REACTIONS OF CYCLOPENTADIENYL COMPOUNDS OF TIN WITH ORGANIC ACIDS

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The reaction of cyclopentadienyl compounds of tin (IV) with acids proceeds under mild conditions with the splitting of the C_5H_5-Sn bond [1, 2]. There is no more detailed information on this subject. For the purpose of synthesizing acylates of cyclopentadienyltin and investigating the comparative stability of the C_5H_5-M bond with respect to acidolysis, we studied the reactions of compounds with the general formula $(C_5H_5)_nSnR_{4-n}$ (n = 1 — 4, R = Alk) with carboxylic acids.

Trialkylcyclopentadienyltin (TACPT) readily reacts with AcOH and other organic acids at ~20°. The corresponding acylates of trialkyltin form with a yield of ~100% over the course of several minutes according to the reaction

$$R_3SnC_5H_5 + R'COOH \rightarrow R_3SnOOCR' + C_5H_6$$

The reaction proceeds exothermically and has a short induction period.

The reaction of dimethyldicyclopentadienyltin (DMDCPT) with organic acids proceeds considerably more slowly. Even after 72 h, a large portion of the original organotin compound remains unreacted. After 5 days, the reaction mixture consists mostly of dimethylcyclopentadineyltin acetate (DMCPTA) and dimethyltin diacetate (DMTDA). The latter can be isolated with a yield of ~100% after storage of the reaction for 7 days at 20°. Here we have the reaction

$$(C_2H_5)_2Sn(C_5H_5)_2 + 2CH_3COOH \rightarrow (C_2H_5)_2(C_5H_5)SnOOCCH_3 + C_5H_6 +$$
$$+ (C_2H_5)_2Sn(OOCCH_3)_2 \rightarrow (C_2H_5)_2Sn(OOCCH_3)_2 + 2C_5H_6$$

Solutions of ethyltricyclopentadienyltin (ETCPT) and tetracyclopentadienyltin (TCPT) in AcOH are still more stable. Heating is needed to complete the reaction.

The heating of TCPT with two moles of AcOH in an inert solvent or without one yields a compound, whose elemental-analysis data correspond to dicyclopentadienyltin diacetate (DCPTDA). However, according to the PMR spectrum, the reaction product is a mixture of the mono-, di-, and triacetates of cyclopentadienyltin in a 1 : 2 : 1 ratio. A product with the same characteristics is also produced by the following reactions:

$$(C_5H_5)_2SnCl_2 + 2\,(C_2H_5)_3SnOOCCH_3 \rightarrow (C_5H_5)_2Sn(OOCCH_3)_2 +$$
$$+ 2\,(C_2H_5)_3SnCl$$
$$Cl_2Sn(OOCCH_3)_2 + 2\,C_5H_5Tl \rightarrow (C_5H_5)_2Sn(OOCCH_3)_2 + 2\,TlCl$$

It is very likely that the following equilibrium processes involving the exchange of cyclopentadienyl groups and acyl residues proceed in DCPTDA, in any case in solution:

$$2\,(C_5H_5)_2Sn(OOCCH_3)_2 \rightleftarrows C_5H_5Sn(OOCCH_3)_3 + (C_5H_5)_3SnOOCCH_3$$

An analogous equilibrium has recently been described for bis(thiophenolato)dicyclopentadienyltin [3].

The high resistance of TCPT to the action of organic acids makes it possible to use this reaction for the synthesis of cyclopentadienyltin triacylates [4], i.e.,

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$$(C_5H_5)_4Sn + 3\,RCOOH \rightarrow C_5H_5Sn(OOCR)_3 + 3\,C_5H_6$$

For the synthesis of derivatives of the higher carboxylic acids, it is wise to employ the reacidification reaction

$$C_5H_5Sn(OOCC_3H_7\text{-}i)_3 + 3\,C_{11}H_{23}COOH \rightarrow C_5H_5Sn(OOCC_{11}H_{23})_3 + \\ + 3\,i\text{-}C_3H_7COOH$$

The complete acidolysis of TCPT by organic acids occurs only following the prolonged boiling of a solution of TCPT in an excess of the acid according to the reaction

$$(C_5H_5)_4Sn + 4\,RCOOH \rightarrow Sn(OOCR)_4 + 4\,C_5H_6$$

The data obtained show that the successive replacement of the alkyl groups in TACPT by electron — acceptor acyl residues results in a significant increase in the strength of the $C_5H_5 - Sn$ bond with respect to acidolysis. A similar effect is caused by the replacement of the alkyl groups by cyclopentadienyl groups. The strength of the $C_5H_5 - Sn$ bond with respect to the action of organic acids increases along the series $R_3SnC_5H_5 < R_2Sn(C_5H_5)_2 < RSn(C_5H_5)_3 \leq Sn(C_5H_5)_4$.

According to [5, 6], a characteristic feature of the electronic structure of compounds with the general formula $C_5H_5MR_3$ (M = Si, Ge, Sn) is the pronounced hyperconjugation (σ-π conjugation) of the C — M bond with the diene system of the ring. This is manifested as a significant decrease in the first ionization potential, as well as the appearance of an effective positive charge on the metal atom and a negative charge on the C atoms of the cyclopentadienyl ring. This effect is most clearly displayed in the case of tin compounds. It also determines a very interesting feature of these compounds, viz., the ability to undergo rapid degenerate intramolecular C — C metallotropic rearrangements [5-7]. Thus the h^1-cyclopentadienyl radical acts an electron-acceptor group with respect to the R_3Sn radical. The value of the total effective negative charge on the C atoms of the ring is, in the final analysis, the factor which determines the acidolysis rate. This charge obviously decreases regularly along the series cited above from TACPT to TCPT, and this series, therefore, finds a logical explanation.

In the PMR spectra of compounds with the general formula $(C_5H_5)_nSnR_{4-n}$ the signals of the protons of the cyclopentadientyl ring appear in the form of sharp singlets in the 6.0-ppm region, and the satellites, which are caused by the spin — spin interaction between the protons of the ring and the ^{117}Sn and ^{119}Sn magnetic isotopes, are retained. This fact indicates that there are intramolecular metallotropic rearrangements which are fast in the NMR time scale at ~20°. The averaged signals of the cyclopentadienyl ring are shifted regularly in the weak-field direction as we go from TACPT to TCPT and as the number of acyl residues on the tin atom is increased. This serves as additional evidence for the changes indicated above in the effective negative charge on the C atoms of the cyclopentadienyl ring.

EXPERIMENTAL METHOD

The original alkylcyclopentadienyltin compounds $R_3SnC_5H_5$, $R_2Sn(C_5H_5)_2$, and TCPT were synthesized according to [1]. Methyltricyclopentadienyltin (MTCPT) was obtained in the form of a yellow solid with an mp of 45-46° after vacuum sublimation at $7 \cdot 10^{-4}$ mm Hg and 90°. Found: C, 58.44; H, 5.51; Sn, 36.17%. $C_{16}H_{18}Sn$. Calculated: C, 58.41; H, 5.47; Sn, 36.12%. Tri-n-propylcyclopentadienyltin (TPCPT) was obtained by reacting diethylaminotri-n-propyltin with cyclopentadiene according to the method for the synthesis of trimethylcyclopentadienyltin. The yield was 72% and the bp 99-100° (1 mm). Found: C, 53.81; H, 8.41; Sn, 37.88%. $C_{14}H_{26}Sn$. Calculated: C, 53.72; H, 8.32; Sn, 37.96%. The experiments were carried out in an atmosphere of dry argon. The course of the reactions and the composition of the mixtures formed were monitored by collecting samples with the aid of PMR. The PMR spectra were recorded on a Varian T-60 spectrometer in CCl_4 at 20° with the use of TMS as an internal standard.

Reaction of Alkylcyclopentadienyltin Compounds with Acids. a) The addition of 0.57 g (0.095 mole + a 10% excess) of AcOH to 2.971 g (0.095 mole) of TPCPT produced two salts, and a solution of a light yellow color appeared after 3-4 min. An exothermic reaction took place after 10 min, and the mixture crystallized completely. After the removal of the volatile products in a vacuum, 2.914 g (a quantitative yield) of tri-n-propyltin acetate [7] with an mp of 82° (from hexane) were obtained. The reaction between 2.767 g (0.08 mole) of tri-n-butylcyclopentadienyltin and 0.468 g (0.08 mole + a 10% excess) of AcOh occurred in a similar manner. The yield of tri-n-butyltin acetate was 2.72, and its mp was 84-85° (from hexane). A mixed sample with the compound obtained by an independent method did not display any melting point depression.

The reactions between dimethyl-, diethyl-, methyl-, and ethyl-tricyclopentadienyltin with AcOH were carried out in a similar manner. In the case of DMDCPT, dimethyltin diacetate [8] with an mp of 66-67° was obtained in a ~100% yield.

Reaction of Tetracyclopentadienyltin with Acids (1 : 2). a) A solution of 1.512 g (0.0252 mole) of AcOH in 10 ml CCl_4 was added dropwise over the course of 30 min with stirring to a solution of 4.772 g (0.0126 mole) of TCPT in 20 ml of absolute CCl_4 heated to boiling. The mixture was boiled for 2 h, and the solvent and the cyclopentadiene formed as a result of the reaction were vacuum distilled at ~20°. The residue yielded 3.90 g (84.4%) of a crystalline yellow powder with an mp of 85-86° (from hexane). Found: C, 45.74; H, 4.37; Sn, 32.28%. $C_{14}H_{16}O_4Sn$. Calculated: C, 45.81; H, 4.36; Sn, 32.28%. According to the PMR spectrum, the reaction product is probably a mixture of three compounds, viz., the acetates of mono-, di-, and tricyclopentadienyltin in a 1 : 2 : 1 ratio.

b) The same result was obtained by gradually adding 2.376 g (0.0270 mole) isobutyric acid to a solution of 5.112 g (0.0135 mole) of TCPT in 15 ml of CCl_4 heated to boiling. The removal of the volatile compounds in a vacuum and the maintenance of the residue at $3 \cdot 10^{-3}$ mm Hg to constant weight yielded an orange oil, which, according to the PMR spectrum, is a mixture of the mono-, di-, and triisobutyrates of cyclopentadienyltin. The composition of the reaction product remained unchanged following a twofold molecular distillation in a vacuum of $3 \cdot 10^{-3}$ mm Hg at a bath temperature of 130-140°. The same product was obtained by adding 5.205 g (0.01375 mole) of TCPT in 10 ml of CCl_4 to a solution of 2.4193 g (0.0275 mole) of isobutyric acid in 5 ml of CCl_4 heated to boiling or by heating stoichiometric amounts of TCPT and isobutyric acid without a solvent in a water bath.

Reaction of Dicyclopentadienyltin Dichloride with Triethyl Tin Acetate. Dicyclopentadienyltin dichloride (DCPTDC) was obtained by gradually adding 3.65 g (0.014 mole) of $SnCl_4$ in 10 ml of CCl_4 to a solution of 5.302 g (0.014 mole) of TCPT in 15 ml of CCl_4 at 5°. On the next day the solution was filtered to remove the small amount of precipitate, and the filtrate was evaporated in a vacuum. The product contained 7.17 g (80%) of DCPTDC in the form of a light yellow powder with an mp of 42-43° (from hexane, in a sealed capillary). Found: C, 37.38; H, 3.19; Cl, 22.27; Sn, 37.21%. $C_{10}H_{10}Cl_2Sn$. Calculated: C, 37.53; H, 3.13; Cl, 22.21; Sn, 37.13%. The product DCPTDC is highly soluble in dioxane, $CHCl_3$, and CCl_4, dissolved in hexane or petroleum ether with heating, and is moderately soluble in pyridine and ether. Dicyclopentadienyltin dibromide (DCPTDB) was obtained in a similar manner with a 7.48-g (78.9%) yield (from 4.393 g of TCPT and 5.09 g of $SnBr_4$) and an mp of 45-46° (in a sealed capillary). Found: C, 29.28; H, 2.37; Br, 39.07; Sn, 29.36%. $C_{10}H_{10}Br_2Sn$. Calculated: C, 29.37; H, 2.45; Br, 39.13; Sn, 29.04%. The product DCPTDB dissolves well in the common organic solvents except cold hexane and petroleum ether.

A solution of 4.619 g (0.0113 mole) of DCPTDC in 15 ml of absolute benzene was added dropwise with stirring to a suspension of 5.981 g (0.0226 mole) of triethyl tin acetate in 50 ml of absolute hexane. After the reactants were mixed, a transparent solution containing a small amount of precipitate formed. The precipitate was filtered off, and the filtrate was evaporated in a vacuum. The residue contained a mixture of a liquid and crystals. The product consisted of 3.1 g (74.8%) of a light yellow crystalline compound with an mp of 85-86° (from hexane). The compound dissolves well in AcOH, dioxane, $CHCl_3$, benzene, toluene, THF, and pyridine and moderately in CCl_4 and ether. The compound is moderately soluble in hexane and petroleum ether even upon heating. Found: C, 45.73; H, 4.30; Sn, 32.34%. $C_{14}H_{16}O_4Sn$. Calculated: C, 45.81; H, 4.36; Sn, 32.38%. According to the PMR spectrum, the reaction product is probably a mixture of three compounds, viz., the acetates of mono-, di-, and tricyclopentadienyltin in a 1 : 2 : 1 ratio.

Reaction of Tin Dichloride Diacetate with Cyclopentadienylthallium. A solution of 4.922 g (0.016 mole) of tin dichloride diacetate in 20 ml of THF was added dropwise over the course of 1 h at −10° with vigorous stirring to a suspension of 8.672 g (0.032 mole) of cyclopentadientylthallium in 30 ml of absolute THF. The mixture was stirred at ~20° for 2 h, and the TlCl precipitate was filtered, washed with ether, and dried. The yield was 7.66 g (~100%). The solvents were evaporated from the filtrate in a vacuum. The residue was a light yellow powder with an mp of 85-86° (from hexane). The solubility of the compound was the same as that for the product obtained in the preceding experiment. Found: C, 46.00; H, 4.39; Sn, 32.37%. According to the PMR spectrum, the reaction product is probably a mixture of three compounds, viz., the mono-, di-, and triacetates of cyclopentadienyltin in a 1 : 2 : 1 ratio.

Cyclopentadienyltin Tripropionate. A mixture of 10.35 g (0.0273 mole) of TCPT and 6.073 g (0.0819 mole + a 5% excess) C_2H_5COOH was heated for 20 min at 85-90°. The excess acid and the cyclopentadiene formed as a result of the reaction were driven off in a vacuum, and the residue was purified by distillation. The product contained 10.29 g (93.2%) of cyclopentadienyltin tripropionate in the form of a light yellow liquid with a bp of 130-140° (bath temperature) ($8 \cdot 10^{-4}$ mm Hg). Found: C, 41.64; H, 4.94; Sn, 29.27%. $C_{14}H_{20}O_6Sn$. Calculated: C, 41.72; H, 4.99; Sn, 29.46%.

Cyclopentadienyltin Triisobutyrate. This compound was obtained in analogy to the preceding compound. The yield was 94.5%, and the bp was 120° (bath temperature ($3 \cdot 10^{-3}$ mm). Found: C, 46.01; H, 5.73; Sn, 26.76%. $C_{17}H_{26}O_6Sn$. Calculated: C, 45.95; H, 5.89; Sn, 26.67%.

Cyclopentadienyltin Trilaurate. A mixture of 1.512 g (0.034 mole) of cyclopentadienyltin triisobutyrate and 2.04 g (0.0102 mole) of lauric acid was heated in 25 ml of absolute benzene for 1 h. The benzene and the isobutyric acid formed as a result of the reaction were driven off in a vacuum (1 mm), and the residue was maintained under a vacuum of $8 \cdot 10^{-3}$ mm Hg to constant weight. The product contained 2.655 g (~100%) of cyclopentadienyltin trilaurate in the form of a waxy yellow compound. Found: C, 63.18; H, 9.61; Sn, 15.34%. $C_{41}H_{74}O_6Sn$. Calculated: C, 63.00; H, 9.49; Sn, 15.18%.

Tin Tetraacetate. A mixture of 2.03 g (0.0053 mole) of TCPT and 1.4 g (0.0212 mole + a 10% excess) of AcOH was heated in a water bath, the cyclopentadiene evolved was collected in a dry ice trap, and then the mixture was boiled for 30 min. When cooled to ~20°, the contents of the flask crystallized completely. Two recrystallizations from AcOH yielded 1.336 g (71%) tin tetraacetate with an mp of 238-239° (in a sealed capillary). A mixed sample with the compound obtained as previously described in [9] did not show any melting point depression. Found: C, 26.96; H, 3.41; Sn, 33.54%. $C_8H_{12}O_8Sn$. Calculated: C, 27.07; H, 3.38; Sn, 33.47%.

Tin Tetraisobutyrate. In an analogous manner tin tetraisobutyrate was obtained from 3.56 g (0.0094 mole) of TCPT and 3.64 g (0.0376 + a 10% excess) of isobutyric acid. The yield was 3.31 g (75.4%) and the bp was 115-116° (in a sealed capillary). A mixed sample melts without any depression. Found: C, 41.11; H, 6.08; Sn, 25.39%. $C_{16}H_{28}O_8Sn$. Calculated: C, 41.13; H, 6.00; Sn, 25.43%.

CONCLUSIONS

1. The strength of the $C_5H_5 - Sn$ bond with respect to acidolysis by carboxylic acid increases along the series $R_3SnC_5H_5 < R_2Sn(C_5H_5)_2 < RSn(C_5H_5)_3 \leq (C_5H_5)_4Sn$ (R = Alk) in agreement with the decrease in the effective negative charge in the ring and the degree of σ-π conjugation between the C — Sn bond and the diene system of the cyclopentadienyl ring.

2. Dicyclopentadienyltin diacylates undergo reactions involving the exchange of pentadienyl groups and acyl residues and the formation of a mixture of mono-, di-, and tricyclopentadienyltin acylates.

3. The acidolysis of tetracyclopentadienyltin by carboxylic acids may be used as a preparative method for the synthesis of cyclopentadienyl triacylates.

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