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THE PREPARATION OF SUBSTITUTED ALLYLLITHIUM REAGENTS FROM ALLYLTIN COMPOUNDS BY TRANSMETALATION *

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Summary

The reaction of substituted allyltrimethyltin compounds with methyllithium in tetrahydrofuran gave substituted allyllithium reagents. Reactions of the latter with trimethylchlorosilane, iodomethane (or benzyl bromide) and carbonyl compounds were examined.

Introduction

Allylic lithium reagents may be prepared by direct lithiation of the appropriate olefin, by lithium metal cleavage of allyl aryl ethers or by the action of an alkyl- or aryl-lithium reagent on an allylic derivative of a heavy metal such as tin, lead to mercury [2,3]. In previous studies we have used the latter route (transmetalation) to prepare allyllithium itself [4] and crotyllithium [5] from the respective allylic tin compound and *gem*-dichloroallyllithium [6] and *gem*-chloro(trimethylsilyl)allyllithium [7] from the respective allylic lead compounds. The transmetalation procedure has some advantages: (1) It does not require the basic additives (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine, hexamethyl phosphoric triamide, potassium t-butoxide, etc.) which must be used in olefin lithiation procedures. (2) It does not produce a nucleophilic co-product such as the lithium aryloxide formed in the allyl aryl ether cleavage method. (3) It can be used to prepare the pure, solid allylic lithium compound, as in our isolation [4] and proton NMR investigation [8] of allyllithium.

Our recent research has made available a number of allylic tin compounds by a Wittig route (Scheme 1) [1], and we have used these products to prepare the derived allylic lithium reagents. We report here the full details of this work.

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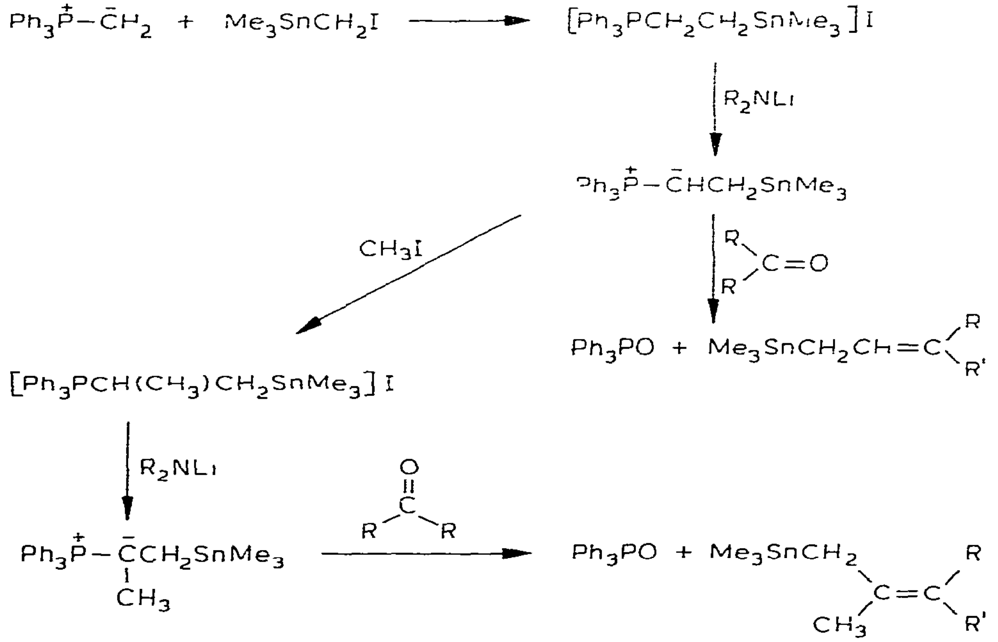
* Dedicated to Professor Henri Normant on the occasion of his 72nd birthday, June 25, 1979. Preliminary communication ref. 1.

Scheme 1

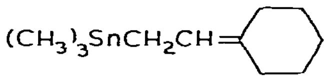


Results and discussion

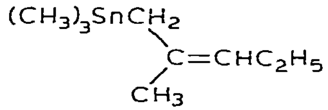
The allylic tin derivatives which were available for this study were the following compounds I (30/70 *cis/trans* isomer ratio), II (*trans* isomer), III and IV (50/50 *E/Z* isomer ratio).

$(CH_3)_3SnCH_2CH{=}CHC_6H_{13}\text{-}n$ (I)

$(CH_3)_3SnCH_2CH{=}CHC_6H_5$ (*trans* isomer) (II)



(III)



$(CH_3)_3SnCH_2C(CH_3){=}CHC_2H_5$

(IV)

The four allylic tin compounds I—IV undergo ready conversion to the respective allylic lithium reagents, as shown for IV in eq. 1. In a typical reaction,

$$Me_3SnCH_2C(CH_3){=}CHC_2H_5 + MeLi \xrightarrow{THF} Li(CH_2C(CH_3)CHC_2H_5) + Me_4Sn \qquad (1)$$

this tin compound, in tetrahydrofuran (THF) solution under nitrogen at 0°C, was treated with 1.1 molar equivalents of methyllithium in diethyl ether. The resulting yellow solution was stirred for 30 min at 0°C and then an excess of acetone was added. After 30 min, hydrolytic work-up was followed by examination of the organic phase by gas chromatography (GLC). It was determined

TABLE 1

REACTIONS OF $Li(CH_2CHCHC_6H_{13})$

Substrate	Product (% yield)	α/γ ratio
Me_3SiCl	$Me_3SiCH_2CH{=}CHC_6H_{13}$ (98)	0/100
CH_3I	$CH_3CH(C_6H_{13})CH{=}CH_2$ (40) $CH_3CH_2CH{=}CHC_6H_{13}$ (45)	47/53
Me_2CO	$Me_2C(OH)CH(C_6H_{13})CH{=}CH_2$ (80) $Me_2C(OH)CH_2CH{=}CHC_6H_{13}$ (13)	86/14
Me_2CHCHO	$Me_2CHCH(OH)CH(C_6H_{13})CH{=}CH_2$ (63) $Me_2CHCH(OH)CH_2CH{=}CHC_6H_{13}$ (28)	69/31
$(CF_3)_2CO$	$(CF_3)_2C(OH)CH(C_6H_{13})CH{=}CH_2$ (30) $(CF_3)_2C(OH)CH_2CH{=}CHC_6H_{13}$ (63)	32/68

that the carbonyl addition product, $(CH_3)_2C(OH)CH(C_2H_5)C(CH_3){=}CH_2$, had been produced in 88% yield

Each allylic lithium compound generated from compounds I—IV was allowed to react with three carbonyl compounds, iodomethane and trimethylchlorosilane The results of these experiments are given in Tables 1—4 and are summarized and compared in Table 5 Excellent product yields were obtained in all reactions and the results compare reasonably well with those reported in the literature for similar reactions of comparable reagents For example, Barbot, Chan and Miginiac [9] conducted a series of reactions of $Li(CH_2\text{-}CHCMeEt)$ with carbonyl compounds, among them $(CH_3)_2CO$, CH_3CHO and $CH_3C(O)CF_3$ They obtained branched/linear (or α/γ) * product ratios of, respectively, 100/0, 70/30 and 0/100 These results obtained with a *gem*-dialkylallyllithium reagent may be compared with those seen with the reagent derived from III, $Li(CH_2CHC(CH_2)_5\text{-cyclo})$, which on reaction witn $(CH_3)_2CO$, $(CH_3)_2\text{-}CHCHO$ and $(CF_3)_2CO$ showed similar α/γ ratios 100/0, 79/21 and 0/100, respectively

Reactions of $Li(CH_2CHCHC_6H_5)$ had been investigated previously by Gerard and Miginiac [10] In reactions of this reagent with $(C_2H_5)_2CO$ and $(CH_3)_2\text{-}CHCHO$ the α/γ product ratios were found to be 63/37 and 62/38, respectively In the present study, this reagent, derived from II rather than from the allylic ether as in the French study [10], reacted with $(CH_3)_2CO$ and $(CH_3)_2CHCHO$, giving α/γ product ratios of 79/21 and 56/44, respectively Finally, Miginiac reported reactions between the monoalkylallyllithium reagent $Li(CH_2CHCHC_2H_5)$ and a number of ketones [11] In the case of its reaction with $n\text{-}C_3H_7C(O)CH_3$ an α/γ ratio of 86/14 was observed The same ratio was obtained in the reaction of the reagent derived from $Li(CH_2CHCHC_6H_{13}\text{-}n)$ (I), in its reaction with

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* When the new C-C bond is formed at the CH_2 terminus of the allylic lithium reagent the product is defined as the γ product when it is formed at the substituted terminus it is defined as the α product

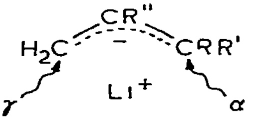


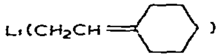
TABLE 2

REACTIONS OF $Li(CH_2CHCHPh)$

Substrate	Product (% yield)	α/γ ratio
Me_3SiCl	$Me_3SiCH_2CH=CHPh$ (96)	0/100
CH_3I	$CH_3CHPhCH=CH_2$ (76)	84/16
	$CH_3CH_2CH=CHPh$ (14)	
Me_2CO	$Me_2C(OH)CHPhCH=CH_2$ (70)	79/21
	$Me_2C(OH)CH_2CH=CHPh$ (19)	
Me_2CHCHO	$Me_2CH(OH)CHPhCH=CH_2$ (54)	56/44
	$Me_2CH(OH)CH_2CH=CHPh$ (43)	
	$(CF_3)_2C(OH)CHPhCH=CH_2$ (20)	
$(CF_3)_2CO$	$(CF_3)_2C(OH)CH_2CH=CHPh$ (67)	24/76

acetone, and an α/γ ratio of 100/0 was obtained in the reaction of the IV-derived reagent, $Li(CH_2CMeCHEt)$, with acetone. Also, Rautenstrauch has studied the reactions of $Li(CH_2CHCMe_2)$ and $Li(CH_2CHCHCH_3)$ with a variety of aldehydes and ketones and observed predominant formation of the new carbon—carbon bond at the substituted terminus of each reagent (α-attack) unless the carbonyl function was highly hindered [12]. A comparison with the results obtained in our previous study of the chemistry of *gem*-dichloroallyllithium also is of interest: here also a reversal in the α/γ product ratio was

TABLE 3

REACTIONS OF 

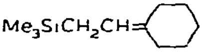
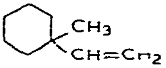
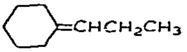
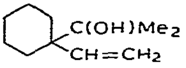
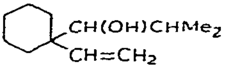
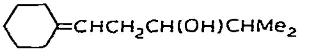
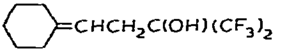
Substrate	Product (% yield)		α/γ ratio
Me_3SiCl		(92)	0/100
CH_3I		(23)	29/71
		(54)	
Me_2CO		(89)	100/0
Me_2CHCHO		(67)	79/21
		(18)	
$(CF_3)_2CO$		(82)	0/100

TABLE 4

REACTIONS OF Li($CH_2CMeCHEt$)

Substrate	Product (% yield)	α/γ ratio
Me_3SiCl	$MeSiCH_2CMe=CHEt$ (91)	0/100
$PhCH_2Br$	$PhCH_2CHEtCMe=CH_2$ (30) $PhCH_2CH_2CMe=CHEt$ (34) $PhCH_2CH_2Ph$ (42)	46/54
Me_2CO	$Me_2C(OH)CHEtCMe=CH_2$ (88)	100/0
Me_2CHCHO	$Me_2CHCH(OH)CHEtCMe=CH_2$ (65) $Me_2CHCH(OH)CH_2CMe=CHEt$ (22)	75/25
$(CF_3)_2CO$	$(CF_3)_3C(OH)CHEtCMe=CH_2$ (33) $(CF_3)_2C(OH)CH_2CMe=CHEt$ (60)	35/65

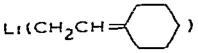
observed on changing the carbonyl reactant from acetone to hexafluoroacetone [6]

The reactions of all of the four allylic lithium reagents which we have studied with trimethylchlorosilane showed exclusive Si—C bond formation at the unsubstituted terminus, an observation made previously with crotyllithium [5], *gem*-dichloroallyllithium [6], trimethylsilylallyllithium [13] and *gem*-chloro (trimethylsilyl)allyllithium [7] This very likely is the result of a steric factor With the unhindered iodomethane, the α/γ product ratios were very reagent-dependent, varying from 86/14 for Li($CH_2CHCHC_6H_5$) to 29/71 for Li($CH_2CHC(CH_2)_5$-cyclo) Generally, the addition of alkyl halides to alkylallyllithium reagents has been to proceed to a greater extent at the less-substituted carbon of the allyl group [3]

Various mechanisms and explanations for the varied regioselectivity of substituted allylic lithium reagents in their reactions with alkylating agents and carbonyl compounds have been discussed in the literature [3,6,7,9,14], but without apparent consensus The rationalization which serves best to account for the results of the present and previous studies involves the hard/soft/acid/base (HSAB) concept of Pearson [15] This approach was applied in our previous discussion of the reactions of *gem*-dichloroallyllithium [6] and used by Barbot, Chan and Miginiac [9] in their more extensive studies of the α/γ regioselectivity

TABLE 5

BRANCHED/LINEAR (α/γ) ADDITION PRODUCT RATIOS

Substrate		Li($CH_2CMeCHEt$)	Li($CH_2CHCHC_6H_{13}$)	Li($CH_2CHCHPh$)
Me_3SiCl	0/100	0/100	0/100	0/100
CH_3I	29/71	46/54 [a]	47/53	84/16
$CH_3C(O)CH_3$	100/0	100/0	86/14	79/21
Me_2CHCHO	79/21	75/25	69/31	56/44
$(CF_3)_2CO$	0/100	35/65	32/68	24/76

[a] $PhCH_2Br$ was used as the alkylating agent since the products of the CH_3I reaction were too low boiling for proper analysis

of substituted allyllithium reagents Discussion of these results in these terms would be meaningful only if we are dealing with products of kinetic control in the reactions of the allylic lithium reagents derived from I—IV with carbonyl compounds. Miginiac and his coworkers have shown that alkyl-substituted allyllithiums react irreversibly with carbonyl compounds [9—11] Phenylallyllithium can add reversibly to C=O compounds, but the reaction conditions used for the Li($CH_2CHCHC_6H_5$) reactions in the present study were those reported by Gerard and Miginiac to give principally kinetic products [10]

Noteworthy is the close agreement in the regioselectivity observed in the reactions of Li($CH_2CHCHC_6H_{13}$-n) and Li($CH_2C(CH_3)CHEt$) The methyl group in the 2-position apparently exerts no significant influence on the course of the reaction If any trend is apparent, it is that the former reagent reacts slightly less at the substituted terminus, which is probably due to the larger bulk of the n-hexyl substituent

It is of interest to consider the stereochemistry of the linear (γ) addition products of these reactions, but before doing so we note that allylic lithium reagents equilibrate in solution [5], so that the stereochemistry of the products should be independent of that of the starting tin compounds

The phenylallyllithium reactions with carbonyl compounds gave linear products of predominantly (>90%) *trans* configuration, in agreement with the observations of Gerard and Miginiac [10] The reaction with trimethylchlorosilane produced a known linear olefin, $Me_3SiCH_2CH{=}CH_2C_6H_5$, the refractive index and NMR spectrum of which matches those for the *trans* isomer as reported by Roberts and Kaissi [16] The linear alcohol derived from the reaction of this reagent with isobutraldehyde also was of a *trans* configuration, with an NMR spectrum matching that reported for this isomer by Gerard and Miginiac [10]. The two linear hexafluoroacetone-derived alcohols were separable by GLC and identified by means of the coupling constants of the olefinic protons ($J_{AB(trans)}$ 16 Hz; $J_{AB(cis)}$ 11 Hz) Again, the *trans* isomer predominated. The major isomers obtained in the other C=O addition reactions also had the *trans* configuration.

The n-hexylallyllithium addition products proved more difficult to analyze since, as with the parent tin compound, I, the isomers were not easily separable by GLC The linear silane derived from the reaction with trimethylchlorosilane was almost exclusively *trans* NMR analysis showed only one Si—Me resonance and its IR spectrum displayed a predominant absorption at 965 cm^{-1} When this compound was prepared by the Wittig reaction [1], both isomers were obtained, each with a slightly different Si—Me resonance One Si—Me peak, therefore, indicates the presence of only one isomer. The 3-decene produced in the iodomethane reaction also was assigned the *trans* configuration on the basis of a prominent IR absorption at 965 cm^{-1}.

The linear alcohols derived from reactions between the carbonyl compounds and n-hexyllithium proved to be mixtures of *cis* and *trans* isomers According to the IR spectrum of the mixture, the *cis* isomer predominated (absence of prominent absorptions in the 965—960 cm^{-1} region). The reactions of Li($CH_2CHCHEt$)

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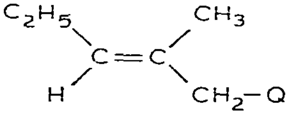
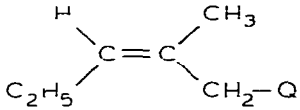
* The discussion of this application of the HSAB approach in ref 6 and 9 is adequete Further discussion as applied to the present cases is given in the Ph D Thesis of R E M (M I T 1977)

with carbonyl compounds also gave a mixture of isomers [11].

The configuration of the trisubstituted olefins resulting from the reactions of $Li(CH_2C(CH_3)CHC_2H_5)$ with carbonyl compounds and with alkylating agents were assigned on the basis of their IR and NMR spectra. Clark [17] has examined a series of trialkylethylenes of type $RCH{=}C(CH_3)R'$ ($R' = CH_3$) and noted that an IR absorption band at 2725 cm^{-1} was characteristic of the *Z* configuration and was absent in the spectra of the *E* isomers. Two groups [18,19], in examining the NMR spectra of the same type of trialkylethylenes (where one alkyl group is methyl), noted that the field position of the methyl substituents on the double bond varied with the geometry of the molecules. The δ-values were seen to be approximately 0.07—0.15 ppm to higher field for the *E* isomer than for the *Z* isomer.



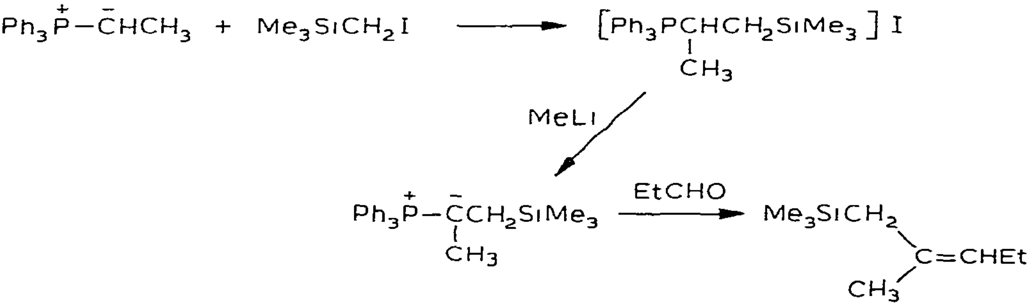
E isomers



Z isomers

The NMR spectrum of the silane product of the $Li(CH_2C(CH_3)CHC_2H_5)/Me_3SiCl$ reaction showed only one $Si—CH_3$ resonance and only one resonance due to a methyl group attached to an olefinic carbon atom. Its IR spectrum showed a band at 2730 cm^{-1}, indicative of the *Z* isomer ($Q = Me_3Si$). A mixture of both *Z* and *E* isomers of this allylic silane was available from a Wittig synthesis (Scheme 2) [1]. The NMR spectrum of this isomer mixture showed the two

Scheme 2



(2)

$Si—CH_3$ resonances, as well as two $=C—CH_3$ methyl resonances which were separated by 0.12 ppm. The single CH_3 resonance of the $Me_3SiCH_2C(CH_3){=}CHEt$ isomer from the organolithium synthesis corresponded to the lower field signal of the pair seen in the spectrum of the isomer mixture, thus confirming its identity as the *Z* isomer. All the other compounds of this series displayed only one methyl resonance in their NMR spectra and an IR absorption in the 2730—2720 cm^{-1} region. On this basis, all were assigned the *Z* configuration.

In the light of the above discussion, it is interesting to note that the preparation of allylic tin and silicon compounds by means of the Wittig reaction, as in Schemes 1 and 2, produces allyl-silanes and -stannanes of varying degrees of isomeric purity [1]. On the other hand, the preparation of allylic silanes by the allyllithium route results in the formation of only one isomer.

The general route illustrated in Scheme 1 for the synthesis of allylic tin compounds should be broadly applicable to the synthesis of allyltins with varied substitution on the α, β and γ carbon atoms of the allyl substituent. Each allyltin compound thus prepared will provide the preparative entry to the corresponding allyllithium reagent

Experimental

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of prepurified nitrogen using rigorously dried solvents Collection of samples for analysis, spectroscopic measurements and refractive index determination and for yield determinations was accomplished using gas chromatography (GLC) Yields were determined using internal standard and empirically determined response factors.

Nuclear magnetic resonance spectra were recorded using a Varian Associates T60 or an Hitachi—Perkin—Elmer R20B spectrometer. Proton chemical shifts are reported in δ units ppm from internal tetramethylsilane Infrared spectra were obtained using a Perkin—Elmer Model 457A grating infrared spectrophotometer.

Methyllithium was purchased from Alfa Division, Ventron Corp The carbonyl compounds were commercial products (Eastman or Aldrich) and were used as received or purified if necessary. The allylic tin compounds were prepared as described in ref. 1.

The new compounds prepared during the course of this study, together with their physical properties, spectroscopic characterizing data and their analyses, are listed in Table 6. Known compounds were identified by comparing their refractive indices and NMR and IR spectra with literature data

The reactions of allylic tin compounds with methyllithium Reactions of the allylic lithium reagents

A few examples of such reactions are given

Reaction of trimethyl(2-nonenyl)tin with methyllithium, trimethylchlorosilane quench A 500 ml, three-necked Morton flask which was fitted with a mechanical stirrer, nitrogen inlet tube and a no-air stopper, was charged with 1.55 g (5.37 mmol) of $Me_3SnCH_2CH{=}CHn\text{-}C_6H_{13}$ (70/30 *trans/cis* isomer ratio, by NMR) and 200 ml of dry THF and cooled in an ice bath. Subsequently, 3.20 ml of 1.88 *M* methyllithium in diethyl ether (5.90 mmol, 10% excess) was added dropwise over a 3—4 min period. The solution immediately turned bright yellow. The resulting mixture was stirred for 30 min at ice bath temperature and then 1 26 ml (ca. 10 mmol) of trimethylchlorosilane was added rapidly The yellow color was discharged and the mixture was stirred at room temperature for 30 min. Subsequently it was trap-to-trap distilled (0 03 mmHg at room temperature) into a receiver cooled to —78°C. An aliquot of the distillate was removed for GLC analysis and the remainder was concentrated at reduced pressure. GLC analysis (General Electric Co SE30 silicone rubber gum, 20% on Chromosorb P, at 120°C) showed the presence of 5 26 mmol (98%) of *trans*-$Me_3SiCH_2CH{=}CHn\text{-}C_6H_{13}$.

TABLE 6

NEW COMPOUNDS

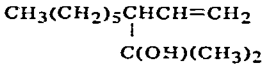
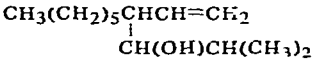
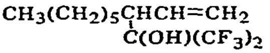
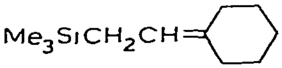
Compound	n_D^{25}	Analysis (Found (calcd) (%))		^1H NMR (in CCl_4) δ (ppm)
		Carbon	Hydrogen	
$Me_3SiCH_2CH=CHC_6H_{13}$ n (*trans* isomer)	1 4395	72 45 (72 64)	13 25 (13 21)	0 18 (s 9 H Me_3Si) 0 85—1 68 (m 13 H) 1 85—2 65 (m 2 H) 5 18—5 48 (m 2 H)
$CH_3CH_2CH=CH(CH_2)_5CH_3$ (*trans* isomer)	1 4233	85 70 (85 63) (mixture with 3-methyl-1-nonene)	14 37 (14 37)	0 77—1 50 (m 14 H) 1 77—2 23 (m 4 H) 5 17—5 45 (m 2 H)
$CH_2=CHCH(CH_3)(CH_2)_5CH_3$	1 4174			0 77—1 38 (m 16 H) 1 70—2 40 (m 1 H) 4 67—6 00 (m 3 H)
 $CH_3(CH_2)_5\underset{\displaystyle C(OH)(CH_3)_2}{\underset{\vert}{C}}HCH=CH_2$	1 4472	78 30 (78 20) (mixture with 1-methyl-4-undecen-2-ol)	13 00 (13 12)	0 70—1 53 (m 20 H) 1 67—2 00 (m, 1 H) 4 82—5 61 (m, 3 H)
$CH_3(CH_2)_5CH=CHCH_2C(OH)(CH_3)_2$ (*cis/trans* mixture)	1 4482			0 78—1 57 (m 18 H) 1 92—2 25 (m 4 H) 5 33—5 58 (m 2 H)
$CH_3(CH_2)_5CH=CHCH_2CH(OH)CH(CH_3)_2$ (*cis/trans* mixture)	1 4512	78 72 (78 73) (mixture with 2-methyl-4-vinyl-decan-3-ol)	13 21 (13 19)	0 58—1 52 (m, 18 H) 1 52—2 25 (m, 5 H), 2 98—3 42 (m 1 H) 5 22—5 58 (m 2 H)
 $CH_3(CH_2)_5\underset{\displaystyle CH(OH)CH(CH_3)_2}{\underset{\vert}{C}}HCH=CH_2$	1 4476			0 52—2 33 (m, 22 H) 3 03—3 23 (m 1 H) 4 67—5 97 (m 3 H)
$CH_3(CH_2)_5CH=CHCH_2C(OH)(CF_3)_2$ (*cis/trans* mixture)	1 3863	49 48 (49 32) (mixture with 1,1-bis-(trifluoromethyl)-2-vinyloctan-1-ol)	6 19 (6 21)	0 67—1 55 (m 17 H), 1 88—2 28 (m, 2 H), 2 55—2 82 (m 3 H), 5 18—5 98 (m, 2 H)
 $CH_3(CH_2)_5\underset{\displaystyle C(OH)(CF_3)_2}{\underset{\vert}{C}}HCH=CH_2$	1 3882			0 67—1 50 (m 13 H) 1 65—2 00 (m 1 H) 2 78 (s 1 H OH) 5 33—5 60 (m 3 H)
	1 4676	72 56 (72 44)	12 27 (12 15)	0 03 (s 9 H) 1 38—1 68 (m 6 H includes d at 1 40 *J* 9 Hz $SiCH_2CH$) 1 93—2 25 (m, 4 H), 5 05 (t *J* 9 Hz, 1 H)

TABLE 6

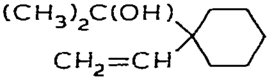
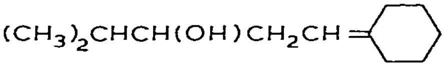
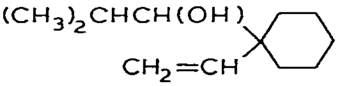
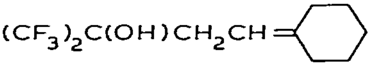
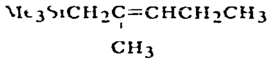
Compound	n_D^{25}	Analysis (Found (calcd.)) (%)		^{1}H NMR (in CCl$_4$) δ (ppm)
		Carbon	Hydrogen	
	1.4862	78.24 (78.51)	12.01 (11.98)	1.08 (s, 6 H), 1.23 (s, 1 H, OH), 1.08—1.92 (m, 10 H), 4.78—5.87 (m, 3 H)
	1.4718	79.22 (79.06) (mixture with 1-(1-vinylcyclohexyl)-2-methylpropanol	11.87 (12.16)	0.77—2.25 (m, 20 H), 2.98—3.25 (m, 1 H), 5.03 (t, J 7 Hz, 1 H)
	1.4773			0.58—2.05 (m, 18 H), 3.02—3.15 (m, 1 H), 4.78—5.95 (m, 3 H)
	1.4069	47.73 (47.83)	5.36 (5.11)	1.38—1.77 (m, 6 H), 2.02—2.37 (m, 4 H), 2.67 (d, J 8 Hz, 2 H), 2.73 (s, 1 H, OH), 5.12 (t, J 8 Hz, 1 H)
$C_6H_5CH{=}CHCH_2C(OH)(CH_3)_2$ (*trans* isomer)	solid m.p. 40—41°C	81.93 (81.77) (mixture with 2-methyl-3-phenyl-4-penten-2-ol)	9.17 (9.15)	1.20 (s, 7 H, Me and OH), 2.27 (d, J 6 Hz, 2 H), 6.10—6.48 (m, 2 H), 7.15 (s, 5 H)
$CH_2{=}CHCH(C_6H_5)C(OH)(CH_3)_2$	1.5225			1.08 and 1.12 (s, 3 H each), 1.18 (s, 1 H, OH), 3.13 (d, J 9 Hz, 1 H), 4.82—6.40 (m, 3 H)
$CH_2{=}CHCH(C_6H_5)C(OH)(CF_3)_2$	1.4380	50.60 (50.72) (mixture with 1,1-bis(trifluoromethyl)-2-phenyl-3-butenol is isomers)	3.87 (3.55)	2.87 (s, 1 H, OH), 3.90 (d, J 10 Hz, 1 H), 5.00—5.40 (m, 2 H), 5.85—6.72 (m, 1 H), 7.28 (s, 5 H)
$C_6H_5CH{=}CHCH_2C(OH)(CF_3)_2$ (*trans* isomer)	1.4601			2.83 (s, 1 H, OH), 2.85 (d, J 7 Hz, 1 H), olefinic AB 6.12 (d of t, 1 H) and 6.58 (d, J 7 Hz), J_{AB} 16 Hz, 7.32 (s, 5 H)

TABLE 6 (continued)

Compound	n_D^{25}	Analysis (Found (calcd) (%)) Carbon	Hydrogen	^{1}H NMR (in CCl$_4$) δ (ppm)
C$_6$H$_5$CH=CHCH$_2$C(OH)(CF$_3$)$_2$ (cis isomer)				2 78—3 11 (broad s 1 H OH) 2 94 (d, J 8 Hz 2 H) olefinic AB 5 44 (d of t 1 H) and 6 51 (d J 8 Hz 1 H) J_{AB} 11 Hz 7 27 (s 5 H)
$\mathrm{Me_3SiCH_2\underset{CH_3}{C}{=}CHCH_2CH_3}$ (Z isomer)	1 4352	69 27 (69 14)	13 01 (12 89)	0 08 (s 9 H) 0 97 (t J 7 Hz 3 H) 1 42—2 22 (m 2 H) 1 50 (s 2 H) 1 68 (s 3 H) 4 97 (t J 7 Hz 1 H)
CH$_3$CH$_3$CH=C(CH$_3$)CH$_2$CH$_2$C$_6$H$_5$ (Z isomer)	1 5041	89 12 (89 59) (mixture with 2-methyl-4-ethyl-4-phenyl-1-butene)	10 60 (10 41)	0 83 (t J 7 Hz 3 H) 1 67 (s, 3 H) 1 78—4 48 (m 6 H) 5 03 (t J 7 Hz 1 H) 7 08 (s 5 H)
CH$_2$=C(CH$_3$)CH(C$_2$H$_5$)CH$_2$C$_6$H$_5$	1 5061			0 77 (t J 7 Hz 3 H) 1 05—1 55 (m 2 H) 1 60 (s 3 H) 1 85—2 32 (m 1 H) 2 47—2 68 (m 2 H) 4 48—4 72 (m 2 H) 7 05 (s 5 H)
CH$_3$CH$_2$CH=C(CH$_3$)CH$_2$CH(OH)CH(CH$_3$)$_2$ (Z isomer)	1 4488	76 80 (76 86) (mixture with 2 5-dimethyl-3-ethyl-1-hexen-4-ol)	12 89 (12 90)	0 72—2 28 (m 18 H) 3 15—3 52 (m 1 H) 4 98—5 38 (m, 1 H)
CH$_2$=C(CH$_3$)CH(C$_2$H$_5$)CH(OH)CH(CH$_3$)$_2$ (1/1 mixture of diastereomers)	1 4463			0 58—2 25 (m 18 H) 3 00—3 33 (m 1 H), 4 65—5 03 (m 2 H)
CH$_3$CH$_2$CH=C(CH$_3$)CH$_2$C(OH)(CF$_3$)$_2$ (Z isomer)	1 3716	43 14 (43 21) (mixture with 1 1-bis-(trifluoromethyl)-3-methyl-2-ethyl-3-buten-1-ol)	4 91 (4 83)	0 98 (t J 7 Hz 3 H) 1 82 (s, 3 H) 1 85—2 22 (m 2 H) 2 68 (s 2 H) 2 80 (s 1 H OH) 5 55 (t J 7 Hz 1 H)
CH$_2$=C(CH$_3$)CH(C$_2$H$_5$)C(OH)(CF$_3$)$_2$	1 3733			0 85 (t, J 7 Hz, 3 H), 0 95—1 45 (m 2 H) 1 52—1 98 (m 1 H) 1 77 (s, 3 H), 3 00 (s, 1 H, OH), 4 98—5 32 (m 2 H)

Reaction of trimethyl(2-cyclohexylideneethyl)tin with methyllithium, iodomethane quench The lithium reagent was prepared using the above procedures from 1.93 g (7.07 mmol) of the tin compound III in 200 ml of THF and 7.78 mmol of methyllithium To the resulting yellow solution was added rapidly 2.6 ml (ca. 40 mmol) of iodomethane. After the reaction mixture had been stirred for 30 min at room temperature, it was trap-to-trap distilled (0.07 mmHg at room temperature) GLC analysis of the concentrated distillate showed the presence of two products 3.82 mmol (54%) of n-propylidenecyclohexane, whose NMR [20] and IR [21] spectra were in agreement with published spectra, and 1.63 mmol (23%) of 1-methyl-1-vinylcyclohexane, n_D^{20} 1.4505 (Lit. [22] n_D^{20} 1.4512), whose NMR spectrum matched that in the literature [22]

Reaction of trimethyl(3-phenylallyl)tin with methyllithium, hexafluoroacetone quench The lithium reagent was prepared by the above procedure from 1.465 g (5.21 mmol) of *trans*-$Me_3SnCH_2CH=CHPh$ in 200 ml of THF and 5.70 mmol of methyllithium in diethyl ether at 0°C, a deep red-orange solution resulted The no-air stopper was replaced with a Dewar condenser filled with dry ice/acetone. Hexafluoroacetone (Peninsular Chem Research) was dried by passing the gas through columns filled with anhydrous calcium sulfate and anhydrous calcium chloride and then was condensed into the reaction flask. The quantity of hexafluoroacetone used was roughly twice the amount necessary to completely discharge the color of the reagent solution After the reaction mixture had been stirred at room temperature for 3 h it was hydrolyzed by addition of 50 ml of water. The mixture was extracted with pentane and the organic layer back-extracted with water. The organic layer was dried and concentrated at reduced pressure GLC analysis of the residue showed the presence of two products 3.23 mmol (62%) of *trans*-1,1-bis(trifluoromethyl)-4-phenyl-3-butanol and 1.04 mmol (20%) of 1,1-bis(trifluoromethyl)-2-phenyl-3-butenol.

Acknowledgments

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