ORGANOMETALLIC COMPOUNDS

IV*. PHENYL-TIN CLEAVAGE BY CHELATING AGENTS

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Cleavage reactions of tetraalkyltin compounds[1] have been studied by others who used compounds such as carboxylic acids, phenol, and mercaptans as cleavage agents. It has been noted that the cleavage reactions between tetraphenyltin[2] and formic or acetic acids proceed with the formation of benzene and the corresponding basic tin(IV) salts. More recently, tin–phenyl cleavage was observed upon heating diphenyltin dichloride[3] with excess acetylacetone on a steam bath. Because the interaction of diphenyltin dichloride and a monoprotic bidentate chelating agent, HCh, is used to prepare metal-chelate compounds $(C_6H_5)_2Sn(Ch)_2$, it was of interest to investigate the conditions under which the tin–phenyl cleavage occurs.

EXPERIMENTAL***

Materials

Diphenyltin dichloride and dimethyltin dichloride, obtained from Columbia Organic Chemicals Co., Inc., as well as triphenyltin chloride, received from M & T Chemicals Inc., were used without further purification, as were the commercially available 8-quinolinol, salicylaldehyde, and β-diketones. Imines were prepared by mixing directly the desired amine and an aldehyde or ketone.

Interaction of diphenyltin dichloride and chelating agents under cleavage conditions (Table 1)

The general procedure consisted in heating a mixture of diphenyltin dichloride and the chelating agent in stoichiometric amounts. Cleavage occurred at temperatures between 100–200°, depending on the compound used, and often the reaction was complete in less than twenty minutes. Products were collected and then purified by recrystallization from mixtures of benzene or toluene and petroleum ether (b.p. 90–110°). The following preparation is typical.

Dichlorobis(1-phenyl-1,3-butanedionato)tin(IV). Benzoylacetone (1.00 g, 0.0062

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[*] For Part III, see ref. 10.

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[***] All microanalyses and molecular weight determinations were performed at the University of Illinois under the direction of Mr. J. NEMETH. Molecular weights in benzene were determined by means of a Mechrolab vapor phase osmometer.

mole) and diphenyltin dichloride (1.06 g, 0.0031 mole) were mixed in a round-bottomed flask, equipped with a reflux condenser, and were heated at 190–200° for twenty minutes. Upon cooling, the residue was dissolved in 10 ml benzene and the product recovered by adding 20 ml petroleum ether (b.p. 90–110°). The product was filtered off, washed with ether, and dried in a vacuum desiccator. The yield was 1.10 g (70 %) of yellow crystals; m.p. 216–218°. Another recrystallization from a 1:5 petroleum ether–toluene mixture raised the melting point to 218–219°.

Quadridentate ligands

The quadridentate bis β-diketo-diimines 4,4′-(trimethylenedinitrilo)di-2-pentanone and 4,4′-(ethylenedinitrilo)di-2-pentanone appeared to effect cleavage when heated with diphenyltin dichloride, but apparently they were not sufficiently acidic to act as diprotic acids at temperatures below 200°, a temperature of rapid thermal decomposition of the ligands. However, 3,3″-(ethylenedinitrilo)dibutyrophenone reacted with diphenyltin dichloride at 180–190° within twenty minutes and 6,6′-[ethylenebis(nitrilomethylidyne)]di-*o*-cresol reacted even more readily.

When equimolar quantities of diphenyltin dichloride and 3,3″-(ethylenedinitrilo)dibutyrophenone were mixed in benzene, a white solid, m.p. 128–130°, formed which could be recrystallized from benzene. The analysis corresponded to that expected for the adduct $[(C_6H_5)_2SnCl_2]_2 \cdot H_2Ch'$. (Found: C, 52.94; H, 4.37; N, 2.83; Cl, 14.79. $C_{46}H_{44}Cl_4N_2O_2Sn_2$ calcd.: C, 53.33; H, 4.28; N, 2.70; Cl, 13.69 %.)

Interaction of tetraphenyltin and bidentate chelating agents

Starting materials were recovered in nearly quantitative yield when tetraphenyltin and 8-quinolinol were heated at 200° for 30 minutes in 1:2 molar ratio. Only when the temperature was raised to 220–230° and the molar ratio increased to 1:5 did cleavage occur with the release of benzene. The product appeared to be a mixture of benzene-insoluble materials. Dibenzoylmethane did not react with tetraphenyltin after 21 hours at 200–220° using a 2:1 ligand-to-tin molar ratio.

Interaction of dimethyltin dichloride and 8-quinolinol

Methyl groups were not readily cleaved by 8-quinolinol even when the temperature was raised to 200° for several hours.

Interaction of triphenyltin chloride and 8-quinolinol

When a mixture of 8-quinolinol (3.33 g, 0.0229 mole) and triphenyltin chloride (4.21 g, 0.0109 mole) was heated at 140° for 80 minutes, an orange solid formed as the last of the benzene was driven off. The orange solid dissolved in 20 ml of refluxing toluene to produce an orange solution. Upon cooling, a sparingly soluble, lemon yellow solid precipitated. Infrared, microanalytical, and ultraviolet solution spectrophotometric data indicated that the yellow material was actually a mixture of dichlorobis(8-quinolinolato)tin(IV) and bis(8-quinolinolato)diphenyltin(IV). The conclusions were further substantiated by a chromatographic experiment using an 87-cm column[4] packed with D-lactose in benzene. No separation of the product into optically active fractions was observed, but instead separation of the sample into two fractions possessing respectively the ultraviolet solution spectra of $Cl_2Sn(Ox)_2$ and $(C_6H_5)_2Sn(Ox)_2$ was noted*.

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* Ox = 8-quinolinolato.

Condensation of tetrachlorotin(IV) and 8-quinolinol

Tetrachlorotin(IV) refluxed with excess 8-quinolinol in toluene gave a yellow compound, $SnCl_4 \cdot 2HOx$, m.p. 263–265° (ethanol). (Found: C, 39.34; H, 2.75; N, 5.00. $C_{18}H_{14}Cl_4N_2O_2Sn$ calcd.: C, 39.25; H, 2.56; N, 5.08%.)

RESULTS

Absorption spectra

The ultraviolet and infrared absorption spectra were determined as described previously[3]. Pertinent spectral bands are listed in Tables 2 and 3.

The ultraviolet absorption spectrum of $Cl_2Sn(Ox)_2$, agrees fairly well with that reported previously for $(C_6H_5)_2Sn(Ox)_2$. Other workers[5] suggest that the 8-quinolinolato moiety is behaving as a bidentate ligand, as it probably is in $Cl_2Sn(Ox)_2$. The spectra of the β-dicarbonyl derivatives, $Cl_2Sn(Ch)_2$, are similar to those of the corresponding diphenyl compounds $(C_6H_5)_2Sn(Ch)_2$[3]. The absorption maxima of the dichloro compounds are displaced somewhat to longer wavelengths and the extinction coefficients of the dichloro compounds are about one-half of the values of the corresponding diphenyl compounds. This is consistent with the expected order of solution stability of the two series.

As is typical of β-dicarbonyl–metal compounds[6], the β-dicarbonyl derivatives have no infrared absorption bands in the usual carbonyl region near 1700 cm^{-1}, but instead have a strong and broad absorption band near 1550 cm^{-1} which may be ascribed to the formation of strong complexes by the carbonyl oxygens with an acidic tin atom. In addition, there is a band near 1590 cm^{-1} which may be assigned to C=C vibration, following previous assignments[7]. The salicylaldehyde derivative differs from the β-dicarbonyl compounds inasmuch as a strong carbonyl band is present at 1669 cm^{-1} which is in the proper location for a conjugated, but not chelated, carbonyl group. There is present in the spectrum of this compound a moderately strong absorption band at 1405 cm^{-1}, which is weak confirmatory evidence of the presence of an aromatic aldehyde group[6].

No band was observed in the spectrum of $(CH_3)_2Sn(Ox)Cl$ which could be ascribed to Sn–Cl vibration, presumably as a result of a shift to below 250 cm^{-1} on coordination[10]. In the spectrum of most compounds of the type $Cl_2Sn(Ch)_2$, there is only one prominent absorption band in the expected[8] 400–250 cm^{-1} region, namely one at or near 325 cm^{-1}. Consequently, this band is attributed to Sn–Cl vibrations. The band is found at 340 cm^{-1} in the spectrum of salicylaldehyde derivative and at 320 cm^{-1} in the spectrum of the dibenzoylmethane derivative, and, in a general way, can be correlated with the chelating tendency of the ligand.

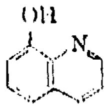
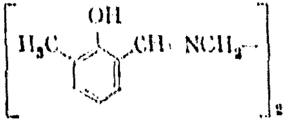
On the basis of absorption spectra and molecular weight data, compounds of the type $Cl_2Sn(Ch)_2$ are probably six-coordinate complexes, having the *trans* structure. The salicylaldehyde derivative is an exception; the infrared spectrum provides evidence that this might best be considered to be a four-coordinate compound with the carbonyl non-coordinated.

DISCUSSION

Because of the large number of organotin halides, either commercially available or prepared[9], which could be used as starting materials, such cleavage reactions of

TABLE 1

PHYSICAL DATA OF CLEAVAGE PRODUCTS OF THE TYPE $Cl_2Sn(Ch)_2$ AND Cl_2SnCh'

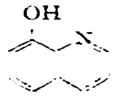
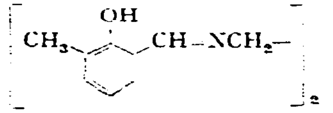
HCh or H_2Ch'	*Reaction conditions: °C, time*	*Product color*	*M.p., °C*	*Yield, %*	*Mol. wt. in C_6H_6*	*Recryst. solvent*	*Analysis calcd. (found)*			
							C	*H*	*N*	*Cl*
$CH_3COCH_2COCH_3$	170–180 30 min	v.lt.yel.	202–203	20	388 (411)	toluene-pet. ether	30.97 (31.25)	3.64 (3.61)	—	18.28 (19.21)
$C_6H_5COCH_2COCH_3$	190–200 20 min	yellow	218–219	70	512 (478)	toluene-pet. ether	46.92 (46.87)	3.54 (3.53)	—	13.85 (13.74)
$C_6H_5COCH_2COC_6H_5$	200–210 45 min	yellow	262–263	62	636 (594)	toluene-pet. ether	56.65 (56.41)	3.48 (3.38)	—	11.14 (11.72)
o-HOC_6H_4CHO	200 1 h	yellow	256–257	49	—	—	38.94 (38.53)	2.33 (2.45)	—	
	170 15 min	yellow	> 350	95	—	—	45.24 (45.69)	2.53 (2.69)	5.86 (5.68)	14.84 (14.65)
$[C_6H_5COCH_2C(CH_3)=NCH_2-]_2$	180–190 20 min	v.lt.yel.	320–321	37	—	—	49.30 (48.53)	4.13 (4.17)	5.22 (5.39)	13.23 (13.67)
	175–180 5 min	yellow	336–337	95	484 (465)	$CHCl_3$	44.67 (45.62)	3.75 (3.86)	5.79 (5.83)	

the type summarized in Table 1 could provide a convenient route for the preparation of new and interesting tin–chelate compounds. Previous work[10] has established the fact that compounds of the type $R_2Sn(Ox)Cl$ are subject to alkylation, chelation, and halogen exchange. It appears likely that compounds of the type $Cl_2Sn(Ch)_2$ would be subject to the same reactions, but the practicality of the use of such reactions depends in large measure upon the ease of preparation of $Cl_2Sn(Ch)_2$. Often such a compound cannot be prepared by direct interaction of ligand and tin(IV) chloride. This is true for 8-quinolinol, even under forcing conditions.

In general, it has been demonstrated that displacement of chlorine from tin in diphenyltin dichloride by chelating agents is favored in the presence of organic solvents such as benzene or ethanol, but tin–phenyl cleavage is favored at temperatures in excess of 100°, provided the ligand is present in high concentration. Moreover, tin–phenyl cleavage occurs preferentially when diphenyltin dichloride is heated above 150° in the absence of solvent with compounds such as 8-quinolinol, salicylaldehyde, and various β-diketones.

TABLE 2

ULTRAVIOLET ABSORPTION SPECTRA OF COMPOUNDS OF THE TYPE $Cl_2Sn(Ch_2)$ AND Cl_2SnCh' IN $CHCl_3$

HCh or H_2Ch'	*Wavelengths of absorption maxima [λ, mμ and corresponding molecular extinction coefficients (ε)]*	
	λ	10^{-4} ε
$CH_3COCH_2COCH_3$	285	1.6
$C_6H_5COCH_2COCH_3$	322	3.0
$C_6H_5COCH_2COC_6H_5$	348 258	4.5 1.9
o-HOC_6H_4CHO	329 258	0.61 2.1
	383 259	0.47 6.7
$[C_6H_5COCH_2C(CH_3){=}NCH_2-]_2$	341 263	4.8 2.9
	374 299 241	0.54 2.9 2.1

Representative quadridentate ligands, 3,3″-(ethylenedinitrilo)dibutyrophenone and 6,6′-[ethylenebis(nitrilomethylidyne)]di-o-cresol, behave similarly to salicylaldehyde. It is interesting to note that the first quadridentate ligand precipitates with diphenyltin dichloride from benzene as a simple adduct, $[(C_6H_5)_2SnCl_2]_2 \cdot H_2Ch$, which can be recrystallized from benzene. Other quadridentate ligands, 4,4′-(trimethylene- and -ethylenedinitrilo)di-2-pentanone, are much less effective in causing tin–phenyl cleavage of diphenyltin dichloride. This is attributable to the fact that these ligands undergo thermal decomposition at the temperatures required for cleavage.

Other compounds examined for ease of carbon–tin cleavage include tetra-

TABLE 3

INFRARED ABSORPTION DATA OF COMPOUNDS OF THE TYPE $Cl_2Sn(Ch)_2$ AND Cl_2SnCh'*

$CH_3COCH_2COCH_3$	$C_6H_5COCH_2COCH_3$	$C_6H_5COCH_2COC_6H_5$	o-HOC_6H_4CHO	$[C_6H_5COCH_2C(CH_3)=NCH_2-]_2$
			1669 s	
			1645 s	
1620 m	1622 m		1615 s	
	1602 m	1600 s	1595 s	1600 s
	1594 m	1590 s		
1540 s	1550 –	1550 –	1540 m	1520 s
	1510 s	1510 s		
585 w	605 w	605 w		
	554 w	560 w	562 m	562 w
			537 m	540 w
			520 m	
460 w	452 w	455 w	455 m	460 w
420 w	438 w		433 m	445 w
411 w	400 w		400 w	
		390 w	390 w	
		360 w		
360 w	325 w	320 w	320 w	

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* Obtained as KBr discs.

phenyltin, triphenyltin chloride, and dimethyltin dichloride. The latter compound was not readily cleaved by 8-quinolinol even at a temperature 30° above that required for diphenyltin dichloride. This order of ease of cleavage is in agreement with that observed by Seyferth[11] for cleavage with protonic acids[11]. Tin–phenyl cleavage of tetraphenyltin by 8-quinolinol is feasible, but is less satisfactory as a synthetic method than is the cleavage of diphenyltin dichloride because a large excess of 8-quinolinol is required.

Phenyl–tin cleavage occurred readily when triphenyltin chloride was heated with 8-quinolinol (1:2 molar ratio). However, the expected product, $C_6H_5SnCl(Ox)_2$, was not isolated, although an orange benzene solution, typical[3] of this product, was obtained. Rather two other compounds, $(C_6H_5)_2Sn(Ox)_2$ and $Cl_2Sn(Ox)_2$ were obtained upon adsorption and elution of the crude solid on a chromatographic column. It seems reasonable to suggest that these are disproportionation products:

$$(C_6H_5)_3SnCl + 2HOx \rightarrow 2C_6H_6 + C_6H_5SnCl(Ox)_2 \xrightarrow[\Delta]{\text{toluene}} Cl_2Sn(Ox)_2 + (C_6H_5)_2Sn(Ox)_2$$

It seems unwarranted to suggest that these products arise from the thermal disproportionation of $(C_6H_5)_2SnCl(Ox)$, which could arise if tin–phenyl cleavage of triphenyltin chloride occurs in two steps. This possible intermediate has been prepared by another method[6], and it is unaffected by recrystallization conditions.

While the mechanism of phenyl–tin cleavage by chelating agents may well be related to the mechanism for cleavage by carboxylic acids, it seems appropriate to defer comment until kinetic data are available. The scope of the method is sufficiently great as to make it a useful procedure for the synthesis of tin–chelate compounds.

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SUMMARY

Acetylacetone, benzoylacetone, dibenzoylmethane, salicylaldehyde, and 8-quinolinol react with diphenyltin dichloride to produce tin–phenyl cleavage products of the type $Cl_2Sn(Ch)_2$, where HCh is a bidentate, monoprotic chelating agent. Two quadridentate diprotic ligands of the type H_2Ch', 3,3″-(ethylenedinitrilo)-dibutyrophenone and 6,6′-[ethylenebis(nitrilomethylidyne)]di-*o*-cresol, react with diphenyltin dichloride under similar conditions to give products of the general type Cl_2SnCh'.

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