Journal of Organometallic Chemistry, 129 (1977) C36—C38

Preliminary communication

REACTION OF ALLYLTIN COMPOUNDS

II*. FACILE PREPARATION OF ALLYL KETONES VIA ALLYLTINS

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(Received December 27th, 1976)

Summary

In the presence of catalytic amounts of chlorotris(triphenylphosphine)-rhodium(I), the reaction of acyl chlorides with allyltri-n-butyltin proceeded smoothly under mild conditions to afford the corresponding allyl ketones.

A few years ago, we reported that substitution of organic halides by allylic organotin compounds proceeded by a free radical mechanism [1]. Elegant and conclusive support for the proposed mechanism was provided subsequently by Grignon and Pereyre [2].

$R_3SnCH_2CH{=}CH_2 \rightarrow R_3Sn^\cdot$

$R_3Sn^\cdot + R'X \rightarrow R_3SnX + R'^\cdot$

$R'^\cdot + R_3SnCH_2CH{=}CH_2 \rightarrow R'CH_2CH{=}CH_2 + R_3Sn^\cdot$

X = halogen

During the course of our investigation we found that acyl chlorides do not react with organotin compounds to give alkyl ketones.

We report here that chlorotris(triphenylphosphine)rhodium(I) catalyzes the formation in good yields of allyl ketones from acyl chlorides and allylic organotin compounds. Thus, in the presence of chlorotris(triphenylphosphine)-rhodium(I), the reaction of acyl chlorides with allyltri-n-butyltin (prepared from allylmagnesium chloride and tri-n-butyltin chloride [2]) proceeded smoothly under mild conditions to afford the corresponding allyl ketones (Table 1).

Allyl ketones generally are difficult to isolate from acidic or basic reaction mixtures because they can isomerize very easily to the corresponding conjugated

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[*] For part I see ref. 1.

TABLE 1

THE REACTION OF ACYL CHLORIDES WITH ORGANOTIN COMPOUNDS

Reactants (mmol)			Catalyst (mmol)	Solvent	Reaction conditions (°C/h)	Product yield (%)
		$CH_2{=}CHCH_2SnBu_3$				$RCOCH_2CH{=}CH_2$[a]
CH_3COCl	3	2	0.02	CH_2Cl_2	40/3	51
CH_3CH_2COCl	4	2	0.02	CH_2Cl_2	40/5	70
$(CH_3)_2CHCOCl$	2.4	2	0.02	PhH	80/12	37
$(CH_3)_3CCOCl$	2.2	2	0.02	PhH	80/10	72
PhCOCl	4	2	0.02	PhH	80/5	86
		$CH_3CH{=}CHCH_2SnBu_3$				$RCOCH_2CH{=}CHCH_3$[b]
CH_3CH_2COCl	1	1.2	0.01	PhH	80/12	64
		$PhCH_2SnBu_3$				$RCOCH_2Ph$[a]
CH_3COCl	1.5	1	0.01	PhH	80/12	69

[a] Based on tin compounds. [b] Based on propionyl chloride.

enones under such conditions [3]. It was found, however, that the allyl ketones could be isolated readily from our reaction mixtures by GLC or by distillation under reduced pressure. It is necessary to keep the column temperature of GLC (column: 1.8 m, 10% SF 96 on Celite 545) below 100°C.

In a typical procedure, 0.66 g (2 mmol) of allyltri-n-butyltin and 0.37 g (4 mmol) of propionyl chloride were allowed to react in the presence of 0.019 g (0.02 mmol) of the rhodium complex in 1 ml of dichloromethane in a sealed tube at 40°C. After 5 h, the resulting mixture was examined by GLC to determine that allyl ethyl ketone and tri-n-butyltin chloride had been obtained in 70 and 100% yield, respectively, based on the allyltri-n-butyltin. The structure of allyl ethyl ketone [3] was determined by spectroscopic analysis. Mass spectrum: (m^+/e), 98(7% M^+), 69(23%), 57(100%), 41(32%), 29(69%). NMR: in CCl_4, (δ ppm), 1.01(t, J 7.2 Hz, 3H), 2.40(q, J 7.2 Hz, 2H), 3.09(d, J 7.0 Hz, 2H), 4.82—6.25(m, 3H). IR: neat, (cm^{-1}), 3075(H_2C—CH—), 1722(—C=O), 1640($H_2C{=}CH$—), 996($H_2C{=}CH$—). Tri-n-butyltin chloride was identified by comparison of its IR spectrum with that of the authentic sample. Starting from 9.25 g (0.1 mol) of propionyl chloride and 36.4 g (0.11 mol) of allyltri-n-butyltin containing 0.93 g (1 mmol) of the rhodium complex, 5.4 g (56%) yield of allyl ethyl ketone could be obtained by careful fractional distillation under reduced pressure (b.p. 54°C/60 mmHg).

The reaction between propionyl chloride and crotyltri-n-butyltin (E,Z mixture) gave crotyl ethyl ketone (E,Z mixture), but not α-methylallyl ethyl ketone. The rhodium-catalyzed reaction of acetyl chloride with benzyltri-n-butyltin gave benzyl methyl ketone. From these results it is unlikely that the reaction involves the type of mechanism proposed for such reactions under free radical conditions [1].

Recently, Hegedus et al. reported that alkylrhodium(I) complexes prepared from organolithiums or from Grignard reagents and chloro(carbonyl)bis(triphenylphosphine)rhodium(I) can be used to alkylate acyl chlorides, giving alkyl ketones and regenerating the complex [4]. In view of this, it is reasonable to suggest that an allylic rhodium(I) intermediate derived from the $RhClL_3$ catalyst and the allylic tin compound is the actual allylating agent.

From the viewpoint of synthetic chemistry, the present organotin systems are more useful than the organo-lithium or -magnesium systems. The latter require stoichiometric amounts of rhodium complex, because the organo-lithium and -magnesium compounds, which react with the ketones produced as well as with acyl halides, must be converted completely to the organorhodium complex at −78°C in the initial step. Organotin compounds can be mixed with acyl halides at room temperature without reaction and subsequent addition of only a trace amount of the rhodium complex to the mixture can induce the allylation reaction.

Further studies of the scope and limitation and of the mechanism of these reactions are in progress.

References

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