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ORGANOTIN HYDRIDE ADDITIONS TO *E*- AND *Z*-TRISUBSTITUTED ETHYLENES. SYNTHESIS OF SOME NEW FUNCTIONALLY SUBSTITUTED ORGANOTIN COMPOUNDS

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Summary

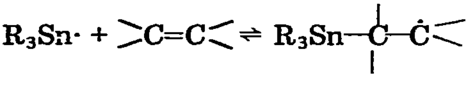
The syntheses of some new functionally substituted organotin compounds are reported. The results indicate that the additions of tri-n-butyltin and triphenyltin hydrides to trisubstituted ethylenes (where one substituent is either a carbomethoxy or a nitrile group) proceed smoothly to give high yields of organotin adducts and that the reactions are stereoselective. Evidence concerning the reversibility of the free radical forming step is presented.

Introduction

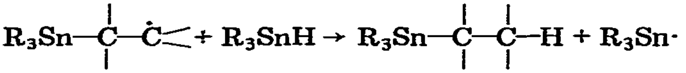
Hydrostannation is the most useful reaction for synthezing organotin compounds containing functional groups. Although in certain cases an ionic mechanism has been demonstrated [1], more commonly the reactions proceed by a free radical mechanism of the type shown below [2,3]. The reversibility of step 3 has been demonstrated by Neumann [4] and Kuivila [5,6], using both internal and terminal olefins.

$$\text{Initiator} \rightarrow \text{Rad.} \qquad (1)$$

$$R_3SnH + Rad\cdot \rightarrow R_3Sn\cdot + RadH \qquad (2)$$



$$R_3Sn\cdot + \rangle C{=}C\langle \rightleftharpoons R_3Sn{-}\overset{|}{\underset{|}{C}}{-}\dot{C}\langle \qquad (3)$$



$$R_3Sn{-}\overset{|}{\underset{|}{C}}{-}\dot{C}\langle + R_3SnH \rightarrow R_3Sn{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H + R_3Sn\cdot \qquad (4)$$

In the present work we report the synthesis of new functionally substituted organotin compounds of type R_3SnR' by the hydrostannation of *E*- and *Z*-tri-

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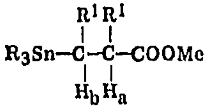
TABLE 1

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



$$R_3Sn{-}\underset{H_b}{\overset{R^1}{C}}{-}\underset{H_a}{\overset{R^1}{C}}{-}COOMe$$

Compound	R	R¹	R²	Time[b]	M.p. (°C) or n_D[c]	PMR[d] (H_a and H_b)	Elemental analyses (%)			
							Calculated		Found	
							C	H	C	H
I	n-Bu	Me	Me	240	1.4875	2.14(m)[f]	53.35	9.45	52.91	9.27
II	n-Bu	Me	Ph	180	1.5192	2.88(m)	59.12	8.63	59.43	8.35
III	n-Bu	Ph	Me	60	1.5120[e]	underneath n-Bu_3Sn-	59.12	8.63	58.78	8.29
IV	n-Bu	Ph	Ph	240	1.5438	H_a: 4.21 (d, J 12.5) H_b: 3.23 (d, J 12.5)	63.57	8.00	63.78	8.09
V	Ph	Me	Me	90	1.6002	H_a: 2.39 (q, J 3.5)[f] H_b: 1.89 (q, J 3.5)	61.97	5.63	62.19	5.85
VI	Ph	Me	Ph	60	107–108[g]	3.38(m)	66.06	5.35	65.78	5.11
VII	Ph	Ph	Me	90	146–147	2.50(m)	66.06	5.35	65.64	5.15
VIII	Ph	Ph	Ph	90	158–159	H_a: 4.45 (d, J 13.5) H_b: 3.91 (d, J 13.5)	69.29	5.13	68.84	5.38

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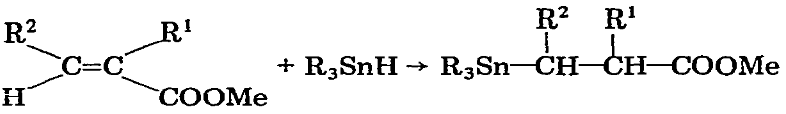
[a] Quantitative yield of adducts obtained in all reactions using a 50% excess of hydride, at 80°C, in nitrogen atmosphere and in presence of ABIN (0.05 mol per mol of hydride). [b] In minutes. [c] Refractive indices determined at 22°C, except when indicated otherwise. [d] Chemical shifts in ppm relative to TMS as internal standard, and J values in Hz; CCl_4 used as solvent, except when indicated otherwise. [e] Determined at 21.5°C. [f] $CDCl_3$. [g] All solids were recrystallized from benzene.

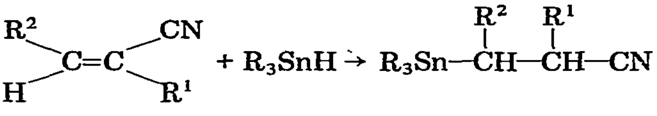
substituted olefins. These compounds will be used in toxicological studies. The particular systems investigated were the additions of tri-n-butyltin and triphenyltin hydrides to methyl *E*-α,β-disubstituted propenoates (eq. 5) and *Z*-α,β-disubstituted acrylonitriles (eq. 6).



E

(5)

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



Z

(6)

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

Results and discussion

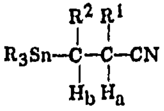
All the additions were carried out under conditions favoring a free radical reaction, e.g., at 80°C, in the absence of solvent, in a nitrogen atmosphere, and in the presence of azobisisobutyronitrile (ABIN) as a free radical initiator. The reactions were followed by IR spectroscopy (by observing the disappearance of the Sn—H absorption) and by PMR spectroscopy (by observing product formation). For all the reactions a quantitative yield of adduct was obtained when a 20—50% excess of the organotin hydride was used.

The new organotin compounds obtained, as well as some of their physical characteristics, elemental analysis (C, H) and the reaction conditions are summarized in Tables 1 and 2.

The PMR spectra indicate 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. However, since it is not possible to say which diastereoisomer has been formed, it is not known whether a *trans* or a *cis* addition has occurred. A possible solution to this problem would be to hydrolyze and esterify the adducts obtained from the *Z*-α,β-disubstituted acrylonitriles, and compare the resulting compounds with those obtained directly by the hydrostannation of the corresponding methyl *E*-α,β-disubstituted propenoates. Unfortunately it was found that this approach was unsatisfactory, since both acid or alkaline hydrolysis of the organotin adducts of the nitriles resulted in demetallation. Such demetallations have been reported previously in other organotin systems by Eaborn [7]. An alternative method, which would not only confirm the stereoselectivity, but might also decide whether the reactions are stereospecific, would be to examine the additions of organotin hydrides to the geometric isomers of the esters and nitriles used previously.

TABLE 2

ADDUCTS OBTAINED FROM THE REACTIONS OF ORGANOTIN MONOHYDRIDES AND Z-α,β-DISUBSTITUTED ACRYLONITRILES [a]



$$R_3Sn{-}\overset{R^2}{\underset{H_b}{C}}{-}\overset{R^1}{\underset{H_a}{C}}{-}CN$$

Compound	R	R^1	R^2	Time [b]	M.p. (°C) or n_D^{v}	PMR [d] (H$_a$ and H$_b$)	Elemental analyses (%)			
							Calculated		Found	
							C	H	C	H
IX	n-Bu	Ph	Me	180	1.5175 [e]	H$_a$: 3.25 (d, J 3.5)	60.85	8.59	60.83	8.78
X	n-Bu	Ph	Ph	150	1.5519	H$_a$: 3.52 (d, J 4.5) H$_b$: 2.37 (d, J 4.5)	65.34	7.92	65.08	8.20
XI	Ph	Ph	Me	120	110–111 [f]	H$_a$: 4.06 (d, J 6) [g] H$_b$: 2.52(m)	68.04	5.09	67.78	5.22
XII	Ph	Ph	Ph	120	151–153	H$_a$: 3.58 (d, J 5) H$_b$: 2.98 (d, J 5)	71.25	4.89	71.35	5.11

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[a] Quantitative yield of adducts obtained in all reactions using a 50% excess of hydride, at 80°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] Chemical shifts in ppm relative to TMS as internal standard, and J values in Hz; CCl_3D used as solvent, except when indicated otherwise. [e] Determined at 21.5°C. [f] All solids were recrystallized from ethanol. [g] In CCl_4.

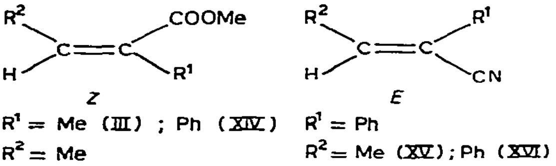
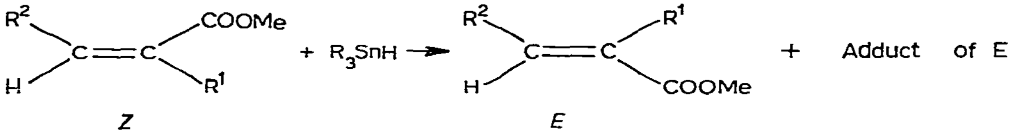


Fig. 1. Methyl *Z*-α,β-disubstituted propenoates and *E*-α,β-disubstituted acrylonitriles used.

With this aim, the additions of tri-n-butyltin and triphenyltin hydrides to methyl *Z*-α,β-disubstituted propenoates and *E*-α,β-disubstituted acrylonitriles were examined (Fig. 1).

In all these reactions it was found that single adducts were again obtained in high yields if an excess of organotin hydride was used. However, these adducts were found to be identical to the adducts obtained starting from the more stable olefins, e.g., both methyl *Z*- and *E*-α,β-disubstituted propenoates gave the same addition product. The same applied to the *Z*- and *E*-nitriles. When the reactions were repeated using an insufficiency of hydride (1 : 1 or 1 : 0.5 ratio), the addition product was again formed, together with quantities of the isomeric olefin of the starting material (eq. 7), the relative amounts varying according to the type of organotin hydride used (Table 3).



(7)

In separate experiments it was shown that the methyl *Z*-α,β-disubstituted propenoates and the *E*-α,β-disubstituted acrylonitriles do not undergo isomerization under the reaction conditions (i.e., at 80°C, under a nitrogen atmosphere in the presence of ABIN) in the absence of the organotin hydride, even after 4 h, demonstrating that the olefin isomerization results from reaction of the olefin with the tin hydride.

The present results, therefore, do not enable the steric course of the reaction to be clearly established, but it is possible to say that the reaction is stereoselective. Previously reported data on the stereochemistry of hydrostannation

TABLE 3

ADDITIONS OF ORGANOTIN MONOHYDRIDES TO METHYL *Z*-α,β-DISUBSTITUTED PROPENOATES AND *E*-α,β-DISUBSTITUTED ACRYLONITRILES, OLEFIN : HYDRIDE RATIO 1 : 0.5.

Compound	n-Bu_3SnH		Ph_3SnH	
	Adduct [a]	Isomer [a]	Adduct [a]	Isomer [a]
XIII	5	95	44	56
XIV	5	95	40	60
XV	2	98	32	68
XVI	4	96	30	70

[a] Yields calculated on the basis of the amount of olefin used (PMR).

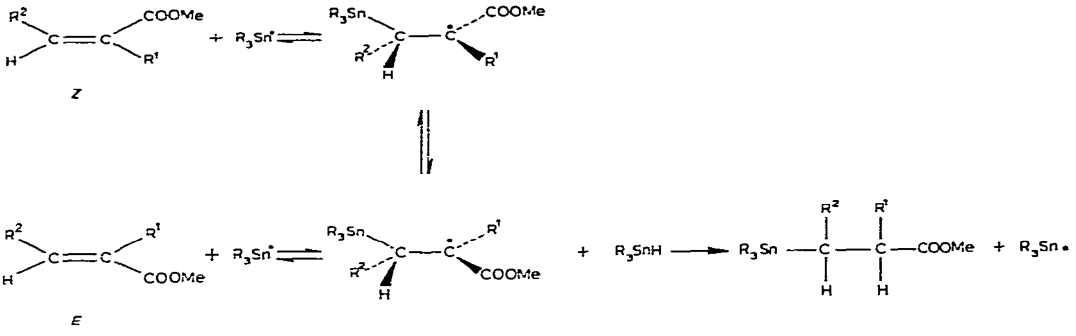


Fig. 2. Intermediates in the free-radical attack on *Z*- and *E*-propenoates.

is not necessarily applicable to the systems used here, because the results relate either to cyclic olefins [8,9] (which give *trans*-addition), or acyclic olefins with different steric requirements, such as *cis*- and *trans*-β-deuteriostyrenes [10] (which undergo non-stereoselective addition) where the differences in energy between the possible conformations of the intermediate radicals are likely to be smaller than for the tri-substituted olefins. The observed stereoselectivity in the present work could be connected with the preferred conformations of the intermediate radicals [11,12] (Fig. 2).

The observed isomerizations of the thermodynamically less stable trisubstituted olefins (XIII—XVI) confirm the reversibility of the radical addition step (eq. 3 and Fig. 2).

The results also demonstrate that whether the radical intermediate gives adduct or starting material (or isomeric olefin) depends on the hydride-donating ability of the organotin hydride used. Since more addition is observed in the presence of triphenyltin hydride (Table 3), this suggests that the triphenyltin is a better hydride donor, a result in agreement with the work of Ingold [13].

Experimental

PMR spectra were obtained with Varian A60-D and XL-100 instruments. 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 the Departamento de Química Orgánica, Universidad Nacional de Buenos Aires. All the olefins used but tiglic acid (Fluka) were synthesized in our Laboratory following standard procedures [14—18]. The organotin hydrides were obtained by reduction of the corresponding chlorides with sodium borohydride [19]. All the organotin adducts were purified by column chromatography (silica gel, Kieselgel 60, 70—230 mesh, Merck).

Additions of organotin hydrides to the olefins

A similar procedure was used in the preparation of all the organotin compounds. Two experiments are described in detail to illustrate the methods used:

A. Reaction of methyl E-α,β-diphenyl propenoate with tri-n-butyltin hydride. Synthesis of methyl α-phenyl-β-tri-n-butylstannyl cinnamate (IV). Methyl *E*-α,β-diphenyl propenoate (5 g, 0.021 mol) was hydrostannated with 6.11 g (0.0315 mol, 50% excess) of tri-n-butyltin hydride, using ABIN as a catalyst, in a nitrogen atmosphere, at 80°C, during 4 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 IV was obtained. The crude product was directly purified by column chromatography using silica gel 60. The adduct IV was eluted with Petroleum ether 30—60 as an oily colorless liquid; n_D^{22} 1.5438; PMR (CCl_4, δ, ppm) 4.21 (H_a, d, J 12.5 Hz) and 3.23 (H_b, d, J 12.5 Hz). Analysis: Found: C, 63.78; H, 8.09. $C_{28}H_{42}O_2Sn$ calcd.: C, 63.57; H, 8.00%. The compound on distillation decomposed at 185°C/2 Torr.

B, Reaction of E-α,β-diphenyl acrylonitrile (XVI) with triphenyltin hydride. Isomerization and addition. A mixture of XVI and triphenyltin hydride (1 : 0.5 ratio) and ABIN, was left to react under the above conditions for 2 h. The PMR spectrum of the crude product showed clearly that it consisted of a mixture of about 70% of *Z*-α,β-diphenyl acrylonitrile (geometric isomer of XVI) and 30% of the adduct XII. The mixture was separated by column chromatography (silica gel 60), the addition compound being eluted with $CCl_4$and recrystallized from ethanol, m.p. 151—153°C. Mixed m.p. with the sample (XVI) obtained by hydrostannation of *Z*-α,β-diphenyl acrylonitrile showed no depression of m.p.

Acknowledgement

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References

1 A.J. Leusink and J.G. Noltes, Tetrahedron Lett., (1966) 335.
2 W.P. Neumann, The Organic Chemistry of Tin, Wiley, London, 1970.
3 H.G. Kuivila, Adv. Organometal. Chem., 1 (1964) 47.
4 W.P. Neumann, H.J. Albert and W. Kaiser, Tetrahedron Lett., (1967) 2041.
5 H.G. Kuivila and R. Sommer, J. Amer. Chem. Soc., 89 (1967) 5616.
6 R. Sommer and H.G. Kuivila, J. Org. Chem., 33 (1968) 802.
7 a) R.W. Bott, C. Eaborn and T.W. Swaddle, J. Chem. Soc., (1963) 2342; b) R. Alexander, C. Eaborn and T.G. Traylor, J. Organometal. Chem., 21 (1970) P 65.
8 S. Kikkawa, N. Masakatsu and K. Hosoya, Nippon Kagaku Kaishi, (1973) 1130; Chem. Abs., 79 (1973) 66494b.
9 H.G. Kuivila and P.P. Patnode, J. Organometal. Chem., 129 (1977) 145.
10 J.P. Quintard and M. Pereyre, Compt. Rend. Acad. Sci., Ser. C, 284 (1977) C397.
11 a) J.K. Kochi, Acc. Chem. Research, 9 (1974) 351; b) T. Kawamura, P. Meakin and J.K. Kochi, J. Amer. Chem. Soc., 94 (1972) 8065.

12 a) D. Griller and K.U. Ingold, Acc. Chem. Research, 9 (1976) 13; b) D. Griller and K.U. Ingold, J. Amer. Chem. Soc., 96 (1974) 6715.

13 D.J. Carlsson and K.U. Ingold, J. Amer. Chem. Soc., 90 (1968) 1055.

14 H. Zimmermann and J. English Jr., J. Amer. Chem. Soc., 76 (1954) 2291.

15 R.E. Buckles and K. Bremer, Org. Synth., 33 (1953) 70.

16 S. Wawzonek and E.M. Smolin, Org. Synth., Coll. Vol. III, (1955) 715.

17 P. Pfeiffer, I. Engelhardt and W. Alfuss, Ann., 467 (1928) 158.

18 R.E. Buckles and G.V. Mock, J. Org. Chem., 15 (1950) 680.

19 A.B. Chopa and J.C. Podestá, Anal. Asoc. Quim. Arg., 65 (1977) 181.