REACTIONS OF MONO-AND DI-CARBOXYLIC ACIDS WITH TRIALKYLBORINES AND TRIALKYLALUMINUMS

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The reactions of carboxylic acids with alkyl and aryl derivatives of boron have been little studied. In 1936 Meerwein and co-workers [1] described the reaction of triethylborine with acetic and o-chlorobenzoic acids, which proceeds with the replacement of one of the boron-attached ethyl groups by an acyloxy group; the authors state that under more severe conditions the other boron-attached ethyls may also be replaced. In the reaction between chlorodiphenylborine and acetic acid, instead of the expected mixed diphenylborinic acetic anhydride, i.e., diphenylboron acetate, Mikhailov and Fedotov [2] isolated a mixed diphenylpyroboronic acetic anhydride, i.e., bis(acetoxyphenylboron) oxide, which was probably formed as a result of the further reaction of the initially formed product with acetic acid. Mikhailov and Shchegoleva [3] carried out the reaction between butyl 1-propanechloroboronate and acetic acid, and as a result of a series of transformations they isolated bis(acetoxypropylboron) oxide as final product. Until recently there was no information in the literature on the reaction between trialkyl(or aryl)aluminums and carboxylic acids. In 1961 Zakharkin, Kolesnikov, and co-workers [4] described the reaction of trialkylaluminums with various saturated carboxylic acids. In the present paper we present the results of a study of the reaction of trialkylborines with saturated and unsaturated carboxylic acids

$$\mathrm{RCOOH} + \mathrm{BR}_3' \rightarrow \mathrm{RCOOBR}_2' + \mathrm{R'H}$$

in which

$$\mathrm{R} = \mathrm{CH_3},\ \mathrm{C_2H_5},\ \mathrm{CH_2} = \mathrm{C}\ (\mathrm{CH_3});\ \mathrm{R}^1 = \mathrm{p\text{-}C_4H_9}\ .$$

The reaction was carried out in an inert solvent, and during the reaction a saturated hydrocarbon was liberated in an amount close to that calculated. By this method we obtained the mixed anhydrides of dibutylborinic and acetic acids, dibutylborinic and propionic acids, and dibutylborinic and methacrylic acids; the properties of these are presented in Table 1.

However, mixed anhydrides of dialkylborinic and carboxylic acids are obtained only when the molar ratio of carboxylic acid to trialkylborine is 0.75 : 1; with equimolecular amounts of the reactants, in addition to these dialkylboron alkanoates we obtained also the mixed pyroboronic carboxylic anhydrides bis(acetoxybutylboron) oxide, bis[buty(propionyloxy)boron] oxide, and bis[(benzoyloxy)butylboron] oxide of general formula $\mathrm{R'B(OOCR)-O-B \cdot (OOCR)R'}$, in which $\mathrm{R = CH_3, C_2H_5, C_6H_5}$; $\mathrm{R' = n\text{-}C_4H_9}$. The properties of these products are presented in Table 2.

A study was made of the mass thermal polymerization and polymerization in presence of initiators (azodiisobutyronitrile, t-butyl hydroperoxide, tributylborine) of dibutylboron methacrylate. As a result we obtained viscous liquids or waxlike solid polymers, which were insoluble in the usual organic solvents, but soluble in N,N-dimethylformamide. Dibutylboron methacrylate copolymerizes with methyl methacrylate and with styrene in all proportions with formation of semitransparent glasslike polymers which are almost insoluble in organic solvents. We examined also the extension of this reaction of alkylborines and alkylaluminums with carboxylic acids to dicarboxylic acids. At a molar ratio of trialkylborine or trialkylaluminum to dicarboxylic acid of 2 : 1, under the conditions described above we obtained bisdialkylboron dicarboxylates and also bisdialkylaluminum dicarboxylates of general formula $\mathrm{R_2MOOC(CH_2)_xCOOMR_2}$, in which $\mathrm{R = C_3H_7}$, n- and $\mathrm{i\text{-}C_4H_9}$; x = 4 and 7; M = B and Al. The properties of the compounds obtained are presented in Table 3.

TABLE 1. Properties of Mixed Anhydrides of Dialkylborinic and Carboxylic Acids of the Type $RCOOBR'_2$ (dialkylboron alkanoates)

R	R¹	B.p. in °C (p in mm)	Yield (%)	n_D^{20}	d_{20}^{20}	B (%)	
						found	calc.
CH_3—	n-C_4H_9	78—80 (4)	28,6	1,4202	—	5,59 5,38	5,88
C_2H_5—	n-C_4H_9	84—85 (4)	25,2	1,4318	0,8582	5,53 5,21	5,46
$CH_2=$ $=C(CH_3)$	n-C_4H_9	81—83 (3)	62,0	—	0,8667	5,42* 5,20	5,10

*Found: C 68.92, 69.20; H 12.24, 12.32%. Calculated: C 68.59; H 11.03%.

TABLE 2. Properties of Mixed Anhydrides of Dialkylpyroboronic and Carboxylic Acids of the Type R'B(OOCR)−O−B(OOCR)R' [Bis(acyloxy)alkylboron Oxides]

R	R¹	B.p. in °C (p in mm)	Yield (%)	B (%)	
				found	calc.
CH_3—	n-C_4H_9	M.p. 45	54,8	7,95	8,02
C_2H_5—	n-C_4H_9	119—121(3)	50,0	6,84 7,03	7,26
C_6H_5—	n-C_4H_9	170 (2) M.p. 68°	42,0	4,64 * 4,63	5,49

*Found: C 68.09, 67.86; H 7.10, 6.96%. Calculated: C 67.05; H 7.16%.

It must be mentioned that in the case of the reaction between triisobutylaluminum and adipic acid in equimolecular proportions we isolated a white powder, which decomposed in air and was difficultly soluble in organic solvents; it was possibly a polymer of the type $[-Al(C_4H_9)-OOC(CH_2)_4COO-]_n$. In reaction between tributylborine and adipic acid in equimolecular proportions we isolated bisdibutylboron adipate, but in a considerably reduced yield.

EXPERIMENTAL

Dibutylboron acetate. A three-necked flask fitted with stirrer, reflux condenser, and a special funnel for dropwise addition in a stream of nitrogen was charged with a solution of 10 g (0.05 mole) of tributylborine in 10 ml of dry hexane; a solution of 3.3 g (0.05 mole) of carefully purified acetic acid in an equal volume of hexane was then added with external cooling of the flask with cold water. In a gas holder connected to the apparatus 800 ml of gaseous butane collected. At the end of the reaction the contents of the flask were heated gently for two hours, and the reaction mixture was vacuum-fractionated. We obtained 2.5 g (28.6%) of a colorless liquid. The residue from the distillation was bis(acetoxybutylboron) oxide, a white crystalline substance which readily hydrolyzes in air; m. p. 45° (in a sealed capillary).

TABLE 3. Properties of Bisdialkylboron or Bisdialkylaluminum Dicarboxylates of the Type $R_2MOOC(CH_2)_xCOOMR_2$

M	x	R	B.p. in °C (p in mm)	Yield (%)	n_D^{20}	B (%)	
						found	calc.
B	4	p-C_4H_9	82—83 (3)	29,8	1,4169	5,22,5,32	5,49
B	4	p-C_3H_7	39—42 (3)	30,0	1,4051	6,53,6,73	6,39
B	7	p-C_4H_9	110—111 (9)	22,3	1,4221	5,30,5,54	4,95
Al	4	i-C_4H_9	158—159 (6)	33,3	—	12,03	12,65

Dibutylboron propionate. This was prepared analogously from 7.6 g (0.04 mole) of tributylborine and 2.25 ml (0.03 mole) of purified propionic acid: a colorless liquid, yield 2.4 g (41.8%).

Bis[butyl(propionyloxy)boron] oxide. This was obtained in the form of the residue remaining after solvent and dibutylboron propionate had been distilled off after the reaction between 10 g (0.005 mole) of tributylborine and 4 g (0.05 mole) of propionic acid. We obtained 1.4 g (50.0%) of viscous liquid.

Bis[(benzoyloxy)butylboron] oxide. The above-described apparatus was charged with 7.6 g (0.04 mole) of tributylborine in 10 ml of dry benzene, and a solution of 5.1 g (0.04 mole) of freshly crystallized benzoic acid in 50 ml of benzene was added gradually; the reaction was carried out without cooling. The reaction mixture was heated for two hours with gently boiling of the solvent. Volatile substances were distilled off, and the residue was vacuum-distilled through an air condenser. We obtained 3.5 g (42%) of white crystals, m. p. 68°C.

Dibutylboron methacrylate. The above-described apparatus was charged with a solution of 10 g (0.05 mole) of tributylborine in 13 ml of dry hexane, and a little cuprous chloride was added as a polymerization inhibitor. A solution of 2.8 g (0.032 mole) of purified methacrylic acid in an equal volume of hexane was then added with external cooling of the flask with a mixture of ice and salt (−12°); in a gas holder connected to the apparatus we collected about 1 liter of gaseous butane. When the dropwise addition was complete, the contents of the flask were kept at room temperature and stirred for one hour. Vacuum fractionation of the mixture gave 4.15 g (62.0%) of a colorless liquid.

Bisdibutylboron adipate was prepared in the above-described apparatus by adding 31 g (0.17 mole) of tributylborine in 30 ml of hexane to a suspension of 12.5 g (0.085 mole) of recrystallized adipic acid in 13 ml of hexane. The mixture was heated gently for two hours, and 950 ml of butane was collected. Unchanged adipic acid (8.9 g, m. p. 149°) was filtered off. Found: C 49.98, 49.44; H 7.54, 7.62%. $C_6H_{10}O_4$. Calculated: C 49.31; H 6.90%. The filtrate was evaporated and vacuum-distilled. We obtained 9.6 g (29.8%) of the mixed anhydride as a colorless liquid which hydrolyzed in air.

Bisdibutylboron adipate was obtained also in 18.5% yield by the reaction of 10 g (0.05 mole) of tributylborine with 7.3 g (0.05 mole) of adipic acid.

Bisdipropylboron adipate was prepared by the addition of 11.2 g (0.08 mole) of tripropylborine in 15 ml of hexane to a suspension of 5.8 g (0.04 mole) of adipic acid in 10 ml of hexane. We obtained 4 g (30.0%) of product as a colorless readily hydrolyzed liquid; in addition we collected 650 ml of propane and recovered 1.8 g of adipic acid, m. p. 149°.

Bisdibutylboron azelaate was prepared analogously from 14.5 g (0.08 mole) of tributylborine and 15 g (0.04 mole) of recrystallized azelaic acid in 37 ml of hexane; it formed a colorless readily hydrolyzed liquid; yield 10 g (22.3%). We collected 650 ml of butane and recovered 12.9 g of azelaic acid.

Bisdiisobutylaluminum adipate was prepared analogously from 4.5 g (0.03 mole) of purified adipic acid in 5 ml of hexane and 12 g (0.06 mole) of triisobutylaluminum in 15 ml of hexane. We obtained 500 ml of gas, 3.0 g of unchanged adipic acid, m. p. 150°, and 4 g (33.0%) of a clear viscous liquid which rapidly decomposed in air.

Poly(isobutylaluminum) adipate was obtained under analogous conditions from equimolecular amounts of triisobutylaluminum and adipic acid as a powderlike precipitate in 30.0% yield. The product decomposed rapidly in air; it was partially soluble in highly polar solvents (amyl acetate). Found: C 52.33; H 9.05; Al 12.70%. $[-(C_4H_9)-OOC(CH_2)_xCOO-]$. Calculated: C 52.62; H 7.50; Al 11.82%.

SUMMARY

1. Mixed anhydrides of dialkylborinic with saturated and unsaturated carboxylic acids were prepared. The mixed anhydride of dibutylborinic and methacrylic acids is capable of polymerizing and copolymerizing with certain monomers in presence of initiators.

2. In the reaction of trialkylborines with carboxylic acids in equimolecular proportions, as well as the above mixed anhydrides, mixed pyroboronic-carboxylic anhydides, namely dialkylboron acetate, propionate, and benzoate, were isolated.

3. As a result of the reaction of trialkylborines and trialkylaluminums with dicarboxylic acids the mixed anhydrides bisdibutylboron adipate, bisdipropylboron adipate, bisdibutylboron azelaate, and bisdibutylaluminum adipate were obtained; from equimolecular amounts of triisobutylaluminum and adipic acid a product of possibly polymeric character was formed.

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