Synthesis of Ocimenol and Related Compounds from 5-Chloro-2-pentanone

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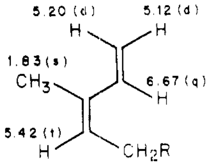
Extensive studies have been made to obtain versatile synthetic intermediates for terpene compounds. One of the successful examples is 6-methyl-5-hepten-2-one which has been widely used for the preparation of mono- or sesquiterpene alcohols having terminal prenyl groups. Fewer studies have been made on the synthesis of terpene alcohols with 2-methylbutenyl or 2-methylbutadienyl groups. In the search for novel useful intermediates for introducing these groups in terpene syntheses, we employed 5-chloro-2-pentanone (**1**) as a starting material.

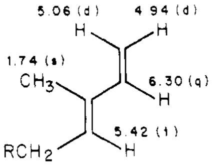
The Grignard reactions of **1** with ethyl- or vinylmagnesium bromide followed by dehydration gave C_7 mono- or diunsaturated chlorides. Another Grignard reaction of the unsaturated chlorides with carbonyl compounds was expected to afford terpene alcohols and their analogues. This paper describes the results of the syntheses of ocimenol (2,6-dimethyl-5,7-octadien-2-ol, **4**), dihydroalloocimenol (2,6-dimethyl-5-octen-2-ol, **9a**), and their analogues, which are considered to be useful fragrant materials. Ocimenol has been prepared by acid isomerization of myrcenol[1] or by the hydrolysis of myrcene hydrochloride.[2]

When 6-chloro-3-methyl-1-hexen-3-ol (**2**), obtained by the reaction of **1** with vinylmagnesium bromide in THF, was treated with diphosphorus pentoxide in benzene, a mixture of 6-chloro-3-methyl-1,3-hexadiene (**3a**, 85%) and 2-(3-chloropropyl)-1,3-butadiene (**3b**, 15%) was obtained in 70% yield (Scheme I). Fractional distillation gave 95% pure **3a**. Aqueous sulfuric acid (10%), potassium hydrogen sulfate, sodium sulfate, and aluminum oxide were also examined as dehydration reagents for **2**, but the contents of **3a** in the product mixtures were always lower than that obtained by diphosphorus pentoxide.

The ^{1}H NMR spectrum of the product showed two vinyl methyl groups at δ 1.74 and 1.83. Since it has been shown that in nonsymmetrical trisubstituted double bonds a vinyl methyl group occurs at a lower field in the cis relative to the trans isomer,[3] peaks at δ 1.74 and 1.83 were assigned to the trans and cis isomers of **3a**, respectively. Two doublets of the terminal vinyl protons and a quartet of a vinyl proton also exhibit different chemical shifts for the cis and trans isomers. The assignments shown were made on the basis of the changes of chemical shifts generally observed for different configurations of butadiene derivatives.[4] The pronounced shift of the vinyl proton at 6.67 ppm in *cis*-**3a** may be the consequence of a steric interaction of the proton with the chloropropyl group.[4] The integration of the resonance peaks of vinyl methyl protons suggests that the ratio of trans to cis isomer of **3a** is approximately 2.

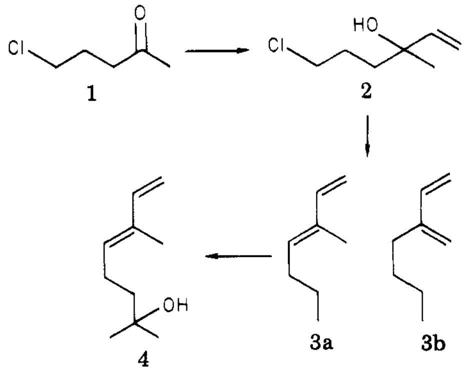


cis-3a



R = CH_2CH_2Cl

Scheme I



The Grignard reaction of **3a** with acetone in THF gave ocimenol (**4**), the structure of which was confirmed by NMR,[3b] IR, and mass spectral fragmentation. The ^{1}H NMR spectrum of **4** at lower field is very similar to that of **3a**, except that the relative intensities of the peaks due to cis isomer are much lower than those of **3a**. This seems to suggest that the reactivity of *cis*-**3a** in the Grignard reaction is lower than that of the trans isomer.

The mass spectrum of **4** shows some characteristic features of the fragmentation. The primary fragmentations are loss of H_2O and OH, and the abundance of these and the parent ions are in the order $M - H_2O > M - OH > M$. The formation of hydroxy carbonium ions (RR′COH) and C_5H_8 ions (m/e 68) is observed for all the alcohols prepared in this work. The formation of the ion at m/e 93 may occur by the loss of an isopropyl group from the dehydrated fragment of **4**. Analogous fragmentations are also observed for all the compounds prepared in this work.

The reactions of the Grignard reagent of **3a** with propionaldehyde and methyl ethyl ketone afforded 7-methyl-3-hydroxy-6,8-nonadiene (**5**) and 3,7-dimethyl-3-hydroxy-6,8-nonadiene (**6**), respectively. They exhibited quite similar mass spectral fragmentations to that of **4**, except that **5** did not give M − OH ion.

The reaction of **1** with ethylmagnesium bromide in THF gave 6-chloro-3-methyl-3-hexanol (**7**) in 65% yield. The subsequent dehydration of **7** with 10% sulfuric acid gave a mixture of 6-chloro-3-methyl-2-hexene (**8a**) and 6-chloro-3-methyl-3-hexene (**8b**) in 60% yield. The chlorination of **7** with concentrated HCl followed by dehydrochlorination with DMF afforded **8** in 75% yield. Gas chromatographic analysis and NMR spectrum indicate that the ratio of **8a** to **8b** is approximately 1.5. No *exo*-methylene compounds were detected. The structure of **8a** was confirmed also by comparison with an authentic sample prepared by the reaction of ethyltriphenylphosphonium bromide with 5-chloro-2-pentanone (**1**) in ether in the presence of *n*-butyllithium.

The reaction of the Grignard reagent of **8** with acetone gave a mixture of 2,6-dimethyl-5-octen-2-ol (dihydroalloocimenol, **9a**) and 2,6-dimethyl-6-octen-2-ol (**9b**), which are useful fragrant materials.[5] Analogous unsaturated

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(1) International Flavors & Fragrances Inc., Netherlands Appl., 6512236 (1966); *Chem. Abstr.*, **65**, 7225*d* (1966).

(2) B. J. Kane and R. A. von Genk, U.S. Patent, 3932539 (1976); *Chem. Abstr.*, 84, 135883 (1976).

(3) (a) R. B. Bates, R. H. Carnighan, R. O. Rakutis, and J. H. Schauble, *Chem. Ind.* (*London*), 1020 (1962); (b) K. L. Stevens, L. Jurd, and G. Manners, *Tetrahedron*, 28, 1939 (1972).

(4) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, New York, 1969, p 225.

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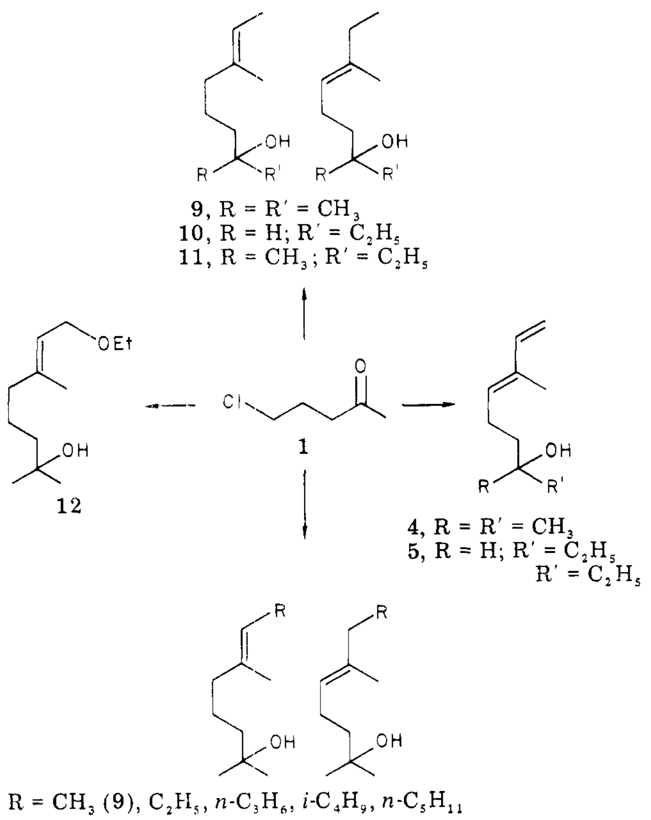
Scheme II



alcohols (**10** and **11**) were obtained by the reactions of **8** with propionaldehyde or methyl ethyl ketone.

The reactions of **1** with *n*-propyl-, *n*-butyl-, isoamyl-, and *n*-hexylmagnesium halides and the subsequent reactions with acetone similar to those described above afforded alkyl-substituted derivatives of **9**. It is interesting to note that contrary to the diene alcohols described above, these monounsaturated alcohols do not give parent ions or M − OH ions in their mass spectra. Dehydration seems to be a predominant process for these compounds.

Another type of compound obtained from **1** is hydroxygeranyl ethyl ether (**12**). The treatment of 6-chloro-3-methyl-1-hexen-3-ol (**2**) with aqueous hydrobromic acid gave an isomerized product 1-bromo-6-chloro-3-methyl-2-hexene, which was then converted to an ethyl ether by the reaction with sodium ethoxide. The Grignard reaction of the chloro ether with acetone in THF afforded **12** in 70% yield.

As summarized in Scheme II, the above described syntheses of terpene alcohols and their homologues seem to exhibit the utility of 5-chloro-2-pentanone (**1**) as a building block of compounds having 3-methyl-1,3-hexadienyl, 3-methyl-2- or -3-hexenyl, or related structures.

Experimental Section

5-Chloro-2-pentanone (**1**) was prepared by the treatment of α-acetyl-γ-butyrolactone with hydrochloric acid.[6] Halides, ketones, and aldehydes were distilled before use. IR spectra were taken on a JASCO-IRA2 instrument, and NMR spectra were determined in carbon tetrachloride on a Hitachi R-20A instrument; chemical shifts are reported in ppm downfield from tetramethylsilane. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet, q, quartet. Coupling constants are given in hertz. Mass spectra were recorded on a Hitachi RMU-7M high-resolution mass spectrometer at an ionizing voltage of 70 eV and a sample chamber temperature of 150 °C. Gas chromatograms were taken on a Hitachi 023 gas chromatograph using a 1-m column packed with 20% SE-30 on Celite. Reactions requiring anhydrous conditions were carried out under nitrogen.

6-Chloro-3-methyl-1-hexen-3-ol (2). To a mixture of THF (250 mL) and magnesium (35.1 g, 1.44 mol) were added ethyl bromide (2 mL) and iodine (0.5 g). After the mixture was stirred at room temperature for 5 min, a solution of vinyl bromide (123.8 g, 1.16 mol) in THF (135 mL) was added dropwise at room temperature. After being stirred for 1 h, the mixture was cooled by an ice bath below 10 °C, and a solution of **1** (146.5 g, 1.22 mol) in THF (120 mL) was added dropwise for about 2 h. The mixture was then warmed up to room temperature and stirred for 2 h. After the reaction, the reaction mixture was poured into 700 mL of 10% HCl solution saturated by NaCl and extracted with ether, and the ether solution was washed with 5% sodium hydrogen carbonate solution and water and then dried on sodium sulfate. The solution was concentrated in vacuo, and the residual oil was distilled at reduced pressure to yield 96.4 g (56%) of **2**: bp 52–53 °C (1.5 mm); IR 3450 (OH), 1640 (C═C), 1300, 1100, 995, 920 ($\mathrm{CH{=}CH_2}$); NMR 1.26 (s, 3 H, $\mathrm{CH_3}$), 1.4–2.2 (m, 4 H, $\mathrm{ClCH_2CH_2CH_2}$), 3.50 (t, *J* = 5 Hz, 2 H, $\mathrm{ClCH_2}$), 4.8–5.3 (m, 2 H, $\mathrm{{=}CH_2}$), 5.86 ppm (q, *J* = 11 and 18 Hz, 1 H, CH═).

6-Chloro-3-methyl-1,3-hexadiene (3a). To a mixture of benzene (300 mL) and phosphorus pentoxide (37.9 g, 0.27 mol) was added **2** (30.0 g, 0.20 mol) dropwise at room temperature. After 1 h of reaction, the precipitates were filtered off, and the filtrate was washed with 5% sodium hydrogen carbonate solution and saturated NaCl solution and dried on sodium sulfate. The solution was concentrated in vacuo, and the residual oil was distilled at reduced pressure to yield a mixture of **3a** and 2-(3-chloropropyl)-1,3-butadiene (**3b**). The content of **3a** was determined to be 85% by GLC. After repeated distillations, **3a** with purity of 95% was obtained: yield 70%; bp 60–61 °C (15 mm); IR 1643 and 1608 (C═C), 1442, 1292, 985, 900 ($\mathrm{CH{=}CH_2}$); NMR 1.74 and 1.83 (s, 3 H, $\mathrm{CH_3}$), 2.56 (q, *J* = 6 Hz, 2 H, $\mathrm{CH_2CH{=}}$), 3.45 (t, *J* = 6 Hz, 2 H, $\mathrm{ClCH_2}$), 4.94 (d, *J* = 11 Hz, 1 H, cis $\mathrm{{=}CH_2}$), 5.06 (d, *J* = 17 Hz, 1 H, trans $\mathrm{{=}CH_2}$), 5.42 (t, *J* = 7 Hz, 1 H, $\mathrm{CH_2CH{=}}$), 6.30 and 6.67 ppm (2 q, *J* = 10 and 18 Hz, 1 H, $\mathrm{CH{=}CH_2}$); MS *m/e* 132 and 130 (parents), 95 ($\mathrm{C_7H_{11}}$), 94 ($\mathrm{C_7H_{10}}$, M − HCl), 81 ($\mathrm{C_6H_9}$), 68 ($\mathrm{C_5H_8}$), 53 ($\mathrm{C_4H_5}$).

2,6-Dimethyl-5,7-octadien-2-ol (Ocimenol, 4). To a mixture of THF (20 mL) and magnesium (2.0 g, 0.08 mol) were added ethyl bromide (0.15 mL) and iodine (0.1 g). The mixture was heated and refluxed, and a solution of **3a** (9.0 g, 0.07 mol) in THF (17 mL) was added dropwise. After the mixture was refluxed for 2 h, acetone (4.1 g, 0.07 mol) in THF (10 mL) was added dropwise at 15–20 °C. The mixture was stirred for 3 h, poured into 50 mL of 10% HCl solution saturated with NaCl, and extracted with ether. The ether solution was washed with 5% sodium hydrogen carbonate solutions and water and dried over sodium sulfate. The concentration of the solution in vacuo and the distillation of the residual oil gave 4.9 g (47%) of **4**: bp 57–59 °C (2 mm), purity by GLC 96%; IR 3370 (OH), 1648 and 1614 (C═C), 1385, 1210, 990, 900 ($\mathrm{CH_2{=}CH}$); NMR 1.18 (s, 6 H, $\mathrm{CH_3COH}$), 1.3–1.7 (m, 2 H, $\mathrm{CH_2COH}$), 1.71 (s, 3 H, $\mathrm{CH_3C{=}}$), 1.9–2.4 (m, 2 H, $\mathrm{CH_2CH{=}}$), 4.83 (d, *J* = 10 Hz, 1 H, cis $\mathrm{{=}CH_2}$), 4.97 (d, *J* = 18 Hz, 1 H, trans $\mathrm{{=}CH_2}$), 5.4 (t, *J* = 6 Hz, 1 H, $\mathrm{CH_2CH{=}}$), 6.25 and 6.72 ppm (2 q, *J* = 10 and 17 Hz, 1 H, $\mathrm{CH{=}CH_2}$); MS *m/e* 154 (parent), 137 ($\mathrm{C_{10}H_{17}}$, M − OH), 136 ($\mathrm{C_{10}H_{16}}$, M − $\mathrm{H_2O}$), 121 ($\mathrm{C_9H_{13}}$), 93 ($\mathrm{C_7H_9}$), 81 ($\mathrm{C_6H_9}$), 68 ($\mathrm{C_5H_8}$), 59 ($\mathrm{C_3H_7O}$).

Similar reactions of **3a** with propionaldehyde and methyl ethyl ketone afforded 7-methyl-3-hydroxy-6,8-nonadiene (**5**) and 3,7-dimethyl-3-hydroxy-6,8-nonadiene (**6**), respectively. The yield of **5** was 50%: bp 64–65 °C (2 mm); IR 3350 (OH), 1645 and 1612 (C═C), 1465, 1120, 992, 895 ($\mathrm{CH_2{=}CH}$); NMR 0.94 (t, *J* = 7 Hz, 3 H, $\mathrm{CH_3CH_2}$), 1.1–1.7 (m, 4 H, $\mathrm{CH_2C(OH)CH_2}$), 1.74 (s, 3 H, $\mathrm{CH_3C{=}}$), 1.9–2.5 (m, 2 H, $\mathrm{CH_2CH{=}}$), 3.44 (quintuplet, *J* = 6 Hz, 1 H, CHOH), 4.85 (d, *J* = 6 Hz, 1 H, cis $\mathrm{{=}CH_2}$), 4.98 (d, *J* = 17 Hz, 1 H, trans $\mathrm{{=}CH_2}$), 5.42 (t, *J* = 7 Hz, 1 H, $\mathrm{CH_2CH{=}}$), 6.27 and 6.72 ppm (2 q, *J* = 11 and 17 Hz, 1 H, $\mathrm{CH{=}CH_2}$); MS *m/e* 154 (parent), 136 ($\mathrm{C_{10}H_{16}}$, M − $\mathrm{H_2O}$), 121 ($\mathrm{C_9H_{13}}$), 93 ($\mathrm{C_7H_9}$), 81 ($\mathrm{C_6H_9}$), 68 ($\mathrm{C_5H_8}$), 59 ($\mathrm{C_3H_7O}$). Yield of **6** was 45%: bp 84–85

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(5) (a) R. Kitaoka and Y. Fujita, *Nippon Kagaku Kaishi*, **74**, 76 (1953); (b) R. L. Webb, U.S. Patent, 2 902 510 (1959); *Chem. Abstr.*, **54**, 1292*d* (1960); (c) H. Kroesche and H. Pasedach, German Offen., 1 927 845 (1970); *Chem. Abstr.*, **74**, 41 899 (1971).

(6) G. W. Cannon, R. C. Ellis, and J. R. Leal, "Organic Syntheses", Collect. Vol. 4, Wiley, New York, 1963, p 597.

°C (2.5 mm); IR 3400 (OH), 1640 and 1605 (C=C), 1460, 1376, 1120, 985 and 892 (CH_2=CH); NMR 0.90 (t, *J* = 7 Hz, 3 H, CH_3CH_2), 1.14 (s, 3 H, CH_3COH), 1.2–1.7 (m, 4 H, CH_2C(OH)CH_2), 1.74 (s, 3 H, CH_3C=), 1.8–2.5 (m, 2 H, =CHCH_2), 4.85 (d, *J* = 6 Hz, 1 H, cis =CH_2), 5.00 (d, *J* = 17 Hz, 1 H, trans =CH_2), 5.42 (t, *J* = 6 Hz, 1 H, CH_2CH=), 6.29 and 6.75 ppm (2 q, *J* = 9 and 17 Hz, 1 H, CH=CH_2); MS *m/e* 168 (parent), 151 ($C_{11}H_{19}$, M – OH), 150 ($C_{11}H_{18}$, M – H_2O), 121 (C_9H_{13}), 93 (C_7H_9), 81 (C_6H_9), 73 (C_4H_9O), 68 (C_5H_8).

6-Chloro-3-methyl-2-hexene (8a) and 6-Chloro-3-methyl-3-hexene (8b). 6-Chloro-3-methyl-3-hexanol (7) was prepared by a method similar to that described for the preparation of **2**: yield 65%, bp 71–73 °C (2 mm). A mixture of **7** (45.2 g, 0.30 mol) and concentrated HCl (50 mL) was stirred for 1 h at room temperature. The solution was extracted with ether, and the extract was washed with 5% sodium carbonate solution and water. After evaporation of ether under reduced pressure, DMF (50 mL) was added, and the mixture was heated at 130 °C for 3 h. Water was then added to the solution, and it was extracted with ether. The ether solution was dried over sodium sulfate and concentrated in vacuo. Subsequent distillation under reduced pressure afforded a mixture of **8a** and **8b**: 75% yield, bp 70–73 °C (35 mm).

An authentic sample of **8a** was prepared by the Wittig reaction of **1** with ethylidenetriphenylphosphorane. Thus, to a mixture of ethyltriphenylphosphonium bromide (72.5 g, 0.20 mol) with ether (500 mL) was added under nitrogen a 15% hexane solution of *n*-butyllithium (0.20 mol), and the mixture was stirred for 3 h at room temperature. **1** was then added dropwise at room temperature, and the mixture was refluxed for 2 h. Water was added to stop the reaction, and the mixture was extracted with hexane. After the solution was dried over sodium sulfate, ether and hexane were evaporated under reduced pressure, and the distillation of the residual oil afforded pure **8a** in 20% yield: bp 64–65 °C (23 mm); IR 1670 (C=C), 1440, 1380, 1260, 1015, 808 (CH=C); NMR 1.4–1.8 (several s, 6 H, CH_3C=), 1.8–2.3 (m, 4 H, CH_2CH_2C=), 3.45 (t, *J* = 6 Hz, 2 H, CH_2Cl), 5.0–5.5 ppm (m, 1 H, =CH); MS *m/e* 134 and 132 (parent), 83 (C_6H_{11}), 69 (C_5H_9).

2,6-Dimethyl-5-octen-2-ol (Dihydroalloocimenol, 9a) and 2,6-Dimethyl-6-octen-2-ol (9b). A mixture of **9a** and **9b** was obtained in 76% yield by a reaction of **8a** and **8b** with acetone similar to that described for the preparation of **4**: bp 69–71 °C (2 mm); IR 3390 (OH), 1670 (C=C), 1470, 1380, 1200, 1150, 905; NMR 0.89 (t, *J* = 6 Hz, CH_2CH_3), 1.18 (s, CH_3COH), 1.2–1.7 (m, CCH_2C), 1.60 (s, CH_3C=), 1.7–2.3 (m, CH_2C=), 4.8–5.3 ppm (m, CH=); MS *m/e* 138 ($C_{10}H_{18}$, M – H_2O), 123 (C_9H_{15}), 95 (C_7H_{11}), 83 (C_6H_{11}), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O).

Similarly, 7-methyl-6- or -7-nonen-3-ol (**10**) and 3,7-dimethyl-6- or -7-nonen-3-ol (**11**) were obtained by the reactions of **8** with propionaldehyde and methyl ethyl ketone, respectively. Yield of **10** was 55%: bp 79–82 °C (3 mm); 3350 (OH), 1660 (C=C), 1450, 1370, 1110, 960; NMR 0.90 (t, *J* = 7 Hz, CH_3CH_2CHOH), 0.95 (t, *J* = 7 Hz, CH_3CH_2C=), 1.2–1.7 (m, CCH_2C), 1.58 (s, CH_3C=), 1.7–2.3 (m, CH_2C=), ca. 3.3 (m, CHOH), 4.8–5.3 ppm (m, CH=); MS *m/e* 156 (parent), 139 ($C_{10}H_{19}$, M – OH), 138 ($C_{10}H_{18}$, M – H_2O), 127 ($C_8H_{15}O$), 95 (C_7H_{11}), 83 (C_6H_{11}), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O). Yield of **11** was 70%: bp 79–81 °C (1 mm); IR 3420 (OH), 1670 (C=C), 1450, 1370, 1175, 1140, 925; NMR 0.86 (t, *J* = 7 Hz, CH_3CH_2COH), 0.96 (t, *J* = 7 Hz, CH_3CH_2C=), 1.10 (s, CH_3COH), 1.2–1.7 (m, CCH_2C), 1.58 (s, CH_3C=), 1.7–2.3 (m, CH_2C=), 4.8–5.3 ppm (m, CH=); MS *m/e* 152 ($C_{11}H_{20}$, M – H_2O), 123 (C_9H_{15}), 95 (C_7H_{11}), 83 (C_6H_{11}), 73 (C_4H_9O), 69 (C_5H_9).

When *n*-propyl bromide, *n*-butyl chloride, isoamyl chloride, or *n*-hexyl chloride were used in place of ethyl bromide in the reaction with **1**, subsequent dehydration and Grignard reaction with acetone gave alkyl substituted dihydroalloocimenol and their isomers, $(CH_3)_2C(OH)(CH_2)_3C(CH_3)$=$CHCH_2R$ and $(CH_3)_2C(OH)(CH_2)_2CH$=$C(CH_3)(CH_2)_2R$. The substituent R, yield, boiling point, and mass spectral fragments are as follows: CH_3, 68%, 78–80 °C (2 mm), MS *m/e* 152 ($C_{11}H_{20}$, M – H_2O), 137 ($C_{10}H_{17}$), 109 (C_8H_{13}), 97 (C_7H_{13}), 95 (C_7H_{11}), 83 (C_6H_{11}), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O); C_2H_5, 70%, 92–94 °C (2 mm), MS *m/e* 166 ($C_{12}H_{22}$, M – H_2O), 151 ($C_{11}H_{19}$), 123 (C_9H_{15}), 95 (C_7H_{11}), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O); $(CH_3)_2CH$, 67%, 100–103 °C (2 mm), MS *m/e* 180 ($C_{13}H_{24}$, M – H_2O), 165 ($C_{12}H_{21}$), 137 ($C_{10}H_{17}$), 95 (C_7H_{11}), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O); $CH_3(CH_2)_3$, 65%, 109–113 °C (2 mm), MS *m/e* 194 ($C_{14}H_{26}$, M – H_2O), 179 ($C_{13}H_{23}$), 139 ($C_{10}H_{19}$), 123 (C_9H_{15}), 95 (C_7H_{11}), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O).

Hydroxygeranyl Ethyl Ether (12). A mixture of **2** (0.30 mol) and 47% HBr solution (80 mL) was stirred at room temperature for 3 h. The mixture was extracted with ether, and the ether solution was washed with water and dried over sodium sulfate. After evaportion of the ether, distillation gave 1-bromo-6-chloro-3-methyl-2-hexene in 60% yield; bp 84–86 °C (1 mm). The bromide was added to a solution of sodium (0.16 mol) in ethanol (150 mL), and the solution was stirred at room temperature for 2 h. After evaporation of ethanol, the mixture was extracted with ether, and the extract was washed with water and dried over sodium sulfate. The ether was evaporated off, and the distillation of the residue gave 6-chloro-1-ethoxy-3-methyl-2-hexene in 85% yield: bp 79–81 °C (1 mm); IR 1670 (C=C), 1436, 1372, 1100 (C-O-C); NMR 1.14 (t, *J* = 7 Hz, 3 H, CH_3CH_2), 1.64 and 1.72 (2 s, 3 H, CH_3C=), 1.7–2.4 (m, 4 H, $ClCH_2CH_2CH_2$), 3.37 (q, *J* = 7 Hz, 2 H, OCH_2CH_3), 3.46 (t, *J* = 7 Hz, 2 H, $ClCH_2$), 3.86 (d, *J* = 6 Hz, 2 H, =$CHCH_2O$), 5.33 ppm (t, *J* = 7 Hz, 1 H, =CH).

The Grignard reaction of 6-chloro-1-ethoxy-3-methyl-2-hexene with acetone was carried out in a similar manner to that for **4**, and **12** was obtained in 70% yield: bp 102–103 °C (1 mm); IR 3420 (OH), 1662 (C=C), 1450, 1370, 1095 (C-O-C); NMR 1.14 (s, 6 H, CH_3COH), 1.14 (t, *J* = 7 Hz, 3 H, CH_2CH_3), 1.3–1.6 (m, 4 H, $CH_2CH_2CH_2$C=), 1.8–2.3 (m, 2 H, CH_2C=), 3.39 (q, *J* = 7 Hz, 2 H, OCH_2CH_3), 3.89 (d, *J* = 7 Hz, 2 H, =CCH_2O), 5.30 ppm (t, *J* = 7 Hz, 1 H, =CH); MS *m/e* 182 ($C_{12}H_{22}O$, M – H_2O), 167 ($C_{11}H_{19}O$), 139 ($C_9H_{15}O$), 137 ($C_{10}H_{17}$), 113 ($C_7H_{13}O$), 99 ($C_6H_{11}O$), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O).

Registry No. 1, 5891-21-4; 2, 42448-57-7; *cis*-3a, 61432-63-1; *trans*-3a, 42448-59-9; 3b, 26831-14-1; *cis*-4, 7643-59-6; *trans*-4, 7643-60-9; *cis*-5, 71616-37-0; *trans*-5, 71616-38-1; *cis*-6, 71616-39-2; *trans*-6, 71616-40-5; 7, 71616-41-6; 8a, 60379-90-0; 8b, 71616-42-7; 9a, 59861-43-7; 9b, 30385-25-2; 10, 71616-23-4; 11, 71616-25-6; 12, 71616-43-8; α-acetyl-γ-butyrolactone, 517-23-7; vinyl bromide, 593-60-2; acetone, 67-64-1; propionaldehyde, 123-38-6; methyl ethyl ketone, 78-93-3; ethyltriphenylphosphonium bromide, 1530-32-1; *n*-propyl bromide, 106-94-5; *n*-butyl chloride, 109-69-3; isoamyl chloride, 107-84-6; *n*-hexyl chloride, 544-10-5; ethyl bromide, 74-96-4; 2,6-dimethyl-5-nonen-2-ol, 71616-44-9; 2,6-dimethyl-5-decen-2-ol, 71616-45-0; 2,6,9-trimethyl-5-decen-2-ol, 71616-46-1; 2,6-dimethyl-5-dodecen-2-ol, 71616-47-2; 2,6-dimethyl-6-nonen-2-ol, 71616-48-3; 2,6-dimethyl-6-decen-2-ol, 71616-49-4; 2,6,9-trimethyl-6-decen-2-ol, 71616-50-7; 2,6-dimethyl-6-dodecen-2-ol, 71616-51-8; 1-bromo-6-chloro-3-methyl-2-hexene, 71616-52-9; 6-chloro-1-ethoxy-3-methyl-2-hexene, 71616-53-0.

Synthesis of Certain Bipyranylidene and Bi(thiopyranylidene) Derivatives

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Since the first report on the high electrical conductivity of the charge-transfer salt of tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ),[1] there has been much interest in the synthesis of tetrathiafulvalene (TTF) and its derivatives and analogues. We have been interested in the synthesis of 2,2′,6,6′-tetraaryl-4,4′-bipyranylidenes, the sulfur analogues, and related compounds, as this type of compound also forms highly conducting salts with TCNQ.[2]

These dimers are prepared by heating a 4*H*-pyran-4-thione or a 4*H*-4,4-dichloropyran with copper in a solvent

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