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Alkoxysilanes. VIII. The Preparation of Alkoxysiloxy Derivatives of Aluminum and Boron

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In order to obtain a polymer containing a heterosiloxane linkage in the molecular main chain, we have already reported on the preparation of alkoxysiloxy derivatives of metals (Sb,[1] Ti,[2] Zr,[3] Sn). In the present experimental work, the preparation of the derivatives of aluminum and boron was attempted.

The reaction of triiso-propoxyaluminum or tri-*n*-butyl borate with tri-*t*-butoxysilanol was investigated; it was difficult to isolate the reaction product in 1:1 molar ratio of the silanol to triisopropoxyaluminum by recrystallization and distillation because of its high solubility in solvents or because of its decomposition. The reaction in the 3: 1 molar ratio caused decomposition during the removal of the solvent from the reaction mixture and led to the formation of a gel insoluble in organic solvents. The gas evolved during the decomposition was identified as isobutylene by means of gas chromatography. Therefore, it was considered that, in this reaction, the rupture of the alkoxy group attached to silicon occurred along with alcohol exchange. This reaction is very different from that of the metal alkoxides with the silanol. The difference may be attributed to the property as Lewis acids of aluminum compounds. In the 2:1 molar ratio, however, bis(tri-*t*-butoxysiloxy)-isopropoxyaluminum (I) was isolated by recrystallization (mp 75—76°C). The results of the molecular-weight determination indicated that it was associated. On the other hand, tri-*t*-butoxydi-*n*-butoxy (II) and bis(tri-*t*-butoxysiloxy)*n*-butoxysiloxyboron (III) were easily obtained as viscous liquids, however, it seems difficult to replace the last *n*-butoxy group attached to boron by the butoxysiloxy group because of its steric hindrance.

$$\mathrm{M(OR)_3} + n(\mathrm{Bu}^t\mathrm{O})_3\mathrm{SiOH} \longrightarrow [(\mathrm{Bu}^t\mathrm{O})_3\mathrm{SiO}]_n\mathrm{M(OR)}_{3-n} + n\mathrm{ROH}$$

where $\mathrm{M}=\mathrm{Al}$, $\mathrm{R}=\mathrm{Pr}^i$, and $n=2$ (I); $\mathrm{M}=\mathrm{B}$, $\mathrm{R}=\mathrm{Bu}^n$ and $n=1$ (II) or 2 (III)

The reaction of acetylacetonatodiisopropoxyaluminum with the silanol gave bis(tri-*t*-butoxysiloxy)acetylacetonatoaluminum (IV), as in the case of titanium, zirconium, and tin. Bis(tri-*t*-butoxysiloxy)isopropoxyaluminum is associated, while this compound is monomeric (Table 1). The difference seems to be ascribed to the coordination of the carbonyl group in the acetylacetonato to aluminum.[4] These compounds were identified by means of elemental analysis, as is shown in Table 1, and by studying the IR spectra, which were essentially identical and which showed the IR absorption peaks at 1050—1075 ($\nu_{\mathrm{Si-O-C}}$ and $\nu_{\mathrm{Si-O-Al}}$[5]) and 1320 ($\nu_{\mathrm{B-O-C}}$), 1500—1600(AcAc) cm^{-1}. The reaction products from bis(acetylacetonato)isopropoxyaluminum, however, were almost all tri(acetylacetonato)-aluminum. In this case, therfore, disproportionation

Table 1. Alkoxysiloxy derivatives of Al and B

Reagents (g)		Product						
$\mathrm{M(OR)_3}$	$\mathrm{(BuO)_3}$-SiOH		Yield (%)	Mp, °C Bp °C/mmHg	n_{D}^{20} or mol wt Found (Calcd)	Anal. Found % (Calcd)		
						C	H	Si
5.6	16.5	(I)	36.4	75—76[b]	1300 (613)	52.29 (52.92)	10.18 (9.96)	9.71[c] (9.50)
7.6	8.7	(II)	38.1	125—121.5/2	1.4102	57.22 (57.30)	10.54 (10.75)	6.60 (6.70)
2.7	6.2	(III)	41.0	167—169/1.5	1.4128	54.58 (55.02)	10.80 (10.30)	8.92 (9.22)
5.6[a]	11.8	(IV)	29.3	60—61[b]	710 (685)	54.26 (54.60)	8.97 (9.73)	8.45[d] (8.61)
3.5[a]	8.4	(V)	—	280 (Decomp)	—	49.68 (48.77)	8.95 (8.75)	11.78[e] (11.79)
3.2	2.9	(VI)	—	290/2 (Decomp)	650 (625)	45.00 (45.40)	8.47 (8.52)	12.83 (13.31)

Benzene was used as a solvent. a) $\mathrm{(AcAc)Al(OPr^{\mathit{i}})_2}$ as reagent. b) Recrystallized from benzene (IV) or *n*-hexane. c) Al%, Found: 3.91 (Calcd: 4.41); d) 8.45 (8.61); e) 8.12 (8.79).

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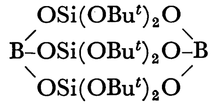
may occur:

$$(AcAc)Al(OPr^i)_2 + 2(Bu^tO)_3SiOH \longrightarrow [(Bu^tO)_3SiO]_2Al(AcAc) + 2Pr^iOH$$
(IV)

$$3(AcAc)_2Al(OPr^i) + 2(Bu^tO)_3SiOH \longrightarrow 2Al(AcAc)_3 + [(Bu^tO)_3SiO]_2Al(OPr^i) + 2Pr^iOH$$

In order to obtain a polymeric substance, the reaction of acetylacetonatodiisopropoxyaluminum or tri-*n*-butyl borate with di-*t*-butoxy and bis(tri-*t*-butoxysiloxy)silanediol was carried out: with di-*t*-butoxysilanediol, a little tri(acetylacetonato)aluminum and a powder (decomposed at 200°C) soluble in organic solvents were formed, whereas with bis(tri-*t*-butoxysiloxy)silanediol, needle crystals (decomposed at 280°C) almost insoluble in solvents were obtained (V). It was shown, by means of studying the IR spectra and by the elemental analysis, that these substances contained the Si–O–Al bond together with the acetyl-acetonato groups, and that the former had an atom ratio of C: H: Si equal to 6: 13: 1 and that the latter has a unit structure of $[-Al(AcAc)-O-Si[OSi(OBu^t)_3]_2-O-]_n$, although the structures were not confirmed. On the other hand, it was difficult to isolate the products formed by the reaction of tri-*n*-butyl borate with the diols by recrystallization or distillation, however, the results of the study of the IR spectra, the elemental analysis, and the molecular weight determination showed that the raw material obtained by the reaction of the alkoxide with di-*t*-butoxysilanediol was in accordance with the following formula:



$$B\begin{cases} OSi(OBu^t)_2O \\ OSi(OBu^t)_2O \\ OSi(OBu^t)_2O \end{cases}B$$

(VI)[6]

Experimental

Materials. The alkoxysilanols were prepared by the method already described.[2,7] Commercially-available aluminum triisopropoxide was redistilled before use. The tri-*n*-butyl borate was obtained by the reaction of boric anhydride with *n*-butyl alcohol according to the procedure of Walton and Rosenbaum;[8] bp 107—109°C/1 mmHg, n_D^{20} 1.4089. The acetylacetonatodiisopropoxyaluminum was afforded by Thomas method;[4] bp 147—148°C/2 mmHg.

Preparation of Compounds (I) and (II). A mixture of metal alkoxide or acetylacetonato chelate, silanol, and benzene was refluxed for 1 hr. The solvent was then removed, and the residue was fractionally distilled *in vacuo* or recrystallized from *n*-hexane or benzene. The results are shown in Table 1.

Reaction of Acetylacetonatodiisopropoxyaluminum with Silanediols. A mixture of 3.5 g (0.014 mol) of the acetylacetonato chelate, 8.4 g (0.014 mol) of bis(tri-*t*-butoxysiloxy)silanediol, and 30 m*l* of benzene was heated. White needle crystals appeared at 70°C; then the mixture was further heated for 30 min. The crystals were filtered and washed with benzene (yield 8.1 g). The analytical data are shown in Table 1.

In another run, a mixture of 4.0 g (0.016 mol) of the chelate, 3.4 g (0.016 mol) of di-*t*-butoxysilanediol, and 30 m*l* of toluene was refluxed for 1 hr. The solvent was then removed, and the residue was recrystallized from *n*-hexane, giving 0.5 g of needle crystals; mp 187—190°C. Found: C, 54.42; H, 6.38; Al, 8.41% (tris(acetylacetonato)aluminum). The filtrate gave a yellow powder (3.7 g) after the removal of the solvent; mp about 200°C (decomposed).

Analysis. The silicon was determined by a method already described. The aluminum was determined to be aluminum oxide after a weighed sample had been decomposed by an aqueous alcohol solution.

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