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STANNYLDIENES, NEW TOOLS FOR ORGANIC SYNTHESIS. PREPARATION AND REACTIVITY.

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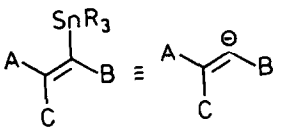
Summary. Tributylstannyl-1,3-dienes could be considered synthetic equivalents of conjugated dienic anions. The preparation of differently substituted 2- and 3-trialkylstannyl-1,3-dienes is reported starting from propargyltrimethylsilane. The position of the stannyl moiety on the dienic skeleton can be controlled by hydrostannylation of (trimethylsilyl)propargyl alcohols or stannyl cupration of (trimethylsilyl)propargyl ketones. The so obtained stannyldienes are submitted to Diels Alder reaction and the corresponding cycloadducts functionalized through the C-Sn bond. Stannyldienes are also suitable for a regiocontrolled transfer of the dienic structure by : a)tin-lithium exchange and further reaction with aldehydes to give conjugated dienic alcohols; b)coupling with acyl chlorides in the presence of palladium catalysts to give conjugated dienic ketones; c) $AlCl_3$ promoted reaction with acyl chlorides to give allenic ketones.

The chemistry of vinylstannanes[1] is of considerable importance since a variety of compounds containing the olefinic or the 1,3 dienic unit have been prepared using this class of compounds[2]. The development of such reagents in recent times can be explained with their stability to different agents as water, air, acids and bases, silica gel, that is relatively high for an organometallic species and that allows more easy procedures working with them as the possibility of long time storage. Analogously there have been developed methods that allow the selective functionalization of the C-Sn bond of vinylstannanes. They undergo a stereospecific Sn-Li exchange,[3] in the presence of methyllithium or butyllithium, to generate the highly reactive vinyllithium species, or they can be also successfully used in cross coupling reactions with organic halides catalyzed by palladium.[4] The foregoing observations warrant the following equality

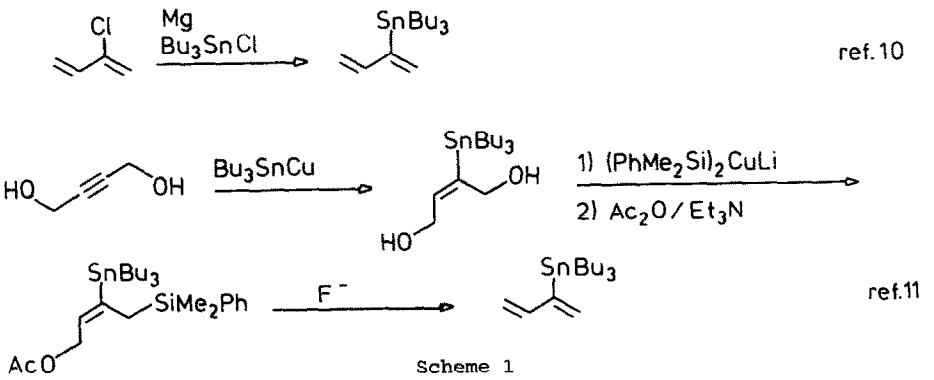


which presents a vinylstannane as a synthetic equivalent of a vinyl carbanion.

The same observations can be extended to conjugated dienes carrying a stannyl group, so that the access to stannyldienes opens a way to the synthetically attractive class of conjugated dienic anions. The possibility to use specifically functionalized 1,3-dienes is moreover attractive, particularly if such functional group can either activate the diene and is able to undergo subsequent elaboration.[5] 2-Stannyl- and 3-stannyl-1,3-dienes[6] accomplish well the previously described tasks. They are synthetic equivalents of 1,3-dienic anions,[7] species otherwise accessible with difficulty.[8] They can be also used in Diels Alder reactions with further elaboration of the vinylstannanes so obtained through the C-Sn bond.[9]

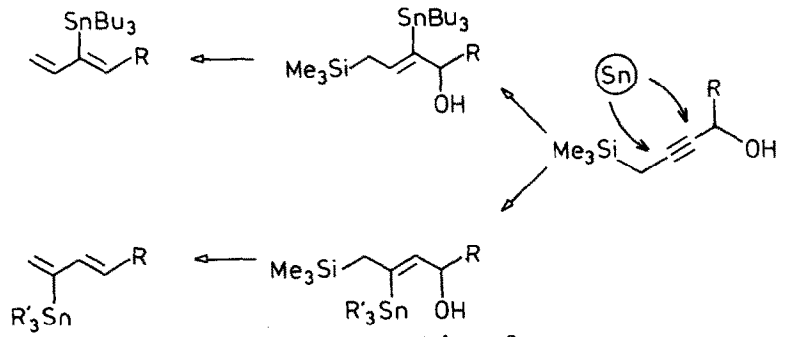
We report here our strategies for the preparation of 2- and 3-stannyl-1,3-dienes with different substituents in the position 4 of the conjugated system, and a complete study on their reactivity which shows the potential and the limitations in the use of this class of organostannanes in organic synthesis.

2-Tributylstannyl-1,3-butadiene was prepared[10] by coupling of the Grignard reagent obtained from chloroprene and chlorotributylstannane, or by stannyl cupration[11] of 2-butyn-1,3-diol followed by silyl cupration and subsequent 1,4 elimination reaction. (Scheme 1)



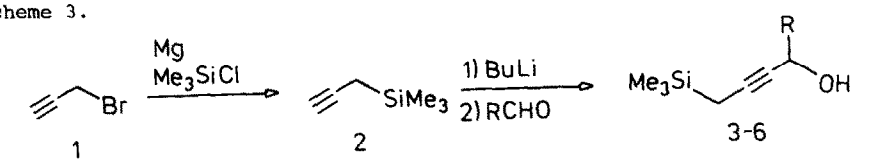
Scheme 1

To carry out a general synthesis of differently substituted stannyldienes we looked carefully to the second method identifying the last reaction as the key step for this preparation. To perform the 1,4 elimination of an acetate and a trimethylsilyl groups we needed to introduce in a regiocontrolled way the tin moiety on a propargylsilane. (Scheme 2)



Scheme 2

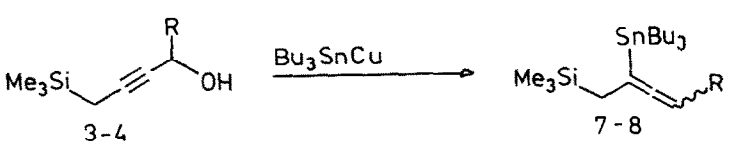
We prepared the trimethylsilylpropargylic alcohols **3-6** by coupling of the lithium salt of trimethylpropargylsilane **2** with several aldehydes as described in Scheme 3.



3 R=H (51%). 4 R=CH_3 (76%). 5 R=C_3H_7 (66%). 6 R=C_6H_5 (90%).

Scheme 3

Surprisingly, first attempts to perform a stannyl cupration on **3** and **4** gave very poor yields of the stannyl allenes **7** and **8**, and no traces of the expected vinylstannanes. (Scheme 4)



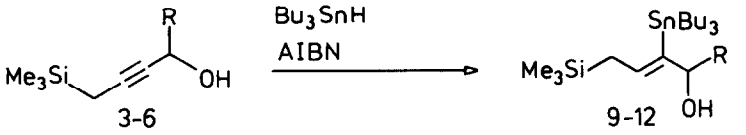
7 R=H (5%). 8 R=CH_3 (9%)

Scheme 4

The increased hindrance of **3** respect to 2-butyn-1,4-diol and the presence of a

single OH (probably not sufficient to move the equilibrium towards the products[12]) can explain the lack of reactivity of **3** in comparison with the propargylic diol used in ref. 11.

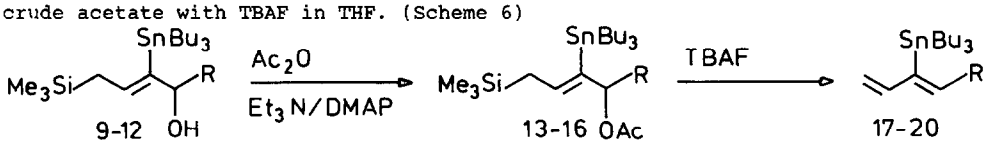
The tributylstannyl moiety was introduced by hydrostannylation of propargylic alcohols **3-6** with tributylstannyl hydride at 60°-70°C for 1-4 h in the presence of catalytic amounts of AIBN. (Scheme 5)



9 R=H (71%). 10 R=CH_3 (63%). 11 R=C_3H_7 (76%). 12 R=C_6H_5 (65%).

Scheme 5

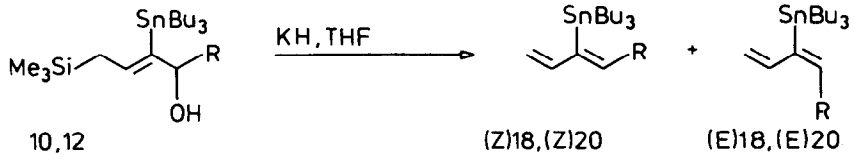
The reaction described in Scheme 5 presented a good regio- and stereoselectivity[13] because the Z product with the tributylstannyl group in the position close to the oxygen was obtained. After transformation of the alcohols **9-12** into the corresponding acetates **13-16** with acetic anhydride, triethylamine and catalytic amounts of DMAP, we accomplished the 1,4 Peterson elimination treating the crude acetate with TBAF in THF. (Scheme 6)



13,17 R=H (66%). 14,18 R=CH_3 (92%). 15,19 R=C_3H_7 (65%). 16,20 R=C_6H_5 (70%).

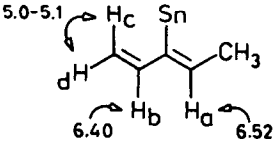
Scheme 6

This reaction resulted very efficient, giving, in 10-30 minutes at room temperature, a quantitative conversion of the acetates **13-16** into dienes **17-20** which were isolated by column chromatography on silica gel. After purification, compounds **18**, **19** and **20** resulted formed respectively by a mixture of the Z and the E isomers in a ratio respectively of 8:1, 10:1 and 15:1. The high stereocontrol of the fluoride induced elimination of the trimethylsilyl and the acetate group was proved by the result of the KH induced elimination performed on alcohols **10** and **12** which gave 25% ca. of an approximately 1:1 mixture of Z and E **17** and **20**. (Scheme 7)



Scheme 7

The comparison between the ^1H NMR of the products obtained from the acetates and the products obtained from the alcohols made the correct attribution of (Z)-**17-20** easier. Looking to the spectrum of **18**, selective decoupling of the methylic



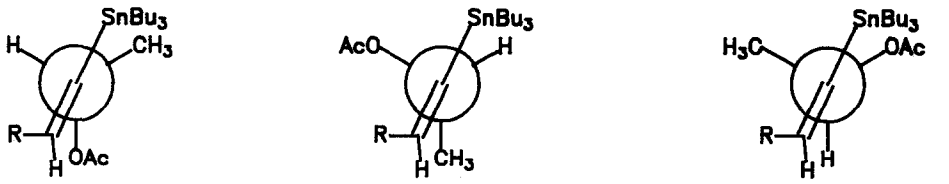
protons indicated that the terminal protons H_c and H_d showed a higher field frequencies whereas the internal protons H_a and H_b were respectively at 6.40 and 6.52 ppm. In the other isomer obtained with the elimination catalyzed by KH, the same protons had a chemical shifts of 6.7-6.9 ppm, typical[14] of internal protons in a dienic system with the E configuration. Moreover the ^1H-^{119}Sn J value found for H_a resulted of 110 Hz, confirming the Z configuration of the product arising from the TBAF induced elimination.

From a Z-allylsilyl alcohol (as **10**, **11** and **12**) a Z diene (as **18**, **19** and **20**) was predominantly obtained and the merit of this stereocontrol can be ascribed to the presence of the tin. Analogous eliminations carried out on allylsilanes **21** and **22** gave mainly a mixture of the Z and the E dienes **23** and **24**. (Scheme 8)

21,23 R=H (E/Z 1.2/1). 22,23 R=CH_3 (E/Z 1/1.3).

Scheme 8

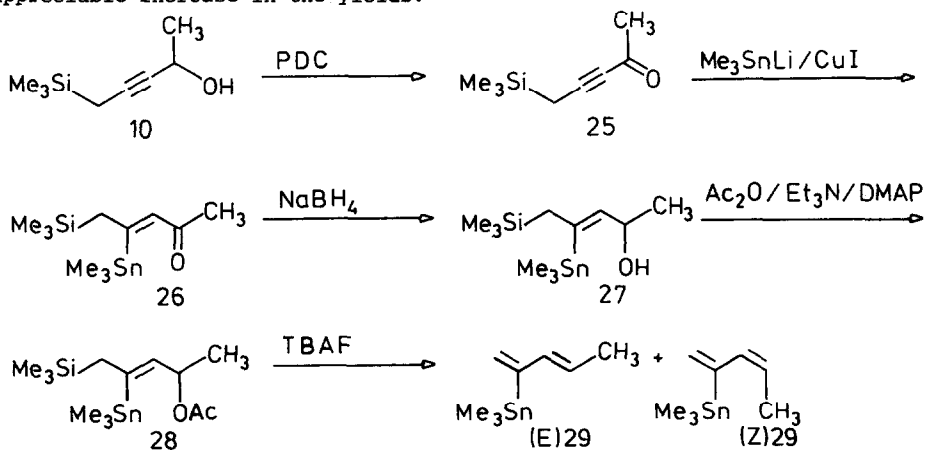
An interpretation of this behavior was attempted regarding the tributylstannyl group as a "masked proton with no effective steric interactions" due to the long C-Sn bond. Assuming that TBAF attack the trimethylsilyl group with subsequent elimination of the acetate ion, it should be possible to describe the system as in Scheme 9 where the Newmann projections of the possible conformations are reported.



Scheme 9

If we consider the tributylstannyl group sufficiently far away to really interact with the substituents at C_4, the only destabilizing interaction should be between the proton at C_2 and the substituents at C_4, with the higher populated conformation (formula C in Scheme 9) that gave the Z isomer.

The synthesis of the 1,3-dienes with the tin in the other "internal" position was also accomplished (Scheme 10). Trimethylpropargylsilane **10**, the same starting material employed in the preparation of **18-20**, was oxidized to the propargylic ketone **25** with PDC in CH_2Cl_2. Yields were not very good (40% ca) and attempts to use other oxidizing reagents (PCC, PCC/$Me_3SiOOSiMe_3$, CrO_3/pyridine) did not give appreciable increase in the yields.[15]



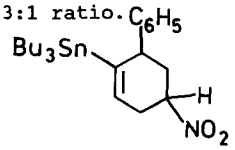
Scheme 10

Ketone **25** underwent 1,4 conjugated addition with trimethylstannyllithium (prepared from chlorotrimethylstannane and lithium shots in THF) in the presence of 10% molar amounts of CuI, to give the ß-stannyl-α,ß-unsaturated ketone **26**, isolated as a crude and directly reduced to the alcohol **27**. The stannyl derivative **22** was the Z isomer as revealed by the sharp singlet at 6.52 ppm of the proton α

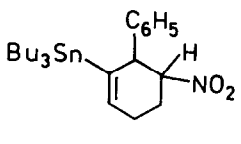
to the CO, which showed also a (^{1}H-^{119}Sn)J = 125 Hz, typical of a trans H-Sn relation. After acetylation of **27** with acetic anhydride, triethylamine and catalytic amounts of DMAP, TBAF induced 1,4-elimination to give 2-trimetylstannyl-1,3-pentadiene **28** as a mixture of Z and E isomers approximately in a 1:1 ratio.

The possibility to realize the functionalization of these stannyldienes was then studied. For the cycloaddition reactions compounds **17,18** and **20** were used because they were isomerically pure.

Cycloaddition reaction of **17, 18** and **20**, and a variety of dienophiles including an enone, an enol ether and an acetylenic ester were conducted without solvent at room temperature or at 80°-100°C, or in toluene solution containing boron trifluoride etherate at 0°C. The development of the reaction was monitored by tlc analysis and after 2-15 h, the reaction mixture was subjected to silica gel chromatography to separate the adducts. The results of these cycloaddition reactions are reported in Table I. The structural and stereochemical assignments of the cycloadducts were based on complete spectroscopic data. Characteristic ^{1}H and ^{119}Sn NMR spectroscopic parameters for these substances allowed the assignments of relative stereochemistry at the chiral centers of these adducts. The absence of a detectable ^{1}H-^{119}Sn coupling constant for the proton at C_4 in products **32, 35, 36** and **39**, suggested that we were in the presence of the 1-4 derivatives. In fact in the case of product **39** we obtained a mixture of the 1-4 (**39a**) and the 1-3 (**39b**) adducts in a 3:1 ratio.



39a

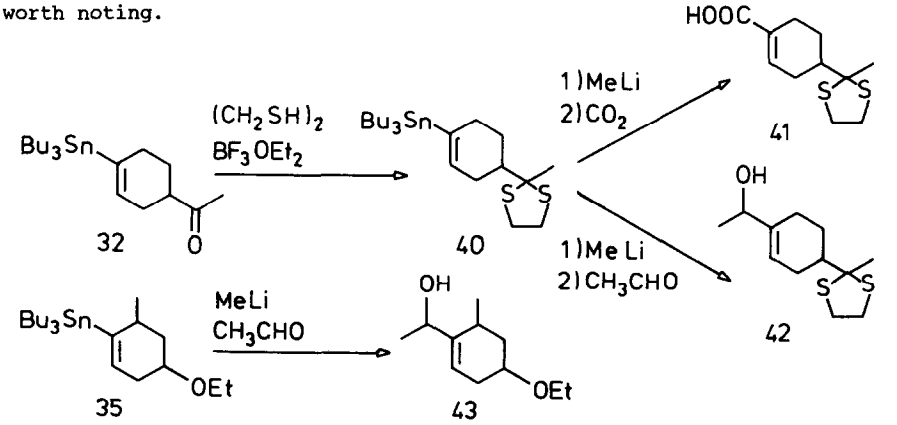


39b

It was possible to detect a (^{1}H-^{119}Sn)J = 35 Hz for the minor component, absent in the case of the major, suggesting that this last was the 1-4 adduct. Comparison of the ^{1}H NMR and the ^{119}Sn NMR spectra of **39** with that of **32, 36** and **38** allowed to us to make the assignment reported in Table I.

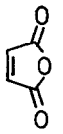
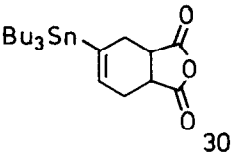
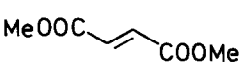
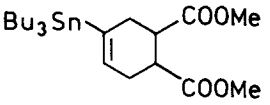
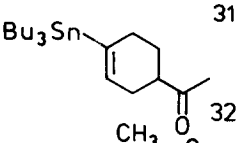
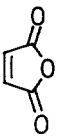
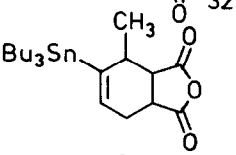
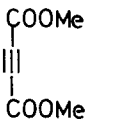
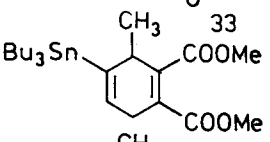
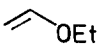
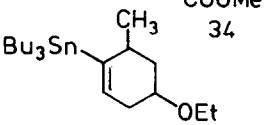
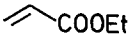
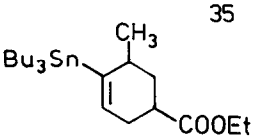
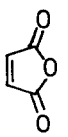
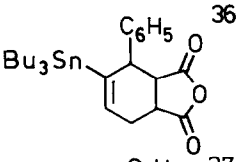
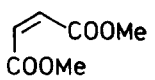
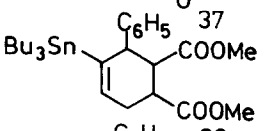
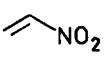
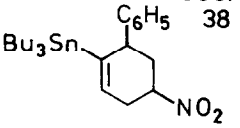
Tributylstannyl-1,3-dienes did not present a different reactivity from other 2-substituted dienes. They have a similar reactivity to the analogous silyl derivatives[16], showing also a higher regioselectivity under the action of boron trifluoride etherate. The Lewis acid has a noteworthy effect in the reaction with non symmetrical dienophiles as the presence of the methyl or the phenyl group in position 4 on the dienic system, that disfavor the formation of the 1,3 (*meta* like) adduct. Unfortunately the presence of boron trifluoride etherate generally induced a decrease of the yields, probably for the instability of the substituted diene to acidic conditions.

The further transformation of the stannylcyclohexenes through the Sn-C bond is worth noting.



Scheme 11

TABLE I Cycloaddition reactions of dienes **17**, **18** and **20**.

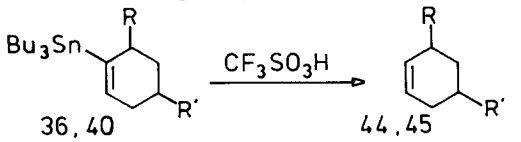
Diene	Dienophile	Reaction Conditions	Products	Yields[a]
17		Neat, r.t., 2 h	 30	75%
17		Neat, 100°C, 8 h	 31	69%
17		BF_3 OEt_2, Toluene, 0°C, 3h	 32	55%[b]
18		Neat, 80°, 12 h	 33	68%
18		Neat, 80°, 12 h	 34	81%
18		Benzene, Reflux, 9 h	 35	62%[c]
18		BF_3 OEt_2, Toluene 0°, 5 h	 36	20%[d]
20		Neat, 80°C, 2 h	 37	66%
20		Neat, 100°, 10 h	 38	40%
20		Toluene, Reflux, 2 h	 39	49%[e]

a)Yields of products isolated by column chromatography and fully characterized. b)Ratio between the *trans*-1,4 and the 1,3 isomers 8:1 (by ^{119}Sn NMR).c)Ratio between the *cis*-1,4 and the 1,3 isomers 5:1 (by ^{119}Sn NMR). d)Ratio between the *cis*-1,4 and the 1,3 isomers 6:1 (by ^{119}Sn NMR). e)Ratio between the 1,4 and the 1,3 isomers 3:1 (by ^{119}Sn NMR).

From adducts **32** and **35** it was possible to generate the corresponding lithium derivatives "via" Sn-Li exchange with methyllithium in ether/THF at -78°C and the following reaction with suitable electrophiles afforded compounds **41, 42** and **43** as reported in Scheme 11. Electrophiles had to be very reactive towards the lithium salts. In the reaction of **32** with methyllithium followed by addition of acetone or allyl bromide, only **32** was recovered, and no traces of the destannylated derivative **44** was also detected.

In line of principle other possible developments of these adducts, especially in the presence of functional groups incompatible with the use of lithiated reagents, could be the coupling with organic halides in the presence of palladium catalysts[17] or reactions in the presence of radical initiators[18], but they were not tried at this stage of the work.

Destannylation occurred only in moderate yields with trifluoromethansulfonic acid in THF to give products **44** and **45**. (Scheme 12)

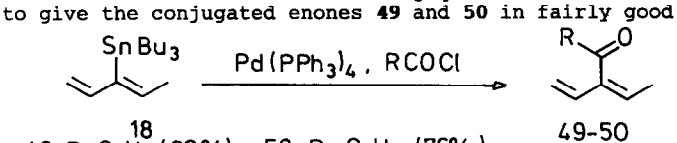


40, 44 R=H, R'= . 36, 45 $R=CH_3$, R'=COOEt

Scheme 12

Much more complex resulted the reaction of stannyldienes with electrophiles. Tin-lithium exchange worked well only in the case of compound **17** giving the products described in Table II. The presence of the allenic alcohols was strictly related to the solvent employed and their amounts, negligible using THF, increased with the presence of hexane. Attempts to perform the Sn-Li exchange with the substituted stannyldienes **18, 19** and **20** did not give appreciable results, we obtained mainly the starting materials.

The introduction of an electrophile was possible only using the Stille[17] procedure, in the presence of $Pd(PPh_3)_4$ and acyl chlorides as reported in Scheme 13, to give the conjugated enones **49** and **50** in fairly good yields.

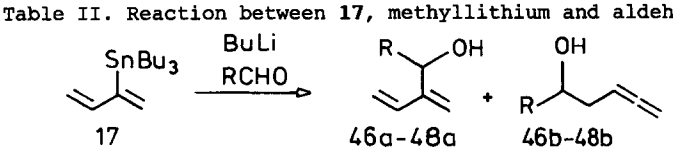


18
49 $R=C_6H_5$ (82%). 50 $R=C_6H_{13}$ (76%).

Scheme 13

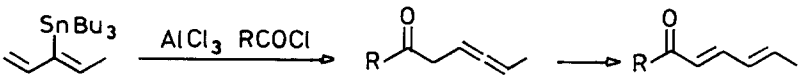
Acyl chlorides reacted with stannyl dienes also in the presence of $AlCl_3$ to give the allenic derivatives **51-53** as described in Scheme 14.

Table II. Reaction between **17**, methyllithium and aldehydes.



46a, 46b $R=C_6H_5$. 47a, 47b $R=C_6H_{13}$. 48a, 48b $R=(CH_3)_2CH$

Aldehyde	Reaction conditions	Products	Ratio	Yields
C_6H_5CHO	THF, -78°C, 2 h	**46a 46b**	9 : 1	62%
C_3H_7CHO	THF, -78°C, 2 h	**47a 47b**	10 : 1	55%
C_3H_7CHO	THF/Hexane, -78°C, 3 h	**47a 47b**	3 : 1	73%
$(CH_3)_2CHCHO$	THF, -78°C, 3 h	**48a 48b**	9 : 1	73%
$(CH_3)_2CHCHO$	THF/Hexane, -78°C, 3 h	**48a 48b**	2 : 1	62%
$(CH_3)_2CHCHO$	Hexane, -50°, 6 h	**48a 48b**	1 : 1	41%



18 51-53 54-56

51,54 R= C_3H_7 (51%) . 52,55 R= $(CH_3)_2CH$ (49%) . 53,56 R= C_6H_5 (59%).

Scheme 14

This reaction was performed by slow addition at -20°C of the stannyl diene to a dark red solution obtained adding at 0°C the acyl chloride to $AlCl_3$ dispersed in toluene. After few minutes the color changed to pale yellow and the solution was treated with ethanol and directly submitted to silica gel chromatography. Products **51-53** were isolated in appreciable yields, sometimes together with the dienyl ketones **54-56**, in which the allenic derivatives could be quantitatively transformed by treatment with triethylamine/DMAP in THF/ethanol. Finally no attempts have been made to use dienes **17-20** in free radical induced reactions.

EXPERIMENTAL SECTION

Propargyltrimethylsilane (2). In a 4 necked 1000 mL flask, equipped with mechanical stirrer, dropping funnel, thermometer and condenser, Magnesium turnings (14.6 g, 0.6 mol) were covered with dry ether (60 mL) under nitrogen atmosphere. To this stirred mixture $HgCl_2$ (0.2 g) was added followed by propargyl bromide (6 g, 0.05 mol) in a single portion. After few minutes the reaction started (the solvent become dark and started to boil), the flask was cooled to 20°C and propargyl bromide (65.4 g, 0.55 mol) in dry ether (400 mL) was added at such a rate to maintain the internal temperature of the flask at 20°C (±2°C). At the end of the addition the stirring was continued for 20 minutes. The flask was cooled at 0°C and chlorotrimethylsilane (65 g, 0.6 mol) was added during 30 minutes. The mixture was than stirred at room temperature for 12 h and, after cooling at 0°C, a saturated solution of ammonium chloride (50 mL) was added, followed by diethyl ether (100 mL). The ethereal layer was separated, dried on anhydrous magnesium sulfate and the solvent carefully evaporated under vacuum. The residual yellow oil was fractionated collecting the fraction boiling at 90°-92°C, and obtaining 36 g of **2** (57% yield). ^1H NMR ($CDCl_3$) δ 0.3 (s, 9H, Me_3Si), 1.65 (d, 2H, J=2Hz, CH_2), 1.90 (t, 1H, J=2Hz, CH)ppm.

Preparation of (Trimethylsilyl)propargyl Alcohols. General Procedure. 1-(Trimethylsilyl)-2-butyn-4-ol (3). To a solution of 2 (11.2 g, 0.1 mol) in dry THF (60 mL) at -78°C, butyllithium (62.5 ml of a 1.6 M solution in diethyl ether, 0.1 mol) was added dropwise with a syringe. After 10 min. at this temperature, gaseous formaldehyde, generated by depolymerization of trioxymethylene (90 g, 1 mol), at 180°C, was carried over through a wide glass tube, into the mixture by a slow current of dry nitrogen. Then the mixture was allowed to warm to room temperature for 3 h and it was treated with 30 mL of a saturated ammonium chloride solution and then poured into 50 mL of diethyl ether. The ethereal layer was separated and dried over anhydrous sodium sulfate. Evaporation of the solvent and final distillation gave the alcohol (**3**). Obtained 7.3 g (51% yield) , b.p. 170-172°C/105 mmHg; ^1H NMR (CCl_4) δ 0.50 (s, 9H, Me_3Si), 1.9 (m, 2H, CH_2), 3.47 (s, 1H, OH), 4.5 (m, 2H, CH_2O-)ppm. The resultant product is 98% pure according to glc analysis.

1-(Trimethylsilyl)-2-pentyn-4-ol (4) . Distillation gave (**4**). Obtained 12 g (76% yield), b.p. 100-102°C/25 mmHg. ^1H NMR (CCl_4) δ 0.43 (s, 9H, Me_3Si), 1.7 (m, 5H, CH_3CH_2), 2.97 (s, 1H, OH), 4.7 (m, 1H, CH-O)ppm. The resultant product is 95% pure (glc analysis).

1-(Trimethylsilyl)-2-heptyn-4-ol (**5**). Distillation gave (**5**). Obtained 4 g (66% yield), b.p. 125-127°C/55 mmHg. ^{1}H NMR (CCl_4) δ 0.43 (s, 9H, Me_3Si), 1.2 (m, 5H, CH_3, CH_2), 1.8 (m, 4H, CH_2Si, CH_2), 2.57 (s, 1H, OH), 4.5 (m, 1H, CH)ppm. The product is pure (glc analysis).

1-(Trimethylsilyl)-4-phenyl-2-butyn-4-ol (**6**). Distillation gave (**6**). Obtained 21 g (90% yield), b.p. 109-111°C/0.04 mmHg. ^{1}H NMR (CCl_4) δ 0.20 (s, 9H, Me_3Si), 1.57 (d, 2H, J=3Hz, CH_2), 2.5 (s, 1H, OH), 5.4 (m, 1H, CH-O), 7.3-7.6 (m, 5H, Arom.)ppm. The resultant product is 98% pure (glc analysis).

Stannyl Cupration of (Trimethylsilyl)propargyl Alcohols. General Procedure. 1-(Trimethylsilyl)-2-(tributylstannyl)-2,3-pentadiene (**8**). Lithium diisopropylamide (5.2 mmol) in dry THF (10 mL) and tributylstannyl hydride (1.5 g, 5.1 mmol) were stirred at 0°C for 30 minutes. The mixture was then cooled at -50°C and copper(I) bromide/dimethyl sulfide complex (1.0 g, 5.1 mmol) added in small portions. The dark red solution was kept at -50°C for 30 minutes, and then cooled at -78°C. 1-(Trimethylsilyl)-2-pentyn-4-ol (**4**) (0.78 g, 5.0 mmol) in THF (1 mL) was added stirring and the mixture kept at -78°C for 6 h. Ammonium chloride solution (3 mL) is added followed by diethyl ether. After the usual work up glc/mass analysis showed the presence of starting material and little amounts of **8**. Mass spectrum m/z 428(M^+), 155, 73(base).

Hydrostannylation of Propargyl Alcohols 2-19 . General Procedure. (Z)-1-(Trimethylsilyl)-3-(tributylstannyl)-2-penten-4-ol (**10**). The reaction was performed in a sealed tube. Tributylstannyl hydride (0.7 mmol), **4** (1.44 g, 9.2 mmol) and AIBN (3 mg,0.02 mmol), were heated at 60°C for 1 h. ^{1}H NMR analysis of the crude product mixture showed the quantitative reduction of **4**. Vinylstannane (**10**) was isolated by column chromatography on silica gel with hexane : ethyl acetate (11:1). Obtained 2 g (63% yield). ^{1}H NMR ($CDCl_3$) δ 0.0 (s, 9H, Me_2Si), 0.7-1.7 (m, 33H, Bu_3Sn, CH_3CH_2 and OH), 4.2 (m, 1H, CH-O), 6.08 (t, 1H, J=6Hz, CH=)ppm.

(Z)-1-(Trimethylsilyl)-3-(tributylstannyl)-2-buten-4-ol (**9**). 71% Yield ^{1}H NMR ($CDCl_3$) δ 0.0 (s, 9H, Me_3Si), 0.8-1.5 (m, 30H, Bu_3Sn, CH_2Si and OH), 3.97 (s, 2H, CH_2O), 6.07 (t, 1H, J=7Hz, CH=)ppm.

(Z)-1-(Trimethylsilyl)-3-(tributylstannyl)-2-hepten-4-ol (**10**). 76% Yield. ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9H, Me_3Si), 0.7 (m, 7H, CH_3, CH_2 and CH_2Si), 1.4 (m, 28H, Bu_3Sn and OH), 4.03 (s, 1H, CHO), 6.06 (t,1H, J=7Hz, CH=)ppm.

(Z)-1-(Trimethylsilyl)-3-(tributylstannyl)-4-phenyl-2-buten-4-ol (**11**). 65% Yield. ^{1}H NMR ($CDCl_3$) δ 0.08 (s, 9H, Me_3Si), 0.6-1.7 (m, 30H, Bu_3Sn, CH_2 and OH), 5.18 (s, 1H, CH-O), 6.18 (t, 1H, J=7Hz, CH=), 7.3 (m, 5H, Arom.)ppm.

Preparation of Acetates 13-16. General Procedure. (Z)-1-(Trimethylsilyl)-3-(tributylstannyl)-4-acetyl-2-butene (**13**). Alcohol **9** (11.9 g, 27 mmol), was dissolved in dry dichloromethane (25 mL) and cooled at 0°C. To this solution was added DMAP (0.03 g, 0.3 mmol), triethylamine (10.6 mL, 73 mmol), and, after 5 minutes and very slowly, acetic anhydride (3.5 mL, 33.7 mmol). The mixture was stirred at room temperature for 1 h, then cooled at 0°C and a solution of HCl 10% (5 mL) was added. The ethereal layer was separated, dried on anhydrous sodium sulfate and the solvent evaporated. A glc analysis showed that the crude was sufficiently pure to be used directly in the following step without any purification. Obtained 11. 5 g of **9**, 89% yield.

Preparation of (Tributylstannyl)-1,3-dienes. General Procedure. 2-(Tributylstannyl)-1,3-butadiene (**17**). To a solution of the acetyl derivative **13** (9 g, 19.6 mmol) in dry THF (20 mL) at 0°C, TBAF (6.2 g, 19.6 mmol) was added in small portions. The mixture was warmed to room temperature and the stirring continued until tlc analysis showed the disappearance of the starting material. Hexane (80

mL) was added and the organic layer separated from the yellow oil so formed. The hexane solution was then washed with water and the organic layer dried on anhydrous sodium sulfate. After evaporation of the solvent the product was purified by column chromatography on silica gel (eluant hexane). Obtained 4.4 g of **17**. (66% yield). ^{1}H NMR ($CDCl_2$) δ 0.9-1.7 (m, 27H, Bu_3Sn), 5.1-6.0 (m, 4H, 2 CH=), 6.7 (m, 1H, CH=)ppm. Mass spectrum m/z : 342.7(M^+), 232.6(base).

3-(Tributylstannyl)-1,3-pentadiene (**18**). 92% Yield. ^{1}H NMR ($CDCl_3$) δ 0.8-1.6 (m, 27H, Bu_3Sn) 1.7 (d, 3H, J=6Hz, CH_3), 4.7 (m, 1H, CH=), 4.8 (m, 1H, CH=), 6.4 (m, 1H, CH=), 6.5 (m, 2H, CH=)ppm. Mass spectrum m/z : 357.1(M^+), 232.6(base).

3-(Tributylstannyl)-1,3-heptadiene (**19**). 65% Yield. ^{1}H NMR (CCl_4) δ 0.7-2.0 (m, 32H, Bu_3Sn, CH_2, CH_3), 2.1 (m, 2H, CH_2), 4.9 (m, 1H, CH=), 5.0 (m, 1H, CH=), 6.6 (m, 2H, 2CH=)ppm. Mass spectrum m/z : 385.2(M^+), 232.6(base).

2-(Tributylstannyl)-1-phenyl-1,3-butadiene (**20**). 70% Yield.^{1} H NMR (CCl_4) δ : 0.7-2.0 (m, 27H, Bu_3Sn), 5.1 (m, 1H, CH=), 5.2 (m, 1H, CH=), 6.6 (m, 2H, 2CH=), 7.2 (m, 5H Arom.)ppm. Mass spectrum m/z : 419.2(M^+), 232.6(base).

Preparation of (Tributylstannyl)-1,3-dienes in the Presence of KH. Potassium hydride (0.26 g of a 33% dispersion in mineral oil, 2.3 mmol) was washed with hexane, then covered with dry THF (5 mL) and to this mixture, cooled at 0°C, alcohol **10** (1 g, 2.3 mmol) was added slowly. The mixture was refluxed for 24 h, cooled at -20°C and water (3 mL) added dropwise followed by diethyl ether (10 mL). The organic layer was separated and dried on anhydrous sodium sulfate. After evaporation of the solvent column chromatography on silica gel (eluant hexane) gave **18** as a mixture of the Z and the E isomers. Obtained 0.2 g, 25% yield. (E)-**19**. ^{1}H NMR ($CDCl_3$) δ 0.8-1.6 (m, 27H, Bu_3Sn) 1.7 (d, 3H, J=6Hz, CH_3), 4.6 (m, 1H, CH=), 5.0 (m, 1H, CH=), 6.8 (m, 2H, 2CH=)ppm.

1-(Trimethylsilyl)-2-pentyn-4-one (**25**). To a solution of propargyltrimethylsilane **2** (3.0 g, 27.6 mmol) in dry THF (20 mL), under nitrogen at -78°C, butyllithium (16.7 mL of a 1.6 M solution in hexane, 26.7 mmol) was added slowly and the solution stirred for 1 h. Ethyl acetate (1.18 g, 13.4 mmol) was added, immediately followed by boron trifluoride etherate (3.5 g, 24.4 mmol). The mixture was stirred for 30 minutes at -78°C, then a saturated solution of ammonium chloride (15 mL) was added, the organic layer separated and dried on anhydrous magnesium sulfate. After evaporation of the solvent, the product was purified by column chromatography on Florisil (eluant hexane/ethyl acetate 8/1) to give **25**. Obtained 2 g (50% yields). ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9H, Me_3Si), 1.55 (s, 2H, CH_2), 2.05 (s, 3H, CH_3)ppm. IR (neat) 2980, 2190, 1670, 1250 cm^{-1}). Mass spectrum m/z 139(M^+-15), 73(base).

(Z)-1-(Trimethylsilyl)-2-(trimethylstannyl)-2-penten-4-one (**26**). Lithium shots (0.5 g, 7.1 mmol) was dispersed in THF (10 mL) in a flask equipped with a mechanical stirrer, under nitrogen at 0°C. A solution of chlorotrimethylstannane (1.4 g, 7.1 mmol) in THF (10 mL) was added slowly and the mixture stirred at room temperature overnight. The green dark solution containing trimethylstannyllithium was added, "via cannula", to a solution of ketone **25** (1 g, 6.5 mmol) and copper-(I) iodide (0.13 g, 0.7 mmol) cooled at 0°C. The reaction mixture was stirred at room temperature for 3 h, then a saturated solution of ammonium chloride (5 mL) was added, followed by diethyl ether (20 mL). The ethereal layer was separated, washed with water and brine and dried on anhydrous magnesium sulfate. After evaporation of the solvent the crude resulted sufficiently pure to be use directly in the next step. Obtained 1.7 g, 83% yield. ^{1}H NMR ($CDCl_3$) δ 0.21 (s, 18H, Me_3Si, Me_3Sn), 2.1 (m, 5H, CH_3, CH_2), 6.52 (s, 1H, CH=)ppm. IR (neat) 2980, 1660, 1250, 960 cm^{-1}. Mass spectrum M/z 303(M^+-15), 155(M^+-$SnMe_3$), 73(base).

(Z)-1-(Trimethylsilyl)-2-(trimethylstannyl)-2-penten-4-ol (**27**). Sodium borohy-

dride (1.1 g, 30 mmol) was dissolved in methanol (10 mL) and to this mixture, cooled at 0°C, a solution of the stannyl ketone **26** (4.5 g, 30 mmol) in THF (5 mL) was added slowly and the mixture stirred at room temperature for 2 h. The mixture was hydrolyzed with a saturated solution of ammonium chloride, extracted with diethyl ether and the organic layer was separated and washed with brine. After drying and evaporation of the solvent, the product was purified by column chromatography on silica gel (eluant hexane/ethyl acetate 8/1) to give 8.5 g of **27** (88% yields). ^{1}H NMR ($CDCl_3$) δ 0.3-0.6 (m, 18H, Me_3Si, Me_3Sn), 1.4-1.7 (m, 5H, CH_2, CH_3), 3.9-4.2 (m, 1H, OH), 4.3-4.6 (m, 1H, CH-O), 6.0-6.3 (m, 1H, CH=)ppm. IR (neat) 3300-3500, 2950, 1250 cm^{-1}. Mass spectrum 320(M^+), 315, 73.

2-(Trimethylstannyl)-1,3-pentadiene (**29**). 65% Yield. ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 9H, Me_3Sn), 1.7 (d, 3H, J=8Hz, CH_3), 4.9 (m, 1H, CH=), 5.1 (m, 1H, CH=), 6.6 (m, 1H, CH=), 6.8 (m, 1H, CH=)ppm. Mass spectrum m/z 230(M^+), 215, 163, 41(base).

Thermal Cycloaddition of Stannyldienes. General Procedure. 4-(Tributylstannyl)-3-methyl-4-cyclohexen-1,2-dicarboxyl anhydride (**33**). The stannyldiene **18** (0.8 g, 2.2. mmol) and maleic anhydride (0.2 g, 2.2 mmol) were mixed in a sealed tube in presence of hydroquinone (10 mg) and the mixture heated at 80°C for 3 h. The mixture was dissolved in ether, the solution dried on anhydrous sodium sulphate, the solvent evaporated and the adduct **33** was isolated by column chromatography on silica gel. Obtained 0.6 g (61% yield). The characterization of the product is reported in Table III.

Cycloaddition of Stannyldienes in the Presence of Boron Trifluoride Etherate. General Procedure. 4-(Tributylstannyl)-3-methyl-4-cyclohexenyl-ethylcarboxylate (**36**). Ethyl acrilate (0.2 g, 2 mmol) in toluene (4 mL) was cooled at -78°C and boron trifluoride etherate (0.28 g, 2 mmol) was added slowly. To this solution stannyldiene **18** (0.8 g, 2.2 mmol) was added and the mixture warmed to 0°C and stirred 2 h. The solution was then poured on sodium carbonate (2 g), the solvent separated, evaporated and the product **36** isolated by column chromatography on silica gel (eluant hexane/ethyl acetate 1/1). Obtained 0.18 g (20% yield). The characterization of the product is reported in Table III

2-[1-(Tributylstannyl)-1-cyclohexen-4-yl]-2-methyl-1,3-dithiolane (**40**). A solution containing the adduct **28** (0.7 g, 1.65 mmol), ethandithiol (0.17 g, 1.8 mmol) and boron trifluoride etherate (5 mL) in benzene (10 mL) was refluxed for 10 h. To this mixture water was added followed by a saturated solution of sodium carbonate. The organic layer was separated, dried on anhydrous magnesium sulfate, and the solvent evaporated. The crude resulted sufficiently pure to be used in the next steps.

Functionalization of Stannyl Cycloadducts. General Procedure. 2-[1-Carboxy-1-cyclohexen-4-yl]-2-methyl-1,3-dithiolane (**41**). To a solution of **40** (0.7 g, 1.43 mmol) in dry THF (2mL), cooled at 0°C and under nitrogen, methyllithium (1mL of a 1.6 M solution in diethyl ether, 1.6 mmol), was added and the yellow solution was stirred at 0°C for 3 h. After cooling to -78°C, dry ice (CO_2) was added and the mixture raised to room temperature. Ethyl acetate (10 mL) was added and the organic layer washed with a saturated solution of ammonium chloride and brine. After separation of the solvent, drying on anhydrous magnesium sulfate and evaporation of the solvent, compound **41** was isolated by PTLC (eluant ethyl acetate). Obtained 0.2 g (56% yield). ^{1}H NMR ($CDCl_3$) δ 1.9 (m, 3H, CH_2, CH), 2.1 (s, 3H, CH_3), 2.2 (m, 4H, $2CH_2$), 2.7 (m, 4H, $2CH_2S$), 5.9 (m, 1H, CH=), 10.0 (s, 1H, COOH)ppm. IR (KBr) 3200-2800, 2960, 1670, 960 cm^{-1}. Mass spectrum 244(M^+), 226, 132(base). Calcd. C 54.06 H 6.60; Found C 54.67 H 6.58.

2-[1-(1-Ethanol-1-yl)-1-cyclohexen-4-yl)-2-methyl-1,3-dithiolane (**42**). 66% Yield ^{1}H NMR ($CDCl_3$) 1.8 (m, 3H, CH_2, CH), 2.0 (d, 2H, J=8Hz, CH_3), 2.2 (m, 7H, CH_3, $2CH_2$), 2.6 (m, 4H, $2CH_2S$), 3.0 (s, 1H, OH), 3.9 (m, 1H, CH), 6.3 (m, 1H, CH=)ppm.

Table III. Analytical data of cycloadducts **30-39**.

Product	^{1}H NMR ($CDCl_3$) δ	^{119}Sn NMR	Elemental Analysis
30	0.8-1.8 (m, 27H, Bu_3Sn), 1.9-2.5 (m, 4H, $2CH_2$), 3.1 (m, 2H, CHCO), 6.1 (m, 1H, CH=).	-66.6	Calcd. C 54.45; H 7.75 Found C 54.65; H 7.70
31	0.6-1.8 (m, 27H, Bu_3Sn), 1.9-2.7 (m, 6H, $2CH_2$, CH(4), CH(5)), 3.3 (s, 6H, Me), 6.2 (m, 1H,CH=).	-60.0	Calcd. C 54.23; H 8.27 Found C 54.65; H 8.20
32	0.9-1.7 (m, 29Hm Bu_3Sn, CH_2), 2.1 (s, 3H, CH_3), 2.2 (m, 2H, CH_2C=), 2.4 (m, 3H, CH_2CSn, CHCO), 5.8 (m, 1H, CH=).	-55.6	Calcd. C 58.42; H 8.82 Found C 58.92; H 8.67
33	0.4-1.6 (m, 30H, Bu_3Sn, CH_3), 2.2-2.8 (m, 3H, CH_2, CH(3)), 3.0-3.4 (m, 2H, CH(1), CH(2)), 6.1 (m, 1H, CH=).	-69.7	Calcd. C 55.41; H 7.97 Found C 55.97; H 7.50
34	0.4-1.7 (m, 30H, Bu_3Sn, CH_3), 2.7-3.0 (m, 3H, CH_2, CH), 3.41 (s, 3H, CH_3), 3.50 (s, 3H, CH_3), 7.0 (s, 1H, CH=).	-74.9	Calcd. C 55.24; H 8.25 Found C 55.85; H 8.07
35	0.6-1.9 (m, 33H, Bu_3Sn, $2CH_3$), 2.5-2.8 (m, 4H, $2CH_2$), 3.7 (q, 2H, J=8Hz, OCH_2), 4.1 (m, 1H, CH-O), 7.0 (m, 1H, CH=).	-61.0	Calcd. C 58.76; H 9.86 Found C 58.98; H 9.23
36	0.9-1.8 (m, 35H, Bu_3Sn, $2CH_3$, CH_2), 2.2-2.7 (m, 4H, CH_2C=, 2CH), 3.9 (q, 2H, J=9Hz, OCH_2), 6.4 (m, 1H, CH=).	-58.9	Calcd. C 57.78; H 9.26 Found C 57.98; H 9.12
37	0.6-1.7 (m, 27H, Bu_3Sn), 2.8-3.0 (m, 3H, CH(3), CH_2), 3.2 (m, 2H, 2CH), 6.9 (m, 1H, CH=), 7.3 (m, 5H, Arom.).	-87.8	Calcd. C 60.37; H 7.40 Found C 60.87; H 7.10
38	0.7-1.8 (m, 27H, Bu_3Sn), 2.6-2.9 (m, 3H, CH(3), CH_2), 3.1 (m, 2H, 2CH), 3.8 (s, 3H, CH_3), 3.9 (s, 3H, CH_3), 6.7 (m, 1H, CH=), 7.2 (m, 5H, Arom.).	-81.9	Calcd. C 59.71; H 7.87 Found C 60.09; H 7.00
39	0.6-1.9 (m, 29H, Bu_3Sn, CH_2), 2.5-2.9 (m, 3H, CH_2, CH), 4.9 (m, 1H, $CHNO_2$), 6.3 (m, 1H, CH=).	-86.8	Calcd. C 60.52; H 8.25 Found C 60.79; H 8.07

Mass spectrum 244(M^+), 211, 41(base). Calcd. C 58.97; H 8.25 Found C 59.12; H 8.33.

1-(Ethanol-1-yl)-4-ethoxy-6-methyl-1-cyclohexene (43). 72% Yield. ^{1}H NMR ($CDCl_3$) δ 1.1 (t, 3H, J=8Hz, CH_3), 1.6-2.9 (m, 11H, $2CH_2$, $2CH_3$, CH), 3.0 (bs, 1H, OH), 3.4 (q, 2H, J=8Hz, OCH_2), 3.9 (m, 1H, CH-O), 4.1 (m, 1H, CH-O), 5.9 (m, 1H, CH=) ppm. Mass spectrum 184(M^+), 44(base). Calcd. C 71.69%; H 10.94 Found C 71.43; H 11.09.

Destannylation of the Stannyl Cycloadducts. General Procedure. 2-(1-Cyclohexen-4-yl)-2-methyl-1,3-dithiolane (44). To a solution of the stannylcyclohexene **40** (0.1 g) in THF (1 mL), cooled at 0°C, trifluoromethanesulfonic acid (0.1 mL) was added slowly and the dark solution stirred at room temperature overnight. Glc/mass analysis showed the disappearance of the starting material and the formation of the destannylated product. **40** mass spectrum m/z 200(M^+), 185, 134(base).

Reaction Between 2-(Tributylstannyl)-1,3-butadiene, Butyllithium and Aldehydes. General Procedure. 2-Methylene-1-phenyl-3-buten-1-ol[7] **(46a).** To a solution of butyllithium (3 mmol) in THF (3 mL), cooled at -78°C, under nitrogen and magnetic stirring, stannyldiene **17** (0.85 g, 2.5 mmol) was added and the mixture was stirred at -78°C for 2 h. The solution became deep yellow and to that benzaldehyde (0.31 g, 3 mmol) was added in a single portion. The color of the solution disappeared immediately, and after 10 minutes, a saturated solution of ammonium chloride (1 mL) was added followed by diethyl ether, and the organic layer separated. After drying on anhydrous magnesium sulfate, the solvent was evaporated and product **46** isolated by column chromatography on silica gel (eluant hexane/ethyl acetate 1/2). The product isolated was composed by **46a** and **46b** (ratio determined by glc analysis). Obtained 0.26 g, (62% yield). ^{1}H NMR ($CDCl_3$) δ 2.3 (bs, 1H, OH), 4.5 (d, 1H, J=11 Hz, CH=), 5.1 (d, 1H, J=18 Hz, CH=), 5.3 (m, 3H, CH_2, CH), 6.3 (m, 1H, CH=), 7.3 (m, 5H, Arom.)ppm. Mass spectrum m/z 160(M^+), 79(base).

3-Methylene-1-decen-4-ol (47a). ^{1}H NMR ($CDCl_3$) δ 0.9 (m, 3H, Me), 1.1-1.9 (m, 10H, CH_2), 2.5 (bs, 1H, OH), 4.4 (m, 1H, CH), 5.0 (d, 1H, J=11 Hz, CH=), 5.2 (bs, 2H, CH_2), 5.3 (d, 1H, J=15Hz, CH=), 6.3 (m, 1H, CH=)ppm. Mass spectrum m/z 168 (M^+), 83(base).

3-Methylene-5-methyl-1-hexen-4-ol (48a). ^{1}H NMR ($CDCl_3$) δ 1.1 (d, 6H, J=5Hz, CH_3), 1.4 (m, 1H, CH), 3.1 (bs, 1H, OH), 4.3 (m, 1H, CH), 5.2 (d, 1H, J=15Hz, CH=), 5.3 (m, 3H, CH_2, CH=), 6.3 (m, 1H, CH=)ppm. Mass spectrum m/z 126(M^+), 43(base).

6-Methyl-1,2-heptadien-5-ol (48b). ^{1}H NMR ($CDCl_3$) The diagnostic signals are: 2.23 (m, CH_2), 4.7 (m, $=CH_2$)ppm. IR (neat) 1950, 1050 cm^{-1}. Mass spectrum m/z 126(M^+), 75(base).

Reaction of Stannyldienes in Presence of Palladium Catalysts. General Procedure. 2-(1-Ethen-1-yl)-1-phenyl-2-buten-1-one (50). In a flask, $Pd(PPh_3)_4$ (6 mg) was submitted to a vacuum-nitrogen treatment. Dry toluene (1 mL) was added followed by benzoyl chloride (35 mg, 0.25 mmol) and diene **18** (100 mg, 0.28 mmol). The mixture was refluxed until tlc analysis showed disappearance of the starting material. The solution was directly deposed on a PTLC plate eluted with hexane/ethyl acetate 3/1 to give **49**. Obtained 35 mg, 82% yield. ^{1}H NMR ($CDCl_3$) δ 1.83 (d, 3H, J=6Hz, CH_3), 4.7 (m, 1H, CH=), 5.0 (m, 1H, CH=), 5.9 (m, 1H, CH=), 6.4 (m, 1H, CH=), 7.3 (m, 5H, Arom.)ppm.

Reaction of Stannyldienes in Presence of $AlCl_3$ and Acyl Chlorides. General Procedure. 2,3-Nonadienyl-6-one (51). Aluminum trichloride (0.4 g, 3 mmol) was dispersed in toluene (5 mL), cooled at -20°C and diene **18** (1 g, 3 mmol) was added. After 5-15 minutes ethanol (5 mL) was added and the mixture directly deposed on a PTLC, eluted with hexane/ethyl acetate 8/1 to give product **51**. Obtained 0.27 g (51% yield) . ^{1}H NMR ($CDCl_3$) δ 1.2 (m, 3H, CH_3), 1.4-1.9 (m, 7H, $2CH_2$, CH_3), 3.6 (d, 2H, J=5 Hz, CH_2C=), 5.6 (m, 1H, CH=), 5.8 (m, 1H, CH=)ppm. Mass spectrum 138(M^+), 43(base). Calcd. 78.21; H 10.21. Found C 78.01; H 11.21.

7-Methyl-2,3-octadienyl-6-one (52). 49% Yield. ^{1}H NMR ($CDCl_3$) δ 1.1 (d, 6H, J=6 Hz, $2CH_3$) 1.5 (m, 1H, CH), 3.3 (d, 2H, J=5Hz, CH_2C=), 5.9 (m, 2H, 2CH=)ppm. Mass spectrum 138(M^+), 43(base). Calcd. 78.21; H 10.21. Found C 78.67; H 10.38.

6-Phenyl-2,3-hexadienyl-6-one (53) . 59% Yield. ^{1}H NMR ($CDCl_3$) δ 2.1 (d, 3H, J=6Hz, CH_3), 3.5 (d, J=5Hz, CH_2), 5.8 (m, 2H, CH=), 7.6 (m, 5H, Arom.)ppm. Mass spectra m/z 172 (M^+), 43 (base). Calcd. C 83.68%; H 7.02. Found C 83.21; H 6.99.

Isomerisation of Allenic Ketones. General Procedure. 2,4-Nonadienyl-6-one (54). A solution of **51** (0.1 g, 0.7 mmol) was stirred together with triethylamine (0.1g, 1 mmol) and DMAP (10 mg) in dichloromethane (2 mL) for 3 h. Ethanol (2 mL) was then

added and the mixture stirred 2 h. Water (2 mL) was added, the organic layer separated, dried on anhydrous sodium sulphate and the solvent evaporated to give **54**. Obtained 94 mg, 94% yield. ^{1}H NMR (CCl_4) δ 1.0 (t, 3H, J=8Hz, CH_3), 1.6 (m, 2H, CH_2), 1.9 (d, 3H, CH_3), 2.5 (m, 2H, CH_2), 5.9 (m, 1H, CH=), 6.2 (m, 1H, CH=), 6.8 (m, 1H, CH=), 7.5 (m, 1H, CH=)ppm. Mass spectrum m/z 138(M^+), 41(base).

7-Methyl-2,4-octadienyl-6-one (55). 89% Yield. ^{1}H NMR ($CDCl_3$) δ 1.2 (d, 6H, J=6Hz, $2CH_3$), 1.8 (m, 1H, CH), 2.1 (d, 3H, CH_3), 5.7 (m, 1H, CH=), 6.2 (m, 1H, CH=), 6.6 (m, 1H, CH=), 7.4 (m, 1H, CH=)ppm. Mass spectrum m/z 138(M^+), 41(base).

6-Phenyl-2,4-hexadienyl-6-one (56). 93% Yield. ^{1}H NMR ($CDCl_3$). δ 1.8 (d, 3H, J=7Hz, CH_3), 5.9 (m, 1H, CH=), 6.8 (m, 1H, CH=), 7.3-7.7 (m, 7H, Arom., 2CH=)ppm. Mass spectrum m/z 172(M^+), 41(base).

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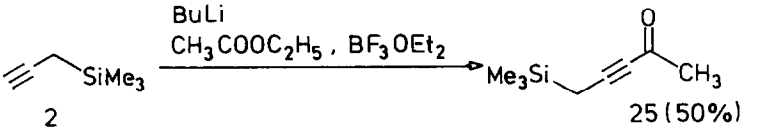
15)Ketone **25** could be prepared also in slightly higher yields (50% ca) by coupling of the lithium derivative of propargyl silane and ethyl acetate in the presence of boron trifluoride etherate.



2 25 (50%)

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