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REACTION OF α-CHLORO KETONES WITH ALLYLTRI-n-BUTYLTIN.$^{1)}$
CONTROL OF REACTION SITE BY THE VARIATION OF REACTION CONDITIONS

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Reaction of α-chloro ketones with allyltri-n-butyltin proceeds to afford 4-butenyl ketones in the presence of azobisisobutyronitrile, while in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium allyl epoxides are obtained.

Previously we reported that some organic halides react with allylic organotin compounds to give allylated products in the presence of azobisisobutyronitrile (AIBN).$^{2,3)}$ We also showed that wider variety of organic halides underwent the same type of coupling reaction with allyltin compounds in the presence of catalytic amounts of transition metal complexes.$^{1,4)}$

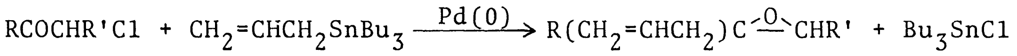
$$\mathrm{R'X + R_3SnCH_2CH{=}CH_2 \xrightarrow[\text{Transition Metal Complex}]{\text{AIBN or}} R'CH_2CH{=}CH_2 + R_3SnX}$$

Now, we wish to report that catalytic amounts of tetrakis(triphenylphosphine)palladium induce the reaction of α-chloro ketones with allyltri-n-butyltin to yield epoxides as coupling products quite different from those obtained by the reaction initiated by radical generators.

The reaction of α-chloro ketones with allyltri-n-butyltin proceeds normally to afford 4-butenyl ketones in the presence of AIBN.

$$\mathrm{RCOCHR'Cl + CH_2{=}CHCH_2SnBu_3 \xrightarrow{AIBN} RCOCHR'CH_2CH{=}CH_2 + Bu_3SnCl}$$

However, α-chloro ketones react with allyltri-n-butyltin to afford allyl epoxides in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium.



$$\mathrm{RCOCHR'Cl + CH_2{=}CHCH_2SnBu_3 \xrightarrow{Pd(0)} R(CH_2{=}CHCH_2)C\overset{O}{\frown\!\!-}CHR' + Bu_3SnCl}$$

The reaction was carried out by heating a degassed homogeneous solution of an equimolar mixture of α-chloro ketone (2 mmol) and allyltri-n-butyltin (2 mmol) including 5 mole % of AIBN or 1 mole % of Pd(0) complex in dichloromethane (1 ml) or benzene (1 ml) in a sealed tube. Products were analyzed by glc and their structures were determined by spectroscopic analysis. Results are summerized in Table.

TABLE. Reaction of α-chloro ketones with allyltri-n-butyltin

Ketone	Conditions				Product	Yields
	Addenda	Temp.	Time	Solvent		%
CH_3COCH_2Cl	AIBN	80 °C	5 h.	CH_2Cl_2	$CH_3COCH_2CH_2CH{=}CH_2$	39
	Pd(0)	80	20	CH_2Cl_2	$CH_3(CH_2{=}CHCH_2)C\overset{O}{\frown}CH_2$	63
$CH_3COCHClCH_3$	AIBN	80	5	CH_2Cl_2	$CH_3COCH(CH_2CH{=}CH_2)CH_3$	36
	Pd(0)	100	20	CH_2Cl_2	$CH_3(CH_2{=}CHCH_2)C\overset{O}{\frown}CHCH_3$	53
$EtCOCHClCH_3$	AIBN	80	5	PhH	$EtCOCH(CH_2CH{=}CH_2)CH_3$	58
	Pd(0)	100	20	PhH	$Et(CH_2{=}CHCH_2)C\overset{O}{\frown}CHCH_3$	30
$C_6H_5COCH_2Cl$	AIBN	80	5	PhH	$C_6H_5COCH_2CH_2CH{=}CH_2$	59
	Pd(0)	100	20	PhH	$C_6H_5CH(CH_2CH{=}CH_2)CHO$	65
$p\text{-}ClC_6H_4COCH_2Cl$	Pd(0)	100	20	PhH	$p\text{-}ClC_6H_4CH(CH_2CH{=}CH_2)CHO$	39

In the Pd(0) catalyzed reaction of aryl chloromethyl ketones, isolated products were not epoxides, but allylated aldehydes, which may be produced by a rearrangement of the epoxide once formed under the reaction conditions. It should be noted that allylation occurs at the carbonyl carbon atom in the Pd(0) catalyzed reaction, but at the halogenated carbon atom in the AIBN initiated reaction. The reaction initiated by AIBN is thought to proceed by the free radical chain mechanism proposed elsewhere.[2,3] Mechanistic investigations on reaction catalyzed by Pd(0) complex are in progress.

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