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SYNTHESIS OF THE PRINCIPAL COMPONENTS OF THE SEX ATTRACTANT FROM MALE *IPS CONFUSUS* FRASS: 2-METHYL-6-METHYLENE-7-OCTEN-4-OL, 2-METHYL-6-METHYLENE-2,7-OCTADIEN-4-OL, AND (+)-*CIS*-VERBENOL

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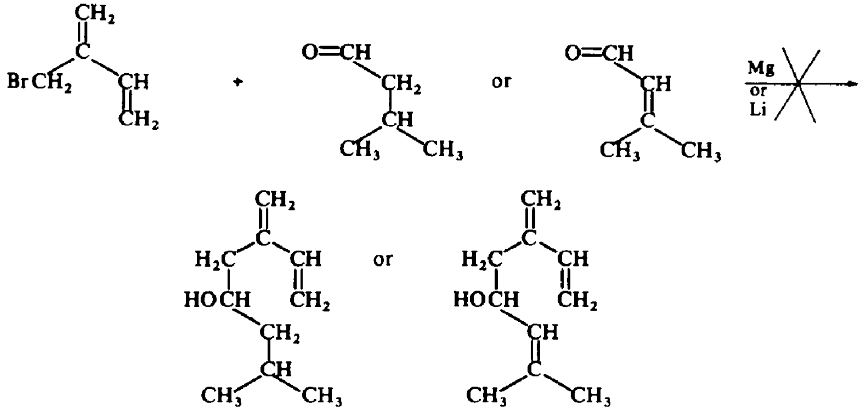
Abstract—We have synthesized the three terpene alcohols previously identified as the principal components of the sex attractant produced by the bark beetle, *Ips confusus*. The compounds are: 2-methyl-6-methylene-7-octen-4-ol (I), 2-methyl-6-methylene-2,7-octadien-4-ol (II), and (+)-*cis*-verbenol (XIII).

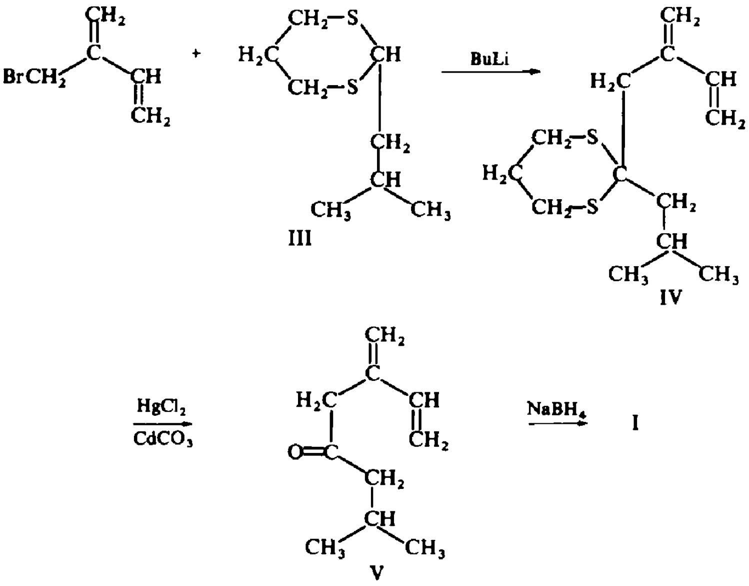
The title compounds have been identified as the principal components of the sex attractant produced in the frass of the male bark beetle, *Ips confusus*, boring in ponderosa pine.[1] We carried out their synthesis to confirm identification and to furnish materials for laboratory and field bioassays, the successful results of which will be reported elsewhere.

We were unable to prepare the Grignard reagent or the lithium reagent from 2-bromomethylbutadiene[2] and to react them with isovaleraldehyde and/or with β,β-dimethylacrolein to synthesize respectively 2-methyl-6-methylene-7-octen-4-ol (I), and 2-methyl-6-methylene-2,7-octadien-4-ol (II).



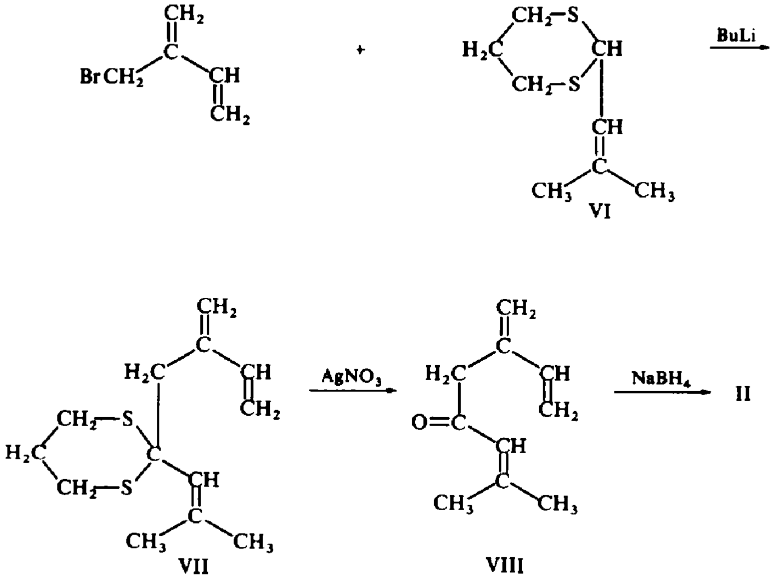
I II

A procedure recently developed by Corey[3] that utilizes the anion of a blocked aldehyde to form a blocked ketone was the initial step in the sequence leading to Compound I (III → IV → V → I). The reaction of 2-isobutyl-1,3-dithiane (III) with 2-bromomethylbutadiene in the presence of butyl lithium gave 2-methyl-6-methylene-7-octen-4-one propanedithioketal (IV). Deblocking with the commonly used mixture



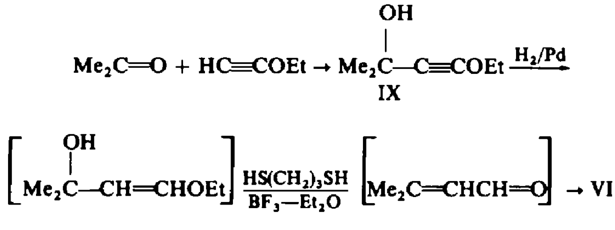
of mercuric chloride and cadmium carbonate gave 2-methyl-6-methylene-7-octen-4-one (V), which on sodium borohydride reduction gave compound I.

A similar sequence was utilized to prepare compound II (VI → VII → VIII → II)



The reaction of 2-isobutenyl-1,3-dithiane (VI) with 2-bromomethylbutadiene gave 2-methyl-6-methylene-2,7-octadien-4-one propanedithioketal (VII). Deblocking with mercuric chloride and cadmium carbonate resulted in non-distillable material and a minute amount of 2-methyl-6-methylene-2,7-octadien-4-one (VIII); no improvement could be effected by using mercuric salts under various conditions. Acceptable yields were finally achieved by deblocking with silver nitrate.[*]

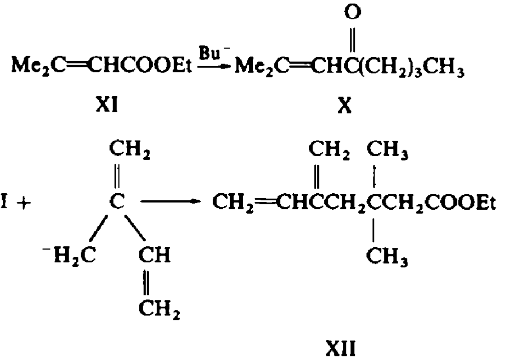
2-Isobutenyl-1,3-dithiane (VI) was prepared by treating the crude product from the hydrogenation of dimethylethoxyethynyl carbinol (IX) with propanedithiol and boron trifluoride–etherate. Compound IX was prepared from acetone and ethoxyacetylene (Humphrey Chemical Co., North Haven, Conn.) by the procedure of Nazarov, *et al.*[5]



$$\mathrm{Me_2C{=}O + HC{\equiv}COEt \rightarrow \underset{IX}{Me_2\overset{OH}{\overset{|}{C}}{-}C{\equiv}COEt}} \xrightarrow{H_2/Pd}$$

$$\left[\mathrm{Me_2\overset{OH}{\overset{|}{C}}{-}CH{=}CHOEt}\right] \xrightarrow[BF_3{-}Et_2O]{HS(CH_2)_3SH} \left[\mathrm{Me_2C{=}CHCH{=}O}\right] \rightarrow \mathrm{VI}$$

Two by-products were identified in the reaction mixture that contained 2-methyl-6-methylene-2,7-octadien-4-one (VIII): 2-methyl-2-octen-4-one (X) probably resulted from the reaction of butyl lithium with the carbonyl group of ethyl β,β-dimethylacrylate (XI), whereas ethyl 3,3-dimethyl-5-methylene-6-heptenoate (XII) probably results from a Michael attack by the isoprenyl anion on ethyl β,β-dimethylacrylate (XI). The latter may have resulted from acid-catalyzed rearrangement of IX during the workup of the magnesium alkoxy intermediate, or from any unreduced IX that remained after hydrogenation.

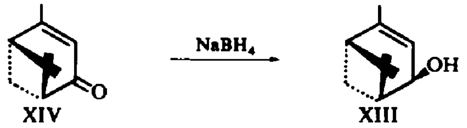


$$\underset{XI}{\mathrm{Me_2C{=}CHCOOEt}} \xrightarrow{Bu^-} \underset{X}{\mathrm{Me_2C{=}CH\overset{O}{\overset{\|}{C}}(CH_2)_3CH_3}}$$

$$\mathrm{XI} + \mathrm{{}^-H_2C{-}\overset{CH_2}{\overset{\|}{C}}{-}CH{=}CH_2} \longrightarrow \mathrm{CH_2{=}CH\overset{CH_2}{\overset{\|}{C}}CH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2COOEt}$$

XII

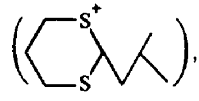
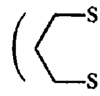
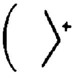
cis-Verbenol has been reported several times in the literature. The conflicting reports are summarized[6] by Banthorpe and Whittacker who conclude that "further studies, monitored by GLC, are urgently needed to elucidate these discrepancies concerning the *cis* isomer." We report the synthesis of (+)-*cis*-verbenol (XIII) by sodium borohydride reduction of (−)-verbenone (XIV), and the properties of a GLC cut of XIII.

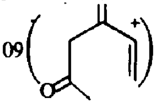
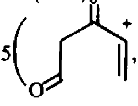
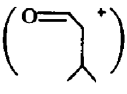


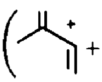
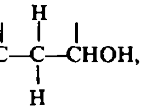
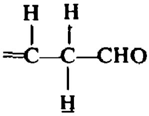
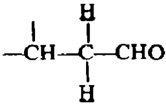
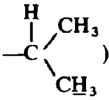
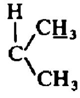
XIV XIII

[*] Silver nitrate has been used to prepare dithiols from dithianes.[4]

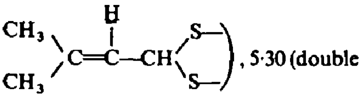
EXPERIMENTAL

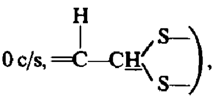
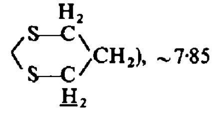
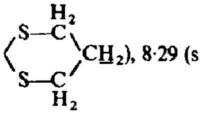
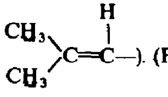
2-Methyl-6-methylene-7-octen-4-one propanedithioketal (IV). To a stirred soln of 5·8 g (0·033 mole) 2-isobutyl-1,3-dithiane[7] (b.p. 61°/0·17 mm) in 75 ml anhyd THF at −40°, was added under N_2, over a period of 5 min, 21 ml (0·033 mole) of n-BuLi (1·6M in hexane, Foote Mineral Co.). The soln was held at −20° for 5 hr, cooled to −40°, and treated with 3·6 ml (4·9 g, 0·033 mole) 2-bromomethylbutadiene[2] and 200 mg NaI. The mixture (stirred) was allowed to come to room temp over a period of 5 hr, and poured onto ice. 1N HCl was added to pH 6; the soln was extracted with pentane; the pentane soln was washed successively with 3% $NaHSO_3$aq, 1N KOH, and water, dried over K_2CO_3, and concentrated to 8 g of yellow oil. The oil was distilled (short-path) at 110°/0·1 mm. The distillate (4·5 g), which was used in the next step, was 89% pure (51% yield) by GLC (Aerograph 204, 10% Carbowax 20M on 60/80 mesh Chromosorb W, 5 ft × ⅛ in aluminium tubing, 155°, 29 cm³ He/min, retention time 16 min). A GLC cut melted at 32–35°, and gave the following spectral data. Calc. M^+ for $C_{13}H_{22}S_2$: 242. Mass spectrum (*m/e*): M^+ not detected, 175 (), 107 ( +H, base), 43 () IR (λ_{max}^{film}, μ) 3·28 (olefinic CH), 6·12 and 6·26 (conj. double bond), 10·1 and 11·0 vinyl), 11·1 sh (terminal methylene).

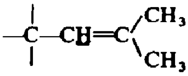
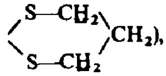
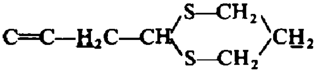
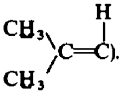
2-Methyl-6-methylene-7-octen-4-one (V). A mixture of 4·4 g (0·018 mole) of IV, 20·2 g moist $CdCO_3$, and 20·2g $HgCl_2$ in 120 ml acetone and 23 ml water was stirred at 50° under N_2 for 15 min. Another 10·1 g $CdCO_3$ was added and the mixture was stirred at 50° for an additional 30 min. KI (26·1 g) was added and the mixture was stirred at room temp for 15 min. The mixture was filtered and the solid material was washed with acetone. The filtrate and washings were concentrated under reduced press to 60 ml and extracted with pentane. The pentane soln was washed with KIaq, dried with Na_2SO_4, and concentrated to a yellow oil (1·6 g, 59% yield), which showed a strong C=O band in the IR spectrum at 5·84 μ. The ketone was distilled (short-path) at 110°/10 mm, and the distillate was used in the next step. The following spectral and combustion data were obtained on a GLC cut (8% Carbowax 20M on Chromosorb G, 60/80 mesh, 12 ft × ¼ in aluminium tubing, 115°, 44 cm³ He/min, retention time 30 min). Calc. M^+ for $C_{10}H_{16}O$: 152. Mass spectrum (*m/e*): M^+ 152 (11·2% of base), $M^+ + 1$ (11·3% of P; calc.: $M^+ + 1$ = 11·1%), 137 ($M^+ - CH_3$), 109 (), 95 (, base), 85 (). IR (λ_{max}^{film}, μ): 3·28 (olefinic CH), 5·84 (C=O), 6·26 (conj. double bond), 10·1 and 11·1 (vinyl). (Found: C, 78·74; H, 10·39. Calc. for $C_{10}H_{16}O$ (152·2): C, 78·89; H, 10·59%).

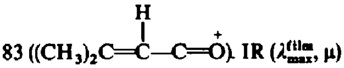
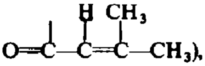
2-Methyl-6-methylene-7-octen-4-ol (I). $NaBH_4$ (0·40 g, 0·0105 mole) was added to a soln of 0·54 g (0·0035 mole) of the distilled ketone V in 15 ml MeOH and 4 ml water in an ice bath, and the soln was held at 0° for 3 hr. Pentane extraction, removal of the pentane, and distillation (short-path) of the residue at 110°/10 mm gave 0·45 g of an oil whose IR spectrum showed an OH band but no CO absorption. The distillate was 80% compound I (66% yield) by GLC analysis (Aerograph 204, 10% Carbowax 20M on 60/80 mesh Chromosorb W, 5 ft × ⅛ in aluminium tubing, 115°, 30 cm³ He/min, retention time 7·25 min). Pure compound I was isolated by preparative GLC (Aerograph A90P3, 20% Carbowax 20M on 45/60 mesh Chromosorb W, 6 ft × ⅜ in aluminium tubing, 100 cm³ He/min slowed to 40 cm³ He/min during collection of the major peak, retention time 15 to 37 min). The spectral data on the GLC isolated compound I were congruent with those of the compound isolated from frass.[8] Calc. M^+ for $C_{10}H_{18}O$: 154. Mass sepctrum (*m/e*): M^+ 154 (1·1% of base), base 68 ( + H). IR (λ^{film}, μ): 2·96 (OH), 3·23 (olefinic CH), 6·25 (conj. double bond), 7·21 and 7·29 (*gem*-dimethyl), 10·1 and 11·1 (vinyl), 11·26 sh (terminal methylene). NMR ($CDCl_3$, τ): 3·60 (doublet of doublets, 1 proton, J_{trans} 18 c/s, J_{cis} 12 c/s, —C—CH=CH₂), 4·65–5·10 (multiplet, 4 protons, terminal methylenes), 6·20 (multiplet, 1 proton, —CHOH), 7·53 (doublet of doublets, 1 proton, J_{gem} 14 c/s, J_{vic} 4 c/s,  $=\overset{|}{C}-\underset{H}{\overset{H}{C}}-\overset{|}{C}HOH$, 7·82 (doublet of doublets, 1 proton, J_{gem} 14 c/s, J_{vic} 9 c/s,  $=\overset{H}{C}-\underset{\underline{H}}{\overset{H}{C}}-CHOH$), ~8·25 (multiplet, 1 proton, —C$\underline{H}$(CH$_3$)$_2$), 8·40 (singlet, 1 proton, OH), ~8·65 (multiplet, 2 nonequivalent protons,  $-\overset{|}{C}H-\underset{\underline{H}}{\overset{\underline{H}}{C}}-CHOH$), 9·08 (doublet, 3 protons, 7 c/s,  $-\overset{H}{C}{<}^{CH_3}_{C\underline{H}_3}$), 9·10 (doublet, 3 protons,  $\overset{H}{C}{<}^{C\underline{H}_3}_{CH_3}$). UV (mμ): λ_{max}^{hexane} 226 (ε_{max} 20,000). (Found: C, 77·60; H, 11·64. Calc. for $C_{10}H_{18}O$ (154·2): C, 77·86; H, 11·76%.)

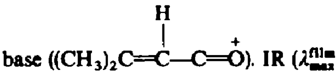
2-*Isobutenyl*-1,3-*dithiane* (VI). Compound IX[5] (38 g, 0·296 mole) in 60 ml ether was hydrogenated at atm press in the presence of 5 g of 10% Pd—CaCO$_3$.[5] The reaction slowed after about two thirds of the calculated amount of H$_2$ was absorbed; therefore 3 g of additional catalyst was added, and the reaction was continued until 0·296 moles of H$_2$ was absorbed. The catalyst was filtered, and to the filtrate was added 26·5 ml (0·25 mole) propanedithiol. To this soln, cooled in an ice–salt slurry, was added, slowly with stirring, 64 ml (0·5 mole) BF$_3$-etherate. (*Warning*: rapid addition may cause a violent exothermic reaction). The soln was stirred for 15 min at 0°, poured into 10% NaOH aq, and extracted 3 times with equal volumes of CHCl$_3$. The CHCl$_3$ soln was washed with water and dried over Na$_2$SO$_4$; the CHCl$_3$ was removed under vacuum. Short-path distillation at 100°/0·1 mm gave 22·3 g (40% based on dimethylethoxyethynyl carbinol) of distillate, which was used in the next step; it was 90% pure by GLC analysis (Aerograph A90P3, 20% Carbowax M on 60/80 mesh Chromosorb W, 6 ft × ¼ in aluminium tubing, 150°, 50 cm^3 He/min, retention time 13·4 min). The following structural data were obtained on a GLC cut: IR (λ^{film}, μ): 6·01 (C=C). NMR (CCl$_4$, τ): 4·99 (doublet with additional allylic splitting of ~1 c/s, 1 proton, J = 10 c/s,

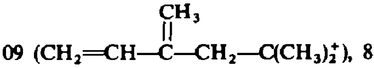
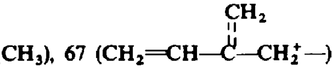


$(CH_3)_2C{=}\overset{\underline{H}}{C}-CH{<}^{S-}_{S-}\big)$, 5·30 (doublet, 1 proton, J = 10 c/s,  $=\overset{H}{C}-C\underline{H}{<}^{S-}_{S-}\big)$, ~7·0 to ~7·45 (multiplet, 4 protons,  $\big\langle{}^{S-\overset{H_2}{C}}_{S-\underset{\underline{H}_2}{C}}{>}CH_2$), ~7·85 to ~8·2 (multiplet, 2 protons,  $\big\langle{}^{S-\overset{H_2}{C}}_{S-\underset{H_2}{C}}{>}C\underline{H}_2$), 8·29 (singlet with allylic splitting of ~1 c/s, 6 protons,  $(C\underline{H}_3)_2C{=}\overset{H}{C}-$). (Found: C, 55·03; H, 8·23. Calc. for $C_8H_{14}S_2$: C, 55·16; H, 8·10%).

2-*Methyl*-6-*methylene*-2,7-*octadien*-4-*one propanedithioketal* (VII). To a stirred soln of 10·2 g (0·058 mole) of VI in 100 ml dry THF at −40°, was added under N$_2$ over a period of 5 min a soln of 39 ml (0·0586 mole) n-BuLi (1·5M in hexane). The soln was held at −20° for 6 hr, cooled to −40°, and treated with 8·8 g (0·060 mole) 2-bromomethylbutadiene and 200 mg NaI. The cooling bath was removed, and the stirred mixture was allowed to come to room temp. After overnight stirring, the mixture was poured on to ice and extracted with three 100 ml portions ether. The ether soln was washed successively with 100 ml 3% NaHSO$_3$ aq, 100 ml 10% NaOH aq and two 100 ml portions water. The ether soln was dried over NaSO$_4$, and, after removal of the ether, the oily residue was distilled (short-path) at 100–112°/0·15 mm to give 6·8 g of distillate, which was used in the next step; it was 57% pure (28% yield) by GLC analysis (Aerograph 204, 10% Carbowax 20M on 60/80 mesh Chromosorb G, 5 ft × ⅛ in, 155°, 40 cm^3 He/min, retention time 14·0 min). The following structural data were obtained on a GLC cut. IR (λ_{max}^{film}, μ) 3·29 (olefinic CH), 6·01 and 6·26 (conj. C═C), 10·1 and 11·1 (vinyl). NMR (CCl_4, τ): 3·72 (doublet of doublets, 1 proton, J_{trans} 17 c/s, J_{cis} 11 c/s, $=\overset{|}{C}-C\underline{H}=CH_2$), 4·62 (singlet with allylic splitting of ~1 c/s, 1 proton,  $-\overset{|}{\underset{|}{C}}-C\underline{H}=C\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$), ~4·7 to ~5·15 (multiplet, 4 olefinic protons), ~7·23 (multiplet, 4 protons,  $\left\langle\begin{matrix}S-C\underline{H}_2\\S-C\underline{H}_2\end{matrix}\right\rangle CH_2$), ~8·1 (multiplet, 4 protons,  $C=C-\underline{H}_2C-CH\left\langle\begin{matrix}S-CH_2\\S-CH_2\end{matrix}\right\rangle C\underline{H}_2$), ~8·10 and 8·30 (singlets, 3 protons each, allylic splitting of ~1 c/s,  $\left.\begin{matrix}C\underline{H}_3\\C\underline{H}_3\end{matrix}\right\rangle C=\overset{\overset{H}{|}}{C}$).

2-*Methyl-6-methylene-2,7-octadien-4-one* (VIII). To a stirred soln of 2·57 g (1·65 g pure material, 0·00687 mole) of VII in 100 ml 95% EtOH held at 50°, was added dropwise a soln of 2·4 g (0·0143 mole) $AgNO_3$ in 5 ml water. The soln was stirred at 50° for 20 min; the ppt was removed, and the filtrate was poured into 200 ml saturated NaCl aq, which was extracted with three 20 ml portions pentane. The pentane soln was dried over Na_2SO_4, and the pentane was removed. The residue was distilled (short-path) at 100°/7 mm. The distillate weighed 0·387 g and was used in the next step; it contained 55% VIII, 26% X, and 19% XII which were separated by preparative GLC. (GLC of VIII: Aerograph 204, 10% Carbowax 20M on 60/80 mesh Chromosorb G, 5 ft × ⅛ in, 100°, 31 cm³ He/min, retention time 5·9 min. Preparative conditions: Aerograph A90P3, 8% Carbowax 20M on 60/80 mesh Chromosorb G, 5 ft × ¼ in aluminium column, 105°, 50 cm³ He/min, retention time 40 min.) Calc. M^+ for $C_{10}H_{14}O$: 150. Mass spectrum (*m/e*): M^+ 150 (5·15% of base), base 83 ( $(CH_3)_2C=\overset{\overset{H}{|}}{C}-C=\overset{+}{O}$). IR ($\lambda_{max}^{film}$, μ): 3·29 (olefinic CH), 5·91 (conj. C═O), 6·01 and 6·25 (conj. C═C), 10·08 and 11·05 (vinyl). NMR (CCl_4, τ): 3·70 (doublet of doublets, 1 proton $=\overset{|}{C}-\overset{|}{C}\underline{H}=CH_2$), 3·98 (singlet with allylic splitting of ~1 c/s, 1 proton,  $O=\overset{|}{C}-\overset{\overset{\underline{H}}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$), ~4·75 to ~5·1 (multiplet, 4 olefinic protons), 6·85 (singlet, 2 protons, $O=\overset{|}{C}-\overset{|}{C}H_2$), 7·91 and 8·17 (singlets, each 3 protons, $(C\underline{H}_3)_2C=C$).

2-*Methyl-2-octen-4-one* (X). This by-product was isolated by GLC from the distillate that contained VIII. The retention time under the preparative conditions described for VIII was 15 min. Calc. M^+ for $C_9H_{16}O$: 140. Mass spectrum (*m/e*): M^+ 140, 83 base ( $(CH_3)_2C=\overset{\overset{H}{|}}{C}-C=\overset{+}{O}$). IR ($\lambda_{max}^{film}$, μ): 5·91 and 6·12 (C═C—C═O). NMR (CCl_4, τ): 4·1 (singlet with allylic splitting of ~1 c/s, 1 proton, $(CH_3)_2C=C\underline{H}-C=O$), 7·73 (triplet, 2 protons, J = 7 c/s, $-CH_2-C\underline{H}_2-C=O$), 7·92 and 8·20 (two singlets, each 3 protons, $(CH_3)_2C=C$), ~8·4 to 8·95 (multiplet, 4 protons, 2 CH_2 groups), 9·12 (distorted triplet, 3 protons, $C\underline{H}_3CH_2$).

Ethyl 3,3-dimethyl-5-methylene-6-heptenoate (XII). This by-product was isolated by preparative GLC from the distillate that contained VIII. The retention time under the preparative conditions described for VIII was 42 min. Calc. M^+ for $C_{12}H_{20}O_2$: 196. Mass spectrum: M^+ 196, $M^+ + 1 = 13·1\%$ of M^+, $M^+ + 2 = 1·37\%$ of M^+ (Calc. for $C_{12}H_{20}O_2$: $M^+ + 1 = 13·37$, $M^+ + 2 = 1·22$), 181 ($M^+ - CH_3$), 167 ($M^+ - C_2H_5$), 151 ($M^+ - OCH_2CH_3$), 129 ($((CH_3)_2CCH_2COOCH_2\overset{+}{C}H_3)$), 109 ( $CH_2=CH-\overset{\overset{CH_3}{\|}}{C}-CH_2-C(CH_3)_2^{+}$), 87 (base, $-CH_2COOCH_2CH_3$), 67 ( $CH_2=CH-\overset{\overset{CH_2}{\|}}{C}-CH_2^{+}-$). IR ($\lambda_{max}^{film}$, μ): 3·31 (olefinic CH), 5·77 (C═O, 6·10 and 6·25 (conj. C═C), ~8·7 (C—O—C), 10·08 and 11·1 (vinyl). NMR (CCl_4, τ): 3·70 (doublet of doublets, 1 proton, $CH_2=C\underline{H}-\overset{|}{C}=CH_2$), ~4·67 to ~5·15 (multiplet, 4 olefinic protons), 5·96 (quartet, 2 protons, $J = 7$ c/s, $-COC\underline{H}_2CH_3$), 7·72 and 7·87 (singlets, 2 protons each, $-\overset{\|}{C}-C\underline{H}_2-\underset{|}{\overset{|}{C}}-C\underline{H}_2-\overset{\|}{C}O-$), 8·75 (triplet, 3 protons, $J = 7$ c/s, $-OCH_2C\underline{H}_3$), 0·01 (singlet, 6 protons, $(CH_3)_2\overset{|}{C}-$).

2-*Methyl-6-methylene-2,7-octadien-4-ol* (II). To a soln of the distillate (0·144 g) that contained 0·070 g (0·465 mmole) of VIII in 3 ml isopropyl alcohol and 1 ml water, was added 0·038 g (1·0 mmole) $NaBH_4$ at 25°. The soln was poured into sat NaClaq after it had been stirred at 25° for 4·5 hr. Extraction with three 10 ml portions of pentane followed by drying of the pentane soln over Na_2SO_4, filtration, pentane removal, and short-path distillation (110°/5 mm) gave 0·091 g of distillate from which 0·022 g (31% yield) of the desired product was obtained by preparative GLC (Aerograph A90P3, 8% Carbowax 20M on 60/80 mesh Chromosorb G, 6 ft × $\frac{1}{4}$ in aluminium tubing, 120°, 50 cm^3 He/min, retention time 25·5 min). The IR and NMR spectra of this synthesized compound were congruent with those of the isolated compound[1] for which mass and UV spectra were also reported. IR (λ_{max}^{film}, μ): 3·02 (OH, 6·26 (conj. $C{=}C$), 9·80 ($C-OH$), 10·08 and 11·10 (vinyl). NMR (CCl_4, τ): 3·72 (doublet of doublets, 1 proton, $CH_2{=}C\underline{H}-\overset{|}{C}{=}CH_2$, J_{trans} 18 c/s, J_{cis} 11 c/s), ~4·7 to ~5·12 (multiplet, 5 olefinic protons), 5·68 (multiplet, 1 proton, $-CH_2-C\underline{H}OH-CH{=}$), 7·71 (apparent doublet, 2 protons, $-\overset{\|}{C}-C\underline{H}_2-\overset{|}{C}HOH$), 8·31 and 8·39 (2 singlets, 3 protons each, $(CH_3)_2C{=}C$), 8·44 (singlet, 1 proton, OH). (Found: C, 79·27; H, 10·77. Calc. for $C_{10}H_{16}O$ (152·2): C, 78·89; H, 10·59%.)

(+)-cis-*Verbenol* (XIII). A mixture of 5·0 g (0·033 mole) of (−)-verbenone (90%, Glidden Co.), 1·25 g (0·033 mole) $NaBH_4$ in 75 ml isopropyl alcohol was stirred at 25° for 3·5 hr. Water (150 ml) was added, and the mixture was extracted with three 100 ml portions ether. The ether soln was dried over Na_2SO_4, the ether was removed, and the residue was distilled (short-path) at 80°/1 mm. The distillate (3·0 g) consisted of 70% (+)-*cis*-verbenol (47% yield) and 30% (−)-verbenone. A pure sample of (+)-*cis*-verbenol was obtained by preparative GLC (Aerograph A90P3, 8% Carbowax 20M on 60/80 mesh Chromosorb G, 12 ft × $\frac{3}{8}$ in aluminum tubing, 130°, 120 cm^3 He/min, retention time 43–58 min), m.p. 69°, $[\alpha]_D^{21°}$ +7·6 ± 1·3° ($c = 2·5$, acetone). The mass, IR, NMR and UV spectra were congruent with those of the compound isolated from frass.[1] Calc. M^+ for $C_{10}H_{16}O$: 152. Mass spectrum (m/e): M^+ 152, 137 ($M^+ - CH_3$), 134 ($M^+ - H_2O$), 119 ($M^+ - CH_3$ and H_2O), base 43. IR ($\lambda_{max}^{CCl_4}$, μ): 2·98 (OH), 6·04 ($C{=}C$), 7·27 (notched, $C(CH_3)_2$), 9·65 and 9·90 ($C-OH$). NMR (CCl_4, τ): 4·73 (broadened, $=CH$), 5·71 (broadened, $C\underline{H}OH$), ~7·5 to ~8·2 (multiplet, 4 protons), 8·30 (singlet, $=C-CH_3$), 8·68 (singlet, CH_3), 8·77 (singlet, 1 proton, OH), 8·97 (singlet, 3 protons, CH_3). UV (λ_{max}^{hexane}, mμ): 215 ($\varepsilon = 4000$). (Found: C, 78·88; H, 10·39. Calc. for $C_{10}H_{16}O$ (152·2): C, 78·89; H, 10·59%.)

Instrumentation. The IR spectra were run on a Perkin–Elmer 221 and 137, the NMR on a Varian HA100, the UV spectra on a Perkin–Elmer 202, the mass spectra on a CEC 21-103C, and the optical rotation on a Perkin–Elmer 141.

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The NMR spectra were run by W. R. Anderson, Jr., the optical rotation by P. Lim, and the mass spectra by W. N. Tuttle. J. I. DeGraw suggested the blocked aldehyde approach, and D. W. Henry suggested the direct conversion step in the preparation of Compound VI.

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