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SHORT COMMUNICATION

Mono- and trititanates of cyclic nitrilotriethylene triorganotin titanate(IV)

Introduction

The isolation of a series of "mono-", "di-" and "trititanates" of cyclic nitrilotriethylene triorganosilyl titanate(IV) was previously reported from our laboratory[1]. This paper describes the preparation of the tin analogs of the mono- and trititanates: cyclic nitrilotriethylene triphenyltin titanate(IV) (I), cyclic nitrilotriethylene tributyltin titanate(IV) (II), and cyclic nitrilotriethylene tributyltin titanate(IV) bis(nitrilotriethylene) titanate(IV) (III).

$$\mathrm{Ti(OR)_4 + (HOC_2H_4)_3N \rightarrow ROTi(OC_2H_4)_3N + 3\,ROH} \tag{1}$$

$$\mathrm{ROTi(OC_2H_4)_3N + (C_6H_5)_3SnOH \rightarrow \underset{(I)}{(C_6H_5)_3SnOTi(OC_2H_4)_3N} + ROH} \tag{2}$$

$$\mathrm{3\,(C_4H_9)_3SnOAc + 3\,Ti(OR)_4 \rightarrow 3\,(C_4H_9)_3SnOTi(OR)_3 + 3\,ROAc} \tag{3}$$

$$\mathrm{3\,(C_4H_9)_3SnOTi(OR)_3 + 3\,(HOC_2H_4)_3N \rightarrow 3\,\underset{(II)}{(C_4H_9)_3SnOTi(OC_2H_4)_3N} + 9\,ROH} \tag{4}$$

$$\mathrm{3\,(C_4H_9)_3SnOTi(OC_2H_4)_3N \rightarrow (C_4H_9)_3SnOSn(C_4H_9)_3 + \underset{(III)}{[(C_4H_9)_3SnOTi(OC_2H_4)_3N][N(C_2H_4O)_3TiOTi(OC_2H_4)_3N]}} \tag{5}$$

Discussion and results

In the previous paper it was shown that di-, and trititanates of cyclic nitrilotriethylene triorganosilyl titanate(IV) could be formed, depending upon the R groups attached to the silicon and the order of combining the reactants. The possibility of the direct preparation of the trititanate from the monotitanate was suspected, but no experimental evidence was found to prove this hypothesis.

In the case of the tin analogs, (I), cyclic nitrilotriethylene triphenyltin titanate (IV) and (III), cyclic nitrilotriethylene tributyltin titanate(IV) bis(nitrilotriethylene) titanate(IV) could be isolated owing to their insolubility in toluene solvent. However, the monotitanate (II), cyclic nitrilotriethylene tributylstannyl titanate(IV) is a liquid, and on attempted distillation only a small yield of monotitanate (II) is obtained because of rapid conversion to the trititanate (III) (eqn. 4 and 5). A substantially larger yield of monotitanate (II) could probably be achieved by molecular distillation. To form (I), the triphenyltin hydroxide must be carefully purified[2] to eliminate the presence of bis(triphenyltin) oxide and water. The water decomposes the organotitanate[3] preventing the formation of the Sn–O–Ti linkage[4].

Experimental

The solvents were purified by distillation over sodium, and triethanolamine was purified by distillation. All manipulations were carried out in an atmosphere of dry nitrogen. Analyses were performed by The Glidden Company laboratories

(Baltimore, Maryland) and Schwartzkopf Microanalytical Laboratories (Woodside, New York). Molecular weights were measured with a Mechrolab Vapor Pressure Osmometer Model 301A in chloroform or benzene at 37°.

(*a*) *Preparation of cyclic nitrilotriethylene triphenylstannyl titanate*(*IV*) (*I*). Triethanolamine (13.27 ml, 0.10 mole) was added to a solution of tetraisopropyl titanate (29.76 ml, 0.10 mole) in toluene (1000 ml). The isopropanol/toluene azeotrope was removed. Triphenyltin hydroxide (36.70 g, 0.10 mole) recrystallized from ethanol was added as a powder and the isopropanol/toluene azeotrope was removed. The reaction mixture was cooled and filtered, and the residue was washed with toluene/ petroleum ether and dried (25.93 g, 46%), m.p. 205–208° (decomp.). (Found: N, 2.53; Sn, 21.66; Ti, 8.52; mol. wt. VPO in chloroform, 575. $C_{24}H_{27}NO_4SnTi$ calcd.: N, 2.50; Sn, 21.19; Ti, 8.55%; mol. wt., 560.)

The above reaction was repeated in cyclohexane yielding the product in 97% yield. (Found: N, 2.48; Sn, 20.49; Ti, 8.65%.)

(*b*) *Preparation of cyclic nitrilotriethylene tributylstannyl titanate*(*IV*) (*II*). Tributyltin acetate (90.0 g, 0.267 mole) was added to tetrabutyl titanate (90.8 g, 0.267 mole) and the butyl acetate was removed by distillation (28.8 g, 93%). Triethanolamine (35.4 ml, 0.267 mole) was added, and butanol was removed under vacuum. Heat was applied and cyclic nitrilotriethylene tributyltin titanate(IV) was isolated at 74°/0.05 mm; n_D^{28} 1.4592 (3.0 g, 2%). (Found: N, 2.63; Sn, 23.00; Ti, 9.17; mol. wt. VPO in benzene, 530. $C_{18}H_{39}NO_4SnTi$ calcd.: N, 2.80; Sn, 23.74; Ti, 9.58%; mol. wt., 500.) The quantity of distillate was not sufficient to maintain thermal equilibrium at the thermometer bulb and the true boiling point probably is higher than reported.

(*c*) *Preparation of cyclic nitrilotriethylene tributyltin titanate*(*IV*) *bis*(*nitrilotriethylene*) *titanate*(*IV*) (*III*). On standing, cyclic nitrilotriethylene tributyltin titanate(IV) formed a precipitate. This precipitate was filtered and washed with petroleum ether and dried at 110° for one hour, yielding cyclic nitrilotriethylene tributyltin titanate(IV) bis(nitrilotriethylene) titanate(IV). (Found: C, 39.82; H, 7.35; N, 4.39; Sn, 13.23; Ti, 15.24. $C_{30}H_{63}N_3O_{11}SnTi_3$ calcd.: C, 39.85; H, 7.02; N, 4.65; Sn, 13.13; Ti, 15.89%.)

Reaction (*b*) was repeated on a 0.1 mole scale. During attempted distillation of the monotitanate (II), a solid formed in the reaction pot. The precipitate was isolated by filtration, washed with petroleum ether and dried. Analysis shows that the trititanate (III), m.p. 177° (decomp.), was isolated. (Found: C, 39.65; H, 7.27; N, 4.69; Sn, 13.16; Ti, 15.24. $C_{30}H_{63}N_3O_{11}SnTi_3$ calcd.: C, 39.85; H, 7.02; N, 4.65; Sn, 13.13; Ti, 15.89%.)

Preparation of (*III*) *in toluene*. Sublimed tributyltin acetate (16.85 g, 0.05 mole) was added to tetrabutyl titanate (17.11 ml, 0.05 mole) in toluene (600 ml) and the azeotrope was removed and checked by infrared spectra until no butyl acetate could be detected. Triethanolamine (6.64 ml, 0.05 mole) was added, and the butanol/ toluene azeotrope was removed. The precipitate was filtered and washed with petroleum ether yielding cyclic nitrilotriethylene tributyltin titanate(IV) bis(nitrilotriethylene) titanate(IV), m.p. 177° (decomp.). (Found: C, 40.42; H, 7.11; N, 4.63; Sn, 12.63; Ti, 15.78. $C_{30}H_{63}N_3O_{11}SnTi_3$ calcd.: C, 39.85; H, 7.02; N, 4.65; Sn, 13.13; Ti, 15.89%.) The filtrate was distilled, yielding toluene and bis(tributyltin) oxide. (Found: C, 48.55; H, 9.28; Sn, 38.40. $C_{24}H_{54}OSn_2$ calcd.: C, 48.36; H, 9.13; Sn, 39.93%.)

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