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REACTIONS OF TRI- AND DI-ORGANOTIN(IV) COMPOUNDS WITH 2-THENOYLTRIFLUOROACETONE

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Summary

Reactions of tri- and di-organotin(IV) with 2-thenoyltrifluoroacetone in dry benzene yield five and six coordinated tin compounds respectively. These non-ionic compounds are hydrolytically stable in air, and monomeric in refluxing benzene.

Introduction

There are only a few reports on the complexes formed by reaction of tri- and di-organotin(IV) halides with bidentate ligands; these involve, as ligands, carboxylates [1], dithiocarbamates [2], dithiophosphinates [3], 8-hydroxyquinoline [4-7], tropolone [8], dithiozone [9, 10], 1,10-phenanthroline and 2,2'-bipyridine [11-13], acetylacetone and picolinic acid [14-16] and 1-nitroso-2-naphthol [17, 18]. In most cases these complexes are thought to have a chelated structure containing penta- and hexa-coordinated tin.

Very little work has been done on the reactions of tri- and di-organotin(IV) compounds with halogen substituted β-diketones such as 2-thenoyltrifluoroacetone and *p*-bromobenzoylacetone. We previously reported [19] the reactions of tin(IV) halides with 2-thenoyltrifluoroacetone and *p*-fluorobenzoylacetone, and we describe below the preparation of tri- and di-organotin(IV) 2-thenoyltrifluoroacetonates. The ligand 2-thenoyltrifluoroacetone is denoted by HTTA.

Results and discussion

Dialkyltin bis(2-thenoyltrifluoroacetonate) was obtained by refluxing dialkyltin oxide and HTTA in 1/2 molar ratio in dry benzene for 15-20 h (eqn. 1).

$$(R_2SnO)_x + 2x\ HTTA \rightarrow x\ R_2Sn(TTA)_2 + x\ H_2O \qquad (1)$$

$$(R = CH_3,\ C_2H_5 \text{ and } C_4H_9)$$

The water—benzene azeotrope was fractionated off between 67-80°C, and compounds were either crystallised or distilled under reduced pressure.

TABLE 1

PREPARATION AND PROPERTIES OF COMPOUNDS OF THE TYPE $R_2Sn(TTA)_2$

Wt. of R_2SnO (g)	Wt. of HTTA (g)	Molar ratio	Refluxing period (h)	Colour and state	Yield (g)	M.p/B p. (°C)	Tin assay (%)		Mol. wt. found (calcd.)	Mol. Complexity	Conductivity in nitrobenzene (in micromhos)
							found	calcd			
(I) $(CH_3)_2Sn(\overline{SCHCHCHC}COCHCOCF_3)_2$											
0.82	2.22	1/2	15-20	Light brown solid	2.0	129-132	19.97	20.07	585 (591)	0.99	1.00×10^{-3} $(1.03 \times 10^{-3} M)$ [a]
(II) $(C_2H_5)_2Sn(\overline{SCHCHCHC}COCHCOCF_3)_2$											
0.96	2.22	1/2	12-18	Yellow viscous liquid	2.10	—	19.05	19.16	610 (619)	0.99	2.00×10^{-3} $(1.10 \times 10^{-3} M)$
(III) $(C_4H_9)_2Sn(\overline{SCHCHCHC}COCHCOCF_3)_2$											
1.25	2.22	1/2	18-20	Orange liquid	2.80	148/0.5mm	17.45	17.57	661 (675)	0.98	1.00×10^{-3} $(1.30 \times 10^{-3} M)$

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[a] Concentration in parentheses.

Triorganotin(IV) 2-thenoyltrifluoroacetonate was prepared by adding an equimolecular quantity of triorganotin chloride to the sodium salt of 2-thenoyltrifluoroacetone in dry methanol and refluxing the mixture for 4-5 h (eqns. 2-4).

$$CH_3OH + Na \rightarrow CH_3ONa + \tfrac{1}{2} H_2\uparrow \qquad (2)$$

$$HTTA + CH_3ONa \rightarrow Na^+(TTA^-) + CH_3OH \qquad (3)$$

$$R_3SnCl + Na^+(TTA^-) \rightarrow R_3Sn(TTA) + NaCl\downarrow \qquad (4)$$

($R = CH_3, C_2H_5, C_3H_7, C_4H_9$ and C_6H_5)

Sodium chloride was filtered off and the products were recrystallised or distilled under reduced pressure.

Ebullioscopic determinations of molecular weights in benzene (Tables 1 and 2) show the compounds to be monomeric, and conductivity measurements in nitrobenzene show them to be non-ionic. The conductivities fall in the region $1.0\text{-}2.0 \times 10^{-3}$ micromhos.

There is some controversy concerning the structure of the compounds of the type $R_2Snacac_2$. McGrady and Tobias [20] and Nelson and Martin [21] in 1965 assigned a *trans* configuration on the basis of IR, NMR and dipole moment studies respectively. Moore and Nelson [22], noting the temperature variation of the measured dipole moment for a number of structurally related tin complexes, have inferred by analogy that $(C_6H_5)_2Snacac_2$ exists as the *cis* isomer. Several workers [23-31] have assigned a *cis* structure to these compounds on the basis of dipole moment measurements or NMR chemical shift values. Recently, X-ray diffraction studies [32] of the compound $Me_2Snoxin_2$ (oxin = 8-hydroxyquinolate) revealed a *cis* disposition of methyl groups although the octahedron is somewhat distorted. On the basis of the values of Mössbauer isomer shift δ, and quadrupole splitting ΔE, Fitzsimmons and coworkers [33] have assigned a *cis* configuration to a large number of organotin complexes. In view of the above a *cis* octahedral configuration is proposed for the compounds of the type $R_2Sn(TTA)_2$. (Fig. 1).

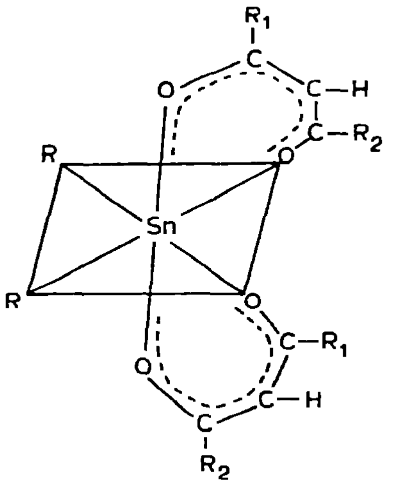

Fig. 1.

(continued on p. 364)

TABLE 2

PREPARATION AND PROPERTIES OF COMPOUNDS OF THE TYPE $R_3Sn(TTA)$

Wt. of R_3SnCl (g)	Wt. of HTTA (g)	Molar ratio	Refluxing period (h)	Colour and state	Yield (g)	M p/B.p. (°C)	Tin assay (%)		Mol. wt. found (calcd.)	Mol. Complexity	Conductivity in nitrobenzene (in micromhos)
							found	calcd.			
(IV) $(CH_3)_3Sn(\overline{SCHCHCHC}COCHCOCF_3)$											
1.00	1.11	1/1	5	White solid	1.90	204 (dec.)	30.69	30.82	360 (385)	0.96	1.00×10^{-3} $(1.30 \times 10^{-3} M)$ [a]
(V) $(C_2H_5)_3Sn(\overline{SCHCHCHC}COCHCOCF_3)$											
1.20	1.11	1/1	4	Low-melting yellow solid	1.80	65/0.8mm	27.65	27.77	402 (427)	0.94	1.00×10^{-3} $(1.10 \times 10^{-3} M)$
(VI) $(C_3H_7)_3Sn(\overline{SCHCHCHC}COCHCOCF_3)$											
1.41	1.11	1/1	4	Low-melting yellow solid	2.00	79/2mm	25.14	25.28	454 (469)	0.96	1.00×10^{-3} $(1.01 \times 10^{-3} M)$
(VII) $(C_4H_9)_3Sn(\overline{SCHCHCHC}COCHCOCF_3)$											
1.62	1.11	1/1	5	Yellow liquid	2.10	142-145/0.3mm	23.12	23.20	495 (511)	0.96	2.00×10^{-3} $(1.05 \times 10^{-3} M)$
(VIII) $(C_6H_5)_3Sn(\overline{SCHCHCHC}COCHCOCF_3)$											
1.92	1.11	1/1	5	Light yellow solid	2.60	152	20.60	20.76	560 (571)	0.98	1.00×10^{-3} $(1.20 \times 10^{-3} M)$

[a] Concentration in parentheses.

TABLE 3. INFRARED DATA (cm^{-1})

(I) $(CH_3)_2Sn(\overline{SCHCHCHC}COCHCOCF_3)_2$	2954-2844 s, 1614-1594 m (br), 1540-1500 m (br), 1454 m, 1406 s, 1376-1352 m (sh), 1290 s (br), 1180 m (br), 1150 m, 931 m, 796-793 m (sh), 732-726 m (sh), 683 s, 648 s, 608-580 s (sh), 520 m, 492 s.
(II) $(C_2H_5)_2Sn(\overline{SCHCHCHC}COCHCOCF_3)_2$	3100-3080 s (br), 1603-1575 s (br), 1540 m, 1450-1411 s (sh), 1352 s, 1310-1290 m (sh), 1225 m, 1190-1185 m, 1145-1135 s, 1070 m, 1060 s, 928 s, 860 s, 790-785 m (br), 772 s, 750 m, 698-680 s (sh), 648 s, 605 s, 588-575 s, 545 w, 520-510 w (br), 490-480 w (br).
(III) $(C_4H_9)_2Sn(\overline{SCHCHCHC}COCHCOCF_3)_2$	2960-2910 s (br), 2870-2850 s (br), 1616-1590 s (br), 1532 m, 1472 m, 1416 s, 1375 m, 1360 s, 1325-1300 m (sh), 1270 m, 1225 m, 1067 m, 960 m, 935 s, 880-860 m (sh), 850-840 m (br), 799 s, 770 w, 755-729 s (sh), 648 s, 610 m, 590 m, 520 s.
(IV) $(CH_3)_3Sn(\overline{SCHCHCHC}COCHCOCF_3)$	2950-2850 s, 1620 s, 1540-1530 m (doublet), 1475 m (br), 1420 s, 1385-1350 s (doublet), 1290 s, 1180 m (br), 1150-1118 s (br), 1052 m, 963-953 m (br), 935-930 m (sh), 856 s, 842-833 s, 748-715 s (sh), 673 s (sh), 588 s, 570 m, 513 s.
(V) $(C_2H_5)_3Sn(\overline{SCHCHCHC}COCHCOCF_3)$	3102-3072 s (br), 2950 s, 2862 s, 1610 m, 1510 s, 1454 s, 1362 w, 1355 s, 1270 s, 1232 m, 1205-1173 m (vbrsh), 1150-1135 m (brsh), 1083 w, 1065-1055 m (br), 1018-1008 m (br), 985-970 s, 932 s, 860-850 s, 795-780 s (doublet), 765 vw, 725-718 s (sh), 694 m, 678 s, 655 s, 645 s, 605 s, 590-570 s (sh).
(VI) $(C_3H_7)_3Sn(\overline{SCHCHCHC}COCHCOCF_3)$	2950-2920 s, 2860 s, 1625 s, 1515 s, 1455 s, 1415 s, 1357 s, 1335 s, 1270 s, 1210 m, 1140 w (br), 1062 m, 930 m, 860 s, 840 m, 800 s, 720 s, 610 m, 590 s, 520 m.
(VII) $(C_4H_9)_3Sn(\overline{SCHCHCHC}COCHCOCF_3)$	2950 m, 2920 m, 2870-2850 m (sh), 1602 s (br), 1540 s, 1470 w, 1410 s, 1375-1352 s (sh), 1315-1280 s (sh), 1195-1180 s (br), 1145-1138 s (br), 1080-1060 s (sh), 960-932 s (sh), 880-860 s (sh), 790 s, 772 s, 720 s, 698-680 s (sh), 642 s, 608-592 s (sh), 520-512 m (br).
(VIII) $(C_6H_5)_3Sn(\overline{SCHCHCHC}COCHCOCF_3)$	2950-2912 s (sh), 2860-2850 s (sh), 1607 s, 1542 s, 1515 m, 1472 s, 1404 s, 1375 s, 1352 s, 1304 s, 1253 s, 1230 s, 1200-1190 s (br), 1146-1140 s (br), 1080-1065 s (sh), 935 s, 863 m, 800 s, 773 s, 748-732 s (sh), 698 s, 685 w, 660-650 s (sh), 606 m, 590 s, 452-440 s (sh).
(IX) $(\overline{SCHCHCHC}COCH_2COCF_3)$	3400-3200 s (vbr), 3100 w, 2920 m, 2849 m, 1650 m, 1460 s, 1405 s, 1360 w, 1200-1190 m (br), 1160-1150 m (br), 1110 m, 1070-1060 m, 905 w, 862 s, 777 w, 749 m, 740-732 s (sh), 682 s, 640 s, 609 w, 582 m, 565-559 m (sh).

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[a] Spectra for I, IV, VIII and IX recorded in nujol and II, III, V, VI, VII neat.

Discussion

The IR frequencies of various derivatives of tri- and di-organotin(IV) with 2-thenoyltrifluoroacetone are shown in Table 3. Three important absorptions have been used in elucidating the structures of the compounds [34].

A detailed assignment of infrared spectra of a large number of metal acetylacetonates was made by Nakamoto and coworkers [35]. The strong bond occurring in the unchelated ligand near 1650 cm^{-1} is lowered to 1625-1600 cm^{-1} in all the organotin(IV) 2-thenoyltrifluoroacetone complexes. These bands are consistent with the presence of an oxygen-chelated 2-thenoyltrifluoroacetonate ligand.

McGrady and Tobias [20] have reported Sn—O stretching vibrations in the region 700-400 cm^{-1} for β-diketonate derivatives of diorganotin(IV). In the complexes I to VIII three to four peaks are observed around 750-600 cm^{-1}. Medium to strong intensity bands at higher frequency have been assigned to ν_{as}(Sn—O) and lower ones to ν_s(Sn—O). The other medium intensity bands may be due to skeletal vibrations of the thienyl group coupled with ν_{as}(Sn—O) and ν_s(Sn—O).

The IR spectrum of the compounds I to VIII show two strong intensity bands in the region around 590-510 cm^{-1}. The high frequency band is assigned to ν_{as}(Sn—C) and the lower one to ν_s(Sn—C). Some weak absorptions may be due to skeletal vibrations coupled with Sn—C or Sn—O vibrations. Presence of symmetric and antisymmetric Sn—C bands lend support to the *cis* position of organic moiety in compounds of the type $R_2Sn(TTA)_2$.

Experimental

All solvents were carefully dried and purified before use. 2-Thenoyltrifluoroacetone, obtained from BDH, was dried under vacuum. Organotin compounds, a gift from Nitto Kasei & Co., Japan, were used after distillation. Dimethyl- and diethyl-tin oxides were prepared by established procedures. Details of elemental analyses, molecular weights, conductivity measurements, and IR spectra are given elsewhere [19].

Preparation of complexes

Preparation of compounds of the type $R_2Sn(TTA)_2$. (R = CH_3, C_2H_5, C_4H_9 and HTTA = 2-thenoyltrifluoroacetone). In a typical synthesis, dimethyltin oxide (0.005 mol, 0.8235 g) was added to 2-thenoyltrifluoroacetone (0.01 mol, 2.22 g) in 40 ml of dry benzene and the mixture was refluxed for 15-20 h. The benzene—water azeotrope was fractionated off between 67-80°C. Remaining solvent was removed under vacuum (30°C/0.1mm). A light brown solid (2.0 g) was obtained after recrystallisation from chloroform (Table 1).

Preparation of compounds of the type $R_3Sn(TTA)$. (R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5). In a typical preparation trimethyltin chloride (0.005 mol, 1.0 g) was added to 100 ml of dry methanol to which 2-thenoyltrifluoroacetone (0.005 mol, 1.11 g) and clean sodium (0.005 mol, 0.11 g) had been dissolved. The mixture was refluxed for 4-5 h and about 75% methanol was fractionated off between 63-65°C on the column. The remaining methanol solution was filtered to remove sodium chloride. From the filtrate dry compound was obtained by removing the residual methanol under vacuum. A white solid, insoluble in hot chloroform, but soluble in hot benzene and cold methanol was obtained. Other derivatives were prepared in a similar fashion (Table 2).

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