A Highly Atom Efficient, Solvent Promoted Addition of Tetraallylic, Tetraallenic, and Tetrapropargylic Stannanes to Carbonyl Compounds

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Tetraallylic, tetraallenic, and tetrapropargylic stannanes (0.25 equiv) react with aldehydes in methanol to provide unsaturated alcohols in good to excellent yields (56−99%). These reactions proceed exclusively with allylic rearrangement for tetra(2-butenyl)tin **2b** and tetra(1,2-butadienyl)-tin **16c** and predominantly with allylic rearrangement for tetrapropadienyltin **16a** and tetra(2-butynyl)tin **6e**. Allylation reactions also proceeded smoothly with reactive ketones such as ethyl pyruvate (**9a**) and cyclohexanone (**9b**). The corresponding TFA-catalyzed reactions of dimethyl acetals **4d** and **4e** are regiospecific with allylic rearrangement.

Introduction

It has long been known that the allylation of carbonyl groups provides homoallylic alcohols possessing useful functionality suitable for further elaboration.[1] Not surprisingly, numerous protocols have been developed allowing this transformation to be achieved with high levels of regio- and stereocontrol.[2] A large body of work revolves around the use of allylstananne reagents to act as allyl donors and their use in the synthesis of complex natural products.[3] Although these reactions are typically regioselective and high yielding, environmental concerns regarding disposal and poor atom efficiency abound. One of the great remaining difficulties associated with the use of allylstannane reagents, which has not been adequately addressed, is the removal of the stannane byproducts.[4] Recently, we and others reported a particularly mild, convenient, environmentally friendly procedure for the chemoselective allylation of aldehydes[5] and Weinreb amides[6] with commercially available tetraallylstannane. In this procedure the carbonyl compound and stannane (0.25 equiv) react rapidly in methanol, water,[7] or ionic liquid[8] over a range of temperatures from room temperature (aldehydes) to 100 °C (ketones over approximately 4−20 h; Weinreb amides over 5 days). The resulting homoallyl alcohol can be easily separated from insoluble tin methoxide salts. (Weinreb amides afford moderate to good yields of the corresponding allylic ketones.) Unlike the corresponding reactions of allyltrialkylstannanes, this procedure does not require anhydrous conditions, the use of expensive catalysts, or chromatography to remove the organotin byproduct. Acetals are also allylated with this reagent, but require the addition of TFA or silica gel.[9] This latter procedure is particularly suited to the reaction of unstable amino aldehydes, which are more conveniently handled as the corresponding acetals.

The related propargylation and allenylation of aldehydes has also received considerable attention over the past decade. We[10] and others and have developed a variety of methods to achieve regio- and stereocontrol which have been employed for the asymmetric synthesis of complex natural products.[11]

We have previously suggested that the methanol-promoted allylation of carbonyl compounds might be concerted with the activating influence of the solvent primarily as a result of hydrogen bonding to the carbonyl oxygen.[5d] (The reaction in ionic liquids is believed, in part, to be due to the encapsulation of small quantities of water in the "dry" liquid and the serendipitous entrainment of water within the extracting solvent (diethyl ether).[12]) Thus, the allylation should be regiospecific with addition

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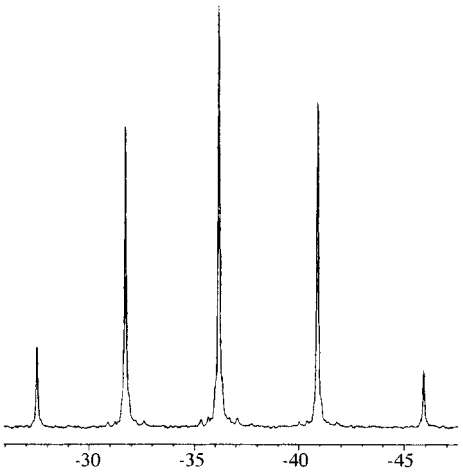
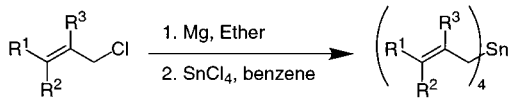


Figure 1. ^{119}Sn {^{1}H} NMR spectrum of **2b** in $CDCl_3$. Assignments (from L to R): cis,cis,cis,cis (δ −27.53, 7.2%); cis,cis,-cis,trans (δ −31.73, 26.6%); cis,cis,trans,trans (δ −36.18, 37.2%); cis,trans,trans,trans (23.9%); trans,trans,trans,trans (δ −45.92, 5.1%).[15]

Scheme 1



1 **2**

a: $R^1 = R^2 = H$, $R^3 = CH_3$
b: $R^1 = H$, $R^2 = CH_3$, $R^3 = H$
c: $R^1 = R^2 = CH_3$, $R^3 = H$

of the aldehyde or ketone to the γ-position of the allylic triad. As part of an ongoing investigation into the regiochemistry of this reaction, we have extended it to the analogous propargylation and allenylation reactions.

Results and Discussion

Synthesis of Tetraallylic Stannanes 2a−c. Using a slight modification of the literature procedure, that is allowing the magnesium metal to stir at room temperature overnight under an nitrogen atmosphere (formation of a "magnesium mirror"), Grignard methodology (Scheme 1) and the readily available allylic chlorides **1** rapidly afforded the methyl-substituted teraallylic stannanes **2a−c** in excellent yield.[13]

Chloride **1b** (E/Z = 90:10) yielded a mixture of tetraorganostannanes that isomerized to an almost perfect binomial distribution of the five diastereomers of **2b** on standing (Figure 1). Stereochemical assignments were based on comparisons with the corresponding ^{13}C and ^{119}Sn NMR data for 2-butenyltributylstannane.[14]

Reactions of Tetraallylic Stannanes (2a−c) with Aldehydes and Acetals. The addition of allylic stannanes **2a−c** to aldehydes **3a−f** was examined under a variety of reaction conditions, including stirring in methanol at room temperature (30 °C), methanol reflux, methanol reflux in the presence of dimethyldimethoxystannane (DDS) and in acidic (HCl) THF. With **2a** only **5**, with **2b** a mixture of **6** and **7**, and with **2c** only **8** were expected as the products of these reactions (Scheme 2).

As can be seen from Table 2, aldehyde addition to stannane **2a** proceeded cleanly, under all of the conditions examined, and in high yield (ca. 90%) affording the expected β-methyl homoallylic alcohols **5a−f** (Table 2, entries 1−6) as the sole product of the reaction. The corresponding reaction with stannane **2b** was regiospecific proceeding with allylic rearrangement, but with low diastereoselectivity in favor of the syn isomers **6a−f** over the anti isomers **7a−f** (de = 0−30%). As with stannane **2a**, the yields of homoallylic alcohols from **2b** were excellent (Table 2, 65−80%, entries 9−26). Finally in this series, tetraalylic stannane **2c** also afforded good to excellent yields of the β-methyl homoallylic alcohols **8a−f** (Table 2, 57−82%, entries 29−34). In all instances, the product could be isolated by aqueous workup or by evaporation of the solvent and washing the resulting slurry of allylated product **5−8** and stannane salts with dichloromethane followed by Kugelrohr distillation or filtration through silica gel. This procedure is markedly simpler than those associated with allyltrialkylstannanes.

Several of the allylation experiments with stannane **2b** and aldehydes **3** were conducted both at room temperature in methanol and at methanol reflux. Comparison of the outcomes of these reactions indicates that there is no significant change in the final reaction yield; however, elevated temperature shows a slight syn isomer **6** preference with aromatic aldehydes **3d−f**. For example, the room-temperature reaction with **3d** affords **6d** + **7d** as a 50:50 mixture (Table 2, entry 16, 83%); at methanol reflux 55:45 (Table 2, entry 17, 80%); with **3e** at room-temperature yielding **6e** + **7e** as a 56:44 mixture (Table 2, entry 20, 71%); and at methanol reflux 59:41 (Table 2, entry 21, 71%).

In previous studies from our laboratories, we have noted a significant acceleration in reaction rate after transfer of the first allyl group from tetraallylstannane to the carbonyl compound.[5d] We postulated that this acceleration was due, at least in part, to the in situ generation of triallylmethoxystannane, which acted as a Lewis acid catalyst the addition of the remaining allyl groups. We envisaged that the addition of a methoxystannane Lewis acid, would yield ostensibly the same outcome in these reactions by mimicking the in situ generated Lewis acid, further strengthening our initial hypothesis. Accordingly, we examined the effect of conducting allylation reactions in the presence of dimethyldimethoxystannane (DDS, 10 mol %).

Interestingly, DDS acted in an almost identical fashion to HCl (in THF) allowing a slight increase in reaction yield and a change in the ratio of products. For example, the reaction of stannane **2b** and aldehyde **3d** in methanol with added DDS (Table 2 entry 18) affords **6d** + **7d** as a 60:40 mixture (Table 2, entry 18, 92%). The corresponding reaction in HCl/THF affords identical products as a 62:38 mixture (Table 2, entry 19, 88%). Indeed, in our hands, the HCl/THF-mediated reactions proceeded in a fashion analogous to those conducted with added DDS, that is, an average of a 10% increase in product yield and a concurrent slight increase in syn (**6**) selectivity (de = 0−33%). However, we note that this HCl/THF methodology is not suited to reactions involving acid-sensitive groups.

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Scheme 2

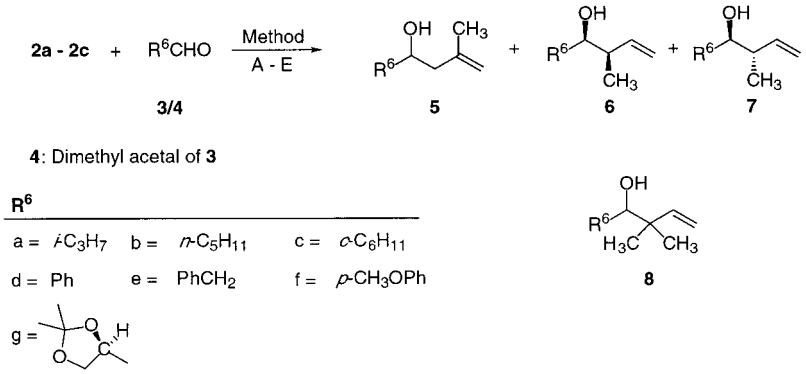

Table 1. Synthesis of Tetraallylic Stannanes (2a−c)

allylic halide	tetraallylic stannane	yield[a] (%)
1a	**2a**	80
1b	**2b**[b]	94
1c	**2c**	88

[a] Isolated yield. [b] Consists of five diastereomers (Figure 1).

Table 2. Reaction of Tetraallylic Stannanes 2a−c with Aldehydes 3 and Selected Dimethyl Acetals 4

entry	stannane	aldehyde/ acetal	method[a]	product	ratio[b]	yield[c] (%)
1	**2a**	**3a**	A	**5a**		99
2	**2a**	**3b**	A	**5b**		92
3	**2a**	**3c**	A	**5c**		90
4	**2a**	**3d**	A	**5d**		94
5	**2a**	**3e**	A	**5e**		88
6	**2a**	**3f**	A	**5f**		66
7	**2a**	**4d**	E	**5d**		75
8	**2a**	**4e**	E	**5e**		trace
9	**2b**	**3a**	B	**6a** + **7a**	38:62	77
10	**2b**	**3b**	B	**6b** + **7b**	45:55	72
11	**2b**	**3b**	C	**6b** + **7b**	54:46	78
12	**2b**	**3b**	D	**6b** + **7b**	63:37	86
13	**2b**	**3c**	A	**6c** + **7c**	65:35	67
14	**2b**	**3c**	B	**6c** + **7c**	57:43	68
15	**2b**	**3c**	D	**6c** + **7c**	54:46	90
16	**2b**	**3d**	A	**6d** + **7d**	50:50	83
17	**2b**	**3d**	B	**6d** + **7d**	55:45	80
18	**2b**	**3d**	C	**6d** + **7d**	60:40	92
19	**2b**	**3d**	D	**6d** + **7d**	62:38	88
20	**2b**	**3e**	A	**6e** + **7e**	56:44	71
21	**2b**	**3e**	B	**6e** + **7e**	59:41	71
22	**2b**	**3e**	C	**6e** + **7e**	49:51	77
23	**2b**	**3e**	D	**6e** + **7e**	52:48	82
24	**2b**	**3f**	B	**6f** + **7f**	57:43	65
25	**2b**	**3f**	C	**6f** + **7f**	60: 40	72
26	**2b**	**3f**	D	**6f** + **7f**	67:33	80
27	**2b**	**4d**	E	**6d** + **7d**	61:39	71
28	**2b**	**4e**	E	**6e** + **7e**		trace
29	**2c**	**3a**	D	**8a**		64
30	**2c**	**3b**	D	**8b**		78
31	**2c**	**3c**	D	**8c**		70
32	**2c**	**3d**	D	**8d**		82
33	**2c**	**3e**	D	**8e**		74
34	**2c**	**3f**	D	**8f**		62
35	**2c**	**4d**	E	**8d**		56
36	**2c**	**4e**	E	**8e**		trace

[a] Methods: (A) MeOH, rt, 4−24 h; (B) MeOH, reflux, 48 h; (C) MeOH + DDS, reflux, 24 h; (D) THF/HCl, rt, 24 h; (E) MeOH/TFA, rt, 24 h. [b] Ratios determined by ^{1}H NMR and ^{13}C NMR. [c] Isolated yields.

We have previously noted that the solvent-promoted addition of tetraallylic stannanes to aldehydes requires a protic solvent and does not proceed in polar, aprotic solvents such as dimethyl sulfoxide.[5b] This previous study also noted no observable, structural change on solvation of the tetraallylic stannane in either polar protic or polar aprotic solvents, suggesting an ion-pair mechanism was unlikely. We have therefore proposed an eight-membered transition state involving tin−solvent coordination and concomitant H-bonding activation of the aldehyde. The present study confirms regiospecific addition with allylic rearrangement for the allylic stannanes studied, even for the highly hindered substrate **2c**, which is consistent with this cyclic mechanism. An equivalent activated species can be drawn for the HCl- and DDS-promoted reactions. With respect to the stereochemistry of addition, there are no clear stereoisomeric preferences or trends that can be unambiguously assigned to a particular transition state conformation (Scheme 3). This is perhaps not surprising if the transition state does indeed resemble a flexible, eight-membered heterocycle.

The corresponding reactions of tetrapropargylic and tetraallenic stannanes are not so invariably regiospecific. There is no literature precedence for S_E, rather than S_E', electrophilic cleavage of allylic stannanes, which suggests to us allylic rearrangement of either the starting stannanes or product alcohols. Treatment of the starting stannanes under the reaction conditions does not result in any isomeric chang,e and so, regioleakage resulting from allene−propargyl isomerization of the product alcohols seems a likely possibility.

We also briefly examined the TFA catalyzed addition of dimethylacetals **4** and stannanes **2a−c**; however, the expected allylated products were only observed in the case of **4d** (Table 2, entries 7, 27, and 35), and only trace quantities were observed with **4e** (Table 2, entries 8, 28, and 36). Additionally, the isolated yields are also lower than those observed with the parent aldehyde, e.g., with benzaldehyde **3d** affords **5d** 94% (Table 2, entry 4), whereas the corresponding reaction with **4d** affords **5d** 75% (Table 2, entry 7). Notwithstanding this, the allylation of **4d** and related compounds has possible synthetic utility for unstable aldehydes.[9,10]

Reaction of Tetrallylic Stannanes 2a−c with Ethyl Pyruvate 9a. Given the success of these allylation reactions with aldehydes, we also investigated the reaction of **2a−c** with activated ketones, specifically with ethyl pyruvate (**9a**) (Scheme 3).

For simplicity in analysis, the mixture of methyl and ethyl ester-formed esters (trans-esterification) were saponified with NaOH and subsequently neutralized with HCl to afford the corresponding acids in good to excellent yields (Table 3). However, only poor diastereoselctivity was apparent with **2b**; essentially equal quantities of syn (**11**) and anti (**12**) products were observed.

Scheme 3

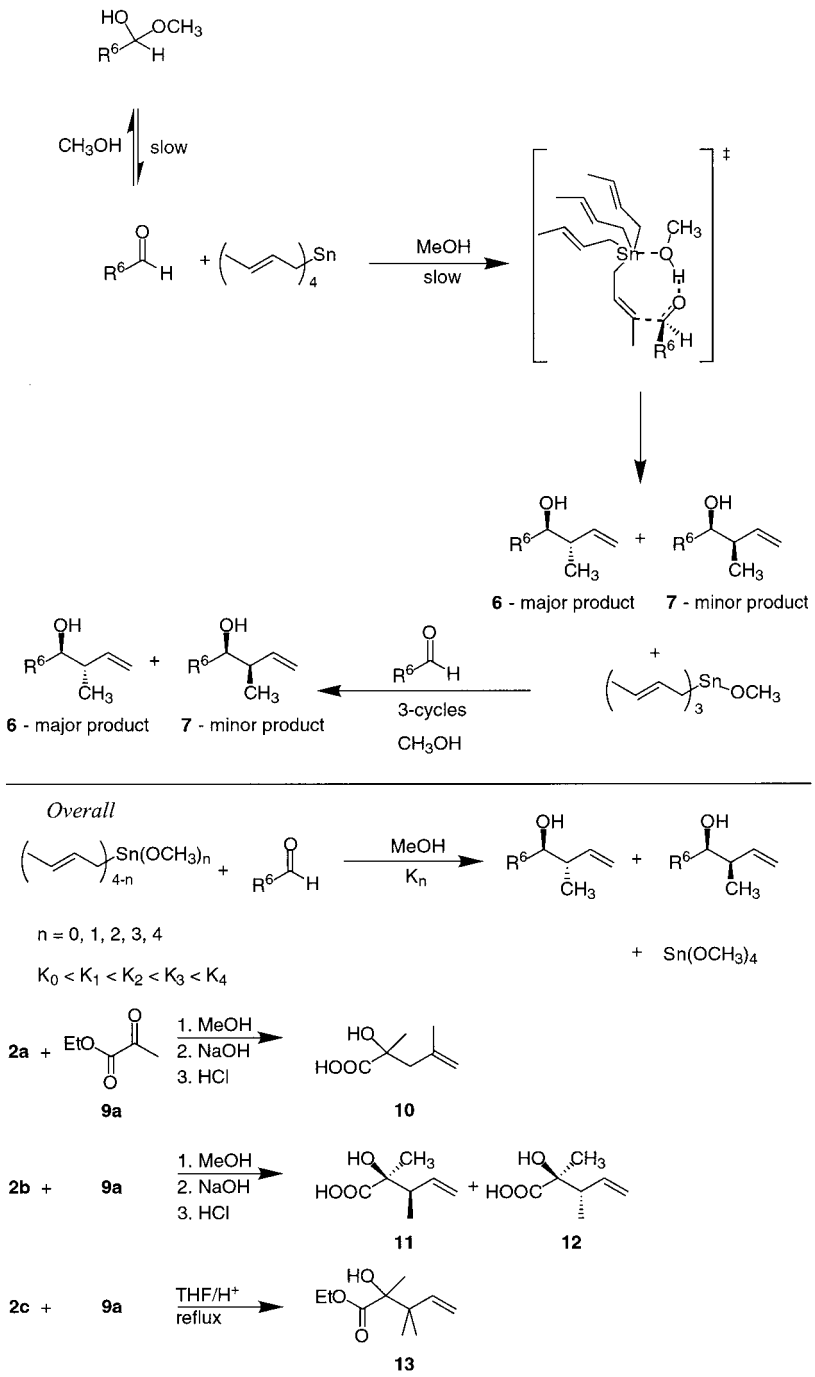

Table 3. Reaction of Tetraallylstannanes 2a−c with Ethyl Pyruvate 9a

stannane	method[a]	product	ratio[b]	yield[c] (%)
2a	A	**10**		79
2b	A	**11/12**	56:44	64
2b	D	**11/12**	46:54	70
2c	D	**13**		49

[a] Methods: (A) MeOH, rt, 4−24 h; (D) THF/HCl, rt, 24 h. [b] Ratios determined by ^{1}H NMR and ^{13}C NMR. [c] Isolated yields.

Synthesis of Tetraallenic and -propargylic Stannanes 16a,c and 17c,d. Tetraallenic **16** and tetrapropargylic **17** stannanes were prepared, in moderate yields, from the corresponding propargylic chlorides **14** and bromides **15** by a Grignard reaction in the presence of a catalytic amount of $HgCl_2$ (ca. 2 mol %) (Scheme 4).[16]

Each tetraorganostannane was obtained as a single regioisomer determined by the substitution pattern of starting propargylic halide (Table 4). Thus, propargylic halides **14c** and **15c**,**d** with a methyl/ethyl group at the terminal position yielded tetrapropargylic stannanes

(15) NMR data for tetra(2-butenyl)stannane **2b**. ^{1}H NMR ($CDCl_3$): δ 1.59 (br, s, $J(^{119}Sn)$ = 19.0 Hz, 12H), 1.67 (br s, $J(^{119}Sn)$ = 77.8 Hz, $J(^{117}Sn)$ = 59.4 Hz, 8H), 1.71 (br s, $J(^{119}Sn)$ = 24.9 Hz, 12H), 5.28 (m, 4H). ^{13}C NMR: cis,cis,cis,cis [$\delta(J(^{117}Sn), J(^{119}Sn))$] 10.60 (240.4, 251.1), 12.51, 118.87 (50.2), 128.00 (48.4); cis,cis,cis,trans 11.09 (240.3, 251.8), 12.51, 14.51[a] (255.6, 267.0), 17.92[a] (13.08), 119.01 (49.7), 121.10[a] (51.9), 128.06 (48.6), 128.87[a] (48.2); cis,cis,trans,trans 11.09 (240.3, 251.8), 12.51, 14.78[a] (254.9, 267.0), 17.92[a] (13.08), 119.16 (49.7), 121.22[a] (51.9), 128.13 (48.9), 128.94[a] (47.8); cis,trans,trans,trans 11.30 (241.2, 251.9), 12.51, 15.01[a] (254.8, 267.1), 17.92[a] (13.08), 119.32 (50.2), 121.34[a] (51.9), 128.20 (48.5), 129.01[a] (48.1); trans,trans,trans,trans 15.23 (255.6, 267.8), 17.92 (13.08), 121.46 (52.5), 129.09 (48.7). Note [a] = trans butenyl units

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Scheme 4

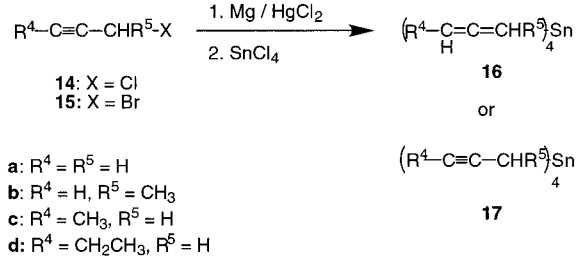
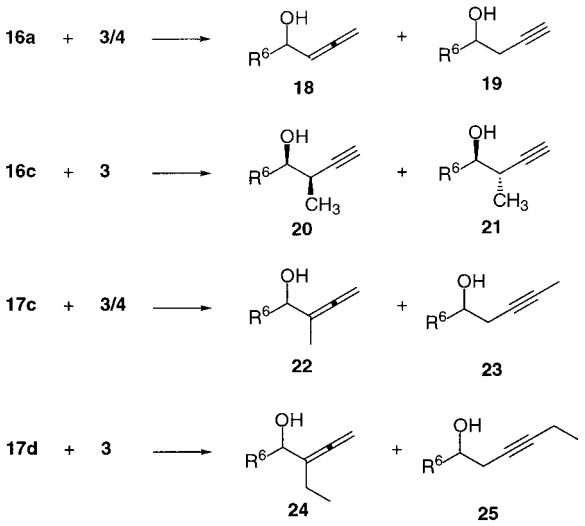


Table 4. Synthesis of Tetraallenic and -propargyic Stannanes (16a,c and 17c,d)

propargyl halide	tetraallenic and propargylic stannanes	yield[a] (%)
14a	**16a**	61
15a	**16a**	61
14b	**16c**[b]	59
15b	**16c**[b]	63
14c	**17c**	61
15c	**17c**	62
15d	**17d**	55

[a] Isolated yields. [b] Consists of three diastereomers in the ratio 50:37:13 as determined by ^{119}Sn NMR spectroscopy.

Scheme 5



17c,**d** while the other propargylic halides not substituted at this position provided tetraallenic stannanes **16a** or **16c** exclusively. Propargylic triarylstannanes are reported to isomerize in methanol to the corresponding allenyl isomer depending on the substitution pattern.[17] No isomerization of **16a**, **16c**, **17c**, or **17d** was observed in methanol after 48 h at room temperature, suggesting that the Grignard reaction yields the thermodynamically favored product in each case.

Reactions of Tetraallenic- and -propargylic Stannanes (16a,c and 17c,d) with Aldehydes 3 and Acetals 4. As with **2a**−**c**, the corresponding reactions of tetraallenic stannanes **16a**,**c** and tetrapropargylic stannanes **17c**,**d** with aldehydes **3** (Scheme 5) in methanol at room temperature and with HCl/THF in a limited number of cases were also examined. As expected the room temperature reaction typically proceeded cleanly and in good to excellent yields (Table 5, entries 1, 3, 5, 7, 9, 12−20, and 23−27, 72−88%).

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Table 5. Reaction of Tetraallenic (16a,c) and -propargylic Stannanes (17c,d) with Aldehydes and Acetals

entry	stannane	aldehyde/ acetal	method[a]	product	ratio[b]	yield[c] (%)
1	**16a**	**3a**	A	**18a/19a**	30:70	77
2	**16a**	**3a**	D	**18a/19a**	28:72	85
3	**16a**	**3c**	A	**18c/19c**	30:70	78
4	**16a**	**3c**	D	**18c/19c**	35:65	86
5	**16a**	**3d**	A	**18d/19d**	25:75	79
6	**16a**	**3d**	D	**18d/19d**	50:50	88
7	**16a**	**3e**	A	**18e/19e**	27:73	79
8	**16a**	**3e**	D	**18e/19e**	54:46	86
9	**16a**	**3g**	A	**18g/19g**	81:19[d]	73
10	**16a**	**4d**	E	**18d/19d**	0:100	74
11	**16a**	**4e**	E	**18e/19e**	0:100	78
12	**16c**	**3c**	A	**20c/21c**	85:15	88
13	**16c**	**3d**	A	**20d/21d**	63:37	84
14	**16c**	**3e**	A	**20e/21e**	74:26	80
15	**16c**	**3g**	A	**20g/21g**	82[e]:18[f]	72
16	**17c**	**3a**	A	**22a/23a**	89:11	75
17	**17c**	**3c**	A	**22c/23c**	90:10	85
18	**17c**	**3d**	A	**22d/23d**	83:17	87
19	**17c**	**3e**	A	**22e/23e**	94:6	77
20	**17c**	**3g**	A	**22g/23g**	90[g]:10[h]	75
21	**17c**	**4d**	E	**22d/23d**	100:0	81
22	**17c**	**4e**	E	**22e/23e**	100:0	79
23	**17d**	**3a**	A	**24a/25a**	88:12	79
24	**17d**	**3c**	A	**24c/25c**	93:7	82
25	**17d**	**3d**	A	**24d/25d**	91:9	81
26	**17d**	**3e**	A	**24e/25e**	92:8	83
27	**17d**	**3g**	A	**24g/25g**	90[i]:10	76

[a] Methods: (A) MeOH, rt, 4−24 h; (D) THF/HCl, rt, 24 h; (E) MeOH/TFA, rt, 24 h. [b] Ratios determined by ^{1}H NMR and ^{13}C NMR. [c] Isolated yields. [d] Two diastereomers (68:13) were observed in the ^{13}C NMR spectrum. [e] Two diastereomers (68.4:12.8) of 19 g were observed in the ^{13}C NMR spectrum. [f] Two diastereomers (52:30) were observed in the ^{13}C NMR spectrum. [g] Two diastereomers (46.4:43.8) were observed in the ^{13}C NMR spectrum. [h] Two diastereomers (7.0:2.8) were observed in the ^{13}C NMR spectrum. [i] Two diastereomers (74.8:15.0) were observed in the ^{13}C NMR spectrum.

The addition of aldehydes to tetrapropadienylstannane **16a** was regioselective in favor of the allylically rearranged homopropargylic alcohols **19** but contaminated with up to 30% of the isomeric allenyl alcohols **18**. Tetra(1,2-butadienyl)tin **16c**, however, reacted exclusively with allylic rearrangement to provide diastereomeric homopropargylic alcohols **20** (syn) and **21** (anti) with a predominance of the former (Table 5, entries 12−15, de = 26−70%). Tetra(2-butynyl)tin **17c** yielded a mixture of regioisomers favoring the allylically rearranged allenyl alcohols **22** over the homopropargylic alcohols **23**.

Reactions of **16a** and aldehydes conducted in HCl/THF also proceeded smoothly (Table 5, entries 2, 4, 6, and 8), with modest improvements in reaction yields compared with equivalent reactions conducted at room temperature in methanol. For example, the reaction of **16a** with **3d** in methanol affords **18d** + **19d** in a 79% yield (Table 5, entry 5, 25:75), whereas in HCl/THF **18d** + **19d** were isolated in an 88% yield (Table 5, entry 6, 50:50). Interestingly, with aromatic aldehydes (**3d** and **3e**) reactions conducted in acidic media show preferential formation of the rearranged proparagylic isomers **19**, increasing from 25 to 50% (Table 5, entries 5 and 6 respectively) of the reaction mixture (compared with methanol). The corresponding acetal reactions afford **19d** and **19e** exclusively (Table 5, entries 10 and 11).

With **17c**, the corresponding TFA-mediated additions to acetals **4d** and **4e** also gave rise to a single isomeric

Scheme 6

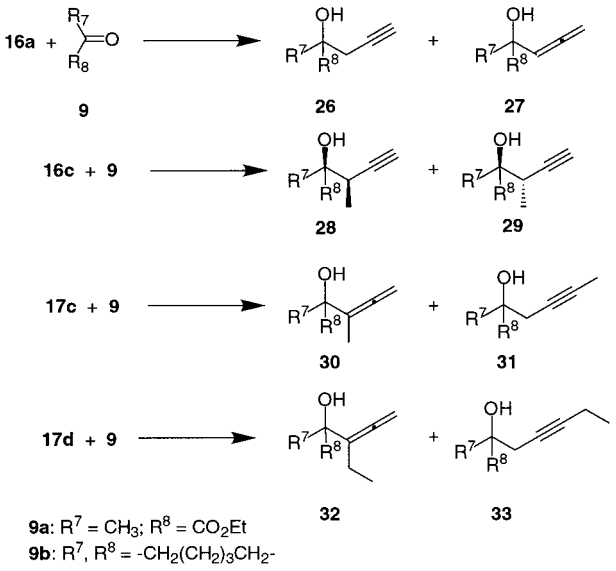

Table 6. Reaction of Tetraallenic (16a,c) and -propargylic Stannanes (17c,d) with Activated Carbonyl Compounds 9a and 9b

stannane	ketone	method[a]	product	ratio[b]	yield (%)
16a	**9a**	A	**26a/27a**	74:26	54[c]
16a	**9b**	B	**26b/27b**	64:34	36
16c	**9a**	A	**28a/29a**	63:37	56[c]
16c	**9b**	B	**28b/29b**		38
17c	**9a**	A	**30a/31a**	100:0	50[c]
17d	**9b**	A	**32a**:**33a**	100:0	52

[a] Methods: (A) MeOH, rt; (B) MeOH reflux. [b] Determined by ^{1}H and ^{13}C NMR. [c] Isolated as the carboxylic acid.

product, in these instances, the allylically rearranged allenyl alcohols **22** (Table 5, entries 21 and 22).

Reaction of Tetraallenic 16a,c and Propargylic Stannanes 17c,d with Ethyl Pyruvate 9a and Cyclohexanone 9b. We have also examined the reactions of tetra- allenic **16a**,**c** and propargylic stannanes **17c**,**d** with activated ketones, with ethyl pyruvate (**9a**), and cyclohexanone (**9b**) (Scheme 6).

Again, for simplicity in analysis, the reactions involving additions to ethyl pyruvate (**9a**) were saponified with NaOH and subsequently neutralized with HCl to afford the corresponding acids in good to excellent yields (Table 6). With **16a**, moderate yields and moderate selectivities were noted with the major homopropargylic alcohol **26** being contaminated with up to 34% of the homoallenyl alcohol **27**, with both **9a** and **9b**. No such contamination was observed with **16c**, with these additions giving rise to moderate diastereoselectivity of syn (**28**) versus anti (**29**), and no allenyl alcohol products were observed. A single product, **28**, was isolated after addition of **16c** to **9b**. Addition of **17c** and **17d** to ethyl pyruvate afforded exclusively the allenyl alcohols **30a** and **32a**, respectively.

Conclusions

We have developed experimentally simple, high yielding and atom economic procedures for the selective addition of unsaturated carbon fragments to carbonyl compounds under a variety of extremely mild conditions. Diastereoselectivities are low, but regioselectivity is generally high, with addition to the γ-position of the allylic triad.

Experimental Section

Materials. All reagents were of commercial quality and were used as received (Aldrich). Solvents were dried and purified using standard techniques. Reactions were monitored by TLC, on aluminum plates coated with silica gel with fluorescent indicator (Merck 60 F_{254}). Boiling points are uncorrected. Unless otherwise noted, NMR spectra were recorded in $CDCl_3$ at 200, 300 or 400 MHz for ^{1}H and at 50, 75 MHz for ^{13}C (Varian Gemini 200 MHz, Bruker Avance 300MX, Varian Unity 400 MHz). Elemental analyses were determined by the University of Strathclyde Microanalysis service and the University of Queensland Microanalysis Service. Mass spectra (*m*/*e*) were obtained in the EI (70 eV) mode at the Organic Mass Spectrometry Facility at the University of Tasmania using a Kratos Analytical Concept ISQ high-resolution mass spectrometer.

General Procedure for Reaction of Tetraallylic, -allenic, and -propargylic Stannanes with Carbonyl Compounds. Method A. The stannane (1.0 mmol) and aldehyde **3** (4.0 mmol) were dissolved in methanol (4 mL) and the mixture stirred at room temperature (ca. 25 °C) for approximately 16−24 h (overnight). Water (10 mL) was then added, and the resulting white precipitates were allowed to settle. The solvent was filtered and the solid was washed with dichloromethane (2 × 10 mL). The aqueous methanol was then extracted with dichloromethane (3 × 15 mL) and the combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The crude allylated product was purified by distillation.

Method B. The stannane (1.0 mmol) and aldehyde **3** (4.0 mmol) were dissolved in methanol (4 mL) and refluxed for 48 h. Water (10 mL) was then added and the resulting white precipitate allowed to settle. The mixture was filtered, and the solid was washed with dichloromethane (2 × 10 mL). The aqueous methanol was then extracted with dichloromethane (3 × 15 mL) and the combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. The crude allylated product was purified by distillation.

Method C. The stannane (1.0 mmol) and dimethyldimethoxystannane (DDS) (0.1 mmol) were dissolved in methanol (4 mL) and stirred at room temperature (ca. 25 °C) for 2 h. Aldehyde **3** (4.0 mmol) was added, and the mixture was refluxed for 24 h. Water (10 mL) was then added to the cooled mixture, and the resulting white precipitates were allowed to settle. The mixture was filtered, and the solid was washed with dichloromethane (2 × 10 mL). The aqueous methanol was then extracted with dichloromethane (3 × 15 mL), and the combined organic extract was dried (Na_2SO_4) and concentrated in vacuo. The crude allylated product was purified by distillation.

Method D. The stannane (1.0 mmol) and aldehyde **3** (4.0 mmol) were dissolved in THF (4 mL). A solution of HCl (0.5 mL, 2 N) was added, and the mixture was stirred at room temperature (ca. 25 °C) for 24 h. A solution of saturated sodium hydrogen carbonate $NaHCO_3$ (10 mL) was added, and the aqueous THF was then extracted with dichloromethane (3 × 15 mL) and the combined organic extract was dried (Na_2SO_4) and concentrated in vacuo. The crude allylated product was purified by distillation.

Method E. The stannane (1.0 mmol) and acetal **4** (4.0 mmol) were dissolved in methanol (4 mL). TFA (0.5 mL) was added, and the mixture was stirred at room temperature (ca. 25 °C) for 24 h. A solution of saturated sodium hydrogen carbonate $NaHCO_3$ (10 mL) was added. The aqueous methanol was then extracted with dichloromethane (3 × 15 mL), and the combined organic extract was dried (Na_2SO_4) and concentrated in vacuo. The crude allylated product was purified by distillation.

Allylation Products. Homoallylic, -allenic, and -propargylic alcohols (**5**−**8**, **10**−**13**, and **18**−**33**) obtained herein were characterized by ^{1}H and ^{13}C NMR spectroscopy, microanalysis, and high-resolution mass spectrometry (where appropriate), and by comparison with literature values: **5a**,[18] **5b**,[19] **5d**,[20] **5f**,[21]

6a,[18b] **7a**,[18b] **6b**,[22] **7b**,[22] **6c**,[23] **7c**,[23] **6d**,[24] **7d**,[24] **6f**,[25] **7f**,[25] **8a**,[18a] **8b**,[26] **8d**,[22,26] **8f**,[27] **11**,[28] **12**,[29] **18a**,[29] **19a**,[29] **18c**,[30] **19c**,[30] **18d**,[20a,31] **19d**,[20a,31] **18e**,[32] **19e**,[32] **20c**,[33] **21c**,[33] **20d**,[34] **21d**,[34] **24d**,[35] **25d**,[35] **26b**,[34] **27b**,[34] **28b**,[34] **29b**.[34]

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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