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ALLYLSTANNATION

VII *. PREPARATION OF CARBOXYLIC ACID 1-ALKENE-4-YL AND 1-ALKYNE-4-YL ESTERS BY TRANSALKOXYLATION OF 4-n-DIBUTYLCHLOROSTANNOXY-1-ALKENES AND 4-n-DIBUTYLCHLOROSTANNOXY-1-ALKYNES WITH ACYL CHLORIDES

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Summary

Carboxylic acid 1-alkene-4-yl and 1-alkyne-4-yl, esters ($RCH(CH_2CH{=}CH_2)OCOR'$ ad $RCH(CH_2C{\equiv}CH)OCOR'$, $R = R'$ or $R \neq R'$ = alkyl or alkenyl group) can be readily prepared in high yields by transalkoxylation reactions between 4-n-dibutylchlorostannoxy-1-alkenes or 4-n-dibutylchlorostannoxy-1-alkynes with acyl chlorides. This represents a general route for preparation of esters containing allyl or propargyl groups.

Introduction

Organotin alkoxides are known to be very useful reagents in transalkoxylation reactions [1]. The reactions of tin alkoxides with acyl halides or anhydrides to form organic esters [2,3] has been taken into account in the present work, which is concerned with reactions of 4-n-dibutylchlorostannoxy-1-alkenes and 4-n-dibutylchlorostannoxy-1-alkynes ($RCH(OSnBu_2Cl)CH_2CH{=}CH_2$ (I) and $RCH(OSnBu_2Cl)CHC{\equiv}CH$(II), respectively) with acyl chlorides R'COCl, where R and R' are alkyl or alkenyl groups.

Alkoxides I and II can be easily prepared as adducts by reaction of $Bu_2Sn(CH_2CH{=}CH_2)Cl$ (III) and $Bu_2Sn(CH{=}C{=}CH_2)Cl$ (IV) with neat aldehydes [4,5]. Reactions of the adducts I and II and acyl chlorides readily gave the corresponding esters.

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* For part VI, see Ref. 5.

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TABLE 1

TRANSALKOXYLATION REACTIONS BETWEEN NEAT 4-n-DIBUTYLCHLOROSTANNOXY-1-ALKENES AND R′COCl AT 0°C

Run	$\underset{\mathrm{OSnBu_2Cl}}{\mathrm{RCHCH_2CH{=}CH_2}}$ [a]	R′COCl [a]	Prepared compound			Ref.
	R	R′		g	Yield (%)	
1	C_2H_5	CH_3	$C_2H_5CH(CH_2CH{=}CH_2)OCOCH_3$	3.5	~100	6
2	C_2H_5	C_2H_5	$C_2H_5CH(CH_2CH{=}CH_2)OCOC_2H_5$	3.8	98	7
3	C_2H_5	CH_2Cl	$C_2H_5CH(CH_2CH{=}CH_2)OCOCH_2Cl$	4.0	91	– [b]
4	C_2H_5	n-C_3H_7	$C_2H_5CH(CH_2CH{=}CH_2)OCOC_3H_7$	4.0	95	– [b]
5	C_2H_5	$(CH_3)_3C$	$C_2H_5CH(CH_2CH{=}CH_2)OCOC(CH_3)_3$	3.7	80	– [b]
6	C_2H_5	$(CH_3)_3CCH_2$	$C_2H_5CH(CH_2CH{=}CH_2)OCOCH_2C(CH_3)_3$	4.2	85	– [b]
7	C_2H_5	$CH_2{=}CH$	$C_2H_5CH(CH_2CH{=}CH_2)OCOCH{=}CH_2$	3.5	91	– [b]
8	C_2H_5	(E)-$CH_3CH{=}CH$	$C_2H_5CH(CH_2CH{=}CH_2)OCOCH{=}CHCH_3(E)$	4.1	98	– [b]
9	CH_3	CH_3	$CH_3CH(CH_2CH{=}CH_2)OCOCH_3$	2.8	87	8
10	$(CH_3)_2CH$	CH_3	$(CH_3)_2CHCH(CH_2CH{=}CH_2)OCOCH_3$	3.6	92	9
11	$(CH_3)_3C$	CH_3	$(CH_3)_3CCH(CH_2CH{=}CH_2)OCOCH_3$	3.8	89	10
12	(E)-$CH_3CH{=}CH$	CH_3	(E)-$CH_3CH{=}CHCH(CH_2CH{=}CH_2)OCOCH_3$	3.5	91	11
13	C_2H_5	$\begin{array}{l}\mathrm{CH_3CO}\\ \mathrm{CH_3CO}\end{array}\mathrm{O}$	$C_2H_5CH(CH_2CH{=}CH_2)OCOCH_3$	3.2	90	6

[a] 25 mmol. [b] Literature data seem to be completely lacking.

Experimental

Allyldibutyltin and allenyldibutyltin chlorides were prepared as previously described [4,5]. Commercial samples of the carbonyl compounds were of reagent grade, and were freshly distilled before use.

The recovered esters were fully characterized by their IR spectra, and by GLC [5]. In the case of known compounds, the properties were compared with those previously reported [6–11].

Reaction of 4-n-dibutylchlorostannoxy-1-alkenes and acyl chlorides

Equimolecular amounts (25 mmol) of allyldibutyltin chloride and carbonyl compound (RCHO) were mixed at 0°C, to form the appropriate 4-n-dibutylchlorostannoxy-1-alkene. The allylstannation was very rapid, and after 30 min the relevant R'COCl (25 mmol) was added and the mixture was allowed to warm to room temperature. The transalkoxylation took a few minutes, and after 20 min the mixture was treated with 20 ml of an aqueous $NaHCO_3$ solution (2 *M*). After extraction with diethyl ether the organic layer was separated and distilled, to give the corresponding ester.

Reaction of 4-n-dibutylchlorostannoxy-1-alkynes and acyl chlorides

Equimolecular amounts (25 mmol) of allenyldibutyltin chloride and C_2H_5CHO * were mixed at 0°C to form the appropriate 4-n-dibutylchlorostannoxy-1-alkyne. After 30 min the relevant R'COCl (25 mmol) was added, and the stirred mixture was allowed to warm to room temperature. Work-up as above gave the expected ester.

Results and discussion

The results are shown in Tables 1 and 2. Table 1 shows data for the allylic esters which were isolated in 80–100% yields. Run 13 of Table 1 shows an example of the use of acetic anhydride in such reactions. Only six of the isolated esters were previously known, their earlier preparations having involved conventional organic synthetic methods [6–11].

Table 2 lists the results for the transalkoxylations involving reactions of 4-n-dibutylchlorostannoxy-1-alkynes or 4-n-dibutylchlorostannoxy-1,2-dienes with acyl chlorides. The products were mixtures of two esters **, the major product (92%) being the 1-alkyne-4-yl ester.

Scheme 1 accounts for the results.

The reactions were monitored by infrared spectroscopy: a mixture of adducts I and II shows the IR bands centered at 2100 and 1932 cm^{-1} arising from $\nu(C{\equiv}C)$ and $\nu(C{=}C{=}C)$, respectively [12]. Analysis of these mixtures showed that the ratio of I/II was 92/8, the same as was found for the recovered esters. This means that the transalkoxylation reactions occur without any rearrangement, as expected since this involve nucleophilic substitutions at the tin centre [1].

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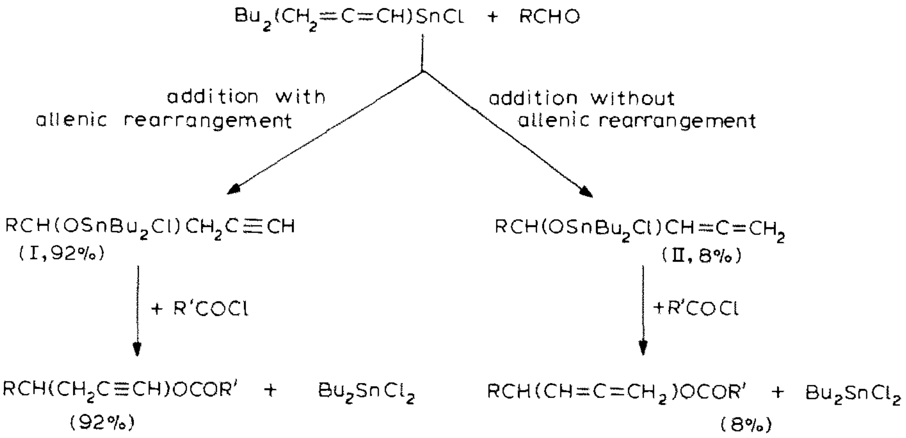
* We report results only for C_2H_5CHO because other aldehydes behave in the same way.

** There appears to be no literature data on the propargylic esters.

SCHEME 1



We should emphasize that organotin chlorides can be used for synthetic purposes without special precautions under very simple conditions [13]. All the reactions give high yields, and several of them are quantitative.

The present work shows that, as expected, transalkoxylation of adducts formed from crotyltin chlorides and aldehydes, as previously described [14,15], give rise to esters containing crotyl or α-methylallyl moieties.

TABLE 2

TRANSALKOXYLATION REACTIONS OF MIXTURES [a] OF 4-n-DI-BUTYLCHLOROSTANNOXY-1-HEXYNE AND 4-n-DI-BUTYLCHLOROSTANNOXY-1,2-HEXADIENE WITH NEAT R'COCl AT 0°C

Run	R'COCl R'=	Prepared compounds		Yield [b] (%)
		g	Yield (%)	
14	CH_3	$C_2H_5CH(CH_2C\equiv CH)OCOCH_3$		92
		$C_2H_5CH(CH=C=CH_2)OCOCH_3$		8
		3.0	83	
15	CH_2Cl	$C_2H_5CH(CH_2C\equiv CH)OCOCH_2Cl$		92
		$C_2H_5CH(CH=C=CH_2)OCOCH_2Cl$		8
		3.2	75	
16	C_2H_5	$C_2H_5CH(CH_2C\equiv CH)OCOC_2H_5$		92
		$C_2H_5CH(CH=C=CH_2)OCOC_2H_5$		8
		2.8	74	
17	n-C_3H_7	$C_2H_5CH(CH_2C\equiv CH)OCOC_3H_7$		92
		$C_2H_5CH(CH=C=CH_2)OCOC_3H_7$		8
		3.0	71	
18	$(CH_3)_3C$	$C_2H_5CH(CH_2C\equiv CH)OCOC(CH_3)_3$		91
		$C_2H_5CH(CH=C=CH_2)OCOC(CH_3)_3$		9
		3.2	71	
19	(*E*)-$CH_3CH=CH$	$C_2H_5CH(CH_2C\equiv CH)OCOCH=CHCH_3$		92
		$C_2H_3CH(CH=C=CH_2)OCOCH=CHCH_3$		8
		3.0	74	

[a] The mixture of the propargylic and allenic adduct, in the ratio 92/8, is formed in an amount (25 mmol) equimolecular with the R'COCl compound. [b] Yield of the recovered isomeric ester.

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