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Synthesis of Chloro(organo-oxy)tin(IV) from Organo-hydroxylic Compound and Tin(II) Chloride

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The reaction of an organo-hydroxylic compound and tin(II) chloride with a chlorine compound containing positively polarizable chlorine was found to yield trichloro(organo-oxy)tin(IV) or its disproportionation products, dichlorobis(organo-oxy)tin(IV) and tin(IV) chloride. The reaction of tin(II) chloride and *N*-chlorosuccinimide (NCS) with methanol or ethanol afforded methoxy- or ethoxy-trichloro(succinimide)tin(IV) (**1**), while the reaction with *n*-butanol led to the formation of dibutoxydichlorotin(IV) (**2**) and tetrachlorobis(succinimide)tin(IV) (**3**). The reaction of tin(II) chloride and NCS with alcohols in the presence of cyclohexanone oxime gave dialkoxydichloro(cyclohexanone oxime)tin(IV) (**6**). Cyclohexanone oxime and hexahydro-2*H*-azepin-2-one (3,4,5,6-tetrahydro-2*H*-azepin-7-ol) could be used as the organo-hydroxylic reagent in the reaction, while 1-chloronitrosocyclohexane and *N*-chlorohexahydro-2*H*-azepin-2-one were also useful as the chlorine compound. Thus, dichlorobis(cyclohexanone oximato)tin(IV) (**9**), dichlorobis(hexahydro-2*H*-azepin-2-onato)tin(IV) (**13**), and an adduct of **9** with tetrachlorobis(hexahydro-2*H*-azepin-2-one)tin(IV) (1 : 1) were prepared. Two stable complexes, bis(benzophenone oximato)dichlorobis(hexahydro-2*H*-azepin-2-one)tin(IV) (**15**) and dichlorobis(2-pyridinethiolato)tin(IV) (**11**), were synthesized by the reactions of **13** with benzophenone oxime and 2-pyridinethiol respectively. The complex **13** was also synthesized by the reaction of *N*-trimethylsilylhexahydro-2*H*-azepin-2-one with tin (IV) chloride.

Halogeno(organo-oxy)tin(IV), such as alkoxychlorotin(IV), can be prepared *via* substitution reactions from tin(IV) halides,[1] tetraalkoxytin(IV),[2] and other organotin(IV) compounds.[3] However, these reactions have some limitations on their use as general preparative methods, as has been shown in the literature. There have been two reports on the formation of halogeno (organo-oxy)tin(IV) from tin(II) halides. Nesmejanov and Kozechkow[4] have suggested the probable formation of dichlorodiethoxytin(IV) in the reaction of tin (II) chloride with diarylmercury in ethanol, based upon the isolation of the corresponding aromatic hydrocarbon and metallic mercury. Melinichenko *et al.*[5] reported briefly a reaction of mercury acetate with tin(II)chloride in acetic acid, the reaction gave diacetoxydichlorotin (IV) and mercury.

This paper will describe a new, convenient method for the synthesis of trichloro(organo-oxy)tin(IV) or dichlorobis(organo-oxy)tin(IV), which consists of the reaction of hydroxylic compounds with tin(II) chloride in the presence of a chlorine compound containing positively polarizable chlorine, such as *N*-chlorosuccinimide(NCS), *N*-chlorohexahydro-2*H*-azepin-2-one(NCC), and 1-chloro-1-nitrosocyclohexane(CNC). This reaction is illustrated in Scheme 1. In the first step of the reaction, trichloro(organo-oxy)tin(IV) is formed as a complex with a ligand(YH) derived from the chlorine compound (Y-Cl), which is isolated in a good yield in several cases. The second step is a disproportionation of the complex, giving dichlorobis-(organo-oxy)tin(IV) and a complex of tin(IV) chloride with the ligand (YH). The disproportionation occurs, depending on the nature of the organo-oxy group (RO-) and the ligand (YH), under the conditions used for the first-step reaction.

$$\mathrm{ROH + SnCl_2 + Y\text{-}Cl \xrightarrow{\text{1st step}} ROSnCl_3\cdot YH}$$

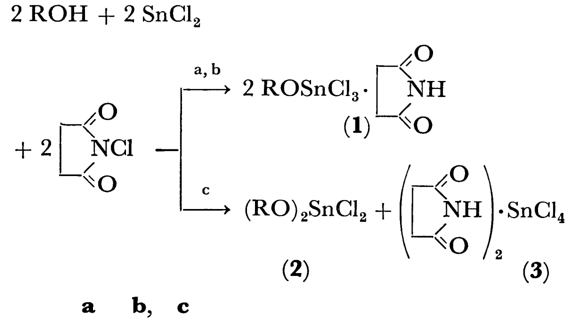
$$\mathrm{2\,ROSnCl_3\cdot YH \xrightarrow{\text{2nd step}} (RO)_2SnCl_2 + (YH)_2SnCl_4}$$

ROH: Methanol, Ethanol, *n*-Butanol, Cyclohexanone oxime, and Hexahydro-2*H*-azepin-2-one.
Y-Cl: *N*-Chlorosuccinimide, 1-Chloro-1-nitrosocyclohexane, and *N*-Chlorohexahydro-2*H*-azepin-2-one.

Scheme 1.

Results and Discussion

When methanol, tin(II) chloride, and NCS were allowed to react in a molar ratio of 1 : 1 : 1 in ethylene dichloride (EDC), trichloromethoxy(succinimide)tin (IV) (**1a**) was produced in an 86% yield. An analogous treatment of ethanol, in place of methanol, afforded trichloroethoxy(succinimide)tin(IV) (**1b**) in an 87% yield. However, the treatment of *n*-butanol, tin(II) chloride, and NCS under similar conditions gave di-*n*-butoxydichlorotin(IV) (**2c**) and tetrachlorobis(succinimide)tin(IV) (**3**) instead of *n*-butoxytrichloro(succinimide)tin(IV) (**1c**).

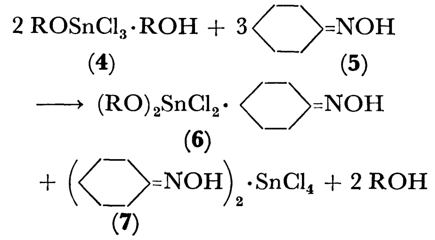


a b, c
R: Me, Et, *n*-Bu

These facts indicate that **1c** readily undergoes disproportionation, while **1a** and **1b** are stable under similar conditions.

The complexes **1a** and **1b** were identified with specimensprepared by the reactions of trichloro(methanol)methoxytin(IV) (**4a**) and trichloro(ethanol)ethoxytin(IV) (**4b**) respectively with succinimide. Such a ligand-exchange reaction has also been reported by Paul *et al.*,[6] who, however, observed only the formation of complexes of trichloromethoxytin(IV) with various ligands including amides, primary amines and nitrogen heterocycles. Analogously, ligand-exchange reactions occurred when **4a** was treated with an equimolar amount of hexahydro-2*H*-azepin-2-one, its *N*-methyl derivative, or cyclohexanone oxime.

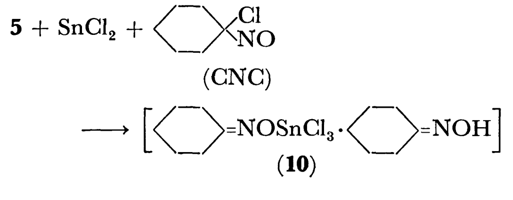
However, when **4a** was treated with a 1.5 fold molar amount of cyclohexanone oxime (**5**), a disproportionation reaction occurred and dichloro(cyclohexanone oxime)dimethoxytin(IV) (**6a**) and tetrachlorobis(cyclohexanone oxime)tin(IV) (**7**) were formed in 94 and 97% yields respectively.

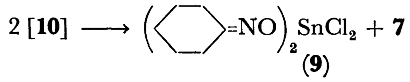


A similar treatment of **1b** or **4b** with **5** gave dichloro(cyclohexanone oxime)diethoxytin(IV) (**6b**) in a good yield. Di-*n*-butoxydichloro(cyclohexanone oxime)tin(IV) (**6c**) was obtained by the treatment of **2c** with an equimolar amount of **5**, providing a confirmation for the formation of **2c** in the reaction mentioned above. The complexes **6** were unexpectedly stable enough to be handled in atmosphere, while dialkoxydichlorotin(IV) or its complexes are, in general, very sensitive to moisture and readily decompose in atmosphere.

The complexes **6** could also be obtained by the reactions of **5**, tin(II) chloride and NCS in the alcohols. In these reactions, the development of blue color was transiently observed, indicating the formation of 1-chloro-1-nitrosocyclohexane (CNC) as one of the reaction intermediates. Since the reaction of **5** with NCS was experimentally confirmed to result in the formation of CNC and succinimide,[7] the use of CNC as a chlorine compound (Y-Cl)[8] in the reaction of Scheme 1 was examined.

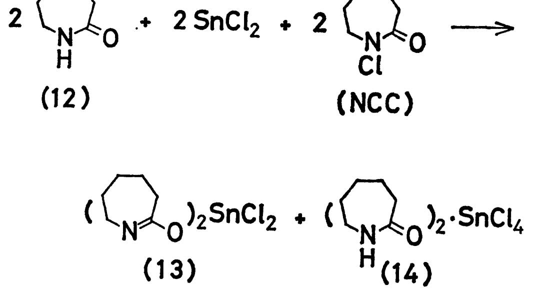
As a variation of the hydroxylic compound in the reaction of Scheme 1, **5** was used. The reaction of **5**, tin(II) chloride, and CNC in a molar ratio of 1 : 1 : 1 afforded dichlorobis(cyclohexanone oximato)tin(IV) (**9**) and **7** in good yields. These results shows that trichloro(cyclohexanone oximato)(cyclohexanone oxime)-tin(IV) (**10**), formed in the first step, readily undergoes a disproportionation, while trichloro(cyclohexanone oxime)methoxytin(IV) (**8**) is stable under similar conditions. The complex **9** is very sensitive to atmospheric moisture, and the formation of **9** was confirmed by several reactions. The treatment of **9** with alcohols afforded **6** in good yields, and the reaction of **9** with double the molar amount of 2-pyridinethiol gave dichlorobis(2-pyridinethiolato)tin(IV) (**11**) and **5** in 83 and 72% yields respectively.



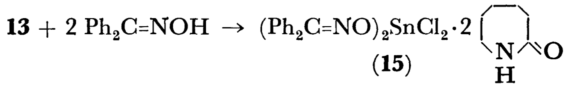


The complex **11** was very stable and was also obtained quantitatively from the reaction of bis(acetylacetonato)-dichlorotin(IV) with 2-pyridinethiol in a molar ratio of 1 : 2.

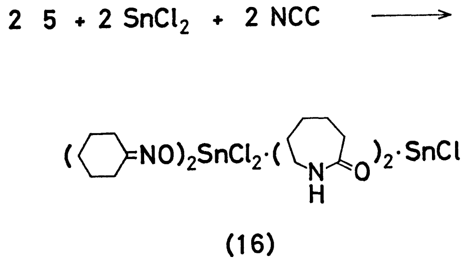
N-Chlorohexahydro-2*H*-azepin-2-one (NCC) was also useful as a chlorine compound for the reaction shown in Scheme 1. When hexahydro-2*H*-azepin-2-one (**12**), tin(II) chloride, and NCC were allowed to react in a molar ratio of 1 : 1 : 1 in benzene, dichlorobis-(hexahydro-2*H*-azepin-2-onato)tin(IV) (**13**) and tetrachlorobis(hexahydro-2*H*-azepin-2-one)tin(IV) (**14**) were both formed in good yields. The complex **13** was isolated as an adduct with benzene (3 : 1), an alternative synthesis of which will be described below.



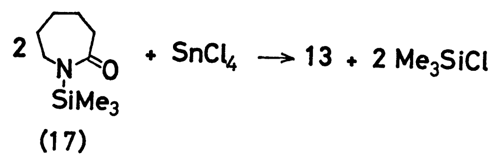
The formation of **13** was supported by two reactions. The first is the reaction with 2-pyridinethiol affording **11** and **12**, while the second reaction consists of a treatment with benzophenone oxime, yielding bis(benzophenone oximato)dichlorobis(hexahydro-2*H*-azepin-2-one)tin(IV) (**15**).[9]



When **5**, tin(II) chloride, and NCC were allowed to react in a molar ratio of 1 : 1 : 1 in benzene, an adduct of **9** with **14** (1 : 1) (**16**) was formed in a good yield. The adduct **16**[10] was also isolated from the reaction of **13** with **7**.



As an alternative synthesis of **13**, the reaction of *N*-trimethylsilylhexahydro-2*H*-azepin-2-one (**17**) with tin(IV) chloride was performed. When **17** was treated with tin(IV) chloride in a molar ratio of 2 : 1 in benzene, and when trimethylsilyl chloride and the solvent were then removed by evaporation, **13** was obtained as a residue in an elemental analytically pure state. The structural supports for **13** were obtained by a study of the IR, NMR, and mass spectra.


(17)

The IR spectrum of **13** exhibits three strong intensity bands at 1620, 1520, and 330 cm^{-1}. The last band[11] can be assigned to the Sn–Cl vibration in a six-coordinated octahedral tin(IV) complex,[6,12,13] the appearance of only one band in the 300—350 cm^{-1} region suggests a *trans* configuration for two Sn–Cl bonds.[13–15] The C=O stretching band of **12** at 1660 cm^{-1} shifts to a spectral region lower by 30 and 50 cm^{-1} on *O*-coordinated complex formation with boron trifluoride and tin(IV) chloride respectively, indicating that the band at 1620 cm^{-1} of **13** may be due to C=O stretching. Furthermore, the band at 1520 cm^{-1} can be assigned to C=N stretching on the basis of the facts that dichlorobis(3,4,5,6-tetrahydro-2*H*-azepin-7-yl sulfato)-tin(IV) shows only one band, at 1520 cm^{-1}, in the 1500—1700 cm^{-1} spectral region, a band which can be assigned to C=N stretching,[16] and that **17** exhibits no band in the 1500—1700 cm^{-1} spectral region except for a carbonyl band at 1630 cm^{-1}.[16,17]

The proton NMR spectrum of **13** shows three peaks, at 8.20 (12H in β, γ, and δ positions), 7.35 (4H in α) and 6.60 (4H, in ε), and no remarkable splitting of the peaks is observed. This indicates that the two azepine rings in **13** are identical or very similar, because the NMR peaks of α or ε protons may be expected to split when one azepine ring in **13** is bonded only on the nitrogen atom with the tin atom and the other is bonded only on the oxygen atom with the tin atom. This supposition follows from the NMR data of several *N*- or *O*-substituted **12** which are shown in Table 1.

TABLE 1. NMR-SPECTRA OF HEXAHYDRO-2*H*-AZEPIN-2-ONE AND ITS DERIVATIVES (τ, in CHCl$_3$)

Compounds	β,γ and δ(6H)	α(2H)	ε(2H)
Unsubstituted	8.25	7.55	6.80
O-Methyl-	8.30	7.60	6.58
N-Methyl-	8.30	7.47	6.60
N-Chloro-	8.20	7.40	6.10
N-Trimethylsilyl-	8.30	7.48	6.78

These spectral observations lead to a probable structure for **13**, which is shown in Fig. 1, although it is not yet clear whether the two oxygen-tin bonds are *cis* or *trans*.

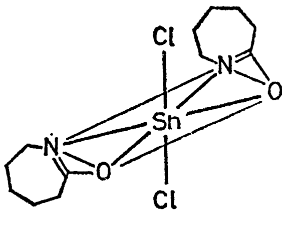
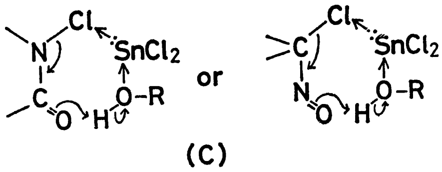


Fig. 1. A probable structure for **13**. An alternative structure, in which two oxygen-tin bonds are *trans*, is also possible.

The complex **13** could not be prepared by the conventional methods of synthesis mentioned in the above introductory part. The recrystallization of **13** from benzene-ethyl ether afforded the adduct with benzene (3 : 1).

Some comments can be made about the mechanism of the reaction shown in Scheme 1, although there has not, so far as we aware, been any report on the oxidation of bivalent tin into a tetravalent state with a halogen compound containing positively polarizable halogen under non-aqueous conditions.[18] Three modes of the pathway can be postulated for the first step reaction. The first involves an initial reaction of tin (II) chloride with the chlorine compound giving a trichlorotin(IV) derivative (A), followed by the replacement of the latter with the hydroxylic compound. The second involves the initial formation of a hypochlorite-type compound (B) from the hydroxylic compound and the chlorine compound and the subsequent reaction of B with tin(II) chloride. The third pathway consists of a concerted mechanism involving a cyclic transition state (C).

$\mathrm{Y{-}SnCl_3}$ (A) $\qquad$ ROCl (B)


(C)

The first-step reaction or the overall reaction of Scheme 1 is independent of the order in which the hydroxylic compound or the chlorine compound is added to tin(II) chloride, although in several cases some reactions have been observed between the two reactants before the addition of the third reactant. For instance, a reaction was observed to occur when NCS was added to tin(II) chloride; the reaction gave a product which might be an *O*-coordination complex of tin(II) chloride with NCS or trichloro(succinimidato)-tin(IV). Although the product could not be confirmed because of its very hygroscopic character, the reaction is so slow as still to be incomplete after stirring for 12 hr at room temperature or for several hours at 80 °C. On the other hand, the reaction of NCS and tin(II) chloride with alcohols or **12** is essentially completed within several hours at room temperature or within 1 hr at 80 °C. Furthermore, the reaction between **5**, tin(II) chloride, and CNC proceeds smoothly in benzene at room temperature, while scarcely no reaction of CNC with tin(II) chloride occurred under the same conditions. It is clear, therefore, that the first pathway is not predominant. The second pathway seems also not to be favored, since NMR spectral investigations do not indicate an isomerization of CNC or NCC into the corresponding hypochlorite-type compound (B) in the presence of **5** or **12**, in spite of the successful reactions of **5**, tin(II) chloride, and CNC and of **12**, tin(II) chloride, and NCC.

At present, in view of these observations, it seems that the first-step reaction of Scheme 1 can best be explained by the third pathway, although the first and second pathways may be competitive to some extent according to the combination of reactants.

Experimental

All the compounds containing tin or silicon atoms, except the $(acac)_2SnCl_2$, **6** and **11**, were handled in a dry nitrogen atmosphere. The reagents and organic solvents for the reactions were used as anhydrous states. All the melting points are uncorrected. The products were identified, unless otherwise mentioned, by comparisons of the melting points and IR spectra with those of authentic samples.

Trichloromethoxy(succinimide)tin(IV) (1a). *a) From Methanol, $SnCl_2$, and NCS*: To a solution of NCS (3.34 g, 25 mmol) in EDC (120 ml) was added $SnCl_2$ (4.74 g, 25 mmol) with stirring at room temperature. A slightly exothermic reaction occurred, and the temperature of the mixture rose by 3.5—5 °C. To the stirred mixture was added drop by drop a solution of methanol (0.9 g, 28 mmol) in EDC (30 ml) at room temperature, after which the mixture was refluxed for 1 hr. The resulting solid was collected by filtration, washed with EDC, and dried to give 7.62 g (86%) of **1a**; mp 192.5—197.5 °C(decomp). IR(KBr): 3140, 3050, 1785, 1700, 1640, 515, 445, 360, 340(sh), 320, 300 and 285 cm^{-1}.

Found: C, 16.95; H, 2.46; N, 3.79; C, 29.63%. Calcd for $C_5H_8Cl_3NO_3Sn$: C, 16.91; H, 2.27; N, 3.94; Cl, 29.95%.

*b) From **4a** and Succinimide*: A mixture of **4a**[1a)] (7.20 g, 25 mmol) and succinimide (2.45 g, 25 mmol) in EDC (250 ml) was heated under atmospheric pressure until 100 ml of the solvent had been distilled off. The resultant solid was collected by filtration, washed with EDC, and dried to give 8.26 g (93%) of **1a**; mp 192.5—197.5 °C (decomp).

Trichloroethoxy(succinimide)tin(IV) (1b). *a) From Ethanol, $SnCl_2$ and NCS*: In a manner similar to Method *a)* used for **1a**, NCS (3.34 g, 25 mmol) was treated with $SnCl_2$ (4.74 g, 25 mmol) in EDC (120 ml) and subsequently with ethanol (1.2 g, 26 mmol) in EDC (30 ml), thus giving 8.0 g (87%) of **1b**; mp 188.5—189.5 °C (decomp). IR (KBr): Essentially identical in pattern with that described in *a)* for **1a**.

Found: C, 19.68; H, 2.87; N, 3.60; Cl, 28.63%. Calcd for $C_6H_{10}Cl_3NO_3Sn$: C, 19.52; H, 2.73; N, 3.79; Cl, 28.81%.

*b) From **4b** and Succinimide*: In a manner similar to Method *b)* used for **1a**, **4b**[1a)] (7.90 g, 25 mmol) was treated with succinimide (4.90 g, 50 mmol) in benzene (250 ml) to give 8.42 g (91%) of **1b**.

Trichloro(hexahydro-2H-azepin-2-one)methoxytin(IV) (18). In a manner similar to Method *b)* used for **1a**, **4a** (14.41 g, 50 mmol) was treated with **12** (5.66 g, 50 mmol) in benzene (300 ml) to give 17.86 g (97%) of **18**; mp 196—199 °C (decomp). IR (KBr): 3350, 1610, 530, 510, 350, 320, 295 and 285 cm^{-1}.

Found: C, 22.95; H, 3.61; N, 3.51; Cl, 29.10%. Calcd for $C_7H_{14}Cl_3NO_2Sn$: C, 22.77; H, 3.61; N, 3.51; Cl, 28.80%.

Trichloromethoxy(1-methylhexahydro-2H-azepin-2-one)tin(IV) (19). In a manner similar to Method *b)* used for **1a**, **4a** (7.20 g, 25 mmol) was treated with 1-methylhexahydro-2*H*-azepin-2-one (3.18 g, 25 mmol) in benzene (170 ml) to give 8.76 g (91%) of **19**; mp 217.5—219 °C (decomp.) IR (KBr): 1600, 525, 450, 350, 325, 310 and 280 cm^{-1}.

Found: C, 25.04; H, 4.29; N, 3.63; Cl, 27.91%. Calcd for $C_8H_{16}Cl_3NO_2Sn$: C, 25.07; H, 4.21; N, 3.66; Cl, 27.75%.

Trichloro(cyclohexanone oxime)methoxytin(IV) (8). In a manner similar to Method *b)* used for **1a**, **4a** (14.41 g, 50 mmol) was treated with **5** (5.66 g, 50 mmol) in benzene (300 ml) to give 14.76 g (80%) of **8a**; mp 158.5—160 °C (decomp). IR (KBr): 3180, 3100, 1130, 1080, 1060, 510, 490, 345, 320 and 310 cm^{-1}.

Found: C, 22.70; H, 3.78; N, 4.05; Cl, 28.63%. Calcd for $C_7H_{14}Cl_3NO_2Sn$: C, 22.77; H, 3.82; N, 3.79; Cl, 28.80%.

Dichloro(cyclohexanone oxime)dimethoxytin(IV) (6a). *a) From **4a** and **5***: To a solution of **4a** (7.20 g, 25 mmol) in methanol (100 ml) was added **5** (4.24 g, 37.5 mmol): the mixture was then stirred for 2 hr at room temperature. The resulting precipitates were collected by filtration, washed with methanol and dried to give crude **6a** (4.28 g, 94%). Recrystallization from EDC-methanol gave an analytical sample as colorless crystals; mp 156 °C (decomp). IR (KBr): 2760—2260 (centered at 2500), 2200—1800 (centered at 2050), 1110, 1040, 1010, 590, 520, 475, 350, 310 and 275 cm^{-1}.

Found: C, 26.24; H, 4.74; N, 3.71; Cl, 19.47%. Calcd for $C_8H_{17}Cl_2NO_3Sn$: C, 26.30; H, 4.66; N, 3.84; Cl, 19.45%.

The methanolic filtrate and washings were concentrated to dryness, and the residue was treated with benzene to give colorless precipitates. Filtration afforded 5.92 g (97%) of **7**.[19)]

*b) From Methanol, $SnCl_2$, NCS and **5***: To a suspension of NCS (3.34 g, 25 mmol) in methanol (100 ml) was added $SnCl_2$ (4.74 g, 25 mmol) at room temperature: the temperature of the mixture thereby rose by 11 °C. The resultant solution was stirred for 2 hr at room temperature. To the solution was added **5** (4.24 g, 37.5 mmol) at room temperature, after which stirring was continued for 2 hr. The resultant solid was collected by filtration, washed with methanol (50 ml), and dried to give 4.41 g (97%) of **6a**.

The combined filtrate and washings were then concentrated, and the residue was treated with EDC (150 ml) to give 5.19 g (85%) of **7** as colorless precipitates.

The EDC solution was concentrated, and the residue was extracted with boiling benzene (100 ml). After the insoluble residue had been removed by filtration, the hot benzene solution was allowed to stand at room temperature, thus affording 2.08 g (85%) of succinimide, as colorless crystals.

Dichloro(cyclohexanone oxime)diethoxytin(IV) (6b). *a) From **4b** and **5***: In a manner similar to Method *a)* used for **6a**, **4b** (7.90 g, 25 mmol) was treated with **5** (4.24 g, 37.5 mmol) in ethanol (200 ml), thus affording crude **6b** (4.51 g, 92%). Recrystallization from EDC-ethanol gave colorless crystals; mp 157—158 °C (decomp). IR (KBr): Essentially identical in pattern with that described in *a)* for **6a**.

Found: C, 30.47; H, 5.45; N, 3.47; Cl, 18.30%. Calcd for $C_{10}H_{20}Cl_2NO_3Sn$: C, 30.57; H, 5.39; N, 3.57; Cl, 18.05%.

The ethanolic filtrate and washing were concentrated and the residue was treated with EDC (100 ml), thus affording 5.75 g (94%) of **7** as colorless precipitates.

*b) From Ethanol, $SnCl_2$, NCS and **5***: In a manner similar to Method *b)* used for **6a**, NCS (3.34 g, 25 mmol) was treated with $SnCl_2$ (4.74 g, 25 mmol) in ethanol (200 ml) and subsequently with **5** (4.24 g, 37.5 mmol). 4.68 g (96%) of **6b** were thus obtained, together with 5.6 g (92%) of **7** and 1.99 (81%) of succinimide.

Di-n-butoxydichloro(cyclohexanone oxime)tin(IV) (6c). *a) From **2c** and **5***: The reaction of NCS (3.34 g, 25 mmol), $SnCl_2$ (4.74 g, 25 mmol), and *n*-butanol (1.9 g, 25.6 mmol) in EDC (120+30 ml) was performed in a manner identical with that described in *a)* for **1a**. The resulting reaction mixture was filtered to give 3.11 g (54%) of **3**. Recrystallization from EDC gave an analytical sample as colorless needles; mp 149.5—152.5 °C (decomp). Found C, 20.95;

H, 2.43; N, 5.90%. Calcd for $C_8H_{10}Cl_4N_2O_4Sn$: C, 20.95; H, 2.26; N, 6.11%.

Since it became clear that **3** was partially soluble in the EDC used as the solvent, but was scarcely soluble in benzene, the same reaction was repeated, but in benzene (90+30 ml), in order to make the separation of **3** from the reaction mixture easy. The resulting reaction mixture was filtered to give 4.76 g (83%) of **3**. To the filtrate was added **5** (2.83 g, 25 mmol) and the mixture was stirred for 2 hr at room temperature. The resultant solid was collected by filtration, washed by being suspended in EDC (50 ml×2), and dried to give 0.85 g of **7**. The combined filtrate and washings were concentrated, and the residue was treated with *n*-butanol to give 3.15 g (56%) of **6c** as colorless precipitates. Recrystallization from EDC–*n*-butanol gave an analytical sample; mp 152—156 °C (decomp). IR (KBr): Essentially identical in pattern with that described in *a)* for **6a**.

Found: C, 37.55; H, 6.24; N, 3.06; Cl, 16.00%. Calcd for $C_{14}H_{29}Cl_2NO_3Sn$: C, 37.45; H, 6.51; N, 3.21; Cl, 15.79%.

b) From n*-Butanol,* $SnCl_2$*, NCS and* ***5***: In a manner similar to Method *b)* used for **6a**, NCS (3.34 g, 25 mmol) was treated with $SnCl_2$ (4.74 g, 25 mmol) in *n*-butanol and subsequently with **5** (4.24 g, 37.5 mmol). The resultant reaction mixture was filtered to give 8.71 g of a mixture of **6c** and **7** as a powdery solid. This mixture was then treated with EDC (100 ml) to give 2.49 g (41%) of **7** as an insoluble solid. The EDC solution separated from **7** was concentrated, and the residue was treated with *n*-butanol (100 ml) to afford 3.94 g (70%) of **6c** as colorless precipitates. The solution separated from **6c** was combined with the *n*-butanolic filtrate separated from the above mixture, and then concentrated. The residue was treated with boiling benzene (150 ml) to give 2.58 g (42%) of **7** as an insoluble solid. Thus, the total yield of **7** was 5.07 g (83%). The hot benzene solution separated from **7** was allowed to stand at room temperature to give 1.94 g (79%) of succinimide as colorless crystals. The benzene solution separated by filtration was concentrated, and the residue was treated with *n*-butanol (30 ml) to give a further 1.55 g portion (28%) of **6c**. Thus, the total yield of **6c** was 5.49 g (98%).

1-Chloro-1-nitrosocyclohexane (CNC). To a solution of **5** (11.31 g, 100 mmol) in benzene (100 ml) was added NCS (13.35 g, 100 mmol); the mixture was then stirred for 5 hr at room temperature, whereby a intensive blue color was developed. The resultant solid was collected by filtration, washed with benzene, and dried to give 9.18 g (93.6%) of succinimide. The combined filtrate and washing were washed with water (50 ml×2), dried over Na_2SO_4, and concentrated to give crude CNC (11.74 g, 80%). Distillation gave 7.42 g (50%) of CNC; bp 54—54.5 °C/15 mmHg (lit,[7a] 52 °C/12 mmHg).

*Dichlorobis(cyclohexanone oximato)tin(IV) (**9**).* To a stirred mixture of $SnCl_2$ (9.47 g, 50 mmol) and **5** (5.65 g, 50 mmol) in benzene (70 ml) was added drop by drop a solution of CNC (7.38 g, 50 mmol) in benzene (30 ml) below 12 °C with ice cooling. The mixture was stirred overnight at room temperature, and then the resulting solid was collected by filtration, washed with EDC (50 ml), and dried to give 11.96 g (98%) of **7**. The benzene filtrate was concentrated to dryness, giving crude **9** as a very hygroscopic, semicrystalline solid (10.58 g). IR (KBr): 2940, 2850, 1600, 1435, 990, 970 and 590 cm^{-1}.

Structural support for **9** was obtained by reactions with alcohols, and 2-pyridinethiol. The reaction with the latter reagent is described in the *b)* section for **11**.

Reaction with Alcohols: Crude **9** (3.0 g) was added to 50 ml of methanol, ethanol, or *n*-butanol, and the mixture was stirred for 1 hr at room temperature. The resulting precipitates were collected by filtration to give **6a** (1.79 g, 67%), **6b** (1.92 g, 67%) or **6c** (2.4 g, 74%). The products were confirmed by means of their melting points and IR spectra, which were identical with those of the respective authentic samples prepared above.

The alcoholic filtrate was concentrated, and the residue was extracted with boiling *n*-hexane (50 ml×3). The combined extracts were concentrated to dryness, giving **5** as a crystalline residue. The yields of **5** in reactions with methanol, ethanol and *n*-butanol were 0.70 g (85%), 0.64 g (79%) and 0.75 g (91%) respectively.

*Dichlorobis(hexahydro-2H-azepin-2-onato)tin(IV) (**13**). a) From* ***17*** *and* $SnCl_4$: To a stirred solution of **17**[17] (9.27 g, 50 mmol) in benzene (60 ml) was added drop by drop a solution of $SnCl_4$ (6.51 g, 25 mmol) in benzene at room temperature, after which the stirring was continued for 5 hr. The resultant solution was concentrated to dryness on an oil bath at 40 °C under reduced pressure in order to remove the benzene and trimethylsilyl chloride. **13** was obtained as a colorless crystalline residue (10.64 g, theoretical yield is 10.35 g); mp 85—86 °C. An analytical sample was obtained by drying the residue at 70 °C. IR (KBr): 1620, 1520, 1455, 530, 470, 330 and 275 cm^{-1}. MS (*m/e*): 414 (M^+), 379 (M−Cl), 302 ($M-C_6H_{10}NO$) and ($M-Cl-C_6H_{10}NO$).

Found: C, 34.95; H, 5.06; N, 6.63; Cl, 17.54%. Calcd for $C_{12}H_{20}Cl_2N_2O_2Sn$: C, 34.82; H, 4.87; N, 6.77; Cl, 17.13%.

b) Adduct of ***13*** *with Benzene (3 : 1)*: A solution of **13** (8.30 g of the crystalline residue obtained above) in benzene (50 ml) was stirred for 4 hr at room temperature and allowed to stand overnight. A trace of an insoluble substance was filtered off, and ethyl ether (60 ml) was added to the filtrate. After stirring for 7 hr, the resulting colorless solid was collected by filtration, washed with a small quantity of benzene, and dried at room temperature to give 1.15 g of the adduct; mp 100—101 °C. IR (KBr): 1620, 1550 and 680 cm^{-1}. MS: Identical peaks shown in *a)* for **13**.

Found: C, 38.22; H, 5.08; N, 6.10; Cl, 16.32%. Calcd for $(C_{12}H_{20}Cl_2N_2O_2Sn)_3C_6H_6$: C, 38.19; H, 5.00; N, 6.36; Cl, 16.14%.

c) Preparation of a Solution of ***13*** *(from* ***12****,* $SnCl_2$*, and NCC)*: To a suspension of $SnCl_2$ (4.74 g, 25 mmol) in benzene (60 ml) was added **12** (2.83 g, 25 mmol), after which the mixture was stirred for 30 min at room temperature. To the resultant solution was added drop by drop a solution of NCC[20] (3.69 g, 25 mmol; bp 55 °C/4×10^{-3} mmHg) in benzene (40 ml) below 10 °C, with ice cooling. After the addition, the mixture was stirred for 15 hr at room temperature, and then it was filtered to give **14**[21] as a colorless powdery solid (5.89 g, 96.7%) and a solution, which was confirmed to contain **13** (12.5 mmol in the theoretical yield) by treatment with 2-pyridinethiol or benzophenone oxime, and by the isolation of the adduct of **13** with benzene.

d) Isolation of the Benzene Adduct from the Solution Prepared in c) for ***13***: The solution was concentrated to give a caramel-like residue, which was then dissolved in benzene (10 ml) after which the solution was stirred for 20 hr at room temperature. The resultant solid was collected by filtration, washed with a small quantity of benzene, and dried at room temperature to give 2.61 g (47%) of the adduct, whose mp, IR and MS were identical with those of the specimen obtained in *b)* for **13**. Found: C, 38.23; H, 5.14; N, 6.01; Cl, 16.45%.

Dichlorobis(2-pyridinethiolato)tin(IV) (II). a) From Bis *(acetylacetonato)dichlorotin(IV)* (**20**) *and 2-Pyridinethiol*: To a stirred solution of **20** (3.88 g, 10 mmol) in benzene (100 ml) was added 2-pyridinethiol (2.22 g, 20 mmol), after which the mixture was refluxed for 30 min. The resultant solid was collected by filtration, washed with EDC, and dried to give 3.86 g (94%) of **11** as a slightly pale yellow, powdery solid; mp 275—277 °C (decomp). IR (KBr): 1580, 1550, 1435, 1420, 410, 400, 310, 300 and 270 cm^{-1}. MS (*m/e*): 410 (M$^+$), 375 (M−Cl), 340 (M−Cl$_2$), 300 (M−PyS) and 265 (M−Cl−PyS).

Found: C, 29.38; H, 1.83; N, 6.87; Cl, 17.24; S, 15.81%. Calcd for $C_{10}H_8Cl_2N_2S_2Sn$: C, 29.30; H, 1.97; N, 6.83; Cl, 17.30; S, 15.64%.

b) From **9** *and 2-Pyridinethiol*: A solution of **9** was prepared by the reaction of 25 mmol portions of SnCl$_2$, **5**, and CNC in benzene (100 ml), followed by a separation from the resultant **7**. To the solution was added 2-pyridinethiol (2.78 g, 25 mmol) at room temperature, and the mixture was stirred for 2 hr. The resulting solid was collected by filtration, washed with EDC (50 ml), and dried to give 4.28 g (83%) of **11**; mp 275—277 °C (decomp.)

The combined filtrate and washings were concentrated, and the residue was extracted with boiling *n*-hexane (50 ml × 3). The combined extracts were then concentrated to dryness to give 2.05 g (72%) of **5** as crystals.

c) From **13** *and 2-Pyridinethiol*: To the solution of **13** in benzene, prepared by Method *c)* for **13** was added 2-pyridinethiol (2.78 g, 25 mmol), and the mixture was treated in a manner identical with that described in *b)* for **11**, thus giving 4.67 g (91%) of **11**.

Bis(benzophenone oximato)dichlorobis(hexahydro-2H-azepin-2-one)tin(IV) (**15**). To a solution of **13** (5.28 g, 12.75 mmol, prepared by Method *a)* for **13**) in benzene (100 ml) was added benzophenone oxime (5.03 g, 25.5 mmol), and the mixture was stirred overnight. The resultant solid was collected by filtration, washed with benzene (70 ml), and dried in a nitrogen atmosphere at room temperature to give 9.34 g (90.5%) of **15**; mp 178.5—180.5 °C. IR (KBr); 3280, 1630, 940, 700, 540, 450, 340(sh), 330, 320 and 295 cm^{-1}.

Found: C, 56.50; H, 5.05; N, 6.74; Cl, 8.75%. Calcd for $C_{38}H_{42}Cl_2N_4O_4Sn$: C, 56.41; H, 5.20; N, 6.93; Cl, 8.78%.

A similar treatment of the solution of **13** in benzene prepared by Method *c)* for **13** with benzophenone oxime (4.93 g, 25 mmol) afforded 8.39 g (83%) of **15**.

An Adduct of **9** *and* **14** *(1 : 1)* (**16**). *a) From* **13** *and* **7**: To a solution of **13** (5.44 g, 13.15 mmol, prepared by Method *a)* for **13**) in benzene (100 ml) was added **7**[16] (6.40 g, 13.15 mmol), and the mixture was stirred for 15 hr at room temperature. The resultant solid was collected by filtration, washed with benzene (40 ml), and dried overnight at 70 °C under reduced pressure to give 11.19 g (94.5%) of **16** as a colorless, powdery solid; mp 103—108 °C (sintering begins at 98 °C). IR (KBr): 3330, 3280, 3190, 1630, 1010, 990, 525, 510, 350(sh), 320—310 and 290 cm^{-1}.

Found: C, 32.34; H, 4.72; N, 5.90; Cl, 23.83%. Calcd for $C_{24}H_{42}Cl_6N_4O_4Sn_2$: C, 31.97; H, 4.66; N, 6.22; Cl, 23.62%.

b) From **5**, *SnCl$_2$, and NCC*: A solution of NCC (7.38 g, 50 mmol) in benzene (30 ml) was added drop by drop to a stirred mixture of **5**, (5.66 g, 50 mmol) and SnCl$_2$ (9.48 g, 50 mmol) in benzene (90 ml) below 14 °C; the stirring was continued overnight at room temperature after the addition. The resulting solid was collected by filtration, washed with benzene, and dried at room temperature under reduced pressure for 7 hr to give 21.03 g (81%) of **16** containing benzene (1.82 mol per 1 mol of **16**) as a colorless powdery solid; mp 97—98 °C.

Found: C, 40.21; H, 5.07; N, 5.34; Cl, 20.68%. Calcd for $C_{24}H_{42}Cl_2N_4O_4Sn \cdot (C_6H_6)_{1.82}$: C, 40.22; H, 5.12; N, 5.37; Cl, 20.40%. The solid was further dried for 6.5 hr at 50 °C and then for 7.5 hr at 70 °C under reduced pressure to give benzene-free **16**. Found: C, 32.44; H, 4.75; N, 6.11; Cl, 23.94%.

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References

1) a) D. C. Bradley, E. V. Caldwell, and W. Wardlaw, *J. Chem. Soc.*, **1957**, 3030, 4775. b) R. Piekos and A. Radecki, *Roczniki Chem.*, **39**, 765 (1965). c) R. Ueeda, Y. Kawasaki, T. Tanaka, and R. Okawara, *J. Organometal. Chem.*, **5**, 194 (1966). d) R. C. Mehrotra and V. D. Gupta, *J. Indian Chem. Soc.*, **40**, 911 (1963).

2) R. C. Mehrotra and V. D. Gupta, *ibid.*, **43**, 155 (1966).

3) a) W. H. Nelson and D. F. Martin, *J. Organometal. Chem.*, **4**, 67 (1965). b) Y. Kawasaki and R. Okawara, *J. Inorg. Nucl. Chem.*, **27**, 1168 (1965).

4) A. N. Nesmejanow and K. A. Kozeschkow, *Ber.*, **63**, 2496 (1930).

5) L. S. Melnichenko, N. N. Zemlyanski, K. A. Samurskaya, and K. A. Kozeschkow, *Dokl. Akad. Nauk SSSR*, **190**, 351 (1970): Eng. Ed. p. 48.

6) R. C. Paul, H. S. Makhni, P. Singh, and S. L. Chadha, *Z. Anorg. Allg. Chem.*, **377**, 108 (1970).

7) The reaction of **5** with *N*-bromosuccinimide is known to give 1-bromo-1-nitrosocyclohexane: a) D. C. Iffland and G. X. Criner, *J. Amer. Chem. Soc.*, **75**, 4047 (1953), but the reaction of **5** with NCS has not been reported, in spite that several methods for the preparation of CNC have been described: b) H. Diekmann and W. Luttke, *Angew. Chem. Int. Ed. Engl.*, **7**, 387 (1968) and references cited therein.

8) A positively polarizable character of chlorine in CNC has been observed in the reaction of CNC with triphenylphosphine; M. Ohno and J. Sakai, *Tetrahedron Lett.* **1965**, 4541.

9) An alternative structure, bis(benzophenone oxime)-dichlorobis(hexahydro-2*H*-azepin-2-onato)tin(IV), can be excluded on the basis of the fact that benzophenone oxime does not form a complex even with tin(IV) chloride, while **12** readily forms complexes with chlorotin(IV)'s, such as alkoxytrichlorotin(IV) and tin(IV) chloride.

10) The structural consideration of the adduct (**16**) is now in progress; the results will be published elsewhere, together with other experimental results.

11) A referee suggested the possibility that the band at 330 cm^{-1} may be due to the Sn–O vibration. Although positive evidence is lacking to date, we still favor the assignment of the band to the Sn–Cl vibration. This is based on the facts that, in the literature,[6,13,22] the strong-intensity bands in the 300—350 cm^{-1} region in the spectra of most hexa-coordinated tin(IV) complexes containing both Sn–O and Sn–Cl bonds have been assigned to the Sn–Cl vibration and the bands in the 400—600 cm^{-1} region have been assigned to the Sn–O vibration. The spectrum of **13** shows a medium-intensity band at 515 cm^{-1} which can be assigned to Sn–O vibration, because the complexes **1**, **18**, **19**, **8**, **6**, **15**,

and **16** exhibit absorption bands in the 500—550 cm^{-1} region in the respective spectra, while no band is observed in the 500—600 cm^{-1} region in the IR spectrum of **11**.

12) I. R. Beattie and M. Milne, *J. Inorg. Nucl. Chem.*, **28**, 1651 (1966).

13) R. C. Paul and S. L. Chadha, *Aust. J. Chem.*, **22**, 1381 (1969).

14) J. P. Clark and C. J. Wilkins, *J. Chem. Soc., A*, **1966**, 871.

15) I. R. Beattie, G. P. McQuilian, L. Rule, and M. Webster, *ibid.*, **1963**, 1514.

16) M. Masaki *et al.*, unpublished results.

17) K. Ruhlmann and B. Rupprich, *Ann. Chem.*, **686**, 226 (1965).

18) Although the oxidation of tin(II) halide with a molecular halogen is known to give tin(IV) halide, molecular chlorine can not be used as a chlorine compound in this method. Even if molecular chlorine caused the first step reaction competitively with the formation of tin(IV) chloride, the final product would be only a complex of tin(IV) chloride with an organo-hydroxylic compound, because the trichloro-(organo-oxy)tin(IV) formed in the reaction would be immediately converted into the complex by the by-produced hydrogen chloride (Y=Cl, in Scheme 1).

19) M. Masaki, K. Fukui, M. Uchida, K. Yamamoto, and I. Uchida, This Bulletin, **46**, 3179 (1973).

20) G. Caprata, G. Lemetre, and A. Vercellone, *Ann. Chim.* (Rome), **49**, 1167 (1959).

21) Inventa AG., Swiss Pat. 326,165 (1958).

22) a) R. Chand and S. L. Chadha, *J. Inorg. Nucl. Chem.*, **31**, 2753 (1969). b) S. H. Hunter, V. M. Langford, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc., A*, **1968**, 305.