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FACILE SYNTHESIS OF TIN(II) CHELATE COMPOUNDS

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Metallic tin reacted readily with bis(1,3-diketonato)copper compounds in an organic solvent to give corresponding bis(1,3-diketonato)tin(II) compounds in excellent yields.

Organic tin(II) compounds bearing Sn-OC bonds have been obtained mainly by the methods of (A), protolysis of dimethoxotin(II), diethoxotin(II), or dicyclopentadienyltin(II),[1-4] and (B), protolysis of blue-black tin(II) oxide in the presence of copper.[5] However, the former procedure requires preliminary preparation of the alkoxotin(II) or dicyclopentadienyltin(II) compounds and the latter is appreciated only in the organic tin(II) compounds having a high degree of thermal stability, such as heterocycles containing Sn-O bonds. Although J.J.Zuckerman[6] have also reported on the action of cathechol and 2,2'-dihydroxybiphenyl on a tin-copper contact mass, the reaction must be conducted at elevated temperature under a high pressure of hydrogen.

We now report on a convenient method for preparing of tin(II) chelate compounds from metallic tin and bis(1,3-diketonato)copper :

$$2\ \mathrm{Sn} + \mathrm{Cu(OR)_2} \xrightarrow[\text{solvent}]{130\ °\mathrm{C},\ 2\ \mathrm{hrs}} \mathrm{Sn(OR)_2} + \mathrm{Sn,\ Cu}$$

R : $CH_3\overset{|}{C}{=}CHCOCH_3$, $CH_3\overset{|}{C}{=}CHCO_2C_2H_5$, $C_6H_5\overset{|}{C}{=}CHCOCH_3$, $C_6H_5\overset{|}{C}{=}CHCOC_6H_5$.

All operations were carried out in nitrogen atmospher dried with liquid nitrogen. The typical procedure is as follows: Metallic tin (5.74 g, 48.4 mmol) and bis(acetylacetonato)copper (6.10 g, 23.3 mmol) were placed in 100 ml of acetylacetone, and heated at 130 °C for 2 hrs with stirring. During the course of the reaction the solution changed in color from dark purple to pale yellow, with the appearance of copper powders. After filtrating the unreacted tin and the resulting copper, the solvent was removed under reduced pressure and the residue was dissolved in 30 ml of hexane. Removing of the resulting solids followed by distillation in vacuo gave 5.80 g (78.5 %) of a pale yellow, air-sensitive bis(acetylacetonato)tin(II). The analytical and physical data were shown in Table. Its spectrum coincides with that of the authentic sample. In the case of the reaction with bis(1-phenyl-1,3-butanedionato)copper and bis(1,3-diphenyl-1,3-propanedionato)-copper, the filtrate was concentrated under reduced pressure and the residue was crystallized from 10 ml of benzene.

The reaction did not occur in refluxing benzene, ethanol, acetonitril, and tetrahydrofurane and in xylene at 115 °C, with recoveries of the starting materials.

Table Preparation of tin(II) chelate compounds[a)]

Reactant		Product		
$Cu(O\underset{CH_3}{C}=CHCOCH_3)_2$	solvent	yield(%)[b)]	bp(°C/mmHg) or mp [°C]	Sn(%) (Calcd)
$Cu(O\underset{CH_3}{C}=CHCOCH_3)_2$	acetylacetone	78.5	87-95/1.5	36.97 (37.49)
	xylene	88.7		
	chlorobenzene	89.9 (86.1)[c)]		
	o-dichlorobenzene	35.2		
$Cu(O\underset{CH_3}{C}=CHCO_2C_2H_5)_2$	chlorobenzene	76.6 (78.5)[c)]	106-108/2	31.78 (31.49)
$Cu(O\underset{C_6H_5}{C}=CHCOCH_3)_2$	chlorobenzene	96.5 (54.6)[c)]	122-124	26.46 (26.93)
$Cu(O\underset{C_6H_5}{C}=CHCOC_6H_5)_2$	chlorobenzene	78.5 (37.0)[c)]	149-151	20.71 (21.00)

a) Reaction conditions : temp.; 130 °C, time; 2 hrs, molar ratio; [Sn]/[Cu]=2.

b) Yield refers to pure isolated products.

c) The figure in parenthesis indicates the yield from the reaction of diethoxotin(II) with the corresponding 1,3-diketone.

As shown in Table, however, the reactions at 130 °C for 2 hrs in acetylacetone, xylene, and chlorobenzene afforded bis(acetylacetonato)tin(II) in high yields, although the reaction in o-dichlorobenzene gave the product in a low yield. The prolonged reaction time also diminished the yield of bis(acetylacetonato)tin(II). The reaction did not proceed in anisol and diglyme even at 130 °C. From these facts, it is considered that the solvents strongly interacting with bis(acetylacetonato)copper are undesirable for the reaction.

Similarly, other bis(1,3-diketonato)copper compounds such as bis(1-ethoxy-1,3-butanedionato)copper, bis(1-phenyl-1,3-butanedionato)copper, and bis(1,3-diphenyl-1,3-propanedionato)copper reacted with metallic tin at 130 °C for 2 hrs in chlorobenzene to give the corresponding bis(1,3-diketonato)tin(II) compounds in yields higher than that of the reaction between diethoxotin(II) and the corresponding 1,3-diketone (see Table). These results show that the present method for preparing tin(II) chelate compounds is superior to the ordinary method.

References

1) a) P.G.Harrison, J. Chem. Soc. Chem. Comm. 1972 544. b) A.B.Cornwell and P.G. Harrison, J. Chem. Soc. Dalton, 1975 1722. c) P.F.R.Ewings and P.G.Harrison, J. Chem. Soc. Dalton, 1975 821, 2015

2) a) I.Wakeshima and I. Kijima, Chem. Lett., 1972 325. b) I.Wakeshima and I. Kijima, Nippon Kagaku Kaishi, 1974 536.

3) K.D.Bos, et al., Inorg. Nucl. Chem.Lett., 9 961 (1973).

4) R.Gsell and M.Zeldin, J. Inorg. Nucl. Chem., 37 1133 (1975)

5) a) G.T.Cocks and J.J.Zuckermann, Inorg. Chem. 4 592 (1965). b) D.E.Fenton et al., Inorg. Chim. Acta., 4 235 (1970).

6) J.J.Zuckerman, J. Chem. Soc., 1963 1322 ; Adv. Inorg. Chem. Radiochem., 6 383 (1964).

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