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Preliminary communication

The reaction of organic halides with allyltrimethyltin

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We have recently reported that allyl sulfides or bromide react with a radical according to the $S_H{}'$ type scheme[1]. Such a process is also expected in the reaction of allyltrimethyltin, since the reversibility of the addition of organotin radical to an olefinic double bond has been established[2]. On the other hand, it is accepted that the reduction of alkyl halides by organotin hydrides proceeds by a free-radical mechanism involving halogen abstraction by organotin radical[3]. Then, the following radical chain reactions involving $S_H{}'$ type reaction may also be expected:

$$R^{\bullet} + CH_2{=}CHCH_2SnMe_3 \rightarrow RCH_2CH{=}CH_2 + {}^{\bullet}SnMe_3$$

$${}^{\bullet}SnMe_3 + R{-}X \rightarrow XSnMe_3 + R^{\bullet}$$

X = halogen

From these view-points, radical reactions of allyltrimethyltin were investigated.

The reactions were carried out in a reaction tube, degassed, and sealed *in vacuo*. Products were analyzed by GLC and their structures were determined by spectroscopic analysis. The main products obtained in the reaction of halides with allyltrimethyltin under various conditions are summarized in Table 1. As expected, the corresponding terminal olefin and trimethyltin chloride were obtained. Generally, the reaction was found to be promoted by benzoyl peroxide (BPO), a radical generator, and retarded by *p*-quinone, a radical scavenger. These findings support the free-radical chain mechanism cited above. The possibility of the following alternative addition–elimination mechanism[4] may be eliminated except for the reaction with carbon tetrachloride, since free-radical addition involving chlorine abstraction by carbon radical has not been known with the substrates other than carbon tetrachloride.

$$R^{\bullet} + CH_2{=}CHCH_2SnMe_3 \rightarrow RCH_2\dot{C}HCH_2SnMe_3$$

$$RCH_2\dot{C}HCH_2SnMe_3 + RCl \rightarrow RCH_2CHClCH_2SnMe_3$$

$$\downarrow$$

$$RCH_2CH{=}CH_2 + ClSnMe_3$$

The reason why the reaction with carbon tetrachloride was not retarded effectively by *p*-quinone is not known.

TABLE 1

THE REACTIONS OF SOME CHLORIDES WITH ALLYLTRIMETHYLTIN AT 80°C FOR 15 h

Substrates (molar ratio)				*Products (yield[a] (%))*	
$C_3H_5SnMe_3$	CCl_4	BPO	*p*-Quinone	$CH_2{=}CHCH_2CCl_3$	Me_3SnCl
1	2	1/100	–	47	57
1	2	–	–	12	16
1	2	1/100	2/100	15	20
1	2	–	2/100	16	21
$C_3H_5SnMe_3$	$CHCl_3$	BPO	*p*-Quinone	$CH_2{=}CHCH_2CHCl_2$	Me_3SnCl
1	2	1/100	–	37	56
1	2	–	–	11	16
1	2	1/100	1/100	1	9
1	2	–	1/100	1	5
$C_3H_5SnMe_3$	$ClCH_2CO_2Me$	BPO	*p*-Quinone	$CH_2{=}CHCH_2CH_2CO_2Me$	Me_3SnCl[b]
1	2	1/100	–	24	+
1	2	–	–	5	+
1	2	1/100	1/100	0.5	+
1	2	–	1/100	0.4	+
$C_3H_5SnMe_3$	CH_3CCl_3	BPO	*p*-Quinone	$CH_2{=}CHCH_2CCl_2Me$	Me_3SnCl
1	2	1/100	–	14	37
1	2	–	–	5	17
1	2	1/100	1/100	2	8
1	2	–	1/100	2	3

[a] Based on allyltrimethyltin.

[b] Trimethyltin chloride was detected by GLC. However, separation was not satisfactory for quantitative analysis.

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