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# Alkoxysilanes. VI. The Preparation of Alkoxysiloxy Derivatives of Zirconium and Tin

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Tetrakis(tri-*t*-butoxysiloxy)zirconium (I) or tin (III), bis(tri-*t*-butoxysiloxy)diisopropoxyzirconium (II) or di-*t*-butoxytin (IV), and bis(tri-*t*-butoxysiloxy)bis(acetylacetonato)zirconium (V) or tin (VI) were prepared in the same way as in the cases of antimony[1] and titanium:[2]

$$\mathrm{M(OR)_4} + n\mathrm{(Bu^tO)_3SiOH} \longrightarrow [\mathrm{(Bu^tO)_3SiO}]_n\mathrm{M(OR)}_{4-n} + n\mathrm{ROH}$$

where M=Zr, $n=4$ (I); $n=2$ (II) and M=Sn, $n=4$ (III); $n=2$ (IV)

$$\mathrm{(Acac)_2M(OR)_2} + 2\mathrm{(Bu^tO)_3SiOH} \longrightarrow [\mathrm{(Bu^tO)_3SiO}]_2\mathrm{M(Acac)_2} + 2\mathrm{ROH}$$

where M=Zr (V) and M=Sn (VI).

The results of the elemental analysis and of the measurements of the IR and NMR spectra are given in Table 1. As compared to the cases of silicon[3] and titanium, (I) and (III) were more easily formed, probably indicating that the increase in the atomic radii of these metals led to an easy introduction of the tri-*t*-butoxysiloxy group. The results of the molecular-weight determination indicated that (I) and (II) are dimeric.[4] They may have an associated structure built up by a zirconosiloxane bridge similar to the alkoxy bridge in metal alkoxide.[5] It was observed that the absorption peaks due to the Si–O–M bond[6] shifted toward higher wave numbers with an increase in the atomic weight of the metals (Ti<Zr<Sn), and that the proton signals of the *t*-butyl group shifted toward an appreciably lower field in the sequence of Ti<Zr<Sn. (V) was very stable and could be distilled, while the other products were decomposed at relative low temperatures.

The preparation of a polymeric substance with Si–O–M bond was attempted; the reaction of zirconium tetraisopropoxide with di-*t*-butoxysilanediol in the molar ratio of 1:2 or 1:3 (alkoxide: silanediol) gave a glassy solid with a relatively low decomposition point (140—150 or 120—130°C). With bis(tri-*t*-butoxysiloxy)silanediol, a highly viscous liquid was obtained. On the other hand, the reaction of tin tetra-*t*-butoxide with this diol gave a white crystal which was identified as having a unit structure $[-\mathrm{Sn(OBu^t)_2{-}O{-}Si[O{-}Si(OBu^t)_3]_2{-}O{-}}]_n$. The reaction of bis(acetylacetonato)-diisopropoxyzirconium with di-*t*-butoxysilanediol afforded polybis(acetylacetonato)zirconosiloxane, which was confirmed to have the structure of $[-\mathrm{Zr(Acac)_2{-}O{-}Si(OBu^t)_2{-}O{-}}]_n$ ($n\fallingdotseq4$). In order to compare the thermal stability of this compound with that of polytitanosiloxane,[2] the TGA curve was measured. The results showed that the polyzirconosiloxane was more stable than the polytitanosiloxanes; the weight loss of

TABLE 1. TRI-*t*-BUTOXYSILOXY DERIVATIVES OF Zr AND Sn

| Compd | IR (cm$^{-1}$) Si-O-M | NMR (τ) | | Mp[d] Bp°C/mmHg | Yield (%) | Anal, Found (Calcd) (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Bu$^t$ and Me | =CH- | | | C | H | Si | M |
| I[a] | 940 | 8.68 | | 150—160 | 75 | 45.98<br>(46.31) | 8.43<br>(8.68) | 9.36<br>(9.03) | 7.80<br>( 7.35) |
| II[b] | 960 | 8.69, 8.22<br>8.73 (sh) | 5.30—5.91[e]<br>(sep) | 166—170 | 65 | 48.49<br>(48.95) | 9.57<br>(9.24) | 8.09<br>(7.64) | 12.50<br>(12.40) |
| III | 1005 | 8.65 | | 121—122 | 24 | 48.74<br>(49.23) | 9.62<br>(9.29) | 9.22<br>(9.56) | 10.14<br>(10.10) |
| IV[c] | — | 8.48 | | 161 | 19 | 48.44<br>(48.55) | 9.33<br>(9.16) | 6.97<br>(7.09) | 14.51<br>(14.81) |
| V | 930 | 9.80, 9.95<br>9.83 (sh) | 5.69 (s) | 69—70<br>210—215/1 | 84 | 50.60<br>(50.10) | 8.43<br>(8.35) | 6.57<br>(6.88) | 11.03<br>(11.17) |
| VI | 930<br>904 (sh) | 8.75<br>8.02, 7.97 (d) | 4.59 (s) | 115 | 56 | 48.32<br>(48.40) | 8.41<br>(8.12) | 6.59<br>(6.66) | 13.89<br>(14.07) |

Mol wt for a, b, and c; Found: 2400, 1280, and 795; Calcd: 1145, 734, and 792.
d: Decomposed; Recrystallized from *n*-hexane.
e: $-\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{H}$; methyne proton.
sh: shoulder, s: singlet, d: doublet, sep: septet

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[1] Y. Abe and I. Kijima, This Bulletin, **42**, 1148 (1969).

[2] Y. Abe and I. Kijima, *ibid.*, **43**, 466 (1970).

[3] Y. Abe and I. Kijima, *ibid.*, **42**, 1118 (1969).

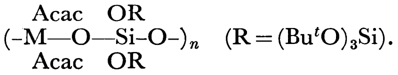
[4] D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, **1959**, 4304.

[5] W. Wardlow, *ibid.*, **1952**, 2027, 4204, 5020.

[6] H. Schmidbaur and M. Schmidt, *J. Amer. Chem. Soc.*, **83**, 2963 (1961).

the former was about 30% at 200°C, whereas that of the latter was about 50% at the same temperature.

The reaction of the zirconium or tin acetylacetonato chelate with bis(tri-*t*-butoxysiloxy)silanediol, on the other hand, gave recrystallizable products with a Si–O–M bond. Although the molecular weight was not measured, the results of the elemental analysis and a study of the IR and NMR spectra indicated that the structure may correspond to:



$$\left(-\overset{\text{Acac}}{\underset{\text{Acac}}{\text{M}}}-\text{O}-\overset{\text{OR}}{\underset{\text{OR}}{\text{Si}}}-\text{O}-\right)_n \quad (\text{R}=(\text{Bu}^t\text{O})_3\text{Si}).$$

## Experimental

*Materials.* The alkoxysilanols were prepared by a method previously described.[2,3] Zirconium tetraisopropoxide was obtained by the distillation of a commercially-available zirconium tetraisopropoxide isopropyl alcohol adduct (bp 195—196°C/3 mmHg).[7] Bis(acetylacetonato)diisopropoxyzirconium was afforded by the distillation of the reaction mixture after a mixture of zirconium tetraisopropoxide, acetylacetone, andbenzene had been refluxed for 1 hr (bp 140—142°C/2 mmHg). Tin tetra-*t*-butoxide (bp 82—83°C/1 mmHg) was prepared by the reaction of tin tetrachloride with *t*-butyl alcohol in the presence of diethylamine. The isolation of bis(acetylacetonato)di-*t*-butoxytin was attempted, but the attempt failed because of its decomposition upon distillation (at about 160°C/1—2 mmHg). The refore, the unpurified tin chelate obtained by the reaction of tin tetra-*t*-butoxide with acetylacetone in benzene was used as the starting material.

*Preparation of Compounds (I)—(IV).* A mixture of metal tetraalkoxide or bis(acetylacetonato)dialkoxymetal, tri-*t*-butoxysilanol (the molar ratio of the silanol to metal alkoxides was 2: 1 or 4: 1),[8] and benzene was refluxed for 1 hr. After the solvent had been removed along with the alcohol formed, the residue was distilled or recrystallized. The compounds thus obtained are given in Table 1.

*The Reaction of Zirconium Tetraisopropoxide with Di-*t*-butoxysilanediol.* A mixture of 4.5 g (0.0137 mol) of the alkoxide, 5.7 g (0.0274 mol) of the diol, and 40 m*l* of ethyl ether was refluxed for 1 hr. The removal of the solvent *in vacuo* gave 7.3 g of a pale yellow solid; mp 140—150°C (decomposed). Found: C, 31.40; H, 6.80; Si, 9.73; Zr, 29.42%. On the other hand, the reaction of 3.2 g (0.098 mol) of the alkoxide and 8.2 g (0.391 mol) of the diol gave 8.1 g of a pale yellow solid; mp 120—130°C (decomposed). Found: C, 30.06; H, 6.75; Si, 15.31; Zr, 15.93%. These polymeric substances were very soluble in common organic solvents.

*Polybis(acetylacetonato)zirconosiloxane.* A mixture of bis(acetylacetonato)diisopropoxyzirconium, di-*t*-butoxysilanediol, and toluene was refluxed for 1 hr. After the solvent had been removed at 100°C *in vacuo*, the residue was further heated for 2 hr to give a dark brown solid; mp 80—90°C. Found: C, 42.65; H, 6.45; Si, 5.43%; mol. wt, 2000. Calcd for $C_{18}H_{32}O_8SiZr$: C, 43.60; H, 6.52; Si, 5.76%; mol. wt, 495×*n*.

*The Reaction of Bis(acetylacetonato)diisopropoxyzirconium or di-*t*-butoxytin with Bis(tri-*t*-butoxysiloxy)silanediol.* A mixture of 8.2 g (0.0201 mol) of bis(acetylacetonato)diisopropoxyzirconium, 11.9 g (0.0201 mol) of the diol, and 40 m*l* of toluene was refluxed for 1 hr. After the solvent had been removed at 160°C, the subsequent evaporation of the solvent *in vacuo* yielded 17.6 g of a dark yellow solid, which was then recrystallized from *n*-hexane to give 10.6 g (56%) of white granular crystals; mp 222—223°C. Found: C, 45.85; H, 7.97; Si, 10.03%. Calcd for $(C_{34}H_{68}O_{14}Si_3Zr)_n$: C, 46.60; H, 7.82; Si, 9.61%. IR: 960 and 925 (shlouder) ($\nu_{Si-O-Zr}$) cm$^{-1}$. NMR: 8.72 (Bu$^t$), 8.06 (Me), and 4.52 (=CH–)τ.

On the other hand, the reaction between bis(acetylacetonato)di-*t*-butoxytin (5.3 g, 0.0112 mol) and the diol (6.6 g, 0.0112 mol) in 50 m*l* of benzene gave 3.2 g of white needle crystals; mp 138—145°C (recrystallized from *n*-hexane; decomposed at 185—190°C). Found: C, 46.27; H, 8.26; Si, 9.48; Sn, 13.19%. Calcd for $(C_{34}H_{68}O_{14}Si_3Sn)_n$: C, 46.84; H, 7.86; Si, 9.67; Sn, 13.61%. IR: 960, 934, and 904 (shoulder) ($\nu_{Si-O-Zr}$) cm$^{-1}$. NMR: 8.72 (Bu$^t$), 8.82 (Me), and 4.76 (=CH–, doublet) τ.

*Analysis.* The silicon was determined by a method described in a previous report. The zirconium was determined to be zirconium dioxide after a weighed sample had been hydrolyzed by means of an aqueous alcohol solution. The tin was determined by iodometry after a weighed sample had been decomposed in concentrated hydrochloric acid containing lead under a carbon dioxide atmosphere.

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[7] The authors wish to thank the Matsumoto Pharmaceutical Co. for supplying the zirconium tetraisopropoxide isopropyl alcohol adduct.

[8] Reagents for (I): 6.3 g (0.0193 mol, $Zr(OPr^i)_4$), 21.1 g (0.0799 mol, $(Bu^tO)_3SiOH$; (II): 11.2 (0.0343), 18.8 (0.0712); (III): 5.8 (0.0141, $Sn(OBu^t)_4$), 14.9 (0.0564); (IV): 9.4 (0.0229), 12.1 (0.0458); (V): 9.6 (0.0236, $(Acac)_2Zr(OPr^i)_2$), 12.5 (0.0473); (VI): 5.9 (0.0128, $(Acac)_2Sn(OBu^t)_2$, 7.1 (0.0269).
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