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Synthesis and odor characteristics of isomeric 3,3,7-trimethyl-4-octen-1-ols and their 3-sila analogues

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Synopsis

The isomeric (E) and (Z) 3,3,7-trimethyl-4-octen-1-ols and their 3-sila analogues were synthesized. The (Z) 3,3,7-trimethyl-4-octen-1-ol was obtained by the isomerization of E alcohol via its epoxide deoxygenation according to the Vedejs method. Both sila analogues were synthesized from 4-methyl-1-pentyne. The carbon chain was elongated by alkyne silylation with dimethylvinylchlorosilane (synthesis of Z isomer) or by hydrosilylation with dimethylchlorosilane followed by Reformatsky reaction with ethyl bromoacetate (synthesis of isomer E). Odors of alcohols obtained and their acetates have been also evaluated. The odors of carbon compounds are more intense and more fresh than their silicon analogues.

INTRODUCTION

Naturally occurring acyclic monoterpene alcohols are used in many fragrance compositions because of their pleasant and original odors. Synthesized by us, 3,7-dimethyl-4-octen-1-ol, the structural analogue of citronellol (1), and its homologue with an additional methyl group at C-7 are also characterized by pleasant, floral odors (2). The 7-sila analogue of the last alcohol was also obtained.

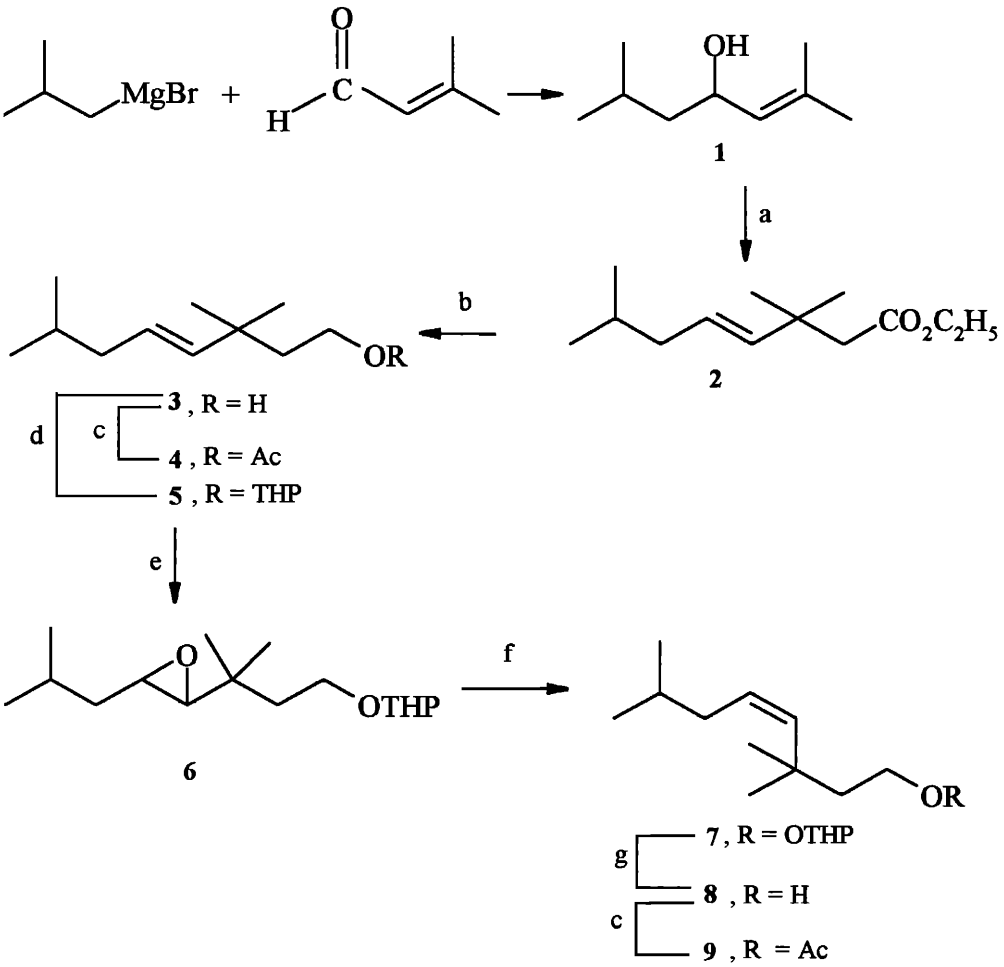
One of the reasons for our interest in the synthesis of silaisoprenoid compounds are studies on the influence of the presence of silicon in the molecule on the biological activity or odoriferous properties of the compound. The influence on biological activity was documented, for example, for sila-antimuscarinic agents (3,4) sila-pyrethroids (5), and sila-juvenoids (6,7). The effect on odoriferous properties of the replacement of the carbon atom with silicon in the molecule has been studied by Wannegat *et al.* (8–10). Their interesting results encouraged us in synthesizing acyclic silaisoprenoids.

As an extension of our studies, we have synthesized a new homologue of our synthetic terpene alcohol (3,7-dimethyl-4-octen-1-ol), with an additional methyl group at C-3 and its 3-sila analogue. Both alcohols were obtained in pure isomeric (E and Z) forms.

RESULTS AND DISCUSSION

The (E) isomer of the title compound was obtained in three-step synthesis from 3-

methyl-2-buten-1-al (Scheme 1). The first step, the Grignard reaction of this aldehyde with isobutylmagnesium bromide, afforded the alcohol 1 in 72% yield. Allyl alchol 1 was transformed via the Claisen rearrangement (orthoacetate modification) into the ester 2 (78% yield), which was reduced with lithium aluminum hydride (yield 89%) to the desired alcohol 3. The E configuration of the double bond formed in the Claisen rearrangement was confirmed by ^1H NMR ($J_{H\text{-}4,H\text{-}5}$ = 15.6 Hz) as well as by IR (v = 970 cm^{-1}) spectral data. The (Z) isomer of 3,3,7-trimethyl-4-octen-1-ol (8) was obtained by four-step isomerization of (E) alcohol 3. Thus alcohol 3 was transformed into tetrahydropyrane ether 5, which was oxidized with m-chloroperbenzoic acid to epoxyether 6. The key step of this isomerization, deoxygenation of epoxy ether, was carried out according to the procedure described by Vedejs and Fuchs (11). Deprotection of



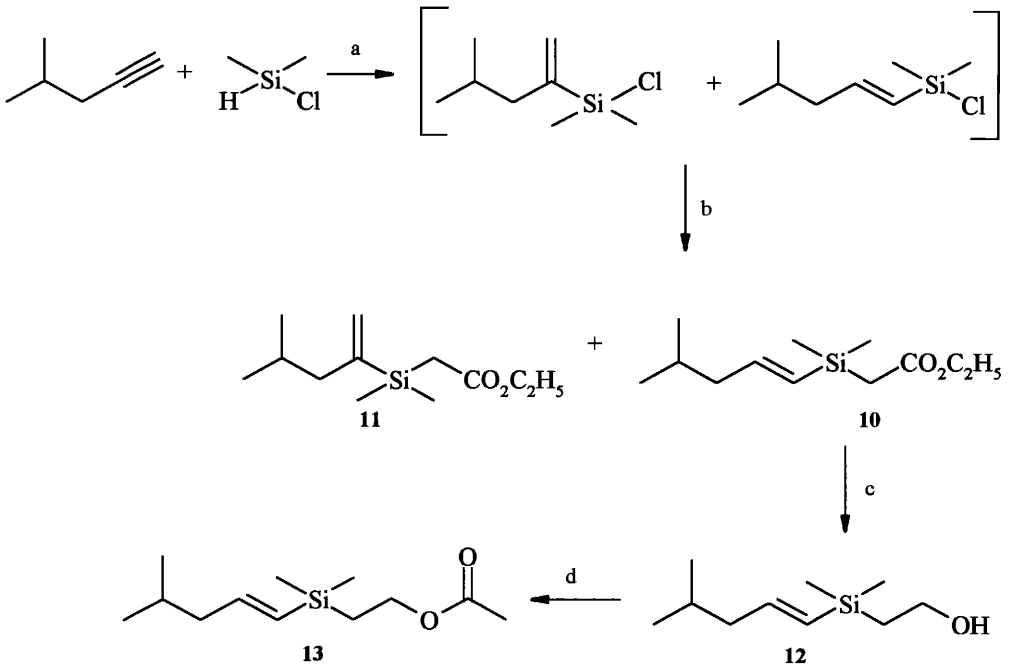
a) $CH_3C(OC_2H_5)_3$, C_2H_5COOH, 138° C; b) $LiAlH_4$; c) AcCl, Py; d) PPTS, DHP; e) MCPBA, CH_2Cl_2; f) 1. $(C_6H_5)_2PLi$, THF, 2. CH_3I; g) PPTS

Scheme 1

ether 7 leads to (Z) alcohol **8**. The yield of isomerization based on alcohol **3** was 37%. The (Z) configuration of the double bond was confirmed by ^{1}H NMR ($J_{H\text{-}4,H\text{-}5}$ = 12.2 Hz) and IR (712 cm^{-1}).

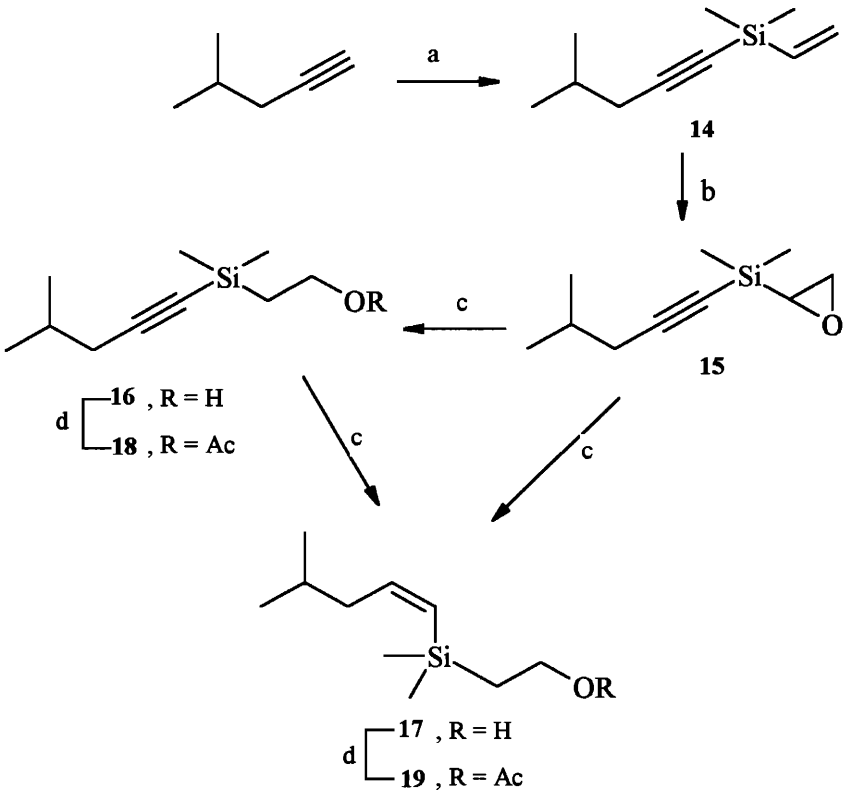
3-Sila analogues of alcohol **3** as well as alcohol **8** were obtained from 4-methyl-1-pentyne. Ethyl silaester **10** was synthesized in a two-step procedure: hydrosilylation of alkyne with dimethylchlorosilane in the presence of hexachloroplatinic acid as a catalyst (12) followed by the Reformatsky reaction of alkenechlorosilane intermediate with ethyl bromopropionate (Scheme 2). Unfortunately, the product mixture isolated from this synthesis (yield 75%) contained, according to GC, 90% of ester **10**, 8% of regioisomer **11**, and a small amount of the Z isomer of **10**. Separation of this mixture by column chromotography on silica gel impregnated with $AgNO_3$ (4%) afforded pure (above 97%) ester **10**. In the last step of synthesis, ester **10** was reduced with lithium aluminum hydride to alcohol **12** in 84% yield.

The 3-sila analogue of alcohol **8** was also obtained from 4-methyl-1-pentyne (Scheme 3). Lithium alkyne was silylated at −78°C with vinyl dimethylchlorosilane, and the resulting vinylsilane **14** (yield 84%) was oxidized with m-chloroperbenzoic acid to epoxide **15** in 81% yield. Then epoxide was reduced with diisobuthylaluminum hydride (DIBAL) to alkynesilanol **16**. The application of lithium aluminum hydride for this reduction gave the mixture of products in which the content of alcohol **16** was 30% only. The secondary α-silenol was obtained as the second main (20%) component in this mixture. Further reduction of alcohol **16** with DIBAL gave the final (Z)-silenol, **17**. More effective



a) H_2PtCl_6 ; b) $BrCH_2CO_2C_2H_5$, Zn, THF; c) $LiAlH_4$; d) AcCl, Py

Scheme 2



a) 1. nBu-Li, Et_2O, - 78 ° C, 2. $ClSi(CH_3)_2CH{=}CH_2$, Et_2O; b) MCPBA; c) DIBAL; d) AcCl, Py

Scheme 3

(yield 79%) was the one-step reduction of epoxide 15 with two equivalents of diisobutyloaluminum hydride, which led directly to 17. Acetates 4, 9, 13, 18, and 19 were obtained in good yield (60–90%) by esterification of corresponding alcohols 3, 8, 12, 16, and 17 with acetyl chloride in the presence of anhydrous pyridine.

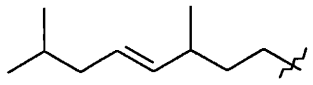
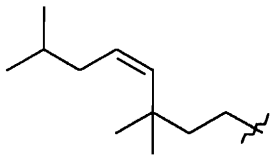
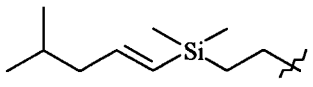
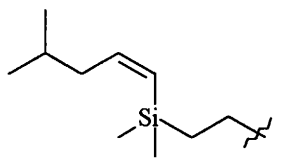
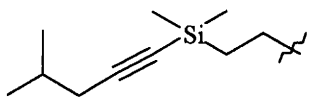
The odor characteristics of the compounds obtained are given in Table I. Comparison of the odors of carbon compounds and their silicon analogues indicates that the odors of carbon compounds are more intensive and more fresh than silicon ones. The odors of carbon alcohols can be generally described as fresh-green, whereas sila alcohols are described as floral-fruity or fruity. Acetates, with the exception of 19, are characterized by a fruity or a fruity-floral odor. The comparative olfactory analysis of compounds with different geometry of the double bond shows differences in notes of odors. The most distinctive difference was observed for E and Z isomers of sila acetates (13 and 19). Alcohol with a triple C–C bond is characterized by the most floral odor among the compounds evaluated.

EXPERIMENTAL

STARTING MATERIALS AND REAGENTS

4-Methyl-1-pentyne (b.p. 61–62°C lit. (13) 61°C) was synthesized from 4-methyl-1-

Table I
Odor Descriptions of Compounds Synthesized*

Compound	-OH	$-OC(O)CH_3$
	Medium-intensive, fresh-green, floral-fruity, with rose and grapefruit notes	Intensive, agreeable, fruity, with apricot note
	Intensive, more than E isomer, agreeable, fresh-green, with tomato leaf and citrus notes	Medium-intensive, fresh, fruity, with desiccated-apricot note
	Weak, agreeable, floral-fruity	Weak, fruity, with wild strawberry note
	Medium-intensive, less than C analogue, fresh, fruity, with melon fruit note	Medium-intensive, agreeable, fresh, balsamic-vegetable note
	Weak, agreeable, floral-fruity, with lime flower note	Weak, agreeable, fresh, fruity-floral

* The odor was evaluated for samples that were above 97% (gc) purity.

pentene by bromination followed by elimination of 1,2-dibromide with potassium hydroxide. All other reagents used in this work were purchased from Fluka.

ANALYTICAL METHODS

^1H NMR spectra were measured for solutions ($CDCl_3$) on Bruker Avance DRX 300 (300 MHz). IR spectra were determined with a Specord M-80 infrared spectrophotometer. Gas chromatographic analyses were performed on a Hewlett-Packard instrument, using an HP-5 capillary column (30 m × 0.31 mm). Analytical TLC was carried out on silica gel G (Merck) with different developing systems. Compounds were detected by spraying the plates with 7% H_2SO_4 in ethanol containing *ca* 0.1% of p-anisaldehyde, followed by heating to 120°C. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck) with petroleum ether-ethyl acetate 7:1 (for alcohols) or 50:1 (for esters) systems as eluents.

OLFACTORY EVALUATION

Odorous properties of the compounds synthesized were determined by Prof. J. Góra strictly following the described procedure (14).

2,6-Dimethyl-2-hepten-4-ol (1). The Grignard reaction of 3-methyl-2-buten-1-al (16.8 g, 0.2 mole) with isobutyl magnesium bromide formed from isobutyl bromide (34.2 g, 0.25 mole) and magnesium (6.0 g, 0.25 mole) was carried out in ethyl ether by a method described earlier (2). The crude alcohol 1 was distilled *in vacuo* (b.p. 50–51°C/5 mm Hg) to afford (21.0 g, 75% yield) pure alcohol 3: n_D^{20} = 1.4455 (lit. (15) b.p. 74–76°C/12 mm Hg, n_D^{20} = 1.4410). ^{1}H NMR (δ): 0.83 (d, J = 6.5 Hz, 6H, $-CH(C\underline{H}_3)_2$), 1.05–1.42 (m, 3H, $-C\underline{H}_2C\underline{H}(CH_3)_2$), 1.62, (s, 6H, $=C(C\underline{H}_3)_2$), 4.30 (dt, J = 8.3 and 7.3 Hz, 1H, $-C\underline{H}$ (OH)–).

Ethyl (E)-3,3,7-trimethyl-4-octenoate (2). A mixture of alcohol 1 (20.0 g, 0.14 mole), triethyl orthoacetate (180 ml, 1 mole), and 0.3 ml of propionic acid was heated (138–139°C) with a simultaneous removal of ethanol. Then unreacted orthoacetate was distilled off and the residue was distilled *in vacuo* (b.p. 74–76°C/5 mm Hg). In this way 23.2 g (yield 78%) of pure ester 2 was obtained, n_D^{20} = 1.4475; ^{1}H NMR (δ): 0.83 (d, J = 6.6 Hz, 6H, $-CH(C\underline{H}_3)_2$), 1.09 (s, 6H, $-C(C\underline{H}_3)_2-$) 1.21 (t, J = 7.2 Hz, 3H, $-OCH_2C\underline{H}_3$), 1.54 (m 1H, $-C\underline{H}(CH_3)_2$), 1.81 (t, J = 6.7 Hz, 2H, $-C\underline{H}_2CH=CH$), 2.23, (s, 2H, $-C\underline{H}_2CO_2-$), 4.07 (q, J = 7.2 Hz, 2H, $-OC\underline{H}_2CH_3$), 5.32 (dt, J = 15.6 and 6.7 Hz, 1H, $-CH_2C\underline{H}=CH-$), 5.43 (d, J = 15.6 Hz, $-CH_2CH=C\underline{H}-$); IR (cm^{-1}): 1736 (s), 1384 (m), 1368 (m), 1136 (s), 976 (s). Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.53, H, 11.39. Found C, 73.25; H, 11.45.

(E)-3,3,7-Trimethyl-4-octen-1-ol (3). Reduction of ester 3 (2.2 g, 0.01 mole) with lithium aluminium hydride (0.2 g, 0.006 mole) afforded alcohol 3 in high yield (1.5 g, 89%): b.p. 89–91°C/6 mm Hg; n_D^{20} = 1.4450; ^{1}H NMR (δ): 0.84 (d, J = 6.3 Hz, 6H, $(C\underline{H}_3)_2CH-$), 1.01 (s, 6H, $-C(C\underline{H}_3)_2-$), 1.86 (t, J = 6.6 Hz, 2H, $-C\underline{H}_2-CH=CH-$), 3.64 (t, J = 7 Hz, 2H, $-C\underline{H}_2OH$), 5.31 (dt, J = 15.6 and 6.6 Hz, 1H, $-CH_2C\underline{H}=CH-$), 5.39 (d, J = 15.6 Hz, 1H, $-CH_2CH=C\underline{H}-$); IR (cm^{-1}): 3320 (s,b), 1364 (m), 1384 (m), 1024 (s), 876 (s). Anal Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.12. Found: C, 77.40; H, 13.41.

Tetrahydropyranyl ether of alcohol 3 (5). A mixture of alcohol 3 (11.1 g, 0.065 mole), 3,4-dihydro-2*H*-pyran (5.7 g, 0.07 mole), and pyridinium p-toluenosulfonate (0.15 g) was stirred for 46 h at room temperature. Then the reaction mixture was diluted with ethyl ether (200 cm^3). The ethereal solution was washed with saturated $NaHCO_3$ and water, and dried ($MgSO_4$). The crude product was purified by column chromatography (silica gel, petroleum ether–ethyl acetate, 40:1). Thus 15.3 g (yield 92%) of 5 was obtained: n_D^{20} = 1.4530; ^{1}H NMR (δ): 0.86 (d, J = 6.7 Hz, 6H, $-CH(C\underline{H}_3)_2$), 1.00 (s, 6H, $-C(C\underline{H}_3)_2-$), 3.32–3.57 and 3.70–3.86 (m, 4H, $-O-C\underline{H}_2-$), 4.55 (m, 1H, $-O-C\underline{H}-O$), 5.29 (dt, J = 15.6 and 6.5 Hz, 1H, $CH_2-C\underline{H}=CH-$); 5.36 (d, J = 15.6 Hz, 1H, $-CH_2-CH=C\underline{H}-$); IR (cm^{-1}): 1384 (s), 1376 (s), 1136 (s), 1080 (s), 1032 (s), 976 (s). Anal. Calcd. for $C_{16}H_{30}O_2$: C, 75.52; H, 11.88. Found C, 75.41; H, 11.94.

Tetrahydropyranyl ether of 3,3,7-trimethyl-4,5-epoxyoctan-1-ol (6). m-Chloroperbenzoic acid (4.0 g, 0.023 mole) CH_2Cl_2 (25 cm^3) was added dropwise at 0°C to a solution of ether 5 (5.1 g, 0.02 mole) in 30 cm^3 of CH_2Cl_2, and the reaction mixture was warmed to room temperature and stirred for 48 h. Then it was diluted with ethyl ether (200 cm^3), washed alternately with saturated solutions of Na_2SO_3 and Na_2CO_3, and dried ($MgSO_4$). A preparative column chromatography of the crude product accorded 4.5 g (84% yield) of pure epox ether 6: n_D^{20} = 1.4570; ^{1}H NMR (δ); 0.89, 0.90, 0.92 and 0.93 (four s 6H, $-C(C\underline{H}_3)_2-$), 0.96 and 0.98 (two d, J = 6.6 Hz, 6H, $-CH(C\underline{H}_3)_2$), 2.51 (d, J = 2.4 Hz,

1H,–CH_2–CH–C<u>H</u>–), 2.87 (m, 1H, –CH_2–C<u>H</u>–CH–), 3.44–3.53 (m, 2H, –O$C\underline{H}_2$– THP part), 3.80–3.91 (m, 2H, –OCH_2–, alcohol part), 4.57 (m, 1H, –OC<u>H</u>O–); IR (cm^{-1}): 1032 (s), 1080 (s), 1140 (s), 1372 (m), 1380 (m), 1382 (m).

Tetrahydropyranyl ether of (Z)-3,3,7-trimethyl-4-octen-1-ol (7). Epoxy ether **6** (3.4 g, 0.0125 mole) in (50 cm^3) THF was added at room temperature and under nitrogen to a solution of lithium diphenylphosphide prepared in THF (40 cm^3) from chlorodiphenyphosphine (6.2 g, 0.028 mole) and lithium (0.4 g, 0.056 mole). The reaction mixture was stirred at room temperature for 16 h. Then methyl iodide (3.8 cm^3, 0.06 mole) was added, and the mixture was kept at room temperature for the next 1 h. The reaction mixture was quenched with water and the product was extracted with ethyl ether. The ethereal solution was washed with brine and dried ($MgSO_4$). The crude product was purified by column chromatography. Thus 3.4 g (50% yield) of pure ether **7** was obtained: n_D^{20} = 1.4583; ^{1}H NMR (δ): 0.90 (d, J = 6.6 Hz, 6H, –CH($C\underline{H}_3$)$_2$), 1.12 (s, 6H, –C($C\underline{H}_3$)$_2$–), 2.05 (t, J = 6.5 Hz, 2H, –$C\underline{H}_2$–CH=CH–), 3.41–3.46 (m, 2H, –$C\underline{H}_2$O– THP part), 3.78–3.87 (m, 2H, –$C\underline{H}_2$O– alcohol part), 4.56 (m, 1H, –OC<u>H</u>O–), 5.21 (dt, J = 12.1 and 6.5 Hz, 1H, –CH_2–C<u>H</u>=CH–), 5.27 (d, J = 12.1 Hz, 1H, –CH_2CH=C<u>H</u>–); IR (cm^{-1}): 1384 (s), 1376 (s), 1120 (s), 1080 (s), 1032 (s), 712 (m).

(Z)-3,3,7-Trimethyl-4-octen-1-ol (8). Ether **7** (2.3 g, 0.009 mole) in ethyl alcohol (25 cm^3) with pyridinium p-toluenosulfonate (0.3 g) was heated at 50°C for 12 h. The reaction mixture was diluted with ethyl ether (100 cm^3), washed with brine, and dried ($MgSO_4$). Pure alcohol **8** (1.5 g, 96% yield) was obtained after column chromatography. Its physical and spectroscopic data are as follows: b.p. 60°C/2 mm Hg; n_D^{20} = 1.4523; ^{1}H NMR (δ): 0.89 (d, J = 6.6 Hz, 6H, –CH($C\underline{H}_3$)$_2$), 1.11 (s, 6H, –C($C\underline{H}_3$)$_2$–), 1.54 (s, 1H, –O<u>H</u>), 1.58 (m, 1H, –C<u>H</u>(CH_3)$_2$), 1.68 (t, J = 7.2 Hz, 2H, –$C\underline{H}_2$–CH_2–O–), 2.05 (t, J = 6.5 Hz, 2H, –$C\underline{H}_2$CH=CH–), 3.68 (m, 2H, –$C\underline{H}_2$OH), 5.23 (d, t, J = 12.2 and 6.5 Hz, 1H, –CH_2C<u>H</u>=CH–), 5.28 (d, J = 12.2 Hz, 2H, –CH_2CH=C<u>H</u>–); IR (cm^{-1}): 3336 (s,b), 1460 (s), 1384 (s), 1976 (s), 1240 (m), 1056 (s), 1024 (s), 712 (s). Anal. Calcd. For $C_{11}H_{22}O$: C, 77.58; H, 13.12. Found: C, 77.65; H, 13.15.

Ethyl dimethyl-(4-methyl-1(E)-penten-1-yl)silylacetate (10). A mixture of 4-methyl-1-pentyne (4.5 g, 0.055 mole), chlorodimethylsilane (5.8 cm^3, 0.052 mole) and five drops of 7% solution of hexachloroplatinic acid in ethanol was placed in a hermetically closed flask (50 cm^3) and was stirred for 1 h at room temperature and 3 h at 60°C. Crude 4-methyl-1-pentene-1-yl-dimethylchlorosilane, together with ethyl bromoacetate (5.8 cm^3, 0.052 mole) in THF (30 cm^3), was added through a dropping funnel under nitrogen to zinc (3.6 g, 0.055 mole) in THF (10 cm^3). The reaction was activated by adding an iodine crystal. The reaction mixture was diluted with petroleum ether (200 cm^3), the solid ZnBrCl was filtered off, and the solvent was evaporated. Crude product (7.35 g, 62% yield), a mixture of esters **10** and **11**, was purified by means of preparative column chromatography on silica gel impregnated with $AgNO_3$ (4%) and activated at 250°C. In that way, pure (above 95%) ester **10** (4.7 g) was obtained: n_D^{20} = 1.4430; b.p. 70°C/2 mm Hg; ^{1}H NMR (δ): 0.13 (s, 6H, –Si(–$C\underline{H}_3$)$_2$–), 0.84 (d, J = 6.6 Hz, 6H, –CH($C\underline{H}_3$)$_2$), 1.21 (t, J = 7.0 Hz, 3H, –$OCH_2C\underline{H}_3$), 1.63 (m, 1H, –C<u>H</u>(CH_3)$_2$), 1.98 (m, 2H, –$C\underline{H}_2$CH=CH_2–), 4.04 (q, J = 7.0 Hz, 2H, –O$C\underline{H}_2CH_3$), 5.56 (d, J = 18.5 Hz, 1H, –CH_2CH=C<u>H</u>–), 6.05 (dt, J = 18.5 and 6.7 Hz, 1H, –CH_2C<u>H</u>=CH–); IR

(cm^{-1}): 1724 (s), 1384 (m), 1375 (m), 1244 (s), 1092 (s), 972 (m), 832 (s). Anal. Calcd. for $C_{12}H_{24}OSi$: C, 63.10; H, 1059. Found: C, 63.02; H, 10.70.

2-{Dimethyl-(4-methyl-1(E)-penten-1-yl)silyl}ethanol (12). The reduction of ester **10** (2.0 g, 0.0088 mole) with $LiAlH_4$ (0.25 g, 0.0066 mole) in ethyl ether (50 cm^3) afforded alcohol **12** (1.4 g, 84% yield). Its physical and spectral data are as follows: b.p. 62°C/2 mm Hg; n_D^{20} = 1.4527; ^{1}H NMR (δ): 0.46 (s, 6H, $-Si(C\underline{H}_3)_2-$), 0.86 (d, J = 6.5 Hz, 6H, $-CH(C\underline{H}_3)_2$), 0.98 (m, 2H, $-C\underline{H}_2CH_2OH$), 1.23 (s, 1 H, $-O\underline{H}$), 1.66 (m, 1H, $-C\underline{H}(CH_3)_2$), 1.98 (td, J = 6.7 and 1.5 Hz, 2H, $-C\underline{H}_2CH=CH-$), 3.71 (m, 2H, $-C\underline{H}_2OH$), 5.56 (dt, J = 18.5 and 1.5 Hz, 1H, $-CH_2CH=C\underline{H}-$), 6.01 (dt, J = 18.5 and 6.7 Hz, 1H, $-CH_2C\underline{H}=CH-$); IR (cm^{-1}): 3320 (s,b), 1615 (m), 1384 (m), 1375 (m), 1240 (s), 1035 (s), 992 (s), 835 (s). Anal. Calcd. for $C_{10}H_{22}OSi$: C, 64.44; H, 11.90. Found: C, 64.51; H, 12.01.

Dimethyl-(4-methyl-1-pentyn-1-yl)-vinylsilane (14). n-BuLi (54 cm^3 of 1.6 M solution in hexane, 0.086 mole) was added dropwise under nitrogen to a cooled (−78°C) solution of 4-methyl-1-pentyne (10 cm^3, 0.086 mole) in ethyl eter (50 cm^3). After 20 minutes, dimethylvinylchlorosilane (11 cm^3, 0.08 mole) was added and the reaction mixture was warmed to room temperature. Then the mixture was diluted with ethyl ether (100 cm^3) and quenched with water (20 cm^3). The ethereal solution was washed with brine and dried ($MgSO_4$). The product was distilled *in vacuo*: (b.p. 64–66°C/16 mm Hg) to give 11.2 g (yield 84%) of pure silane **14**. Its physical and spectral data are as follows: n_D^{20} = 1.4270; ^{1}H NMR (δ): 0.18 (s, 6H, $-Si(C\underline{H}_3)_2-$), 0.96 (d, J = 6.6 Hz, 6H, $-CH(C\underline{H}_3)_2$), 1.80 (m, 1H, $-C\underline{H}(CH_3)_2$), 2.11 (d, J = 6.6 Hz, 2H, $-C\underline{H}_2-$), 5.82 (dd, J = 19.5 and 4.4 Hz, 1H, $-CH=C\underline{H}_2$ trans), 5.97 (dd, J = 14.5 and 4.4 Hz, 1H, $-CH=C\underline{H}_2$ cis), 6.12 (dd, J = 19.5 and 14.5 Hz, 1H, $-C\underline{H}=CH_2$); IR (cm^{-1}): 3048 (m), 2176 (s), 1248 (s), 824 (s). Anal. Calcd. for $C_{10}H_{18}Si$: C, 72.21; H, 10.90. Found: C, 72.07; H, 10.95.

Dimethyl-(4-methyl-1-pentyn-1-yl)epoxyethylsilane (15). Vinyl silane **14** (6.0 g, 0.036 mole) was added to a dried solution of m-chloroperbenzoic acid (9.5 g, 0.0433 mole) in CH_2Cl_2 (100 cm^3), and the mixture was stirred at room temperature for 48 h. The reaction mixture was concentrated *in vacuo* up to 3/4 of volume and then was diluted with petroleum ether (250 cm^3). m-Chlorobenzoic acid was filtered off, and the crude product was purified by column chromatography. Pure epoxide **15** (5.4 g, yield 82%) had the following physical and spectral data: n_D^{20} = 1.4513; ^{1}H NMR (δ): 0.14 and 0.21 (two s, 6H, $-Si(C\underline{H}_3)_2-$), 0.95 (d, J = 6.6 Hz, 6H, $-CH(C\underline{H}_3)_2$), 1.80 (m, 1H, $-C\underline{H}(CH_3)_2$), 2.10 (d, J = 6.6 Hz, 2H, $-C\underline{H}_2-$), 2.24 (dd, J = 5.4 and 3.9 Hz, 1H, $-CH(O)-C\underline{H}_2$), 2.66 (dd, J = 5.9 and 3.9 Hz, 1H, $-CH(O)-C\underline{H}_2$), 2.92 (dd, J = 5.9 and 5.4 Hz, 1H, $-C\underline{H}(O)-CH_2$); IR (cm^{-1}): 2176 (s), 1248 (s), 1232 (m), 880 (s), 824 (s).

2-{Dimethyl-(4-methyl-1-pentyn-1-yl)silyl}ethanol (16). Epoxide **15** (1.3 g, 0.0071 mole) in hexane (35 cm^3) was reduced with diisobuthylaluminum hydride (8 cm^3 of 1M solution in hexane). After purification of the crude product (column chromatography) 1.05 g (80% yield) of alcoohol **16** was obtained: b.p. 65°C/2 mm Hg; n_D^{20} = 1.4540; ^{1}H NMR (δ): 0.12 (s, 6H, $-Si(C\underline{H}_3)_2-$), 0.93 (d, J = 6.6 Hz, 2H, $-CH(C\underline{H}_3)_2$), 0.99 (t, J = 7.9 Hz, 2H, $C\underline{H}_2CH_2OH$), 1.75 (m, 1H, $-C\underline{H}(CH_3)_2$), 1.93 (s, 1H, $-O\underline{H}$), 2.07 (d, J = 6.6 Hz, 2H, $-C\underline{H}_2-C\equiv C$), 3.77 (t, J = 7.9 Hz, 2H, $-C\underline{H}_2OH$); IR (cm^{-1}): 3368

(s,b), 2176 (s), 1248 (s), 1172 (m), 1036 (s), 840 (s). Anal. Calcd. for $C_{10}H_{20}OSi$: C, 65.15; H, 10.93. Found: C, 65.03; H, 10.78.

2-{Dimethyl-(4-methyl-1(Z)-penten-1-yl)silyl}ethanol (17). Diisobutylaluminum hydride (4 cm^3 of 1M solution in hexane) was added under nitrogen to a hexane (10 cm^3) solution of alcohol **16** (0.3 g, 1.63 mmole), and the reaction mixture was stirred for 4 h. Then the reaction mixture was diluted with ethyl ether (50 cm^3) and a 10% solution of NaCl (20 cm^3). The product was extracted with ethyl ether and after work-up was purified by column chromatography. In this way, 0.25 g of pure alcohol **17** was obtained: b.p. 63°C/2 mm Hg; n_D^{20} = 1.4539; ^{1}H NMR (δ): 0.11 (s, 6H, $-Si(C\underline{H}_3)_2-$), 0.88 (d, J = 6.7 Hz, 2H, $-CH(C\underline{H}_3)_2$), 1.03 (t, J = 8.3 Hz, 2H, $-C\underline{H}_2CH_2OH$), 1.48 (s, 1H, -OH), 1.63 (m, 1H, $-C\underline{H}(CH_3)_2$), 1.99 (ddd, J = 7.3, 6.9 and 1.3 Hz, 2H, $-C\underline{H}_2CH=CH$), 3.72 (t, J = 8.3 Hz, 2H, $-CH_2OH$), 5.46 (d,t, J = 14.2 and 1.3 Hz, 1H, $-CH_2CH=C\underline{H}-$), 6.33 (dt, J = 14.2 and 7.3 Hz, 1H, $-CH_2C\underline{H}=CH-$); IR (cm^{-1}): 3344 (s,b), 1604 (m), 1248 (s), 1172 (m), 1036 (s), 836 (s), Anal. Calcd. for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90. Found: C, 64.32; H, 11.74. Alcohol **17** was also obtained in 79% yield by the reduction of epoxide **15** with two equivalents of diisobutylaluminum hydride.

Synthesis of acetates 4, 9, 13, 18, and 19. General procedure: A solution of acetyl chloride (0.0025 mole) in ethyl ether (5 cm^3) was added to a cooled (0°C) solution of alcohol (0.002 mole) and anhydrous pyridine (0.004 mole) in ethyl ether (30 cm^3), and the reaction mixture was stirred for 2 h. Then water (20 cm^3) was added and the product was extracted with ethyl ether (2 × 20 cm^3). The combined ethereal solution was washed with 10% $CuSO_4$ solution, 10% $NaHCO_3$ solution, and brine, and dried ($MgSO_4$). The crude acetates were purified by column chromatography. Their physical and spectral data are given below:

4: Yield: 94%; b.p. 62°C/2 mm Hg; n_D^{20} = 1.4356; ^{1}H NMR (δ): 0.84 (d, J = 6.6 Hz, 6H, $-CH(C\underline{H}_3)_2$), 0.99 (s, 6H, $-C(C\underline{H}_3)_2$), 1.56 (m, 1H, $-C\underline{H}(CH_3)_2$), 1.60 (t, J = 7.6 Hz, 2H, $-C\underline{H}_2CH_2O-$), 1.84 (m, 2H, $-C\underline{H}_2CH=CH-$), 2.00 (s, 3H, $-C(O)C\underline{H}_3$), 4.02 (m, 2H, $-C\underline{H}_2O-$), 5.23–5.30 (m, 2H, $-C\underline{H}=C\underline{H}-$); IR ($cm^{-1}$): 1740 (s), 1384 (s), 1368 (m), 1244 (s), 1032 (s), 976 (s). Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.41; H, 11.42.

9: Yield: 95%; b.p. 65°C/2 mm Hg; n_D^{20} = 1.4410; ^{1}H NMR (δ): 0.88 (d, J = 6.6 Hz, 6H, $-CH(C\underline{H}_3)_2$, 1.11 (s, 6H, $-C(C\underline{H}_3)_2-$), 1.54 (m, 1H, $-C\underline{H}(CH_3)_2$), 1.71 (t, J = 6.7 Hz, 2H, $C\underline{H}_2CH_2O-$), 2.01 (s, 3H, $-C(O)C\underline{H}_3$), 2.02 (m, 2H, $-C\underline{H}_2CH=CH-$), 4.09 (t, J = 6.7 Hz, 2H, $-CH_2C\underline{H}_2O-$), 5.21–5.24 (m, 2H, $-C\underline{H}=C\underline{H}-$); IR ($cm^{-1}$): 1748 (s), 1468 (s), 1384 (s), 1364 (s), 1236 (s), 1032 (s), 712 (m). Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.35; H, 11.45.

13: Yield: 78%; b.p. 64°C/2 mm Hg; n_D^{20} = 1.4420; ^{1}H NMR (δ): 0.07 (s, 6H, $-Si(C\underline{H}_3)_2-$), 1.02 (m, 2H, $-C\underline{H}_2CH_2O$), 0.85 (d, J = 6.6 Hz, 6H, $-CH(C\underline{H}_3)_2$), 1.40 (m, 1H, $-C\underline{H}(CH_3)_2$), 1.98 (m, 2H, $-C\underline{H}_2CH=CH-$), 2.00 (s, 3H, $-C(O)C\underline{H}_3$), 4.11 (m, 2H, $-CH_2C\underline{H}_2O-$), 5.56 (dt, J = 18.5 and 1.3 Hz, 1H, $-CH_2CH=C\underline{H}-$), 6.00 (dt, J = 18.5 and 6.7 Hz, 1H, $-CH_2C\underline{H}=CH-$); IR (cm^{-1}): 1740 (s), 1616 (w), 1372 (m), 1360 (m), 1244 (s), 1048 (s), 952 (m), 826 (s). Anal. Calcd. for $C_{12}H_{12}O_2Si$: C, 64.23; H, 8.98. Found: C, 64.15; H, 9.05.

18: Yield: 60%; b.p. 63.5°C/2 mm Hg; n_D^{20} = 1.4432; ^{1}H NMR (δ): 0.16 (s, 6H, $-Si(C\underline{H}_3)_2-$), 0.95 (d, J = 6.6 Hz, 6H, $-CH(C\underline{H}_3)_2$), 1.05 (t, J = 8.4 Hz, 2H, $-C\underline{H}_2CH_2O-$), 1.80 (m, 1H, $-C\underline{H}(CH_3)_2$), 2.01 (s, 3H, $-C(O)C\underline{H}_3$), 2.08 (d, J = 6.6 Hz, $-CH_2C\equiv$), 4.20 (t, J = 8.4 Hz, $-CH_2C\underline{H}_2O-$); IR (cm^{-1}): 2176 (s), 1740 (s), 1240 (s), 1040 (s), 824 (s). Anal. Calcd. for $C_{12}H_{22}O_2Si$: C, 63.67; H, 9.79. Found: C, 63.75; H, 9.85.

19: Yield 91%; b.p. 67°C/2 mm Hg; n_D^{20} = 1.4440, ^{1}H NMR (δ): 0.13 (s, 6H, $-Si(C\underline{H}_3)_2-$), 0.88 (d, J = 6.8 Hz, 6H, $-CH(C\underline{H}_3)_2$, 1.04 (t, J = 8.4 Hz, 2H, $-C\underline{H}_2CH_2O-$), 1.61 (m, 1H, $-C\underline{H}(CH_3)_2$), 1.98 (ddd, J = 7.3, 6.9 and 1.3 Hz, 2H, $-CH_2CH=CH-$), 1.99 (s, 3H, $-C(O)C\underline{H}_3$), 4.14 (t, J = 8.4 Hz, $-CH_2C\underline{H}_2O-$), 5.44 (dt, J = 14.2 and 1.3 Hz, 1H, $-CH_2CH=C\underline{H}-$), 6.33 (dt, J = 14.2 and 7.3 Hz, 1H, $-CH_2C\underline{H}=CH-$); IR (cm^{-1}): 1740 (s), 1608 (m), 1240 (s), 1048 (s), 712 (m). Anal. Calcd. for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 63.01; H, 10.72.

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REFERENCES

(1) C. Wawrzeńczyk, Z. Przepiórka, and A. Zabża, Insect growth regulators. Part IX. Syntheses of aryl 3,7-dimethyl-4-octen-1-yl ethers, *Pol. J. Chem.,* 55, 819 (1981).
(2) R. Obara, T. Olejniczak, and C. Wawrzeńczyk, Odoriferous derivatives of (E)-3,7,7-trimethyl-4-octen-1-ol and its 7-sila analogue, *J. Soc. Cosmet. Chem.,* 46, 321–328 (1995).
(3) R. Tacke, M. Strecker, G. Lambrecht, U. Moser, E. Mutschler, Bioisosteric C/Si exchange in parasympatholytics of the pridinol type sila drugs, *Arch. Pharm.,* 317, 207 (1984).
(4) R. Tacke, M. Strecker, G. Lambrecht, U. Moser, and E. Mutschler, (2-Aminoethyl) cycloalkylphenylsilanole: Bioisosterer CSi—Austausch bei parasympatholytika vom typ des trihexylphenidyls, Lycrimins und Procyclidins, *Liebigs Ann. Chem.,* 922–930 (1983).
(5) S. McN. Siebruth, S. Y. Lin, J. F. Engel, J. A. Greenblatt, S. E. Burkart, and D. W. Gammon, "Silane Analogues of MTI-800: Biology and Chemistry," in *Recent Advances in the Chemistry of Insect Control,* J. Crombie, Ed. (Royal Society of Chemistry, Cambridge, 1989), pp. 142–150.
(6) I. Ujvary, A. Kis-Tamas, L. Varjes, and L. Nowak, Syntheses of silicon-containing juvenile hormone analogues, *Acta Chimica Hungarica,* 113, 165–175 (1983).
(7) T. Olejniczak, S. Łakota, A. Raszka, and C. Wawrzeńczyk, "Synthesis and Biological Activity of Some Sila-Juvenoids," in *Insects: Chemical, Physiological and Environmental Aspects,* D. Konopińska, Ed., 1985, pp. 271–275.
(8) R. Munstedt and U. Wannagat, Sila-Riechstoffe und Riechstoffe-Isostere, Ein neur Weg zu Sila-β-Jonon, *Monatsh,* 116, 693–700 (1985).
(9) R. Munstedt and U. Wannagat, α-Formylopropenylsilane als Modellsubstanzen für b-cyclocitral, *Liebigs Ann. Chem.,* 944–945 (1985).
(10) U. Wannagat, R. Munstedt, and U. Horder, Sila β-jonon und verwandte Verbindungen, *Liebigs Ann. Chem.,* 950–958 (1985).
(11) E. Vedejs and P. L. Fuchs, Inversion of acyclic olefins by the phosphorus betaine method: Scope and limitations, *J. Am. Chem. Soc.,* 95, 822–825 (1973).
(12) L. Birkofer and T. Kühn, Einfache Synthesen von symmetrischen bis (trimethylsilyl)-ethen, *Chem. Ber.,* 111, 3119–3123 (1978).
(13) H. N. Miller, K. W. Greenlee, J. M. Derfer, and C. E. Boord, Mono- and dialkylacetylenes from vicinal dihalides and sodium amide in liquid ammonia, *J. Org. Chem.,* 19, 1882–1888 (1954).
(14) P. M. Müller and D. Lamparsky, *Perfumes—Art, Science and Technology* (Elsevier Applied Science, London, 1991), pp. 278–286.
(15) L. Bateman, J. I. Cunneen, and E. S. Waight, Geranidenes the decomposition of 2,6-dimethylhept-5-en-2-ol and some derivatives thereof, *J. Chem. Soc.,* 1714–1718 (1952).