

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

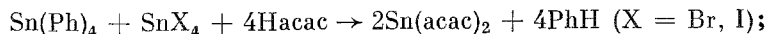
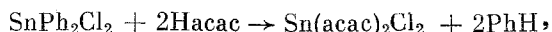
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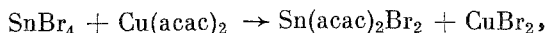
Dihalo-bis(acetylacetonato)tin(IV) complexes may be prepared by the substitution of two halide ions by acetylacetonate (Hacac):



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



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



The oxidation state of tin is not altered.

In the present work, we discovered that  $\text{Sn}(\text{acac})_2\text{X}_2$  compounds ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) are obtained relatively easily upon passing  $\text{O}_2$  through a solution or suspension of  $\text{SnX}_2$  in acetylacetone:  $\text{SnX}_2 + \frac{1}{2}\text{O}_2 + 2\text{Hacac} \rightarrow \text{Sn}(\text{acac})_2\text{X}_2 + \text{H}_2\text{O}$  as a result of the oxidation of  $\text{Sn}(\text{II})$  to  $\text{Sn}(\text{IV})$  ions.

#### EXPERIMENTAL

Samples of  $\text{SnF}_2$  and  $\text{SnI}_2$  were obtained according to standard procedures [9]. A sample of  $\text{SnCl}_2$  was obtained from pure-grade  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  by dehydration with acetic anhydride [10]. Pure-grade  $\text{SnBr}_2$  was used without further purification. Pure-grade acetylacetone was purified by distillation, bp  $139^\circ\text{C}$ . 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 mmol) finely ground  $\text{SnF}_2$  in 30 ml acetylacetone at  $\sim 70-90^\circ\text{C}$  for 1 h. Acetylacetone was removed in vacuum and 50 ml  $\text{CHCl}_3$  was added to the dry white residue. Unreacted  $\text{SnF}_2$  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 mmol)  $\text{SnCl}_2$  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.  $\text{Sn}(\text{acac})_2\text{Cl}_2$  was also obtained as a result of maintaining a solution of  $\text{SnCl}_2$  or  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in acetylacetone for several days.  $\text{Sn}(\text{acac})_2\text{Cl}_2$  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 mmol)  $\text{SnBr}_2$  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  $\text{Sn}(\text{acac})_2\text{Br}_2$ . 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  $\text{Sn}(\text{acac})_2\text{Br}_2$ . The total yield was 82%.

Diiodo-bis(acetylacetonato)tin(IV). Oxygen was passed through a suspension of 7.10 g (19.1 mmol)  $\text{SnI}_2$  in 30 ml acetylacetone at about  $40^\circ\text{C}$  for 20 min until red  $\text{SnI}_2$  was completely dissolved. The white precipitate formed was filtered off, washed with 10 ml absolute

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TABLE 1. Indices of  $\text{Sn}(\text{acac})_2\text{X}_2$  Complexes Prepared (the PMR spectral indices were obtained in  $\text{CDCl}_3$  at 293 K using a Bruker CXP-300 spectrometer at 300.066 MHz)

Compound	Mp, °C	Chemical shift, $\delta$ , ppm from TMS**		Found/Calculated, %		
		$\text{CH}_3$ ***	$-\text{CH}=\text{C}-$	H	C	X
$\text{Sn}(\text{acac})_2\text{F}_2$	Not determined	2,14;2,22	5,72	3,58	33,55	11,47
		2,18 ****	5,67	3,98	33,84	10,71
$\text{Sn}(\text{acac})_2\text{Cl}_2$	204,5–205,5	2,12;2,21	5,72	3,25	29,91	18,35
				3,64	30,97	18,28
$\text{Sn}(\text{acac})_2\text{Br}_2$	189,5–191,5	2,10;2,20	5,71	2,90	24,35	33,73
				2,96	25,20	33,52
$\text{Sn}(\text{acac})_2\text{I}_2$	179–181	2,07;2,17	5,74	2,56	20,17	43,41
				2,48	21,00	44,47

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

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

\*\*\*The two signals for the  $\text{CH}_3$  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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