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Abstract

Full Text

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A NEW METHOD FOR THE SYNTHESIS OF TRIS(TRIALKYL(ARYL)SILYL)BORATES

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Up to the present time, only fragmentary information has been available in the literature on the preparation of silicon-organic esters of boric acid ([1–4]).

The present work is a continuation of our investigations on the dehydrocondensation of trialkyl(aryl)silanes with organic molecules containing oxy-, oxo-, and polyoxy groups.

We previously noted ([5,6]) that trialkyl(aryl)silanes react smoothly with oxy-, carboxy-, and polyoxyorganic compounds in the presence of catalysts of a non-alkaline nature.

We have found that trialkyl(aryl)silanes dehydrocondense with boric acid, without the formation of by-products, in the presence of small additions, 0.01–1% (based on the trialkyl(aryl)silane), of anhydrous halides of cobalt, nickel, palladium, and platinum, giving the corresponding tris(trialkyl(aryl)silyl)borates in yields of up to 90–95% of theory.

The reaction is carried out by heating a mixture of the starting components at 100–130° and is readily controlled by the rate and amount of hydrogen evolved. The process proceeds according to the simplest scheme:

$$3R_3SiH + (OH)_3B \longrightarrow (R_3SiO)_3B + 3H_2.$$

The tris(trialkyl(aryl)silyl)borates obtained by this method are of high purity and are colorless liquids with a characteristic odor, distilling without decomposition. They are readily hydrolyzed by water and by dilute alkalis and acids.

Table 1 gives the physical constants, yields, and analytical data for the tris(trialkyl(aryl)silyl)borates obtained by us.

Table 1

Tris(trialkyl(aryl)silyl)borates

$(R_3SiO)_3B$ R_3Si—	b.p., °C/mm Hg	d_4^{20}	n_D^{20}	B, %, calc.	B, %, found	Si, %, calc.	Si, %, found	Reaction duration, min	Yield, %
$(C_2H_5)_3Si$—	195/9.5*	0.8921	1.4380	2.68	2.67; 2.65	20.83	20.88; 21.00	480	94.1
$(n\text{-}C_3H_7)_3Si$—	215–217/1	0.8662	1.4425	2.04	2.08; 2.00	15.87	15.60; 15.68	52	90.6
$(n\text{-}C_4H_9)_3Si$—	273–274/3	0.8753	1.4488	1.65	1.62; 1.69	12.82	12.73; 12.85	55	88.7
$CH_3(n\text{-}C_3H_7)_2Si$—	185/3	0.8661**	1.4308	2.42	2.40; 2.45	18.86	18.68; 18.90	45	95.5
$CH_3(n\text{-}C_4H_9)_2Si$—	232/4	0.8736	1.4370	2.04	2.01; 2.09	15.87	15.70; 15.86	210	89.8
$CH_3(n\text{-}C_6H_{11})_2Si$—	273–274/9	0.8613	1.4410	1.76	1.74; 1.79	13.70	13.59; 13.36	42	94.2
$C_2H_5(n\text{-}C_3H_7)_2Si$—	214/3	0.8768	1.4410	2.21	2.23; 2.30	17.24	16.20; 16.77	180	96.7
$C_2H_5(n\text{-}C_4H_9)_2Si$—	235/3	0.8875	1.4462	1.89	1.91; 1.96	14.70	14.75; 15.21	219	95.8
$C_2H_5(n\text{-}C_6H_{11})_2Si$—	297–298/11	0.8753	1.4480	1.65	1.72; 1.62	12.82	12.82; 12.74	47	95.1
$C_2H_5(C_6H_5)_2Si$—	354–358/8	1.086***	1.5796*	1.56	1.60; 1.57	12.16	12.17; 12.13	147	92.5

* Literature data (4): b.p. 178-179°/13 mm; d_4^{20} 0.8918; n_D^{20} 1.4382.

** Literature data (4): b.p. 157-160°/1 mm; d_4^{20} 0.8668; n_D^{20} 1.4332.

*** At 50° (viscous liquid).

Experimental Part

Starting reagents. Trialkyl(aryl)silanes were obtained by the reaction of trichlorosilane, methyldichlorosilane, and ethyldichlorosilane with the corresponding magnesium haloalkyls and were purified on a column (high-boiling in vacuum).

Boric acid—a chemically pure preparation—was ground to a fine powder and dried over calcium chloride.

Halides of cobalt, nickel, palladium, and platinum—pure preparations—were carefully dehydrated according to the general procedure (7).

Analysis. Boron in tris(trialkyl(aryl)silyl)borates was determined as boric acid by titrating a weighed sample of the substance in an aqueous-alcoholic medium in the presence of mannitol with 0.2 N KOH solution (thymol blue indicator).

The titer of the alkali solution was determined using an aqueous-alcoholic solution of pure boric acid of the same concentration, in which the boric anhydride content had previously been determined (by the gravimetric method).

Silicon was determined from the difference between the sum of the oxides of silicon and boron formed upon mineralization of a weighed sample of the substance with a mixture of oleum and conc. nitric acid, followed by ignition of the oxides at 900–950° (4).

Typical synthesis of tris(ethyldi-iso-amylsilyl)borate. A mixture of 34 g (0.17 g-mole) of ethyldi-iso-amylsilane, 3.1 g (0.05 g-mole) of orthoboric acid, and 0.1 g (0.0077 g-mole) of anhydrous nickel chloride was heated until the evolution of hydrogen had completely ceased (47 min) at a temperature of 110–120°. Distillation of the reaction mixture gave 31.3 g of tris(ethyldi-iso-amylsilyl)borate with b.p. 296–300°/11 mm, i.e., 95% of theory. After a second distillation, tris(ethyldi-iso-amylsilyl)borate had b.p. 297-298°/11 mm; d_4^{20} 0.8757; n_D^{20} 1.4480.

Found, %: B 1.72; 1.62; Si 12.82; 12.74
$C_{36}H_{81}Si_3O_3B$. Calculated, %: B 1.65; Si 12.82

Syntheses of other tris(trialkyl(aryl)silyl)borates were carried out analogously to the preceding one at a temperature of 100–130° and a molar ratio $R_3SiH : (OH)_3 : B : MX$ equal to 0.17 : 0.05 : 0.0077.

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