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ORGANOTIN COMPOUNDS

III *. ORGANOTIN CHLOROHYDRIDE ADDITIONS TO METHYL *E*-DISUBSTITUTED PROPENOATES

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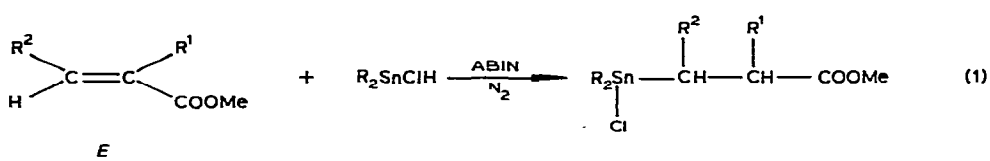
Summary

The syntheses of new functionally substituted organotin compounds are reported. The results indicate that the additions of di-n-butyltin and diphenyltin chlorohydrides to methyl *E*-disubstituted propenoates give high yields of organotin adducts and that the reactions are stereoselective. Evidence supporting a *trans*-stereospecific addition is discussed.

Introduction

The use of organotin chlorohydrides as hydrostannation reagents has already been described by Neumann and Pedain [1], who applied this reaction to the synthesis of several functionally substituted organotins.

Following our studies [2] on the synthesis of new functionally substituted organotin compounds in order to use them in toxicological investigations, now we report results obtained in the synthesis of compounds of type $R_2R'SnCl$ by hydrostannation of methyl *E*-α,β-disubstituted propenoates, according to eq. 1.



E

R = n-Bu, Ph ; R^1 = Me , Ph ; R^2 = Me , Ph

(1)

* For part II see ref. 2.

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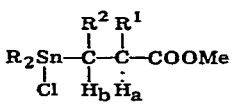
Results and discussion

The additions were carried out under conditions favouring a free radical reaction, e.g. in the absence of solvent, in a nitrogen atmosphere and in the presence of azobisisobutyronitrile (ABIN) as a free radical initiator. The reaction temperature was kept at 40°C in order to avoid the decomposition of the organotin chlorohydrides. The reactions were followed by IR (by observing the disappearance of the Sn—H absorption) and by PMR (by observing product formation). For all the reactions a quantitative yield of adduct was obtained using a 50% excess of the organotin chlorohydride. The new organotin compounds obtained as well as some of their physical characteristics, elemental analyses (C, H) and the reaction conditions are summarized in Table 1.

In agreement with previous results [2], the analysis of the PMR spectra indicates that for each of the systems studied, only one of the two possible diastereoisomers was obtained as a product, showing that the additions are stereoselective. In order to decide whether the reactions are stereospecific, additions of organotin chlorohydrides to the geometric isomers of the esters used previously, i.e. *Z* in place of *E*, were attempted. However, as in the case of the monoorganotin hydride additions [2], the single adducts obtained were identical to those obtained starting from the more stable olefins, e.g. both methyl *Z*- and *E*-α,β-disubstituted propenoates gave the same addition product. Using an insufficiency of hydride (1 : 1 or 1 : 0.5 ratio), the addition product was formed together with quantities of the isomeric olefin of the starting material (eq. 2).

TABLE 1

ADDUCTS OBTAINED FROM THE REACTIONS OF ORGANOTIN CHLOROHYDRIDES AND METHYL-*E*-α,β-DISUBSTITUTED PROPENOATES [a]

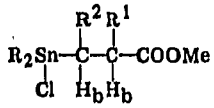


Compound	R	R^1	R^2	Time [b]	M.p. (°C) or n_D [c]	Elemental analyses (%)			
						Calculated		Found	
						C	H	C	H
I	n-Bu	Me	Me	120	1.5019	43.84	7.62	43.42	7.84
II	n-Bu	Me	Ph	210	1.5339	51.21	7.01	50.99	7.11
III	n-Bu	Ph	Me	270	1.5300 [d]	51.21	7.01	50.85	6.90
IV	n-Bu	Ph	Ph	180	1.5609 [e]	56.77	6.55	56.25	6.74
V	Ph	Me	Me	60	1.5880	51.04	4.99	51.37	5.15
VI	Ph	Me	Ph	180	161—163 [f]	56.84	4.74	56.58	4.90
VII	Ph	Ph	Me	150	1.5989 [d]	56.84	4.74	56.72	4.85
VIII	Ph	Ph	Ph	180	134—136 [g]	61.41	4.60	60.91	4.33

[a] Quantitative yield of adducts obtained in all reactions using a 50% excess of hydride, at 40°C, in nitrogen atmosphere and in presence of ABIN (0.05 mol per mol of hydride). [b] In minutes. [c] Refractive indices determined at 22°C, except when indicated otherwise. [d] At 21.5°C. [e] At 22.5°C. [f] Recrystallized from benzene. [g] Recrystallized from petroleum ether (30—60°).

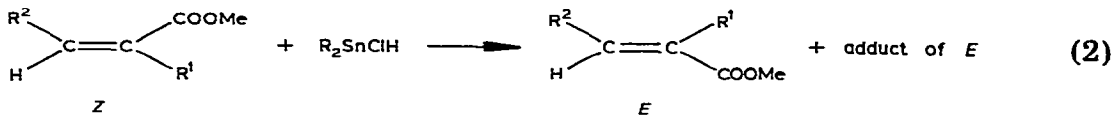
TABLE 2

PMR DATA OF THE ORGANOTIN ADDUCTS



Compound	R	R^1	R^2	Chemical shifts (δ, ppm) [a]		
				H_a	H_b	Others
I	n-Bu	Me	Me	3.00(m, 1 H)	underneath n-Bu	3.83 (s, 3 H); 1.4 (broad complex signal, 25 H)
II	n-Bu	Me	Ph	3.05 (complex signal, 2 H)		3.91 (s, 3 H); 1.26 (complex signal, 21 H); 7.1 (m, 5 H)
III	n-Bu	Ph	Me	partially under —OMe	underneath n-Bu	3.76 (two s [b], 4 H); 1.38 (complex signal, 22 H); 7.2 (m, 5 H)
IV	n-Bu	Ph	Ph	4.40 (d, *J* 2 Hz)	3.20 (d, *J* 2 Hz)	3.90 (s, 3 H); 1.2 (m, 18 H); 7.1 (m, 10 H)
V	Ph	Me	Me	3.12 (m, 1 H)	2.23 (m, 1 H)	3.94 (s, 3 H); 1.26 (d, 3 H, *J* 7.5 Hz); 1.45 (d, 3 H, *J* 8.5 Hz); 7.8 (m, 10 H)
VI	Ph	Me	Ph	3.22 (complex signal, 2 H)		3.91 (s, 3 H); 1.15 (d, 3 H, *J* 6.5 Hz); 7.36 (complex signal, 15 H)
VII	Ph	Ph	Me	partially under —OMe	2.20 (m, 1 H)	3.72 (two s [b], 4 H); 1.40 (d, 3 H, *J* 7.0 Hz); 7.32 (complex signal, 15 H)
VIII	Ph	Ph	Ph	4.32 (d, *J* 3 Hz)	3.33 (d, *J* 3 Hz)	3.89 (s, 3 H); 7.28 (complex signal, 20 H)

[a] Chemical shifts relative to TMS; spectra recorded in CCl_4 solution. [b] One strong and one weak signal too close.



Z E

As the methyl *Z*-α,β-disubstituted propenoates do not undergo isomerization under the reaction conditions [2] in the absence of the organotin hydride, it is concluded that the olefin isomerization results from reaction of the olefin with the tin hydride. These results confirm the reversibility of the radical addition step reported by Neumann [3] and Kuivila [4,5].

A study of the spectroscopic data, PMR and IR, ν(C=O), of the adducts obtained (Tables 2 and 3) gives some evidence about the possible stereochemistry of the reaction.

Without exception the carbonyl stretching frequencies in these compounds lie between 1656 and 1680 cm^{-1} (Table 3), i.e. between 50 and 80 cm^{-1} to lower frequency than the parent saturated esters. The PMR data (Table 2) indicate that the ester signals are situated downfield from the corresponding signal in the saturated analogues of the methyl disubstituted propenoates. For example III (—OMe, 3.76 ppm) and VII (—OMe, 3.72 ppm) compared with $CH_3CH_2CHPhCOOMe$ (—OMe, 3.44 ppm). These values are consistent with intramolecular carbonyl coordination to Sn, because this phenomenon reduces the carbonyl stretching frequency [6], and also has a deshielding effect on the methoxy group protons. That the carbonyl coordination to Sn is intramolecular

TABLE 3

IR DATA OF THE ORGANOTIN ADDUCTS [a]

Compound (see Tables 1 and 2)	Frequency (cm^{-1})	
	ν(C=O)	Others
I	1677s	2890s; 1555w; 1447s(br); 1366m; 1330m; 1269m; 1250m; 1219w; 1176w; 1149w; 1130m; 1075m; 1018m; 962w; 873s(br); 768m(br); 733m
II	1676s	2890s; 2833m(sh); 1488w; 1458s(br); 1374w; 1333w; 1266m(br); 1225m; 1183w; 1155w; 1116m; 1065m; 1020w; 873w; 763s(br); 696s
III	1681s	2817s; 1629w; 1470w; 1437m; 1412m; 1353w; 1235s(br); 1183m(br); 1163m; 1093w; 1062w; 1031m; 1018w; 767m(br); 745w; 727m; 697s.
IV	1680s	2907s; 2825m(sh); 1603w; 1492w; 1439s(br); 1337m(br); 1228s; 1182m; 1080w; 1053w; 1031w; 965m; 877m(br); 806w; 762m; 749w; 697s
V	1667s	3030w; 2941m; 1428s(br); 1374w; 1333m; 1266m(br); 1219s; 1183m; 1131m; 1070m; 1022m; 995m; 966w; 877w; 730s; 694s
VI	1668s	3060w; 2994w; 1484w; 1453m; 1429m; 1385w; 1353w; 1338m; 1280m; 1243m(br); 1193w; 1155w; 1075m; 1070m; 1053m; 1017m(br); 994w; 956m; 923m; 844w; 801w; 767m; 755m; 725s(br); 690s(br)
VII	1656s	3030w; 2907w; 1460w; 1412s; 1316w(sh); 1282w; 1219m(br); 1176w; 1065m; 1015w; 990m; 900w; 775m(br); 728s; 693s
VIII [b]	1681s	3030w; 2915w; 1600w; 1580w; 1496m; 1482w; 1450w; 1442m; 1432m; 1364m; 1340w; 1310w; 1230s; 1186m; 1078m; 1050w; 1035w; 1026w; 1000w; 965w; 822w; 780w; 760m; 740s; 700s

[a] Spectra recorded as pure compounds, except when indicated otherwise. [b] As KBr pressed disc.

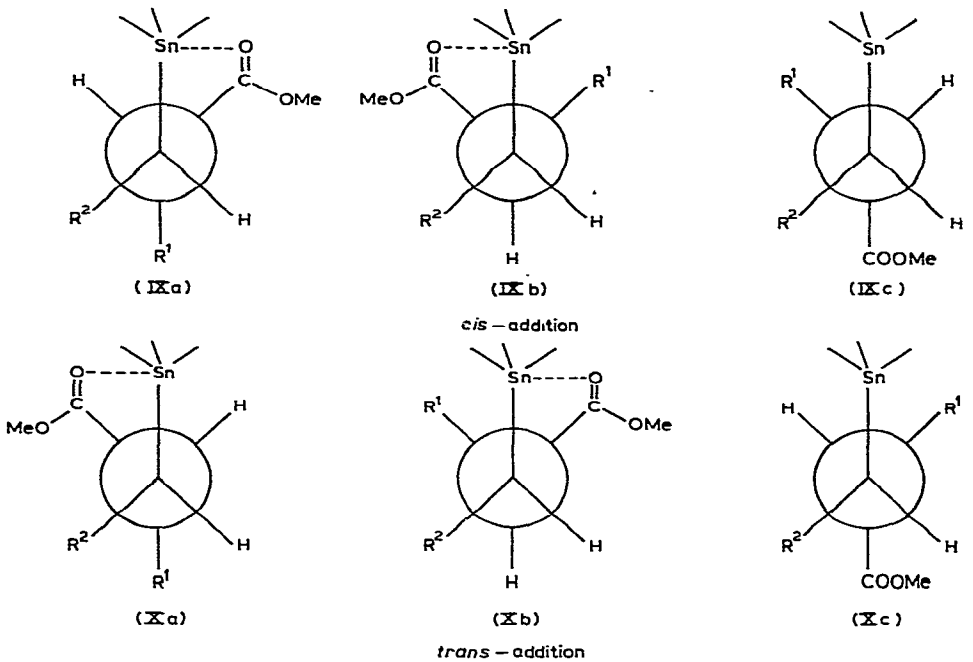


Fig. 1.

is demonstrated by the fact that the carbonyl stretching frequency of the compounds does not change in solution. The possible conformations resulting from a *cis*-attack (IXa—IXc) and from a *trans*-attack (Xa—Xc) are shown in Fig. 1.

Only structures IXab and Xab are consistent with intramolecular coordination. The structures IXb and Xb could be discarded because both are sterically unfavourable. Now, taking into account the small coupling constants $J(H_a—H_b)$ of 2 and 3 Hz observed for compounds IV and VIII (Table 2) it is possible to conclude that the structure Xa is the one which is in agreement with the spectroscopic data (both IR and PMR), because structure IXa should give much larger coupling constants (ca. 10 Hz).

Therefore these results strongly suggest that the reactions take place following a *trans*-addition stereochemistry.

Further work is in progress in order to obtain more evidence about the stereochemistry of these addition reactions.

Experimental

PMR spectra were obtained with a Varian A60-D instrument. Infrared spectra were recorded with a Perkin-Elmer 137-B spectrophotometer. The refraction indices were measured with a Universal Abbe, Zeiss Jena VEB instrument and the melting points were determined on a Kofler hot stage and are uncorrected. Microanalyses were performed in Dortmund University, Federal Republic of Germany. All the olefins used but tiglic acid (Fluka) were synthesized in our laboratory following standard procedures [7—11]. The organotin chlorohydrides

were obtained from the equilibrium mixtures of di-n-butyltin and diphenyltin dichlorides with the corresponding dihydrides [1,12], the latter being obtained by reduction of the dichlorides with sodium borohydride [13]. All the organotin adducts obtained were purified by column chromatography (silica gel, Kiesel gel 60, 70—230 mesh, Merck).

Additions of organotin chlorohydrides to the olefins

A similar procedure was used in the preparation of all the organotin compounds. One experiment is described in detail to illustrate the methods used:

Reaction of methyl-E-α,β-diphenylpropenoate with diphenyltin chlorohydride. Synthesis of methyl-α-phenyl-β-(di-n-butyl)chlorostannyl cinnamate (VIII). Methyl-*E*-α,β-diphenylpropenoate (5 g, 0.021 mol) was hydrostannated with 9.745 g (0.0315 mol, 50% excess) of diphenyltin chlorohydride, using ABIN as a catalyst (0.0015 mol), in a nitrogen atmosphere, at 40°C, during 3 h (optimal time of reaction and adequate excess of organotin hydride were determined in previous runs by both monitoring the reaction by taking samples at intervals and observing the disappearance of the Sn—H absorption by IR and also by checking that the PMR spectrum of the reaction mixture did not show the presence of unreacted olefin). The PMR spectrum showed that under these conditions a quantitative yield of adduct VIII was obtained. The crude product was directly purified by column chromatography using silica gel 60. The adduct VIII was eluted with carbon tetrachloride. M.p. 134—136°C, recrystallized from petroleum ether (30—60); PMR (CCl_4, δ, ppm), 4.32 (H_a, d, J 3 Hz), 3.33 (H_b, d, J 3 Hz), 3.89 (s, —OMe); IR (Kbr disc), ν(C=O) 1681 cm^{-1}. Analysis: Found: C, 60.91; H, 4.33. $C_{28}H_{25}O_2ClSn$ calcd.: C, 61.41; H, 4.60%.

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