Free Radical Chain Reaction of Allylic Tin Compounds with Organic Halides Involving S_H' Process

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Negatively substituted halomethanes were allylated easily by allyltin compounds *via* radical chain reaction involving S_H' process. Aryl, aralkyl, and alkyl halides underwent similar chain reactions only when the tin compound was charged in excessive amounts.

Since stannyl radical has been known to add to a double bond reversibly[1] and to abstract halogen atoms from organic halides,[2] the following radical chain reaction involving S_H' process is expected to proceed.

$$\rangle Sn\cdot + R\text{-}X \longrightarrow \rangle Sn\text{-}X + R\cdot$$

$$R\cdot + CH_2{=}CHCH_2Sn\langle \longrightarrow R\text{-}CH_2CH{=}CH_2 + \rangle Sn\cdot$$

Since the first examples of the chain reaction have been presented in 1973,[3] several applications were carried out with various organic halides.[4,5] In those reports, however, experimental details are frequently not provided. In this study, in order to survey scope and limitation of the chain reaction, various organic halides were subjected to the reaction of allylic tin compounds under ordinary reaction conditions where the radical chain carrier could be produced. As a result, negatively substituted aliphatic halides such as polyhaloalkanes, α-halo esters, and α-halo nitrile were found to be good substrates, whereas aryl, benzyl, and alkyl halides were shown to be poor substrates.

Results and Discussion

Reaction of Radical Generators with Allyltin Compounds. Table 1 shows the products detected in the reaction mixtures which were obtained by decomposing the common radical generators in benzene containing allyltin compounds. With α,α'-azobisisobutyronitrile (AIBN), about 75% of 1-cyano-1-propyl radical can be explained by the products: 50% were captured by allyltin compounds giving 2,2-dimethyl-4-pentenenitrile, and 25% dimerized under these conditions. Although the fate of the stannyl groups is uncertain, the fact suggests capability of AIBN as an initiator of the reaction of the tin compounds with organic halides.

Phenyl radical derived from phenylazotriphenylmethane (PAT) was also found to react with allyltin compounds, giving allylbenzene in 50%. Formation of biphenyl indicates that some of phenyl radical (*ca.* 10%) are consumed by phenylation of the solvent benzene. The product which is expected for S_H' process between triphenylmethyl radical and allyltin compounds was not detected.

Benzoyl peroxide (BPO) reacts with allyltin compounds, giving allyl benzoate and organotin benzoate in good yield. However, these products are explained most reasonably in terms of bimolecular mechanism between BPO and allyltin, instead of S_H' involving benzoxyl radical.[6] The detailed chemistry of the reaction will be shown elsewhere.

Reaction of Allylic Tin Compounds with Negatively Substituted Halomethanes. Reaction of halides such as polyhalomethanes, α-halo carboxylic esters, α-halo ketones, and α-halo nitriles with allyltributyltin was initiated by AIBN and gave the results as shown in in Table 2. Halogen atoms in the organic halides were displaced by an allyl group in moderate yield. In all cases, tributyltin halides were produced in almost quantitatively. In the absence of AIBN the reaction occurred hardly, and the reactants were almost remained unchanged at these temperature, although at much higher temperature considerable conversion was reported to be observed.[4] The presence of galvinoxyl (10 mol%) inhibited the AIBN (3 mol%) induced reaction completely. These facts indicate that the reaction proceeds by a radical chain mechanism.

Table 3 shows the results of the reaction of these halides with crotyltributyltin under similar conditions. Halogen atoms in the substrates were displaced by 1-methyl-2-propenyl group, but not by 2-butenyl group. The observed yields were lower than those in the reaction of allyltin compound. These findings support that the radical derived by abstraction of a halogen atom reacts with allylic tin compounds by a S_H' manner.

Table 1. Reaction of radical generators with allyltin compounds[a]

$R_3SnCH_2CH{=}CH_2$		Generator		Temp	Products			
R	mmol		mmol	°C		mmol		mmol
Me	2.0	AIBN	0.1	80	$Me_2C(CN)CH_2CH{=}CH_2$	0.10	$[Me_2C(CN)\text{-}]_2$	0.02
Bu	5.0	AIBN	0.1	80	$Me_2C(CN)CH_2CH{=}CH_2$	0.10	$[Me_2C(CN)\text{-}]_2$	0.023
Me	2.0	PAT	0.1	60	$PhCH_2CH{=}CH_2$	0.05		
Bu	2.0	PAT	0.1	60	$PhCH_2CH{=}CH_2$	0.05	Ph-Ph	0.01
Me	5.0	BPO	0.25	80	$BzOCH_2CH{=}CH_2$	0.15	$BzOSnMe_3$	0.2
Bu	5.0	BPO	0.25	80	$BzOCH_2CH{=}CH_2$	0.09	$BzOSnBu_3$	0.2

a) Solvent PhH 1 ml.

Table 2. Thermal reaction of allyltributyltin with negatively substituted aliphatic halides[a)]

Halide	mmol	Additives[b)]	mmol			Solvent	ml	Product	mmol
CCl_4	1.1	None				PhH	1	CH_2=$CHCH_2$–CCl_3	Trace
CCl_4	1.1	A	0.03			PhH	1	–CCl_3	0.73
CCl_4	1.1	A	0.03	G	0.1	PhH	1	–CCl_3	Trace
CCl_4	10	None				—		–CCl_3	0.70
$CHCl_3$	1.1	A	0.03			PhH	1	–$CHCl_2$	0.40
$CHCl_3$	1.1	A	0.03	G	0.1	PhH	1	–$CHCl_2$	0
CH_3CCl_3	1.1	A	0.03			PhH	1	–CCl_2CH_3	0.42
CH_3CCl_3	1.1	A	0.03	G	0.1	PhH	1	–CCl_2CH_3	0
$BrCH_2CO_2Me$	1.1	A	0.03			PhH	1	–CH_2CO_2Me	0.60
$ClCH_2CO_2Me$	1.1	A	0.03			PhH	1	–CH_2CO_2Me	0.53
$ClCH_2COCH_3$	1.1	A	0.03			PhH	1	–CH_2COCH_3	0.43
$ClCH_2COPh$	1.1	A	0.03			PhH	1	–CH_2COPh	0.51
$ClCH_2CN$	1.1	A	0.03			PhH	1	–CH_2CN	0.40
$ClCH_2CN$	1.1	A	0.03	G	0.1	PhH	1	–CH_2CN	0

a) Using Bu_3SnCH_2CH=CH_2 1 mmol at 80 °C, 3 h. b) A: AIBN, G: galvinoxyl.

Table 3. Thermal reaction of crotyltributyltin with negatively substituted aliphatic halides[a)]

Halide	mmol	Additive	mmol	Solvent	ml	Product	mmol
CCl_4	1.1	AIBN	0.03	$PhCH_3$	1	CH_2=$CHCHMe$–CCl_3	0.26
CCl_4	10	AIBN	0.03	—		–CCl_3	0.45
$CHCl_3$	10	AIBN	0.03	—		–$CHCl_2$	0.22
$ClCH_2CN$	10	AIBN	0.03	—		–CH_2CN	0.49
$BrCH_2CO_2Me$	10	AIBN	0.03	—		–CH_2CO_2Me	0.36

a) CH_3CH=$CHCH_2SnBu_3$ 1 mmol, 80 °C, 3 h.

Table 4. Photoreaction of allyltributyltin with negatively substituted aliphatic halides[a)]

R–$SnBu_3$ R	Halide	mmol	Irradiated time/h	Product	mmol
Allyl	CCl_4	1.1	1	CH_2=$CHCH_2$–CCl_3	0.62
	$CHCl_3$	1.1	1	–$CHCl_2$	0.28
	CH_3CCl_3	1.1	3	–CCl_2CH_3	0.57
	$BrCH_2CO_2Me$	1.1	1	–CH_2CO_2Me	0.70
	$ClCH_2CO_2Me$	1.1	1		0.54
	$ClCH_2COCH_3$	1.1	1	–CH_2COCH_3	0.42
	$ClCH_2COPh$	1.1	1	–CH_2COPh	0.54
	$ClCH_2CN$	1.1	3	–CH_2CN	0.51
Crotyl	CCl_4	1.1	1	CH_2=$CHCH(CH_3)$–CCl_3	0.34
		1.1	3		0.50
		1.1	5		0.67
		1.1	24		0.65
	$CHCl_3$	1.1	5	–$CHCl_2$	0.15

a) Allylic tin compound 1 mmol, solvent: PhH 1 ml, at 21—22 °C, irradiated by high pressure Hg lamp.

$$R\cdot + CH_3CH = CHCH_2Sn\langle \longrightarrow$$
$$R\text{–}CH(CH_3)CH = CH_2 + \rangle Sn\cdot$$

Lower yields in the reactions of crotyltin may be due to crowdiness at the position being attacked by R·.

Quite similar reactions between these halides and allyl- or crotyltin compounds proceeded under irradiation by a high pressure mercury lamp. As shown in Table 4, tendencies in dependence of yield on the structure of halide are quite resembling to those in the AIBN induced reaction. This implies the nature of radical chain mechanism of the photoreactions.

Reaction of Aryl, Aralkyl, and Alkyl Halide with Allyltributyltin. Under conditions similar to those for the above reactions, AIBN- as well as photoinduced reactions of aryl, benzyl, and alkyl halides with allyltin compound were quite sluggish. Thus, as shown in Tables 5 and 6, with equimolar reactants only few % of conversion were observed, and with large excess of halide reactions did not take place almost at all. In these cases, the reactants were recovered almost quantitatively. This inactiveness of aryl halide might be surprising at a glance, since both halogen abstraction from aryl halide by stannyl radical[2)] and S_H' process involving phenyl radical have been well known.[7)]

Table 7 shows the effect of additives on the yield of

TABLE 5. THERMAL REACTION OF ALLYLTRIBUTYLTIN WITH ALKYL, ARALKYL, AND ARYL HALIDES

Allyl–$SnBu_3$ mmol	Halide	mmol	AIBN mmol	Solvent	ml	Product	mmol
1	PhI	1	0.05	PhH	1	$PhCH_2CH=CH_2$	0.05
1		10	0.05	—			Trace
2		1	0.5	PhH	1		0.35
5		0.5	0.1		1		0.29
5		0.5	0.05		1		0.10
1	PhBr	10	0.03	—			Trace
5		0.5	0.1	PhH	0.5		0.29
5	PhCl	0.5	0.1		0.5		0
1	$PhCH_2Cl$	1.1	0.03		1	$PhCH_2CH_2CH=CH_2$	Trace
1		10	0.05		1		Trace
5		0.5	0.1		1		0.34
5		0.5	0.03		1		0.09
1	$PhCH_2Br$	1.1	0.05		1		0.03
5		0.5	0.1		1		0.43
5		0.5	0.03		1		0.11
5	*n*-$C_8H_{17}Br$	0.5	0.1		1	*n*-$C_9H_{19}CH=CH_2$	0.48
5	*cyclo*-$C_6H_{11}Br$	0.5	0.1		1	*cyclo*-$C_6H_{11}CH_2CH=CH_2$	0.43

TABLE 6. PHOTOREACTION OF ALLYLTRIBUTYLTIN WITH ALKYL, ARALKYL, AND ARYL HALIDES

Halide	mmol	Tin compd mmol	Solvent	ml	Irradiated time/h	Product	mmol
PhI	1.1	1	PhH	1	1	$PhCH_2CH=CH_2$	0.08
	1.1	1		1	24		0.20
	1.5	5		1	5		0.29
PhBr	1.1	1		1	1		Trace
	1.1	1		1	24		0.18
	0.5	5	$PhCH_3$	0.5	5		0.29
PhCl	0.5	5		0.5	5		0
	0.5	5	—		25		0
$PhCH_2Cl$	1.1	1	PhH	1	24	$PhCH_2CH_2CH=CH_2$	0.10
	0.5	5		1	5		0.18
$PhCH_2Br$	1.1	1		1	24		0.24
	0.5	5		1	5		0.28
n-$C_8H_{17}Br$	0.5	5	—		5	*n*-$C_9H_{19}CH=CH_2$	0.45
cyclo-$C_6H_{11}Br$	0.5	5	—		5	*cyclo*-$C_6H_{11}CH_2CH=CH_2$	0.42

benzene produced by reduction of iodobenzene by organotin hydride for which Kuivila proposed the radical chain mechanism involving halogen abstraction by stannyl radical.[2] Even without any additive,

$$R_3SnH + PhX \longrightarrow R_3SnX + PhH$$

benzene was formed in *ca.* 30% yield by heating a mixture of iodobenzene and tributyltin hydride at 80 °C for 24 h. The yield did not diminish in the presence of radical scavengers such as galvinoxyl and *p*-benzoquinone, indicating that the reduction occurring under the conditions is not a radical chain process. However, in the presence of AIBN yield of benzene was increased up to 80%, which again fell to *ca.* 40% by the addition of a radical scavenger. This fact means that AIBN assisted reaction was suppressed almost completely by a radical scavenger. This suggests that Kuivila's chain mechanism is sound at least for the AIBN assisted reaction, and stannyl radical once formed in a medium containing iodobenzene abstracts an iodine atom quite effectively.

TABLE 7. REACTION OF IODOBENZENE BY TRIBUTYLTIN HYDRIDE[a]

Additive	mmol	Yield of PhH/%[b]
—		33
Galvinoxyl	0.04	35
p-Benzoquinone	0.04	35
AIBN	0.04	80
AIBN 0.04,	*p*-Benzoquinone 0.1	42

a) PhI 10 mmol, Bu_3SnH 1 mmol, 80 °C, 24 h. b) Based on Bu_3SnH.

On the other hand, the fact that biphenyl was formed in a considerable amount by decomposing PAT in benzene containing allyltributyltin (Table 1) suggests that S_H' reaction of phenyl radical with allyltin compound is not enough fast to construct an effective chain process. Some of phenyl radical may be consumed by non-chain by-pass such as phenylation of aryl halide

or the solvent benzene.

Employing more inert solvents, then, might be one of possible ways to enhance the efficiency of the chain reaction. However, since among the usual solvents,[8] benzene has been known to be relatively unreactive toward phenyl radical, and phenyl radical has been known to undergo S_H' with allyl sulfides 15—20 times faster than it adds to benzene,[8] increasing the relative concentration of allyltin is expected to give better results. Actually, when large excess of allyltin was employed, iodo- and bromobenzene were converted into allylbenzene in good yield, in either AIBN- or photo-induced reaction (Tables 5 and 6). However, even under these conditions, considerable amount of AIBN or prolonged irradiation is necessary to realize satisfactory yield, indicating very small kinetic chain length.

Chlorobenzene which is reduced by organotin hydride only in poor yield,[2] did not react even in the presence of large excess of allyltin, perhaps due to difficulty in chlorine abstraction by stannyl radical.

Benzyl and alkyl bromide also react under similar conditions, giving the corresponding displacement products. During the course of the study, we met the communication that the AIBN initiated reaction of cyclohexyl bromide with allyltributyltin gave allylcyclohexane in 88% yield, when 2 equiv. of tin compound was employed.[5]

Conclusion

Efficiency of free radical chain reaction between allylic tin compounds and organic halide depends on the nature of the halide, and is affected by easiness of halogen abstraction by stannyl radical and more subtly by efficiency of S_H' process. Negatively substituted halomethanes which are classified as acceptor subtrates in Huyser's sense[9] produce electron seeking radicals which will easily attack the π-bond of allyltin compound, giving S_H' product. Aralkyl and alkyl radicals, donor radicals, are less reactive toward the π-bond of allyltin. As a result, the expected chain reaction proceeds smoothly only when an excess amount of allyltin is employed. And at least concerning with the present reaction aryl radicals fall into the latter category.

Experimental

Materials. Allyltributyltin[10] was prepared by treating allylmagnesium chloride in ether. Bp 106—107 °C/1.6 mmHg (1 mmHg=133.322 Pa). Crotyltributyltin[4] was prepared by similar method or by the reaction of tributyltin-lithium with *trans*-crotyl chloride: In a three-necked flask (300 ml), tributyltin chloride (32.5 g) was placed and 7 g of metal lithium. The mixture was stirred for about 2 h. under argon atmosphere. To the mixture cooled by ice-water, was added dropwise tetrahydrofuran (100 ml) during 4 h. After the mixture turned to deep green, the mixture was stirred for one night at room temperature. After removal of unchanged lithium, a solution of *trans*-crotyl chloride (9.5 g) in tetrahydrofuran (50 ml) was added to the mixture cooled at −20 °C by means of ice–salt, during 1 h. The reaction mixture was stirred at the temperature for a half day, and for further one night, cooling by water. The mixture was treated with a saturated solution of ammonium chloride, then the product was extracted by ether. After the ethereal solution was dried over magnesium sulfate, removal of the ether and distillation under reduced pressure gave 20.9 g of the product (61%), bp 115—118 °C/2.0 mmHg. Tributyltin hydride[11] was prepared by reducing tributyltin chloride with $LiAlH_4$. Commercial organic halides were used as substrates after distillation.

Reaction Procedure. A solution containing reactants and solvent of amounts noted in the Tables is placed in a Pyrex tube and degassed. The tube was sealed and immersed in a bath kept at designated temperature for the thermal reactions. For photoinduced reaction, the tube was immersed in running water and irradiated with a high pressure mercury lamp (200 W). The products were collected by GLPC and identified NMR and IR spectroscopically. Amounts of products were determined by also GLPC.

Products. Except the well known compounds, the structures of the products were deduced based on the analytical and spectroscopic data recorded here.

4,4,4-Trichloro-1-butene: IR (neat) 1865 (C–H, out of plane), 1640 (C=C), and 645 cm^{-1} (C–Cl): ^1H NMR (CCl_4) δ=3.40 (2H, d, J=6.6 Hz) and 5.80 (3H, m). Found: C, 30.38; H, 3.08; Cl, 66.30%. Calcd for $C_4H_5Cl_3$: C, 30.13; H, 3.16; Cl, 66.71%.

4,4-Dichloro-1-butene: IR (neat) 1860 (C–H, out of plane), 1640 (C=C), 670 and 610 cm^{-1} (C–Cl): ^1H NMR (CCl_4) δ=2.87 (2H, t, J=6.4 Hz) and 5.60 (4H, m). Found: C, 38.81; H, 4.60; Cl, 56.38%. Calcd for $C_4H_6Cl_2$: C, 38.44; H, 4.84; Cl, 56.72%.

4,4-Dichloro-1-pentene: IR (neat) 1860 (C–H, out of plane), 1640 (C=C), 1380 (C–H, in plane), and 673 cm^{-1} (C–Cl): ^1H NMR (CCl_4) δ=2.17 (3H, s), 3.05 (2H, d, J=6.0 Hz), and 5.65 (3H, m). Found: C, 43.67; H, 5.45; Cl, 50.68%. Calcd for $C_5H_8Cl_2$: C, 43.20; H, 5.80; Cl, 51.00%.

4,4,4-Trichloro-3-methyl-1-butene: IR (neat) 1860 (C–H, out of plane), 1640 (C=C), and 575 cm^{-1} (C–Cl): ^1H NMR (CCl_4) δ=1.47 (3H, d, J=6.8 Hz), 3.20 (1H, m), and 5.60 (3H, m). Found: C, 34.91; H, 4.11; Cl, 61.03%. Calcd for $C_5H_7Cl_3$: C, 34.60; H, 4.02; Cl, 61.38%.

4,4-Dichloro-3-methyl-1-butene: IR (neat) 1643 (C=C) and 680 cm^{-1} (C–Cl): ^1H NMR (CCl_4) δ=1.28 (3H, d, J=7.2 Hz), 2.80 (1H, m), and 5.65 (4H, m). Found: C, 43.01; H, 5.52; Cl, 50.70%. Calcd for $C_5H_8Cl_2$: C, 43.20; H, 5.80; Cl, 51.00%.

3-Methyl-4-pentenenitrile: IR (neat) 2240 (C≡N) and 1640 cm^{-1} (C=C): ^1H NMR (CCl_4) δ=1.18 (3H, d, J=6.2 Hz), 2.49 (3H, m), and 5.60 (3H, m). Found: C, 75.49; H, 9.29; N, 15.01%. Calcd for C_6H_9N: C, 75.74; H, 9.54; N, 14.72%.

Methyl 3-Methyl-4-pentenoate: IR (neat) 1740 (C=O ester) and 1640 cm^{-1} (C=C): ^1H NMR (CCl_4) δ=1.11 (3H, d, J=6.2 Hz), 2.50 (3H, m), 3.70 (3H, s), and 5.55 (3H, m). Found: C, 65.35; H, 9.20%. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.43%.

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