thod.[7] The most relevant data found for 1-4 are shown in Table II. The calculated bond lengths for 2 compare reasonably well with those reported from X-ray investigations.[5]

Experimental Section

The PE spectra of 1 and 2 were recorded on a PS18 photoelectron spectrometer (Perkin-Elmer Ltd., Beaconsfield) at room temperature. Calibration was achieved with argon and xenon. A resolution of about 20 meV on the $^2P_{3/2}$ Ar line was obtained.

The sample of 1 contained a trace of benzene (see Figure 1). Compounds 1 and 2 were prepared by the methods described previously in the literature.[9,10]

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Registry No. 1, 63001-13-8; 2, 3350-02-5; 3, 87803-52-9; 4, 31519-30-9.

(9) Zefirov, N. S.; Averina, N. V.; Boganov, A. M.; Kuznetsova, T. S.; Yarovoi', S. S. *Dokl. Akad. Nauk SSSR* **1977**, *233*, 373; *Chem. Abstr.* **1978**, *87*, 22530*w*.

(10) Von E. Doering, W.; Pomerantz, M. *Tetrahedron Lett.* **1964**, 961.

Notes

Easy Synthesis of a Structural Isomer of Citronellal

Tiberio Corona, Paolo Crotti, Franco Macchia,* and Maria Ferretti

Istituti di Chimica Organica e Chimica Farmaceutica della Facoltà di Farmacia, Università di Pisa, 56100 Pisa, Italy

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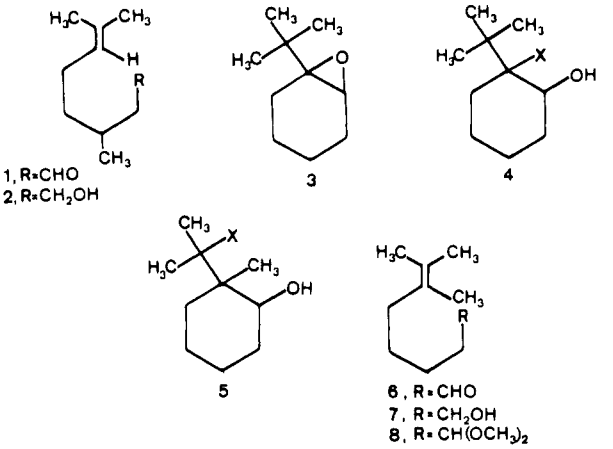
The well-known monoterpene citronellal (**1**, Chart I) is one of the unsaturated aldehydes naturally occurring in essential oils such as Citronella and Lemongrass oils.[1] Few structural isomers either of 1 or of its corresponding alcohol citronellol (**2**) have been found in nature or have been synthesized.

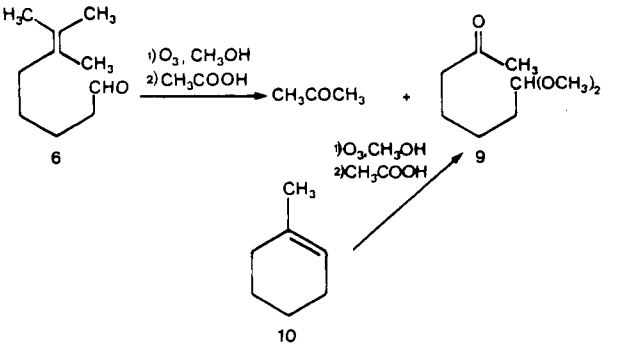
In the course of our studies on the mechanism and the stereochemistry of the reactions of substituted oxiranes under acidic conditions,[2] we examined 1-*tert*-butylcyclohexene oxide (**3**), structurally analogous to other oxiranes previously examined.[2] The large steric hindrance of the *tert*-butyl and the possibility of 1,2-shifts in the intermediate carbocation formed in the oxirane ring-opening process led us to anticipate that the chemical behavior of **3** could be different from that of other simple alkyl-substituted oxiranes.[2]

The reactions of **3** under acidic conditions afforded complex mixtures[3] consisting of the primary 1,2-addition products (**4**), the secondary 1,3-addition products (**5**), which can be assumed to be originated by rearrangement of the original skeleton of **3** by migration of a methyl, and other rearrangement products.[4] Somewhat surprisingly, among these last compounds, the aldehyde **6**, which lacks both the *tert*-butyl group and the cyclohexane skeleton, was isolated. The aldehyde **6** is a structural isomer of citronellal (**1**) and differs from **1** only in the position of one

Chart I



Scheme I



methyl group. The amount of **6** formed in the reactions of **3** changes markedly with the reaction conditions. In the trichloroacetolyses of **3** in nonprotic solvents the amounts of **6** are noticeable: when the reaction is carried out in CH_2Cl_2, the aldehyde **6** is the main product (42% yield, GC). When the acid-catalyzed ring opening of **3** is carried out in methanol or in methanol containing solvents, the dimethyl acetal of **6** (**8**) is obtained. The structure of the aldehdye **6** has been clarified by its ^1H NMR and mass spectrum and unequivocally confirmed through chemical transformations. The aldehyde **6** can be easily transformed into its dimethyl acetal **8** by treatment with anhydrous methanol in the presence of a catalytic amount of sulfuric

(1) Brettle, R. In Barton, D.; Ollis, W. D. "Comprehensive Organic Chemistry"; Stoddart, J. F., Ed.; Pergamon Press: Oxford, 1979; Vol. 1, p 946.

(2) Costantino, P.; Crotti, P.; Ferretti, M.; Macchia, F. *J. Org. Chem.* **1982**, *47*, 2917.

(3) The complete details and the mechanism and the stereochemistry of the reactions of epoxide **3** will be published in a forthcoming publication.

(4) The ring-opening reactions of **3** are largely regioselective; the large majority of the reaction products arises from the ring opening between the oxirane oxygen and the tertiary carbon.[3]

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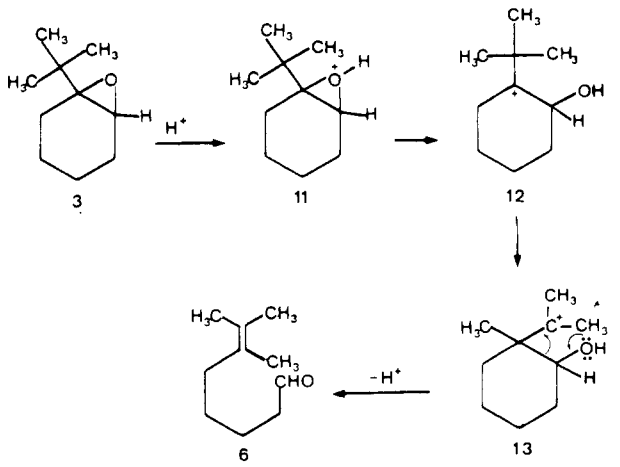
Scheme II



acid at room temperature. The $LiAlH_4$ reduction of **6** gives the alcohol **7**. The ozonolysis of **6** (Scheme I) in MeOH at −40 °C, followed by treatment with AcOH, affords acetone and the dimethyl acetal of 6-oxoheptanal (**9**). This product, formed very likely by reaction of the free 6-oxoheptanal with methanol under the acidic conditions, has been also obtained, as the sole product, by ozonolysis of 1-methylcyclohexene (**10**) under the same conditions as used for **6**. Reaction of **9** with 2,4-dinitrophenylhydrazine[5] gave, through the free 6-oxoheptanal, the corresponding bis 2,4-DNP.

A rationalization of the formation of **6** in the acid-catalyzed reaction of **3** can be attempted through a mechanism (Scheme II) implying protonation of the oxirane oxigen to give **11**. Breaking of the tertiary C–O bond affords the tertiary carbocation **12**, which can undergo methyl migration to give the new tertiary carbenium ion species **13**.[6] This latter carbenium ion, **13**, can give , via a retro-Prins fragmentation with cleavage of the C–C bond, the citronellal isomeric aldehyde **6**. Analogous mechanisms have been proposed for the acid-catalyzed cleavage of 1,3-diols,[8] and the reverse has been suggested for the acid-catalyzed cyclization of citronellal (**1**) to isopulegol.[9]

Experimental Section

Melting points were determined on a Kofler apparatus and are uncorrected. IR spectra for comparison between compounds were taken on paraffin oil mulls on a Perkin-Elmer Infracord Model 137. ^1H NMR spectra were determined on ~10% $CDCl_3$ solutions with a Varian EM 360 spectrometer by using Me_4Si as an internal standard. Mass spectra for **6** and **8** were recorded at 70 eV on a Varian MAT CH-7 GC/MS system. The mass spectrum for **6** was also recorded at 70 eV on a VG 7070 EQ mass spectrometer with a direct introduction probe. GC analyses were performed on a Carlo Erba Fractovap GV apparatus with a flame-ionization detector with glass columns (2 m × 2.5 mm) packed with 10% diethylene glycol succinate on 80–100-mesh silanized Chromosorb W [column temperature: low isotherm 100 °C (6 min), high isotherm 190 °C (increase 3 °C/min)]. Preparative TLC was performed on 2-mm-layer silica gel plates (Merck F_{254}) containing a fluorescent indicator: the TLC plates were visualized first by UV light (254 nm) and then by spraying with 1 N $K_2Cr_2O_7$ in 40% aqueous sulfuric acid.

1-*tert*-Butylcyclohexene Oxide (3). A solution of 1-*tert*-butylcyclohexene[10] (10 g, 72.4 mmol) in $CHCl_3$ (300 mL) was treated (under stirring) with 90% MCPBA (14.82 g, 79.7 mmol) in small portions while the temperature was kept at −14 °C. The resulting reaction mixture was left 20 h at 5 °C and then washed (water, saturated $NaHCO_3$, and water), dried, and evaporated to yield crude **3** (9.5 g) as a liquid. This residue was chromatographed through a 2.0 × 28 cm column of silica gel by elution with petroleum ether (bp 40–70 °C) and collecting fractions of about 80 mL. Fractions 2–5 gave pure **3**: 8.9 g; liquid; IR 917, 869, 847 cm^{-1}; NMR δ 3.10 (m, 1, O–CH–C<), 0.73 [s, 9, $C(CH_3)_3$] [lit.[11] bp 64–68 °C (13 mm)]. Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.50; H, 11.35.

Reaction of Epoxide 3 with Trichloroacetic Acid in CH_2Cl_2. A solution of **3** (0.65 g, 4.2 mmol) in anhydrous CH_2Cl_2 (65 mL) was treated at 25 °C with a 1 M solution of trichloroacetic acid in anhydrous CH_2Cl_2 (4.6 mL). The resulting mixture was stirred for 20 min at the same temperature, washed (saturated $NaHCO_3$ and water), filtered, and evaporated to dryness to give an oily residue which was subjected to preparative TLC (a 9/1 mixture of petroleum ether and ether was used as the eluant; elution was repeated twice). Extraction of the band with R_f 0.45 afforded pure **6,7-dimethyl-6-octenal (6)**: 0.24 g (GC); colorless liquid; IR 2717, 1715 cm^{-1}; NMR δ 9.86 (m, 1, CHO), 1.63 [s, 9, $CH_3C{=}C(CH_3)_2$]; MS, *m/e* (relative intensity) 154 (M^+, 50), 110 ($M^+ - CH_2{=}CHOH$, 38), 95 (58), 83 (70), 69 (40), 55 (72), 41 (72), 39 (55), 27 (45). Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.59; H, 11.63.

Reaction of Epoxide 3 with Acidic Methanol. A solution of **3** (0.50 g) in 0.2 N H_2SO_4 in anhydrous methanol (50 mL) was stirred 15 min at room temperature, treated with solid $NaHCO_3$, diluted with water, and extracted with ether. Evaporation of the washed (water) and dried ether extracts yielded an oily residue which was subjected to preparative TLC (a 9/1 mixture of petroleum ether and ether was used as the eluant; elution was repeated twice). Extraction of the band with R_f 0.75 afforded pure **6,7-dimethyl-6-octenal dimethyl acetal (8)**: 0.020 g (GC); liquid; IR 1129, 1081, 1058 cm^{-1}; NMR δ 4.33 [m, 1, $CH(OCH_3)_2$], 3.33 [s, 6, $CH(OCH_3)_2$], 1.63 [s, 9, $CH_3C{=}C(CH_3)_2$]; MS, *m/e* 200 (M^+). Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.94; H. 12.07. Found: C, 71.71; H, 12.24.

When the same reaction on **3** (0.30 g) was carried out by using a solution of MeOH in anhydrous CH_2Cl_2 in the presence of TsOH (prepared in such a way that the molar ratio between epoxide **3**, TsOH, and MeOH was 1:0.1:6), the crude product obtained gave, through a preparative TLC procedure (see above), pure **8** (0.035 g).

Treatment of Aldehyde 6 with 0.2 N H_2SO_4–MeOH Solution. Aldehyde **6** (0.020 g) was treated with 0.2 N H_2SO_4 in anhydrous MeOH (5 mL) under stirring for 5 min at room temperature. Dilution with saturated $NaHCO_3$, extraction with ether, and evaporation of the washed (water) and dried ether extracts afforded an oily residue consisting of pure **8** (GC).

Reduction of Aldehyde 6 with $LiAlH_4$. A stirred solution of the aldehyde **6** (0.10 g) in anhydrous ether (10 mL) was treated with $LiAlH_4$ (0.10 g) in small portions and stirred for 1 h at room temperature. The excess of hydride was destroyed by adding water and 10% aqueous NaOH solution. Evaporation of the filtered and dried organic solvent afforded a liquid product consisting of pure **6,7-dimethyl-6-octenol (7)**: 0.075 g (GC); IR 3378 cm^{-1}; NMR δ 3.53 (m, 2, CH_2OH), 1.53 [s, 9, $CH_3C{=}C(CH_3)_2$].

Ozonolysis of Aldehyde 6. A stream of O_3 and O_2 was passed through a cold (−40 °C) solution of **6** (0.12 g) in anhydrous MeOH (15 mL) until O_3 was detected (aqueous KI solution) in the exit gases. The solution was gently swept with N_2 to remove dissolved

(5) Shriner, R. L.; Fuson, R. C; Curtin, D. Y. "Systematic Identification of Organic Compounds", 4th ed.; Wiley: New York, 1957; p 219.
(6) The facility of the rearrangement of a tertiary carbenium ion, the *tert*-butyl-substituted one, **12**, to another tertiary carbocation, **13**, could be due to the higher stability of the latter carbocation **13** compared to **12**, because the former oxirane oxygen in **13** is further from the positive charge and should therefore exert its electron-withdrawing inductive effect to a much smaller degree. Other effects such as the relief of steric strain on passing from **12** to **13** could be relevant, but the difference in strain in a similar case has been recently questioned.[7]
(7) Fry, J. L.; Saba, J. A. *Tetrahedron Lett.* **1982**, *23*, 1743.
(8) Zimmerman, H. E.; English, J. Jr. *J. Am. Chem. Soc.* **1954**, *76*, 2285.
(9) Eschinazi, H. E. *J. Org. Chem.* **1961**, *26*, 3072.
(10) Goering, H. L.; Reeves, R. L.; Espy, H. H. *J. Am. Chem. Soc.* **1956**, *78*, 4926.
(11) Drefahl, G.; Heublein, G.; Lochner, S. *J. Prakt. Chem.* **1966**, *32*, 69.

O_3, treated with glacial AcOH (4 mL), and transferred to a microdistillation apparatus. When the distillation started, the distillate was cautiously collected in a solution of 2,4-dinitrophenylhydrazine in a H_2SO_4–EtOH mixture.[5] The first distillate produced in the collecting tube a precipitate which was filtered while the distillation stopped. The filtered product was washed and dried and turned out to be the 2,4-DNP of acetone: 0.010 g; mp 127–128 °C (lit.[12] mp 128 °C).

The liquid residue of the distillation was diluted with water and extracted with ether. Evaporation of the washed (water, saturated $NaHCO_3$, water) and dried ether extracts gave **6-oxoheptanal dimethyl acetal (9)**: 0.050 g; oil; IR 1718, 1129, 1081, 1052 cm^{-1}; NMR δ 4.30 [m, 1, $CH(OCH_3)_2$], 3.26 [s, 6, $CH(OCH_3)_2$], 2.07 (s, 3, $COCH_3$). The addition of a portion of **9** (0.010 g) to a solution of 2,4-dinitrophenylhydrazine in H_2SO_4–EtOH[5] afforded the bis 2,4-DNP of **9**: mp 187–188 °C. Anal. Calcd for $C_{19}H_{20}N_8O_8$: C, 46.72; H, 4.09; N, 22.95. Found: C, 46.61; H, 4.05; N, 23.22.

Ozonolysis of 1-Methylcyclohexene (10). The ozonolysis of **10**[13] (0.50 g) was performed as described above for **6**. The methanolic solution from the ozonolysis tube, after acidification with glacial AcOH, was gently warmed at 50–60 °C for 5 min, cooled, diluted with water, and extracted with ether. Evaporation of the washed (water, saturatred $NaHCO_3$, water) and dried ether extracts afforded pure **9** (0.41 g).

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Registry No. **3**, 7583-74-6; **6**, 87830-76-0; **7**, 87830-77-1; **8**, 87830-78-2; **9**, 36727-64-7; **10**, 591-49-1.

(12) Vogel, A. "Textbook of Practical Organic Chemistry", 4th ed.; Longman: London, 1978; p 1194.
(13) For the preparation of **10** see: Barili, P. L.; Bellucci, G.; Macchia, B.; Macchia, F.; Parmigiani, G. *Gazz. Chim. Ital.* **1971**, *101*, 300.

Synthesis and Structure of Side Chain Haloallenes in the Steroid Series

Cornelis J. Elsevier, Hendrik J. T. Bos, and Peter Vermeer*

Organisch Chemisch Laboratorium, Rijksuniversiteit Utrecht, Croesestraat 79, 3522 AD, The Netherlands

Anthony L. Spek* and Jan Kroon

Laboratorium voor Structuurchemie, Rijksuniversiteit Utrecht, Padualaan 8, Utrecht, The Netherlands

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Recently we developed a stereoselective route to 1-haloallenes by reacting optically active 2-propynylic methanesulfonates with lithium dihalocuprates.[1] In one case, viz., reaction of mestranol methanesulfonate (**1**) with lithium dibromocuprate, the allene formation even proceeded stereospecifically. Unfortunately, the well-known and valuable Lowe–Brewster rules[2] may be violated in the case of trisubstituted allenes,[3,4] so that the absolute configuration of the bromoallenes derived from **1** was still a matter of doubt. The present paper concerns an unequivocal determination of its structure together with a more elaborate study of the haloallene formation in the steroid series.

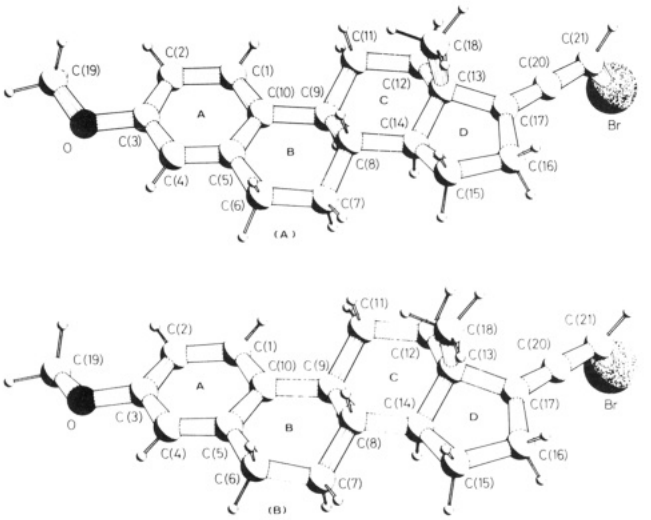
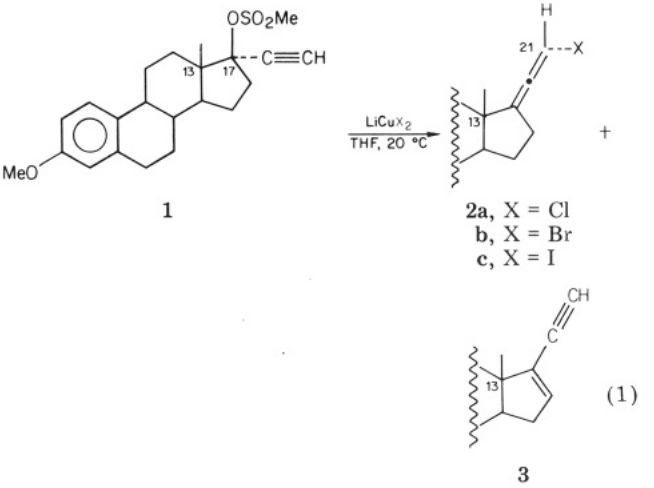


Figure 1. Molecular structure of the two independent molecules labeled A and B in the unit cell.

Equation 1 shows the stereospecific conversion of the



1 **2a**, X = Cl; **b**, X = Br; **c**, X = I **3** (1)

sulfonate **1** by lithium dichloro–, dibromo– (cf. ref 1), and diiodocuprate in tetrahydrofuran. In all cases only one of the two possible epimeric haloallenes **2** was obtained, together with ca. 10–15% of enyne **3** when X was Cl or Br. Allene **2** could easily be purified from **3** by crystallization. The produced halides **2** all showed high negative specific rotations $[\alpha]^{20}_D$ ($CHCl_3$), viz., −110° for **2a** (X = Cl), −173° for **2b** (X = Br), and −252° for **2c** (X = I). As the parent compound **2** in which X is hydrogen is dextrorotatory ($[\alpha]_D$ +41.2°),[5] Lowe–Brewster rules predict the 21β-haloallene structure instead of the 21α structure indicated in eq 1. Nevertheless, the rules appear to predict the wrong configuration for **2**. This follows from an X-ray study of allene **2b**. The result of this study is given in Figure 1; the α-position of X in this case is evident. In view of our previous study[1] which was mainly focussed on the preparation of 1-halo-3-phenylpropadienes, compounds for which Lowe–Brewster rules can be used, allenes **2a** and **2c** will also contain the halogen atom in the α-position as Cl and I influence the optical rotation in the same direction as Br does. As the 21α-haloallenes **2** were now readily accessible, we wondered whether also their 21-epimers could be prepared. For that study we first attempted to prepare and

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(2) (a) Lowe, G. *Chem. Commun.* **1965**, 411. (b) Brewster, J. H. *Top. Stereochem.* **1967**, *2*, 33.
(3) Bertrand, M.; Gil, G.; Kumar, A. *Nouv. J. Chim.* **1980**, *4*, 69.
(4) Elsevier, C. J.; Meijer, J.; Westmijze, H.; Vermeer, P.; Van Dijck, L. A. *J. Chem. Soc., Chem. Commun.* **1982**, 84.
(5) Van Dijck, L. A.; Lankwerden, B. J.; Vermeer, J. G. C. M.; Weber, A. J. M. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 801.

0022-3263/84/1949-0379$01.50/0