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ADDITION OF STANNYLATED CARBOXYLIC ACID DERIVATIVES TO THE CARBONYL GROUP OF ALDEHYDES *

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Summary

Addition reactions of Bu_3SnCH_2COOEt with PhCHO at 75°C in the presence of Bu_3SnI and reactions of Et_3SnCH_2X (X = COOEt, CN, $CONMe_2$) with benzaldehyde, cinnamaldehyde and furfural at 20°C in DMSO in the presence of Me_4NF (2 mol %) were investigated. Adducts obtained in high yield in these reactions readily undergo hydrolysis (when treated with aqueous KF) and acetolysis (when treated with AcCl) with quantative formation of 3-hydroxy and 3-acetoxy derivatives of esters, nitriles and amides. We show that interaction of Et_3SnCH_2COOEt with the above-mentioned aldehydes and isovaleraldehyde in the presence of equimolar amounts of Et_4NCl in CH_2Cl_2/HMPTA (10/1) at 20°C followed by treatment of the reaction mixture with AcCl readily gives 3-acetoxyesters. Reactions of $PhCH(SnMe_3)COOEt$ with acrolein, crotonaldehyde and cinnamaldehyde and the hydrolysis of the obtained adducts lead exclusively to 1,2-addition products, these reactions are virtually non-stereoselective. The reaction of $PhCH(SnMe_3)COOEt$ with benzaldehyde at 20°C in DMF, CH_2Cl_2 or without solvent gives mainly *threo*-ethyl(2,3-diphenyl-3-hydroxy)propionate whereas at −78°C in CH_2Cl_2 in the presence of $BF_3 \cdot Et_2O$ *erythro* isomer is mainly formed. The data obtained are discussed within the framework of the mechanism involving the participation of the O-isomer $CH_2{=}C(OEt)OSnR_3$. This active intermediate is formed via metallotropic rearrangement of the starting organotin compound.

Addition reactions of organotin compounds to the carbonyl group of aldehydes are extensively used for carbon–carbon bond formation [1,2]. These reactions proved to be stereoselective giving *threo* [3,4] or *erythro* isomers [5,6] depending on the reaction conditions. This seems to be very important since it helps to solve a synthesis problem for stereo-regulated aldol condensation.

* Dedicated to Prof. Oleg A. Reutov on the occasion of his 65th birthday on September 5th, 1985.

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In recent years addition reactions of allyltin compounds to the carbonyl group [3,5] as well as organotin derivatives of aldehydes and ketones [4,6,8] have been studied in detail. Reactions of other α-substituted stannanes including stannylated esters, nitriles and amides are investigated to a lesser extent. The reactions only proceed easily with aldehydes containing electron-withdrawing substituents [9,10].

To obtain new data on synthetic possibilities of the latter class of organotin compounds we used activated organotin compounds to extend the scope of the participating aldehydes. The activation of the organotin substrate was performed by a well-known organometallic chemistry technique: nucleophilic catalysis [11]: the reaction was carried out in the presence of halide ions. Recently we found a new specific type of activation for stannylated esters by addition of trialkyltin halide [12] and also used it in the present research. In the study of these reactions special attention was paid to both stereoselectivity of the addition reactions and regioselectivity in the case of α, β-unsaturated aldehydes.

Results

Reaction of Bu_3SnCH_2COOEt with PhCHO in the presence of Bu_3SnI

In accordance with ref. 9 and 10 tributyl(carboethoxymethyl)tin failed to react with benzaldehyde in DMSO even at elevated temperature. However, the reaction is completed in 6 h in the presence of Bu_3SnI at 75°C yielding the adduct (85%) after distillation (eq. 1).

$$Bu_3SnCH_2COOEt + PhCHO \xrightarrow[DMSO]{Bu_3SnI} PhCH(OSnBu_3)CH_2COOEt \quad (1)$$

Hydrolysis of the adduct gave ethyl(3-hydroxy-3-phenyl)propionate (93%). The corresponding acetoxy derivative was isolated in 75% yield after reaction of the adduct with Ac_2O (50°C, 2 h) (eq. 2).

$$PhCH(OSnBu_3)CH_2COOEt \xrightarrow{H_2O} PhCH(OH)CH_2COOEt \quad (2)$$
$$PhCH(OSnBu_3)CH_2COOEt \xrightarrow{Ac_2O} PhCH(OAc)CH_2COOEt$$

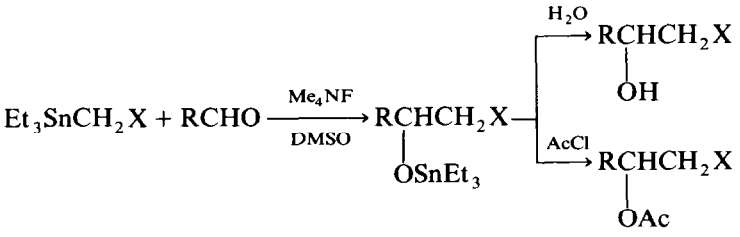
The attempted addition of Bu_3SnCH_2COOEt to acetophenone in the presence of Bu_3SnI as an activator failed. The transmetallation reaction took place under the same conditions yielding ethylacetate (82%) and stannylated ketone in 36 h (eq. 3).

$$Bu_3SnCH_2COOEt + PhCOCH_3 \xrightarrow[DMSO]{Bu_3SnI} CH_3COOEt + PhCOCH_2SnBu_3 \quad (3)$$

Me_4NF-catalyzed reactions of Et_3SnCH_2X ($X = COOEt$, $CONMe_2$, CN) with aldehydes

Nucleophilic catalysis by fluoride-ion derived from Me_4NF (2 mol %) has been

used in the reactions of stannylated carboxylic acid derivatives with aldehydes. The reactions of the organotin compounds mentioned above with benzaldehyde, cinnamaldehyde and furfural in DMSO have been investigated. After 2 d ^{1}H NMR spectroscopy indicated that the reaction was finished. In the case of Et_3SnCH_2COOEt the adducts were isolated and characterized by elementary organic analysis and ^{1}H NMR spectroscopy. As far as other compounds are concerned the corresponding adducts (without isolation) were hydrolyzed and alcohols formed or treated with acyl chloride to give the corresponding esters (eq. 4).



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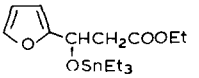
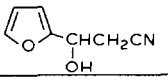
Yields of organotin adducts and the corresponding alcohols are given in Table 1.

TABLE 1

PRODUCTS YIELDS OF THE REACTIONS OF Et_3SnCH_2X WITH ALDEHYDES IN THE PRESENCE OF Me_4NF (2 mol%), DMSO, 20°C, *c* 2 *M*

X in Et_3SnCH_2X	R in RCHO	Product	Yield (%)
COOEt	Ph	PhCHCH$_2$COOEt OSnEt$_3$	76
COOEt	PhCH=CH–	PhCH=CHCHCH$_2$COOEt OSnEt$_3$	69
COOEt			61
$CONMe_2$	Ph	PhCHCH$_2$CONMe$_2$ OH	75
$CONMe_2$	PhCH=CH	PhCH=CHCHCH$_2$CONMe$_2$ OH	71
CN	Ph	PhCHCH$_2$CN OH	80
CN	PhCH=CH–	PhCH=CHCHCH$_2$CN OH	73
CN			65

In order facilitate the reactions and to increase the product yields we used some other solvents. We studied the solvent effect on the reaction rate of Et_3SnCH_2COOEt with benzaldehyde in the presence of Me_4NF (2 mol %). The reaction conversion rate was determined by the yield of ethyl(3-hydroxy-3-phenyl)propionate formed after hydrolysis of the reaction mixture. The yield of the reaction product determined by GLC analysis depends on the nature of the solvent as follows:

Solvent	HMPTA	DMF	THF	CH_2Cl_2
Yield (%) (after 25 h)	77	53	21	2

The best yield is achieved in HMPTA, however it was less then 80% even at prolonged reaction time.

Reaction of Et_3SnCH_2COOEt with aldehydes in the presence of Et_4NCl

Tetraethylammonium chloride may also be used to activate the reactions of Et_3SnCH_2COOEt with aldehydes. However, Et_4NCl in catalytic amounts is somewhat less efficient than Me_4NF. For instance, in HMPTA the product yield in the reaction with benzaldehyde in the presence of Me_4NF (2 mol%) is 38% and in the case of Et_4NCl, even in a larger amount (5 mol%) is 37%. The reaction acceleration is especially high in the presence of equimolar amounts of Et_4NCl. For example, reflux of the reaction mixture in CH_2Cl_2/HMPTA (10/1) under these conditions leads to a quantitative yield of the product in 2 h. Treament of the reaction mixture with AcCl (1 h reflux) afforded the ethyl ester of the corresponding 3-acetoxylic acid.

$$Et_3SnCH_2COOEt + PhCHO \xrightarrow[(2)\ AcCl]{(1)\ Et_4NCl\ (CH_2Cl_2/HMPTA)} PhCH(OAc)CH_2COOEt \quad (5)$$

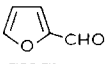
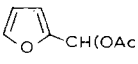
The product yields of these reactions are presented in Table 2.

Reactions of $PhCH(Me_3Sn)COOEt$ with α,β-unsaturated aldehydes

According to the data in Table 2 the reaction of Et_3SnCH_2COOEt with cinnamaldehyde occurs with 1,2-addition, and no conjugated addition products have been observed. To investigate the regioselectivity of organotin ester derivatives interaction

TABLE 2

YIELDS OF PRODUCTS OF THE REACTIONS OF Et_3SnCH_2COOEt WITH ALDEHYDES IN THE PRESENCE OF EQUIMOLAR AMOUNTS OF Et_4NCl IN CH_2Cl_2/HMPTA (10/1) UNDER REFLUX, 2 h, *c* 0.4 *M*

Aldehyde	Product [a]	Yield (%) [b]
PhCHO	$PhCH(OAc)CH_2COOEt$	93 (84) [c]
PhCH=CHCHO	$PhCH=CHCH(OAc)CH_2COOEt$	89
		81
Me_2CHCH_2CHO	$Me_2CHCH_2CH(OAc)CH_2COOEt$	62

[a] Obtained under reflux of the reaction mixture with AcCl for 1 h. [b] GLC data. [c] Separated by distillation.

TABLE 3

^{1}H NMR [a] DATA (δ, ppm, $CDCl_3$) AND *erythro/threo* RATIO OF RCH=CHCH(OH)CH(Ph)COOEt [b]

R	Isomer	CH_3 [c] (t)	CH_2 [c] (q)	H_α (d)	$J_{\alpha\beta}$ (Hz)	R–C=C (d)	J (Hz)	Ratio (%)
Ph	*erythro*	1.122	4.056	3.744	7.4	–		45
Ph	*threo*	1.167	4.118	3.710	9.0	–		55
Me	*erythro*	1.185	4.118	3.629	7.8	1.674	6.6	51
Me	*threo*	1.190	4.127	3.587	8.9	1.538	6.2	49
H	*erythro*	1.206	4.115	3.649	7.4	–		60
H	*threo*	1.206	4.143	3.616	8.8	–		40

[a] Other protons are characterized by average shifts: R = Ph, 4.84 (1H, H_β), 3.15 (1H, OH), 6.35 (2H, CH=CH), 7.25 (10 H, 2Ph); R = Me, 4.60 (1H, H_β), 2.71 (1H, OH), 5.53 (2H, CH=CH), 7.30 (5H, Ph); R = H, 4.67 (1H, H_β), 2.44 (1H, OH), 5.39 (3H, $CH=CH_2$), 7.31 (5H, Ph). [b] Classification of ^{1}H NMR signals is made by the following correlations [13]: $\delta\ (CH_3)_{erythro} < \delta(CH_3)_{threo}$, $\delta\ (CH_2)_{erythro} < (CH_2)_{threo}$, $\delta\ (H_\alpha)_{erythro} > \delta\ (H_\alpha)_{threo}$, $J_{\alpha\beta erythro} < J_{\alpha\beta threo}$. [c] All compounds have $J(CH_3,CH_2)$ 7.1 Hz.

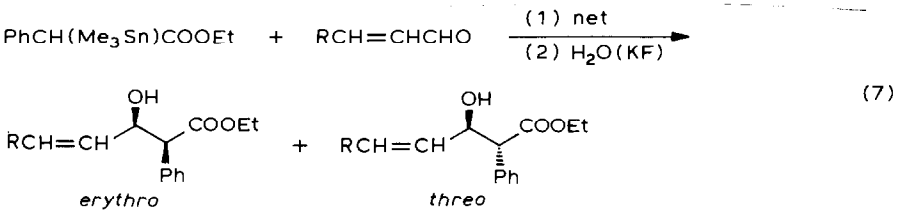
with α,β-unsaturated aldehydes we used acrolein and crotonaldehyde, which are sterically less hindered aldehydes. However, in the presence of activators such as halide ions these aldehydes were found to polymerize easily. That is why the reactions were carried out with $PhCH(Me_3Sn)COOEt$, which is rather active at room temperature even in the absence of halide ions.

The reaction with aldehydes was carried out by mixing equimolar amounts of the reactants. In all cases the products of 1,2-addition were obtained after hydrolysis (eq. 6).

$$PhCH(Me_3Sn)COOEt + RCH{=}CHCHO \xrightarrow[(2)\ H_2O(KF)]{(1)\ \text{net 1–5 h}} RCH{=}CHCH(OH)CHPhCOOEt \quad (6)$$

(R = H, 79%
R = Me, 80%
R = Ph, 88%)

The diastereoisomer content was determined by ^{1}H NMR spectroscopy. The proton signals were classified with regard to the characteristic chemical shifts and coupling constants of compounds of similar structure [13] and the ratio of diastereoisomers was found from integrals of signals. Table 3 shows that the yields of *erythro* and *threo* isomers are virtually the same. Thus the reactions do not seem to be stereoselective.



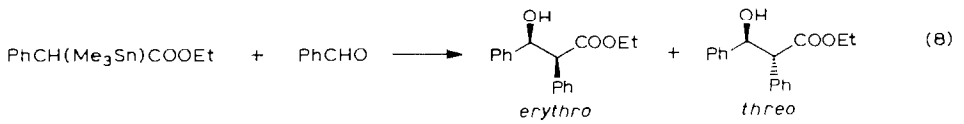
(7)

TABLE 4

EFFECT OF REACTION CONDITIONS ON THE STEREOSELECTIVITY OF ADDITION REACTIONS OF PhCH(Me_3Sn)COOEt WITH PhCHO AT 20°C, *c* 0.2 *M*

Solvent	Addition (1 equiv.)	Time (h)	Yield (%)	*erythro/treo*
–	–	0.1	94	41/59
DMF	–	24	88	40/60
DMF	Me_3SnI	24	85	42/58
CH_2Cl_2	–	24	90	22/78
CH_2Cl_2	$BF_3 \cdot Et_2O$	5 [a]	63	65/35

[a] At −78°C.



(8)

Reaction of PhCH(Me_3Sn)COOEt with PhCHO

The addition reactions of stannylated esters with aldehydes can be stereoselective as was shown in the reaction of PhCH(Me_3Sn)COOEt with benzaldehyde. Hydrolysis of the reaction products gave the known *erythro* and *threo* isomers of ethyl (2,3-diphenyl-3-hydroxy)propionate [13,14] (eq. 8).

The reactions were carried out by mixing the reactants either without solvent, in DMF, or in CH_2Cl_2 without additions and in the presence of Me_3SnI or $BF_3 \cdot Et_2O$. The reaction products were separated by TLC [14] and were identified by ^1H NMR spectroscopy. In all cases the reaction rate was rather high. Without solvent a slight raise in temperature of the reaction mixture was observed. The product yields after hydrolysis of the reaction mixture and also the isomer ratios are given in Table 4.

The *threo* isomer is the predominant product in all cases except where $BF_3 \cdot Et_2O$ was used (Table 4). The reaction's stereoselectivity is the highest in CH_2Cl_2 and somewhat lower in DMF. Addition of Me_3SnI does not alter the isomer ratio. The stereoselectivity of the reaction is changed at −78°C in the presence of $BF_3 \cdot Et_2O$, the main product being the *erythro* isomer.

Discussion

As mentioned above the stannylated esters, amides and nitriles only react with those carbonyl compounds, containing electron-withdrawing substituents, e.g. C_6F_5CHO or $PhCOCF_3$ [10]. To carry out the reactions involving ordinary carbonyl compounds a special method is required [15]: the organotin compound is introduced into the reaction with the carbonyl compound as triorganotin enolate in the presence of $TiCl_4$. The use of this technique is limited since it is required to carry out a rather difficult synthesis of organotin O-isomer.

A substantial acceleration of the reaction of organotin carbonyl compounds, amides and nitriles with ordinary aldehydes was achieved by addition of trialkyliodostannane and halide ions. Tables 1 and 2 show that the yield of the corresponding addition products is rather high.

The use of the CH_2Cl_2/HMPTA mixture in the presence of equimolar amounts of Et_4NCl is very convenient in these reactions. In this case the reactions proceed easily and yield addition products which are converted to the corresponding acetoxy derivatives by treatment with acetyl chloride. The yield of α-acetoxy esters thus obtained is rather high, sometimes almost quantitative (Table 2).

The mechanism of catalysis is of special interest. Different catalytic mechanisms for different activators should be expected; e.g., catalysis by fluoride ion may be described as shown in eq. 9 similar to that for the reactions of organosilicon compounds [16]:

$$\begin{array}{l} R_3SnCH_2COOEt + F^- \longrightarrow [{}^-CH_2COOEt] + R_3SnF \\ [{}^-CH_2COOEt] + R'CHO \rightleftharpoons [R'\underset{\displaystyle O^-}{\underset{|}{C}}HCH_2COOEt] \\ [R'\underset{\displaystyle O^-}{\underset{|}{C}}HCH_2COOEt] + R_3SnF \longrightarrow R'\underset{\displaystyle OSnR_3}{\underset{|}{C}}HCH_2COOEt + F^- \end{array} \qquad (9)$$

Another reaction (eq. 10) mechanism which is rather likely in the presence of chloride ion is suggested taking into account that organotin derivatives of esters can react with electrophilic reagents apparently in the enolates formed in a fast metallotropic rearrangement [12].

$$R_3SnCH_2COOEt \overset{Cl^-}{\rightleftharpoons} CH_2{=}C(OEt)OSnR_3 \xrightarrow{R'CHO} R'\underset{\displaystyle OSnR_3}{\underset{|}{C}}HCH_2COOEt \qquad (10)$$

The chloride ion in reaction 10 seems to play a double role. On the one hand it can accelerate the metallotropic rearrangement by ionization of the C–Sn bond when Cl^- coordinates at the tin atom and an ion-pair is formed [17]. On the other hand the chloride ion is capable of nucleophilic assistance [11] in the reaction of triorganotin enolate with carbonyl compounds facilitating cleavage of O–Sn bonds for release of R_3Sn groups.

$$\begin{array}{l} R_3SnCH_2COOEt + Et_4NCl \rightleftharpoons \left[\begin{array}{l} R_3\overset{+}{Sn}\,{}^-CH_2COOEt \\ \;\uparrow \\ Et_4NCl \end{array}\right] \rightleftharpoons \\ CH_2{=}C(OEt)OR_3Sn \leftarrow ClNEt_4 \rightleftharpoons CH_2{=}C(OEt)OR_3Sn + Et_4NCl \end{array} \qquad (11)$$

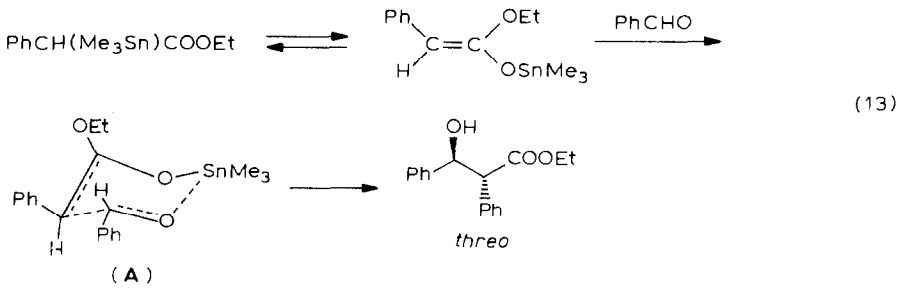
Participation of tin enolate might explain the acceleration of the reactions in the presence of trialkyliodostannane. According to the proposed mechanism (eq. 12) the

act of catalysis involves R_3SnI attack of the carbonyl group resulting in displacement of the R_3Sn group with reaction center transfer. As a result the tin enolate is formed which is an active species in these reactions.

$$R_3SnCH_2COOEt \xrightarrow{R_3SnI} CH_2{=}C(OEt)OSnR_3 \xrightarrow{R'CHO} R'\underset{\displaystyle OSnR_3}{\underset{|}{C}}HCH_2COOEt \qquad (12)$$

The proposed catalysis mechanism differs from that usually accepted for organometallic reactions (both from nucleophilic catalysis when the nucleophile coordinated to the metal atom activates the substrate and from electrophilic catalysis related to activation of the electrophilic agent, e.g. by a Lewis acid [11]). The catalytic contribution of the latter type is also possible in the reaction under investigation since trialkyliodostannane is able, as a Lewis acid, to active the carbonyl group towards nucleophilic agents.

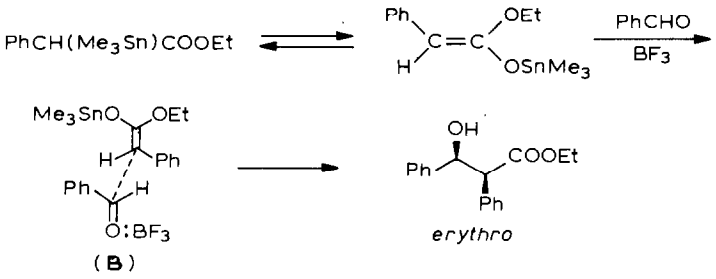
The stereochemical features of the reaction of $PhCH(Me_3Sn)COOEt$ with PhCHO can be explained within the framework of the mechanisms 10 and 12. The predominant formation of the *threo* isomer in this reaction is believed to be due to participation of the O-tautomer $PhCH{=}C(OEt)OSnMe_3$ as an active species. This intermediate can be formed rather quickly due to structural features of the starting organotin compound even if accelerating additives are absent. The transition state of the reaction is considered to be cyclic as it usually is in similar cases [1]. The most probable state is the six-membered activated complex **A** in chair conformation where bulky phenyl groups are located in equatorial positions.



(13)

The accepted point of view assumes that the enolate has the *E*-configuration, in which the bulky phenyl and trimethyltin groups are both in the remotest possible position. Such an arrangement of groups is known for stannylated ketoenols [6]. The proposed mechanism can also account for the fact that the stereoselectivity of the reaction increases if CH_2Cl_2 is used instead of DMF. Reduction of solvent's polarity must be favourable for realization of the cyclic transition state with intramolecular coordination.

In the presence of $BF_3 \cdot Et_2O$ which forms a complex with benzaldehyde the coordination of tin to the carbonyl group is rather difficult [1] and an acyclic transition state (**B**) is preferred. The *erythro* isomer being predominant in this case [6].



(14)

The low stereoselectivity of the reaction of $PhCH(Me_3Sn)COOEt$ with α,β-unsaturated aldehydes (Table 3) in the adopted reaction scheme can be explained by the fact that the phenyl group in transition state **A** is in equatorial position whereas the less bulky vinyl group may occupy both equatorial and axial positions.

Experimental

The ^1H NMR spectra were recorded on "Varian T-60" and "Bruker 200" spectrometers. The IR spectra were obtained on UR-20 apparatus (KBr). Chromatographic analysis of reaction products was made using a "LHM-8MD" chromatograph model IV with nitrogen as the carrier gas (3/m 3 mm column packed with 10% E-301 on Chromosorb W silanized with dimethyldichlorsilane).

The organotin compounds Et_3SnCH_2COOEt [18], Et_3SnCH_2CN [19], $Et_3SnCH_2CONMe_2$ [20], Bu_3SnCH_2COOEt [15], Me_3SnI and Bu_3SnI [21] were prepared according to literature methods. The new compound $PhCH(Me_3Sn)COOEt$ was prepared by the reaction of Et_2NSnMe_3 with ethyl (phenylacetate) analogous to the procedure in ref. 22 (93% yield, b.p. 85–87°C/0.05 mmHg; n_D^{20} 1.5345. ^1H NMR (CCl_4) (δ, ppm): 0.2(s, 9H, Me_3Sn), 1.3 (t, 3H, CH_3), 3.6(s, 1H, SnCH), 4.0(q, 2H, CH_2O), 7.2(m, 5H, Ar); IR spectrum: ν(C=O) 1720 cm^{-1}; Analysis. Found: C, 47.99; H, 6.17; Sn, 36.07. $C_{13}H_{20}O_2Sn$ calcd.: C, 47.75; H, 6.16; Sn, 36.30%).

The synthesis of standards for GLC analysis is described in ref. 23.

Reactions of Bu_3SnCH_2COOEt with carbonyl compounds in the presence of Bu_3SnI

Bu_3SnCH_2COOEt (1.89 g, 5 mmol) was added to benzaldehyde (0.53 g, 5 mmol) and Bu_3SnI (2.09 g, 5 mmol) in DMSO-d_6 under argon. After heating at 75°C for 6 h the reaction was completed as shown by ^1H NMR spectroscopy. Distillation of the reaction mixture afforded 2.06 g (yield 85%) $Bu_3SnOCH(Ph)CH_2COOEt$, b.p. 145°C/0.02 mmHg, ^1H NMR (CCl_4) (δ, ppm): 1.1 (m, 27H, Bu_3Sn); 2.52 (m, 3H, CH_3CO); 4.12 (q, 2H, OCH_2); 5.06 (m, 1H, CH); 7.3 (m, 5H, Ar). GLC analysis showed that hydrolysis of $Bu_3SnOCHPhCH_2COOEt$ (0.242 g, 0.5 mmol) in benzene (1 ml) by action of saturated aqueous KF afforded ethyl (3-hydroxy-3-phenyl)propionate) in 93% yield and after treatment of the adduct with AcCl (0.0785 g, 1 mmol) in CH_2Cl_2 (3 h reflux) ethyl (3-acetoxy-3-phenyl)propionate is formed in 93% yield.

The reaction of Bu_3SnCH_2COOEt with acetophenone was carried out similarly. According to ^1H NMR data the conversion of the reaction was 80% after 36 h. After treatment of the reaction mixture with bromine it was found by GLC that ethyl (bromoacetate) (10%), ethyl acetate (82%), α-bromoacetophenone (75%) and acetophenone (15%) were formed.

Reactions of Et_3SnCH_2COOEt with aldehydes in DMSO in the presence of Me_4NF

A solution of Et_3SnCH_2COOEt (1.47 g, 5 mmol), aldehyde (5 mmol) and Me_4NF (0.0073 g, 0.1 mmol) in DMSO (total volume 2.5 ml) was stirred at room temperature for 45–50 h. Distillation of the reaction mixtures at reduced pressure afforded the following compounds [23]: $Et_3SnOCH(Ph)CH_2COOEt$ (76%), b.p. 109–111°C/0.1 mmHg; $PhCH{=}CHCH(Et_3SnO)CH_2COOEt$ (69%), b.p. 136–138°C/0.1 mmHg; $(C_4H_3O)CH(Et_3SnO)CH_2COOEt$ (61%), b.p. 117–120°C/0.1 mmHg.

A solution of Et_3SnCH_2COOEt (0.293 g, 1 mmol), PhCHO (0.102 g, 1 mmol) and Me_4NF (0.0019 g, 0.02 mmol) in DMSO (total volume 0.5 ml) was stirred for 50 h at 20°C. After hydrolysis of the reaction mixture, extraction with benzene and drying of the extract with $MgSO_4$ ethyl (3-hydroxy-3-phenyl)propionate (0.243 g, 90%) was isolated by TLC on silica gel (hexane/ether, 2/1), b.p. 106°C/0.2 mmHg. The following products were similarly obtained by reactions of benzaldehyde, cinnamaldehyde and furfural with the corresponding organotin compounds:

$PhCH(OH)CH_2CONMe_2$ (75%), b.p. 112–115°C/0.1 mmHg; ^1H NMR (CCl_4) (δ, ppm): 2.4(d, 2H, CH_2), 2.7(s, 6H, NMe_2), 3.3(s, 1H, OH), 4.9(t, 1H, CHO), 7.1(m, 5H, Ar); Analysis, Found: C, 68.08; H, 8.02. $H_{11}H_{15}NO_2$ calcd.: C, 68.37; H, 7.82%.

$PhCH{=}CHCH(OH)CH_2CN$ (73%), b.p. 95–96°C/0.01 mmHg; ^1H NMR (CCl_4) (δ, ppm): 2.4(d, 2H, CH_2), 3.5(s, 1H, OH), 4.8 (m, 1H, CHO), 6.3 (m, 2H, CH=CH), 7.2(m, 5H, Ar). Analysis. Found: C, 76.71; H, 6.78. $C_{11}H_{11}NO$ calcd.: C, 76.28; H, 6.40%.

$PhCH{=}CHCH(OH)CH_2CONMe_2$ (71%), b.p. 105–106°C/0.01 mmHg; ^1H NMR (CCl_4) (δ, ppm): 2.4(d, 2H, CH_2CO), 2.9(d, 6H, NMe_2), 3.8(s, 1H, OH), 4.7 (m, 1H, CHO), 6.4(m, 2H, CH=CH), 7.2(m, 5H, Ar). Analysis. Found: C, 71.12; H, 7.83. $C_{13}H_{17}NO_2$ calcd.: C, 71.21; H, 7.81%.

$(C_4H_3O)CH(OH)CH_2CN$ (65%), b.p. 104–106°C/0.1 mmHg; ^1H NMR (CCl_4) (δ, ppm): 2.5(d, 2H, CH_2), 3.7(s, 1H, OH), 5.0(m, 1H, CHO), 6.1 (m, 2H, C_4H_3O), 7.2 (m, 1H, C_4H_3O). Analysis. Found: C, 61.44; H, 5.10. C_7H_7NO calcd.: C, 61.31; H, 5.14%.

Reactions of Et_3SnCH_2COOEt with benzaldehyde in CH_2Cl_2/HMPTA in the presence of Et_4NCl

A solution of Et_3SnCH_2COOEt (1.47 g, 5 mmol), PhCHO (0.51 g, 5 mmol) and Et_4NCl (0.83 g, 5 mmol) in CH_2Cl_2/HMPTA (10/1) (total volume 12 ml) was refluxed for 2 h. Then AcCl (0.54 g, 7 mmol) was added and the mixture was refluxed for 1 h again. Hydrolysis of the reaction mixture by aqueous KF followed by filtration of Et_3SnF, extraction with benzene, drying of the extract with $MgSO_4$, removal of the solvent and distillation afforded 0.99 g (84%) of $PhCH(OAc)$-CH_2COOEt.

Reaction of $PhCH(Me_3Sn)COOEt$ with benzaldehyde

To a solution of PhCHO (0.053 g, 0.5 mmol) in 2.5 ml of DMF$PhCH$-$(Me_3Sn)COOEt$ (0.764 g, 0.5 mmol) was added under argon atmosphere. The

reaction mixture was hydrolyzed by aqueous KF 24 h later, then it was extracted with benzene and the extract dried with $MgSO_4$. The benzene was partly removed and *threo* and *erythro* isomers of ethyl (2,3-diphenyl-3-hydroxy)propionate were isolated by TLC on "Silpearl" (ether/hexane, 2/3). The yield of products obtained and ratio of the isomers are given in Table 4.

A solution $PhCH(Me_3Sn)COOEt$ (0.164 g, 0.5 mmol) in 1 ml of CH_2Cl_2 was added dropwise to a solution of PhCHO (0.053 g, 0.5 mmol) and $BF_3 \cdot Et_2O$ (0.07 g, 0.5 mmol) in 1.5 ml of CH_2Cl_2 cooled at $-78°C$ under argon. The reaction mixture was stirred for 5 h at $-78°C$ and after warming up to room temperature it was treated as described above.

Reaction of $PhCH(Me_3Sn)COOEt$ with α,β-unsaturated aldehydes

To cinnamaldehyde (0.212 g, 1 mmol) under argon atmosphere $PhCH(Me_3Sn)COOEt$ (0.328 g, 1 mmol) was added. The reaction mixture was treated with aqueous KF 3 h later, extracted by benzene and dried with $MgSO_4$. The solvent was partly removed and PhCH=CHCH(OH)CH(Ph)COOEt (0.26 g, 88%) was isolated by TLC on "Silpearl" (ether/hexane, 2/3). Mass spectrum (*m/e*): 296(M^+), 278, 163, 133.

The reactions of $PhCH(Me_3Sn)COOEt$ with crotonaldehyde and acrolein were carried out similarly. The following products were isolated: MeCH=CHCH(OH)CH(Ph)COOEt (80%), mass spectrum (*m/e*): 234 (M^+), 217, 216, 189, 163, 71; CH_2=CHCH(OH)CH(Ph)COOEt (79%), mass spectrum (*m/e*): 220 (M^+), 203, 163, 134, 57. The ratio of the isomers is given in Table 3.

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