PREPARATION AND PROPERTIES OF SOME ORGANOTIN COMPOUNDS

II. β-DIKETONE COMPLEXES OF ALKYLTIN COMPOUNDS

R. C. MEHROTRA AND V. D. GUPTA
The Chemical Laboratories, University of Rajasthan, Jaipur (India)
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In Part I we described some distillable dibutyltin glycolates[1]. The present communication deals with the derivatives of β-diketones of alkyltin(IV) compounds. No systematic study of the derivatives of β-diketones and ketoesters in alkyltin series has previously been carried out. One patent[2] describes the dibutyltin bis(acetylacetonate) as a catalyst for formation of polyurethan in foams, and another[3] describes the compounds formed from $Bu_2Sn(OMe)_2$ and acetoacetic esters as being important for the preparation of foamed materials.

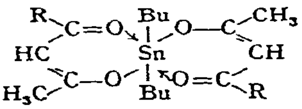
During the present investigations, the reactions of dibutyltin diethoxide with acetylacetone and ketoesters (methyl and ethyl acetoacetates) have been studied. The reactions were carried out in 1:2 molar ratios in dry benzene. The progress of the reaction was checked by the estimation of the ethanol liberated in the fractionated azeotrope. The excess solvent was stripped off under reduced pressure and the products isolated. The equations for the reactions are as follows:

$$2CH_3COCH_2COR + Bu_2Sn(OC_2H_5)_2 \longrightarrow (CH_3COCHCOR)_2SnBu_2 + 2C_2H_5OH$$
$$(R = CH_3,\ OCH_3 \text{ or } OC_2H_5)$$

All the products are highly soluble in benzene and can be distilled under reduced pressure.

Studies of complexes of the dimethyltin(IV) ion[4] in aqueous medium point to the probability of six-coordination at tin, in a chelate complex, in compounds of the type $(CH_3)_2SnL_2$ (L = acetylacetonate). Recently it has been observed[5] that diphenyltin(IV) dioxinate is probably a chelate complex with octahedral stereochemistry. A similar conclusion for the latter type of products was reached by Okawara[6] on the basis of molecular weight, infrared and ultraviolet studies.

In view of the monomeric nature of the derivatives isolated during the course of the present investigations, the following structure can reasonably be suggested for them:



$R = CH_3$, OCH_3 or OC_2H_5

After the above work had been completed, Okawara and coworkers[7] suggested a *trans*-configuration for dimethyltin bis(acetylacetonate), which was shown, on the basis of its spectral similarity with that of copper acetylacetonate, to have four equivalent metal–oxygen bonds.

In view of the strong chelating tendency of acetylacetone, trialkyltin acetylacetonate could be expected to have the tin atom in a 5-coordinated state. The triethyltin acetylacetonate was synthesized by the reaction between triethyltin ethoxide with acetylacetone in equimolar ratio in benzene:

$$CH_3COCH_2COCH_3 + (C_2H_5)_3SnOC_2H_5 \longrightarrow (C_2H_5)_3Sn(CH_3COCHCOCH_3) + C_2H_5OH$$

The product was a white solid, quite soluble in common organic solvents, and could be purified by sublimation under reduced pressure. It was monomeric in boiling benzene.

In recent years, an increasing amount of evidence has accumulated for the presence of five-coordinated tin in the solid state. In the solution state the existence of penta-coordinated tin atom was claimed in Bu_3SnImB where Im = imidiazole and B = basic complexing agent, as a result of viscosity studies[8] in inert solvents. However, it has been claimed[5] on the basis of a spectrophotometric study that triphenyltin oxinate is not a chelate complex and the bonding to the tin atom is presumably tetrahedral.

The existence of 5-coordinated tin in trimethyltin hydroxide[9] has been recently shown by Okawara by infrared studies and by the dimeric nature of the compound in a number of solvents. In view of this it was considered of interest to examine triethyltin ethoxide, but it was found to be monomeric in benzene. Trimethyltin methoxide, in which steric factors, if present in the case of triethyltin ethoxide, would be minimized was prepared by the reaction of trimethyltin chloride with sodium methoxide in presence of benzene. The product, a white solid, which was purified by sublimation under reduced pressure, was found to have only a slight degree (1.2) of association. This was not due to depolymerization at the boiling benzene temperature, because an almost identical result was obtained in ether. It may be that back-coordination from alkoxy oxygen to tin is strong enough in this product to overcome the tendency to polymerization.

EXPERIMENTAL

Apparatus and analytical methods has already been described[1]. Benzene, ethanol and ether were dried as reported[1]. Dibutyltin diethoxide was also synthesized as previously[1]. Methanol was dried over calcium oxide, followed by distillation over magnesium methoxide. Acetylacetone, methyl and ethyl acetoacetates were refluxed over aluminium isopropoxide and fractionated.

Molecular weights were determined by a semimicro-ebulliometer (Gallenkamp) with thermistor sensing.

(i) *Reaction between dibutyltin diethoxide and acetylacetone*

To a benzene (65 g) solution of dibutyltin diethoxide (2.67 g) was added acetylacetone (1.65 g). The reaction mixture was refluxed (bath 110–120°) and the ethanol liberated was fractionated off immediately as the binary azeotrope with benzene. The excess solvent was distilled off. The product was dried under reduced pressure (31°/0.1 mm) and was distilled to yield a light yellow liquid (2.7 g; yield 75 %) at 132°/0.4 mm.

Found: ethanol in the azeotrope 0.72 g (two moles require 0.76 g). (Found: C, 49.1; H, 7.6; Sn, 27.2; mol. wt., 438. $C_{18}H_{32}O_4Sn$ calcd.: C, 50.1; H, 7.48; Sn, 27.5%; mol. wt., 431.)

(ii) Reaction between dibutyltin diethoxide and methyl acetoacetate

Methyl acetoacetate (1.91 g) was added to dibutyltin diethoxide (2.67 g) in benzene (68 g). The mixture was refluxed and the ethanol was fractionated out. The product was dried under reduced pressure (0.2 mm) and distilled to yield a white solid (3.2 g; yield 83%) at 136–138°/0.2–0.3 mm. Found: ethanol in the azeotrope 0.73 g (two moles require 0.76 g). (Found: C, 46.8; H, 7.1; Sn, 25.9; mol. wt., 466. $C_{18}H_{32}O_6Sn$ calcd.: C, 46.6; H, 6.96; Sn, 25.6%; mol. wt., 463.)

(iii) Reaction between dibutyltin diethoxide and ethyl acetoacetate

Ethyl acetoacetate (1.77 g) was added to dibutyltin diethoxide (2.20 g) in the presence of benzene (71 g). The mixture was refluxed and the binary azeotrope of benzene-ethanol was collected at 68–80°. After removal of excess benzene under reduced pressure, the product was distilled which gave a light yellowish liquid (2.07 g, yield 62%) at 154°/0.3 mm. Found: ethanol in the azeotrope 0.60 g (two moles require 0.62 g). (Found: C, 49.0; H, 7.7; Sn, 24.6; mol. wt., 492. $C_{20}H_{36}O_6Sn$ calcd.: C, 48.9; H, 7.38; Sn, 24.1%; mol. wt., 491.)

(iv) Preparation of triethyltin ethoxide

To a refluxing solution of sodium ethoxide (Na, 0.9 g) in ethanol (28 g) was added dropwise triethyltin chloride (8.72 g) in benzene (41 g). The mixture was refluxed for about seven hours and left overnight, and the precipitated sodium chloride was then filtered off. Excess ethanol and benzene were removed under reduced pressure. On distillation (87–88°/10–8 mm) a colourless liquid (7.7 g; yield 85%) was obtained. (Found: C, 37.3; H, 7.94; Sn, 47.0; $C_8H_{20}OSn$ calcd.: C, 38.2; H, 8.03; Sn, 47.3%.) Mol. wt. in benzene, 260, 256, 247, 238 at concentrations 0.0549, 0.108, 0.164, 0.230 g/15 ml. Calcd. 250.9.

(v) Reaction between triethyltin ethoxide and acetylacetone

A mixture of triethyltin ethoxide (2.93 g), acetylacetone (1.17 g) and benzene (49.0 g) was refluxed and the benzene–ethanol azeotrope was removed by fractionation and excess benzene was then distilled off. The residue was dried under reduced pressure, and sublimed (80–100° bath/0.15 mm) to give a white solid (2.49 g; yield 70%). Found: ethanol in azeotrope, 0.51 g (one mole requires 0.53 g). (Found: Sn, 38.2; mol. wt., 298. $C_{11}H_{22}O_2Sn$ calcd.: Sn, 38.8%; mol. wt., 304.9.)

(vi) Preparation of trimethyltin methoxide

A benzene (28.0 g) solution of trimethyltin chloride (6.45 g) was added dropwise to a refluxing solution of sodium (0.87 g) in methanol (22.0 g). It was refluxed for four hours and kept overnight. Sodium chloride was filtered out, and excess methanol and benzene were removed by distillation. The residue was dried under reduced pressure and sublimed (60–80° bath/11–12 mm) to yield a beautiful white solid (4.0 g; yield 63%). (Found: Sn, 60.7; OCH_3, 15.5. $C_4H_{12}OSn$ calcd.: Sn, 60.9; OCH_3, 15.9%.) Mol. wt. in benzene, 237, 230, 234, 226 at concentrations 0.778, 1.229, 1.698, 1.768 g/

15 ml. Mol. wt. in ether 235, 235, 238, 230 at concentrations 0.052, 0.083, 0.128, 0.168 g/15 ml. Calcd. 194.

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SUMMARY

A number of distillable complexes have been obtained from reaction between dibutyltin diethoxide and acetylacetone, methyl acetoacetate or ethyl acetoacetate. The products are monomeric, which indicates possible octahedral configuration. The triethyltin acetylacetonate has also been shown to be monomeric in benzene, and may contain a five-coordinated tin atom. Trimethyltin methoxide also is only slightly associated in benzene or ether.

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