Homologues of Monocyclic Monoterpenes. Tetramethylated Derivatives of Carvone, Carveol, β-Terpineol, Sobrerol, and Related Compounds[1]

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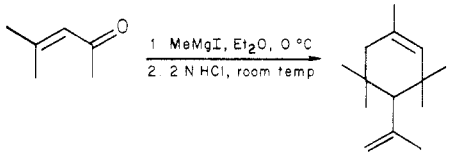
Epoxidation of tetramethyllimonene (1) gave monoepoxide **2t**, which was opened regioselectively to endo and exo tetramethylated *trans*-carveols **3t** and **5t**, respectively. The alcohols were further oxidized to tetramethylcarvone (**4**) and its unstable exocyclic isomer **6**. Reduction of **4** with diisobutylaluminum hydride gave tetramethylated *cis*-carveol **3c** exclusively, whereas analogous reduction of **6** produced an epimeric mixture of **5c**/**5t** = 85:15. Reduction of diepoxide **13** with Super-Hydride gave acid-sensitive tetramethylated α-terpineol 1,2-epoxide **14t**, which on treatment with *N*-lithioethylenediamine yielded tetramethylsobrerol (**15**). Xylene-sensitized irradiation of **1** in weakly acidic solution gave tetramethylated β-terpineols **9c** and **9t**. The postulated intermediate cation **9+** is attacked by water preferentially from the side trans to the isopropenyl group. Dichlorocyclopropanation of **1** also produced preferentially the trans adduct **11t** (**11t**/**11c** = 80:20).

4-Isopropenyl-1,3,3,5,5-pentamethyl-1-cyclohexene (1),[2]



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i.e., 3,3,5,5-tetramethyllimonene, or TM-limonene for short, is now readily available from inexpensive mesityl oxide (4-methyl-3-penten-2-one) and methylmagnesium iodide in batches of at least 25–30 g (see Experimental Section). The reaction proceeds in one pot and involves a biomimetic dehydrative cyclodimerization of the allylic alcohol, viz., 2,4-dimethyl-3-penten-2-ol, which is formed as an intermediate.[2] **1** is the parent of a class of homologous monocyclic monoterpenes. We here describe the preparation of some oxygenated derivatives of **1**, which are of interest inter alia in perfumery.

Attempts to introduce oxygen into **1** with singlet oxygen as enophile,[3] as it has been done with parent limonene,[4] were not promising. Both double bonds in **1** are sterically hindered and **1** reacted only sluggishly to form a mixture of products.

A useful method of oxygenating **1** is the site-selective epoxidation to **2**.[2] In this reaction, as in other electrophilic additions to the internal double bond of **1** to be described below, the trans epoxide **2** is formed preferentially (trans/cis = 93:7). The preference for the *trans*-TM-limonene oxide stereoisomer stands in contrast to the reaction of parent limonene, which on monoepoxidation with *m*-chloroperbenzoic acid gives an approximate 1:1 mixture of trans/cis expoxides.[5]

TM-Carvone 4, 6 and TM-Carveols 3c, 3t as well as 5c, 5t. TM-Limonene oxide (**2**) is a crystalline, sublimable epoxide, which because it is unusually hindered does not react with 6 N aqueous potassium hydroxide on refluxing at 130 °C for 7 days. It is inert to $LiAlH_4$ in toluene or tetrahydrofuran (90 °C, 3 days) and even to Super-Hydride[6] (lithium triethylborohydride) in refluxing tetrahydrofuran! (For comparison, Super-Hydride (1 M in THF) has been reported to react with the epoxide of 1-methylcyclohexene in 5 min at 0 °C to give 1-methylcyclohexanol in 100% yield.)[7] Since epoxides can be regarded as masked allylic alcohols, we tried an E2-like opening of **2** with strong base. A priori, two isomeric allyl alcohols may be formed, i.e., the "thermodynamic" alcohol **3t** and the "kinetic" alcohol **5t** (Scheme I). We have found that the direction of opening can be controlled by the choice of base. The sterically hindered base lithium diisopropylamide gave (3 h at 50 °C) the less stable allyl alcohol **5t** as the single isomer in 95% yield after flash chromatography on silica gel. On the other hand, *N*-lithioethylenediamine,[8] which is an equally strong base and also a very weak proton donor (RNH_2 has a pK_a value of ~33), gave tetramethylated *trans*-carveol **3t** in 90% yield. The expected greater thermodynamic stability of the trisubstituted olefin **3t** over the disubstituted olefin **5t** was confirmed experimentally when a mixture of **3t** and **5t** (30:70), which had been obtained by reaction of **2** with aluminum isopropoxide, was treated with *N*-lithioethylenediamine: Only the more substituted Saytzeff olefin **3t** was obtained.

With the key isomer **3t** at hand, TM-carvone (**4**) could be prepared readily by oxidation with pyridinium chlorochromate (85% yield). Likewise, oxidation of **5t** with PCC and catalytic amounts of pyridine gave the TM-carvone isomer **6** as a sensitive oil that tended to polymerize upon standing at room temperature and on distillation. However, **6** could be kept for several weeks in dilute solution at −20 °C. Attempts to obtain **4** by the classical procedure developed for preparing parent carvone, i.e., nitrosochlorination, elimination of HCl to carvoxime, and hydrolysis[9] failed. Sterically hindered **1** could not be nitrosochlorinated. We also failed to prepare TM-carvoxime from **4** and hydroxylamine. TM-carveols **3t** and **5t** originate from trans epoxide **2**, and therefore have their hydroxyl group trans to the isopropenyl group. Their respective cis isomers **3c** and **5c** were obtained by controlled reduction of **4** and **6**. Thus the sterically demanding diisobutylaluminum hydride (DIBAH) in toluene reacted

(1) Terpenes and Terpenoid Compounds, 9. Part 8: Hoffmann, H. M. R.; Henning, R.; Lalko, O. R. *Angew. Chem.* **1982**, *94*, 464. Part 7: Henning, R.; Hoffmann, H. M. R. *Tetrahedron Lett.* **1982**, *23*, 2305. Part 6: Ismail, Z. M.; Hoffmann, H. M. R. *Chem. Ber.* **1982**, *115*, 1256.

(2) Hoffmann, H. M. R.; Vathke-Ernst, H. *Chem. Ber.* **1981**, *114*, 1182.

(3) Terminology of the ene reaction: Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556.

(4) Schenck, G. O.; Gollnick, K.; Buchwald, G.; Schroeter, S.; Ohloff, G. *Justus Liebigs Ann. Chem.* **1964**, *674*, 93.

(5) Royals, E. E.; Leffingwell, J. C. *J. Org. Chem.* **1966**, *31*, 1937. See also ref 2, footnote 4.

(6) Tradename of Aldrich Chemical Co.

(7) Brown, H. C.; Kim, S. C.; Krishnamurty, S. *J. Org. Chem.* **1980**, *45*, 1.

(8) Reggel, S.; Friedman, S.; Wender, I. *J. Org. Chem.* **1958**, *23*, 1136. Narula, A. S.; Dev, S. *Tetrahedron* **1971**, *27*, 1119. See also Verghese, J. *Perfum. Flavor.* **1981**, *6*, 23.

(9) Cf. Reitsema, R. H. *J. Org. Chem.* **1958**, *23*, 2038. Rothenberger, O. S.; Krasnoff, S. B.; Rollins, R. B. *J. Chem. Educ.* **1980**, *57*, 741.

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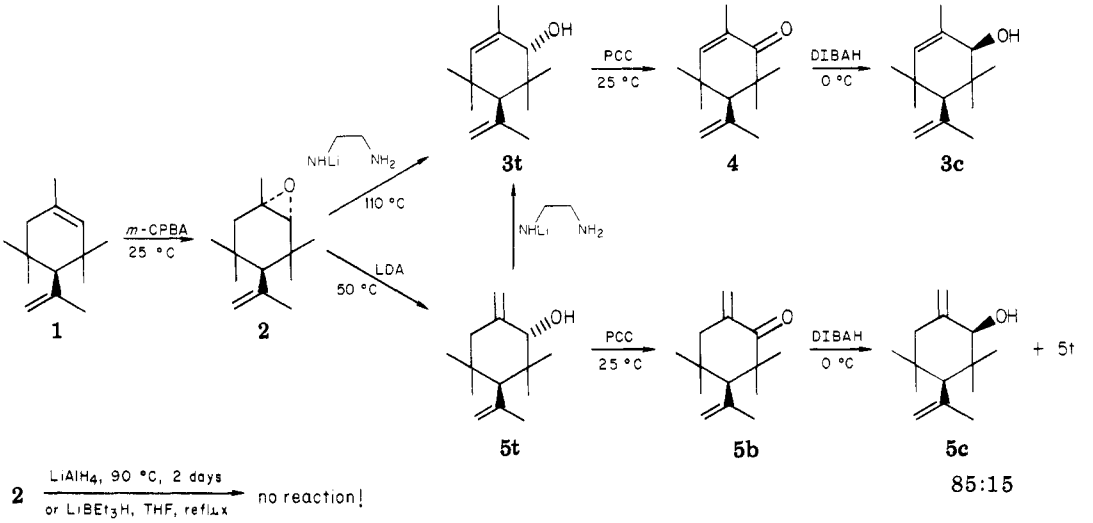
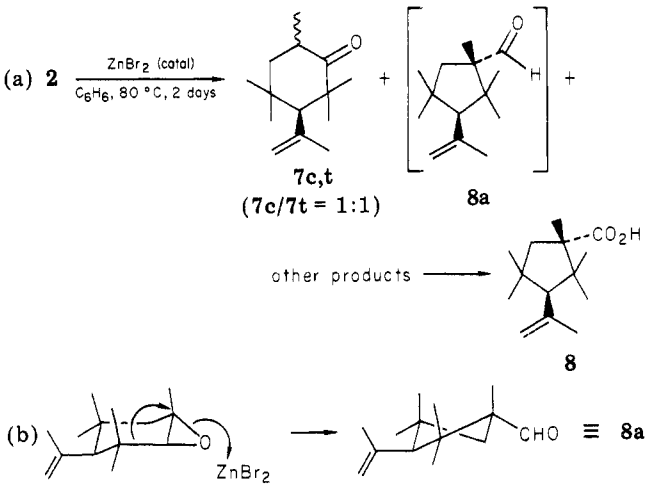
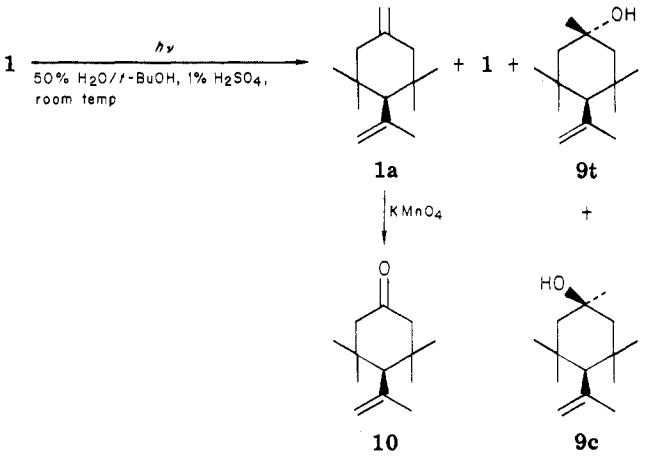
Scheme I



Scheme II



Scheme III

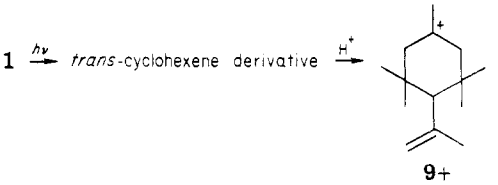


with TM-carvone **4** to give TM-*cis*-carveol **3c** exclusively. Put another way, DIBAH delivers its hydride ion from the more accessible side, i.e., trans to the isopropenyl group. In contrast, the carbonyl carbon of enone **6** must be partly accessible from the cis face: DIBAH reduction of **6** gave **5c** no longer exclusively, but also a minor amount of **5t** (**5c**/**5t** = 85:15).

$ZnBr_2$-Induced Rearrangement of 2. The electrophilic opening of parent limonene oxide with $ZnBr_2$ has been shown to produce two ring-contracted products and dihydrocarvone.[10] The reaction of TM-limonene oxide (**2**) with catalytic amounts of $ZnBr_2$ required heating for 2 days at 80 °C (Scheme IIa) and yielded a 1:1 mixture of isomeric TM-dihydrocarvones **7c** and **7t** and also the ring-contracted cyclopentanecarboxylic acid **8**. The latter acid is assumed to have its carboxylic acid group and isopropenyl group trans to each other on mechanistic grounds (arrows, Scheme IIb).

Aldehyde **8a** is the precursor of carboxylic acid **8** but was generally not isolated. The complex reaction of **2** with $ZnBr_2$ stands in contrast to the clean reactions of **2** with LiN-*i*-Pr_2 and $LiNHCH_2CH_2NH_2$ (cf. Scheme I).

TM-β-Terpineols 9t and 9c. Parent β-terpineol is a versatile perfumery component, which together with some of its isomers is produced in bulk by hydration of the pinenes. almost innumerable methods for preparing these isomers have been described in the literature.[11] Following the photochemical approach of Kropp[12] we obtained **9t** and **9c** in 40% yield (isomeric ratio of **9t**/**9c** = 4:1) by xylene-sensitized irradiation of **1** in weakly acidic aqueous solution. The isomeric alcohols **9t** and **9c** were separable from **1** and **1a** by flash column chromatography using pentane to elute the olefins and then dichloromethane to elute the molar polar alcohols (Scheme III). The assignment of the major alcohol to structure **9t** (OH group equatorial) and of the minor alcohol to structure **9c** (OH group axial) was secured by a number of criteria. For example, **9t** with the more accessible OH group had a longer GC retention time than **9c**, interacted more strongly than **9c** with europium shift reagent [Eu(fod)$_3$], and interacted more strongly with solvent $(CD_3)_2SO$, as observed by ^1H NMR. A rational precursor of the TM-β-terpineols **9** is tertiary cation **9+**, formed by protonation of the highly

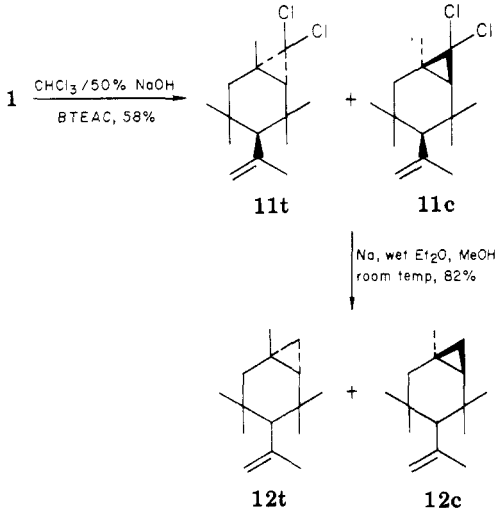


reactive *trans*-cyclohexene isomer of **1**, which is thought to be generated photochemically. **9+** is attacked by water

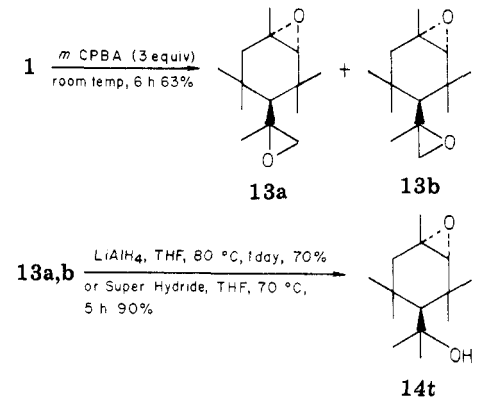
(10) Settine, R. L.; Parks, G. L.; Hunter, G. L. K. *J. Org. Chem.* **1964**, *29*, 616.

(11) Cf., e.g., Merkel, D. "Riechstoffe"; Pergamon Press: Oxford, 1972.
(12) Kropp, P. J. J. *Org. Chem.* **1970**, *35*, 2435.

Scheme IV



Scheme V



preferentially from the more accessible face to give **9t**. Presumably, cation **9+** is also the precursor of **1a**, which is assumed to arise by kinetic deprotonation of **9+**.

TM-Limonene isomer **1a** could not be separated from **1**, but it could be identified by subtractive ^{13}C NMR, by GC/MS, and, more importantly, by oxidation to cyclohexanone derivative **10**.

Further Electrophilic Additions to 1 and 2. Using the standard PTC procedure we dichlorocyclopropanated TM-limonene (**1**). As in the epoxidation of **1** only the trisubstituted, internal double bond was attacked by dichlorocarbene to yield a stereoisomeric mixture of **11t** and **11c** in a ratio of 80:20 (Scheme IV). We assume again that the major isomer is *trans*, i.e., **11t**. The smaller trans/cis ratio relative to the trans/cis ratio of epoxidation of **1** (trans/cis = 93:7) should be due to the greater reactivity and hence lower selectivity of dichlorocarbene. Note also that the dichlorocyclopropanation of *parent* limonene generally gives the product in which both double bonds have reacted.[13] Dechlorination of **11t** and **11c** to **12t** and **12c**, respectively, was straightforward, being conveniently carried out with sodium in moist ether/methanol.[14]

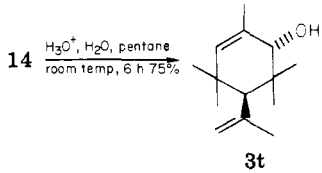
Under which conditions can the isopropenyl group of **1** be attacked? Crawford et al. reported in 1972 that limonene itself can be metalated site selectively with the 1:1 complex of *n*-butyllithium and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) with conversion of the extracyclic isopropenyl group into the allyllithium derivative.[15] In contrast to these results we were unable to lithiate **1** satisfactorily under these conditions, refluxing being required to observe a color change, which as we have confirmed occurs with limonene itself after 1 h at room temperature. An excess of TMEDA, the use of *sec*-butyllithium instead of *n*-butyllithium, and activation of *n*-butyllithium with freshly sublimed potassium *tert*-butoxide[16] followed by quenching with methyl iodide and carbon dioxide were equally unsuccessful. We show elsewhere by temperature-dependent NMR that rotation about the extracyclic sp^2–sp^3 carbon–carbon single bond in **1** is hindered ($\Delta G^{\ddagger}$ = 12.8 kcal/mol) and that two rotamers are equally populated.[17]

Table I. Parallel Reaction of 14t and 2 in Aqueous Acid/Pentane

products,[a] %					
14t	3t	8a	7	8	time, h
(A) **14t** $\xrightarrow{H_3O^+,\ pentane}$ **3t** + other products					
46	35				1.5
36	40	5			3
9	55	10	3.6		6
	44	25	4.6	6.8	26
	34	25	9.3	6.9	50
	30	38	9.3	6.6	120
	29	36	12	7.3	170
(B) **2** $\xrightarrow{H_3O^+,\ pentane}$ **3t** + other products + [8a] → **8**					
90	3.2	4.3			1.5
82	7.8	7.7			3
80	8.5	8.5			6
54	21	10.2		6.8	26
52	29	11	0.8	6.9	50
21	57	12	2.2	7.1	120
13	64	12	3.5	7.3	170

[a] Determined by GLC.

However, despite steric congestion TM-limonene oxide (**2**) could be epoxidized further under more forcing conditions (3 equiv of *m*-chloroperbenzoic acid) to form a mixture of diepoxides **13a** and **13b** (Scheme V). Treatment of **13** with $LiAlH_4$ led to opening of the extracyclic epoxide ring. The nucleophile of choice for this transformation is Super-Hydride, which after 5 h at 70 °C in solvent tetrahydrofuran gave TM-α-terpineol 1,2-epoxide (**14t**) in 90% yield. Consistent with the work on TM-limonene oxide (**2**), the second, annelated epoxide group in **14t** reacted with neither $LiAlH_4$ nor $LiBEt_3H$. Interestingly, on treatment with aqueous *p*-toluenesulfonic acid/pentane, **14t** could be dehydrated and the epoxide group could be opened readily to give TM-*trans*-carveol (**3t**) in good yield (ca. 75%). Under the same conditions



3t

opening of the epoxide ring of the structurally related **2**

(13) Joshi, G. C.; Singh, N.; Pande, L. M. *Tetrahedron Lett.* **1972**, 1461. Makosza, M., personal communication to E. Dehmlow, S. Dehmlow. "Phase Transfer Catalysis"; Verlag Chemie: Weinheim/Bergstr., Germany, 1980; p 181. Julia, S.; Ginebreda, A. *Synthesis* **1977**, *682*.

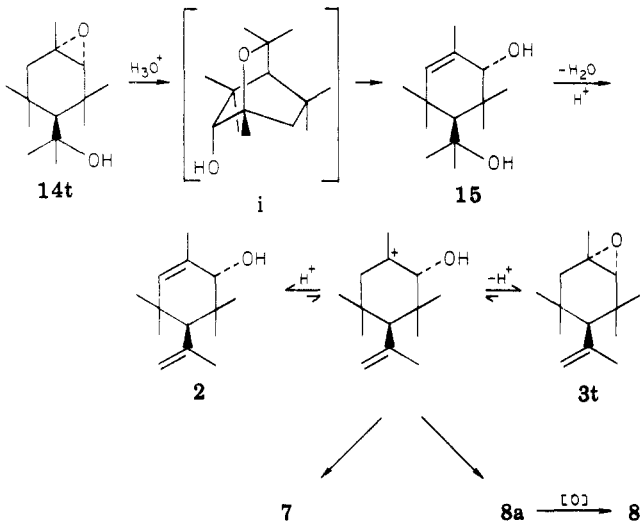
(14) See, e.g., Ghosez, L.; Laroche, P.; Bastens, L. *Tetrahedron Lett.* **1964**, 3745.

(15) Crawford, R. J.; Erman, W. F.; Broaddus, C. D. *J. Am. Chem. Soc.* **1972**, *94*, 4298. See also Crawford, R. J. *J. Org. Chem.* **1972**, *37*, 3543.

(16) Schlosser, M.; Hartmann, J.; David, V. *Helv. Chim. Acta* **1974**, *57*, 1567.

(17) Hoffmann, H. M. R.; Giguere, R. J.; Pauluth, D.; Hofer, E. *J. Org. Chem.*, submitted for publication.

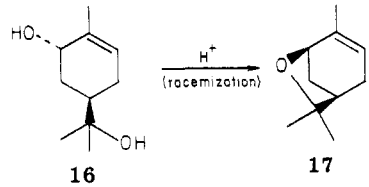
Scheme VI



was sluggish. In order to prove the possibility of neighboring group participation we compared the reactivity of **14t** with that of **2** toward aqueous acid in a two-phase system in more detail. Both **14t** and **2** gave the same products eventually, but the rates and proportion of products were different. As will be seen from Table I, in A) more than half of dioxygenated educt **14t** had disappeared after 1.5 h, and 35% of **3t** had formed, whereas in B 90% of **2** had remained while **3t** (3.2%) and **8a** (4.3%) were present in roughly equal amounts. Clearly, **14t** reacted faster than **2** under the same conditions.

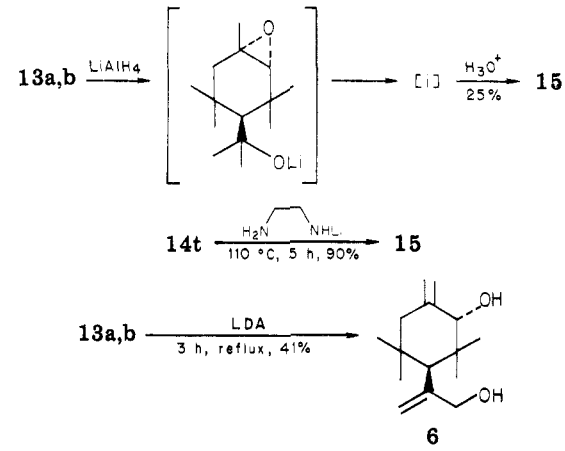
A plausible route to **3t** proceeds via TM-1,8-cineol derivative i (Scheme VI), which arises by neighboring group participation and which is assumed to reopen to TM-sobrerol (**15**) and thence to dehydrate to **3t**. In experiment A the formation of **3t** had reached its maximum after 6 h and then dropped, while five-membered ring **8** and **8a** became the major product. In experiment B **3t** remained the major product throughout, while five-membered ring **8** and also TM-dihydrocarvone **7** remained minor products. Apparently, the aqueous acid has a much better chance of reacting with **3t** in A—**3t** being built up quickly—than in B. The postulated 1,8-cineol derivative i has not yet been isolated, but TM-sobrerol (**15**) has under another set of conditions.

TM-Sobrerol (15). Sobrerol itself has been known for a long time, its discovery being due to Sobrero in 1851.[18] Racemic sobrerol has been reported to have a significant respiratory analeptic action and is used for treating chronic bronchitis.[19] Whereas acid-catalyzed dehydration of optically active sobrerol (**16**) gives *dl*-pinol (**17**), TM-sobrerol (**15**), by virtue of the crowded methyl groups, does not give TM-pinol, but TM-carveol (**3t**), as discussed above. A



route to **15** was discovered by accident: the reaction mixture of $LiAlH_4$ with **13a,b** was worked up with ice water

Scheme VII



(30 mL) and then 2 N H_2SO_4 (30 mL) to dissolve the precipitate. After vigorous stirring for 10 min GLC showed a new peak with a longer retention time than that of diepoxide **13a,b**. On continued stirring with acid, this peak disappeared and TM-carveol (**3t**) was formed, having a shorter GLC retention time than that of **13a,b**. The IR spectrum (OH band) and the ^1H NMR spectrum in $(CD_3)_2SO$ (secondary and tertiary alcohol) suggested the unknown to be **15**, as was confirmed by ^{13}C NMR. It must be borne in mind that an excess of $LiAlH_4$ was used for the reduction of **13a,b**. Consequently, before addition of the acid the solution was strongly alkaline. Since structurally related **2** does not react with $LiAlH_4$, neighboring group participation may again be invoked (cf. Scheme VII) to explain the formation of **15**.

In any event, the concentration of aqueous acid seems to decide whether **15** can be isolated or whether **15** is dehydrated to **3t**.

Finally, a simple route to TM-sobrerol (**15**) was found by epoxide opening of **14t** with *N*-lithioethylenediamine, giving **15** in 90% yield. Opening of diepoxide **13ab** with lithium diisopropylamide produced bis(allylic alcohol) **18**. The comparison of TM-limonene and its derivatives with that of limonene itself illustrates the marked influence of steric factors upon chemical reactivity.

Experimental Section

Note. Rotation about the crowded sp^2–sp^3 carbon–carbon single bond in TM-limonene derivatives is hindered ($\Delta G^{\ddagger} \sim 12$–15 kcal/mol).[17] Hence, NMR spectra are temperature dependent.

1,3,3,5,5-Pentamethyl-4-(1-methylethenyl)-1-cyclohexene (3,3,5,5-Tetramethyllimonene; 1). A 1-L three-necked, round-bottomed flask is fitted with a pressure-equalizing dropping funnel, mechanical stirrer, and reflux condenser protected with a $CaCl_2$ drying tube. The apparatus is charged with magnesium turnings (18.25 g, 0.75 mol) and flame-dried with a Bunsen burner. After the flask has cooled to room temperature, 50 mL of anhydrous ether is introduced, followed by dropwise addition of ca. 20 mL of methyl iodide solution (106.5 g, 0.75 mol in 100 mL of anhydrous ether). The mixture is stirred at room temperature, and within a few minutes an exothermic reaction occurs. The remaining methyl iodide solution is added dropwise at a rate that sustains gentle boiling of the ether. Upon completion of the addition, the reaction mixture is refluxed for 0.5 h and then cooled to ca. 0 °C (ice water/NaCl). 4-Methyl-3-penten-2-one (mesityl oxide; 59 g, 0.6 mol) in anhydrous ether (100 mL) is added dropwise over a period of ca. 2 h (note 1). The reaction mixture is stirred for 1 h at 0 °C, left overnight at room temperature, recooled to 0 °C, and worked up as follows. Ice water (50 mL) is carefully stirred (dropwise addition) into the mixture over a 1-h period, whereby an exothermic reaction is observed and a white precipitate of $Mg(OH)_2$ forms. The cyclodimerization of the allyl alcohol is now carried out in situ by allowing the reaction mixture

(18) Sobrero, A. *Justus Liebigs Ann. Chem.* **1851**, *80*, 106. See also Schmidt, H. *Chem. Ber.* **1953**, *86*, 1437. Lombard, R.; Heywang, G. *Bull. Soc. Chim. Fr.* **1954**, 1210.
(19) Cf. Dalla Valle, V. *Chem. Abstr.* **1971**, *75*, 74770w.
(20) Long-range coupling ($J \sim 1$ Hz).

to come to room temperature and adding 400 mL of 2 N hydrochloric acid (note 2) in 50-mL portions over a 1-h period with vigorous stirring (note 3). The reaction is complete after stirring at room temperature for 3 h. The organic phase is separated and the aqueous phase is washed with ether (2 × 150 mL). The combined organic phases are washed with 150 mL of a 5% $NaHCO_3$ solution and 150 mL of a saturated NaCl solution and dried over Na_2SO_4. Filtration and removal of solvent yields a dark crude oil (ca. 50 g), which is first purified by refluxing at 120–130 °C for 20 min (note 4) followed by flash column filtration (note 5). Final vacuum distillation through a 15-cm Vigreux column (note 6) yields 25.9–29.1 g (51–57%) of 3,3,5,5-tetramethyllimonene as a colorless oil: bp 44–46 °C (≤ 1 torr) (note 7), 95% pure by GLC; IR ($CHCl_3$) 3100–3080 (olefinic CH), 3000–2820 (CH_3, CH_2), 1680–1600 (C=C) cm^{-1}; 90-MHz ^1H NMR ($CDCl_3$) δ 0.92 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3), 1.00 (s, 3 H, CH_3), 1.04 (s, 3 H, CH_3), 1.63 (m,[20] 3 H, cyclohexenyl CH_3), 1.82 (m, 3 H, isopropenyl CH_3), 1.50–1.85 (m, 2 H, allylic CH_2), 1.93 (s, 1 H, allylic H), 4.67–4.74 (m, 1 H, exo methylene H), 4.90–5.00 (m,[20] 1 H, exo methylene H), 5.0–5.13 (m,[20] 1 H, olefinic H); ^{13}C NMR ($CDCl_3$) δ 23.7 (q), 24.0 (q), 25.8 (q), 26.7 (q), 30.9 (q), 33.0 (q), 33.7 (s), 36.1 (s), 47.8 (t), 60.2 (d), 115.0 (t), 128.8 (s), 132.2 (d), 145.2 (s). Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.98. Found: C, 87.31; H, 12.54.

Notes. 1. Mesityl oxide was purchased from Aldrich-Europe (n^{20}_D = 1.445) containing ca. 12% unconjugated enone.

2. After HCl addition the precipitate dissolves and two clear phases are formed.

3. During this procedure the reaction progress may be monitored by gas chromatography (2.0 m, 5% Carbowax glass column, temperature program 40 to 200 °C at 20 °C/min). 3,3,5,5-Tetramethyllimonene has a retention time of ca. 4.0 min and is accompanied by at least two unidentified side products (t_R = 3.0 and 4.3 min, respectively). Monomeric allylic alcohol, 2,4-dimethyl-3-penten-2-ol (t_R = 2.5 min), 2,4-dimethyl-1,3-pentadiene (t_R = 0.5 min), and several trimeric products (t_R = 7.0–8.0 min, ca. 20%) are also observed.

4. Quick heating serves to remove the minor side products (t_R = 3.0 and 4.3 min).

5. Silitech 63-200 (Woelm-Pharma, GmbH, Eschwege, Germany) is used in a 10:1 silica gel/crude product ratio with pentane as eluent. This filtration is necessary to prevent the crude product from strongly foaming during attempted distillation. Approximately 1 L of filtrate is collected, mild pressure (press ball) being used to speed the filtration.

6. Kugelrohr distillation is equally satisfactory.

7. Calculated yield based on purity of mesityl oxide (note 1) and on assumption that the tertiary alcohol derived from the unconjugated enone does not yield 1 under the experimental conditions.

2,4,4,6,6-Pentamethyl-5-(1-methylethenyl)-*trans*-2-cyclohexen-1-ol (TM-*trans*-Carveol; 3t). Lithium metal (0.34 g, 48 mmol) is carefully added, with stirring, to 10 mL of absolute ethylenediamine contained in a flame-dried 25-mL two-necked flask. The mixture is brought to 110 °C until the evolution of hydrogen is complete; a blue solution results. The solution is allowed to cool to 40–50 °C and melted epoxide 2[2] (1.0 g, 4.8 mmol) is added in one portion. The temperature is raised to 110 °C and maintained for 5 h. After cooling to room temperature, the reaction mixture is hydrolyzed by pouring onto 75 mL of ice water and is extracted with dichloromethane (2 × 30 mL). The organic phase is washed with saturated NH_4Cl solution (50 mL) and saturated NaCl solution (50 mL), dried (Na_2SO_4), and concentrated on a rotary evaporator to give a yellow solid (0.95 g). Flash chromatography on silica gel (10:1, CH_2Cl_2) yields a colorless waxy solid, **3t** (0.90 g, 90%), as a single isomer (GLC, NMR): mp 38–40 °C; 90-MHz ^1H NMR ($CDCl_3$) δ 0.98 (s, 6 H, $2CH_3$), 1.03 (s, 6 H, $2CH_3$), 1.43 (br s, 1 H, OH), 1.80 (m,[20] 3 H, isopropenyl CH_3), 1.87 (m,[20] 3 H, cyclohexenyl CH_3), 2.25 (s, 1 H), 3.30 (br s, 1 H), 4.80 (m, 1 H), 5.02 (m, 1 H), 5.23 (m, 1 H) (olefinic H's); IR (CCl_4) 3620 (m, sh OH), 3580 (w, br OH), 1000 (s, CO) cm^{-1}; mass spectrum, *m/z* (relative intensity) 208 (M^+, 15), 175 (6), 152 (10), 151 (7), 147 (12), 145 (14), 123 (10), 121 (15), 112 (100), 110 (15), 109 (12), 97 (45), 96 (46), 95 (7); ^{13}C NMR ($CDCl_3$) δ 22.2 (q), 22.4 (q), 22.9 (q), 24.8 (q), 26.8 (q), 32.8 (q), 36.4 (s), 38.0 (s), 52.8 (d), 79.2 (d), 116.3 (t), 130.6 (s), 136.5 (d), 144.2 (s). Anal Calcd for $C_{14}H_{24}O$: C, 80.70; H, 11.61. Found: C, 80.77; H, 11.46.

2,2,4,4-Tetramethyl-6-methylene-3-(1-methylethenyl)-*trans*-cyclohexan-1-ol (5t). A 50-mL three-necked flask is fitted with a reflux condenser, pressure-equalizing dropping funnel, nitrogen inlet, and rubber septum. The apparatus is flame-dried under nitrogen, charged with 15 mL of absolute ether and diisopropylamine (0.40 g, 5.4 mmol), and cooled to 0 °C (ice bath). *n*-Butyllithium (1.5 M) in hexane (4.0 mL, 6.0 mmol) is added carefully by means of a syringe. After 10 min at 0 °C the solution turns green-yellow and epoxide **2** (1.0 g, 4.8 mmol) dissolved in ether (3 mL) is added dropwise. The ice bath is removed and the solution brought to 50 °C for 3 h. The reaction mixture is worked up by cooling to 0 °C, adding water (15 mL), and extracting with ether (2 × 30 mL). Washing, drying, and flash chromatography as described above for **3t** yield colorless needles of **5t** (0.95 g, 95%) as a single isomer (GLC, NMR): mp 43–45 °C; 90-MHz ^1H NMR ($CDCl_3$) δ 0.93 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3), 0.98 (s, 6 H, $2CH_3$), 1.53 (d, *J* = 5 Hz, 1 H, OH), 1.85 (m,[20] 3 H, isopropenyl CH_3) , 1.77 (d, *J* = 13 Hz, 1 H), 2.25 (s, 1 H), 2.45 (d, *J* = 13 Hz, 1 H), 3.70 (br s, 1 H), 4.77 (m, 1 H), 4.83 (m, 1 H), 4.90 (m, 1 H), 5.00 (m, 1 H) (olefinic H's); IR (CCl_4) 3620 (m, sharp OH), 3490 (w, br OH), 1040 (m, CO) cm^{-1}; mass spectrum, *m/z* (relative intensity) 208 (M^+, 10), 193 (6), 175 (6), 165 (9), 164 (6), 152 (22), 150 (8), 137 (11), 135 (8), 123 (10), 121 (8), 119 (7), 112 (14), 111 (13), 109 (13), 107 (13), 105 (8), 97 (100), 96 (13), 95 (14), 93 (15), 91 (8), 83 (26), 81 (19); *^{13}C NMR* ($CDCl_3$) δ 22.7 (2 q), 22.9 (q), 26.8 (q), 32.7 (q), 36.9 (s), 40.4 (s), 46.0 (t), 54.6 (d), 82.5 (d), 111.7 (t), 113.9 (t), 145.2 (s), 146.9 (s). Anal. Calcd for $C_{14}H_{24}O$: C, 80.70; H, 11.61. Found: C, 80.81; H, 11.50.

2,4,4,6,6-Pentamethyl-5-(1-methylethenyl)-2-cyclohexanone (TM-Carvone) (4). A flame-dried, 25-mL, two-necked flask is charged with pyridinium chlorochromate (0.60 g, 2.7 mmol) and 7.5 mL of absolute CH_2Cl_2. Carveol **3t** (0.5 g, 2.4 mmol), dissolved in ca. 2 mL of CH_2Cl_2, is added in one portion to the well-stirred mixture, which almost immediately turns black. After 2 h at room temperature the tarry reaction mixture is flash filtered through a short column (neutral Al_2O_3, grade III, ca. 10 g; CH_2Cl_2). The flask is washed thoroughly with ether, which serves to granulate the tarry residue, and a combined filtrate of ca. 80 mL is collected, concentrated on a rotary evaporator, and Kugelrohr distilled [80–90 °C (0.1 torr)] to give a colorless oil, **4** (0.42 g, 85%): 90-MHz ^1H NMR ($CDCl_3$) δ 1.14 (s, 6 H, $2CH_3$), 1.21 (s, 6 H, $2CH_3$), 1.67 (s, 3 H, cyclohexenyl CH_3), 1.77 (m,[20] 3 H, isopropenyl CH_3), 2.36 (s, 1 H), 4.75 (m, 1 H), 4.92 (m, 1 H), 6.04 (m,[20] 1 H, enone H) (olefinic H's); IR (CCl_4) 1675 (vs, C=O) cm^{-1}; mass spectrum, *m/z* (relative intensity) 206 (M^+, 29), 191 (8), 163 (11), 137 (8), 135 (11), 121 (20), 110 (100), 109 (9), 95 (40), 82 (15); ^{13}C NMR ($CDCl_3$) δ 16.6 (q), 23.5 (q), 23.9 (q), 26.7 (q), 29.9 (q), 31.9 (q), 35.6 (s), 44.5 (s), 72.6 (d), 116.0 (t), 130.2 (s), 144.6 (s), 152.1 (d), 204.8 (s). Anal. Calcd for $C_{14}H_{22}O$: C, 81.49; H, 10.74. Found: C, 81.20; H, 10.58.

2,2,4,4-Tetramethyl-6-methylene-3-(1-methylethenyl)-cyclohexanone (6). A flame-dried, 25-mL, two-necked flask is charged with 10 mL of absolute dichloromethane, 100 mg of absolute pyridine, and TM-carveol **5t** (0.5 g, 2.4 mmol). The solution is cooled to ca. 0 °C (ice bath) and pyridinium chlorochromate (0.77 g, 3.45 mmol) is added in one portion. After 20 min with the well-stirred reaction mixture is allowed to come to room temperature and after 1 h worked up as follows. The reaction mixture is cooled to 0 °C and 10 mL of absolute ether is added, and the mixture is stirred for 10 min and flash filtered through a short column (neutral Al_2O_3, grade III, ca. 10 g; CH_2Cl_2). The filtrate is kept cold during collection and the solvent is removed under reduced pressure at room temperature or below (heating causes the sensitive exo enone to polymerize) to give a light-yellow oil, **6** (370 mg, 75%). The product is stored in dilute ether solution at −20 °C and is stable under these conditions for weeks. Spectral data for **6**: 90-MHz ^1H NMR ($CDCl_3$) δ 1.03 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.83 (m,[20] 3 H, isopropenyl CH_3), 1.55–2.27 (m, 2 H), 2.44 (s, 1 H), 4.75 (m, 1 H), 5.00 (m, 1 H), 5.15 (m, 1 H), 5.86 (m, 1 H) (olefinic H's); IR (CCl_4) 1690 (vs, C=O) cm^{-1}; mass spectrum, *m/z* (relative intensity) 206 (M^+, 22), 191 (19), 163 (26), 137 (31), 135 (28), 121 (26), 109 (26), 107 (27), 105 (41), 97 (45), 96 (55), 95 (43), 83 (22), 81 (61); ^{13}C NMR ($CDCl_3$) δ 23.9 (q), 24.4 (q), 25.0 (q), 28.1 (q), 31.8 (q), 34.4 (s), 47.3 (s), 47.9 (t), 61.8 (d), 116.2 (t), 121.6 (t), 143.0 (s), 144.0 (s), 207 (s).

2,4,4,6,6-Pentamethyl-5-(1-methylethenyl)-*cis*-2-cyclohexen-1-ol (TM-*cis*-Carveol) (3c). TM-Carvone (4; 206 mg, 1 mmol) is dissolved in 2 mL of absolute toluene in a flame-dried, 25-mL, two-necked flask fitted with a rubber septum and reflux condenser under nitrogen. The solution is cooled to 0 °C (ice bath) and 1.2 M diisobutylaluminum hydride in toluene (1.3 mL, 1.5 mmol) is added slowly through the septum by means of a syringe. After 1 h at 0 °C the reaction solution is quenched with 2 mL of absolute methanol and flash filtered through a short column (silica gel, ca. 3 g, CH_2Cl_2). The filtrate (ca. 40 mL) is concentrated on a rotary evaporator to give white needles, **3c** (200 mg, 96%), as a single isomer (GLC, NMR): mp 63–65 °C; 90-MHz ^1H NMR ($CDCl_3$) δ 0.92 (s, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 1.02 (s, 6 H, $2CH_3$), 1.40 (br s, 1 H, OH), 1.72 (m,[20] 3 H, isopropenyl CH_3), 1.86 (m,[20] 3 H, cyclohexenyl CH_3), 1.94 (s, 1 H), 3.87 (br s, 1 H), 4.77 (m, 1 H), 5.01 (m, 1 H), 5.17 (m, 1 H) (olefinic H's); (CCl_4) 3640, 3610 (m, sharp OH), 1060 (m, CO) cm^{-1}; mass spectrum, *m/e* (relative intensity) 208 (M^+, 4), 193 (4), 137 (5), 135 (7), 123 (7), 121 (9), 112 (100), 109 (12), 97 (39), 83 (16); ^{13}C NMR ($CDCl_3$) δ 15.6 (q), 19.4 (q), 25.1 (q), 26.0 (q), 32.8 (q), 36.4 (s), 38.6 (s), 59.2 (d), 79.9 (d), 116.0 (t), 131.2 (s), 135.0 (d), 144.1 (s); mass spectrum, *m/z* 208.18256 (M^+ calcd for $C_{14}H_{24}O$, 208.18270).

2,2,4,4-Tetramethyl-6-methylene-3-(1-methylethenyl)-*cis*-cyclohexan-1-ol (5c). The reaction is carried out as described for the preparation of **3c**. TM-*exo*-Carvone **6** (206 mg, 1 mmol) yields, after work up, an 85:15 mixture of **5c/5t** (175 mg, 85%) as determined by GLC: 90-MHz ^1H NMR ($CDCl_3$) δ (inter alia) 0.90 (s, 6 H, $2CH_3$), 0.97 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3), 1.60 (d, J = 6 Hz, 1 H, OH), 1.55–1.95 (m, 2 H), 1.83 (m,[20] 3 H, isopropenyl CH_3), 2.02 (s, 1 H), 3.97 (d, J = 6 Hz, 1 H), 4.80 (m, 2 H), 5.00 (m, 2 H) (olefinic H's); IR (CCl_4) 3620 (w, sharp, OH), 905 (s) cm^{-1}.

***cis*- and *trans*-2,2,4,4,6-Pentamethyl-3-(1-methylethenyl)cyclohexanone (7c, 7t).** A 50-mL, three-necked flask, fitted with a reflux condenser, dropping funnel and drying tube, is charged with zinc bromide (100 mg, 0.45 mmol) and then flame-dried. After the flask is cooled, 10 mL of absolute benzene is added and the temperature is raised to 80 °C to dissolve the reagent. The flask is removed from the oil bath and epoxide **2** (5.4 g, 26 mmol), dissolved in 10 mL of absolute benzene, is added dropwise—an exothermic reaction is observed. After addition the solution is refluxed at 80 °C for 48 h. The reaction is worked up by cooling, diluting with CH_2Cl_2 (30 mL), washing with water (75 mL), 5% NH_3 solution (30 mL), and saturated NaCl solution (50 mL). The combined aqueous phase is extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic phase dried (Na_2SO_4) and concentrated to give a crude oil, 4.5 g. Flash column filtration (silica gel, 10:1) with the eluent pentane (150 mL) allows isolation of an "olefinic" fraction, 0.5 g, containing several unidentified products (GLC). Elution with ether (200 mL) gives a second fraction, 3.5 g, containing mainly products **7c/7t** and **8**. Fractional distillation (10-cm Vigreux column) of this fraction allows isolation of **7c/7t** as a colorless oil (2.0 g, 40%) in a 1:1 *cis/trans* ratio (GLC), bp 110–140 °C (≤1 torr). The residue contains acid **8**, which after evaporative recrystallization from light petroleum (bp 60–70 °C) gives **8** as colorless plates (0.6 g, 11%), mp 98–100 °C. Spectral data for **7c/7t**: 90-MHz ^1H NMR ($CDCl_3$) δ 0.91 (s, 3 H), 0.97 (s, 3 H), 1.00 (s, 3 H), 1.04 (s, 3 H), 1.27 (d, J = 6.5 Hz, 3 H), 1.45–1.86 (m, 2 H), 1.80 (s, 3 H), 1.93 (s, 1 H), 2.86 (m, 1 H), 4.83 (m, 1 H), 5.10 (m, 1 H); IR (CCl_4) 3000–2880 (vs), 1710 (vs, C=O) cm^{-1}; mass spectrum, *m/z* (relative intensity) 208 (M^+, 91), 165 (26), 152 (38), 139 (79), 137 (44), 125 (38), 123 (50), 109 (44), 97 (100), 96 (47), 83 (85), 81 (47); mass spectrum, *m/z* 208.18256 (M^+ calcd for $C_{14}H_{24}O$, 208.18270).

Spectral data for *trans*-1,2,2,4,4-pentamethyl-3-(1-methylethenyl)cyclopentane carboxylic acid (8): 90-MHz ^1H NMR ($CDCl_3$) δ 0.92 (s, 3 H), 1.04 (s, 3 H), 1.08 (s, 3 H), 1.13 (s, 3 H), 1.17 (s, 3 H), 1.81 (m,[20] 3 H), 1.86 (AB system, $\nu_1-\nu_3$ = 70.4 Hz, J = 14 Hz, 2 H), 2.52 (s, 1 H), 4.72 (m, 1 H), 5.09 (m, 1 H); IR (CCl_4) 3300–2400 (m, OH), 2980–2880 (s), 1690 (s, C=O) cm^{-1}; mass spectrum, *m/z* (relative intensity) 224 (M^+, 36), 209 (32), 191 (28), 179 (25), 175 (21), 167 (21), 163 (21), 153 (25), 150 (21), 139 (45), 137 (61), 135 (39), 128 (40), 123 (89), 121 (36), 112 (39), 109 (39), 107 (25), 105 (28), 99 (32), 97 (100), 96 (89), 95 (62), 83 (78), 81 (62); ^{13}C NMR ($CDCl_3$) δ 20.7 (q), 21.2 (q), 25.9 (q), 28.6 (q), 30.0 (q), 31.7 (q), 39.6 (s), 48.7 (s), 51.3 (t), 55.2 (s), 63.9 (d), 116.1 (t), 143.1 (s), 184.3 (s); mass spectrum, *m/z* 224.17823 (M^+ calcd for $C_{14}H_{24}O_2$, 224.17761).

***trans*- and *cis*-1,3,3,5,5-Pentamethyl-4-(1-methylethenyl)cyclohexan-1-ol (9t, 9c) and 1,1,3,3-Tetramethyl-5-methylene-2-(1-methylethenyl)cyclohexane (1a).** A mixture of 75 mL of *tert*-butyl alcohol, 75 mL of water, 1.5 mL of concentrated H_2SO_4, and 4.0 mL of xylene was poured into the argon-flushed reaction chamber of a GRÄNTZEL 400 photochemical reactor. Tetramethyllimonene (1) (3.0 g, 15.6 mmol) was added to the mixture, which was then flushed with argon for several minutes, with stirring. The mixture was irradiated at room temperature (water/air cooling systems) with low-vapor mercury lamps (100 mA) for 3 days, the reaction progress being monitored by GLC. The reaction was worked up by neutralizing with 1 N NaOH, extracting with ether, and drying ($MgSO_4$) in the usual manner to give, upon solvent removal, ca. 3.0 g of a crude orange oil. Flash column chromatography (neutral Al_2O_3, grade III, 10:1) using pentane as initial eluent (ca. 300 mL collected) serves to isolate the olefinic fraction containing unreacted **1** and isomer **1a** (1.35 g, 45%) in a ca. 1:1 ratio. Eluent change to CH_2Cl_2 then allows isolation of the TM-β-terpineols **9t/c** as colorless needles (1.2 g, 40%, **9t/9c** ~ 4:1). Two evaporative recrystallizations from light petroleum (bp 60–70 °C) yield **9t**, mp 100–101 °C, as colorless plates.

Spectral data for 1a: GC/MS, *m/e* (relative intensity) 192 (M^+, 5), 177 (24), 164 (12), 149 (48), 136 (12), 134 (10), 121 (34), 107 (23), 97 (64), 81 (78), 55 (96), 41 (100); ^{13}C NMR ($CDCl_3$) of **1** δ 23.7 (q), 24.0 (q), 25.8 (q), 26.7 (q), 30.9 (q), 33.0 (q), 33.7 (s), 36.1 (s), 47.8 (t), 60.2 (d), 115.0 (t), 128.8 (s), 132.2 (d), 145.2 (s); ^{13}C NMR of **1a** (determined from mixed **1/1a** spectra) δ 22.8 (q), 23.0 (q), 24.0 (q), 24.8 (q), 32.7 (q), 33.6 (s), 52.1 (t), 61.8 (d), 109.4 (t), 115.0 (t), 128.8 (s), 145.5 (s).

Spectra data for 9t: 90-MHz ^1H NMR ($CDCl_3$) δ 1.03 (s, 6 H), 1.08 (s, 6 H), 1.00–1.13 (br s, 1 H), 1.38 (s, 3 H), 1.52 (AB system, $\nu_1-\nu_3$ = 25 Hz, J = 18 Hz, 4 H), 1.60 (s, 1 H), 1.78 (m,[20] 3 H), 4.68 (m,[20] 1 H), 4.95 (br s, 1 H); IR (CCl_4) 3600 (m, OH), 3020–2880 (s), 900 (m, CO) cm^{-1}; mass spectrum, *m/z* (relative intensity) 210 (M^+, 3), 195 (3), 192 (10), 177 (14), 149 (9), 137 (14), 136 (11), 135 (11), 121 (15), 100 (51), 97 (37), 96 (100), 82 (32); ^{13}C NMR ($CDCl_3$) δ 23.8 (q), 34.3 (q), 34.5 (q), 35.2 (s), 54.4 (t), 60.9 (d), 70.9 (s), 113.0 (t), 144.6 (s).

3,3,5,5-Tetramethyl-4-(1-methylethenyl)cyclohexanone (10). A mixture of isomers **1/1a** (ca. 1:1, 200 mg, 1 mmol) and 30 mg of $NaHCO_3$ in 1.2 mL of acetone is cooled to 0 °C. $KMnO_4$ (0.63 g, 4 mmol) is added to the cold mixture and stirred at 0 °C for 4 h. The solvent is then removed and the residue dissolved in 2 mL of water, cooled to 0 °C, and acidified with concentrated H_2SO_4 and $NaHSO_3$ until the color disappears. Extraction with ether, drying, and concentration gives a yellow oil, which GLC analysis shows to contain starting isomer **1** and product **10**. Flash column chromatography using the pentane/CH_2Cl_2 solvent switch as described for **9t/c** allows isolation (CH_2Cl_2 fraction) of **10** (30 mg, 20%) as a light-yellow oil: 90-MHz ^1H NMR ($CDCl_3$) δ 1.04 (s, 6 H), 1.08 (s, 6 H), 1.90 (m,[20] 3 H), 2.23 (s, 1 H), 2.27 (AB system, $\nu_1-\nu_3$ = 20 Hz, J = 13 Hz, 4 H), 4.82 (m,[20] 1 H), 5.09 (m,[20] 1 H); IR (CCl_4) 3000–2860 (s), 1715 (s, C=O) cm^{-1}; mass spectrum, *m/z* (relative intensity) 194 (M^+, 10), 139 (13), 138 (13), 123 (31), 112 (5), 97 (100), 81 (27).

***trans*- and *cis*-7,7-Dichloro-1,3,3,5,5-pentamethyl-4-(1-methylethenyl)bicyclo[4.1.0]heptane (11t, 11c).** A 100-mL round-bottomed flask, fitted with reflux condenser, is charged with a solution of tetramethyllimonene (1) (0.6 g, 3.1 mmol) in $CHCl_3$. Finely ground NaOH (7.0 g, 170 mmol) and benzyl triethylammonium chloride (300 mg, 1.5 mmol) are added to the well-stirred solution. An exothermic reaction ensues (temperature rises to ca. 50 °C), and the solution foams and becomes dark brown. After 1 h the reaction mixture is worked up by cooling to 0 °C (ice bath) and then filtered. The brown precipitate is washed with $CHCl_3$ (3 × 40 mL) and the filtrate dried ($MgSO_4$), concentrated, and flash column filtered (silica gel, 10:1, CH_2Cl_2) to give a crude oil. Kugelrohr distillation serves to remove remaining **1** and yields **11t/11c** as a colorless oil (400 mg, 58%): bp 160 °C (0.5 torr); **11t/11c** = 4:1; 90-MHz ^1H NMR ($CDCl_3$) δ 0.83 (s, 3 H), 1.14 (s, 3 H), 1.24 (s, 6 H), 1.45 (s, 3 H), 1.81 (m,[20] 3 H), 1.30–1.60 (m, 3 H), 1.85 (s, 1 H), 4.72 (m,[20] 1 H), 5.00 (m,[20] 1 H); mass spectrum, *m/z* (relative intensity) 276 (M^+ + 2, 0.5),

274 (M^+, 2), 178 (15), 165 (19), 163 (27), 151 (24), 145 (31), 143 (87), 138 (58), 137 (17), 135 (13), 129 (10), 124 (17), 123 (100), 121 (17), 109 (21), 107 (27), 105 (14), 96 (54), 95 (23), 91 (24), 83 (40), 81 (35), 79 (17), 77 (21).

***trans*- and *cis*-1,3,3,5,5-Pentamethyl-4-(1-methylethenyl)bicyclo[4.1.0]heptane (12t, 12c).** A 50-mL, three-necked flask, fitted with a reflux condensor and dropping funnel, is charged with a solution of **11t/11c** (300 mg, 1.1 mmol) in 10 mL of absolute ether. Sodium metal (2.5 g) is slowly added in small portions while at the same time 15 mL of wet methanol (3% H_2O) is dropped in. After the reaction mixture has been stirred for 6 h, a second portion of sodium (1.0 g) and methanol (5 mL) is added, the mixture being stirred overnight. After addition of water (30 mL) and extraction with ether (3 × 30 mL), the combined organic phase is dried ($MgSO_4$), concentrated, and distilled (Kugelrohr) to give **12t/12c** (200 mg, 82%): bp 60 °C (0.5 torr); **12t/12c** = 4:1; 90-MHz ^1H NMR ($CDCl_3$) δ 0.76 (s, 3 H), 0.91 (s, 3 H), 1.09 (s, 6 H), 1.24 (s, 3 H), 1.08–1.73 (m, 6 H), 1.80 (m,[20] 3 H), 4.70 (m,[20] 1 H), 4.94 (m,[20] 1 H).

1,3,3,5,5-Pentamethyl-4-(1-methyloxiran-1-yl)-7-oxabicyclo[4.1.0]heptane (13a, 13b). A well-stirred solution of **1** (2.6 g, 13.6 mmol) in 30 mL of CH_2Cl_2 is mixed with 30 mL of a 5% $NaHCO_3$ solution. *m*-Chloroperbenzoic acid (6.0 g, 34 mmol) in 45 mL of CH_2Cl_2 is added and the mixture is stirred for 3 h at room temperature. A second portion of *m*-CPBA (2.0 g, 11.5 mmol) is added and the mixture is stirred for an additional hour (GLC shows consumption of **1** to be 95% complete). The organic phase is separated, the aqueous phase washed with CH_2Cl_2 (2 × 20 mL), and the combined organic phase washed with 2 N NaOH (2 × 40 mL), water (1 × 30 mL), and dried ($MgSO_4$). Concentration and flash column filtration (silica gel, 15:1) with pentane elutes starting material **1** and monoepoxide **2**. Elution with CH_2Cl_2 allows isolation of **13a,b** (ratio 3:2 by GLC), which, after Kugelrohr distillation, gives a colorless heavy oil (1.9 g, 63%): bp 165 °C (1 torr); 90-MHz ^1H NMR ($CDCl_3$) δ 1.06 (s, 3 H), 1.12 (s, 3 H), 1.15 (s, 3 H), 1.24 (s, 3 H), 1.30 (s, 3 H), 1.45 (s, 3 H), 1.54 (s, 1 H), 1.57–1.62 (m, 2 H), 2.41–2.70 (m, 3 H); IR (CCl_4) 3050 (w), 3000–2800 (s), 1380–1320 (s) cm^{-1}; mass spectrum, *m/z* (relative intensity) 224 (M^+, 4), 209 (9), 153 (14), 151 (16), 149 (18), 137 (20), 135 (17), 125 (12), 123 (24), 121 (15), 113 (15), 112 (30), 111 (20), 109 (21), 107 (12), 99 (25), 95 (21), 83 (22), 81 (15); ^{13}C NMR ($CDCl_3$) δ 23.4 (q), 24.4 (q), (q), 25.2 (q), 25.9 (q), 29.6 (q), 30.6 (q), 34.6 (t), 34.8 (s), 48.0 (q), 53.6 (d), 54.8 (s), 56.3 (s), 58.9 (s), 70.2 (d). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.96; H, 10.74.

1,1-Dimethyl-1-(3,4-epoxy-2,2,4,6,6-pentamethyl-3-cyclohexen-1-yl)methanol (14t). (a) Reduction with $LiAlH_4$. (a) Reduction with $LiAlH_4$. A 25-mL, two-necked flask is charged with 15 mL of absolute ether and $LiAlH_4$ (180 mg, 4.5 mmol). Diepoxide **13a/13b** (0.5 g, 2.2 mmol) dissolved in 3 mL of absolute THF is added dropwise at room temperature. The mixture is refluxed for 24 h (oil bath, 90 °C) and cooled to 0 °C and ice water (20 mL) is added dropwise. The organic phase is separated and the aqueous phase washed with ether (30 mL). The combined organic phase is washed with saturated NaCl solution (30 mL), dried ($MgSO_4$), and concentrated to give **14t** (350 mg, 70%) as a heavy oil: 90-MHz ^1H NMR ($CDCl_3$) δ 1.04 (s, 3 H), 1.11 (s, 3 H), 1.31 (s, 3 H), 1.33 (s, 3 H), 1.36 (s, 3 H), 1.42 (s, 6 H), 1.64 (s, 1 H), 1.75–1.90 (m, 2 H), 2.54 (s, 1 H), the hydroxy proton lies underneath the seven methyl groups between 1.0 and 1.48; IR (neat) 3600–3200 (m), 3000–2820 (s), 1400–1340 (m), 1120 (s) cm^{-1}; mass spectrum, *m/z* (relative intensity) 226 (M^+, 10), 153 (10), 136 (13), 112 (12), 110 (14), 99 (25), 97 (65), 95 (22), 83 (16); ^{13}C NMR ($CDCl_3$) δ 23.5 (q), 24.7 (q), 25.4 (q), 31.4 (q), 32.4 (q), 32.7 (q), 35.1 (s), 35.9 (s), 51.3 (t), 57.6 (d), 59.5 (s), 73.0 (d), 75.8 (s).

(b) Reduction with Lithium Triethylborohydride. A flamed-dried, 25-mL, two-necked flask fitted with a reflux condenser and drying tube is charged with diepoxide **13a,b** (2.0 g, 8.9 mmol) dissolved in 2–3 mL of absolute ether. At room temperature 10 mL of an ice-cold solution of lithium triethylborohydride (1.5 equiv; 1.3 M in THF) is slowly added by syringe through the septum. After addition the temperature is raised to 65–70 °C for 3 h. Near the end of the reaction a white precipitate forms. After cooling to 0 °C the mixture is worked up by slowly adding water (10 mL), extracting with ether (2 × 50 mL), drying, and concentraing to give a viscous colorless oil of **14t** (1.8 g, 90%). Spectral data were identical with those described above.

2,4,4,6,6-Pentamethyl-5-(1-hydroxy-1,1-dimethylmeth-1-yl)-*trans*-2-cyclohexen-1-ol (15) (TM-Sobrerol). (a) From Acid-Catalyzed Workup of $LiAlH_4$ Reduction. The reaction is carried out as described for the preparation of **14t**, but with a modified workup. Diepoxide **13a,b** (1.0 g, 4.4 mmol) is reduced by refluxing for 20 h and cooled to 0 °C. Ice–water (30 mL) is slowly added and the usual white precipitate forms. Thereafter, 2 N H_2SO_4 (30 mL) is added and the precipitate dissolves. After 10 min the phases are separated, and the aqueous phase is washed with ether (3 × 20 mL), saturated NaCl solution (30 mL), dried ($MgSO_4$), and concentrated. Upon concentration a white precipitate forms, which is recrystallized from pentane to give **15** (250 mg, 25%), mp 130 °C.

(b) From the Reaction of *N*-Lithioethylenediamine with 14t. This procedure is carried out as described for the preparation of **3t**. **14t** (1.0 g, 4.1 mmol) is used. After a reaction time of 5 h workup gives **15** (0.9 g, 90%) as a colorless solid. The product may be evaporatively recrystallized from CH_2Cl_2 to give colorless plates: mp 130 °C; 90-MHz ^1H NMR ($CDCl_3$) δ 0.92 (s, 3 H), 1.21 (s, 3 H), 1.24 (s, 3 H), 1.28 (s, 3 H), 1.45 (s, 3 H), 1.47 (s, 3 H), 1.75 (d, J = 1.5 Hz, 1 H), 1.97 (s, 1 H), 3.09 (s, 1 H), 5.03 (d, J = 1.5 Hz, 1 H), 1.10–1.65 (obscured OH, 2 H); IR ($CHCl_3$) 3600 (s), 3540–3320 (m), 3000–2880 (s), 1020 (s), 990 (vs) cm^{-1}; mass spectrum, *m/z* (relative intensity) 226 (M^+, 4), 211 (6), 208 (4), 193 (4), 115 (13), 103 (9), 102 (11), 101 (25), 97 (16), 96 (100), 73 (10), 69 (12); ^{13}C NMR ($CDCl_3$) δ 21.8 (q), 23.4 (q), 23.8 (q), 28.7 (q), 31.4 (q), 34.0 (s), 35.3 (q), 36.3 (q), 38.3 (s), 53.5 (d), 76.1 (s), 82.5 (d), 123.3 (s), 140.0 (d). Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.28; H, 11.57. Found: C, 74.29; H, 11.53.

3-[1-(Hydroxymethyl)ethenyl]-2,2,4,4-tetramethyl-6-methylenecyclohexanol (16). The procedure is carried out as described for the preparation of **5t** from **2**. **13a,b** (0.5 g, 2.2 mmol) is treated with 2 equiv of lithium diisopropylamide for 3 h at reflux. Usual workup and flash column filtration (silica gel, 10:1, CH_2Cl_2) followed by recrystallization from ether gives **16** (200 mg, 41%): mp 155 °C; 90-MHz ^1H NMR ($CDCl_3$) δ 0.90 (s, 3 H), 0.93 (s, 3 H), 1.01 (s, 6 H), 1.57 (br s, 2 OH, 2 H), 2.15 (AB system, $\nu_1-\nu_3$ = 47 Hz, J = 13 Hz, 2 H), 2.08 (s, 1 H), 3.70 (s, 1 H), 5.10 (br s, 2 H), 4.84 (m, 1 H), 4.93 (m, 1 H), 5.07 (m, 1 H), 5.36 (m, 1 H); IR ($CHCl_3$) 3695 (m), 3600 (m), 3700–3200 (s), 1600 (m), 910 (s) cm^{-1}; *mass spectrum*, *m/z* (relative intensity) 224 (M^+, 21), 206 (54), 193 (16), 191 (19), 177 (15), 175 (22), 163 (21), 154 (16), 150 (25), 137 (21), 135 (25), 133 (17), 123 (17), 121 (23), 112 (39), 111 (41), 109 (23), 107 (30), 105 (18), 97 (52), 96 (61), 95 (66), 93 (36), 91 (22), 85 (23), 83 (40), 81 (40). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.96; H, 10.76.

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Registry No. **1**, 68930-33-6; **1a**, 83379-10-6; **2**, 78310-15-3; **3c**, 81517-80-8; **3t**, 81517-75-1; **4**, 81517-77-3; **5c**, 81517-79-5; **5t**, 81517-76-2; **6**, 81517-78-4; **7c**, 83379-11-7; **7t**, 83379-12-8; **8**, 83379-13-9; **9c**, 83379-14-0; **9t**, 83379-15-1; **10**, 83379-16-2; **11c**, 83379-17-3; **11t**, 83434-85-9; **12c**, 83379-18-4; **12t**, 83434-86-0; **13**, 83379-19-5; **14t**, 83379-20-8; **15**, 83379-21-9; **18**, 83379-22-0; mesityl oxide, 141-79-7.