assignments to **3c**: ^{1}H NMR ($CDCl_3$) δ -12.42 (dd, J_{PH} = 25.6 and 12.1 Hz). FDMS, M^+ at m/e 908 based on ^{187}Re.

Photochemical Reactions of $Re_2(CO)_8(\mu$-L⁀L) (L⁀L = dmpm, dppe, dmpe) with Alkenes. $Re_2(CO)_8(\mu$-dmpm) (0.095 g, 0.130 mmol) and toluene (10 mL) were added into a 50-mL Schlenk flask. After being degassed and saturated with ethylene or propylene, the solution was irradiated at ambient temperature for 48 h. The liquid portion was removed under reduced pressure. The pure product **4** was separated as a yellow solid on silica gel coated preparative TLC plates using methylene chloride and hexane (3:1) and recrystallized from the same solvent system. The yields are 40% for **4a** and 30% for **4b**. The spectroscopic data for **4** are listed in Table II. Anal. Calcd for $C_{13}H_{18}O_6P_2Re_2$ (**4a**): C, 22.16; H, 2.57; P, 8.79. Found: C, 22.06; H, 2.56; P, 8.77. UV (CH_2Cl_2): λ_{max} 297 nm (ϵ 6800, sh).

The corresponding reactions of $Re_2(CO)_8(\mu$-dppe) and $Re_2(CO)_8(\mu$-dmpe) were also carried out for 9 and 24 h, respectively. The pale yellow solid products were separated on preparative TLC plates using methylene chloride and hexane (1:1) and recrystallized from the same solvent system. The yields of **5a**, **5b**, **6a**, and **6b** are 50, 38, 45, and 30%, respectively. The spectroscopic data for **5** and **6** are listed in Table III. Anal. Calcd for $C_{34}H_{28}O_6P_2Re_2$ (**5a**): C, 42.23; H, 2.92; P, 6.41. Found: C, 43.77; H, 3.03; P, 6.38. Anal. Calcd for $C_{14}H_{20}O_6P_2Re_2$ (**6a**): C, 23.40; H, 2.81; P, 8.62. Found: C, 23.62; H, 2.98; P, 8.96.

Acknowledgment. High-field NMR facilities were provided by the National Science Foundation (NSF Grant CHE 79-16100). High resolution mass spectrometer facilities were supported in part by a grant from the National Institute of General Medicine Sciences (GM 27029). The ZAB-HF mass spectrometer was purchased in part with grants from the Division of Research Resources, National Institutes of Health (RR 01575) and the National Science Foundation (PCM 8121494). We thank Professor Ken Suslick for use of the UV-visible spectrophotometer.

Registry No. **1a**, 96041-48-4; **1b**, 96148-97-9; **1c**, 96148-98-0; **1d**, 96148-99-1; **2a**, 96041-49-5; **2b**, 96094-63-2; **2c**, 96094-64-3; **2d**, 96094-65-4; **3a**, 96041-50-8; **3b**, 96041-51-9; **4a**, 96041-52-0; **4b**, 96041-53-1; **4c**, 96094-66-5; **5a**, 96041-54-2; **5b**, 96041-55-3; **6a**, 96041-56-4; **6b**, 96041-57-5; $(\mu$-H)$Re_2(CO)_8(\mu$-CH=$CH_2)$, 82621-42-9; $Re_2(CO)_9(PMe_3)$, 51371-62-1; H_2C=CH_2, 74-85-1; $Re_2(CO)_9(PPh_3)$, 51371-62-1; 1,2-*diax*-$Re_2(CO)_8(PPh_3)_2$, 27770-64-5; $Re_2(CO)_{10}$, 14285-68-8; $Re_2(CO)_8(\mu$-dmpm), 88271-76-5; H_3C-C-H=CH_2, 115-07-1; $Re_2(CO)_8(\mu$-dppc), 88271-77-6; $Re_2(CO)_8(\mu$-dmpe), 88271-78-7; 1,2-*dieq*-$Re_2(CO)_8(PMe_3)_2$, 88035-63-6.

Organotin Compounds. 6. Hydrostannation of Methyl (*E*)-Disubstituted Propenoates with Trimethyltin Hydride and Dimethyltin Chlorohydride

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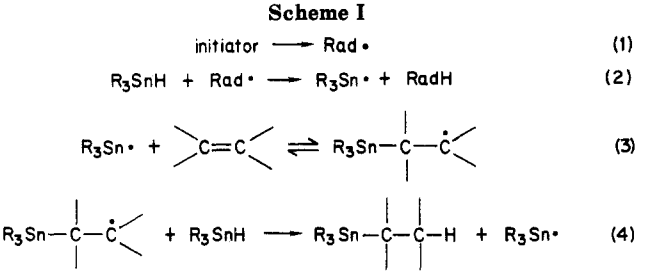
A series of (trimethylstannyl)- and (chlorodimethylstannyl)propyl derivatives having the carboxymethyl functional group has been prepared via free radical additions of trimethyltin hydride and dimethyltin chlorohydride to methyl (*E*)-2,3-disubstituted propenoates giving high yields of mixtures of diastereomeric products. The relationship between the diastereomers obtained in both reactions is demonstrated by quantitative conversion of the (trimethylstannyl)propyl derivatives into the corresponding (chlorodimethylstannyl)propyl derivatives by methyl/chlorine exchange with trimethyltin chloride. The chlorostannyl esters showed intramolecular coordination with the carbonyl group. Evidence concerning the reversibility of the free radical forming step, resulting in a rapid $Z \rightarrow E$ isomerization of the olefin, is presented. The high predominance of one diastereomer in the product might be governed by the preferred conformation of the intermediate radicals.

Hydrostannation is still the most useful reaction for the synthesis of organotin compounds containing organic functional groups. Commonly the reaction proceeds by a well-established free radical mechanism[2,3] according to Scheme I. Besides our interest in the synthesis of organotin esters in order to use them in biochemical studies, the organofunctional organostannes are also of interest because of structure-reactivity relationships like, for example, intramolecular donor-acceptor interactions.[4]

Scheme I



Following our studies[5,6] on the synthesis of new functionally substituted organotin compounds, we now report

(1) Part of the forthcoming Dr. in Chem. Thesis.
(2) Neumann, W. P. "The Organic Chemistry of Tin"; Wiley: London, 1970.
(3) Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47.
(4) Kuivila, H. G.; Karol, T. J.; Swami, K. *Organometallics* **1983**, *2*, 909.
(5) Podestá, J. C.; Chopa, A. B.; Ayala, A. D. *J. Organomet. Chem.* **1981**, *212*, 163.

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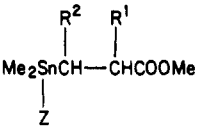
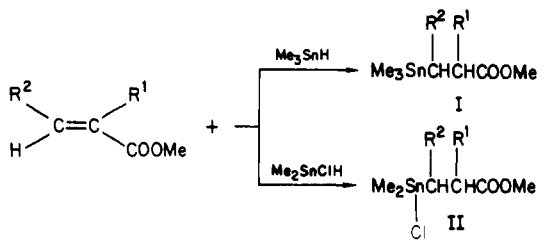
Table I. Adducts Obtained from the Reactions of Methyl (*E*)-Disubstituted Propenoates with Me_3SnH and Me_2SnClH



adducts	Z	R^1	R^2	time, min A[a]	time, min B[b]	hydride/olefin ratio A[a]	hydride/olefin ratio B[b]	yield,[c] %	mp (°C), bp (mm), or n_D	elemental anal. calcd C	calcd H	found C	found H
1	Me	Me	Me	360	240	3:1	1.5:1	(−)[d]	30-31 (0.2)	38.75	7.22	38.60[g]	6.90[g]
2								(+)[d]					
3	Me	Me	Ph	150	60	2:1	1.5:1	20	72-74 (0.2)	49.30	6.50	48.80	6.20
4								80	78-80 (0.3)	49.30	6.50	49.40	6.30
5	Me	Ph	Me	300	270	2:1	2:1	25	82-83 (0.2)	49.30	6.50	49.60	6.60
6								75	80-82 (0.2)	49.30	6.50	49.50	6.40
7	Me	Ph	Ph	270	270	2:1	3:1	20	74-75[e]	56.61	6.00	56.80	6.10
8								80	56-57[e]	56.61	6.00	56.60	5.95
9	Cl	Me	Me	2880	180	2:1	2:1	(−)[d]	1.5024[f,g]	32.09	5.72	31.68[g]	5.58[g]
10								(+)[d]					
11	Cl	Me	Ph	2880	75	2:1	1.5:1	25	88-90[e]	43.20	5.30	43.47	5.41
12								75	100-102[e]	43.20	5.30	43.39	5.50
13	Cl	Ph	Me	2880	50	2:1	1.5:1	15	90-92[e]	43.20	5.30	42.99	5.23
14								85	83-86[e]	43.20	5.30	42.95	5.45
15	Cl	Ph	Ph	2580	75	2:1	2:1	37	103-105[h]	51.04	4.99	51.25	5.16
16								63	94-96[e]	51.04	4.99	51.19	5.09

[a] Radicals thermally generated in the presence of AIBN; 70 °C for Me_3SnH additions and room temperature for Me_2SnClH additions. [b] Radicals generated by irradiation. [c] Relative proportions of diastereoisomers from ^1H NMR spectra. [d] Could not be calculated due to signals overlap in the ^1H NMR spectrum (see text). [e] Recrystallized from ethanol. [f] At 25 °C. [g] Isomer in higher proportion. [h] Extracted from the crude product with petroleum ether (40-60 °C).

Scheme II



R^1=Me, Ph; R^2=Me, Ph

results obtained in the synthesis of compounds of types Me_3SnR and Me_2RSnCl by hydrostannation of methyl (*E*)-2,3-disubstituted propenoates according to Scheme II. The addition of the hydrides to this type of olefins creates simultaneously two new chiral centers, leading to diastereomeric mixtures which could be separated by physical methods. It should be noted that in the chemical literature apart from previous reports[5,6] we have found only two publications[7,8] reporting additions of organotin hydrides to functional olefins leading to adducts with two chiral centers. Kuivila and Patnode[7] reported the addition of trimethyltin hydride to methyl cyclopentene-1-carboxylate, and Rahm et al.[8] reported the addition of organotin hydrides to (*E*)- and (*Z*)-(−)-menthyl crotonate. In the latter, in fact only one new chiral center is formed since the starting olefin already has a chiral center.

Results and Discussion

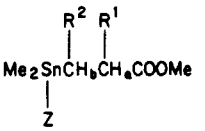
All the additions were carried out under free radical conditions. Two methods were used: (1) The mixture of olefin, excess organotin hydride, and azobis(isobutyronitrile) (AIBN), without solvent and in a nitrogen atmosphere, was stirred (at 70 °C in the case of Me_3SnH additions and at room temperature for Me_2SnClH additions) until all the olefin had reacted. (2) The mixture of olefin and excess organotin hydride, without solvent and in a nitrogen atmosphere, was irradiated (Mercury lamp) with stirring until all the olefin had reacted (temperature inside the photochemical reactor: 25 °C). The reactions were followed by IR spectroscopy (by observing the disappearance of the Sn–H absorption) and by ^1H NMR spectroscopy (by observing product formation). In all cases the optimum times of reaction and hydride/olefin ratios required for a quantative yield (with respect to olefin) were determined. The purification and separation of the diastereoisomers were carried out by column chromatography. The new organotin compounds obtained, as well as some of their physical characteristics, elemental analyses (C, H), reaction conditions, and relative proportions of diastereomers (from ^1H NMR spectra), are summarized in Table I.

Product analysis shows that in the Me_3SnH additions to three of the four olefins studied, mixtures of two diastereoisomers are always obtained, with a relatively high predominance of one of them. In the case of methyl tiglate ($R^1 = R^2 = Me$), the existence of a mixture of stereoisomers was detected by letting the crude product from the Me_3SnH addition react with Me_3SnCl (chlorine/methyl exchange reaction), though the actual ratio between them could not be calculated due to overlap of the ^1H NMR signals (see below).

In the Me_2SnClH additions to the four olefins, mixtures of the two isomers were also found, but in this case it was not possible to effect a chromatographic separation. We were able to elute only the major diastereomers. The others (**11**, **13**, and **15**) were obtained pure from the chlorine/methyl exchange reactions between the corresponding trimethylstannyl adducts (**3**, **5**, and **7**) and Me_3SnCl (see below). The ^1H NMR characteristics of the adducts are summarized in Table II.

(6) Podestá, J. C.; Chopa, A. B. *J. Organomet. Chem.* **1982**, *229*, 223.
(7) Kuivila, H. G.; Patnode, P. P. *J. Organomet. Chem.* **1977**, *129*, 145.
(8) Rahm, A.; Degueil-Castaing, M.; Pereyre, M. *Tetrahedron Lett.* **1980**, *21*, 4649.

Table II. ^{1}H NMR[a] Chemical Shifts and Coupling Constants of Organotin Adducts



adduct (%)	Z	H_a	H_b	MeSn ($^2J(^{119-117}Sn\text{-}C\text{-}H)$)	OMe	R^1	R^2
1 (−)[b] 2 (+)[b]	Me	2.63 (q, 6.8)	1.03-1.89 (m)	0.05 (52.6 and 50.4)	3.64	1.11 (doublets overlap)[c]	
3 (20)	Me	2.9-3.5 (m)	2.58 (d, 10.0)	−0.08 (53.2 and 50.4)	3.70	1.19 (d, 7.2)	6.86-7.5 (m)
4 (80)		2.87-3.33 (m)	2.73 (d, 10.8)	0.00 (53.0 and 50.0)	3.43	1.25 (d, 7.0)	6.80-7.43 (m)
5 (25)	Me	3.43 (d, 12.0)	1.63-2.36 (m)	−0.29 (53.0 and 50.2)	3.60	7.26 (s)	1.18 (d, 7.6)
6 (75)		3.52 (d, 11.0)	1.45-2.12 (m)	0.03 (52.4 and 50.4)	3.61	7.27 (s)	0.96 (d, 7.6)
7 (22)	Me	4.22 (d, 13.6)	3.33 (d, 13.6)	−0.37 (54.0 and 51.0)	3.36	6.90-7.73 (m)	
8 (78)		4.22 (d, 12.0)	3.19 (d, 12.0)	−0.02 (53.2 and 50.8)	3.63	6.71-7.38 (m)	
9 (−)[b]	Cl	2.39-2.84 (m)	1.64-2.19 (m)	0.50 (−)[b] 0.63 (−)[b]	3.81	0.83 (doublets overlap)[c]	
10 (+)[b]		2.80-3.28 (m)	1.64-2.19 (m)	0.54 (60.0 and 64.0) 0.57 (60.8 and 65.6)	3.81	1.32 (doublets overlap)[d]	
11 (25)		3.02-3.48 (m)	2.82 (d, 2.0)	0.12 (61.5 and 65.0) 0.72 (61.0 and 63.6)	3.93	1.49 (d, 7.8)	6.84-7.52 (m)
12 (75)	Cl	2.96-3.49 (m)	3.12 (s)	0.26 (62.6 and 65.6) 0.60 (56.8 and 60.0)	3.89	1.23 (d, 6.8)	6.83-7.48 (m)
13 (15)		4.09 (d, 8.0)	1.84-2.39 (q)	0.49 (−)[b]	3.74	7.06-7.10 (m)	1.21 (d, 7.8)
14 (85)	Cl	3.86 (d, 5.6)	1.85-2.24 (m)	0.53 (56.0 and 60.0) (62.0 and 65.0)	3.83	7.07-7.54 (m)	1.41 (d, 8.0)
15 (37)		4.35 (d, 10.8)	3.39 (d, 10.8)	0.08 0.20 (−)[b]	3.56	6.88-7.62 (m)	
16 (63)	Cl	4.46 (d, 2.0)	3.24 (d, 2.0)	0.16 (59.0 and 63.2) 0.61 (62.0 and 64.0)	3.96	6.86-7.56 (m)	

[a] Chemical shifts in ppm from Me_4Si; multiplicity and J values in parentheses; coupling constants in Hz. [b] Could not be calculated due to signal overlap. [c] Two signals, J = 7.0 Hz. [d] Two signals, J = 7.6 Hz.

As for the two methods employed in the generation of the radicals **1** and **2**, we have found that although the product composition is the same, the irradiation method is usually faster and requires lower hydride/olefin ratios than the thermal method and that it is especially suitable for Me_2SnClH additions where the temperature must be kept at 25 °C in order to avoid chlorohydride decomposition.

In order to establish whether the additions of Me_3SnH and Me_2SnClH followed the same steric course, reactions between the adducts of the former and Me_3SnCl (which should lead to the same compounds obtained in the Me_2SnClH additions) were performed according to eq 5.

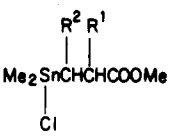
$$\text{I} + Me_3SnCl \rightarrow \text{II} + Me_4Sn \qquad (5)$$

These reactions proceeded smoothly to give quantitative yields of exchange products. The reactions were carried out leaving the mixture of organotin adducts and Me_3SnCl to react at room temperature without solvent, during the time needed in order to obtain a quantitative conversion. Under irradiation the reaction times were lower. Details of reaction conditions are given in Table III.

Our results are consistent with those of Kuivila,[9] in that in this type of reaction where the trimethylstannyl moiety is just two methylene groups apart from the carboxymethyl group, the equilibrium of the reaction is completely displaced to the right due to the gain in stabilization of the products by intramolecular coordination.

These exchange reactions enabled us to establish that starting from the pure adducts of type I, the single products were compounds of type II. Therefore, starting from the adducts obtained in higher yields in the Me_3SnH additions, the only products were the compounds of type II corresponding to the adducts obtained in higher yields in the Me_2SnClH additions. The same applied to the adducts of type I obtained in lower yields in the Me_3SnH additions: they led to the compounds of type II corresponding to the adducts obtained in lower yields in the Me_2SnClH additions.

Table III. Methyl/Chlorine Exchange Reactions: Experimental Conditions[a]



compd no. (adduct no.)	R^1	R^2	time, h A[b]	time, h B[c]
9 (1)	Me	Me	*d*	*d*
10 (2)			15	9
11 (3)	Me	Ph	22	13
12 (4)			20	12
13 (5)	Ph	Me	42	14
14 (6)			42	14
15 (7)	Ph	Ph	40	12
16 (8)			40	12

[a] Me_3SnCl/adduct ratio always 1.2:1. [b] Reactions carried out at room temperature. [c] Reactions carried out by irradiation. [d] Could not be performed because the starting adduct could not be obtained pure.

These results suggest that the additions of Me_3SnH and Me_2SnClH to the olefinic systems under study take the same steric course.

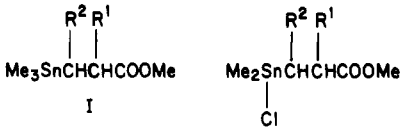
It is to be noted that the exchange reactions enabled us to establish the existence of a second isomer (in less amount) in the Me_3SnH addition to methyl tiglate (adduct 1), which due to spectroscopic similarity with the isomer obtained in higher yield could not be previously detected.

In Table IV a comparison between some spectroscopic data of adducts of types I and II is shown.

Without exception the carbonyl stretching frequencies of the chlorodimethylstannyl esters (type II adducts) lie

(9) Kuivila, H. G.; Dixon, J. E.; Maxfield, P. L.; Scarpa, N. M.; Topka, T. M.; Tsai, K.-H.; Wursthorn, K. R. *J. Organomet. Chem.* **1975**, *86*, 89.

Table IV. Spectroscopic Data Comparison of Organotin Adducts



R¹	R²	¹H NMR (OMe) I	¹H NMR (OMe) II	isomer no. (yields)	IR $\nu_{C=O}$, cm⁻¹ I	IR $\nu_{C=O}$, cm⁻¹ II
		b	3.81[c]	1 and 9 (lower yield)	*b*	*b*
Me	Me	3.64	3.81	2 and 10 (higher yield)	1730	1686
		3.70	3.93	3 and 11 (lower yield)	1725	1681
Me	Ph	3.43	3.89	4 and 12 (higher yield)	1730	1680
		3.60	3.74	5 and 13 (lower yield)	1727	1689
Ph	Me	3.61	3.83	6 and 14 (higher yield)	1726	1692
		3.36	3.56	7 and 15 (lower yield)	1730	1687
Ph	Ph	3.63	3.96	8 and 16 (higher yield)	1725	1680

[a] Chemical shifts in ppm downfield from internal Me_4Si; CCl_4. [b] Could not be obtained pure. [c] From the ¹H NMR spectrum of the mixture.

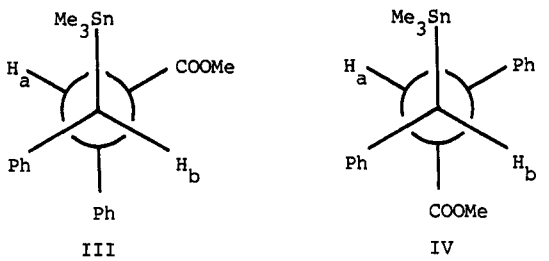


Figure 1.

between 1680 and 1692 cm^{-1} (Table IV), i.e., between 34 and 50 cm^{-1} to lower frequency than the trimethylstannyl esters (type I adducts) and between 44 and 50 cm^{-1} to lower frequency than the parent saturated esters. The ¹H NMR ester signals (Table IV) corresponding to type II adducts are downfield of the corresponding signal both in the trimethylstannyl esters and in the saturated analogues of the methyl disubstituted propanoates (for example, compound **13**, OMe 3.74 ppm, and compound **14**, OMe 3.83 ppm, compared with $CH_3CH_2CHPhCOOMe$, OMe 3.44 ppm). These values clearly indicate that in the case of the chlorodimethylstannyl esters (II), there exists coordination between the carbonyl group of the ester and the Sn atom because this phenomenon reduces the carbonyl stretching frequency[6,9,10] and also has a deshielding effect on the methoxy group protons. That this carbonyl coordination to Sn is intramolecular is demonstrated by the fact that the carbonyl stretching frequency of the compounds is the same both when it is measured in the solid state and in solution. Furthermore, the signal corresponding to the protons of the OMe group in the ¹H NMR spectrum does not change its position upon threefold dilution.

In order to decide whether the reactions are stereospecific with respect to the geometry of the olefin, additions of Me_3SnH to the geometric isomers of the esters used

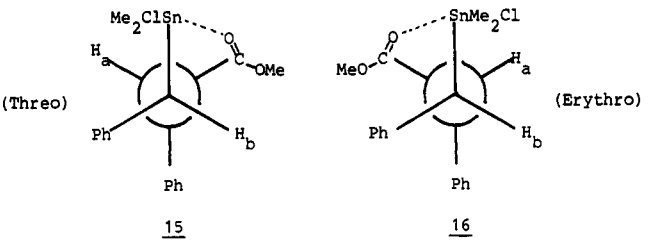
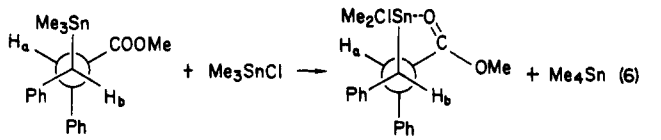


Figure 2.

previously, i.e., *Z* in place of *E*, were attempted. However, as in previous studies,[5,6] the mixtures of adducts obtained were identical with those obtained starting from the more stable olefins, e.g., both methyl (*Z*)- and (*E*)-2,3-disubstituted propenoates gave the same relationship of addition products. Using an insufficient amount of hydride (1:0.75 ratio) the addition products were formed together with quantities of the isomeric olefin of the starting material (eq 6). It follows clearly that the *E* or *Z* identity of the



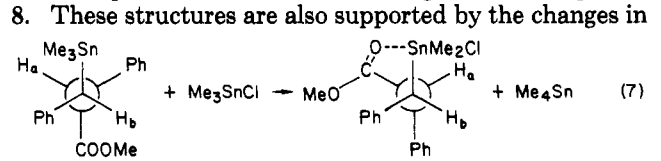
7, $J(H_a-H_b)$ = 13.6 Hz **15**, $J(H_a-H_b)$ = 10.8 Hz

olefin cannot be the reason for the high predominance of one of the two possible diastereomers in the product. As the methyl (*Z*)-2,3-disubstituted propenoates do not undergo isomerization under the reaction conditions[5] in the absence of organotin hydride, it is concluded that the olefin isomerization results from the reversibility of the radical addition step (eq 3 in Scheme I). These results confirm the reversibility reported by Neumann[11] and Kuivila[12,13] for other olefinic systems.

Taking into account the large coupling constants $J(H_a-H_b)$ of 13.6 and 12.0 Hz observed for compounds **7** and **8**, respectively (Table II), it is possible to assume that the preferred conformations for them should be III and IV, Figure 1 (only one of the two possible enantiomers is shown).

These values by themselves do not allow an assignment of the unique configuration of the adducts. However, the ¹H NMR spectra corresponding to the chlorodimethyltin adducts **15** and **16** (Table II) show that the vicinal coupling constants $J(H_a-H_b)$ are 10.8 and 2.0 Hz, respectively. These coupling constant values, together with the demonstrated intramolecular coordination, strongly suggest that the possible configurations and the preferred conformations corresponding to **15** and **16** are those shown in Figure 2 (again, just one of the two possible enantiomers is shown).

Taking into account that compounds **15** and **16** were obtained by the exchange reactions of compounds **7** and **8** with Me_3SnCl, respectively (eq 6 and 7), and the previous discussion, it is possible to attribute structure III (Figure 1) to compound **7** and structure IV (Figure 1) to compound **8**. These structures are also supported by the changes in



8, $J(H_a-H_b)$ = 12.0 Hz **16**, $J(H_a-H_b)$ = 2.0 Hz

(10) Hutton, R. E.; Burley, J. W. *J. Organomet. Chem.* **1976**, *105*, 61.
(11) Neumann, W. P.; Albert, H. J.; Kaiser, W. *Tetrahedron Lett.* **1967**, 2041.
(12) Kuivila, H. G.; Sommer, R. *J. Am. Chem. Soc.* **1967**, *80*, 5616.
(13) Sommer, R.; Kuivila, H. G. *J. Org. Chem.* **1968**, *33*, 802.

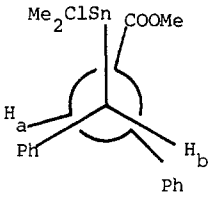
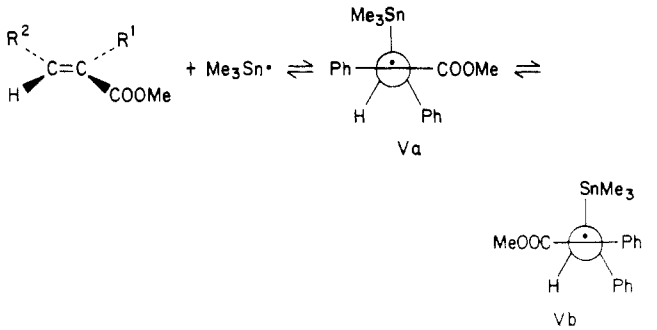


Figure 3.

Scheme III



the vicinal coupling constants observed upon conversion of **7** and **8** into **15** and **16**, respectively (eq 6 and 7). It is clear that only the erythro isomer **8** could give such a great variation when it is converted into **16** (from 12.0 Hz in **8** to 2.0 Hz in **16**). The ^{1}H NMR peaks corresponding to the methyl groups attached to Sn in compounds **15** and **16** are split in both diastereomers. This could be due to chemical surroundings differences originated in intramolecular coordination (the methyl groups become nonequivalent). The values of the vicinal coupling constant $J(H_a-H_b)$ in both **15** and **16** suggest that the structures are however distorted from the ideal ones shown, that of **15** perhaps approaching the one shown in Figure 3.

From these facts the conclusion has to be derived that either by Me_3SnH or by Me_2SnClH addition to both methyl 2,3-diphenylpropenoates, erythro isomers (**8** and **16**) are obtained in much higher yields that the corresponding threo isomers (**7** and **15**). This suggests, in the case of this olefin, the operation of an addition pathway which is sterically governed by an intermediate.

The mechanism leading to the observed mixtures of diastereoisomers can be postulated, therefore, taking into account both the equilibrium between the intermediates radicals Va $\rightleftharpoons$ Vb (Scheme III) and the preferred (because of least steric hindrance) conformations of these radicals. Only conformers Va and Vb have to be considered because Kochi[14] demonstrated that alkyl radicals with β-Sn-substituents exist in a preferred orientation in which the metal substituent (R_3Sn) occupies an eclipsed position relative to the half-filled carbon orbital. Now the bulky tin hydride certainly approaches to Va and Vb ($R^1 = R^2 =$ Ph) from the less hindered side in order to transfer the hydrogen, giving **7** and **8**. Finally, the position of the equilibrium Va $\rightleftharpoons$ Vb will decide the relative amounts of each diastereoisomer.

Further work in order to obtain more information on the stereochemistry of hydrostannations is in progress.

Experimental Section

General Data. Proton nuclear resonance spectra were obtained with a Varian EM 360L instrument. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane. Infrared spectra were recorded with a Perkin-Elmer 137B spectrophotometer. The refraction indices were measured with a Universal Abbe, Zeiss Jena VEB instrument, and the melting points were determined on a Köfler hot stage and are uncorrected. Microanalyses were performed at Dortmund University (FRG). Sample irradiations were carried out in an irradiator constructed in this laboratory which consisted of four water-cooled mercury lamps (two of 250 W and two of 400 W): temperature at the sample site 25 °C.

All the olefins but tiglic acid (Fluka) were synthesized following standard procedures.[15-19] Trimethyltin hydride[9] and dimethyltin dihydride[20] were obtained by reduction of the corresponding chlorides with $LiAlH_4$ in diglyme. The dimethyltin chlorohydride was obtained by the exchange reaction[21] between dimethyltin dihydride and dimethyltin dichloride and was used "in situ". The purification as well as the separation of the diastereoisomeric adducts was carried out by column chromatography (Silica Gel, Kieselgel 60, 70–230 mesh, Merck). For preparative scale separations an RSCo Fraction Collector was used.

Additions of Organotin Hydrides to the Olefins. The same procedure was used in the preparation of all the organotin compounds. One experiment describing the Me_3SnH addition and another the Me_2SnClH addition are developed in detail in order to illustrate the methods used.

A. Reaction of Methyl (*E*)-2-Methyl-3-phenylpropenoate with Me_3SnH. Synthesis of Methyl 2-Methyl-3-phenyl-3-(trimethylstannyl)propanoates (3 and 4). Method I. Methyl (*E*)-2-methyl-3-phenylpropenoate (3.7 g, 0.021 mol) was hydrostannated with Me_3SnH (6.92 g, 0.042 mol), using AIBN as a catalyst in a nitrogen atmosphere at 70 °C, with stirring for 150 min. Optimal times of reaction and the appropriate excess of Me_3SnH were determined in previous runs by checking by ^{1}H NMR spectroscopy that all the olefin had reacted. Under these reaction conditions, the ^{1}H NMR spectrum showed that a quantitative yield (based on starting olefin) of a mixture of diastereoisomeric adducts **3** (20%) and **4** (80%) was obtained. The crude product was purified and separated by column chromatography (Silica Gel): we obtained 1.04 g (0.003 mol) of pure adduct **3**, in the fractions eluted with petroleum ether (40–60)/CCl_4 (1:1), as a liquid of n_D 1.5323 (19.5 °C); bp 72–74 °C (0.2 mm). Adduct **4** (4.93 g, 0.0145 mol) was eluted with petroleum ether (40–60)/CCl_4 (1:2), as a liquid of n_D 1.5324 (19.5 °C); bp 78–80 °C/(0.3 mm). Elemental analyses (C, H) as well as ^{1}H NMR and IR data are included in Tables I, II, and IV respectively.

Method II. To Me_3SnH (5.19 g, 0.035 mol), under a nitrogen atmosphere, was added methyl (*E*)-2-methyl-3-phenylpropenoate (3.7 g, 0.021 mol). The reaction vessel was then placed in the photochemical reactor and stirred during 60 min (the temperature inside the reactor was 25 °C). Under these reaction conditions a quantitative yield of the same diastereoisomeric mixture (**3** and **4**) and in the same proportion as in method I was obtained.

B. Reaction of Methyl (*E*)-2-Methyl-3-phenylpropenoate with Me_2SnClH. Synthesis of Methyl 2-Methyl-3-phenyl-3-(dimethylchlorostannyl)propanoates (11 and 12). Method I. A mixture of methyl (*E*)-2-methyl-3-phenylpropenoate (3.17 g, 0.021 mol) and Me_2SnClH (7.58 g, 0.042 mol) and AIBN was left to react in a nitrogen atmosphere with stirring for 2 days. The ^{1}H NMR spectrum showed that the crude product consisted of a mixture of adducts **11** (25%) and **12** (75%). The mixture was separated by column chromatography (Silica gel); compound **11** could not be eluted alone. Isomer **12** (5.13 g, 0.014 mol) was collected in the fractions eluted with petroleum ether (40–60)/CCl_4 (1:2) as a solid, mp 100–102 °C (ethanol).

Method II. The same products and in the same proportions were obtained when a mixture of methyl (*E*)-2-methyl-3-phenylpropenoate and Me_2SnClH in a 1:1.5 ratio under a nitrogen

(14) a) Kawamura, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 648. (b) Krusic, P. J.; Kochi, J. K. Ibid. **1969**, *91*, 6161. (c) *Ibid.* **1971**, *93*, 846.

(15) Zimmermann, H.; English, J., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 2291.

(16) Buckles, R. E.; Bremer, K. *Org. Synth.* **1953**, *33*, 70.

(17) Wazonek, S.; Smolin, E. M. "Organic Syntheses"; Wiley: New York, 1955; Coll. Vol. III.

(18) Pfeiffer, P.; Engelhardt, I.; Alfuss, W. *Justus Liebigs Ann. Chem.* **1928**, *467*, 158.

(19) Buckles, R. E.; Mock, G. V. *J. Org. Chem.* **1950**, *15*, 680.

(20) Finholt, A. E.; Bond, A. C.; Wilbach, K. E.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69*, 2692.

(21) Neumann, W. P.; Pedain, J. *Tetrahedron Lett.* **1967**, 2461.

atmosphere was irradiated for 75 min in the photochemical reactor (temperature 25 °C).

Exchange Reactions between the Organotin Adducts and Me_3SnCl. C. Reaction of Methyl 2-Methyl-3-phenyl-3-(trimethylstannyl)propanoate (Isomer 3) with Me_3SnCl. Synthesis of Methyl 2-Methyl-3-phenyl-3-(dimethylchlorostannyl)propanoate (Isomer 11). Adduct **3** (5.42 g, 0.015 mol) was added to Me_3SnCl (3.58 g, 0.018 mol) with stirring under nitrogen. The reaction mixture was (a) left at room temperature for 20 h and (b) left for 12 h in the photochemical reactor. The ^1H NMR spectrum showed that under both reaction conditions a quantitative yield of compound **11** was obtained; solid; mp 88–90 °C (ethanol).

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Registry No. 1, 95798-64-4; 2, 95785-30-1; 3, 95798-65-5; 4, 95798-66-6; 5, 95798-67-7; 6, 95798-68-8; 7, 95798-69-9; 8, 95798-70-2; 9, 95841-18-2; 10, 95841-19-3; 11, 95798-71-3; 12, 95798-72-4; 13, 95798-73-5; 14, 95798-74-6; 15, 95798-75-7; 16, 95798-76-8; AIBN, 78-67-1; Me_3SnH, 1631-73-8; Me_2SnClH, 16561-41-4; Me_3SnCl, 1066-45-1; methyl (*E*)-2-methyl-2-butenoate, 6622-76-0; methyl (*E*)-2-methyl-3-phenyl-2-propenoate, 22946-43-6; methyl (*E*)-2-phenyl-2-butenoate, 50415-85-5; methyl (*E*)-2,3-diphenyl-2-butenoate, 36854-27-0.

A MNDO Study of Tin Radical Cations[1]

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Radical cations derived from stannane and its alkyltrimethyl derivatives (Me_3SnR; R = Me, Et, *i*-Pr, *t*-Bu) have been studied, using MNDO. The calculated structures agree with experiment. Fragmentations of the radical cations have also been studied.

Introduction

ESR studies[3-5] of stannane radical cation **1** and its tetraalkyl derivatives have been reported in recent years. The results[3] for the tetramethyl derivative **2a** seemed to indicate a rather unusual C_{3v} structure (**3b**) with the tin and one methyl on the threefold axis of symmetry and the other three methyl groups coplanar with the tin. In the case of **1** both the C_{3v} structure **3a** and the C_{2v} structure **4a** have been observed.[3] No theoretical calculations seem as yet to have been reported for species of this kind other than some early ones for **1** by Hartmann et al.,[6] which, however, were based on an assumed geometry.

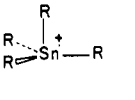
$SnH_4^{+\cdot}$ $Me_3SnR^{+\cdot}$

1 **2a**, R=Me; **2b**, R=Et; **2c**, R=*i*-Pr; **2d**, R=*t*-Bu

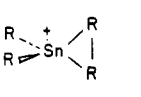
According to the Jahn–Teller theorem, **1** should undergo distortion from tetrahedral symmetry, like the analogous carbon species.[7] Here the distortion can be regarded in another light, as a way to maximize the bonding in an electron-deficient system where there are not enough electrons to form the requisite number of electron-pair bonds. In a molecule MX_4, M being a group 14[19] element, eight electrons are needed to form the four MX bonds. In the corresponding radical cation $MX_4^{+\cdot}$, only three such bonds can be formed. In cases of this kind, the optimum structure can usually be deduced by first forming the best possible set of two-electron bonds and then considering how the odd electron can best be used to bond the extra group. In the case of $MX_4^{+\cdot}$, six of the seven electrons will be used to form normal σ bonds to three of the ligands (X). Since a σ bond is stronger, the greater the s character of the AO's used to form it, the best arrangement is to use sp^2 hybrid AOs of M, the odd electron being left in a p AO. The fourth ligand (X^+) now has to be attached in the best way possible to the radical $\cdot MX_3$.

There are two possible solutions.

In the first type of structure **5**, the singly occupied AO of M is used to form a one-electron bond to the fourth ligand, leading to a triangular pyramid of the kind **3b**



3a R=H; **b** R=CH_3



4a R=H; **b** R=CH_3

postulated by Walther et al.[5] for **2a**. M should in fact lie above the base of the pyramid because this distortion will reduce the repulsions between the ligands and also strengthen the bond to the apical group by introducing s character into the p AO of M used to bind it. While an increase in s character of the apical AO of M will lead to a corresponding decrease in the s character of the three basal AOs, this should not significantly weaken the bonds formed by the latter.

The second alternative is to fuse the fourth ligand (X^+) into one of the existing CX bonds, interaction of the empty

(1) Part 71 of a series of papers reporting applications of quantum mechanical models to chemical problems. For part 70, see: Dewar, M. J. S. *J. Phys. Chem.*, in press.

(2) On sabbatical leave from St. Michael's College, Winooski, VT 05454.

(3) Hasegawa, A.; Kaminaka, S.; Wakabayashi, T.; Hayashi, M.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1199.

(4) Symons, M. C. R. *J. Chem. Soc. Chem. Commun.* **1982**, 869.

(5) Walther, B. W.; Williams, F.; Lau, W.; Kochi, J. K. *Organometallics* **1983**, *2*, 688.

(6) Hartmann, H.; Papula, L.; Strehl, W. *Theor. Chim. Acta.* **1971**, *21*, 69.

(7) (a) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1977**, *99*, 7432. (b) Pople, J. A. *Int. J. Mass. Spectrom. Ion. Phys.* **1976**, *19*, 89. (c) Meyer, W. *J. Chem. Phys.* **1973**, *58*, 1017.

0276-7333/85/2304-1041$01.50/0