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Coordination Chemistry Reviews 249 (2005) 1745–1765
COORDINATION CHEMISTRY REVIEWS
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Review

Organooxotin assemblies from Sn–C bond cleavage reactions☆

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Received 28 December 2004; accepted 23 March 2005
Available online 12 May 2005

Contents

Abstract

Organooxotin compounds can be assembled by using various synthetic methodologies. Although in most instances, organotin oxides and hydroxides are the preferred starting materials for preparing organooxotin compounds, Sn─C bond cleavage reactions involving organotin compounds also offer a rational route. This review deals with the recent progress in this area and examines various reactions, where Sn─C cleavage occurs. A wide range of products are accessible from this approach and these are presented in this article.

Keywords: Sn─C cleavage; Stannoxanes; Organooxotin; Organotin esters; Hydrolytic cleavage

1. Introduction

Organotin compounds have been attracting a lot of interest in recent years [1–4]. Most of these compounds are prepared, in general, by appropriate reactions involving the corresponding organotin halides. Thus, for example, hydrolytic reactions of the organotin halides themselves lead to a wide range of products [5]. Representative examples of the fully hydrolyzed products obtained from tri-, di- and monoorganotin halides are shown in Scheme 1. Thus, the hydrolysis of the triorganotin halides leads to the formation of the triorganotin hydroxides, R_3SnOH, and/or its condensed product the bis(triorganotin)oxide, $R_3SnOSnR_3$ [6]. On the other hand, the complete hydrolysis of diorganotin dihalides leads to the formation of the diorganotin oxide, R_2SnO. The molecular structure of R_2SnO depends on the nature of the 'R'; with substituents, such as *n*-Bu or Ph the compound R_2SnO has a polymeric structure [7]. Presence of bulky substituents, such as *t*-Bu or $CH(SiMe_3)_2$ leads to the formation of six- and four-membered rings [8,9] With the bis(trimethylsilyl)methyl substituent the incompletely condensed product $(R_2SnOH)_2O$ is also formed. Hydrolytic reactions on monoorganotin trihalides leads to the formation of polymeric products. The most common example is *n*-butylstannonoic acid, *n*-BuSn(O)OH. The structure of this compound is unknown, but based on its solid-state ^{119}Sn NMR chemical shift, it has been proposed to have a *football cage* type of structure [4]. A discrete trinuclear compound

☆ Based on the talk given by VC at ICCC-36, Merida-Yucatan, Mexico, July 2004.

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doi:10.1016/j.ccr.2005.03.028

Table 1
Summary of products derived from various Sn—C cleavage reactions

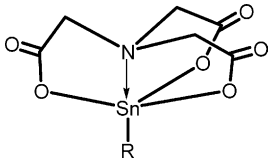
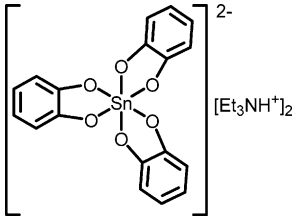
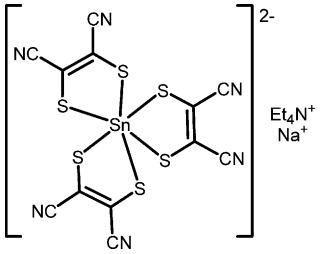
Entry	Substrate	Product	Comments	Ref.
(i) Tin–phenyl cleavage reactions				
1	$[PhSn(O)O_2C\text{-}i\text{-}C_3H_7]_n$ + $i\text{-}C_3H_7CO_2H$	$Sn[O_2C\text{-}i\text{-}C_3H_7]_4$	Reflux conditions	[30]
2	$R^1R^2PS_2H + R^3_4Sn$	$R^3_3SnS_2PR^1R^2$	1:1, 80–100 °C, 5 h R^1 = OMe, OEt, OPr, Me, Et R^2 = OMe, OEt, OPr, Me R^3= Et, Bu, Pr, Ph	[31]
3	$R^1_3SnO_2CR^2 + HgX_2 + H_2O$	$[R^1Sn(OH)_2O_2CR^2]_n$	1:1:1, ether or benzene, reflux, 4 h R^1 = Pr, Bu, Ph R^2 = H, Me, Et X = Cl, Br, I Cleavage order: Ph > Pr ≅ Bu ⋙ cyclohexyl	[32,33]
4	$Ph_3SnO_2CR + HgCl_2 + H_2O$	$[Sn(OH)_4]_n$	3:3:4, ether or benzene, reflux, 4 h R = Me, Et	[32,33]
5	Ph_3SnO_2CMe + 8-hydroxyquinoline	PhSn(8-oxyquinolinate)$_3$	Excess 8-hydroxyquinoline, benzene, reflux	[32,33]
6	$RPhSnO + N(CH_2CO_2H)_3$		1:1, DMF/toluene, reflux, 1 h R = Me, *t*-Bu	[34]
7	$Ph_3Sn–CH_2–SnPh_3 + MeCO_2H$	$(AcO)_3Sn–CH_2–Sn(OAc)_3$	Excess $MeCO_2H$, reflux	[35]
8	$Ph_3SnOH + C_6H_{11}CO_2H$	$[PhSn(O)O_2C–C_6H_{11}]_6$	The Sn–Ph cleaved product is formed by slow hydrolysis of $Ph_3SnO_2C–C_6H_{11}$ during recrystallization Structural type: **drum**	[36]
9	PhSn(O)OH + C_6H_4-1,2-$(OH)_2$ + Et_3N + $Me_2C(OMe)_2$		1:2:1:2, $CH_3CN–H_2O$, 80 °C, 12 h	[37]
10	$PhSnCl_3 + Na_2[(CN)_2C_2S_2] + Et_4N^+Cl^-$		1:2:1, acetone–H_2O, 50 °C, 1 h	[38]
11	$Ph_3SnOH + Cl_3CCO_2H$	$\{[Ph_2Sn(O_2CCCl_3)]_2O\}_2$	See also Scheme 9 MeOH–H_2O, RT, 3 h The product is formed during recrystallization of $Ph_3SnO_2CCCl_3$ from CCl_4–hexane Structural type: **ladder (L3)**	[39]

Table 1 (*Continued*)

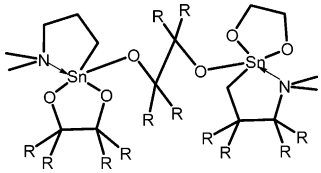
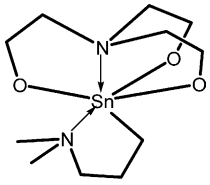
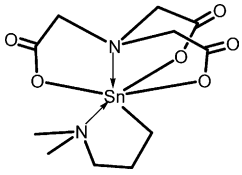
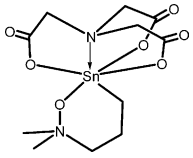
Entry	Substrate	Product	Comments	Ref.
12	$Ph_3SnOH + Cl_3CCO_2H$	$(PhSn)_6(O_2CCCl_3)_{10}O_4$	See also Scheme 9 Benzene, reflux, 24 h Structural type: **ladder (L5)**	[39]
13	$(Ph_3Sn)_2O + Cl_3CCO_2H$	$\{[Ph_2Sn(O_2CCCl_3)]_2O\}_2$	See also Scheme 9 MeOH–H_2O, RT, 3 h The product is formed during recrystallization from CCl_4–light petroleum (30–40 °C) Structural type: **ladder (L1)**	[39]
14	$Ph_2SnO + Cl_3CCO_2H$	$[PhSn(O)O_2CCCl_3]_6$	See also Scheme 9 Benzene, reflux, 12 h Structural type: **drum**	[39]
15	$Me_2N(CH_2)_3SnPh_3 + PhOH$	$Me_2N(CH_2)_3SnPh_{3-n}(OPh)_n$	$n = 1$, 1:1, toluene, reflux, 5 h $n = 2$, 1:2, toluene, reflux, 6 h	[40]
16	$Me_2N(CH_2)_3SnPh_3 + HOCR_2CR_2OH$		R = H, 1:10, 150 °C, 5 h R = Me, 1:3, 150 °C, 22 h	[40]
17	$Me_2N(CH_2)_3SnPh_2(OPh) + (HOCH_2CH_2)_3N$		1:1, xylene, reflux, 24 h	[40]
18	$Me_2N(CH_2)_3SnPh_2(OPh) + (HO_2CCH_2)_3N$		1:1, DMF, 140 °C, 1 h	[40]
19	$Me_2N(CH_2)_3SnPh_3 + (HO_2CCH_2)_3N$		1:1, DMF, 120 °C, 22 h	[40]
20	$R_2SnPh_2 + ClCH_2CO_2H$	$R_2Sn(O_2CCH_2Cl)_2$	1:2, 160 °C, 20 min R = neopentyl, CH_2–$SiMe_3$, 3,3-dimethylbutyl, cyclohexyl R_2 = hexamethylene	[41]
21	$Ph_4Sn + RCO_2H$	$Sn[O_2CR]_4$	See also Scheme 8 R = Me (1:70, benzene, reflux, 25 h) R = CMe_3 (1:40, reflux, 10–24 h) R = $(CH_2)_{12}CH_3$ (1:20, reflux, 10–24 h) R = $(CH_2)_{14}CH_3$ (1:6, xylene, reflux, 10–24 h) R = CH=CHPh (1:6, xylene, reflux, 10–24 h)	[42]

Table 1 (*Continued*)

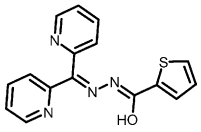
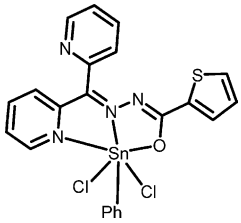
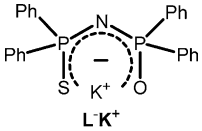
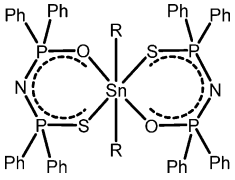
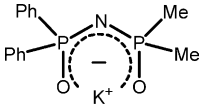
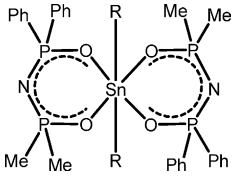
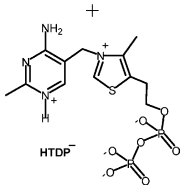
Entry	Substrate	Product	Comments	Ref.
			R = CH_2Ph (1:6, xylene, reflux, 10–24 h) R = $(CH_2)_8CH{=}CH_2$ (1:6, xylene, reflux, 10–24 h) R = 2,4,6-$Me_3C_6H_2$ (1:4, xylene, reflux, 10–24 h) R = $CHPh_2$ (1:6, xylene, reflux, 10–24 h) R = $CH{=}CMe_2$ (1:6, xylene, reflux, 10–24 h)	
22	$Ph_4Sn + (C_6H_{11})_2PO_2H$	$Sn[O_2P(C_6H_{11})_2]_4$	See also Scheme 8 1:6, reflux, 10–24 h	[42]
23	$Ph_4Sn + Ph_2PO_2H$	$PhSn[O_2PPh_2]_3$	See also Scheme 8 1:6, reflux, 10–24 h	[42]
24	$Ph_4Sn + t\text{-}BuPO_3H_2$	$Sn[O_2P(OH)\text{-}t\text{-}Bu]_4$	See also Scheme 8 1:10, toluene, reflux, 10–24 h	[42]
25	$Ph_4Sn + t\text{-}BuPO_3H_2$	$PhSn[O_3P\text{-}t\text{-}Bu][O_2P(OH)\text{-}t\text{-}Bu]$	See also Scheme 8 1:2, reflux, 10–24 h	[42]
26	Ph_2SnCl_2 + 		1:1, absolute EtOH, reflux, 0.5 h	[43]
27	 L^-K^+ + R_3SnCl		1:1, toluene, reflux, 2 h R = Ph, Me The product is formed by a redistribution reaction of R_3SnL	[44]
28	 L^-K^+ + R_3SnCl		1:1, toluene, reflux, 2 h R = Ph, Me The product is formed by a redistribution reaction of R_3SnL	[45]
29	$Ph_3Sn{-}(CH_2)_3{-}SnPh_3 + ClCH_2CO_2H$	$[Sn{-}(CH_2)_3{-}Sn]_6\ (O_2CCH_2Cl)_{14}(OH)_2O_{10}$	See also Scheme 10 1:6, toluene, 120 °C, 2 d Stirring, CH_2Cl_2 Repeated crystallization from CH_2Cl_2–hexane Structural type: **flattened foot-ball**	[46]
30	$Ph_2Sn[(CH_2)_2R_f]_2 + ClCH_2CO_2H$	$[(CH_2)_2R_f]_2Sn(O_2CCH_2Cl)_2$	Excess $ClCH_2CO_2H$, reflux	[47]
31	$PhMeSnCl_2$ + 	$\{[MeSn(HTDP)(OH)]_3O\}^+Cl^-$	1:1, H_2O–$CHCl_3$, pH = 5.6, RT, 16 h Structural type: ***O*-capped**	[48]

Table 1 (*Continued*)

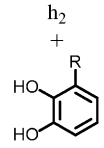
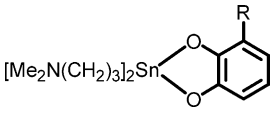
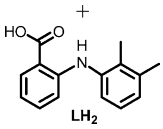
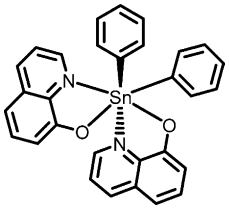
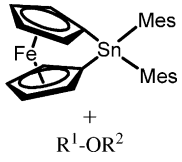
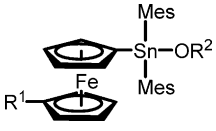
Entry	Substrate	Product	Comments	Ref.
32	$[Me_2N(CH_2)_3]_2SnPh_2$ + ROH	$[Me_2N(CH_2)_3]_2Sn(OR)_2$	Excess phenol, toluene, reflux, 6.5 h R = C_6H_5, 4-*t*-BuC_6H_4, 4-$NO_2C_6H_4$, 2-FC_6H_4	[49]
33	$[Me_2N(CH_2)_3]_2SnPh_2$ + 		1:1, toluene, reflux, 12 h R = H, OCH_3	[49]
34	$[Ph_2SnO]_n$ + 	$[PhSn(O)–LH]_n$	1:1, benzene, reflux, 24 h	[50]
35	$Me_2PhSnI + AgO_2CR$	$\{[Me_2SnO_2CR]_2O\}_2$	1:1, ethanol, RT, 1 h R = Ph, $CHCl_2$ Structural type: **ladder (L1)**	[51,52]
36	$(Ph_3Sn)_2O$ + 2,4,6-$(CF_3)_3C_6H_2$-CO_2H	$[Ph_2Sn(\mu_2\text{-}OH)O_2CC_6H_2\text{-}2,4,6\text{-}(CF_3)_3]_2$	See also Scheme 11 1:2, benzene, reflux, 6 h Crystallized from CH_2Cl_2-*n*-hexane	[54]
37	$(Ph_3Sn)_2O/Ph_3SnOH + CF_3SO_3H$	$[Ph_2Sn(OH)OSnPh_2(O_3SCF_3)]_2$	See also Scheme 11 2:1, MeCN, RT, 1 h Crystallized from CH_2Cl_2-petroleum spirit (60–80 °C) Structural type: **ladder (L6)**	[55]
38	$Ph_3SnCl + C_5H_3N(2\text{-}SH)(3\text{-}CO_2H)$	$\{Ph_2Sn[(C_5H_3N)(2\text{-}S)(3\text{-}CO_2)]\}_3$	See also Scheme 12 2:1, toluene, 90 °C, 1.5 h Et_3N, toluene, 110 °C, 6 h Crystallized from EtOH (95%) or benzene Structural type: **macrocycle**	[56]
39	Ph_3SnCl + 8-hydroxyquinoline		1:1, Et_3N, benzene, reflux, 3.5 h	[57]
40	 + $R^1\text{-}OR^2$		Release of steric strain is the main driving force for this reaction R^1 = H and $R^2 = O_2SCF_3$, 1:1, CH_2Cl_2, −78 to 25 °C, 0.5 h R^1 = Me and $R^2 = O_2SCF_3$, 1:1, CH_2Cl_2, RT, 1–6 h R^1 = *n*-Bu_3Sn and $R^2 = O_2SCF_3$, 1:1, C_6D_6, RT, 1 d R^1 = H and R^2 = Me, 1:1, C_6D_6, RT, 6 d	[58]

Table 1 (*Continued*)

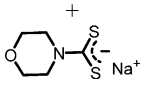
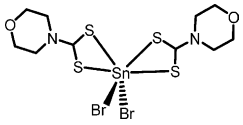
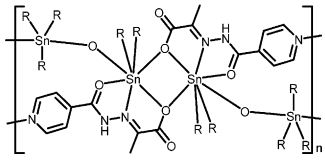
Entry	Substrate	Product	Comments	Ref.
(ii) Tin–benzyl cleavage reactions				
41	$(PhCH_2)_2SnCl_2 + AgO_2P(C_6H_{11})_2$	$[PhCH_2Sn(OH)\{O_2P(C_6H_{11})_2\}_2]_2$	See also Scheme 13 1:2.5, toluene, reflux, 12 h Structural type: **butterfly cluster**	[59]
42	$(PhCH_2)_3SnCl$ or $(PhCH_2)_2SnCl_2$ or $(PhCH_2)_2SnO{\cdot}H_2O$ + *t*-$BuPO(OH)_2$	$\{[PhCH_2Sn(O_2P(OH)$-*t*-$Bu)_2]_2O\}_2$	See also Scheme 13 1:2, toluene, reflux, 4–10 h Structural type: **tetranuclear cage**	[60]
43	$(PhCH_2)_2SnCl_2 + AgO_2CMe$	$\{[(PhCH_2)Sn(O)O_2CMe]_2(PhCH_2)Sn(O_2CMe)_3\}_2$	See also Scheme 14 1:2, toluene, reflux, 20 h Crystallized from CH_2Cl_2 Structural type: **ladder (L5)**	[59]
44	$(PhCH_2)_2SnCl_2 + AgO_2CR$	$[PhCH_2Sn(O)O_2CR]_6$	See also Scheme 14 R = *t*-Bu, C_5H_4N, $CH{=}CMe_2$, $CHPh_2$ 1:2, toluene, reflux, 10 h Structural type: **drum**	[59]
45	$(PhCH_2)_2SnCl_2 + PhCO_2H$	$[PhCH_2Sn(O)O_2CPh]_6$	See also Scheme 14 1:1, EtONa/EtOH, reflux, 12–20 h Structural type: **drum**	[61]
46	$(4\text{-}F\text{-}C_6H_4\text{-}CH_2)_2SnCl_2$ + 		1:2, EtOH (95%), reflux, 6 h Crystallized from EtOH	[62]
47	$[(PhCH_2)_3Sn]_2O + HO_2CR$	$[PhCH_2Sn(O)O_2CR]_6$	1:2, benzene, reflux, 12 h R = C_6H_5, 2-ClC_6H_4, 4-ClC_6H_4, 2-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 4-$OCH_3C_6H_4$, 2-C_4H_3O, 2-C_4H_3S, 2-C_4H_4N, 2-C_5H_4N, 3-C_5H_4N, 4-C_5H_4N Structural type: **drum**	[63,64]
48	$(R_3Sn)_2O$ + 4-PyC(O)NH–N=$C(CH_3)CO_2H$		1:2, benzene, reflux, 6 h R = *n*-Bu, $C_6H_5CH_2$, 4-$NCC_6H_4CH_2$	[65]
(iii) Tin–vinyl and tin–alkyne cleavage reactions				
49	$Et_3Sn{-}CH{=}CH_2 + RCO_2H$	Et_3SnO_2CR	1:1, reflux, 1.5 h R = Me, $CHBr{-}CH_3$	[68]
50	$Et_3Sn{-}CH{=}CH_2 + HSCH_2CO_2Et$	$Et_3Sn{-}S{-}CH_2CO_2Et$	1:3, reflux, 10 h	[68]
51	$Et_3Sn{-}C{\equiv}C{-}P(O)(OEt)_2 + MeCO_2H$	Et_3SnO_2CMe	1:1, ether, RT, 10 min	[70]
52	$R^1Sn(C{\equiv}C{-}R^2)_3 + H_2O$	$[(R^1Sn)_{12}(\mu{-}O)_{14}(\mu{-}OH)_6]{\cdot}(OH)_2$	CH_2Cl_2–aqueous THF or aqueous alcohol, 20 °C, 12 h R^1 = *n*-Bu, $(CH_2)_4C_6H_4$-4-$CH{=}CH_2$, $(CH_2)_5OAc$, $(CH_2)_5O_2CCH{=}CHMe$ R^2 = Me, *n*-Bu, Ph Structural type: **football cage**	[71]

Table 1 (*Continued*)

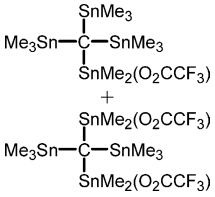
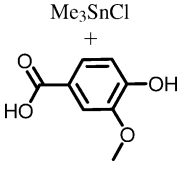
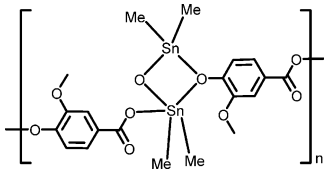
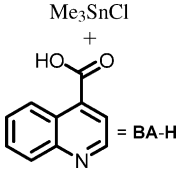
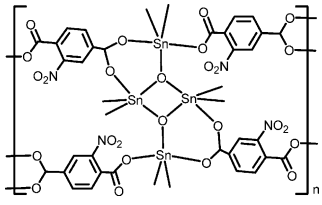
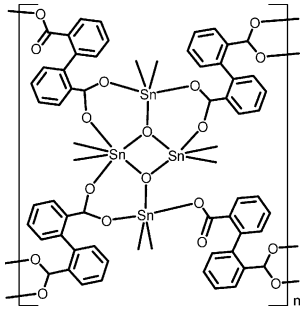
Entry	Substrate	Product	Comments	Ref.
53	$R^1Sn(C{\equiv}C{-}R^2)_3 + R^3OH$	$R^1Sn(OR^3)_3$	1:3, cyclohexane, 60 °C, 16 h R^1 = Me, *n*-Bu R^2 = Me, Ph R^3 = *i*-Pr, *i*-Bu, *s*-Bu, CH_2Ph	[71]
(iv) Tin–ethyl and tin–methyl cleavage reactions				
54	$Et_3SnS_2P(OEt)_2 + Cl_3CCO_2H$	$Et_2Sn[S_2P(OEt)_2][O_2CCCl_3]$	1:1, silica gel, 100 °C, 5 h	[31]
55	$Et_3SnO_2CCCl_3 + HS_2P(OEt)_2$	$Et_2Sn[S_2P(OEt)_2][O_2CCCl_3]$	1:1, silica gel, 100 °C, 5 h	[31]
56	$Me_3SnCl + RCO_2H$	Me_2ClSnO_2CR	Excess acid, 100 °C R = Me, CF_3, C_2F_5, C_3F_7, CF_2Cl, CH_2Cl, CCl_3, CH_2Br, CH_2I	[72]
57	$Me_4Sn + HOTeF_5$	$Me_3SnOTeF_5$	1:1	[73]
58	$Me_3Sn{-}SnMe_3 + ClCH_2CO_2H$	$Me_2SnO_2CCH_2Cl$	1:10, $CHCl_3$, 35 °C, 72 h	[74]
59	$Me_3Sn{-}CHX_2 + n$-PrOH	$Me_3Sn{-}O{-}n$-Pr	NH_3 buffer in *n*-PrOH–H_2O 8:2 v/v X = Cl, Br	[75]
60	$C[SnMe_3]_4 + RCO_2H$		1:1, $CDCl_3$, RT R = Me, CF_3 If excess acid is used, product is $Me_3Sn{-}C[SnMe_2(O_2CR)]_3$	[76]
61			Hydrothermal synthesis 1.2:1, H_2O–pyridine, sealed tube, 130 °C, 48 h Structural type: **bridged ladder**	[77]
62		$[(Me_2Sn{-}BA)_2O]_2$	Hydrothermal synthesis 1.2:1, H_2O–pyridine, sealed tube, 130 °C, 48 h Structural type: **ladder (L1)**	[77]
63	$Me_3SnCl + 2\text{-}NO_2C_6H_3\text{-}1,4\text{-}(CO_2H)_2 + 4,4'$-bipyridine		Hydrothermal synthesis 2:1:1, H_2O, sealed tube, 140 °C, 72 h Cooling 5 h Structural type: **bridged ladder (L1)**	[78]
64	Me_3SnCl + diphenic acid + 4,4′-bipyridine		Hydrothermal synthesis 2:1:1, H_2O, sealed tube, 140 °C, 72 h Cooling 5 h Structural type: **bridged ladder (L4)**	[78]

Table 1 (*Continued*)

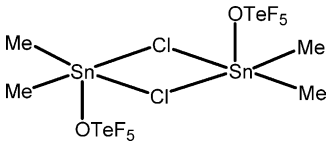
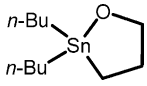
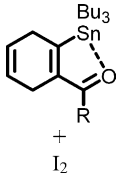
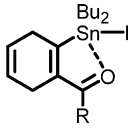
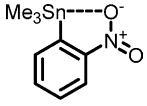
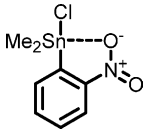
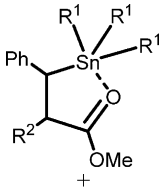
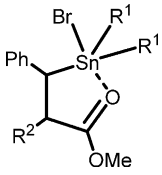
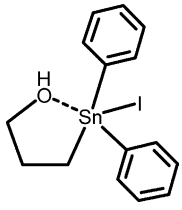
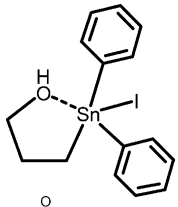
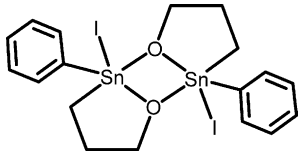
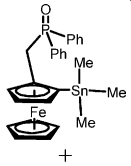
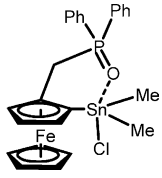
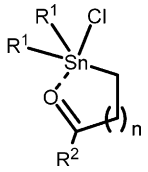
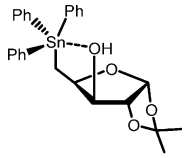
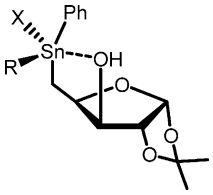
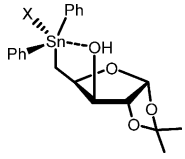
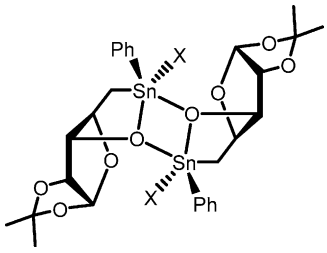
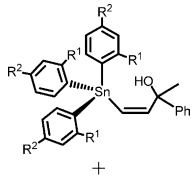
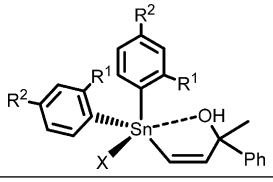
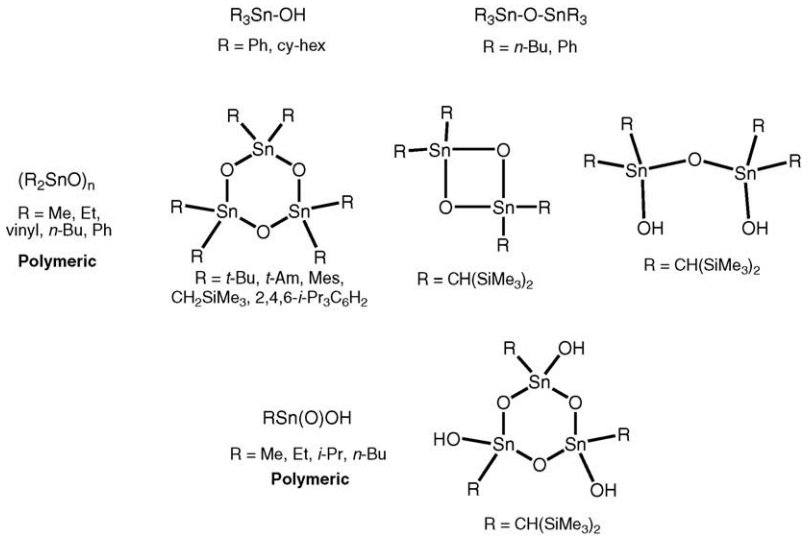
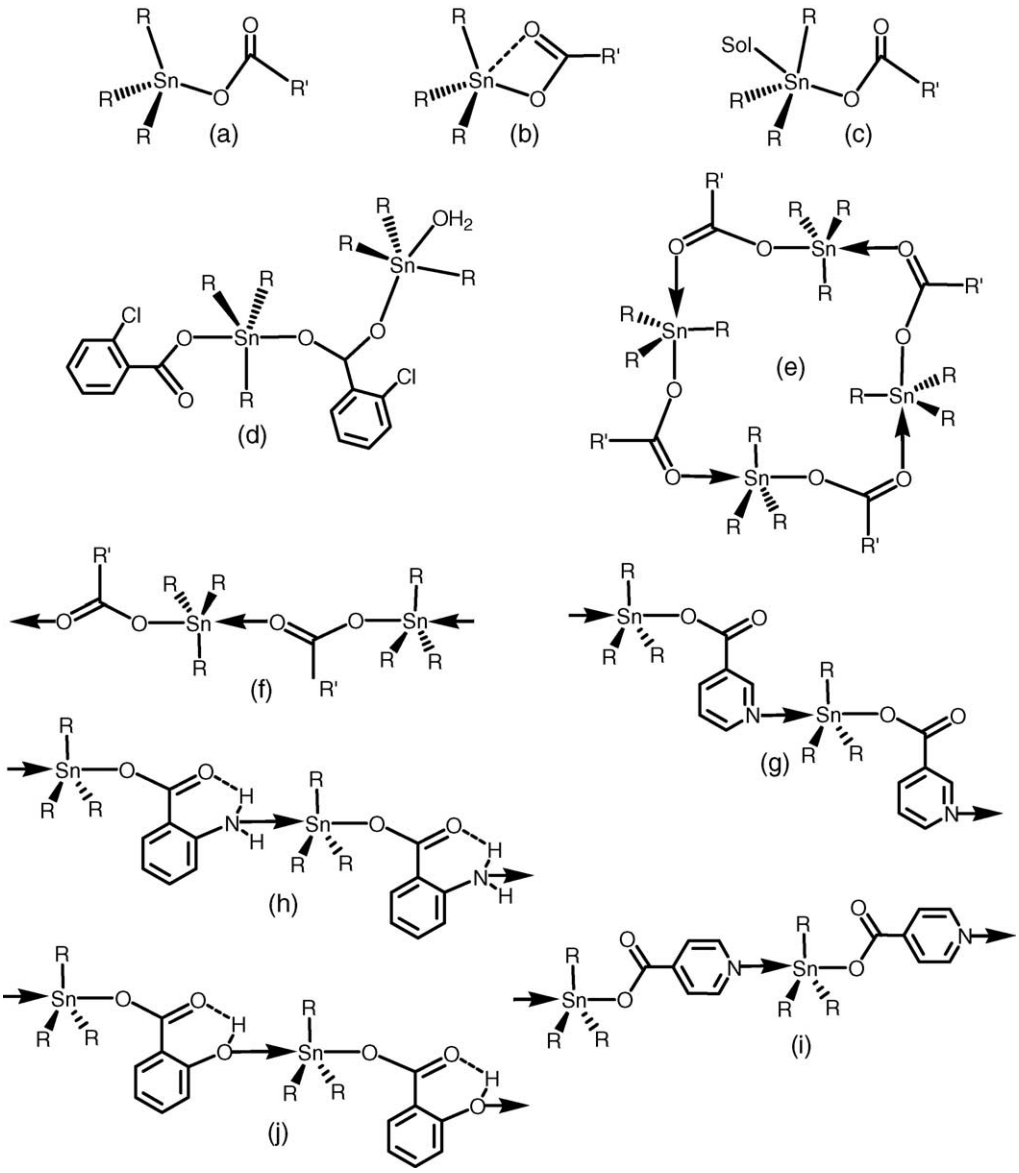
Entry	Substrate	Product	Comments	Ref.
65	$Me_3SnCl + ClOTeF_5$ or $HOTeF_5$		1:1, −196 °C to RT, 12 h	[79]
(v) Tin–butyl cleavage reactions				
66	$(n\text{-}Bu_3Sn)_2O + 1,5\text{-}(HO_3S)_2C_{10}H_6$	$\{n\text{-}Bu_2Sn(OH_2)_3[1,5\text{-}(SO_3)_2C_{10}H_6]\}_2$	See also Scheme 17 1:2, toluene, reflux, 6 h Crystallized from MeOH–THF	[80]
67	$n\text{-}Bu_2SnO + HO_2C\text{–}C_5H_4\text{–}Fe\text{–}C_5H_4\text{–}CO_2H$	$Sn_8O_4(O_2C\text{–}C_5H_4\text{–}Fe\text{–}C_5H_4\text{–}CO_2)_6$	See also Scheme 18 Solvothermal synthesis 1:1, toluene, autoclave, 180 °C, 96 h Structural type: **cubic**	[81]
(vi) Intramolecular neucleophile assisted Sn–C cleavage reactions				
68	$n\text{-}Bu_2Sn\ [CH_2CH_2CH_2\ OH]_2$		RT	[82]
69	 + I_2		$CDCl_3$ or C_6D_6, RT, dark R = Me, OMe No solvent effect in either non-polar (CCl_4, $CHCl_3$, C_6H_6) or polar (MeOH)	[83]
70	 + MeC(O)Cl		$AlCl_3$, CH_2Cl_2, from −20 to +60 °C, 2 h	[84]
71	 + Br_2		1:1, CCl_4–CH_3CN, RT, 1 h R^1 = Me, *n*-Bu R^2 = Me, Ph	[85]
72	$Ph_3SnCH_2CH_2\ CH_2OH + I_2$		1:1, Heating in CCl_4 60 °C for 5 h at 1 Torr	[86]
73			Heating at 120 °C for 10 h at 1 Torr	[86]
74	 + HCl		3:4, MeOH, 50 °C, 30 min	[87]

Table 1 (*Continued*)

Entry	Substrate	Product	Comments	Ref.
75	$R^1_3Sn–CH_2–(CH_2)_n–C(O)R^2$		Electrochemical oxidation, Bu_4NClO_4/CH_2Cl_2, 2,6-lutidine, 4 Å molecular sieves, divided cell Work up: aqueous NaCl R^1 = *n*-Bu, R^2 = Me, *n* = 1–3 R^1 = *n*-Bu, R^2 = OMe, *n* = 1 $R^1 = C_{10}H_{21}$, R^2 = Me, *n* = 1	[88]
76	 + X_2		1:2, CH_2Cl_2, 0 °C R = Ph, X = I; R = Ph, X = Br; R = X = I	[89]
77			Slow decomposition at RT	[89]
78	 + IX or Br_2		1:1, CCl_4, −5 °C to RT, 1 h R^1 and R^2 = H, Me X = Cl, Br, I	[90]



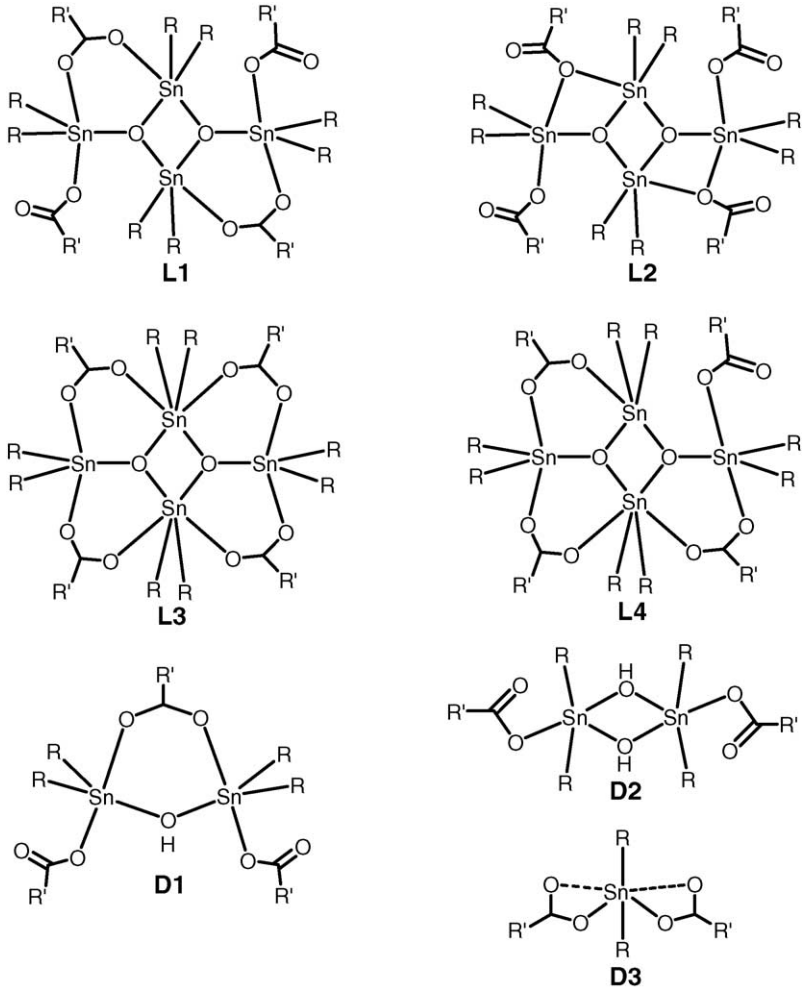
Scheme 1. Organotin oxides and hydroxides in monomeric, dimeric, trimeric and polymeric forms.



Scheme 2. Triorganotincarboxylates: discrete (a–d), macrocyclic (e) and polymeric structures (f–j).

has been isolated in the case RSn(O)OH {R = $CH(SiMe_3)_2$} [10,11]. The presence of the sterically encumbered substituent in the latter is believed to stabilize the trimeric form.

The hydrolyzed products (oxides, hydroxides and oxohydroxides) themselves serve as precursors for reactions with various reagents, such as carboxylic, phosphonic, phosphinic or sulfonic acids. Even restricting ourselves to organotin carboxylates, the diversity of the products formed is quite remarkable. These possibilities are summarized in Schemes 2–4. The nature of the products obtained depends on many factors including nature of the organotin precursor/carboxylic acids and the stoichiometry of the reaction. Triorganotin carboxylates [R_3SnO_2CR'] are found in discrete, macrocylic or polymeric structures [2,4]. Diorganotin carboxylates of the type {$[R_2SnO_2CR']_2O\}_2$ occur in different types of *ladder* structures (L1–L4, Scheme 3). In each of these, a Sn_2O_2 four-membered ring serves as a central core around which the remaining molecular structure is built. Dinuclear compounds {$[R_2SnO_2CR']_2(\mu_2$–OH)$O_2CR'\}$ (R = *n*-Bu; R′ = CCl_3) [12] (D1, Scheme 3) and $[R_2Sn(\mu_2$–OH)$O_2CR']_2$ (R = *t*-Bu; R′ = Me) [8] (D2, Scheme 3) are formed in some instances. Diorganotin dicarboxylates adopt monomeric structures (D3, Scheme 3) [2,4]. In the case of the reactions of RSn(O)OH and carboxylic acids, four important structural types [4,13] are known: (i) mononuclear tricarboxylate $RSn(O_2CR')_3$ (D4); (ii) hexanuclear oxycarboxylate $[RSn(O)O_2CR']_6$ also known as a *drum* structure; (iii) hexanuclear oxycarboxylate {$[RSn(O)O_2CR']_2[RSn(O_2CR')_3]\}_2$ present in a *ladder* structure (L3); (iv) trinuclear oxycarboxylate {$[RSn(X)O_2CR']_3(\mu_3$–O)(μ_2–OH)} (D5) (Scheme 4).



Scheme 3. Diorganooxotin carboxylates: (1) ladder structures (L1–L4) for carboxylates $\{[R_2SnO_2CR']_2O\}_2$; (2) discrete dinuclear structures (D1 and D2) for carboxylates $\{[R_2SnO_2CR']_2(\mu_2\text{–}OH)O_2CR'\}$ and $[R_2Sn(\mu_2\text{–}OH)O_2CR']_2$; (3) discrete mononuclear structure (D3) for carboxylate $R_2Sn(O_2CR')_2$.

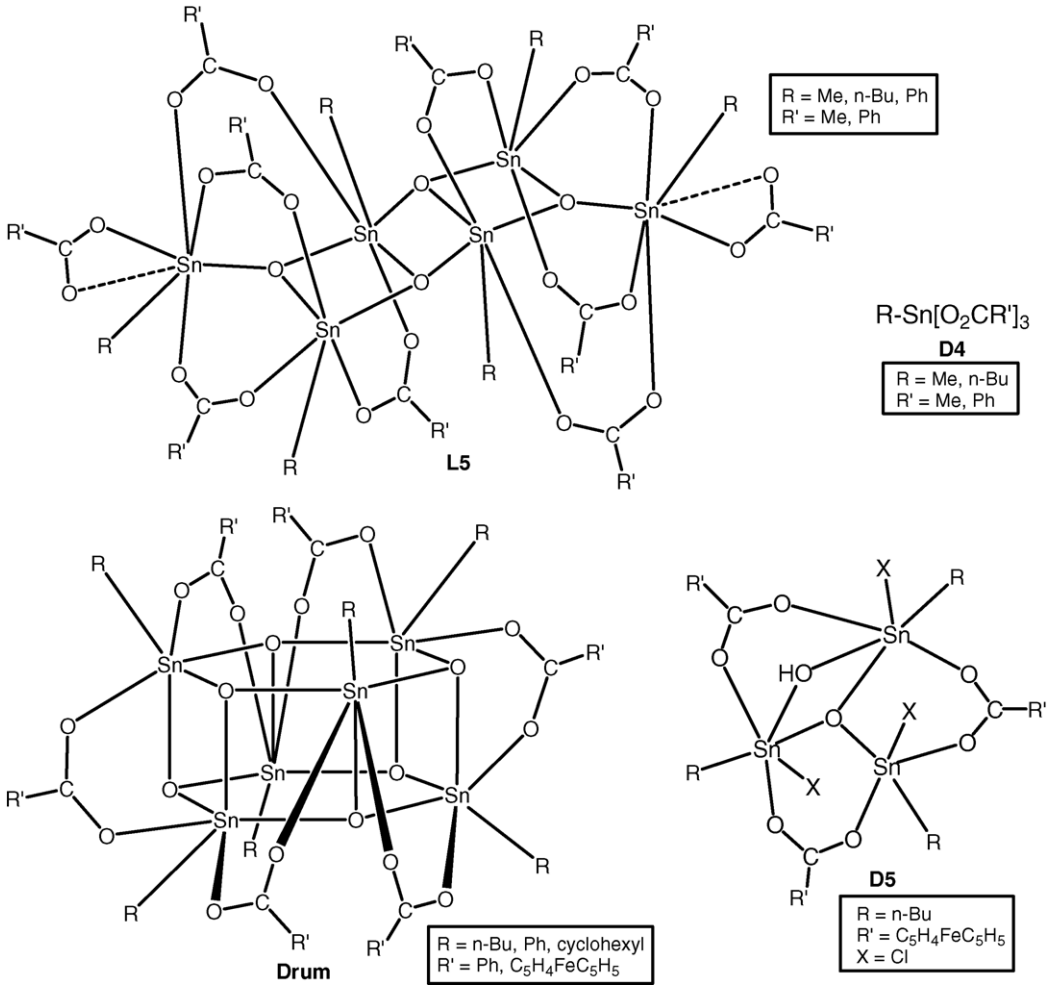
The product diversity is considerably enhanced in the case of the reactions between RSn(O)OH/phosphorus acids [13]. A wide variety of products with considerable structural diversity are realized in these reactions. Some representative examples of the organotin cages obtained in these reactions, are shown in Schemes 5 and 6. Thus, cages, such as *ladder* [14], *drum* [15–17], *cube* [18,19], *O-capped cluster* [19,20], *butterfly cage* [20,21], *crown* [21,22], *extended cage* [22], *football cage* [23,24], *double-O-capped clusters* [25,26], etc., are formed in these reactions.

As can be seen from Schemes 2–6, the products obtained in the reactions between organotin oxides/hydroxides and the acid reagents result in an elaboration of the Sn–O bond of the organotin reactants. The Sn–C bonds are not affected. In contrast to this, a number of reactions are becoming increasingly known, where the Sn–C bond is cleaved leading to Sn–O bond formation. This review focuses on this theme and is presented in the following account. Summary of products derived from various Sn–C cleavage reactions are given in Table 1.

2. Sn–Ph cleavage reactions

The cleavage of Sn–Ph bonds under the influence of strong acids has been known for a long time and has been widely used in synthesis involving organotin compounds [27]. Recent examples of this reaction are illustrated by the selective cleavage of Sn–Ph bonds in the reaction of $(Me_3SiCH_2)_2SnPh_2$ with HX (Scheme 7, Eq. (1)) [28]. In this reaction, the Sn–CH_2SiMe_3 moiety is unaffected by the action of the acid. The organotin dihalides $(Me_3SiCH_2)_2SnX_2$ obtained in the above reaction have been utilized for hydrolysis reactions. Hydrochloric acid or even $SnCl_4$ has been used for the selective cleavage of Sn–Ph bonds [29] in an alkyl chain bridged ditin compound, $Ph_3Sn(CH_2)_3SnPh_3$ (Scheme 7, Eqs. (2) and (3)).

Tetraphenyl tin, $SnPh_4$, has been shown to undergo exhaustive dearylation in reactions with various carboxylic acids or dicyclohexylphosphinic acid to afford tin tetracarboxylates, $Sn(O_2CR)_4$ or the tin tetraphosphinate, $Sn[O_2P(C_6H_{11})_2]_4$, respectively (Scheme 8) (Table 1, Entries



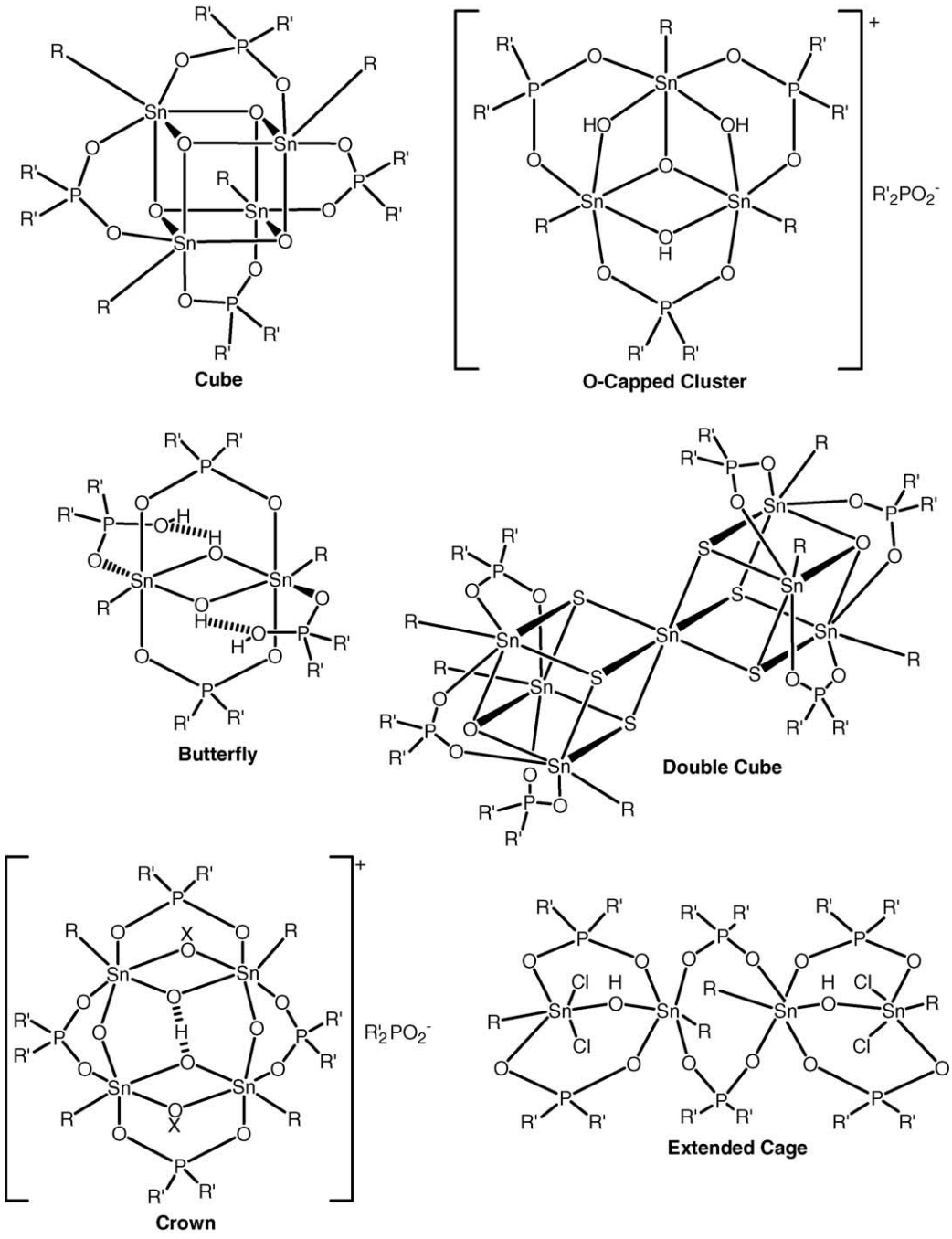
Scheme 4. Monoorganooxotin carboxylates: (1) ladder structure (L5) for the carboxylate $\{[RSn(O)O_2CR']_2[RSn(O_2CR')_3]\}_2$; (2) discrete mononuclear tricarboxylate (D4); (3) drum structure for the carboxylate $[RSn(O)O_2CR']_6$; (4) trinuclear structure (D5) for the carboxylate $\{[RSn(X)O_2CR']_3(\mu_3\text{–}O)(\mu_2\text{–}OH)\}$.

21–25) [42]. A tin tetraphosphonate, $Sn[O_2P(OH)\text{-}t\text{-}Bu]_4$ was obtained in the reaction of $SnPh_4$ with *t*-butylphosphonic acid. However, the reaction of diphenylphosphinic acid leads to a mono aryl product, $PhSn(O_2PPh_2)_3$ (Scheme 8).

Triphenyltin and diphenyltin compounds have been used in dearylation reactions involving carboxcylic acids [4,27]. While use of "normal" carboxylic acids and "normal" reaction conditions do not lead to dearylation, the presence of strong electron-withdrawing substituents on the carboxylic acid facilitates dearylation (Table 1, Entries 11–14, 20). Thus, the reaction of Ph_3SnOH with trichloroacetic acid in mild reaction conditions using methanol affords the expected product, $Ph_3SnO_2CCl_3$ (Scheme 9) [39]. However, the latter under recrystallization conditions affords a dearylated tetrameric *ladder* compound, $\{[Ph_2SnO_2CCl_3]_2O\}_2$. In contrast, the reaction of Ph_3SnOH with CCl_3CO_2H in reflux conditions, using benzene as the solvent, leads to double dearylation and affords the hexameric *ladder* product, $\{[PhSn(O)O_2CCl_3]_2[PhSn(O_2CCl_3)_3]\}_2$. The reaction of Ph_2SnO with CCl_3CO_2H under similar reaction conditions (benzene, reflux) leads to monodearylation and affords the *drum*, $[PhSn(O)O_2CCl_3]_6$ (Scheme 9) [39].

The reaction of $Ph_3Sn(CH_2)_3SnPh_3$ with monochloroacetic acid (Table 1, Entry 29) also leads to dearylation to afford the "*flattened foot ball*", $\{[Sn(CH_2)_3Sn]_6[ClCH_2CO_2]_{14}(OH)_2(O)_{10}\}$ [46]. This reaction is believed to occur in two stages. The first phase of the reaction has been suggested to proceed by a hexa-dearylation to afford a hexacarboxylate. The hydrolysis of the latter affords a dihydroxy intermediate which is eventually transformed to the final product by a condensation reaction (Scheme 10).

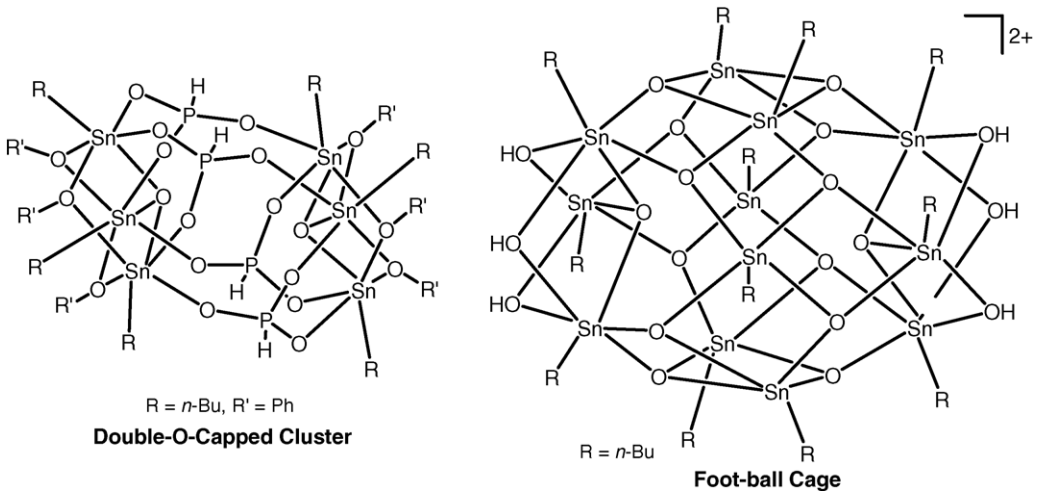
The influence of electron-withdrawing group(s) on the reactivity of the carboxylic acids has been very dramatically demonstrated by us very recently. Thus, 2,4,6-Me_3–$C_6H_2CO_2H$ reacts with Ph_3Sn–O–$SnPh_3$ (toluene, reflux) to afford the normal product, viz., Ph_3SnO_2C–C_6H_2–2,4,6-Me_3 (Scheme 11) [53]. The latter has been shown to possess a discrete structure, such as that shown in Scheme 2, (b). In contrast, the reac-



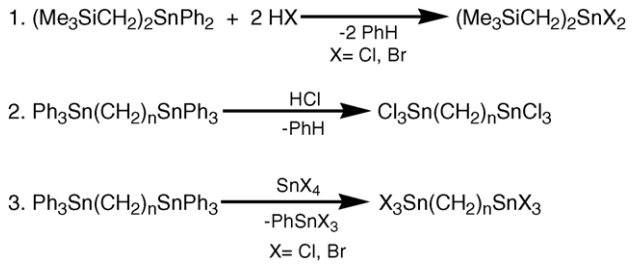
Scheme 5. Monoorganooxotin phosphinates.

tion of 2,4,6-$(CF_3)_3$–$C_6H_2CO_2H$ with Ph_3Sn–O–$SnPh_3$ (under the same reaction conditions) leads to mono dearylation and a hydroxyl bridged ditin compound $\{[2,4,6\text{-}(CF_3)_3\text{–}C_6H_2CO_2]SnPh_2(\mu_2\text{–}OH)\}_2$ is obtained (Scheme 11) (Table 1, Entry 36) [54]. The latter product also shows an interesting 3-dimensional supramolecular structure in the solid-state that results from weak C–H···F and C–H···O intermolecular contacts. Beckmann et al. have also noted that an analogous dearylation occurs in the reaction of Ph_3Sn–O–$SnPh_3$ with triflic acid [55]. The product obtained in this instance has a *ladder* (L6) type of structure (Scheme 11) (Table 1, Entry 37).

Another instance of reactant dependant variation of products is provided in the reactions of triphenyltin chloride with "mercaptonicotinic acid". Triphenyltin chloride reacts with the sodium salt of 2-mercaptonicotinic acid to afford a ditin compound by a simple metathesis reaction [56]. In this product, all the phenyl substituents on tin are intact (Scheme 12). On the other hand, the reaction of Ph_3SnCl with 2-mercaptonicotinic acid in the presence of Et_3N leads

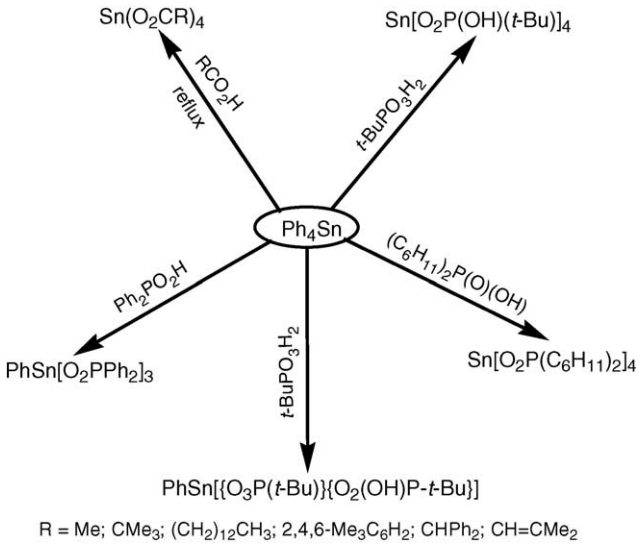


Scheme 6. Monoorganooxotin multinuclear cages.



Scheme 7. Selective dearylation reactions.

to monodearylation to afford an interesting macrocylic product, where the doubly deprotonated 2-mercaptonicotinic acid acts as a bridging ligand (Scheme 12) (Table 1, Entry 38).



Scheme 8. Sn–Ph cleavage reactions of $SnPh_4$ under various reaction conditions.

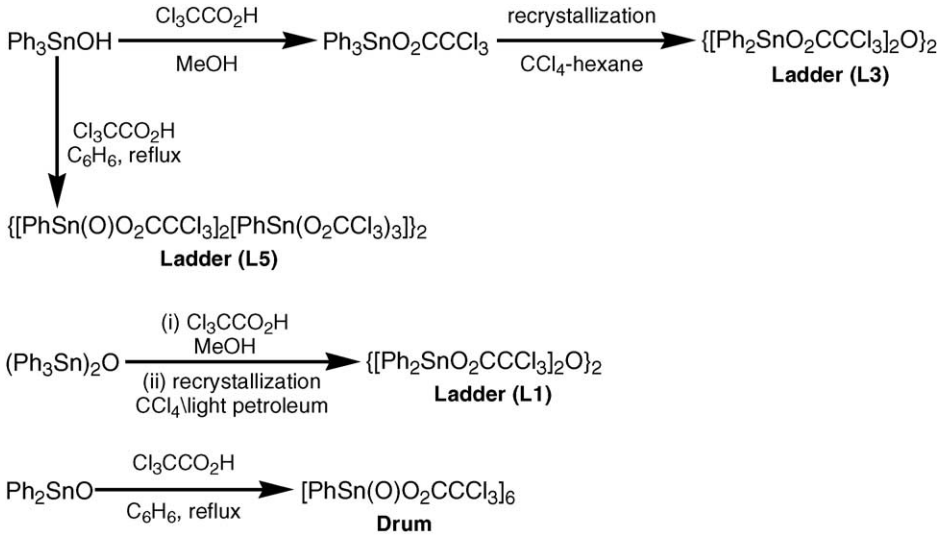
An interesting case of Sn–C bond cleavage reaction involving Sn-cyclopentadienyl bond has been noted [58]. Thus, the reaction of $\{Fe(\eta^5\text{–}C_5H_4)_2\}_2SnMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$) with reagents, such as CF_3SO_3H leads to the release of ring strain, cleavage of Sn–C bond and formation of a ferrocenyltin sulfonate (Table 1, Entry 40).

There have been many other instances of Sn–Ph cleavage reactions. Prominent and representative examples of these have been summarized in Table 1 (Entries 1–39).

3. Sn–CH_2Ph cleavage reactions

Debenzylation reactions offer an excellent possibility for the construction of organotin cages and clusters. Recently, we have utilized the debenzylation strategy for the synthesis of the *tetranuclear organooxotin cage* $[(PhCH_2)_2Sn_2O(O_2P(OH)\text{-}t\text{-}Bu)_4]_2$ [60] (Scheme 13). Accordingly, the reaction of $(PhCH_2)_2SnCl_2$ or $(PhCH_2)_2SnO{\cdot}H_2O$ with *t*-$BuP(O)(OH)_2$ in boiling toluene has been found to afford the mono debenzylated product $[(PhCH_2)_2Sn_2O(O_2P(OH)\text{-}t\text{-}Bu)_4]_2$ in excellent yields (Table 1, Entry 42). In this reaction, the benzyl group is eliminated as toluene. Interestingly, the reaction of $(PhCH_2)_3SnCl$ with *t*-$BuP(O)(OH)_2$ also leads to the same product via a double debenzylation path way. It may be noted that in all these reactions the final product still contains one benzyl group on tin. A careful investigation of these reactions revealed the formation of a *half-cage* intermediate, $\{(PhCH_2)_2Sn_2O[O_2P(OH)\text{-}t\text{-}Bu]_4\}$ (Scheme 13) [60] The latter has been characterized by ^{119}Sn and ^{31}P NMR spectroscopy.

Swamy et al. [59] have also observed debenzylation in reactions involving $(C_6H_{11})_2P(O)OH$ or AgO_2

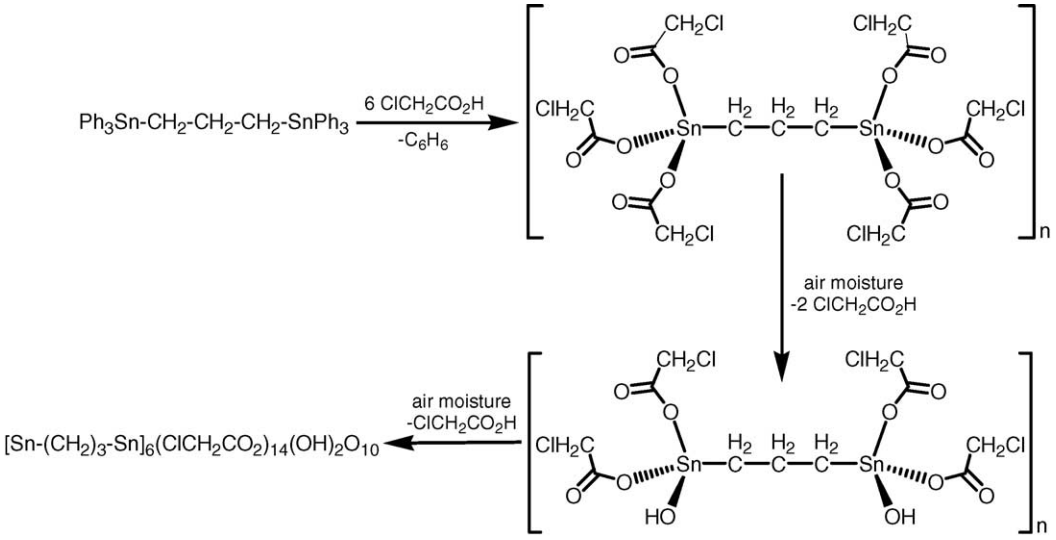


Scheme 9. Sn–Ph cleavage reactions involving the reagent CCl_3CO_2H.

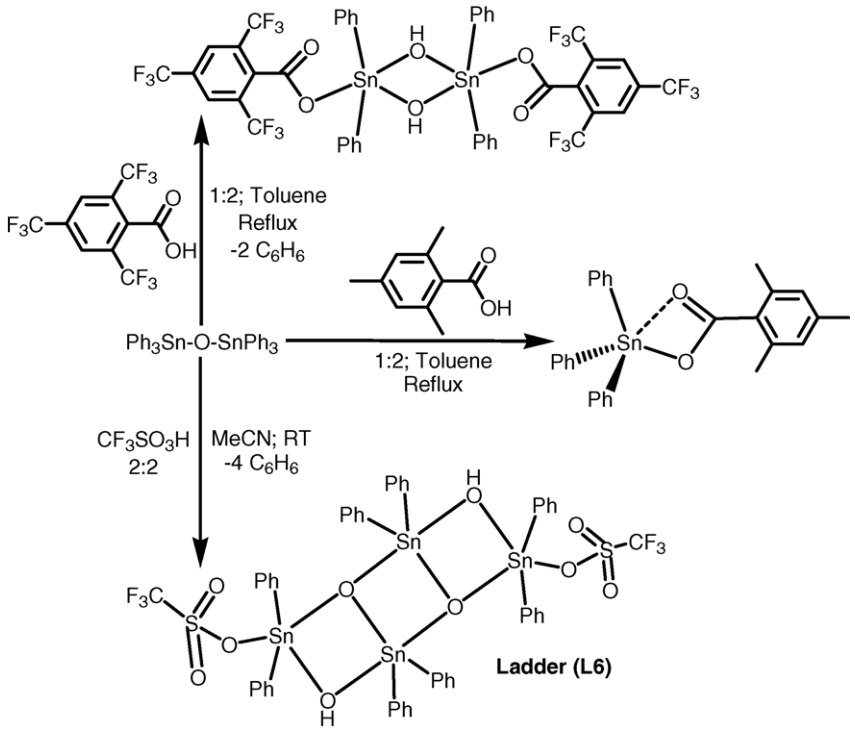
$P(C_6H_{11})_2$ (Scheme 13) (Table 1, Entry 41). Thus, the reaction of $(PhCH_2)_2SnCl_2$ with $AgO_2P(C_6H_{11})_2$ leads to mono debenzylation and the formation of the *butterfly cluster*, $\{PhCH_2Sn(OH)[O_2P(C_6H_{11})_2]_2\}_2$. The latter is transformed to the *O-capped cluster*, $\{[PhCH_2Sn(OH)O_2P(C_6H_{11})_2]_3O\}^+[O_2P(C_6H_{11})_2]^-$ upon slow hydrolysis (Scheme 13). The core structure of the *butterfly* and *O-capped cluster* are shown in Scheme 5. Interestingly, the reaction of $(PhCH_2)_2SnCl_2$ with a mixture of $AgO_2P(C_6H_{11})_2$ and $(C_6H_{11})_2P(O)OH$ leads to the formation of the mononuclear diphosphinate, $\{(PhCH_2)_2Sn[O_2P(C_6H_{11})_2]_2\}\cdot[(C_6H_{11})_2P(O)OH]_2$. The latter is debenzylated in solution at room temperature during the crystallization process to afford the *butterfly cluster* [59].

An interesting transformation of the dibenzyltin dichloride has been recently reported by Zheng et al. Thus, $(PhCH_2)_2SnCl_2$ upon reaction with CO_2 and NaOH affords a carbonate (μ–CO_3) bridged *double-ladder* [61]. The latter can be converted into a *ladder* or a *drum* depending on the reaction conditions. The formation of the *drum* involves debenzylation. These sequences of reactions are summarized in Scheme 14 (Table 1, Entry 45). Similarly, reaction of $(PhCH_2)_2SnCl_2$ with RCO_2Ag (R = *t*-Bu, C_5H_4N, $CH{=}CMe_2$, $CHPh_2$) affords the *drum*. However, a similar reaction with $MeCO_2Ag$ affords the *ladder* (L5) product (Scheme 14).

All the examples of tin–benzyl cleavage reactions are summarized in Table 1 (Entries 41–48).



Scheme 10. Sn–Ph cleavage reactions involving the reagent $ClCH_2CO_2H$.



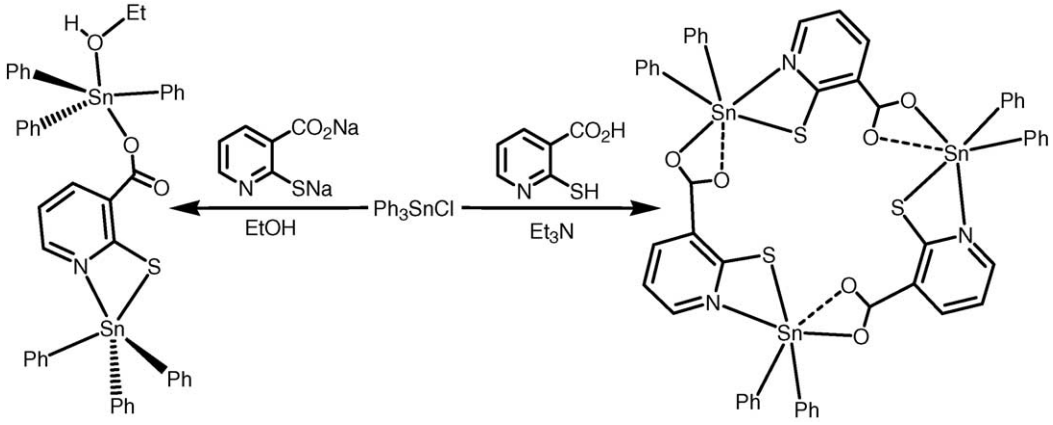
Scheme 11. Sn–Ph cleavage reactions involving the reagents R_fCO_2H [R_f = 2,4,6-$(CF_3)_3C_6H_2$] and CF_3SO_3H.

4. Sn–allyl cleavage and related reactions

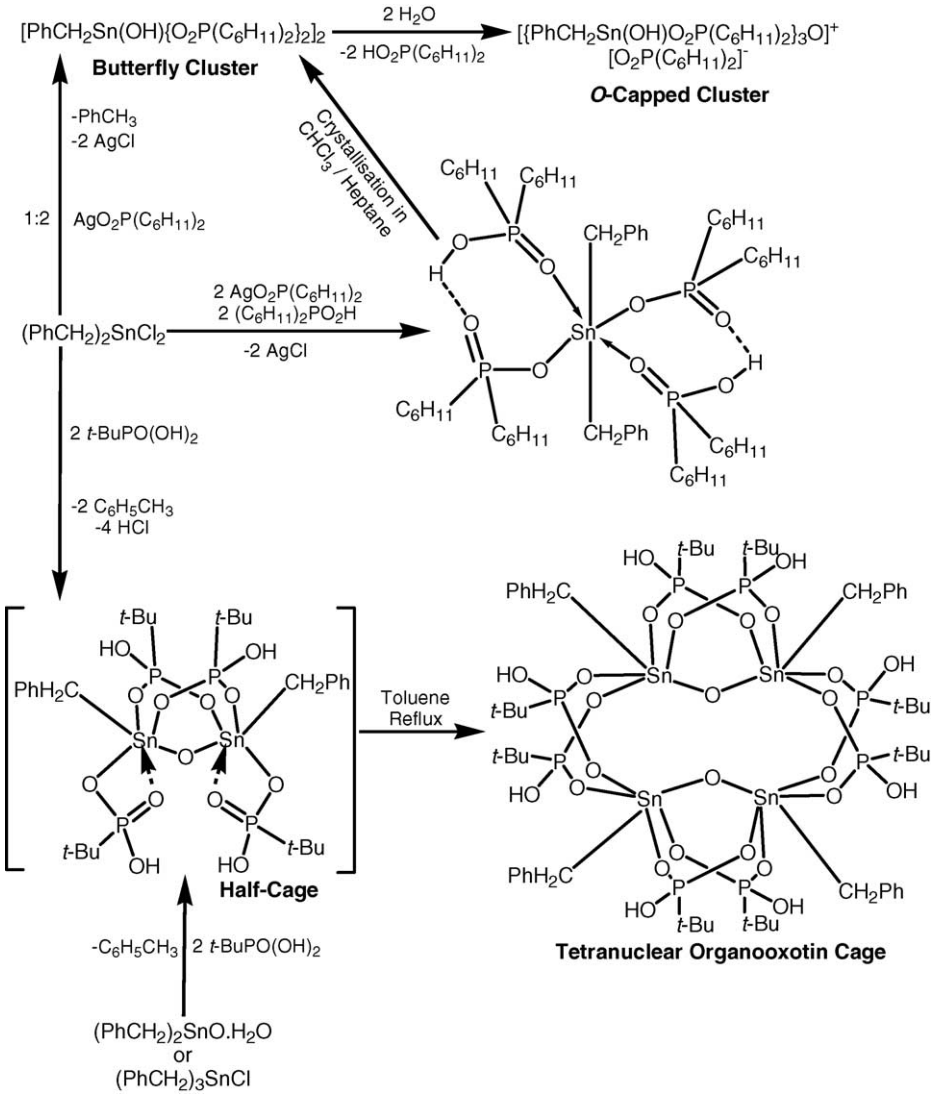
Allyltin compounds are among the most sensitive ones in terms of Sn–C bond cleavage reactions. These compounds are routinely used for allyl transfer reactions [7,66]. Some recent examples of allyl transfer to ketones have been effected by the use of $Sn(CH_2–CH=CH_2)_4$ or *n*-$BuSnCl(CH_2–CH=CH_2)_2$. While the latter has been used in an achiral version, the former has been used in asymmetric synthesis to afford tertiary alcohols in 76–96% of ee (Scheme 15) [67].

Organotin vinyls are also susceptible for Sn–C bond cleavage involving the $Sn–CH=CH_2$ group. Thus, the reaction of $R_3Sn–CH=CH_2$ with X_2 or HX leads to the formation of $R_3Sn–X$ with the elimination of $CH_2=CH–X$ or $CH_2=CH_2$ (Scheme 16) [68]. In order to test the relative labilities of allyl versus vinyl and phenyl versus vinyl groups, diorganotin divinyls have been subjected to reaction with X_2. It was observed that in the reaction involving $R_2Sn(CH=CH_2)_2$ (R = alkyl), the vinyl group is cleaved. On the other hand, if R = Ph, the phenyl group is cleaved (Scheme 16) [68,69]. This gives a relative lability estimate of these three types of substituents.

Organotin compounds containing alkynyl substituents are prone to Sn–C bond cleavage by hydrolysis or alcoholysis reactions [71]. Thus, the reaction of $R^1Sn(C≡C–R^2)_3$



Scheme 12. Sn–Ph cleavage reactions caused by 2-mercaptonicotinic acid.



Scheme 13. Sn—CH_2Ph cleavage reactions effected by phosphinic and phosphonic acids.

(R^1 = Me, *n*-Bu; R^2 = Me, Ph) with R^3OH (R^3 = *i*-Pr, *i*-Bu, *s*-Bu, CH_2Ph) leads to the formation of organotin trialkoxides (Table 1, Entry 53). On the other hand, its hydrolysis leads to the formation of a dodecanuclear oxotin cage, $[(R^1Sn)_{12}(\mu\text{–}O)_{14}(\mu\text{–}OH)_6][OH]_2$ (Table 1, Entry 52).

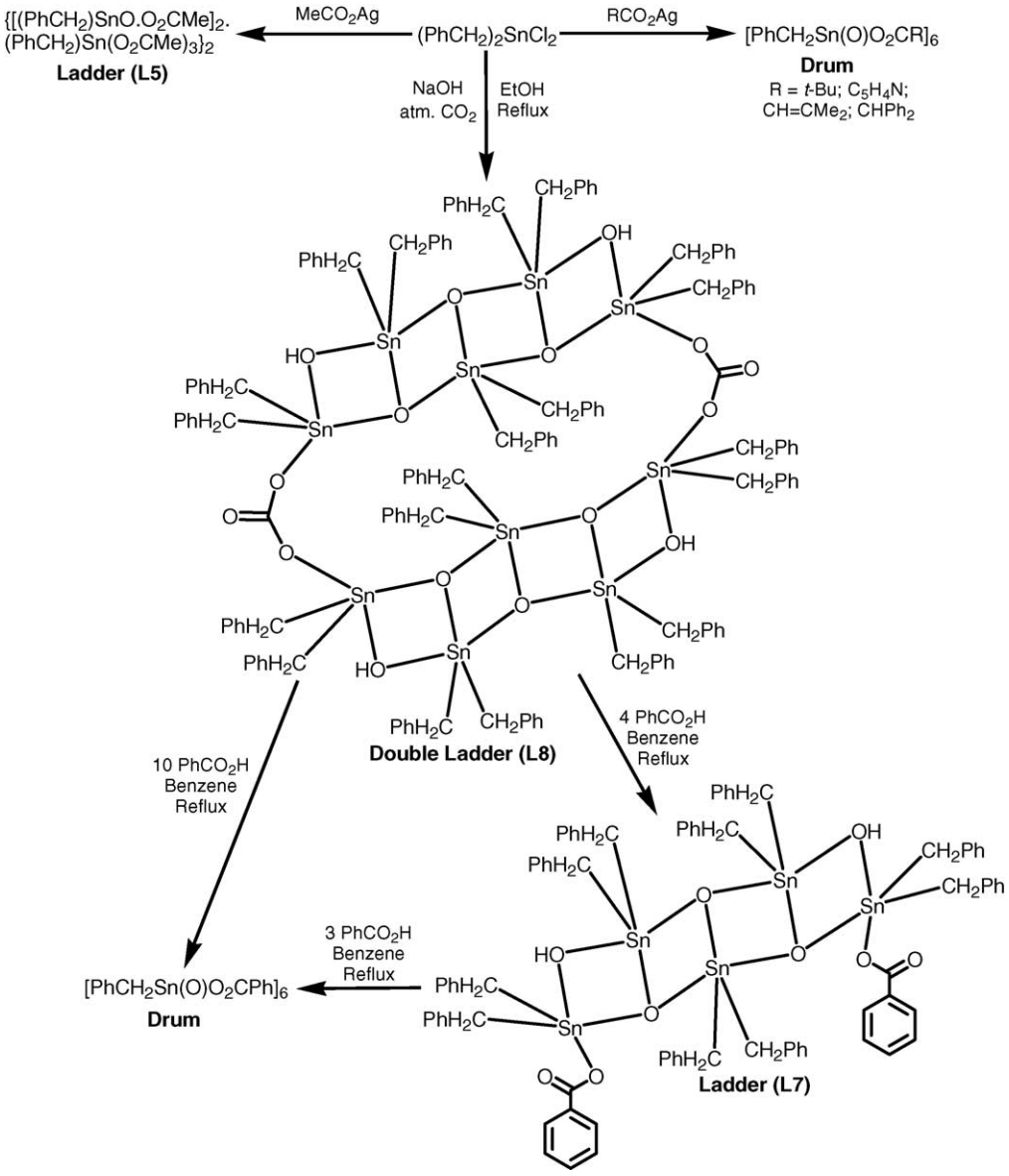
All the examples of these types of reactions are given in Table 1 (Entries 49–53).

5. Sn–alkyl cleavage reactions

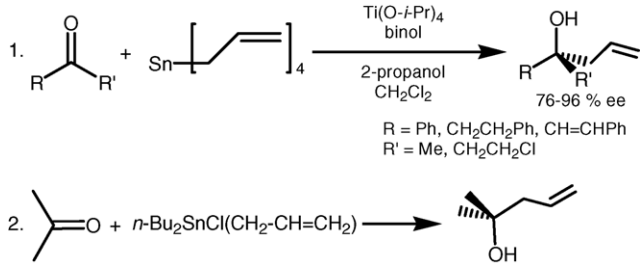
Tin–alkyl cleavage reactions occur mostly under forceful conditions. A number of examples involving Sn–CH_3 cleavage are known [27]. These are summarized in Table 1 (Entries 54–67). Very few examples of Sn–butyl bond cleavage are known. Recently, we have observed that the reaction of 1,5-naphthalenedisulfonic acid with $(n\text{-}Bu_3Sn)_2O$ leads to the cleavage of one *n*-Bu group on the tin atoms and the formation of a dicationic complex, $\{n\text{-}Bu_2Sn(OH_2)_3[1,5\text{-}(SO_3)_2C_{10}H_6]\}_2$ (Scheme 17) (Table 1, Entry 66) [80]. Interestingly, this compound exhibits a very rich supramolecular chemistry in the solid state. Intermolecular O–H···O hydrogen bonding between the disulfonate counter anion and the coordinated water molecules in the tin atoms leads to the formation of a three-dimensional pillared structure.

Zheng et al., have observed that the reaction of $n\text{-}Bu_2SnO$ with ferrocene dicarboxylic acid under solvothermal conditions [81] leads to the complete elimination of the butyl groups on tin atoms and the formation of a mixed-valent octanuclear cage, $Sn_8O_4(O_2C\text{–}C_5H_4\text{–}Fe\text{–}C_5H_4\text{–}CO_2)_6$ (Scheme 18) (Table 1, Entry 67).

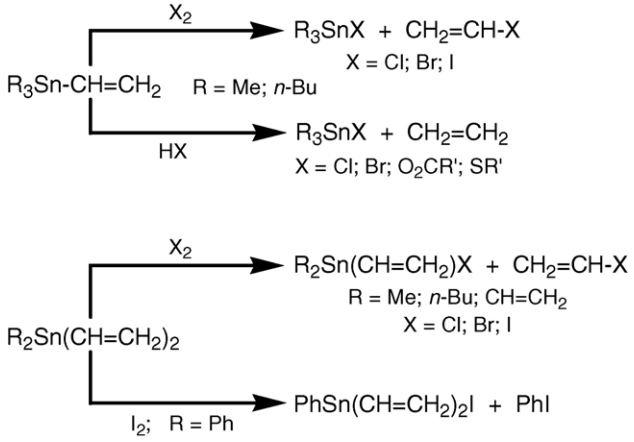
All the reactions discussed vide supra involved a Sn–C bond scission that is mediated by external nucleophiles. Several examples of Sn–C bond cleavage by internal nucleophiles are documented. These are summarized in Table 1 (Entries 68–78).



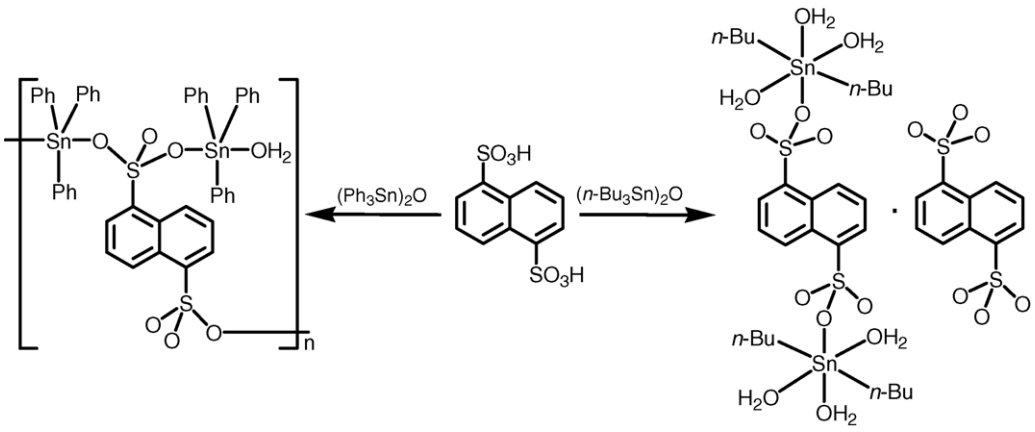
Scheme 14. Tin–benzyl cleavage reactions involving carboxylic acids.



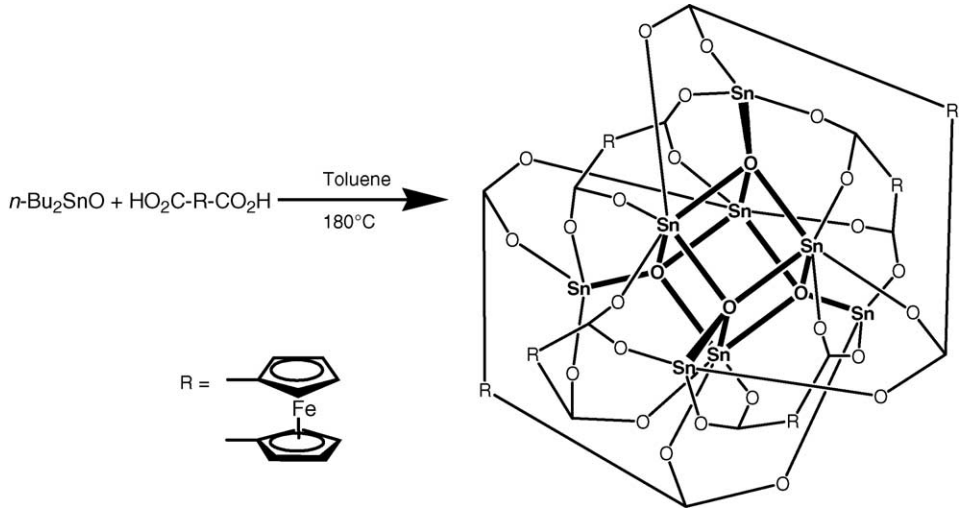
Scheme 15. Allyl transfer reactions.



Scheme 16. Vinyl and phenyl cleavage reactions.



Scheme 17. Sn–butyl cleavage reaction involving naphthalene-1,5-disulfonic acid.



Scheme 18. Sn–butyl cleavage reaction under hydrothermal reaction conditions.

6. Conclusions

Among organometallic main group compounds, organotin compounds are quite unique in possessing reasonably labile Sn–C bonds. While compounds containing Sn–allyl bonds are the most labile, those possessing Sn–benzyl and Sn–phenyl substituents are also sufficiently reactive. The Sn–alkyl bond cleavage is the most difficult to accomplish and occurs under relatively harsh reaction conditions. Even among tin–alkyl compounds those containing Sn–CH_3 scission are the most documented. In contrast, those involving Sn–butyl cleavage are very few. The current state of knowledge of these Sn–C cleavage reactions allows these compounds to be utilized deliberately as synthons. In view of this, it is expected that in addition to organotin halides, oxides and hydroxides compounds containing Sn–alkyl, Sn–benzyl, Sn–phenyl or Sn–allyl bonds will also be very useful as reactants in synthetic procedures for the construction of rings, cages and clusters.

Acknowledgements

We thank Department of Science and Technology (DST), India for financial support. KG, PS and RT thank Council of Scientific and Industrial Research (CSIR), India for senior and junior research fellowships, respectively.

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