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Substitution of the acetoxy groups of dialkoxymethylacetates by organometallic reagents: a route to allyl-, propargyl-, homoallyl-, homopropargyl- and α-stannylacetals

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Abstract

The substitution of the acetoxy groups of dialkoxymethylacetates by organometallic reagents has been examined in a search for new methods of preparing functional acetals. The efficiency of the substitution of the acetoxy group is highly dependent on the nature of the organometallic reagents: soft nucleophiles with strong electrophilic assistance by the counterion are the best reagents. Allyl-, propargyl-, homoallyl-, homopropargyl- and α-stannylacetals have been made by this route, in which dialkoxymethylacetates often function as useful substitutes for dialkylphenylorthoformates.

Introduction

Species bearing an acetal function are valuable as building blocks for organic chemists because of their ability to transfer an organic unit containing a masked aldehyde function. In this context, for instance, the synthesis of β,γ-unsaturated acetals is of interest because of the propensity of the corresponding aldehydes to isomerize into the more stable α,β-enals. The most used route to such unsaturated acetals involves reaction of phenyldialkylorthoformates with appropriate organometallics [1–5].

Although it is efficient, this method requires the use of the mixed orthoformates which are not as easily obtained cleanly from phenol and trialkylorthoformates as

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might be expected (especially in the case of dimethylphenylorthoformate). Thus we decided to examine dialkoxymethylacetates as possible substitutes for the mixed orthoformates *. These reagents are readily accessible from trialkylorthoformates by warming with formic acid and acetic anhydride as described by Scheeren *et al.* [6]:

$$HC(OR)_3 + HCOOH + Ac_2O \longrightarrow AcOCH(OR)_2 + AcOH + HCOOR$$

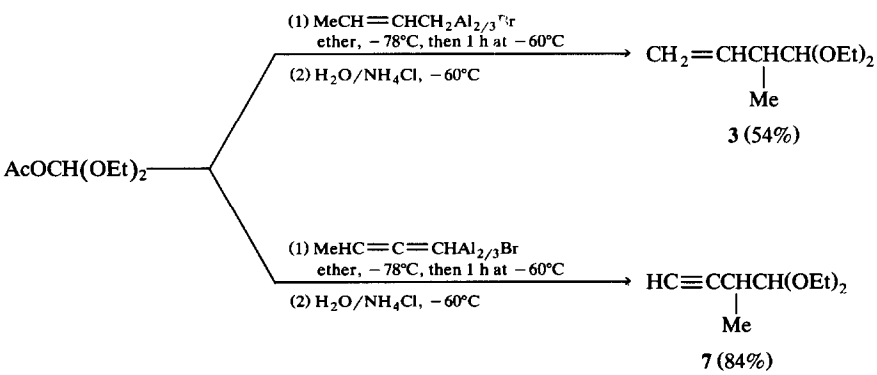
Surprisingly, although dialkoxymethylacetates have often been used in reactions with amines [7,8], to our knowledge they have been largely ignored as possible precursors of acetals via nucleophilic displacement of the acetoxy group by organometallics. We thus decided to examine the reactions of organometallic reagents with dialkoxymethylacetates, focusing mainly on unsaturated organometallic reagents and on tin anionoids.

Results and discussion

Reactivity of simple organometallic reagents

The results involving organometallic compounds and diethoxymethylacetate are presented in Table 1. We were unable to obtain substitution products from n-butyllithium or t-butylmagnesium chloride, but ethylmagnesium bromide and, more efficiently, diethylaluminium chloride gave 1,1-diethoxypropane (Table 1, entries 1, 2). In the allylic series, the allylaluminium bromides appeared to be generally more efficient than allylzinc bromides or allylmagnesium bromides in bringing about substitution of the acetoxy group (entries 3–10). The same was true when allenylmetal reagents were used (entries 11–14).

Of interest is the complete and clean rearrangement observed for the allyl or the allenyl unit using the corresponding organoaluminium bromides **, for instance:

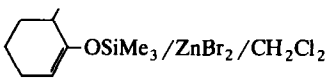
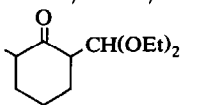


* Diethoxymethylacetate and diethylphenylorthoformate are both commercially available compounds, but for a similar price the first appears to be of higher purity (> 99% compared with 95–97%).

** In the case of allenylmagnesium bromide and allenylzinc bromide the contamination of **6a** with 1,1-diethoxybut-2-yne might be due to isomerization during the hydrolysis steps. The rearrangement of the allyl or of the allenyl unit might occur through an eight centres transition state, as proposed for reactions of allylzinc derivatives with other substrates [9].

Table 1

Reactions of diethoxymethylacetate with organometallic reagents

Entry	Organometallic reagent	Experimental conditions [a]	Acetals obtained		
			Product	No.	Yields [b] (%)
1	EtMgBr/ether	0°C, 12 h, 20°C, A	$Et-CH(OEt)_2$	**1**	(38)
2	Et_2AlCl/ether	20°C, 4 h, 20°C, A	$Et-CH(OEt)_2$	**1**	53
3	AllylMgBr/ether	−30°C, 12 h, 20°C, B	$CH_2=CH-CH_2-CH(OEt)_2$	**2**	(32)
4	AllylZnBr/THF	0°C, 12 h, 20°C, B	$CH_2=CH-CH_2-CH(OEt)_2$	**2**	(75)
5	$AllylAl_{2/3}Br$/ether	−78°C, 1 h, −60°C, B	$CH_2=CH-CH_2-CH(OEt)_2$	**2**	73
6	CrotylMgBr/ether	−30°C, 1.5 h, 0°C, B	$CH_2=CH-CHMe-CH(OEt)_2$	**3**	(20)
7	CrotylZnBr/THF	0°C, 12 h, 20°C, B	$CH_2=CH-CHMe-CH(OEt)_2$	**3**	33
8	$CrotylAl_{2/3}Br$/ether	−78°C, 1 h, −60°C, B	$CH_2=CH-CHMe-CH(OEt)_2$	**3**	54
9	$CH_2=C(COOEt)CH_2ZnBr$/THF	0°C, 12 h, 20°C, A	$CH_2=C(COOEt)-CH_2-CH(OEt)_2$	**4**	60
10	$PhCH=C(COOEt)CH_2ZnBr$/THF	17°C, 12 h, 20°C, A	$CH_2=C(COOEt)-CHPh-CH(OEt)_2$	**5a** [c]	(35)
11	$CH_2=C=CH-MgBr$/ether	0°C, 12 h, 20°C, B	$H-C\equiv C-CH_2-CH(OEt)_2$	**6a** [d]	60
12	$CH_2=C=CHZnBr$/THF	10°C, 4 h, 20°C, A	$H-C\equiv C-CH_2-CH(OEt)_2$	**6a** [d]	51
13	$CH_2=C=CHAl_{2/3}Br$/ether	−78°C, 1 h, −60°C, B	$H-C\equiv C-CH_2-CH(OEt)_2$	**6a**	74
14	$MeCH=C=CHAl_{2/3}Br$/ether	−78°C, 1 h, −60°C, B	$H-C\equiv C-CHMe-CH(OEt)_2$	**7**	84
15	$PhCH_2ZnBr$/THF	0°C, 12 h, 20°C, B	$PhCH_2CH(OEt)_2$	**8**	50
16	$Ph-C\equiv C-MgBr$/ether/THF	0°C, 0.25 h, 0°C, A	$Ph-C\equiv C-CH(OEt)_2$	**9**	(57)
17	$Bu-C\equiv C-MgBr$/ether/THF	0°C, 0.25 h, 0°C, A	$Bu-C\equiv C-CH(OEt)_2$	**10**	(45)
18	$Me_3Si-C\equiv C-MgBr$/ether/THF	0°C, 0.25 h, 0°C, A	$Me_3Si-C\equiv C-CH(OEt)_2$	**11a**	(40)
19	$Ph-CH=CH-CuMe(CN)Li_2$/THF	0°C, 12 h, 20°C, A	$PhCH=CH\sim CH(OEt)_2$	**12** [e]	33
	$E/Z = 85/15$		$E/Z = 86/14$		
20		20°C, 2 h, 20°C, A	 $Z/E = 87/13$	**14**	65

[a] Experimental conditions: after preparation of the organometallic reagents by the methods described in the text, the addition of diethoxymethylacetate on the organometallic reagent (method A) was carried out at the first mentioned temperature and stirring was continued over the above indicated period at the temperature shown. Method B means that the organometallic reagent was added to diethoxymethylacetate. [b] Isolated yields; values in brackets are rates of conversion of diethoxymethylacetate (by GC or NMR analysis). [c] Together with **5b** ($Ph-CH=C(COOEt)-CH_2-CH(OEt)_2$): **5a/5b** = 87/13. [d] Together with $Me-C\equiv C-CH(OEt)_2$, **6b**, *ca.* 10%. [e] (*E,E*)-1,4 diphenylbut-1,3-diene (**13**) was isolated as a side product (7%).

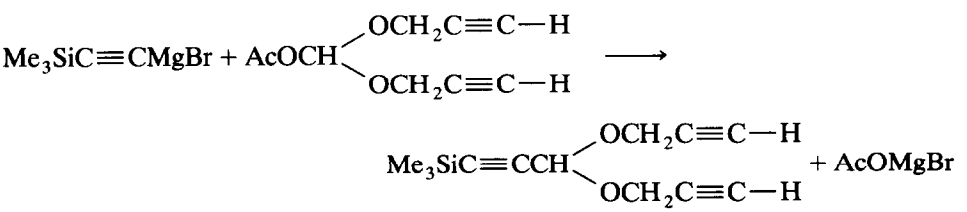
In reactions involving organoaluminium halides, whatever the order of addition of the reagents the temperature must be maintained below −60°C in order to avoid a second substitution at the acetal function [4,10,11]. At such temperatures this reaction appears to provide a valuable route to homopropargylic acetals **6a** and **7**. Hydrostannation readily converts these acetals respectively into 1-tributylstannyl-4,4-diethoxy-but-1-ene and 1-tributylstannyl-4,4-diethoxy-3-methyl-but-1-ene, which are good precursors for homoallylic and homocinnamic skeletons (12).

For bringing about substitution of the acetoxy group of diethoxymethylacetate it can be clearly seen from Table 1 (entries 1–16), that the best species involve soft nucleophiles associated with a counterion able to provide good electrophilic assistance. This is confirmed by the absence of substitution products in reactions involving butyllithium, styryllithium (highly basic species), or t-butylmagnesium chloride (high steric hindrance). With such nucleophiles, addition to the carbonyl group and/or deprotonation reactions probably occur in preference to substitution of the acetoxy group. This is true even with diethoxymethylbenzoate as the electrophile.

If there is no possibility of electrophilic assistance, for example when allyltributyltin is used in the presence of $PdCl_2(CH_3CN)_2$ in dimethylformamide, the expected substitution product is not observed; instead allyl diethyl orthoformate is obtained in low yield (36%). The substitution reaction also failed with styryltributyltin, but when allyltributyltin was used in the presence of $ZnBr_2$, the allylation product **2** was observed in low yield (7% after 5 days at room temperature).

On the other hand, use of less basic and less nucleophilic species (benzyl or alkynyl organometallic reagents) leads to expected functional acetals (entries 15–18). The same is true for soft nucleophiles such as styrylcyanocuprate, which in contrast to styryllithium, gives cinnamic acetal (Table 1, entry 19), and also 2-methyl cyclohexanone trimethylsilyl enol ether in the presence of $ZnBr_2$, which gives the expected β-keto-acetal (65% yield, entry 20).

It is noteworthy that propargylic orthoesters can undergo substitution of the acetoxy group rather than replacement of the acetylenic proton by the metal; this behaviour for organometallics having good nucleophilic rather than strongly basic properties has been confirmed in the case of tin anionoids (*cf.* below):



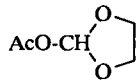
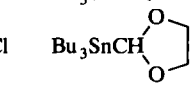
11b

Reactions of tin anionoids

Since the softness of the anionic species is a key factor for bringing about substitution of the acetoxy group of dialkoxymethylacetates, organotin anionoids [13] appear to be good candidates for producing α-stannylacetals [14,15], especially when the counterion can provide electrophilic assistance. Thus, as expected, use of

Table 2

Reactions of tributylstannylmagnesium chloride with dialkoxymethylacetates

Entry	$AcOCH(OR)_2$	Nucleophilic reagent	Product	No.	Yield
1	$AcOCH(OMe)_2$	$Bu_3SnMgCl$	$Bu_3SnCH(OMe)_2$	**15**	33%
2	$AcOCH(OEt)_2$	$Bu_3SnMgCl$	$Bu_3SnCH(OEt)_2$	**16**	70%
3	$AcOCH(Oi\text{-}Bu)_2$	$Bu_3SnMgCl$	$Bu_3SnCH(Oi\text{-}Bu)_2$	**17**	56%
4	$AcOCH(OCH_2C{\equiv}CH)_2$	$Bu_3SnMgCl$	$Bu_3SnCH(OCH_2C{\equiv}CH)_2$	**18**	52%
5		$Bu_3SnMgCl$		**19**	57%

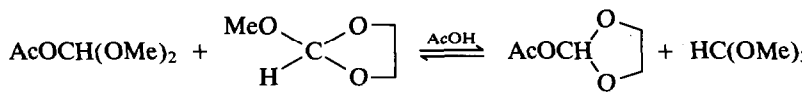
tributylstannylmagnesium chloride gave fairly good yields of α-stannylacetals * (Table 2).

$$AcOCH(OR)_2 + Bu_3SnMgCl \longrightarrow Bu_3SnCH(OR)_2 + AcOMgCl$$

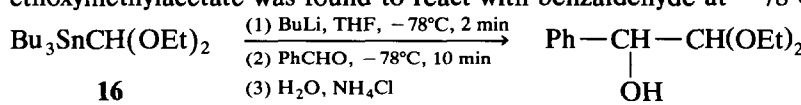
However tributylstannyllithium gave only complex mixtures, of no value for the preparation of α-stannylacetals, and reaction of dimethoxymethylacetate with tributylstannylmagnesium chloride gave dimethoxymethyltributyltin in only low yield (33%). This last result might be due to ready transmetallation of **15**, as suggested by Shiner *et al.* [15]:

$$Bu_3SnCH(OMe)_2 + Bu_3SnMgCl \longrightarrow Bu_6Sn_2 + (MeO)_2CHMgCl$$

Use of trialkylstannylmagnesium halides provides a potential route to a large variety of α-stannylacetals from dialkoxymethylacetates obtained by transesterification [19], for instance



Upon treatment with tributylstannylmagnesium chloride this dialkoxymethylacetate gave 2-tributylstannyl-1,3-dioxolane **19** in 57% yield. This means that this method may often be less efficient than transacetalisation of diethoxymethyltributyltin as a general route to dialkoxymethyltributyltins, including chiral α-stannylacetals [20], but the formation of diethoxymethyltributyltin in good yield without phenolic species (in contrast to the synthesis from diethylphenylorthoformate [14,15]) may be of interest when diethoxymethyltributyltin has to be used as precursor of diethoxymethyllithium after transmetallation with n-butyllithium. Thus diethoxymethyllithium generated from the α-stannylacetal obtained from diethoxymethylacetate was found to react with benzaldehyde at $-78°C$ in THF:



16 **20**

* α-Stannylacetals are as synthons formally d^1 formaldehyde equivalents [14,15], but the possible substitution of one alkoxy group of the acetal function by nucleophiles opens up a range of possibilities for the organic chemist, especially in providing the access to d^1 or d^3 umpolung synthons [16–18].

The α-hydroxyacetal was obtained in 65% yield, whereas Shiner, starting from diethoxymethyltributyltin obtained by another route, observed a fast decomposition of diethoxymethyllithium even at $-95°C$ and recommended trapping at $-110°C$ [15].

Conclusion

The substitution of the acetoxy group of dialkoxymethylacetates by organometallic reagents has been studied in order to establish its potential for the synthesis of functional acetals. The results demonstrate that this reaction is strongly favoured when soft nucleophiles are used and when the counterion is able to provide good electrophilic assistance. In such circumstances use of dialkoxymethylacetates can compete with that of diethylphenylorthoformate for the synthesis of unsaturated acetals or of α-stannylacetals. Diethoxymethyltributyltin was found to be a useful precursor of diethoxymethyllithium, which was trapped with benzaldehyde at $-78°C$ in THF.

Experimental

General

Infrared spectra were recorded with neat compounds (film between NaCl or KBr plates) on a Beckman Acculab 2 or a Perkin–Elmer 1420 spectrometer. The significant absorptions listed below have shapes and intensities consistent with those expected. GLC analyses were performed on a GIRDEL 3000 (FID detector) or a Carlo–Erba 4200 (FID detector, 25 m × 0.3 mm SE 52 capillary column) instrument. The mass spectra were recorded in the EI mode (70 eV) on a Finnigan–Mat 112 apparatus (direct introduction), or by GLC–MS on a Hewlett–Packard apparatus (Engine 5989 A). The isotopic patterns are given for ^{120}Sn in organotin fragments, which means that the reported abundances (values in parentheses) for organotin fragments are roughly one third of the real abundance when compared with organic fragments.

The ^1H NMR spectra were recorded on a Varian EM360 spectrometer (60 MHz) or a Jeol FX90Q spectrometer (89.55 MHz). The latter was also used for the ^{13}C NMR spectra (22.49 MHz) and ^{119}Sn NMR spectra (33.35 MHz). Unless otherwise indicated, the chemical shifts "δ(ppm)" are relative to Me_4Si for ^1H and ^{13}C (internal standard) in deuterochloroform and to Me_4Sn for ^{119}Sn NMR spectra (internal standard) in perdeuterobenzene.

Starting materials

Dialkoxymethylacetates. Dialkoxymethylacetates were obtained as described by Scheeren *et al.* [6,19]; diethoxymethylacetate and dimethoxymethylacetate from the commercially available trialkylorthoformates, dipropargyloxymethylacetate and diisobutyloxymethylacetate from tripropargylorthoformate [21], and triisobutylorthoformate, by treatment with acetic anhydride and formic acid. For the preparation of 2-acetoxy-1,3-dioxolane transesterification was used, starting from

dimethoxymethylacetate and 2-methoxy-1,3-dioxolane (obtained from trimethylorthoformate and ethylene glycol in 90% yield by transacetalation in the presence of sulphuric acid [19]).

Diethoxymethylacetate. A mixture of 165.8 g of acetic anhydride (1.625 mol), 82.8 g of formic acid (1.8 mol), and 222 g of triethylorthoformate (1.5 mol) was stirred for one day and subsequently distilled under reduced pressure (100 mmHg) with the temperature kept below 50°C. After the volatile compounds had been removed diethoxymethylacetate was distilled under vacuum and isolated in 66% yield (160 g, Eb_{15} = 70°C). IR: 3000–2840, 1750, 1375, 1240, 1195, 1010 cm^{-1}. ^1H NMR: 1.22 (6H, t, $^3J_{2H}$ = 7 Hz), 2.09 (3H, s), 3.71 (4H, q, $^3J_{3H}$ = 7 Hz), 6.32 (1H, s).

Dimethoxymethylacetate. (Similar scale, 55% yield). Eb_{35} = 63°C. IR: 3020–2840, 1750, 1370, 1215, 1120, 1090, 1015 cm^{-1}. ^1H NMR: 2.10 (3H, s), 3.41 (6H, s), 6.19 (1H, s).

Dipropargyloxymethylacetate. (1/10 scale, 46% yield). Eb_1 = 81°C. IR: 3300, 2950–2860, 2130, 1730, 1080, 1040, 640 cm^{-1}. ^1H NMR: 2.12 (3H, s), 2.49 (2H, t, $^4J_{2H}$ = 2.7 Hz), 4.37 (4H, d, $^4J_{1H}$ = 2.7 Hz), 6.55 (1H, s), ^{13}C NMR: 20.9, 53.1 (2C), 75.6 (2C), 78.7 (2C), 106.9 and 168.9.

Diisobutyloxymethylacetate. (1/10 scale, 55% yield). Eb_6 = 81°C. IR: 2980–2870, 1750, 1100, 1020. ^1H NMR: 0.93 (12H, d, $^3J_{1H}$ = 6.6 Hz), 1.88 (2H, m, $^3J_{8H}$ = 6.6 Hz), 2.09 (3H, s), 3.41 (4H, d, $^3J_{1H}$ = 6.6 Hz), 6.30 (1H, s). ^{13}C NMR: 19.3 (4C), 20.9, 28.5 (2C), 71.6 (2C), 108.8, 169.3.

2-Acetoxy-1,3-dioxolane. (1/10 scale, 80% yield). Eb_2 = 57°C. IR: 2850–3000, 1730, 1180, 1085 cm^{-1}. ^1H NMR: 1.98 (3H, s), 3.93 to 4.26 (4H, m), 6.85 (1H, s). ^{13}C NMR: 21.1, 64.5 (2C), 111.0 and 170.1.

Organometallic reagents. These reagents are commercially available or were made by previously described methods: allylMgBr [22], crotylMgBr [23] and allenylMgBr [24], allylZnBr, crotylZnBr and allenylZnBr [25], allyl-, crotyl- and allenyl $Al_{2/3}Br$ [4,26–28], $PhCH_2ZnBr$ [25], CH_2=C(COOEt)–CH_2ZnBr [29], PhCH=C(COOEt)–CH_2ZnBr [9], R–C≡CMgBr [30], ^{t}BuMgCl [31], allyltributyltin [32], styryltributyltin [33], styryllithium [34], methyl styrylcyanocuprate [35], 2-methyl-cyclohexanone trimethylsilyl enol ether [36], tributylstannylmagnesium chloride [37].

Reactions of diethoxymethylacetates with organometallic reagents

Experimental procedures. For these reactions the experimental conditions are as shown in Table 1 (solvent, temperature, stirring period, addition mode for the reagents). In initial studies the reactions were carried out on a 10 mmol scale and the concentration of diethoxymethylacetate (8 mmol) in dry ether or THF was adjusted in the light of the concentration of the organometallic reagent in order to give the product mixture as a 50 ml solution. At the end of the reaction, hydrolysis was performed with H_2O/NH_4Cl and the aqueous phase extracted with ether (3 × 20 ml). After drying of the extract over $MgSO_4$ and removal of solvents under vacuum, the residue was distilled (compounds **1**, **2**, **3**, **6**, **7**) or chromatographed on silica gel with an hexane/ether/triethylamine mixture (90/9/1) as eluent.

Subsequently, when promising results had been obtained (entries 13–14 for instance), the reactions were reproduced on a larger scale (0.25 mol) leading to an increase in the isolated yields.

Typical procedure for the preparation of 7. (3-Methylallenyl)aluminium bromide was prepared in ether (200 ml) at 35°C from aluminium (5.4 g) and 3-bromobut-1-yne (33.2 g) in the presence of a catalytic amount of mercuric chloride (28). Diethoxymethylacetate (32.4 g) in ether (200 ml) was placed in a 1 l three-neck flask, and the mixture was cooled to −78°C. The organoaluminium reagent was added slowly enough with stirring to maintain the temperature below −60°C. The reaction was then stirred at −60°C for a further 1 h then treated at this temperature with H_2O/NH_4Cl. After filtration and the usual work-up, compound **7** was distilled as a colourless oil (Eb_{30} = 63°C, 24 g, 84% yield).

Characterization of the obtained acetals. Most of these acetals have been prepared previously and the data obtained for our compounds are consistent with literature values (for instance ref. 3 and references therein). Some relevant data for the compounds are as follows:

1. ^{1}H NMR: 0.91 (3H, t, $^3J_{2H}$ = 7.2 Hz), 1.22 (6H, t, $^3J_{2H}$ = 7.1 Hz), 1.57 (2H, m), 3.3–3.9 (4H, m), 4.41 (1H, $^3J_{2H}$ = 5.6 Hz). ^{13}C NMR; 9.0, 15.4 (2C), 26.7, 61.1 (2C), 104.4. MS: m/z = 103 (41) (M^+ − Et$^\cdot$), 87 (67), 75 (47), 59 (100), 57 (12), 47 (83), 41 (20), 31 (57), 29 (87), 27 (55).

2. ^{1}H NMR: 1.20 (6H, t, $^3J_{2H}$ = 7 Hz), 2.39 (2H, m, $^3J_{1H}$ = 5.7 Hz, $^3J_{1H}$ = 6.7 Hz, $^4J_{2H}$ ~ 1.2 Hz), 3.51 and 3.65 (2 × 2 diastereotopic H, $^2J_{1H}$ = −9 Hz, $^3J_{3H}$ = 7 Hz), 4.52 (1H, t, $^3J_{2H}$ = 5.7 Hz), 5.06 (1H, m, $^3J_{1H}$ = 9.6 Hz, $^2J_{1H}$ = 2.3 Hz, $^4J_{2H}$ ~ 1.2 Hz), 5.10 (1H, m, $^3J_{1H}$ = 17.5 Hz, $^2J_{1H}$ = 2.3 Hz, $^4J_{2H}$ ~ 1.2 Hz), 5.82 (1H, m, $^3J_{1H}$ = 17.5 Hz, $^3J_{1H}$ = 9.6 Hz, $^3J_{2H}$ = 6.7 Hz). ^{13}C NMR: 15.3 (2C), 38.6, 61.1 (2C), 102.5, 117.2 and 133.8. IR: 3075, 2970–2850, 1640, 1125, 1065, 915 cm^{-1}. MS: m/z = 103 (46) (M^+ − $C_3H_5^\cdot$), 99 (30), 75 (52), 71 (42), 47 (100), 43 (64), 41 (34), 39 (19), 29 (69), 27 (40). Anal. Found: C 65.68; H 11.31%. $C_8H_{16}O_2$ calc.: C 66.62; H 11.18%.

3. ^{1}H NMR: 1.03 (3H, d, $^3J_{1H}$ = 6.9 Hz), 1.19 (3H, t, $^3J_{2H}$ = 7.2 Hz), 1.21 (3H, t, $^3J_{2H}$ = 7.2 Hz), 2.48 (1H, m), 3.33 and 3.53 (2 × 2 diastereotopic H; $^2J_{1H}$ = −9.5 Hz, $^3J_{3H}$ = 7.2 Hz), 4.22 (1H, d, $^3J_{1H}$ = 6.3 Hz), 5.01 (1H, m, $^3J_{1H}$ = 9.9 Hz, $^2J_{1H}$ = 2 Hz, $^4J_{1H}$ = 1 Hz), 5.06 (1H, m, $^3J_{1H}$ = 17.6 Hz, $^2J_{1H}$ = 2 Hz, $^4J_{1H}$ = 1.3 Hz), 5.88 (1H, m, $^3J_{1H}$ = 17.6 Hz, $^3J_{1H}$ = 9.9 Hz, $^3J_{1H}$ = 7.1 Hz). ^{13}C NMR: 14.8, 15.3 (2C), 41.4, 62.0, 62.2, 106.2, 114.5, 140.0. IR: 3075, 2860–2970, 1635, 1115, 1065, 920 cm^{-1}. MS: m/z = 113 (15) (M^+ − OEt$^\cdot$), 103 (54), 85 (7), 75 (67), 57 (8), 55 (14), 47 (100), 43 (83), 41 (17), 39 (11), 29 (72), 27 (32). Anal. Found: C 68.11; H 11.29% $C_9H_{18}O_2$ calc.: C, 68.31; H 11.47%.

4. ^{1}H NMR: 1.18 (6H, t, $^3J_{2H}$ = 7.1 Hz), 1.30 (3H, t, $^3J_{2H}$ = 7.1 Hz), 2.64 (2H, dd, $^3J_{1H}$ = 5.8 Hz, $^4J_{1H}$ = 0.9 Hz), 3.50 and 3.66 (2 × 2 diastereotopic H; $^2J_{1H}$ = −9.6 Hz, $^3J_{3H}$ = 7.1 Hz), 4.20 (2H, q, $^3J_{3H}$ = 7.1 Hz), 4.67 (1H, t, $^3J_{2H}$ = 5.8 Hz), 5.66 (1H, m, $^2J_{1H}$ = 1.6 Hz, $^4J_{2H}$ = 0.9 Hz), 6.23 (1H, bd, $^2J_{1H}$ = 1.6 Hz). ^{13}C NMR: 14.3, 15.3 (2C), 36.9, 60.7, 61.7 (2C), 101.8, 127.2, 136.6 and 167.1. IR: 3100, 2860–2970, 1710, 1630, 1175, 1115, 1060, 940, 820 cm^{-1}. MS: m/z = 171 (8) (M^+ − OEt$^\cdot$), 125 (9), 113 (2), 103 (36), 97 (29), 75 (41), 69 (13), 47 (100), 41 (20), 39 (8), 31 (4), 29 (41), 27 (14).

5a. ^{1}H NMR: 1.01 (3H, t, $^3J_{2H}$ = 7 Hz), 1.17 (3H, t, $^3J_{2H}$ = 7 Hz), 1.22 (3H, t, $^3J_{2H}$ = 7 Hz), 3.29 and 3.70 (2 × 2 diastereotopic H; $^2J_{1H}$ = −9.5 Hz, $^3J_{3H}$ = 7 Hz), 4.14 (2H, q, $^3J_{3H}$ = 7 Hz), 4.23 (1H, dd, $^3J_{1H}$ = 7.8 Hz, $^4J_{1H}$ = 0.9 Hz), 4.95 (1H, d, $^3J_{1H}$ = 7.8 Hz), 5.75 (1H, dd, $^2J_{1H}$ = 1.2 Hz, $^4J_{1H}$ = 0.9 Hz), 6.31 (1H, d, $^2J_{1H}$ = 1.2 Hz), 7.1–7.5 (5H, m). ^{13}C NMR: 13.3, 14.1, 14.3, 49.8, 59.9, 61.4, 61.7, 103.4, 125.0,

125.8, 127.3 (2C), 128.3 (2C), 138.6, 139.9 and 166.2. IR: 3080, 3055, 3020, 2860–2970, 1710, 1625, 1365, 1250, 1150, 1110, 1060, 1025, 940, 810, 755, 700 cm^{-1}. MS: $m/z = 247$ (2) ($M^+ - OEt^\cdot$), 201 (4), 173 (6), 145 (2), 117 (6), 116 (5), 115 (10), 103 (100), 91 (6), 75 (79), 47 (72), 29 (22).

5b, regioisomer of **5a**. ^1H NMR: Most of the signals are superimposed on those of **5a**, except 2.92 (2H, bd, $^3J_{1H} = 5.7$ Hz), 4.79 (1H, t, $^3J_{2H} = 5.7$ Hz) and 7.78 (1H, bs). MS: $m/z = 247$ (3) ($M^+ - OEt^\cdot$), 201 (2), 173 (4), 129 (3), 117 (7), 116 (5), 115 (11), 103 (80), 91 (5), 75 (80), 47 (100), 43 (6), 31 (5), 29 (34), 27 (8).

6a. ^1H NMR: 1.20 (6H, t, $^3J_{2H} = 7.2$ Hz), 2.02 (1H, t, $^4J_{2H} = 2.7$ Hz), 2.52 (2H, dd, $^3J_{1H} = 5.6$ Hz, $^4J_{1H} = 2.7$ Hz), 3.56 and 3.69 (2 × 2 diastereotopic H; $^2J_{1H} = -9.6$ Hz, $^3J_{3H} = 7.2$ Hz), 4.66 (1H, t, $^3J_{2H} = 5.6$ Hz). ^{13}C NMR: 15.2 (2C), 24.8, 61.9 (2C), 70.4, 79.8 and 101.0. IR: 3290, 2850–2980, 2125, 1120, 1060, 1020, 640 cm^{-1}. MS: $m/z = 103$ (32) ($M^+ - C_3H_3^\cdot$), 97 (17), 75 (24), 69 (26), 47 (100), 41 (37), 39 (19), 29 (51), 27 (18). Anal. Found: C 67.08 H 9.90% $C_8H_{14}O_2$ calc.: C 67.57; H 9.92%.

6b. ^1H NMR: Spectrum obtained as a mixture with **6a** with meaningful signals at 1.86 (3H, d, $^5J_{1H} = 1.8$ Hz) and 5.18 (1H, q, $^5J_{3H} = 1.8$ Hz).

7. ^1H NMR: 1.19 (3H, d, $^3J_{1H} = 7.1$ Hz), 1.22 (3H, t, $^3J_{2H} = 7.0$ Hz), 1.23 (3H, t, $^3J_{2H} = 7.0$ Hz), 2.04 (1H, d, $^4J_{1H} = 2.5$ Hz), 2.71 (1H, m, $^3J_{3H} = 7.1$ Hz, $^3J_{1H} = 6.2$ Hz, $^4J_{1H} = 2.5$ Hz), 3.55, 3.58, 3.69 and 3.73 (4 diastereotopic H with $^2J_{1H} = -9.3$ Hz and $^3J_{3H} = 7.0$ Hz), 4.36 (1H, d, $^3J_{1H} = 6.2$ Hz). ^{13}C NMR: 15.2 (2C), 16.1, 30.9, 62.6, 62.8, 69.6, 85.2 and 104.6. IR: 3300, 2860–2970, 2115, 1370, 1115, 1060, 1020 cm^{-1}. MS: $m/z = 111$ (11) ($M^+ - OEt^\cdot$), 103 (32), 83 (8), 75 (30), 55 (23), 53 (9), 47 (100), 43 (12), 39 (13), 31 (5), 29 (60), 27 (38).

8. ^1H NMR: 1.15 (6H, t, $^3J_{2H} = 7.1$ Hz), 2.91 (2H, d, $^3J_{1H} = 5.6$ Hz), 3.44 and 3.66 (2 × 2 diastereotopic H; $^2J_{1H} = -9.4$ Hz, $^3J_{3H} = 7.1$ Hz), 4.62 (1H, t, $^3J_{2H} = 5.6$ Hz), 7.24 (5H, bs). ^{13}C NMR: 15.2 (2C), 40.9, 61.7 (2C), 103.4, 126.3, 128.2 (2C), 129.6 (2C) and 137.5. IR: 3020–3080, 2860–2970, 1600, 1480, 1450, 1360, 1340, 1120, 1060, 1020, 745, 700 cm^{-1}. MS: $m/z = 149$ (7) ($M^+ - OEt^\cdot$), 121 (12), 103 (60), 91 (21), 75 (46), 65 (8), 47 (100), 29 (19).

9. ^1H NMR: 1.26 (6H, t, $^3J_{2H} = 7.1$ Hz), 3.66 and 3.82 (2 × 2 diastereotopic H; $^2J_{1H} = -9.4$ Hz, $^3J_{3H} = 7.1$ Hz), 5.48 (1H, s), 7.25–7.60 (5H, m). ^{13}C NMR: 15.2 (2C), 61.0 (2C), 84.7, 85.2, 91.9, 122.1, 128.4 (2C), 128.8, and 132.0 (2C). IR: 3060, 2880–2980, 2240, 1600, 1480, 1440, 1110, 1095, 1050, 1010, 750, 690 cm^{-1}. MS: $m/z = 204$ (1) (M^+), 175 (14), 160 (13) 159 (80), 131 (100), 129 (12), 103 (28), 102 (14), 77 (19), 51 (9), 29 (24).

10. ^1H NMR (CCl_4): 0.8–1.8 (13H including triplet at 1.18, $^3J_{2H} = 7$ Hz), 2.08–2.45 (2H, bm), 3.52 and 3.68 (2 × 2 diastereotopic H; $^2J_{1H} = -9.2$ Hz, $^3J_{3H} = 7$ Hz), 5.13 (1H, $^5J_{2H} = 1.5$ Hz). IR: 2860–2980, 2245, 1080, 1050, 1000 cm^{-1}. MS: $m/z = 183$ (2) ($M^+ - H^\cdot$), 155 (2), 139 (100), 111 (49), 91 (8), 81 (12), 77 (10), 68 (11), 67 (13), 68 (11), 57 (10), 55 (52), 53 (11), 43 (34), 41 (41), 39 (26), 29 (59), 27 (40).

11a. ^1H NMR (CCl_4): 0.18 (9H, s), 1.19 (6H, t, $^3J_{2H} = 7.1$ Hz), 3.50 and 3.66 (2 × 2 diastereotopic H; $^2J_{1H} = -9.4$ Hz, $^3J_{3H} = 7.1$ Hz), 5.10 (1H, s). ^{13}C NMR: −0.3 (3C), 15.2 (2C), 61.0 (2C), 90.4, 91.4 and 100.4. IR: 2870–2990, 2075, 1250, 1115, 1095, 1050, 1010, 850 cm^{-1}. MS: $m/z = 199$ (1) ($M^+ - H^\cdot$), 171 (6), 155 (100), 127 (32), 111 (20), 99 (66), 83 (13), 75 (21), 73 (28), 59 (10), 55 (13), 45 (24), 43 (30), 29 (50), 27 (19).

11b: ^1H NMR (CCl_4): 0.15 (9H, s), 2.43 (2H, t, $^4J_{2H} = 2.5$ Hz), 4.20–4.35 (4H,

m), 5.48 (1H, s); IR: 3300, 2850–2980, 2120, 1250, 1090, 1040, 1025, 850, 635 cm^{-1}.

12*E*. ^1H NMR: 1.25 (6H, t, $^3J_{2H} = 7$ Hz), 3.56 and 3.71 (2 × 2 diastereotopic H; $^2J_{1H} = -9.5$ Hz, $^3J_{3H} = 7$ Hz), 5.06 (1H, dd, $^3J_{1H} = 5$ Hz, $^4J_{1H} = 0.9$ Hz), 6.19 (1H, dd, $^3J_{1H} = 16.1$ Hz, $^3J_{1H} = 5$ Hz), 6.70 (1H, dd, $^3J_{1H} = 16.1$ Hz, $^4J_{1H} = 0.9$ Hz), 7.2–7.5 (5H, m). ^{13}C NMR: 15.3 (2C), 61.1 (2C), 101.6, 126.8 (3C), 128.0, 128.6 (2C), 133.0 and 136.4. IR: 3080, 3060, 3020, 2970–2870, 1650, 1570, 1490, 1450, 1370, 1340, 1140, 1050, 1000, 970, 760, 690 cm^{-1}. MS: $m/z = 206$ (11) (M^+), 161 (100), 135 (33), 133 (75), 132 (13), 131 (28), 115 (33), 105 (41), 104 (26), 103 (31), 91 (19), 77 (40), 55 (74), 51 (20), 47 (19), 29 (90), 27 (34).

12*Z*. ^1H NMR: 1.22 (6H, t, $^3J_{2H} = 7$ Hz), 3.56 and 3.68 (2 × 2 diastereotopic H; $^2J_{1H} = -9.4$ Hz, $^3J_{3H} = 7$ Hz), 5.23 (1H, dd, $^3J_{1H} = 7.3$ Hz, $^4J_{1H} = 0.9$ Hz), 5.78 (1H, dd, $^3J_{1H} = 11.8$ Hz, $^3J_{1H} = 7.3$ Hz), 6.66 (1H, dd, $^3J_{1H} = 11.8$ Hz, $^4J_{1H} = 0.9$ Hz), 7.3–7.5 (5 H, m). ^{13}C NMR: 15.4 (2C), 60.6 (2C), 98.0, 126.4, 127.6, 128.3, 128.8, 129.1, 129.3, 132.8 and 136.4. IR: 3080, 3060, 3020, 2860–2970, 1680, 1600, 1490, 1440, 1050, 1020, 995, 770, 700 cm^{-1}. MS: 206 (7) (M^+), 161 (89), 135 (32), 133 (80), 131 (29), 115 (37), 105 (46), 104 (26), 103 (33), 91 (15), 79 (14), 77 (43), 75 (18), 55 (100), 51 (25), 47 (45), 39 (11), 29 (92), 27 (36).

13*EE*. ^1H NMR: typical AA'BB' system between 6.49 and 7.10 ppm with 16 observable lines, 4H), 7.2–7.5 (10H, m). IR: 3075, 3050, 3010, 2920, 1485, 1440, 990, 965, 740, 690 cm^{-1}. MS: $m/z = 206$ (89) (M^+), 205 (34), 203 (16), 202 (12), 191 (32), 190 (14), 165 (11), 129 (23), 128 (37), 115 (18), 103 (12), 102 (12), 101 (16), 91 (100), 89 (26), 77 (16), 76 (15), 65 (15), 63 (12), 51 (20), 39 (15). For isomers **13***ZZ* and **13***ZE*, similar isotopic patterns were obtained in the GC/MS mode with a slight decrease in the intensity of the molecular ion (relative intensities of ion 206 = 54 for **13***ZZ* and 71 for **13***ZE*, ion 91 remaining the base peak for the spectra).

14*E*. ^1H NMR: 1.04 (3H, d, $^3J_{1H} = 6.7$ Hz), 1.15 (3H, t, $^3J_{2H} = 7.1$ Hz), 1.20 (3H, t, $^3J_{2H} = 7.1$ Hz), 1.3–2.9 (8H, bm), 3.3–3.9 (4 diastereotopic H, $^3J_{3H} = 7.1$ Hz, $^2J_{1H} = -9.5$ Hz), 4.90 (1H, d, $^3J_{1H} = 7.5$ Hz). ^{13}C NMR: 15.0, 15.2 (2C), 21.2, 28.2, 35.9, 53.4, 61.2, 62.0, 101.2 and 211.7.

14*Z*. ^1H NMR: Most of the signals are superimposed on those of **14***E* except 0.99 (3H, d, $^3J_{1H} = 6.5$ Hz) and 4.81 (1H, d, $^3J_{1H} = 6.1$ Hz). ^{13}C NMR: 14.4, 15.4 (2C), 25.2, 29.7, 37.5, 45.9, 55.2, 62.9, 64.0, 102.0 and 211.5. IR (mixture of isomers **14***E*/**14***Z* = 87/13): 2850–2980, 1710, 1450, 1375, 1120, 1060, 920 cm^{-1}. MS (mixture of isomers **14***E*/**14***Z* = 87/13) = m/z 103(26) ($M^+ - C_7H_{11}O^\cdot$), 97 (14), 75 (22), 69 (23), 47 (100), 45 (5), 41 (37), 39 (20), 31 (5), 29 (48), 27 (18).

Reaction of methylstyrylcyanocuprate. The reaction was conducted as indicated in Table 1 and the product mixture was chromatographied on silica gel (eluent, hexane/ether/Et_3N: 90/9/1). The expected acetals were eluted following coupling products of bis-styryl type. The GLC/MS analyses demonstrated the presence of a mixture of isomers, *ZZ*, *EZ* and *EE* 1,4-diphenylbut-1,3-dienes, with **13***EE* the major isomer. R_f values in TLC: **13***ZZ* + **13***ZE* (0.8), **13***EE* (0.76), **12***Z* (0.58), **12***E* (0.50).

Reactions of tin anionoids with dialkoxymethylacetates

Typical experimental procedure preparation of diethoxymethyltributyltin ***16***. To a solution of 0.5 mole of tributylstannylmagnesium chloride in ether in a 500 ml three-neck flask was added dropwise under nitrogen at 0°C during 1 h 78.6 g of

diethoxymethylacetate (0.485 mol) as a 1/1 mixture with ether (the reaction is slightly exothermic). Stirring was maintained for a further 1 h before hydrolysis with H_2O/NH_4Cl. After filtration, decantation and drying over magnesium sulphate, ether was removed under vacuum and the crude mixture was flash-chromatographed on silica gel 60 (eluent: hexane/ether/triethylamine: 95/3/2). After removal of solvents, diethoxymethyltributyltin **16** was obtained as a colourless oil (133.7 g; 70% yield) identical with that previously described [14]. GLC analysis confirmed that tetrabutyltin, hexabutyltin, and tributyltin acetate contained in the crude product had been removed in the purification process. (Distillation is also possible but a higher purity was obtained by chromatography).

Similar experimental conditions, starting from 0.05 mol of tributylstannylmagnesium chloride were used for the syntheses of **15**, **17**, **18** and **19**.

Characterization of the α-stannylacetals 15–19. Physicochemical data were in full agreement with previously reported data for **15** [14,15], **16** [14,15], **18** [20] and **19** [14,20]. Compound **17** was unambiguously identified on the basis of the following data.

IR: 2860–2980, 1470, 1395, 1390, 1380, 1250, 1090, 1030 cm^{-1}. ^1H NMR: 0.5 to 2.1 ppm (41H, n-butyl groups and isopropyl groups absorptions including 12H, d, at 0.93 ppm), 3.17 and 3.31 (2 × 2 diastereotopic H; $^2J_{1H} = -9.7$ Hz, $^3J_{1H} = 6.5$ Hz), 5.17 (1H, s, $^2J_{SnH} = 33$ Hz). ^{13}C NMR: 10.0 (3C, $^1J_{SnC} = 293$ Hz, 13.7 (3C), 19.6 (4C), 27.5 (3C, $^3J_{SnC} = 59.8$ Hz), 29.0 (2C), 29.8 (3C, $^2J_{SnC} = 20$ Hz), 76.4 (4C, $^3J_{SnC} = 32.2$ Hz), 108.8 (1C, $^1J_{SnC} = 490/510$ Hz). ^{119}Sn NMR: $\delta = -56.6$. MS: organotin fragments: $m/z = 377$ (0.5) ($M^+ - O^iBu^\cdot$), 321 (0.3), 291 (1), 235 (2), 179 (3), 177 (2), 121 (3). Organic fragments: $m/z = 159$ (17) ($M^+ - Bu_3Sn^\cdot$), 103 (26), 71 (13), 57 (100), 41 (12), 29 (11).

Transmetallation of diethoxymethyltributyltin with butyllithium and reaction of diethoxymethyllithium with benzaldehyde. A solution of 10 mmol of **16** (3.94 g) in 50 ml of dry THF in a four-neck flask was cooled to −80°C under argon and 6.25 ml of a butyllithium solution (1.6 M) in hexane was added dropwise from a syringe method during 2 min with the temperature in the mixture maintained at −78°C. Benzaldehyde (8 mmol in 2 ml THF) was added, with the temperature still maintained at −78°C. The mixture was stirred for 10 min at −78°C then allowed to warm to 0°C before hydrolysis (H_2O/NH_4Cl). After ether extraction (3 × 50 ml) and drying of the extract over magnesium sulphate and removal of the solvents under vacuum, the α-hydroxyacetal **20** was left as a mixture with benzaldehyde and tetrabutyltin. Purification by chromatography on silica gel with a mixture hexane/ether/triethylamine (85/14/1) as eluent gave 1.09 g (65% yield) of **20**. With such a liquid phase, on TLC plates the R_f value is 0.15. **20** was identified on the basis of the following data. ^1H NMR: 1.03 (3H, t, $^3J_{2H} = 7.3$ Hz), 1.25 (3H, t, $^3J_{2H} = 7.3$ Hz), 2.95 (bs, 1H), 3.20, 3.55, 3.62 and 3.80 (4 diastereotopic H; $^2J_{1H} = -9.7$ Hz, $^3J_{3H} = 7.3$ Hz), 4.32 (1H, d, $^3J_{1H} = 6.4$ Hz), 4.60 (1H, d, $^3J_{1H} = 6.4$ Hz), 6.9–7.6 (5H, m). ^{13}C NMR: 15.0, 15.3, 63.2, 64.2, 74.6, 106.0, 127.4 (2C), 127.6, 127.9 (2C), 140.4. IR: 3440, 3100–3000, 1120, 1070, 1030 cm^{-1}. MS: $m/z = 165$ (12, $M^+ - OEt^\cdot$), 107(8), 103(65), 75(50), 47(100).

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