PREPARATION OF DIHALO-BIS(ACETYLACETONATO)TIN(IV) COMPLEXES BY THE ACTION OF MOLECULAR OXYGEN ON STANNOUS HALIDES IN ACETYLACETONE

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Dihalo-bis(acetylacetonato)tin(IV) complexes may be prepared by the substitution of two halide ions by acetylacetone (Hacac):

$$SnX_4 + 2Hacac \rightarrow Sn(acac)_2X_2 + 2HX \quad (X = F\ [1],\ Cl\ [2\text{--}5],\ Br\ [5]);$$

or the substitution of two phenyl groups [6-8]:

$$SnPh_2Cl_2 + 2Hacac \rightarrow Sn(acac)_2Cl_2 + 2PhH,$$

$$Sn(Ph)_4 + SnX_4 + 4Hacac \rightarrow 2Sn(acac)_2 + 4PhH \quad (X = Br,\ I);$$

and by ligand exchange reactions [1, 3, 5]:

$$SnBr_4 + Cu(acac)_2 \rightarrow Sn(acac)_2Br_2 + CuBr_2,$$

$$SnI_4 + Na(acac) \rightarrow Sn(acac)_2I_2 + 2NaI.$$

The oxidation state of tin is not altered.

In the present work, we discovered that $Sn(acac)_2X_2$ compounds (X = F, Cl, Br, I) are obtained relatively easily upon passing O_2 through a solution or suspension of SnX_2 in acetylacetone: $SnX_2 + \frac{1}{2}O_2 + 2Hacac \rightarrow Sn(acac)_2X_2 + H_2O$ as a result of the oxidation of Sn(II) to Sn(IV) ions.

EXPERIMENTAL

Samples of SnF_2 and SnI_2 were obtained according to standard procedures [9]. A sample of $SnCl_2$ was obtained from pure-grade $SnCl_2 \cdot 2H_2O$ by dehydration with acetic anhydride [10]. Pure-grade $SnBr_2$ was used without further purification. Pure-grade acetylacetone was purified by distillation, bp 139°C. Samples of ether, hexane, and chloroform were purified and dried according to standard procedures [11].

Difluoro-bis(acetylacetonato)tin(IV). Oxygen was passed into a suspension of 6.25 g (39.9 mmoles) finely ground SnF_2 in 30 ml acetylacetone at $\sim$70-90°C for 1 h. Acetylacetone was removed in vacuum and 50 ml $CHCl_3$ was added to the dry white residue. Unreacted SnF_2 was separated by filtration. Separation and drying in vacuum gave 4.6 g (33%) white product.

Dichloro-bis(acetylacetonato)tin(IV). Oxygen was passed through a solution of 5.35 g (28.2 mmoles) $SnCl_2$ in 30 ml acetone for 10 min. The white precipitate formed was separated by filtration and washed with two 10-ml portions of absolute ether to give 9.3 g (85%) product. $Sn(acac)_2Cl_2$ was also obtained as a result of maintaining a solution of $SnCl_2$ or $SnCl_2 \cdot 2H_2O$ in acetylacetone for several days. $Sn(acac)_2Cl_2$ is not formed if this solution is degassed.

Dibromo-bis(acetylacetonato)tin(IV). Oxygen was passed through a suspension of 7.50 g (26.9 mmoles) $SnBr_2$ in 30 ml hot acetylacetone for 1 h. The white precipitate formed was filtered off and washed with 10 ml absolute ether. Drying in vacuum gave 4.9 g $Sn(acac)_2Br_2$. Hexane was added to the mother liquor. The white precipitate formed was filtered off, washed with absolute ether, and dried to give an additional 5.7 g $Sn(acac)_2Br_2$. The total yield was 82%.

Diodo-bis(acetylacetonato)tin(IV). Oxygen was passed through a suspension of 7.10 g (19.1 mmoles) SnI_2 in 30 ml acetylacetone at about 40°C for 20 min until red SnI_2 was completely dissolved. The white precipitate formed was filtered off, washed with 10 ml absolute

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TABLE 1. Indices of $Sn(acac)_2X_2$ Complexes Prepared (the PMR spectral indices were obtained in $CDCl_3$ at 293 K using a Bruker CXP-300 spectrometer at 300.066 MHz)

Compound	Mp, °C	Chemical shift, δ, ppm from TMS**		Found/Calculated, %		
		CH_3-***	—CH=	H	C	X
$Sn(acac)_2F_2$	Not determined	2,14;2,22 2,18 ****	5,72 5,67	3,58 3,98	33,55 33,84	11,47 10,71
$Sn(acac)_2Cl_2$	204,5–205,5	2,12;2,21	5,72	3,25 3,64	29,91 30,97	18,35 18,28
$Sn(acac)_2Br_2$	189,5–191,5	2,10;2,20	5,71	2,90 2,96	24,35 25,20	33,73 33,52
$Sn(acac)_2I_2$	179–181	2,07;2,17	5,74	2,56 2,48	20,17 21,00	43,41 44,47

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*See [1, 3, 5, 8].

**Measured relative to HMDS taking δ_{HMDS} 0.055 ppm; the PMR parameters obtained correspond to the parameters given by Jones [1] and Nelson [8].

***The two signals for the CH_3 group protons are due to the cis arrangement of the acac ligands [1].

****T 310 K. One line appears in the spectrum upon increasing the temperature from 292 to 310 K due to rapid exchange of the acac ligands [1].

ether, and dried in vacuum to give 5.8 g slightly yellowish product. Then, 30 ml hexane was added to the mother liquor. The white precipitate formed was filtered off and washed with hexane and absolute ether. Drying gave an additional 3.9 g of product. The total yield was 89%.

The product indices are given in Table 1.

CONCLUSIONS

A new method has been proposed for the preparation of dihalo-bis(acetylacetonato)tin(IV) complexes by passing oxygen through solutions of stannous halides in acetylacetone.

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