

ALLYLCHLOROTINS AS ALLYLATING AGENTS OF ACYL CHLORIDES

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(Received July 18th, 1983)

Summary

Allylchlorotins of the type $R_{3-n}AllSnCl_n$ ($R = \text{alkyl or All; All} = \text{CH}_2=\text{CHCH}_2$ or *cis/trans*- $\text{CH}_3\text{CH}=\text{CHCH}_2$; $n = 1-3$) undergo uncatalyzed coupling with acyl chlorides under mild conditions. This reaction as well as the corresponding addition reaction to ketones are much faster when Cl is replaced by NCS group in the organotin derivative.

Introduction

Allylchlorotins of the type $R_{3-n}AllSnCl_n$ ($R = \text{alkyl or All; All} = \text{CH}_2=\text{CHCH}_2$ or *cis/trans*- $\text{CH}_3\text{CH}=\text{CHCH}_2$; $n = 1-3$) are much reactive than the corresponding R_3AllSn as allylating agents towards aldehydes and ketones; the reactions take place under mild conditions, in the absence of solvent and catalyst [1-8]. This prompted us to examine the ability of the allylchlorotins to replace the halogens of acyl chlorides by an allyl moiety. Reactions of acyl halides with organometallic derivatives provide a general method of preparing ketones; in particular organotins of the type $R_3(All)Sn$ and even R_4Sn have been employed in rhodium- or palladium-catalyzed reactions [9,10]. The present paper reports the results obtained from the reactions of allylchlorotins with selected acyl chlorides.

Results and discussion

The allylchlorotins examined undergo uncatalyzed coupling reaction with acyl chlorides under mild conditions. The compounds obtained and the reaction conditions are listed in Table 1. Allyl- and crotyl-tributyltin do not react under the conditions used.

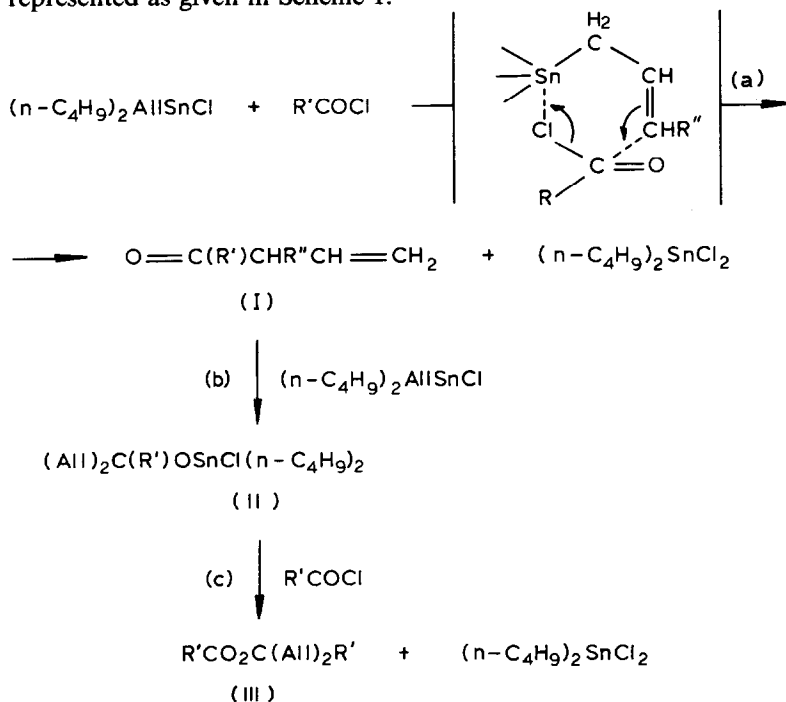
The reaction scheme for the representative compound $(n\text{-C}_4\text{H}_9)_2AllSnCl$ may be

TABLE I
 ALLYLATION OF R'COCl WITH (n-C₄H₉)₂(R''CH=CH-CH₂)₂SnCl

Run	R'	R''	mmol	Reaction conditions (°C/h)	Isolated product and ¹³ C NMR chemical shifts ^a (ppm from int. Me ₄ Si)	IR relevant bands (cm ⁻¹)		Yield (%)	
						ν(C=O)	ν(C=C)		
1	CH ₃	H	58	50/2	118.4 131.1 42.6 83.2 23.6 170.3 22.2 (CH ₂ =CH-CH ₂) ₂ -C-(CH ₃)-O-C-CH ₃ O	1730vs	1240vs	1640s	85
2	(CH ₃) ₃ C	H	16	40/4	26.3 42.5 210.8 41.1 141.5 117.0 (CH ₃) ₃ C-C-CH ₂ -CH=CH ₂ ^{b,c} O	1700vs		1640m	55
3	CH ₂ =CH	H	19	25/15	118.6 132.4 40.9 83.9 129.6 114.4 164.2 139.9 129.8 (CH ₂ =CH-CH ₂) ₂ C(CH=CH ₂)-O-C-CH=CH ₂ O	1720vs	1190vs	1635s 1610m	50
4	CH ₃	CH ₃	17	25/30	27.3 207.6 52.0 15.7 138.5 116.6 CH ₃ -C-CH(CH ₃)-CH-CH ₂ ^d O	1700vs		1630m	90
5	(CH ₃) ₃ C	CH ₃	23	25/24	26.0 44.8 213.9 44.6 19.0 139.8 115.0 (CH ₃) ₃ C-C-CH(CH ₃)CH=CH ₂ O	1700vs		1635s	85

^a The peak assignments were performed using partially relaxed spectra and off-resonance experiments. ^b This compound isomerizes slowly to *trans* 26.1 44.1 201.4 132.6 126.1 17.9 (CH₃)₃C-CO-CH=CH-CH₃, as is known for allylic ketones [14]. ^c The corresponding 2,4-di-nitrophenylhydrazone has m.p. 118°C (uncorrected); analysis: Found: C, 54.12; H, 5.75; N, 18.17; C₁₄H₁₈O₂N₄ calcd.: C, 54.9; H, 5.9; N, 18.3%. ^d The corresponding 2,4-di-nitrophenylhydrazone has m.p. 169°C (uncorrected); analysis: Found: C, 49.05; H, 4.92; N, 19.58; C₁₂H₁₄O₄N₄ calcd.: C, 51.8; H, 5.0; N, 20.1%.

represented as given in Scheme 1.



SCHEME 1

The initial coupling step is normally quite slow and can be followed by an addition reaction of the unreacted allyltin with the formed ketone to give the adduct II. Step (a) is the only one observed for $R' = (CH_3)_3C$ or $R'' = CH_3$. In these cases the absence of the addition is probably caused by steric hindrance, and it has been previously shown that ketones bearing a *t*-butyl group do not insert into the tin-allyl bond under such conditions [1] and that crotyltins are poor allylating agents for ketones [3]. In contrast, both acetyl and pivaloyl chlorides show good reactivity towards allyl and crotyltins. Thus it seems likely that a steric effect is less important in step (a) than in step (b). This can be explained in terms of the lower hindrance at the carbonylic carbon in these substrates than in ketones, since the molecule contains a chlorine instead of an organic group.

Allylic rearrangement was detected by using dibutyl-crotyltin chloride, which gave only methyl allyl ketone with acetyl and pivaloyl chloride. Complete allylic rearrangement has been previously suggested in the reactions of acyl halides with allylmercuric iodide [11]. In contrast, a linear ketone was obtained in the reaction of crotyltributyltin with propionyl chloride in the presence of dichloro-bis(triphenylphosphine)rhodium(II) [9].

Step (b) takes place when $Al = CH_2=CHCH_2$ and $R' = CH_3$ or $CH_2=CH$, and is followed by step (c) to form ester III. The alkoxide II cannot be isolated since reaction (c) is almost instantaneous, as was demonstrated by treating with acetyl chloride the analogous product obtained from the addition of dibutylallyltin chloride to acetone.

The reaction rate increases markedly as the temperature is raised (see runs 1 and

TABLE 2
ALLYLATION ABILITY OF VARIOUS ALLYL TIN DERIVATIVES AT ROOM TEMPERATURE

Run	Allyltin	Substrate	Reaction time (h)	% of Reaction ^a
6	(n-C ₄ H ₉) ₂ (CH ₂ =CHCH ₂)SnCl	Aldehydes ^b	minutes	100
7		CH ₃ COCH ₃ ^b	24	100
8		(CH ₃) ₃ CCOCH ₃ ^b	71 (at 80°C)	50
9		CH ₃ COCl	20	100
10	(n-C ₄ H ₉) ₂ (CH ₂ =CHCH ₂)SnBr	CH ₃ COBr	24	100 ^c
11		Aldehydes	minutes	100
12		CH ₃ COCH ₃	20	100
13		CH ₃ COBr	12	100
14	(n-C ₄ H ₉) ₂ (CH ₂ =CHCH ₂)SnNCS	CH ₃ COCH ₃	2.5	100
15		(CH ₃) ₃ CCOCH ₃	days	no reaction
16		CH ₃ COBr	3	100 ^d
17	(n-C ₄ H ₉) ₂ (CH ₂ =CHCH ₂)SnO ₂ CCH ₃	(CH ₃) ₂ CHCHO	17	50 ^e
18	(n-C ₄ H ₉) ₂ (CH ₂ =CHCH ₂)SnCl ₂	Aldehydes ^f	minutes	100
19		CH ₃ COCH ₃ ^f	20	100
20		(CH ₃) ₃ COCH ₃	42 (at 80°C)	50
21		(CH ₃) ₃ COCl	2 ^g	50 ^h
22		(n-C ₄ H ₉) ₂ (CH ₂ =CHCH ₂)SnCl·HMPA ⁱ	Aldehydes	0.5
23	(n-C ₄ H ₉) ₂ (CH ₂ =CHCH ₂)SnCl ₂ ·HMPA ⁱ	CH ₃ COCH ₃	days	no reaction
24		Aldehydes	minutes	100
25		CH ₃ COCH ₃	24	50 ^e

^a As evaluated from the infrared absorptions of the C=O and C=C stretching. ^b From Ref 1. ^c 80% yield of CH₃(CH₂=CHCH₂)CO₂CCH₃ from a 25 mmol reaction. ^d 70% yield of CH₃(CH₂=CHCH₂)₂CO₂-CCH₃ from a 20 mmol reaction. ^e Unchanged after longer times. ^f From Ref. 2. ^g Other reactions take place if longer times are used. ^h Yield of (CH₃)₃COCH₂CH=CH₂ isolated from a 24 mmol reaction. ⁱ HMPA = hexamethylphosphor amide.

9). Only a small increase of rate is observed on changing from the organotin chloride to the corresponding bromide, and is also the case in the addition reaction to acetone (see runs 7 and 12). A significant shortening of the reaction time is observed when the allyltin isothiocyanate derivative is employed as allylating agent (see Tab. 2). This behaviour may be attributed to the higher acceptor ability of the tin centre in the thiocyanate derivatives than in the corresponding chlorides [12], which favours the coordination of the organic substrate. The importance of the coordination step in the allylations carried out with such compounds has been previously noted [1-3], and is confirmed by the data of Table 2. It should be noted that the allylation ability of the compounds used arises from their ability to reach the pentacoordinate state in the course of the reaction; thus allyltins which are initially pentacoordinated, such as the hexamethylphosphor amide complexes, are much less reactive.

Experimental

Acyl halides, aldehydes and ketones were commercial samples of reagent grade; they were freshly distilled and kept overnight on molecular sieves 4A before use. IR spectra were recorded on a Perkin-Elmer model 599 B spectrophotometer. ¹³C NMR spectra were recorded with a Bruker WH 90 spectrometer operating in FT mode. The allylchlorotins were prepared as previously described [1-4].

Di-n-butylallyltin bromide. This compound was obtained as an oil (b.p. 58–60°C at 0.05 mmHg) by keeping a mixture of di-n-butyltin dibromide and di-n-butyl-diallyltin at 70–80°C for 1 h. IR relevant bands: $\nu(\text{C}=\text{C})$ 1625, $\nu(\text{Sn}-\text{Br})$ 237 cm^{-1} .

Di-n-butylallyltin isothiocyanate. This compound was prepared by treatment of the corresponding chloride with potassium thiocyanate in anhydrous ethanol. The solution was refluxed for 1 h, then filtered and evaporated under reduced pressure. The oil left was dried on P_2O_5 . IR relevant bands: $\nu(\text{C}=\text{C})$ 1625, $\nu(\text{N}-\text{C})$ 2050 cm^{-1} . (For this last assignment see Ref. 13.).

HMPA complexes. The HMPA complexes were prepared as described in ref. 12.

Reactions of allyltins with acyl halides

All the experiments were performed with neat reagents. Equimolar amounts of allyltin and organic substrate were mixed and stirred under the conditions indicated in Table 1 and 2. The progress of the reaction was monitored by infrared spectroscopy. There was progressive decrease in the stretching band of the acyclic $\text{C}=\text{O}$ (about 1800 cm^{-1}) and the growth of a new band at about 1700 cm^{-1} (ketonic or estereal $\nu(\text{C}=\text{O})$). For $\text{R}'' = \text{H}$ (cf. Table 1) the disappearance of the band at 1625 cm^{-1} ($\nu(\text{C}=\text{C})$ of an allylic group bonded to the tin) together with the appearance of a band at 1640 cm^{-1} ($\nu(\text{C}=\text{C})$ of an isolated double bond) were also detectable. This last absorption also appeared in the reactions of crotyltins.

In the experiments summarized in Table 1 the volatile products were pumped off from the reaction mixture (which was kept at 40–50°C) under vacuum and collected at –78°C. The IR and ^{13}C NMR spectra were recorded. The reactions of Table 2 were examined only by IR spectroscopic monitoring, as described above, without further analysis.

Reactions with aldehydes and ketones

The reactions with aldehydes and ketones of the considered new allyltins (i.e. dibutylallyltin bromide, dibutylallyltin isothiocyanate and the HMPA complexes) were performed with neat reagents using the previously described procedure [1]. In a typical run, acetyl chloride was added to the adduct arising from the reaction of the allyltin with acetone. The IR spectrum, recorded immediately after mixing, showed a pattern in the $\nu(\text{C}=\text{O})$ region identical to that exhibited by the final mixture in the reaction with acetyl chloride.

Acknowledgement

We thank the CNR and Ministero della Pubblica Istruzione (Rome) for financial support.

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