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ALLYL-AND BENZYLSTANNANES, NEW REAGENTS IN TERPENIC SYNTHESIS

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Abstract:Terpenic allyl-and benzylstannanes are easily prepared from unsaturated terpene hydrocarbons by metallation followed by quenching with trialkyltin chloride. An isomerization of unsaturated terpenes via allyltin compounds is reported, by which (+)-α-pinene has been converted into (+)-β-pinene. A regioselective acylation of allyl-and benzylstannanes are realized by a rhodium-catalyzed coupling with acyl halides. Mono-and sesquiterpenoid ketones which play an important role in the fragrance industry can be obtained. Hydroxylation and oxidation of terpene hydrocarbons via allyl-and benzylstannanes are also reported.

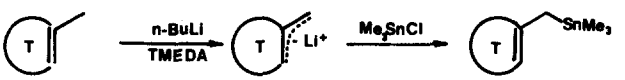
Allylstannanes are versatile reagents that show high reactivity toward electrophilic species[1] and useful precursors for the introduction of a variety of functional groups[2-6]. We report here the use of these organometallic intermediates in the preparation of variously functionalized terpenes providing an access to new compounds of a great potential interest in the area of the fragrance chemistry.

SYNTHESIS OF TERPENIC ALLYL-AND BENZYLSTANNANES

To date, only a few terpenic allystannanes have been obtained, either from allylic halides[7-11] or acetates[12,13], or from unsaturated hydrocarbons[14-16].

In order to introduce the trialkylstannyl group into the allylic position on the terpenic substrates, the availability of starting material were taken into account. As it was difficult to obtain allylic functionnal terpenes in high purity, allyl lithium reagents were first generated from the parent terpene[17] and converted to allylstannanes[1].

The allyl lithium reagents were prepared by metallation of unsaturated terpenic hydrocarbons with n-butyllithium -tetramethylethylenediamine[18,19]. Then the allyl carbanions were quenched with trimethyltin chloride as outlined in Scheme 1.



Scheme 1.

From terpenic hydrocarbons limonene **1**, p-menthene **2**, α-pinene **3**, 2-carene **4** andα-cedrene **5**, readily available natural compounds, we obtained the corresponding allylstannanes **6-10** (Table 1).

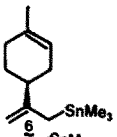
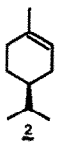
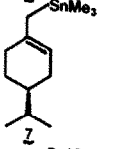
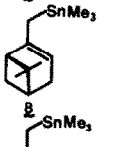
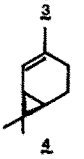
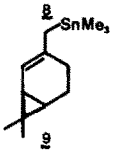
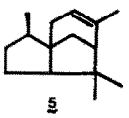
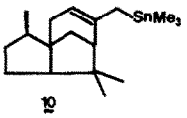
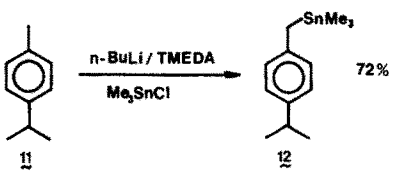
TERPENES	METALLATION Temp. °C	Time hr	ALLYLSTANNANES	Yield %	Bp °C/mmHg
 1	20	4	 6	56	72/0.4
 2	70	8	 7	52	81/0.4
 3	70	8	 8	59	60/0.6
 4	20	48	 9	47	67/0.2
 5	70	8	 10	45	105/0.03

Table 1.

All the compounds were characterized by NMR (^{1}H, ^{13}C and ^{119}Sn). The introduction of the organometallic group appears to go with a very high degree of regioselectivity since allylstannanes with the tin substituent at the less substituted end of the allyl unit were obtained exclusively. We have extended this general procedure to the synthesis of benzylstannane **12** from p-cymene **11**.

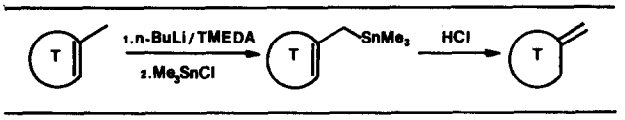


PROTONOLYSIS OF TERPENIC ALLYLSTANNANES : ISOMERIZATION OF UNSATURATED TERPENIC HYDROCARBONS.

Organotin compounds containing an allyl group attached to the metal atom are particularly susceptible to acidic cleavage[20-23]. This reaction which occurs with complete allylic rearrangement, has been applied to the terpenic series.

Treatment of allylstannanes derivatives **7**-**10** with hydrogen chloride at room temperature, in methanol containing 4% water gave terpenic hydrocarbons **13**-**16** (Table 2). Terminal olefins are obtained with good yields and a high degree of purity without contamination with internal ones.

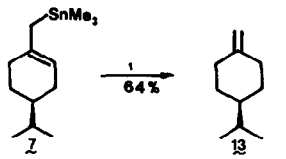
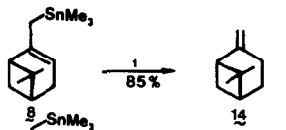
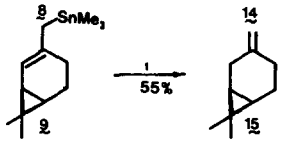
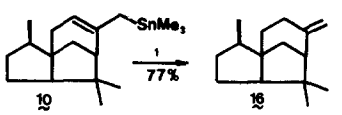
Isomerization of unsaturated terpenic hydrocarbons



Scheme 2

The easy protonolysis of terpenic allyltins, when combined with the preparation of these derivatives from terpenic hydrocarbons provides a synthetic method of isomerization of terpenic hydrocarbons and the formation of energetically less stable terminal olefins. The overall reaction should be formulated as Scheme 2 and the results are summarized in Table 2.

Table 2

ISOMERIZATION OF UNSATURATED TERPENES	overall yield %	b.p °C/mm Hg
	33	68/25
	50	63/25
	26	62/25
	35	89/0.2

Reagents : 1) HCl / MeOH-4% H_2O

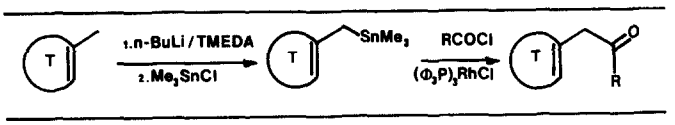
In particular, we propose a new short synthesis of (+)-β-pinene[24]. β-pinene together with its α-isomer is the minor constituent of numerous essential oils, and is the starting material for the manufacture of perfumes, chemicals and polyterpene resins. Also, the conversion of α-pinene into the less easily available β-pinene has been investigated[25], but most of reported methods using various catalysts led to ineffective conversion with poor yields.

More recently, two new synthesis of β-pinene fromα-isomer have been reported. Julia[26] described a four-step method which involves a reductive fission of alkenephosphonates leading to β-pinene with an overall yield of 25%. The conversion proposed by Cao[27] gave a mixture from which β-pinene could only be obtained by careful distillation. Also, our new method converts (+)-α-pinene into (+)-β-pinene with an overall yield of 50% in two steps.

We have obtained (+)-β-pinene with high isomeric and optical purity .This uncommon dextrorotatory form of β-pinene has so far been detected[28,29] in very few plants.

ACYLATION OF TERPENE HYDROCARBONS VIA ALLYL- AND BENZYLSTANNANES

Allyltin compounds undergo a transition metal catalyzed coupling reaction with acid chlorides leading to β,γ-unsaturated ketones. Here, we have extended the work of Migita[30] and Stille[31] to the acylation of allyl-and benzylstannanes **7-9** and **13** with acid chlorides in the presence of chlorotris-(triphenylphosphine)rhodium. The overall transformation from unsaturated terpene hydrocarbons provides a new general method for the acylation of these compounds as illustrated in Scheme **3**.



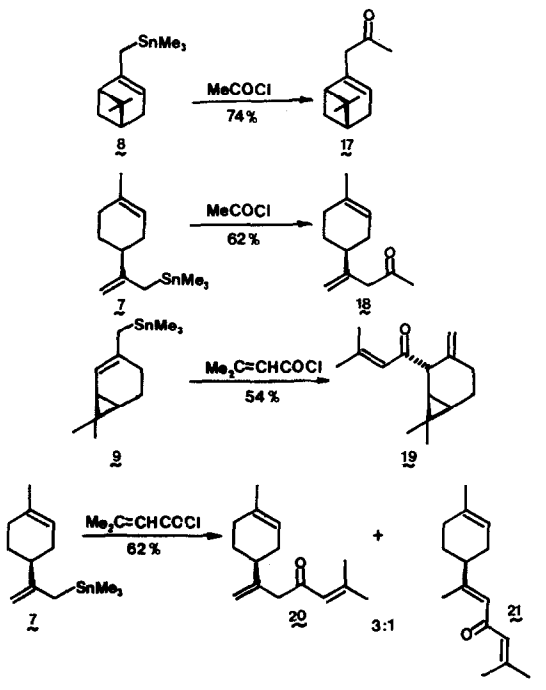
Scheme 3

Thus, we have explored the use of allylstannanes in the synthesis of terpene derivatives[44] not readily obtained by traditional methods (Table 3).

The reaction of acetyl chloride with 10-(trimethylstannyl)-α-pinene **8** gave 10-acetyl-α-pinene **17** in 74% yield while reactions of α-pinene directly with acetic anhydride[32] or β-pinene with acetyl hexachloroantimonate[33] produce **17** in poor yield, often accompanied by rearrangement products.

Table 3

ACYLATION OF UNSATURATED TERPENES



Acylation with acetyl chloride of 10-(trimethylstannyl)limonene 7 gave the exclusive formation of 10-acetyllimonene 18 in 62% yield. The organostannyl group controls the acylation on C-10 carbon whereas direct acylation of limonene with acetyl chloride catalyzed by tin tetrachloride[35] occurs at both C-6 and C-10 to give, after dehydrochloration, a complex mixture of α,β and β,γ-unsaturated ketones.

The reaction of 10-(trimethylstannyl)-2-carene 9 with senecioyl chloride resulted in total allylic rearrangement with the formation of 2-senecioyl-3(10)-carene 19 in 54% yield. To our knowledge this compound has never been described in the literature.

Synthesis of atlantones.

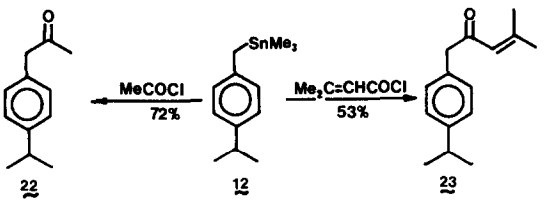
Acylation of allylstannanes with senecioyl chloride offers the potential of introducing an additional isoprene unit and the formation of sesquiterpene ketones. We illustrate this methodology by the synthesis of the atlantones 20 and 21 from limonene.

The rhodium-catalyzed acylation of 10-(trimethylstannyl)limonene 7 with senecioyl chloride proceeded as described earlier to afford a 62% yield of a 75:25 mixture of β-atlantone 20 and α-atlantone 21 .

Again, this reaction proceeded with good regioselectivity whereas direct reaction of limonene with senecioyl chloride under classical reaction conditions affords a complex mixture of unsaturated ketones[36].

Acylation of p-cymene.

The selective transfer of a benzyl group from benzylstannanes has been previously reported by Stille[37]. Consequently we have extended our study to benzyltin derivatives in the terpene series. Thus, 7-(trimethylstannyl)-p-cymene 12 when allowed to react with acetyl and senecioyl chlorides in the presence of chlorotris(triphenylphosphine)rhodium gave 7-acetyl-p-cymene 22 (72%) and 7-senecioyl-p-cymene 23 (53%) respectively.



22 12 23

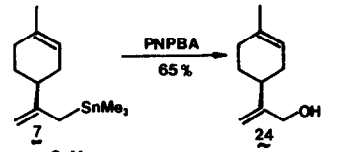
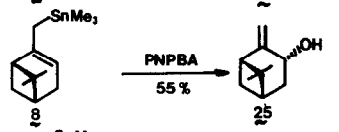
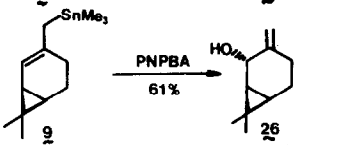
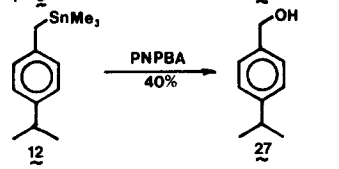
To our knowledge these two compounds have not been previously reported. In comparison, the acylation of p-cymene with acid chlorides in the presence of $AlCl_3$ occurs on the aromatic nucleus to give alkylphenones[38].

The rhodium-catalyzed coupling of acid chlorides with terpene allyl-and benzylstannanes provides a convenient regioselective method for the synthesis of terpenic ketones which are very useful compounds for the aroma industry.

HYDROXYLATION AND OXIDATION OF TERPENE HYDROCARBONS VIA ALLYL-AND BENZYLSTANNANES

Recently Ueno[39] reported that the reaction of m-chloroperbenzoïc acid with allylstannanes led after acid treatment to allylic alcohols. This oxidation have also been used to realize (1,3)-hydroxyl group shifts in allylic alcohols. In order to extend this reaction to terpene series, we have used a solution of p-nitroperbenzoïc acid in chloroform as oxidant. Without acid hydrolysis at the end of reaction, allylstannanes 7-9 and benzylstannane 12 were directly transformed into terpenic alcohols 24-27 respectively, in moderate yields (Table 4).

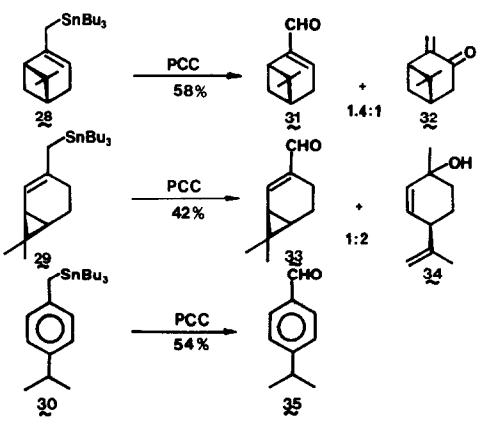
Table 4

HYDROXYLATION OF UNSATURATED TERPENES	b.p °C/mmHg
	75/0.2
	64/0.4
	70/0.3
	75/0.2

Some of them are not easily available with a good purity. This procedure represents a general method that we propose for the transformation of terpene hydrocarbons to the corresponding allylic alcohols via allylstannanes and benzylstannanes.

This methodology can be extended to the introduction of other organic functionality on terpene substrates., In particular this would provide access to terpenic carbonyl compounds - via allyl and benzylstannanes - from terpene hydrocarbons.

Table 5

OXIDATION OF UNSATURATED TERPENES


The oxidation of allyltin derivatives with various oxidant has been reported by Still[40]. Also, when allyl-and benzylstannanes **28**, **29** and **30** are treated with pyridinium chlorochromate in an acetone solution, a mixture of terpenic α,β-unsaturated carbonyl compounds was generally obtained in moderated yields. The results of oxidation are summarized in Table 5 .The poor result may be attribuable in part to the partial hydrolysis of allylorganometallic derivatives under reaction conditions.

Conclusion

We have shown from these various exemples that terpenic allyl-and benzylstannanes - readily obtained from terpenes hydrocarbons, natural compounds easily available - are versatile intermediates for the synthesis of terpenic derivatives, useful in the perfume industry.

EXPERIMENTAL SECTION

IR spectra were obtained with a UNICAM SP 200 spectrophotometer. ^{1}H NMR spectra were recorded at 90 MHz on a BRUKER WH 90 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as an internal standart (ppm). ^{13}C NMR spectra were recorded at 22.63 MHz on a BRUKER WH 90 spectrometer using $CDCl_3$ as solvent. Chemical shifts are reported as δ values in parts per million from internal tetramethylsilane. ^{119}Sn NMR spectra are obtained with a BRUKER WH 90 spectrometer operating at 33.54 MHz with $CDCl_3$ as solvent and $(CH_3)_4Sn$ as external reference. Mass spectra were measured on a Micromass 16F instrument. Elemental microanalyses were performed by Service Central de Microanalyses du CNRS, Vernaison, France. Column chromatography was performed with MERCK silicagel 60, 70-230 mesh ASTM. Solvents were freshly distilled from drying agent in a nitrogen atmosphere before use. α-Pinene, limonene, 2-carene, p-menthene, p-cymene and chlorotris(triphenylphosphine)rhodium were obtained from FLUKA. n-butyllithium in hexane was from ALDRICH CHEMICAL CO. Trimethylstannyl chloride was a generous gift of SCHERING-FRANCE. All reactions were carried out in an atmosphere of dry nitrogen.

PREPARATION OF TERPENE ALLYL-AND BENZYLSTANNANES.

General procedure.

To a stirred solution of 1,5M n-butyllithium in hexane (22 mmol) was added dropwise dry N,N,N',N'-Tetramethylethylenediamine (22 mmol). The temperature of the solution rose to ca.45°C. The yellow resulting solution was stirred with a magnetic stirrer until a temperature of 25°C was regained, whereupon unsaturated terpene (44 mmol) was added. According to the substrate, the solution was stirred in the specific conditions described in Table 1. The solution cooled to 0°C was quenched with a solution of trimethylstannyl chloride (30 mmol) in hexane (10 mL). After 4h the insoluble salts were removed by filtration. The filtrate solvent was poured into a saturated aqueous ammonium chloride solution and extraction with ether. The organic layers were washed with H_2O, dried ($MgSO_4$) and evaporated under reduced pressure. Products are isolated by distillation.
Using the general procedure described above we have obtained these reagents **6**-**10** and **12** from **1**-**5** and **11**:

10-(Trimethylstannyl)limonene 6 ,72°C (0,4mm); MS, m/z (relative intensity) 300 (M+, 5), 165 (100); ^{1}H NMR ($CDCl_3$) δ 0.00 (9H, s), 1.61 (3H, br s), 4.55 and 4.62 (2H, m), 5.40 (1H, m); ^{13}C NMR ($CDCl_3$) δ 153.8 (C-8), 133.2 (C-1), 120.7 (C-2), 102.9 (C-9), 41.1 (C-4), 31.2 (C-6), 30.8 (C-3), 28.3 (C-5), 23.2 (C-7), 20.3 (C-10), -9.7 ($\underline{C}H_3Sn$); ^{119}Sn NMR ($CDCl_3$) δ -0.71. Anal.Calcd for $C_{13}H_{24}Sn$: C, 52.17; H, 8.03; Sn, 39.80. Found: C, 52.21; H, 7.98; Sn, 39.74.

7-(Trimethylstannyl)p-menthene 7 ,81°C (0.4mm); MS, m/z (relative intensity) 302 (M+, 9), 165 (100); ^{1}H NMR ($CDCl_3$) δ 0.04 (9H, s), 0.85 (6H, d), 5.20 (1H, m),; ^{13}C NMR ($CDCl_3$) δ 136.6 (C-1), 116.5 (C-2), 40.0 (C-4), 32.1 (C-8), 31.3 (C-6), 28.9 (C-3), 26.5 (C-5), 21.6 (C-7), 19.8 (C-10), 19.6 (C-9), -9.8 ($\underline{C}H_3Sn$). Anal.Calcd for $C_{13}H_{26}Sn$: C, 51.82; H, 8.64; Sn, 39.53. Found: C, 51.54; H, 8.71; Sn, 39.66.

10-(Trimethylstannyl)-α-pinene 8 ,60°C (0.6mm); MS, m/z (relative intensity) 300 (M+, 4), 165 (100); ^{1}H NMR ($CDCl_3$) δ 0.13 (9H, s), 0.91 (3H, s), 1.33 (3H, s), 5.06 (1H, m); ^{13}C NMR ($CDCl_3$) δ 147.5 (C-2), 110.8 (C-3), 47.9 (C-1), 40.5 (C-5), 37.7 (C-6), 31.4 (C-7), 30.9 (C-4), 26.4 (C-8), 21.7 (C-10), 21.0 (C-9), -9.5 ($\underline{C}H_3Sn$.) ^{119}Sn NMR ($CDCl_3$) δ -4.40. Anal. Calcd for $C_{13}H_{24}Sn$: C, 52.17; H, 8.03; Sn, 39.80. Found: C, 52.10; H, 8.08; Sn, 40.07.

10-(Trimethylstannyl)-2-carene 9 ,67°C (0.2mm); MS, m/z (relative intensity) 300 (M+, 7), 165 (100); ^{1}H NMR ($CDCl_3$) δ 0.06 (9H, s), 0.85 (3H, s), 1.05 (3H, s), 5.35 (1H, m); ^{13}C NMR ($CDCl_3$) δ 137.5 (C-3), 114.8 (C-2), 28.3 (C-3,C-9), 23.5 (C-7), 23.2 (C-1), 22.2 (C-10), 20.5 (C-6), 18.3 (C-5), 15.4 (C-8), -9.7 ($\underline{C}H_3Sn$); ^{119}Sn NMR ($CDCl_3$) δ -1.60. Anal. Calcd for $C_{13}H_{24}Sn$: C, 52.17; H, 8.03; Sn, 39.80. Found: C, 52.09; H, 8;05; Sn, 39.41.

15-(Trimethylstannyl)-α-cedrene 10 ,105°C (0.03mm); MS, m/z (relative intensity) 368 (M+, 3), 165 (100); ^{1}H NMR ($CDCl_3$) δ 0.04 (9H, s), 0.91 (3H, d), 1.02 (3H, s), 1.13 (3H,s), 5.10 (1H,m). Anal. Calcd for $C_{18}H_{32}Sn$: C, 58.86; H, 8.72; Sn, 32.42. Found: C, 59.01; H, 8.64; Sn, 32.54.

7-(Trimethylstannyl)p-cymene 12 ,73°C (0.2mm); MS, m/z (relative intensity) 298 (M+, 8), 165 (100); ^{1}H NMR ($CDCl_3$) δ 0.03 (9H, s), 1.20 (6H,d), 2.30 (2H, s), 2.80 (1H, m), 7.00 (4H, m); ^{13}C NMR ($CDCl_3$) δ 144.3 (C-4), 139.8 (C-1), 126.6 (C-6,C-2), 126.2 (C-3,C-5), 33.4 (C-8), 24.0 (C-9,C-10), 19.4 (C-7), -10.2 ($\underline{C}H_3Sn$). ^{119}Sn NMR ($CDCl_3$) δ + 2.80. Anal. Calcd for $C_{13}H_{22}Sn$: C, 52.52; H, 7.41; Sn, 40.07. Found: C, 52.47; H, 7.39; Sn, 40.18.

PROTONOLYSE OF TERPENE ALLYLSTANNANES.

General procedure.

To a stirred solution of allylstannanes was added at room temperature an appropriate amount of hydrogen chloride in methanol containing 4% water. After stirring for 30 min. a saturated solution of sodium bicarbonate was added. The reaction mixture was extracted with ether, washed with water, dried over $MgSO_4$ and filtered. The solvent was eliminated and the product was isolated by distillation. Product purity and identity were checked by gas chromatography and their structures were firmly established by spectral data.
From allylstannanes 7 and **9-10**, using the general procedure described above, we have respectively obtained after distillation :

1(7)-p-menthene 13, 68°C (25 mm); ^{1}H NMR ($CDCl_3$) δ 0.84 (6H, d), 4.51 (2H, br s).

3(10)-carene 15, 62°C (25 mm); ^{1}H NMR ($CDCl_3$) δ 0.93 (3H, s),0.97 (3H, s), 4.00 (2H, m); ^{13}C NMR ($CDCl_3$) 149.1 (C-3), 107.0 (C-10), 32.2 (C-2), 28.9 (C-4), 28.7 (C-9), 21.4 (C-1,C-5), 19.6 (C-6), 17.7 (C-7), 14.7 (C-8).

β-cedrene 16, 89°C (0.2mm); ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, d), 1.00 (3H, s), 1.10 (3H, s), 4.62 (2H, m).

Obtention of (+)-β-pinene 14.

The reaction of 2.61g (8.7 mmol) of 10-(Trimethylstannyl)-α-pinene **8** prepared from (+)-α-pinene, with HCl (8.7 mmol) in methanol (164 mL) containing 4% H_2O gave 1g (85%) of **(+)-β-pinene 14**, 63°C (25 mm) $[\alpha]_D$ + 14.90°(c 2.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.69 (3H, s), 1.24 (3H, s), 4.61 (2H, m).

ACYLATION OF TERPENE ALLYL-AND BENZYLSTANNANES.

Acylation of 10-(Trimethylstannyl)limonene 7

with acetyl chloride.
A solution of 2.73 g (9.1 mmol) of 10-(Trimethyl stannyl)limonene 7 and 1.07 g (13.7 mmol) of acetyl chloride in 5 mL of dichloromethane was allowed to react in the presence of 0.127 g (0.137 mmol) of chlorotris(triphenylphosphine)rhodium in a sealed tube at 60°C. After 16h, the reaction mixture was hydrolysed with a saturated aqueous NH_4Cl solution and extracted with ether. The organic layers were washed with H_2O and dried. The solvents were removed by evaporation under reduced pressure. The crude product was purified by liquid chromatography on silica gel. Elution with 7:3 petroleum ether - benzene as eluent, gave 1.02 g(62%) of **10-acetyllimonene**[33] **18** : IR, 1715 cm^{-1}; MS, m/z (relative intensity) 178 (M+, 2), 43 (100); ^{1}H NMR ($CDCl_3$) δ 1.64 (3H, br s), 2.10 (3H, s), 3.16 (2H, s), 4.88 and 5.00 (2H, m), 5.37 (1H, m).

with senecioyl chloride.
A solution of 2 g(6.7 mmol) of 10-(Trimethyl-stannyl)limonene 7 and 1.19 g (10 mmol) of senecioyl chloride in 4 mL of dichloromethane are heated (60°C) for 16h in a sealed tube in the presence of 0.062 g (0.067 mmol) of rhodium complex. The reaction mixture was worked up as in the experiment above. The crude product obtained after removing the solvent was purified by liquid chromatography on silica gel. Elution with 6:4 petroleum ether- benzene gave 680 mg (47%) of **β-atlantone**[41-43] **20**: IR 1685 cm^{-1}; MS, m/z (relative intensity) 218 (M+, 3), 83 (100); ^{1}H NMR ($CDCl_3$) δ 1.62 (3H, br s), 1.81 (3H, br s), 2.10 (3H, br s), 3.10 (2H, br s), 4.80 and 4.90 (2H, m), 5.30 (1H, m), 6.00 (1H, m). Elution with 4:6 petroleum ether-benzene gave 220 mg (15%) of **α-atlantone**[41-43] **21** :IR, 1685 cm^{-1}; MS, m/z (relative intensity) 218 (M+, 14), 83 (100); ^{1}H NMR ($CDCl_3$) δ 1.62 (3H, br s), 1.85 (3H, br s), 2.13 (6H, br s), 5.36 (1H, m), 5.97 (2H, m).

Acylation of 10-(Trimethylstannyl)-α-pinene 8 with acetyl chloride.
A solution of 2 g (6.7 mmol) of 10-(Trimethylstannyl)-α-pinene **8** and 0.79 g (10 mmol) of acetyl chloride in 4mL of dichloromethane was heated (60°C) for 48h in a sealed tube in the presence of 0.062 g (0.067 mmol) of chlorotris(triphenylphosphine)rhodium. After 16h, the reaction mixture was hydrolysed and extracted as previously described to give a crude product which was purified by liquid chromatography. Elution with 1:1 petroleum ether- benzene gave 880 mg (74%) of **10-acetyl-α-pinene**[33] **17**: IR, 1715 cm-1; MS, m/z (relative intensity) 178 (M+, 5), 43 (100); ^{1}H NMR ($CDCl_3$) δ 0.75 (3H, s), 1.17 (3H, s), 2.02 (3H, s), 2.97 (3H, br s), 5.28 (1H, m).

Acylation of 10-(Trimethylstannyl)-2-carene 9 with senecioyl chloride.
A solution of 1.5 g (5 mmol) of 10-(Trimethylstannyl)-2-carene **9** and 0.89 g (7.5 mmol) of senecioyl chloride in 3mL of dichloromethane was allowed to react in the presence of 0.047 g (0.05 mmol) of rhodium complex in a sealed tube at 60°C for 24h. The work up previously described gave a reaction mixture which was purified by liquid chromatography. Elution with 2:3 petroleum ether-benzene as an eluent gave 560 mg (51%) of **2-α-senecioyl-3(10)-carene 19**: IR, 1685 cm^{-1}; MS, m/z (relative intensity) 218 (M^+, 3), 83 (100); ^1H NMR ($CDCl_3$) δ 0.95 (3H, s), 1.02 (3H, s), 1.88 (3H, br s), 2.11 (3H, br s), 3.44 (1H, br s), 4.86 (2H, m), 6.22 (1H, m). Anal. Calcd for $C_{15}H_{20}$: C, 82.87; H, 10.10; Found: C, 82.47; H, 10.19.

Acylation of 7-(Trimethylstannyl)-p-cymene 12.
The reactions were conducted in the same fashion as with the allylstannanes. A solution of 0.0106 mol of acid chloride (acetyl or senecioyl chloride) and 0.0067 mol of 7-(Trimethylstannyl)-p-cymene **12** in 5 mL of dichloromethane in the presence of 0.067 mmol of chlorotris(triphenylphosphine)rhodium is heated (60°C) in a sealed tube for 48h.
Using the general procedure described above we have respectively obtained:
7-acetyl-p-cymene 22 : MS, m/z (relative intensity) 176 (M^+, 21), 133 (100); ^1H NMR ($CDCl_3$) δ 1.18 (6H, d), 2.05 (3H, s), 3.55 (2H, s), 7.05 (4H, s). Anal. Calcd for $C_{12}H_{16}O$: C, 81.82; H, 9.09. Found: C, 82.03; H, 9.11.
7-senecioyl-p-cymene 23 : MS, m/z (relative intensity) 216 (M^+, 3), 83 (100); ^1H NMR ($CDCl_3$) δ 1.24 (6H, d), 1.40 (3H, br s), 2.15 (3H, br s), 2.82 (1H, m), 3.66 (2H, s), 6.08 (1H, m), 7.13 (4H, s). Anal. Calcd for $C_{15}H_{20}O$: C, 83.33; H, 9.26. Found: C, 83.51; H, 9.15.

HYDROXYLATION OF TERPENE ALLYL-AND BENZYLSTANNANES.

General procedure

To a solution of allyl-and benzylstannanes (1.6 mmol) in chloroform was slowly added p-nitrobenzoïc acid (1.8 mmol). The mixture was kept at room temperature for 15 min. After filtration, the solution was concentrated under reduced pressure and the products are isolated by distillation.
By use of the above procedure, we have respectively obtained from **7**, **8**, **9** and **12**:

p-mentha-1,8(10)-dien-9-ol 24,[18] : 75°C (0.2 mm); ^1H NMR ($CDCl_3$) δ 1.65 (3H, br s), 4.08 (2H, s), 4.86 and 5.02 (2H, br s), 5.38 (1H, m).

trans-pinocarveol 25,[34] : 64°C (0.4 mm); ^1H NMR ($CDCl_3$) δ 0.64 (3H, s), 1.28 (3H, s), 4.40 (1H, m), 4.79 and 4.99 (2H, m).

3(10)-carene-2-ol 26,[45] : 70°C (0.3 mm); ^1H NMR ($CDCl_3$) δ 0.90 (3H, s), 0.98 (3H, s), 4.01 (1H, br s), 4.66 (2H, m).

p-cymene-7-ol 27,[46] : 75°C (0.2 mm); ^1H NMR ($CDCl_3$) δ 1.24 (6H, d), 2.88 (1H, m), 4.62 (2H, br s), 7.24 (4H, m).
These spectral properties are identical with those previously reported.

OXIDATION OF TERPENE ALLYL-AND BENZYLSTANNANES.

General procedure.

Tributylstannyl derivatives **28**-**30** obtained using the same methodology by trapping allylithium intermediates with tributyltin chloride, were used without isolation.

To a solution of pyridinium chlorochromate (30 mmol) in acetone (40mL) was added terpene allyl-or benzylstannane (10 mmol). After stirring for 1h, 200 mL of ether was added and the reaction mixture was filtered through silica gel column. The solvent was evaporated off, and the residue was purified by liquid chromatography on silica gel.

The oxidation of 10-(Tributylstannyl)-α-pinene **28** according to the general procedure gave **myrtenal 31**[47] MS, m/z (relative intensity) 150 (M^+, 2), 79 (100); ^1H NMR ($CDCl_3$) δ 0.77 (3H, s), 1.36 (3H, s), 6.68 (1H, m), 9.40 (1H, s) and **pinocarvone 32**[48] MS, m/z (relative intensity) 150 (M^+, 18), 81 (100); ^1H NMR ($CDCl_3$) δ 0.84 (3H, s), 1.38 (3H, s), 4.93 and 5.88 (2H, m).

The oxidation of 10-(Tributylstannyl)-2-carene **29** by use of the previous procedure gave **2-carene-10-al 33**[49] MS, m/z (relative intensity) 150 (M^+, 28), 79 (100); ^1H NMR ($CDCl_3$) δ 0.75 (3H, s), 1.10 (3H, s), 6.95 (1H, m), 9.36 (1H, s) and **trans-p-2,8 menthadiene-1-ol 34**[45] MS, m/z (relative intensity) 134 ($M^+ - H_2O$, 2), 59 (100); ^1H NMR ($CDCl_3$) 1.24 (3H, s), 1.77 (3H, br s), 4.67 (2H, m), 5.76 (2H, m).

The oxidation of 7-(Tributylstannyl)-p-cymene **30** according the same procedure gave **p-cymene-7-al 35**[50] ^1H NMR ($CDCl_3$) 1.10 (6H, d), 2.78 (1H, m), 7.44 (4H, m), 9.86 (1H, s)

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