Claisen Rearrangements with Mesityl Oxide Dimethyl Ketal. Synthesis of Ipsdienone, *E*- and *Z*-Ocimenone, 2,6-Dimethyl-2,7-octadien-4-one and 2,6-Dimethyl-2,7-octadien-4-ol

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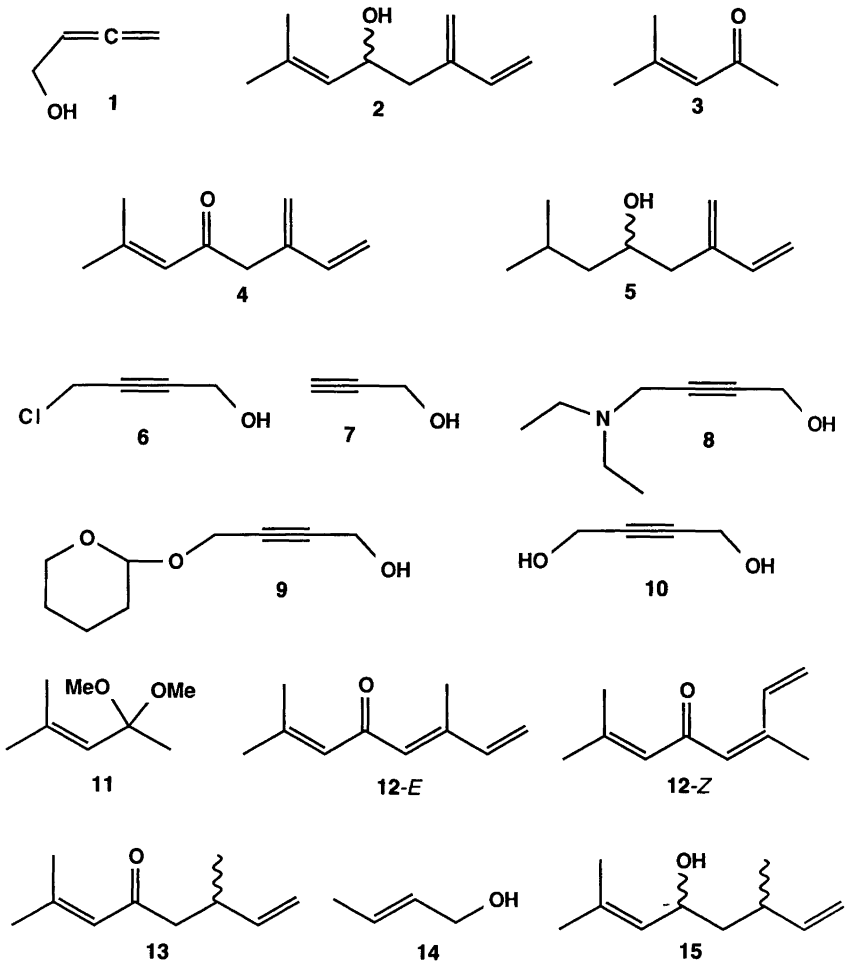
4-Methyl-3-penten-2-one (mesityl oxide) dimethyl ketal was synthesized and utilizied in Claisen rearrangements with 2,3-butadien-1-ol and 2-buten-1-ol to form ipsdienone and 2,6-dimethyl-2,7-octadien-4-one, from which the ocimenones and 2,6-dimethyl-2,7-octadien-4-ol were prepared.

The allene alcohol 2,3-butadien-1-ol (**1**) has been shown to participate in Claisen rearrangements to produce 2-substituted-1,3-butadienes.[1,2] In one case the vinyl ether of **1** was used, with carefully controlled high temperature conditions,[1] and in the other case, Johnson's orthoacetate procedure was employed. The final goal of these reactions was the synthesis of the pheromone components ipsenol[1,2] and ipsdienol.[2] The latter compound is used in lures for mass trapping of species of *Ips* bark beetles and has been synthesized in numerous ways.[3] Since Johnson has shown that methyl or ethyl ketals of α,β-unsaturated ketones can serve as precursors for Claisen rearrangements in a manner similar to orthoesters,[4] it appeared to us that a short route to ipsdienol (**2**) should be a Claisen rearrangement of 2,3-butadien-1-ol (**1**) and a ketal of mesityl oxide (**3**). The resulting ipsdienone (**4**) could then be reduced to ipsdienol (**2**) according to published procedures.[5]

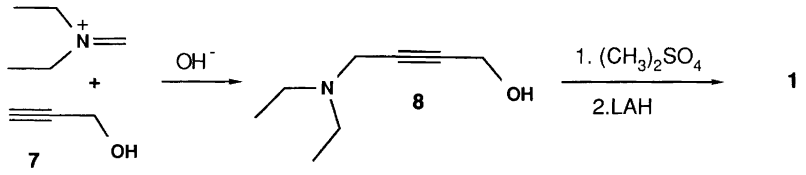
In this paper we describe our experiences and the difficulties encountered while exploring Claisen rearrangements of vinyl ethers obtained from mesityl oxide dimethyl ketal and allylic alcohols.

Three different methods for preparing 2,3-butadien-1-ol (**1**) were compared. At first, lithium aluminium hydride (LAH) treatment of 4-chloro-2-butyn-1-ol (**6**)[1,2] was used, basically according to Skattebøl *et al.*[1] but with a significant simplification of the work-up procedure: The prescribed[1] final 48 h liquid-liquid extraction could be avoided by simply adding sodium sulfate decahydrate and celite to the reaction mixture to destroy excess LAH. Since chlorobutynes are severe skin irritants, alternative routes to 2,3-butadien-1-ol (**1**) were desired. The second method was carried out essentially according to an unpublished procedure developed by Skattebøl and Stenstrøm, and starts with a Mannich reaction with diethylamine, formaldehyde and 2-propynol (**7**). The resulting 4-diethylamino-2-butyn-1-ol (**8**) was methylated with dimethyl sulfate and then treated with an excess of LAH in diethyl ether.[7] Although the intermediate quaternary ammonium salt is insoluble in diethyl ether, which makes vigourous stirring necessary in the final step, this method turned out to be the preferred one (see Scheme 1). A third method was also tried in analogy with published procedures:[8] 4-(2-tetrahydropyranyloxy)-2-butyn-1-ol (**9**) was prepared from 2-butyne-1,4-diol (**10**) and treated with LAH to give a 33 % yield of the allene alcohol **1**. The relatively low yield might be due to butadiene formation.[9]

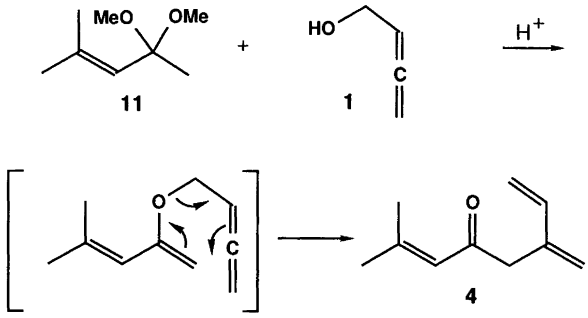
To our knowledge neither the dimethyl nor the diethyl ketal of 4-methyl-3-penten-2-one (mesityl oxide) (**3**) have been described in the literature, and their preparation turned out to be a much more difficult task than expected. Commercial



mesityl oxide (**3**) contains up to 15 % of the deconjugated isomer, but pure mesityl oxide could be obtained by treatment with a dilute solution of KOH in methanol, followed by distillation. Johnson *et al.*[4] have briefly indicated that ketals of α,β-unsaturated ketones can be made by the acid catalyzed reaction of trimethyl orthoformate and excess methanol. Three side reactions were observed during preparation of ketals of mesityl oxide, viz. transposition of the double bond, 1,4-addition of methanol, and vinyl ether formation by loss of methanol, all of which had to be suppressed by carefully selected reaction conditions. A variety of acid catalysts were tried, including pyridinium tosylate.[11] The acidity of the latter turned out to be irreproducible when the com-



Scheme 1.



Scheme 2.

pound was isolated and stored. Reproducible results were obtained only when equivalent amounts of pyridine and *p*-toluenesulfonic acid were mixed *in situ*. In this form the catalyst was found to be very mild and acted too slowly to be of value in connection with this specific problem. Eventually, it was found that *p*-toluenesulfonic acid monohydrate, the amount of which is rather critical, together with short reaction times gave the best results (~ 50 % yield) (see Experimental section).

Provided that methanol was continuously removed by distillation, the Claisen rearrangement to ipsdienone (**4**) proceeded smoothly when 2,3-butadien-1-ol (**1**) and 4-methyl-3-penten-2-one dimethyl ketal (**11**) were heated with catalytic amounts of propionic acid (Scheme 2). Unfortunately, isomerization to give varying amounts of ocimenone (**12**) also took place. The degree of isomerization was found to increase with reaction time and the amount of catalyst used: catalysed transformation of **4** to 100 % of ocimenone was observed, whereas several successful runs without addition of catalyst gave < 10 % of ocimenone. In later experiments these results could not be repeated. A reproducible procedure which gives a ratio of ocimenone:ipsdienone of approximately 40:60 is described in the Experimental section. However, ipsdienone (**4**) could be isolated by repeated chromatography on silica gel. When the reaction mixture was treated with dilute KOH in methanol, total conversion to *E*-ocimenone (**12**-*E*) occurred within a few minutes (see Scheme 3). The product contained < 1 % of the *Z* isomer, which is substantially less than previously reported for syntheses of the ocimenones.[5b,5e,12]

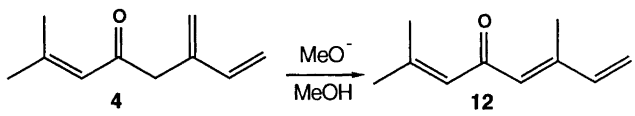
An attempt was also made to prepare and isolate pure *Z*-ocimenone (**12**-*Z*). Photochemical *E*-*Z* isomerization of the ocimenones in hexane with a 254 nm light source gave a photostationary mixture containing 38 % of the *Z* isomer. Chromatography on silica gel impregnated with 20 % (*w*/*w*) silver nitrate gave fractions containing 90 % of the *Z* isomer. Thermal *E*-*Z* isomerization occurred in all samples on storage in the dark, even when kept at −20 °C.

The utility of mesityl oxide dimethyl ketal (**11**) in Claisen rearrangements was extended to the preparation of racemic 2,6-dimethyl-2,7-octadien-4-one (**13**)[13] by using 2-buten-1-ol (**14**) as the allylic alcohol moiety.

For continued investigations of the specificity of receptor cells in *Ips* species by electrophysiological methods,[14] the ketones were reduced with LAH to give the corresponding diastereomeric alcohols **15a** and **15b** which could be separated by repeated chromatography on silica gel.

Experimental

NMR spectra were recorded in $CDCl_3$ on a Bruker WP 200 spectrometer. Analytical GC was performed on a PYE 204 instrument with an FID detector using a 50 m Carbowax 20 M fused silica capillary column. The photochemical isomeriza-



Scheme 3.

tion was carried out in quartz tubes with a Rayonet reactor equipped with 16 RPR 254 nm lamps.

Gradient system for preparative liquid chromatography. All liquid chromatography was performed with gradient elution on silica gel [Merck 60, 230–400 mesh (0.040–0.063 mm)] dry packed in 15 mm or 25 mm i.d. glass colums. The solvent was delivered from an open vessel to the column with a metering pump at a rate of 30 ml min^{-1} for 15 mm i.d., and 80 ml min^{-1} for 25 mm i.d. columns. Gradient elution was accomplished by consecutively adding portions of mixtures of hexane and a polar solvent (0.63, 1.25, 1.88, 2.5, 3.75, 5.0, 7.5, 10, 20, 30, 40, 40, 80 and 100 % of the polar solvent) to a dropping funnel with its stem reaching the surface of the stirred liquid in the vessel originally containing pure hexane. On each addition the stopcock was closed, the solvent mixture was added to the funnel, the funnel was stoppered and the stopcock reopened. In this way, liquid runs to the vessel only when the liquid surface in the vessel is lowered by the pump allowing replacement air to enter through the stem of the dropping funnel, thus maintaining an approximately constant level of the liquid in the vessel. When equal volumes of the added mixtures are used, an S-shaped gradient curve is obtained. All fractions were checked by TLC, which was performed on silica gel (Merck 60, pre-coated aluminium foil) eluted with 20 % ethyl acetate in hexane, and developed with vanillin and sulfuric acid in ethanol.

2,3-Butadien-1-ol (**1**) was prepared in three different ways, described under (a), (b) and (c) below.

4-Chloro-2-butyn-1-ol (**6**) was prepared from 2-Butyn-1,4-diol (**10**) according to Baily and Fujiwara.[6]

(a) *Preparation of* **1** *from* **6**. Under an atmosphere of nitrogen, 4-chloro-2-butyn-1-ol (**6**) (8.8 g, 0.08 mol) in diethyl ether (70 ml) was added to a suspension of LAH (7.7 g, 0.20 mol) in diethyl ether (250 ml) over a period of 2.5 h. The reaction mixture was allowed to react overnight, after which a mixture of sodium sulfate decahydrate and celite (1:1, *v/v*) was added to destroy excess LAH. After 3 h of stirring the solides were removed by filtration and washed with diethyl ether. Removal of the solvent and distillation gave 2,3-butadien-1-ol (**1**). Yield 3.4 g (58 %), b.p. 59–60 °C/40 mmHg.

Preparation of 4-diethylamino-2-butyn-1-ol (**8**). Diethylamine (87.8 g, 1.2 mol) was mixed with water (80 ml). The pH was adjusted to ca. 9 (pH paper) with 50 % H_2SO_4. A 35 % aqueous formaldehyde solution (137.1 g, ca. 1.6 mol CH_2O) was added, followed by 2-propynol (**7**) (56.1 g, 1.0 mol). A solution of $CuSO_4 \cdot 5H_2O$ (7.7 g, 0.031 mol) in water (50 ml) was then carefully added (exothermic reaction). The pH was adjusted to ca. 8. The stirred solution was heated to 80 °C for 1 h, cooled and poured into conc. aqueous ammonia solution (300 ml). Continuous extraction with diethyl ether overnight, drying ($MgSO_4$) and distillation gave **8**. Yield 107 g (75 %), b.p. 98–100 °C/2 mmHg.

(b) *Preparation of* **1** *from methylated* **8**. Dimethyl sulfate (19.0 ml, 25.2 g, 0.20 mol) was added dropwise to the vigourously stirred solution of 4-diethylamino-2-butyn-1-ol (**8**) (24.5 g, 0.17 mol) in dry diethyl ether (600 ml), and the inhomogeneous mixture was heated under reflux overnight. When cooled to room temperature, LAH (15.2 g, 0.40 mol) was added portionwise. The solution was heated under reflux for 4 h, and sodium sulfate decahydrate celite (1:1, *v/v*) (130 g) was added and stirred until the colour of the suspension changed to white (2 h). After filtration, the diethyl ether solution was dried with $MgSO_4$ and the diethyl ether was distilled off at atmospheric pressure. Further distillation gave pure 2,3-butadien-1-ol (**1**). Yield 5.6 g (47 %), b.p. 52–53 °C/30 mmHg.

Preparation of 4-(2-tetrahydropyranyloxy)-2-butyn-1-ol (**9**). Concentrated HCl (0.1 ml) was added to a stirred solution of 2-butyn-1,4-diol (**10**) (8.6 g, 0.1 mol) in diethyl ether (50 ml) in a flask with a condenser, followed by dropwise addition of 2,3-dihydropyrane (5.1 g, 0.06 mol) in diethyl ether (15 ml). After 0.5 h the reaction mixture was washed with saturated sodium bicarbonate solution and water, and then dried with $MgSO_4$. After solvent removal the total reaction mixture was loaded on a 15 mm i.d. column of silica gel (30 g). The column was eluted with diethyl ether hexane (50 ml each of the gradient mixtures described above). This gave a to-

tal separation of the monoprotected and diprotected diols without overlapping fractions. The yield of the monoprotected diol was 5.3 g (51 %). ^{1}H NMR (monoprotected diol): δ 1.67 (br. s, 6H, $-CH_2CH_2CH_2-$), 3.6 (m, 2H, $-CH_2-O-$), 4.33 (s, 4H $-CH_2-\equiv-CH_2-$) and 4.8 (br. s, 1H, -O-CH-O-).

(c) *Preparation of* **1** *from* **9**. LAH (1.14 g, 0.03 mol) was added in portions to a solution of 4-(2-tetrahydropyranyloxy)-but-2-yn-1-ol (**9**) (3.415 g, 0.02 mol) in dry THF (30 ml) and the mixture stirred at room temperature for 2h. Sodium sulfate decahydrate/celite (1:1, *v/v*) (10 g) was then added and the mixture was again stirred until the suspension turned white (< 1 h). The mixture was filtered, THF was removed under reduced pressure and 2,3-butadien-1-ol (**1**) was distilled. Yield 0.459 g (33 %), b.p. 59 °C/40 mmHg. Lit.[16] b.p. 68–69 °C/45 mmHg.

Purification of mesityl oxide (**3**). To commercial mesityl oxide (20 ml), containing 14 % of 4-methyl-4-penten-2-one were added 40 drops of KOH/MeOH (10 g/100 ml) and the mixture was stirred for 2 h at room temperature. The reaction mixture was neutralized with saturated aqueous NH_4Cl solution and the mesityl oxide layer was separated, washed with water and dried with $MgSO_4$. Distillation gave 17.5 ml of pure mesityl oxide (> 99.9 % by GC).

Preparation of 4-methyl-3-penten-2-one dimethyl ketal (**11**). A mixture of mesityl oxide (49.0 g, 0.50 mol), trimethyl orthoformate (80.7 g, 0.76 mol), methanol (100 ml, 79 g, 2.47 mol) and *p*-TsOH · H_2O (380 mg, 0.002 mol) was stirred for 5 min at room temperature under nitrogen atmosphere, after which sodium carbonate (2 g) was added to quench the reaction. Methanol was distilled off using a Vigreux column, and further distillation was carried out with a Teflon spinning band column. This gave 33.8 g (47 %) of **11**, b.p. 41 °C/16 mmHg. ^{1}H NMR: δ 1.39 (s, 3H, $-CH_3$), 1.74 (d, *J* 1.3 Hz, 3H, $-CH_3$), 1.77 (d, *J* 1.3 Hz, 3H, $-CH_3$), 3.16 (s, 6H, two $-OCH_3$), 5.14 (m, 1H, $-CH=$).

Preparation of ipsdienone (**4**) *and ocimenone* (**12**). A flask fitted with a distillation head and containing a mixture of propionic acid (40 mg, 0.5 mmol), 2,3-butadien-1-ol (360 mg, 5.14 mmol) and 4-methyl-3-penten-2-one dimethyl acetal (800 mg, 5.56 mmol) under nitrogen atmosphere was immersed in an oil bath at 170 °C for 5 min, and the methanol formed was distilled off. The reaction mixture was cooled to room temperature and then subjected to column chromatography (diethyl ether/hexane eluent), and a mixture of ocimenone and ipsdienone (40:60) was collected in one fraction. Yield 560 mg (73 %). Repeated chromatography gave the pure compounds. ^{1}H NMR of ipsdienone (**4**): δ 1.87 (d, *J* 1.2 Hz, 3H, $-CH_3$), 2.14 (d, *J* 1.1 Hz, 3H, $-CH_3$), 3.29 (d, *J* 0.9 Hz, 2H, $-CH_2-$), 5.06–5.24 (m, 4H, two $=CH_2$), 6.15 (br. s, 1H, $(CH_3)_2$ $=CH-$), 6.42 (dd, *J* 10.5, 17.5 Hz, 1H, $=CH-$); *E*-ocimenone (**12**-*E*): δ 1.90 (d, *J* 1.1 Hz, 3H, $-CH_3$), 2.18 (d, *J* 1.1 Hz, 3H, $-CH_3$), 2.26 (d, *J* 1.1 Hz, 3H, $-CH_3$), 5.40 (d, also fine coupling, *J* 10.6 Hz, 1H, $=CH_2$), 5.62 (d, also fine coupling, *J* 17.3 Hz, 1H, $=CH_2$), 6.12 (s, with fine coupling, 2H, $=CH-CO-CH=$) and 6.38 (dd, also fine coupling, *J* 10.6, 17.4 Hz, 1H, $=CH-$); *Z*-ocimenone (**12**-*Z*):δ 1.90 (d, *J* 1.1 Hz, 3H, $-CH_3$), 1.99 (d, *J* 1.2 Hz, 3H $-CH_3$), 2.18 (d, *J* 1.1 Hz, 3H, $-CH_3$), 5.42 (dt, *J* 10.8, 0.7 Hz, 1H, $=CH_2$), 5.58 (dt, *J* 17.6, 0.7 Hz, 1H, $=CH_2$), 6.05 (br. s, 2H, $=CH-CO-CH=$) and 7.77 (dd, *J* 10.9, 17.7 Hz, 1H, $=CH-$).

Transformation of ipsdienone (**4**) *to E-ocimenone* (**12**-*E*). To a solution of ipsdienone (112 mg) in diethyl ether (2 ml), 2 drops of KOH/MeOH (10 g/100 ml) were added. The mixture was stirred for 5 min, after which water (2 ml) was added and the diethyl ether layer was separated, washed with water and dried with $MgSO_4$. Concentration of the diethyl ether solution gave *E*-ocimenone (83 mg) containing < 1 % of the *Z*-isomer. A mixture of ipsdienone and ocimenone (3:2) (450 mg) in diethyl ether (2 ml) was transformed completely into *E*-ocimenone in the same way.

Preparation of 2,6-dimethyl-2,7-octadien-4-one (**13**). A flask fitted with a distillation head and containing a mixture of propionic acid (40 mg, 0.5 mmol), 2-buten-1-ol (**14**) (723 mg, 10.04 mmol) and 4-methyl-3-penten-2-one dimethyl acetal (1.672 g, 11.61 mmol) under nitrogen atmosphere was immersed in an oil bath at 140 °C for 1 h and methanol was distilled off. Column chromatography (diethyl ether/hexane eluent) gave 1.09 g (71.5 %) of **13**. ^{1}H NMR: δ 1.02 (d, *J*

6.7 Hz, 3H, $-CH_3$), 1.88 (d, *J* 1.2 Hz, 3H, $-CH_3$), 2.13 (d, *J* 1.1 Hz, 3H, $-CH_3$), 2.32 (dd, *J* 14, 7.5 Hz, 1H, $-CH_2-$), 2.47 (dd, *J* 14, 6.5 Hz, 1H, $-CH_2-$), 2.72 (m, 1H, $-(CH_3)CH-$), 4.92 (dt, *J* 10.4, 1.3 Hz, 1H of $=CH_2$), 4.98 (dt, *J* 17.3, 1.3 Hz, 1H of $=CH_2$), 5.80 (ddd, *J* 17.2, 10.4, 6.8 Hz, 1H, $=CH-$) and 6.05 (br. s, 1H, $(CH_3)_2=CH-$).

Preparation of 2,6-dimethyl-2,7-octadien-4-ol (**15a** and **15b**). LAH (48 mg, 1.26 mmol) was added in portions to a solution of 2,6-dimethyl-2,7-octadien-4-one (**13**) (380 mg, 2.5 mmol) in dry diethyl ether (15 ml) at 0 °C, and the mixture stirred for 10 min. Sodium sulfate decahydrate/celite (1:1, *v/v*) (2 g) was then added and the mixture again stirred for 0.5 h. The mixture was filtered and the diethyl ether was evaporated. The residue after column chromatography (diethyl ether/hexane eluent) gave 250 mg (65 %) of product, which consisted of two diastereomers (49:51 by GC). Repeated chromatography gave the pure compounds **15a** and **15b**. ^1H NMR (first eluted isomer): δ 1.01 (d, *J* 6.8, 3H, $-CH_3$), 1.23–1.63 (m, 2H, $-CH_2-$), 1.67 (d, *J* 1.2 Hz, 3H, $-CH_3$), 1.71 (d, *J* 1.2 Hz, 3H, $-CH_3$), 2.30 (m, 1H, $-(CH_3)CH-$), 4.40 (dt, *J* 5, 8.5 Hz, 1H, $-CH(OH)-$), 4.96 (d, also fine couplings, *J* 10.2 Hz, 1H of $=CH_2$), 5.03 (d, also fine couplings, *J* 17.4 Hz, 1H of $=CH_2$), 5.17 (d, br, *J* 8.5 Hz, 1H, $(CH_3)_2=CH-$) and 5.71 (ddd, *J* 17, 10.1 7.7 Hz, 1H, $=CH-$); ^1H NMR (second eluted isomer): δ 1.02 (d, *J* 6.7 Hz, 3H, $-CH_3$), 1.22–1.45 (m, 2H, $-CH_2$), 1.67 (d, *J* 1.2 Hz, 3H, $-CH_3$), 1.73 (d, *J* 1.3 Hz, 3H, $-CH_3$), 2.19 (m, 1H, $-(CH_3)CH-$), 4.39 (dt, *J* 8.8, 6.8 Hz, 1H, $-CH(OH)-$), 4.88–5.0 (m, 2H, $=CH_2$), 5.14 (br. d, *J* 8.8 Hz, 1H, $(CH_3)_2=CH-$) and 5.73 (ddd, *J* 17, 10, 8 Hz 1H, $=CH-$).

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References

1. Karlsen, S., Frøyen, P. and Skattebøl, L. *Acta Chem. Scand., Ser. B 30* (1976) 664.
2. Bertrand, M. and Viala, J. *Tetrahedron Lett. xx* (1978) 2575.
3. (a) Brand, J. M., Young, J. C. and Silverstein, R. M. In: Herz, W., Grisebach, H. and Kirby, G. W., Eds., *Progress in the Chemistry of Organic Natural Products,* Springer, New York 1979, Vol. p. 37; (b) Mori, K. In: ApSimon, J., Ed., *The Total Synthesis of Natural Products,* Wiley, New York 1981, Vol. 4, p. 1; (c) Baeckström, P., Björkling, F., Högsberg, H.-E. and Norin, T. *Acta Chem. Scand., Ser. B 37* (1983) 1.
4. Johnson, W. S., Brocksom, T. J., Loew, P., Rich, D. H., Werthemann, L., Arnold, R. A., Li, T. and Faulkner, D. J. *J. Am. Chem. Soc. 92* (1970) 4463.
5. (a) Reece, C. A., Rodin, J. O., Brownlee, R. G., Duncan, W. G. and Silverstein, R. M. *Tetrahedron 24* (1968) 4249; (b) Garbers, C. F. and Scott, F. *Tetrahedron Lett.* (1976) 1625; (c) Clinet, J. C. and Linstrumelle, G. *Nouv. J. de Chim. 1* (1977) 373; (d) Sakurai, H., Hosomi, A., Saito, M., Sasaki, K., Iguchi, H., Sasaki, J.-I. and Araki, Y. *Tetrahedron 39* (1983) 883; (e) Rousseau, G. and Drouin, J. *Tetrahedron 39* (1983) 2307.
6. Bailey, W. J. and Fujiwara, E. *J. Am. Chem. Soc. 77* (1955) 165.
7. Skattebøl, L. and Stenstrøm, Y. *Unpublished work.*
8. Cowie, J. S., Landor, P. D. and Landor, S. R. *J. Chem. Soc., Chem. Commun.* (1969) 541.
9. Claesson, A. *Acta Chem. Scand., Ser. B 29* (1975) 609.
10. (a) Herzog, H. L., Jevnik, M. A., Tully, M. E. and Hershberg, E. B. *J. Am. Chem. Soc. 75* (1953) 4425; (b) Nitz, T. J. and Paquette, L. *Tetrahedron Lett. 25* (1984) 3047.
11. Miyashita, M., Yoshikoshi, A. and Grieco, P. A. *J. Org. Chem. 42* (1977) 3772.
12. (a) de Villiers, D. J. J., Garbers, C. F. and Laurie, R. N. *Phytochemistry 10* (1971) 1359; (b) Adams, D. R., Bhatnagar, S. P., Cookson, R. C. and Tuddenham, R. M. *Tetrahedron Lett.* (1974) 3197; (c) Adams, D. R., Bhatnagar, S. P., Cookson, R. C. and Tuddenham, R. M. *J. Chem. Soc., Perkin Trans. 1* (1975) 1741; (d) Park, O. S., Grillasca, Y., Garcia, G. A. and Maldonado, L. A. *Synth. Commun. 7* (1977) 345; (e) Guittet, E. and Julia, S. *Synth,. Commun. 11* (1981) 709.
13. Klein, E. and Rojahn, W. *Chem. Ber. 97* (1964) 2700.
14. Mustaparta, H., Tömmerås, B. Å., Baeckström, P., Bakke, J. M. and Ohloff, G. *J. Comp. Physiol. A 154* (1984) 591.
15. Coxon, J. M., Garland, R. P. and Hartshorn, M. P. *Aust. J. Chem. 25* (1972) 2409.
16. Baily, W. J. and Pfeifer, C. R. *J. Org. Chem. 20* (1955) 1337.

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