Yield (%)	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	Found (%)			Calculated (%)		
					C	H	B	C	H	B
$(n\text{-}C_4H_9)_2BOC_6H_{11}$-cyclo	85,4	120,5—121,0 (9)	0,8416	1,4460	75,21 75,23	13,19 13,14	4,70 4,92	75,00	13,04	4,83
$(n\text{-}C_4H_9)_2BOCH_2C_6H_5$	87,2	141,5—142,0 (8)	0,8871	1,4793	77,55 77,63	10,89 10,76	4,57 4,46	77,59	10,85	4,66
$(i\text{-}C_4H_9)_2BOC_6H_{11}$-cyclo	87,7	104,0—105,0 (7)	0,8331	1,4421	75,28 75,22	13,41 13,30	4,89 5,20	75,00	13,04	4,83
$(i\text{-}C_5H_{11})_2BOC_6H_{11}$- cyclo	86,6	133,5—134,0 (9)	0,8392	1,4472	76,15 76,31	13,01 13,17	4,34 4,44	76,18	13,19	4,29
$(i\text{-}C_5H_{11})_2BOCH_2C_6H_5$	92,3	141,5—142,0 (4,5)	0,8790	1,4760	78,20 78,44	11,37 11,40	4,40 4,45	78,46	11,23	4,16

Trialkylborines react not only with alcohols, but also with phenols, with formation of borinic esters. Thus, heating of a mixture of phenol and triisopentylborine to 170-180° gave phenyl diisopentylborinate.

EXPERIMENTAL

All operations connected with the preparation and transformations of trialkylborines were carried out in a pure dry nitrogen atmosphere.

Synthesis of Trialkylborines

Tributylborine. A benzene solution of 22.5 g (0.075 mole) of isobutyl metaborate was added as quickly as possible to a vigorously stirred solution of butylmagnesium bromide prepared from 18.3 g (0.75 g-atom) of magnesium and 102.8 g (0.75 mole) of butyl bromide in 300 ml of dry ether; no cooling was applied. When the vigorous boiling caused by the reaction between the metaboric ester and butylmagnesium bromide stopped, the reaction mixture was boiled for a further two hours. When cool, the reaction product was treated with 325 ml of 7% hydrochloric acid. The ether layer was separated and mixed with 40 ml of oxygen-free water. Solvents and isobutyl alcohol were removed in a vacuum in presence of excess of water, and the residue was separated and fractionally distilled. This gave 27.8 g (78%) of tributylborine, b.p. 96-97° (17 mm.)

Triisopentylborine. Triisopentylborine was prepared under the same conditions as tributylborine. For reaction we took 18.3 g (0.75 g-atom) of magnesium, 80 g (0.75 mole) of isopentyl chloride, 250 ml of dry ether, and 22.5 g (0.075 mole) of isobutyl metaborate as a 50% solution in benzene. The yield of triisopentylborine, b.p. 114-116° (11 mm) and $n^{20}D$ 1.4321, was 37.9 g (75.1%.)

Triisopropylborine. Over a period of 15 min a solution of 0.9 mole of isopropylmagnesium chloride in 350 ml of dry ether was added with vigorous stirring to 35.9 g (0.095 mole) of cyclohexyl metaborate; no cooling was applied. The reaction mixture was boiled for two hours, and solvent was removed at atmospheric pressure; triisopropylborine was then distilled from the residue of magnesium salts at a residual pressure of 20 mm. Redistillation gave 26.7 g (66.8%) of triisopropylborine, b.p. 76-77° (83 mm.)

Reaction of Trialkylborines with Alcohols

1-Methylheptyl diisopropylborinate. A three-necked flask fitted with reflux condenser, thermometer, and tube for passage of nitrogen was charged with 8.6 g (0.06 mole of triisopropylborine and 8.0 g (0.06 mole) of 2-octanol. The apparatus was connected through a condenser to a gas holder. When the mixture was heated to 130°, a steady evolution of gas began. In the course of 90 min the amount of gas attained 1600 ml and the temperature of the mixture rose to 180°.

When the evolution of gas stopped, the apparatus was cooled and purged with 200 ml of pure nitrogen. Analysis indicated that the gas mixture contained 0.031 mole of propene, 0.0173 mole of hydrogen, and 0.0116 mole of propane. Fractionation of the liquid products gave 10.3 g (74.2%) of 1-methylheptyl diisopropylborinate; b.p. 119-120° (18 mm); $n^{20}D$ 1.4202; d^{20}_4 0.7833. Found: C 74.24; 74.31, H 13.98, 13.74, B 5.24, 4.82%; $C_{14}H_{31}BO$. Calculated: C 74.33, H 13.81, B 4.78%.

Cyclohexyl diisopropylborinate. For reaction we took 9.84 g (0.07 mole) of triisopropylborine and an equimolecular amount of cyclohexanol. The reaction mixture was heated for two hours and the gas liberated amounted to 2900 ml; toward the end of the heating the temperature rose to 190°. Analysis indicated that the gas mixture contained 0.049 mole of propene, 0.047 mole of hydrogen, and 0.013 mole of propane. The liquid reaction products were vacuum-fractionated. This gave 11.5 g (83.5%) of cyclohexyl diisopropylborinate; b.p. 83.0-83.5° (8 mm); d^{20}_4 0.8314; $n^{20}D$ 1.4372. Found: C 73.80, 73.82, H 12.92, 12.74, B 5.36, 5.18%. $C_{12}H_{25}BO$. Calculated: C 73.48, H 12.85, B 5.52%.

Isopentyl dibutylborinate. A mixture of 15.0 g (0.082 mole) of tributylborine and 7.2 g (0.082 mole) of isopentyl alcohol was boiled for two hours. During the boiling the reaction temperature rose from 130° to 210°; simultaneously 2500 ml of gas were liberated, and this contained 0.035 mole of butene, 0.037 mole of hydrogen and 0.33 mole of butane. Distillation of the liquid products gave 14.6 g (83.6%) of isopentyl dibutylborinate; b.p. 114.5-115.5° (15 mm); d^{20}_4 0.7907; $n^{20}D$ 1.4240. Found: C 73.64, 73.36, H 13.85, 14.01, B 5.27, 5.02%. $C_{13}H_{29}BO$. Calculated: C 73.58, H 13.78, B 5.10%.

Phenyl diisopentylborinate. A mixture of 13.2 g (0.06 mole) of triisopentylborine and 5.0 g (0.06 mole) of phenol was heated for 90 min at 170-180°. A mixture (3.25 g) of isopentane and isopentene was condensed in a trap, which was cooled during the experiment to -75°. Vacuum-distillation of the residue gave 10.9 g (75.1%) of phenyl diisopentylborinate, b.p. 122-126° (4 mm.) After redistillation it had: b.p. 121.0-123.5° (3 mm); $n^{20}D$ 1.4712; d^{20}_4 0.8697. Found: C 78.01, 77.98, H 11.27, 11.40, B 4.46, 4.64%. $C_{16}H_{27}BO$. Calculated: C 78.05, H 11.06, B 4.39%.

Synthesis of Dialkylborinic Esters from Metaboric Esters without the Isolation of Trialkylborines

Over a period of 10-15 min 0.055 mole of isobutyl metaborate as a 50% benzene solution was added to a vigorously stirred solution of 0.5 mole of alkylmagnesium halide in 2 moles of ether; no cooling was applied. When the evolution of heat stopped, the reaction mixture was boiled for two hours and then treated with 225 ml of 7% hydrochloric acid. The organoboron layer was separated and evaporated down; it was then heated for two hours with the appropriate alcohol, after which the mixture was vacuum-distilled. The results are given in the table. All the dialkylborinic esters obtained are colorless mobile liquids which mix in all proportions with most organic solvents; they oxidize in air.

SUMMARY

1. Metaboric esters react with alkylmagnesium halides with formation of trialkylborines.

2. When heated with cyclohexanol, benzyl alcohol, 2-octanol, isopentyl alcohol, or phenol, trialkylborines are converted smoothly into the corresponding dialkylborinic esters.

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* Original Russian pagination. See C. B. translation.