0-2° ether to give 9.55 g (46.1%) of white, crystalline **1b**. The ir and pmr spectra of this solid, as well as the behavior on tlc, presented evidence for the presence of 7-oxo-1-cyclooctenecarboxylic acid (**8b**) as an impurity, even though elemental analysis was satisfactory for pure **1b**.

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.42; H, 8.09.

Hydrogenation of 1.703 g of this solid material as in method 1 (above) produced 1.601 g (94.0%) of white, crystalline solids corresponding to pure **1b**: mp 96.5-100.0°; ir 1705 cm^{-1}; nmr δ 10.51 (s, 1).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.61; H, 8.38.

3-Carbomethoxycyclooctanone (**12**).—A solution of 2.00 g (11.7 mmol) of **1b** in 10 ml of methanol was refluxed for 2 hr with 40 ml of 1:2 BF_3–MeOH complex[14] under a nitrogen atmosphere. The solution was cooled, poured into $CHCl_3$, extracted with H_2O, washed with saturated NaCl solution, dried ($MgSO_4$), concentrated, and distilled under reduced pressure to give 1.82 g (84.1%) of a colorless oil: bp 74-75° (0.25 mm); ir 1730, 1700 cm^{-1} (as reported[12]); nmr δ 3.67 (s, 3) (as reported[12]).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.06; H, 8.87.

3-Carboxycyclononanone (**1c**).—A solution of 0.85 g (4.56 mmol) of **8c** in 25 ml of glacial acetic acid was hydrogenated at 40 psig and room temperature over 180 mg of prereduced platinum(IV) oxide until hydrogen absorption ceased (136% theoretical). Work-up as for **1b** (method 1) above gave 0.48 g (55.9%) of a viscous, clear and colorless oil: bp 135-136° (0.2 mm); ir 1700 cm^{-1}; nmr δ 10.30 (s, 1). This oil solidified to a waxy, white solid after storage overnight at 4°.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.12; H, 8.98.

Similar results were produced on hydrogenation of **8c** over 5% palladium on carbon except that the product **1c**, was contaminated with unreacted starting material even after repeated hydrogenation.

3-Carboxycyclodecanone (**1d**).—Hydrolysis and decarboxylation of **7d** was performed by refluxing 20.7 g (76.5 mmol) of **7d** in 250 ml of 10% HCl for 29 hr. Most of the H_2O was removed under reduced pressure. The residue was dissolved in ether, dried ($MgSO_4$), and concentrated under reduced pressure to a heavy slurry, from which 15.8 g (104%) of waxy material was separated by filtration. Recrystallization from ether gave 9.25 g (60.9%) of white crystalline solids: mp 56.0-58.5°; ir 1700 cm^{-1}; nmr δ 11.20 (s, 1).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.48; H. 9.06.

The ethereal mother liquors were concentrated further to give 1.45 g (9.5%) of white solids identical in all respects with the above product.

Registry No.—**1a**, 27531-68-6; **1b**, 27531-69-7; **1c**, 27531-70-0; **1d**, 27531-71-1; **6d**, 27531-72-2; **7a**, 27531-73-3; **7b**, 27531-74-4; **7d**, 27531-75-5; **8a**, 17606-97-2; **8b**, 17606-93-8; **8c**, 27531-78-8; **9**, 27531-79-9; **12**, 17606-96-1; **17**, 18543-37-8.

Absolute Configurations of the *p*-Menthane-2,5-diones and *p*-Menthane-2,5-diols[1]

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The eight diastereoisomeric *p*-menthane-2,5-diols (**1-8**), the four diastereoisomeric *p*-menth-1-ene-3,6-diols (**9-12**), and the two (+)-*p*-menthane-2,5-diones (**13** and **14**), which all have the same absolute configuration at the isopropyl group as (−)-α-phellandrene (**15**), have been prepared, characterized, and interrelated. Absolute configurations have been established for **1-14** by stereoselective chemical interconversions, including hydrogenation of diols **9-12**, Jones oxidation of diols **1-6**, lithium aluminum hydride reduction of diones **13** and **14**, and displacements by formate and hydride ions on monotosylates of diol **4**.

The configurational assignments presented here for the optically active *p*-menthane-2,5-diones and *p*-menthane-2,5-diols formed the basis of our previous definitive report on the *p*-menth-1-ene-3,6-diols.[2] The configurational relationships among the eight diastereoisomeric *p*-menthane-2,5-diols (**1-8**), the four diastereoisomeric *p*-menth-1-ene-3,6-diols[2] (**9-12**), and the two (+)-*p*-menthane-2,5-diones (**13** and **14**), which all have the same absolute configuration at C-4 as (−)-α-phellandrene (**15**), are shown in Scheme I.

Racemic Diones and Diols.—Racemic mixtures containing diones **13** and **14** and diols **3** and **4** have been prepared previously. Lithium–liquid ammonia–ethanol reduction of 2,5-dimethoxy-*p*-cymene followed by acid-catalyzed hydrolysis of the reduction product gave in 96% yield an equilibrium mixture of diones (±)-**13** and (±)-**14**, from which the more stable isomer, (±)-*cis*-*p*-menthane-2,5-dione [(±)-**13**], mp 72-73°, was isolated by fractional crystallization.[3] Hydrogenation of dione (±)-**13** gave (±)-*cis,cis,cis*-*p*-menthane-2,5-diol [(±)-**3**], mp 105°. Assignment of the all-cis configuration, (±)-**3**, to the racemic diol, mp 105°, was based unequivocally upon infrared spectroscopic studies of intramolecular hydrogen bonding.[3,4] Among the *p*-menthane-2,5-diols with hydroxyl groups cis to one another (**1-4**), only diol **3** exhibits detectable intramolecular hydrogen bonding.[4] Diol (±)-**3** has also been prepared by hydrogenation of thymoquinone with rhodium on alumina catalyst at 25°.[5] In addition, a (±)-*p*-menthane-2,5-diol, mp 144°, was isolated from the product of reduction of thymoquinone.[5] The cis configuration of the more stable racemic dione [(±)-**13**], mp 72-73°, was confirmed by its preparation by stereospecific Jones oxidation[6] of the all-cis diol (±)-**3**.[5] Jones oxidation[6] of the racemic diol, mp 144°, gave (±)-*trans*-*p*-menthane-2,5-dione [(±)-**14**], mp 43-43.5°.[5] Therefore, the racemic diol, mp 144°,

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[1] Taken from the Doctoral Dissertation of Krishna Sachdev, Tufts University, June 1966. This paper is dedicated to the memory of the late Dr. Arnold Blumann whose kind encouragement and cooperation contributed in great measure to the successful completion of this work, and the previously reported study of the *p*-menth-1-ene-3,6-diols.[2] This work was supported in part by Public Health Service Research Grant GM-08813 from the National Institutes of Health, in part by the National Science Foundation, and in part by the Research Corporation, and was presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[2] R. D. Stolow and K. Sachdev, *Tetrahedron*, **21**, 1889 (1965).

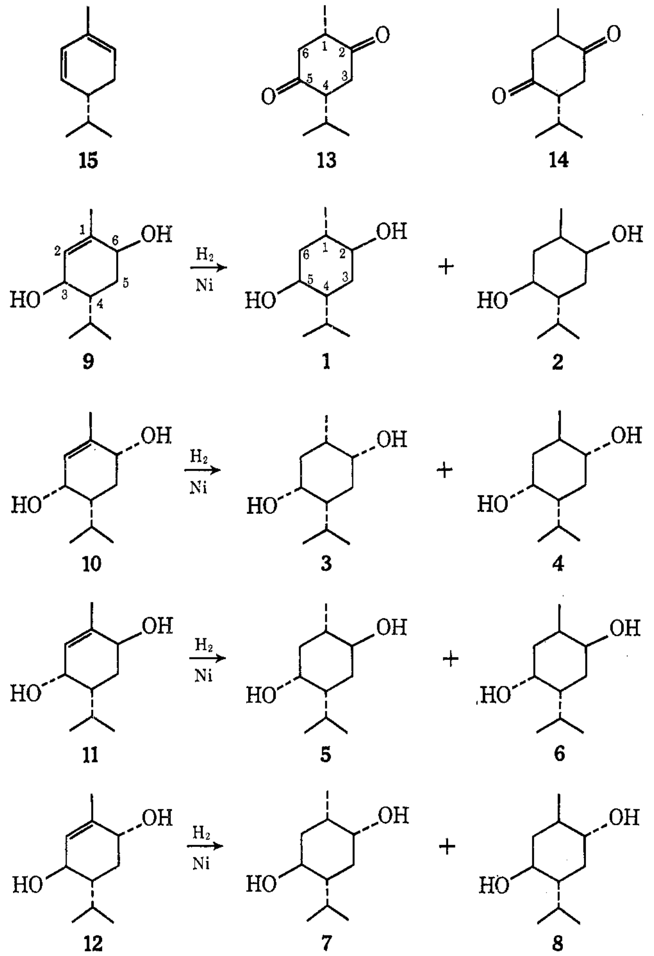
[3] R. D. Stolow, P. M. McDonagh, and M. M. Bonaventura, *J. Amer. Chem. Soc.*, **86**, 2165 (1964).

[4] R. D. Stolow, *ibid.*, **86**, 2170 (1964).

[5] R. D. Stolow and R. R. Krikorian, *Org. Prep. Proced.*, **3**, 39 (1971).

[6] R. G. Curtis, I. Heilbron, E. R. H. Jones, and G. F. Woods, *J. Chem. Soc.*, 457 (1953).

SCHEME I



must have its alkyl groups trans to one another.[5] The (±)-p-menthane-2,5-diol, mp 144°, is here assigned structure (±)-**4** on the basis of its nmr and infrared spectra which are identical with those of optically active diol **4**, described below.[7]

The Optically Active Diols and Diones.—Of the optically active diols (**1**–**12**), nine had been described before this work began.[8,9] However, all but four (diols **1**, **2**, **9**, and **10**) had been reported erroneously.[10]

Although the related monoalcohols, the menthols and carvomenthols, had been studied extensively for many years, the last vestige of confusion concerning structure lingered until recent work was published from several laboratories.[11] In their review of the problem, Schroeter and Eliel[11a] cite work of Blumann, *et al.*,[9] and others,[12] concerning (+)-p-menthane-2,5-diols, mp "134°" and "176°," diols **1** and **2**, respectively. Blumann, *et al.*, degraded diol **1** to monoalcohols, isomenthol and isocarvomenthol.[9] Since firm independent evidence for the structures of the monoalcohols has been provided,[11] assignment of structure **1** to the (+)-p-menthane-2,5-diol, reported mp "134°," has been established beyond reasonable doubt.[9]

Results and Discussion

Preparation.—The eight optically active diastereoisomeric p-menthane-2,5-diols (**1**–**8**) have been prepared by hydrogenation of the four optically active diastereoisomeric p-menth-1-ene-3,6-diols (**9**–**12**).[2] Hydrogenation of each p-menth-1-ene-3,6-diol[2] yielded a corresponding pair of p-menthane-2,5-diols epimeric at C-1 (Scheme I). Hydrogenation of diol **9** to give diols **1** and **2** has been reported[8,9] and confirmed[4] previously. Similarly, hydrogenation of diol **10** gave diols **3** and **4**, as mentioned earlier.[4] Hydrogenation of diol **11** gave diols **5** and **6**, and hydrogenation of diol **12** gave diols **7** and **8**.[2]

Upon hydrogenation with Raney nickel catalyst at *ca.* 25° and 2-atm hydrogen pressure in ethanol solution, diols **9** and **10**, in which the hydroxyl groups are cis to one another, each gave predominantly the product in which hydrogen had added cis to the hydroxyl groups. Diol **9** showed the greatest stereoselectivity, yielding 90% of **1** and 10% of **2**. Diol **9** has its isopropyl group on the opposite side of the ring from its two hydroxyl groups. When the isopropyl group and the two hydroxyl groups are on the same side of the ring (diol **10**), the stereoselectivity is reduced somewhat, but steric hindrance caused by the isopropyl group is not sufficient to overcome the preference for hydrogen addition cis to the hydroxyl groups. Thus diol **10** gave 70% of **4**, and 30% of **3**. This result supports the idea that a net attractive interaction between allylic hydroxyl groups and the catalyst surface exerts a significant influence upon the stereochemistry of the Raney nickel-catalyzed hydrogenation of a carbon–carbon double bond. Related examples have been reported.[13]

Similar hydrogenation of diols **11** and **12**, each of which has one hydroxyl group on each side of the ring, showed little stereoselectivity. In each case, a little more of the product resulted from hydrogen addition cis to the 3-hydroxyl group than from addition cis to the 6-hydroxyl group. Thus diol **11** gave 35% of diol **5** and 65% of diol **6**, while diol **12** gave 60% of diol **7** and 40% of diol **8**.

Each of the four binary mixtures of p-menthane-2,5-diols described above was separable by chromatography on alumina. Four-component diol mixtures, **1**, **2**, **3**, and **4**, and also **1**, **2**, **5**, and **6** were also separable by chromatography on alumina. Therefore, rather than separate the mixture of diols **9** and **10** (prepared as reported previously[2]), it was found advantageous to hydrogenate the mixture of diols **9** and **10** and then separate the four product diols (**1**–**4**) in one operation by chromatography on alumina. The all-cis diol **3**, eluted first, was followed by diols **2**, **4**, and **1**.

(+)-p-Menthane-2,5-diols **7** and **8** were prepared by lithium aluminum hydride reduction of (+)-*cis*- and

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[7] About 60 years ago, hydrogenation of thymohydroquinone was reported to give a mixture from which was isolated a product, mp 112°, a p-menthane-2,5-diol: G. G. Henderson and M. M. J. Sutherland, *ibid.*, **97**, 1616 (1910). We have no clue to the identity of this product.

[8] G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957); see p 592 therein.

[9] A. Blumann, E. W. Della, C. A. Henrick, J. Hodgkin, and P. R. Jefferies, *Aust. J. Chem.*, **15**, 290 (1962), and references cited therein.

[10] Samples previously reported[8] as diols **3** and **4** have been shown to be mixtures.[4] Those previously reported[9] as diols **5** and **11** have been shown to be 1,2-diols,[2] and the diol reported[9] as **12** has been reassigned structure **11**.[2]

[11] (a) S. H. Schroeter and E. L. Eliel, *J. Org. Chem.*, **30**, 1 (1965), and references cited; (b) E. E. Royals and J. C. Leffingwell, *ibid.*, **31**, 1937 (1966), and references cited.

[12] Reference 11a, and ref 49 therein.

[13] M. C. Dart and H. B. Henbest, *J. Chem. Soc.*, 3563 (1960); S. Nishimura and K. Mori, *Bull. Chem. Soc. Jap.*, **36**, 318 (1963); J. E. Anderson, F. G. Riddell, J. P. Fleury, and J. Morgen, *Chem. Commun.*, 128 (1966); S. Mitsui, Y. Senda, and H. Saito, *Bull. Chem. Soc. Jap.*, **39**, 694 (1966), and ref 1 and 2 therein; T. J. Howard and B. Morley, *Chem. Ind.* (*London*), 73 (1967); S. Mitsui, K. Hebiguchi, and H. Saito, *ibid.*, 1746 (1967).

(+)-*trans-p*-menthane-2,5-dione (**13** and **14**), respectively, before the alternate precursor, diol **12**, had been isolated.[2] The (+)-*trans*-dione **14** gave a mixture of the four expected *p*-menthane-2,5-diols: **2** + **4**, 44%; **6**, 6%; and **8**, 50%. The all-equatorial diol **8**, the major product, was isolated by fractional crystallization. The (+)-*cis*-dione **13** gave diols **1**, **3**, **5**, and **7** in the ratio 1:47:33:19. The major product was the all-cis diol **3**. Diol **7** was isolated from the mixture by fractional crystallization. Reduction product mixtures were analyzed by gas chromatography.

The very low yield of diol **1** (1%) from the lithium aluminum hydride reduction of the (+)-*cis*-dione **13** is of interest because it requires at least one highly stereoselective hydride addition step. This point will be discussed more fully elsewhere.

The (+)-*cis*-dione **13** was prepared by Jones oxidation of diol **1**, **3**, or **5**. The (+)-*trans*-dione **14** was prepared by Jones oxidation of diol **4** or **6**. In both the Jones oxidations[6] of diols to diones, and in the lithium aluminum hydride reductions of diones to diols, no significant epimerization of alkyl groups was detected by careful gas chromatographic analysis. In the Raney nickel catalyzed hydrogenations of diols **9–12** described above, in no case was there any detectable epimerization at C-2, C-4, or C-5.

The equilibration of diones (±)-**13** and (±)-**14** has been studied and methods for gas chromatographic analysis of diols **1–8** have been developed.[14] Indeed, the key to the preparative work reported above was analysis by gas chromatography, using columns developed specifically for this purpose by Arthur Clements.[14] Key physical properties and yields of diols **1–8** are summarized in Table I. Conformational studies of diols **1–8** provide the subject for a subsequent publication in which physical properties are treated more fully.

TABLE I
MELTING POINTS, MOLECULAR ROTATIONS, RETENTION TIMES, AND YIELDS OF THE OPTICALLY ACTIVE *p*-MENTHANE-2,5-DIOLS (1–8)

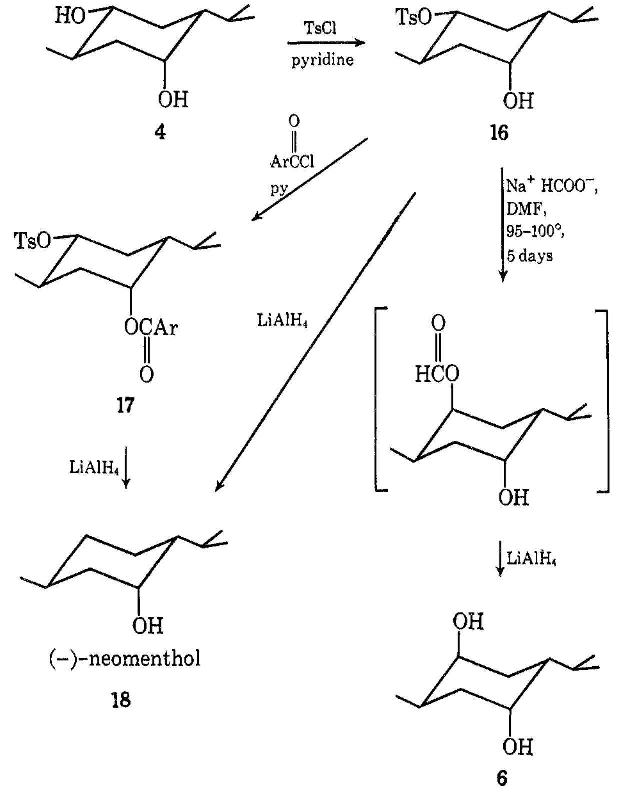
Diol	Mp, °C	$[M]_D$,[a] deg	Time,[b] min	Yield, %,[c] H_2/Ni	Yield, %,[d] $LiAlH_4$
1	137	+58	16.8	90	1
2	177	+150	13.2	10	*e*
3	132	+40	14.5	30	47
4	157	−72	13.2	70	*e*
5	121	+34	12.1	35	33
6	129	+34	9.4	65	6
7	169	+112	18.2	60	19
8	144	+34	15.9	40	50

[a] For diols **1–8**, $[M]_D = 1.723\,[\alpha]_D$. [b] Gas chromatographic retention times in a typical case. [c] Per cent yield upon hydrogenation of the corresponding *p*-menth-1-ene-3,6-diol (**9–12**). [d] Per cent yield from lithium aluminum hydride reduction of the corresponding *p*-menthane-2,5-dione (**13** or **14**). [e] The sum of **2** plus **4** (which have the same retention time) was 44%.

Absolute Configuration.—Diols **9** and **10**, each prepared by opening the oxygen–oxygen linkage of the corresponding cyclic peroxide of (−)-α-phellandrene,[2,8] must each be a *p*-menth-1-ene-3,6-diol with hydroxyl groups cis to one another. Therefore, diols **1–4**, prepared by hydrogenation of diols **9** and **10**, each must have its hydroxyl groups cis to one another.

As described above, Blumann, *et al.*, showed unequivocally that the (+)-*p*-menthane-2,5-diol, observed mp 137°, has structure **1**.[2,9] Assignment of structure **9** to the (−)-*p*-menth-1-ene-3,6-diol, mp 168°, precursor of diol **1**, is therefore required.[2,9] Assignment of structure **2** to the (+)-*p*-menthane-2,5-diol, mp 177°, follows from the fact that it is the coproduct of diol **1** formed upon hydrogenation of diol **9**, and therefore the diol, mp 177°, must have structure **2**, the C-1 epimer of **1**.[2,8,9]

SCHEME II



Assignment of structure **4** to the (−)-*p*-menthane-2,5-diol, mp 157°, was based upon its degradation to (−)-neomenthol (**18**) as shown in Scheme II. The objective was removal of the C-2 hydroxyl group without affecting the stereochemistry at C-1, C-4, or C-5. Treatment of diol **4** with 1 equiv of *p*-toluenesulfonyl chloride in pyridine at *ca.* 25° gave a monotosylate **16**, mp 97°, in 80% yield. The monotosylate **16** was converted to a monotosylate mono-3,5-dinitrobenzoate (**17**), mp 193° dec. Reaction of either **16** or **17** with excess lithium aluminum hydride to bring about displacement of tosylate by hydride gave a total product which contained small amounts of the starting diol **4**, none of the carvomenthols, no neoisomenthol, no isomenthol, <6% of menthol, and >94% of neomenthol, as shown by gas chromatographic comparison with an eight-component mixture containing the four carvomenthols plus the four menthols. Neomenthol had the shortest retention time. The minor component which had the same retention time as menthol was not isolated or identified; the possibility that it was an elimination product has not been ruled out. The major component of the product from **17**, isolated by preparative gas chromatography, gave an infrared spectrum identical with that of an authentic sample of (+)-neomenthol. The neomenthol isolated as the

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(14) A. E. Clements, M.S. Thesis, Tufts University, 1965.

major component from **16** was shown to be (−)-neomenthol (**18**) by conversion into its 3,5-dinitrobenzoate, **19**, mp 154°, $[\alpha]^{27}_{\mathrm{D}}$ −22°, which gave an nmr spectrum identical in all respects with that of an authentic sample of its enantiomer, mp 156°, $[\alpha]^{27}_{\mathrm{D}}$ +23°, prepared from authentic (+)-neomenthol. The isolation of (−)-neomenthol (**18**) requires that the monotosylate of diol **4** must have structure **16** as shown, with the tosyloxy group at C-2 rather than at C-5.[15]

It follows from the unequivocal assignment of structure **4** above that the immediate precursor of diol **4**, the (−)-*p*-menth-1-ene-3,6-diol, mp 149°, with its hydroxyl groups cis to one another, must have structure **10**, as assigned.[2,8,9] Therefore, the (+)-*p*-menthane-2,5-diol, mp 132°, the coproduct of diol **4** formed upon hydrogenation of diol **10**, must have structure **3**, the C-1 epimer of **4**. The all-cis configuration (structure **3**) was confirmed for the (+)-*p*-menthane-2,5-diol, mp 132°, by infrared spectroscopy.[4] Diol **3**, which exhibits significant intramolecular hydrogen bonding, is unique among the *p*-menthane-2,5-diols.[4]

The configuration of diol **6** was established by its preparation from diol **4** by a stereospecific route (Scheme II). The monotosylate **16**, upon treatment with sodium formate in dimethylformamide at 95–100° for 5 days, yielded a monoformate. Reduction of the monoformate with lithium aluminum hydride gave a (+)-*p*-menthane-2,5-diol, mp 129°, assigned structure **6**. When the total product of reaction of the monotosylate **16** with formate ion in dimethylformamide was treated with lithium aluminum hydride, analysis of the resultant total product mixture by gas chromatography showed no detectable amount of diols **1**, **3**, **5**, **7**, and **8**, and showed the presence of diols **4** and **6** in the ratio 1:34. Attack by formate ion upon C-2 of tosylate **16** with inversion of configuration, followed by hydride reduction of the formate without change in configuration, would convert **16** into diol **6**.[16]

The coproducts of hydrogenation of the (−)-*p*-menth-1-ene-3,6-diol, mp 112°, are the (+)-*p*-menthane-2,5-diols, mp 121 and 129°. The latter was identical with diol **6** (prepared from diol **4** as described above) as shown by melting point, mixture melting point, and gas chromatography. The (−)-*p*-menth-1-ene-3,6-diol, mp 112°, which gives diol **6** upon hydrogenation, must therefore have structure **11**, as assigned.[2] The (+)-*p*-menthane-2,5-diol, mp 121°, coproduct of **6** in the hydrogenation of **11**, has been assigned structure **5**, the C-1 epimer of diol **6**.

(+)-*cis*-*p*-Menthane-2,5-dione (**13**) (prepared unequivocally by Jones oxidation of diols **1**, **3**, and **5**), upon lithium aluminum hydride reduction, would be expected to give diols **1**, **3**, **5**, and **7**. The reduction gave a four-component product mixture which contained 19% of a (+)-*p*-menthane-2,5-diol, mp 168–169°, different from diols **1**, **3**, and **5**. The diol, mp 168–169°, was therefore assigned structure **7**.

(+)-*trans*-*p*-Menthane-2,5-dione (**14**) (prepared unequivocally by Jones oxidation of diols **4** and **6**) would be expected to give diols **2**, **4**, **6**, and **8** upon reduction with lithium aluminum hydride. The major component of the product mixture, 50% of a (+)-*p*-menthane-2,5-diol, mp 144°, isolated by fractional crystallization, was different from diols **2**, **4**, and **6**. The diol, mp 144°, was therefore assigned structure **8**.

The coproducts of hydrogenation of the (+)-*p*-menth-1-ene-3,6-diol, mp 123°, gave the same retention times upon gas chromatography as diols **7** and **8**. One of the coproducts, mp 168–169°, isolated by chromatography on alumina, gave the same melting point, optical rotation, and retention time as diol **7** prepared from dione **13** as described above. Therefore, the (+)-*p*-menth-1-ene-3,6-diol, mp 123°, must have structure **12**, as assigned.[2]

The chemical interconversions reported or cited above are more than adequate to establish the absolute configurations of the *p*-menthane-2,5-diols (**1**–**8**), the *p*-menth-1-ene-3,6-diols (**9**–**12**), the (+)-*p*-menthane-2,5-diones (**13** and **14**), and, of course, the complete set of their enantiomers. The configurational relationships among compounds **1**–**15** are shown in Scheme I.

Since the completion of our work,[1] a communication has appeared which reports isolation of diol **8**, mp 143–144°, in 0.003% yield from a natural source.[17] The six infrared absorption peaks reported for this sample[17] are probably consistent with those we found for diol **8**. Jones oxidation was reported[17] to yield a dione, mp 56–57°. Both reported melting points[17] are in excellent agreement with our own values for diol **8**, mp 144–144.5°, and its expected oxidation product, dione **14**, mp 55.5–56°. However, the diol sample isolated from natural sources is reported[17] to give $[\alpha]^{16}_{\mathrm{D}}$ −17.8° (*c* 1.065, ethanol), whereas our sample, the absolute configuration of which has been established above, gave $[\alpha]^{25}_{\mathrm{D}}$ +20° (*c* 0.876, ethanol). If in fact the sample isolated from natural sources is levorotatory, then it *cannot* have structure **8** as claimed.[17,18]

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[15] The equatorial hydroxyl group at C-2 of diol **4** reacted faster to form the mono-*p*-toluenesulfonate ester (**16**) than did the more sterically hindered axial hydroxyl group at C-5. Comparison of the nmr spectra of diol **4** and its monotosylate showed a large downfield shift for the axial C-2 proton of the monotosylate (δ, C-2 proton: **4**, 2.90 ppm; **16**, 4.1 ppm), while the equatorial C-5 proton was affected only slightly. Thus the nmr spectrum of the monotosylate of diol **4** is also consistent with structure **16**, with the electron-attracting tosyloxy group at C-2 rather than C-5.

[16] F. C. Chang and R. T. Blickenstaff, *J. Amer. Chem. Soc.*, **80**, 2906 (1958), reported that β-cholestanyl tosylate, 2.5% in dimethylformamide, 23 hr at 78°, gave 75% of α-cholestanyl formate. This reaction was tested by using it to convert menthol into neomenthol. The total product of the reaction of menthyl tosylate with dimethylformamide for 6 days at 75–80°, still containing some starting tosylate (thin layer chromatography), was reacted with lithium aluminum hydride to give two major components corresponding in gas chromatographic retention time to the expected product, neomenthol, plus menthol. The menthol presumably was formed from the unreacted tosylate. If so, its formation may be analogous to the formation of 57% cholestan-6α-ol (and 38% of cholestane) upon treatment of cholestan-6α-yl tosylate with lithium aluminum hydride, as reported by N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interchemical Corp., New York, N. Y., 1956, pp 855–873.

[17] T. Hashizume and I. Sakata, *Tetrahedron Lett.*, 3355 (1967).

[18] The optical rotation expected for diol **8** may be estimated simply by taking the sum of the observed molecular rotations of the corresponding monoalcohols. Taking (+)-menthol, $[M]_{\mathrm{D}}$ +77°, and (−)-carvomenthol, $[M]_{\mathrm{D}}$ −43°, from J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5483 (1959), Table VII, the sum, $[M]_{\mathrm{D}}$ +34°, is the molecular rotation expected for diol **8**. Diol **8**, prepared in this work, gave $[M]_{\mathrm{D}}$ +34°, as expected (Table I). Similarly, optical rotations for (+)-menthyl acetate, $[\alpha]_{\mathrm{D}}$ +80° (*Beil.*, **6**, III, 143) and (−)-carvomenthyl acetate, $[\alpha]_{\mathrm{D}}$ −28° (*Beil.*, **6**, I, 19), can be used to estimate the expected optical rotation of the diacetate of diol **8**, It was reported[17] that the levorotatory diol gave a dextrorotatory diacetate. mp 66–67°, $[\alpha]^{10}_{\mathrm{D}}$ +15°, a value inconsistent with that expected for either the diacetate of diol **8**, $[\alpha]_{\mathrm{D}}$ *ca.* +40°, or its enantiomer, *ca.* −40°. Unfortunately, no optical rotation was reported for the dione sample prepared from the levorotatory diol.[17] If diol, dione, and diacetate had all been levorotatory, one would have been forced to consider the possibility that the diol reported[17] was the enantiomer of diol **8**. However, this possibility seems very unlikely. From a natural source rich in derivatives of (−)-α-phellandrene,[17] isolation of diol (−)-**8** with absolute configuration at C-4 opposite to that of (−)-α-phellandrene (**15**) would be astounding. In the absence of additional information, the identity of the sample isolated from natural sources[17] remains in question.

Experimental Section

Routine spectral data and analyses by gas chromatography were recorded as described previously.[2,19] Retention times for diols **1**–**8** are given in Table I. Optical rotations at 589 mμ were measured by use of Zeiss and Perkin-Elmer Model 141 polarimeters. ORD curves of diones **13** and **14** were recorded on a Cary Model 60 spectropolarimeter.

Analytical thin layer chromatograms were carried out on 5 × 20 or 10 × 20 cm glass plates uniformly coated with a 0.25-mm layer of aluminum oxide G or silica gel G (E. Merck).[20] The plates were activated by heating at *ca.* 75° for 1 hr. Exposure of the developed plates to iodine vapor allowed detection of separated components.

Melting points were determined in open Pyrex glass capillary tubes by use of an oil bath apparatus and are corrected. Microanalyses were determined by Dr. S. M. Nagy.

Reactions involving lithium aluminum hydride were carried out in a dry nitrogen atmosphere.

(+)-*p*-Menthane-2,5-diols, mp 137 and 177° (1 and 2). Hydrogenation of Diol 9.—The reported procedure[4] gave diol **1** {mp 136.5–137°; $[\alpha]^{27}_{\mathrm{D}}$ +34° (*c* 7.46, ethanol); ir (KBr) 1037, 1002, 984, 962 cm^{-1}} and diol **2** {mp 177–177.5°; $[\alpha]^{25}_{\mathrm{D}}$ +87° (*c* 0.874, ethanol); ir (KBr) 1073, 1025, 998, 979 cm^{-1}} (reported[8,9] for diol **1**, mp 134°, $[\alpha]_{\mathrm{D}}$ +32°; for diol **2**, mp 176°, $[\alpha]_{\mathrm{D}}$ +80°).

(+)-*cis,cis,cis-p*-Menthane-2,5-diol, mp 132° (3), and (−)-*p*-Menthane-2,5-diol, mp 157° (4). A. Hydrogenation of a Mixture of Diols 9 and 10.—Preparation in relatively large quantity of a mixture of diols **9** and **10**, mp 132–145°, has been reported.[2] To a solution of 3.00 g (0.0174 mol) of the mixture in 150 ml of 95% ethanol was added 4.5 g of neutral Raney nickel catalyst (moist with ethanol). Hydrogenation, as above, followed by removal of catalyst and solvent, gave 3.0 g of white solid. Three recrystallizations from benzene gave 1.0 g of diol **4**: mp 156.5–157°; $[\alpha]^{27}_{\mathrm{D}}$ −42° (*c* 6.88, ethanol); ir (KBr) 1049, 1033, 1023 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.90; H, 11.82.

The combined filtrates were evaporated to dryness. Part of the residue, 1.5 g, was chromatographed on 150 g of alumina (Fisher, A-540). Elution with 1% methanol in ether gave first 0.60 g of diol **3**, mp 130–132°, free from detectable amounts of the other diols (gas chromatography). Two recrystallizations from benzene gave diol **3**, mp 132–132.5°, $[\alpha]^{26}_{\mathrm{D}}$ +23° (*c* 7.70, ethanol), which gave infrared spectra (KBr and CCl_4) and a retention time in gas chromatography identical with those of its racemate, (±)-**3**, mp 105°,[3,4] ir (KBr) 1048, 1032, 958 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 70.09; H, 11.80.

Further elution gave 30 mg of solid, mp 176° (diol **2**), followed by 100 mg of solid, mp 146–148° (mixture of diols **2** and **4**: gas chromatography, and thin layer chromatography on alumina), followed by 350 mg of solid, mp 156–157° (diol **4**). Finally, elution with 2% methanol in ether gave 400 mg of solid, mp 137° (diol **1**).

Thin layer chromatography of a mixture of diols **1**–**4** on aluminum oxide plates activated by heating at 73° for 1 hr gave, with 2% methanol in ether, the following R_f values for each diol: **1**, 0.39; **4**, 0.52; **2**, 0.58; **3**, 0.69. These values correspond to the elution order observed during column chromatography on alumina, described above.

B. Hydrogenation of Diol 10.—To a solution of 0.500 g (2.94 mmol) of (−)-*p*-menth-1-ene-3,6-diol (**10**), mp 147–149°,[2] in 30 ml of 95% ethanol was added 0.8 g of neutral Raney nickel catalyst (moist with ethanol). Hydrogenation as above, followed by removal of catalyst and solvent, gave a 3:7 mixture (gas chromatogram of total product) of diols **3** and **4**. Crystallization from 40 ml of benzene gave diol **4**, 0.250 g (50%), mp 156.5–157°. The filtrate, upon evaporation, gave 0.230 g of a mixture of diols **3** and **4**, mp 105–115°, saved for future separation by chromatography on alumina by the method above which gave clean separation of diols **3** and **4**.

(+)-*p*-Menthane-2,5-diols, mp 121 and 129° (5 and 6). A. Hydrogenation of a Mixture of Diols 9 and 11.—To a solution of 2.00 g (0.0118 mol) of a mixture[2] containing 88% of (−)-*p*-menth-1-ene-3,6-diol (**11**), mp 112°, plus 12% of impurity identified by gas chromatography[2] as (−)-*p*-menth-1-ene-3,6-diol (**9**), mp 168°, in 100 ml of 95% ethanol was added 3 g of neutral Raney nickel catalyst (moist with ethanol). At 22° and *ca.* 3-atm hydrogen pressure (Parr apparatus Model 3911), hydrogenation was *ca.* 80% complete in 1 hr and was stopped after 8 hr. Removal of catalyst and solvent gave 2.0 g of colorless semisolid. Upon gas chromatography, a sample of the total product gave two major and two minor peaks, the latter with the same retention times as diols **1** and **2**, the known products of hydrogenation of diol **9** (the impurity[2]). Attempts to isolate diols **5** and **6** by crystallization from ether–hexane or benzene were unsuccessful, since diols **1** and **2** were less soluble. Only diol **1** was isolated. However, chromatography on 140 g of alumina (Fisher Scientific Co., A-540) of the 1.20-g residue, obtained from the combined filtrates of three crystallizations of the product mixture, gave clean separation of the four colorless component diols: **1**, **2**, **5**, and **6**. Elution first with redistilled benzene gave 0.52 g of diol **6**, mp 129°; 1:1 anhydrous ether–benzene next gave 0.50 g of diol **5**, mp 121°; 1% methanol in anhydrous ether then gave 0.02 g of diol **2**, mp 176°, followed by 0.08 g of diol **1**, mp 137°.

Diol **5** after crystallization from 3:1 hexane–ether, gave mp 120.5–121°; $[\alpha]^{28}_{\mathrm{D}}$ +20° (*c* 5.53, ethanol); ir (KBr) 1110, 1048, 1032, 939 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.61; H, 11.45.

Diol **6** after two crystallizations from 10:1 hexane–ether gave mp 128.5–129°; $[\alpha]^{26}_{\mathrm{D}}$ +20° (*c* 7.86 or 0.96, ethanol); ir (KBr) 1030, 998, 972 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.98; H, 11.85.

A second run in which the total hydrogenation product, 2.0 g, was chromatographed as above, gave 0.80 g of recrystallized diol **6**, mp 129°, and 0.39 g of recrystallized diol **5**, mp 121°.

B. Hydrogenation of Diol 11.—To a solution of 0.52 g (3.3 mmol) of pure diol **11**, mp 112°,[2] in 40 ml of 95% ethanol was added 1.1 g of neutral Raney nickel catalyst (moist with ethanol). Hydrogenation, as above, gave 0.50 g of white solid product, containing about 35% of diol **5** and 65% of diol **6** (gas chromatography). Column chromatography on alumina, as above, followed by recrystallization gave 0.120 g of diol **5**, mp 121°, and 0.280 g of diol **6**, mp 129°.

5-Hydroxy-2-*p*-menthyl *p*-Toluenesulfonate 16, a Monotosylate from Diol 4.—To a solution of 0.50 g (2.9 mmol) of diol **4** in 8 ml of dry pyridine in an ice bath was added with stirring, 0.55 g (2.9 mmol) of *p*-toluenesulfonyl chloride over a period of 10 min. The clear solution was stored for 3 days at room temperature. Pyridine was removed at 25° (reduced pressure). The viscous residue was triturated with crushed ice. A white solid, 0.82 g (86%), mp 90–93°, was obtained, Crystallization from hexane gave 0.70 g (67%) of long thin needle-like crystals, mp 96°. Two recrystallizations from hexane gave crystals: mp 97–97.5°, $[\alpha]^{26}_{\mathrm{D}}$ −60° (*c* 0.202, ethanol); nmr peaks (10% solution in $CDCl_3$) at δ (ppm) 7.85, 7.71, 7.37, 7.23 (4 H quartet, aromatic), 4.32–3.89 (2 H), 2.42 (3 H singlet, H_3CAr), 2.18–1.02 (8 H), 0.933, 0.817, 0.71 (9 H, three overlapping doublets, $CH_3)_2CH$ and CH_3CH). The C-2 proton multiplet centered at 4.1 ppm overlapped the C-5 proton multiplet centered at 3.95 ppm.

Anal. Calcd for $C_{17}H_{26}O_4S$: C, 62.55; H, 8.03. Found: C, 62.60; H, 7.99.

The 3,5-Dinitrobenzoate 17, Derived from 16.—To a solution of 0.326 g (1.00 mmol) of the monotosylate **16**, mp 96°, in 5 ml of dry pyridine stirred in an ice bath, was added a solution of 0.250 g (1.08 mmol) of 3,5-dinitrobenzoyl chloride in 5 ml of benzene. The mixture was stirred for 2 days at room temperature. The solvent was removed at 25° (reduced pressure). The residue was triturated with crushed ice. The white solid which separated was collected and washed with four 5-ml portions of water at ~0°. Crystallization of the dried solid from benzene gave 0.350 g (67%) of needle-like crystals, mp 188–191° dec. Two recrystallizations from benzene gave **17**, mp 193° dec, $\nu_{\max}^{\text{Nujol}}$ 1725 cm^{-1}.

Anal. Calcd for $C_{24}H_{28}N_2O_9S$: C, 55.40; H, 5.38; N, 5.38. Found: C, 55.54; H, 5.47; N, 5.27.

Degradation of Diol 4 to Neomenthol (18). A. Reaction of the Monotosylate–Monodinitrobenzoate 17 with Lithium Aluminum Hydride.—To a stirred suspension of 0.60 g (0.016 mol) of lithium aluminum hydride in 150 ml of anhydrous ether was added a solution of 0.280 g (0.538 mmol) of **17** in 80 ml of tetra-

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[19] Nmr and infrared spectra of diols **1**–**12** have been reproduced in the Doctoral Dissertation of K. Sachdev, Tufts University, 1966.

[20] E. Stahl, Ed., "Thin-Layer Chromatography," Academic Press, New York, N. Y., 1965.

hydrofuran (freshly distilled from lithium aluminum hydride)[21] during 7 min. The mixture was heated under reflux for 2 days. Most of the tetrahydrofuran was removed by distillation. To the residue was added 100 ml of ether followed by 4 ml of saturated aqueous sodium sulfate. The salt was separated by filtration and was washed several times with ether. The ether was removed from the filtrate and the residue was crystallized from hexane to give 25 mg of diol **4**, mp 155–156°, identified by mixture melting point, gas chromatography, and infrared spectroscopy. The hexane filtrate was analyzed by gas chromatography on a column[14] capable of resolution of an eight-component mixture of the four menthols and the four carvomenthols. The reaction product showed no detectable amount of any of the carvomenthols or of isomenthol or neoisomenthol (direct comparison by gas chromatography). Two components were observed with a peak ratio of 17:1. The major component was collected. Its retention time and infrared spectrum were identical with those of an authentic sample of (+)-neomenthol.[22] The minor component which had the same retention time as menthol, was not isolated or identified.

B. Reaction of the Monotosylate 16 with Lithium Aluminum Hydride.—To a stirred suspension of 150 mg (3.84 mmol) of lithium aluminum hydride in 70 ml of anhydrous ether was added a solution of 254 mg (0.78 mmol) of monotosylate **16** in 15 ml of ether during 5 min. The mixture was heated gently under reflux for 24 hr. The excess hydride was decomposed with 1 ml of saturated aqueous sodium sulfate. The mixture of salts was collected by filtration and was washed thoroughly with ether. The filtrate was dried ($MgSO_4$). Removal of the solvent (reduced pressure) gave 0.152 g of colorless oil. Analysis by thin layer chromatography on silica gel with 1:1 ether–hexane showed three spots, R_f 0.08, corresponding to diol **4**, 0.48, unidentified, and 0.59, corresponding to neomenthol. No monotosylate **16** was detected. After separation of 5 mg of diol **4**, mp 156.5–157°, by crystallization, the filtrate was subjected to preparative thin layer chromatography on silica gel PF_{254} (E. Merck), to remove the remaining diol **4**. The resulting two component mixture gave a major peak in gas chromatography with the same retention time as neomenthol, and a minor peak, *ca.* 6%, unidentified, but with the same retention time as menthol. The two-component mixture gave $[\alpha]^{27}\mathrm{D}$ $-13°$ (c 0.539, methanol), whereas authentic (+)-neomenthol[22] gave $[\alpha]^{27}\mathrm{D}$ $+20.4°$ (c 0.673, methanol) (reported[23] (+)-neomenthol, $[\alpha]\mathrm{D}$ $+19.7°$).

(−)-Neomenthyl 3,5-Dinitrobenzoate (19).—To a stirred solution of 27.8 mg (0.178 mmol) of the above two-component mixture in 0.5 ml of dry pyridine cooled in an ice–salt bath, was added 50 mg (0.22 mmol) of 3,5-dinitrobenzoyl chloride dissolved in 1 ml of dry benzene. The mixture was allowed to attain room temperature. After 44 hr, most of the solvent was removed at 25–30° under reduced pressure. Trituration of the residue with crushed ice gave 48 mg of solid. Two crystallizations from 5:1 hexane–ether gave 12 mg of **19**, white needle-like crystals, mp 154°, $[\alpha]^{27}_{589}$ $-22°$, $[\alpha]^{27}_{436}$ $-42.2°$ (c 1.027, chloroform). The sample gave the same R_f in thin layer chromatography and the same nmr spectrum (in deuteriochloroform) as an authentic sample of (+)-neomenthyl 3,5-dinitrobenzoate, described below.

(+)-Neomenthyl 3,5-Dinitrobenzoate.—The procedure above was used to prepare the ester from authentic (+)-neomenthol.[22] The derivative gave mp 155.5–156° (reported[23] mp 153°), $[\alpha]^{27}_{589}$ $+23°$, $[\alpha]^{27}_{436}$ $+45.6°$ (c 1.152, chloroform).

Diol 6 from Diol 4 *via* Monotosylate 16.—To a solution of 163 mg (0.500 mmol) of **16**, mp 96°, in 5 ml of dimethylformamide (Fisher reagent) was added 68 mg (0.50 mmol) of sodium formate. The mixture was stirred and heated at 95–100° in a nitrogen atmosphere for 5 days. The product mixture was diluted with 5 ml of water and was extracted with three 40-ml portions of ether. The ether extract was washed with two 15-ml portions of water and then dried ($MgSO_4$). Evaporation of the ether gave 80 mg of yellowish oil, which gave carbonyl absorption at 5.8 μ and two spots on thin layer chromatography on silica gel with anhydrous ether as solvent. The spot of lower R_f corresponded to unreacted tosylate **16**.

To a stirred suspension of 0.100 g of lithium aluminum hydride in 50 ml of anhydrous ether was added slowly a solution of the yellow oil (presumably containing crude monoformate) in 10 ml of ether. The mixture was heated under reflux for 6 hr. Excess hydride was decomposed by addition of 1 ml of saturated aqueous sodium sulfate. The semisolid product, upon gas chromatography, gave three peaks, two of which corresponded in retention time to diols **6** (8.2 min) and **4** (11.4 min) with peak height ratio of 34:1; the third peak, with very short retention time (1.4 min), was not a p-menthane-2,5-diol. No detectable amount of diols **1**, **3**, **5**, **7**, or **8** was observed in the product. Crystallization from hexane gave diol **6**, 35 mg (41%), mp 129°, containing a trace of diol **4**. The sample gave the same melting point, mixture melting point, infrared spectrum, and retention time in gas chromatography as the sample of diol **6** prepared above by hydrogenation of diol **11**.

(+)-*cis*-*p*-Menthane-2,5-dione (13). A. Oxidation of Diol 1.—To a solution of 0.50 g (2.9 mmol) of diol **1**, mp 135–136°, in 25 ml of acetone (redistilled from potassium permanganate) at 0–5°, was added dropwise during 15 min with vigorous stirring, 2.8 ml (100% excess) of 2.8 M chromium trioxide solution.[6] After 10 min more, the reaction mixture was combined with a solution of 0.8 g of sodium hydrogen sulfite in 20 ml of water and the mixture was extracted immediately with three 150-ml portions of ether. The combined ether extract was washed with 50 ml of 10% aqueous ammonium chloride, 50 ml of 10% aqueous sodium bicarbonate, and 30 ml of water. The ether solution was dried ($MgSO_4$). Removal of the ether and recrystallization of the residue from hexane gave 0.40 g (82%) of shiny white plates, mp 68–69°, containing <1% (detected by gas chromatography) of the *trans*-dione **14**. Two recrystallizations from hexane gave the (+)-*cis*-dione **13**: mp 69–69.5°; $[\alpha]\mathrm{D}$ $+294°$ (c 1.58, benzene); ORD [A] +183° (c 1.05, hexane), extrema 325, 275 mμ.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.25; H, 9.71.

B. Oxidation of Diol 5.—A solution of 0.100 g (0.58 mmol) of diol **5**, mp 120.5–121°, in 8 ml of acetone was treated, as above, with 0.55 ml of 2.8 M chromium trioxide solution (100% excess) added during 10 min. The total product contained *ca.* 1% (detected by gas chromatography) of *trans*-dione **14**. Crystallization from hexane gave a first crop of 50 mg (50%) of (+)-*cis*-dione **13**, mp 68–69°, mixture melting point with the analytical sample, mp 68–69°, infrared spectrum identical with that of the analytical sample, $[\alpha]^{26}\mathrm{D}$ $+280°$ (c 0.129, benzene).

(+)-*trans*-*p*-Menthane-2,5-dione (14). A. Oxidation of Diol 4.—A solution of 0.50 g (2.9 mmol) of diol **4**, mp 156.5–157°, in 35 ml of acetone, was treated exactly as above (for part A, preparation of **13**). The total oxidation product contained <1% (detected by gas chromatography) of the *cis*-dione **13**. Crystallization from hexane gave 0.40 g (82%) of the (+)-*trans*-dione **14**, mp 55–56°. Two recrystallizations from hexane gave **14**: mp 55.5–56°; $[\alpha]^{26}\mathrm{D}$ $+49°$ (c 1.29, benzene); ORD [A] +30.4° (c 0.803, n-hexane), extrema 317, 278 mμ.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.28; H, 9.76.

B. Oxidation of Diol 6.—A solution of 0.100 g (0.58 mmol) of diol **6**, mp 128.5–129°, in 8 ml of acetone was treated, as above, with 0.55 ml of 2.8 M chromium trioxide solution (100% excess) added during 10 min. The total product contained a small amount of *cis*-dione **13**. Crystallization from hexane gave 65 mg (67%) of **14**, mp 56°, undepressed mixture melting point with analytical sample.

Reduction of (+)-*cis*-*p*-Menthane-2,5-dione (13) with Lithium Aluminum Hydride.—To a stirred suspension of 0.300 g (8.1 mmol) of lithium aluminum hydride in 80 ml of anhydrous ether was added slowly a solution of 0.280 g (1.67 mmol) of (+)-*cis*-dione **13** in 10 ml of ether during 5 min. The mixture was heated under reflux for 3 hr. Excess hydride was decomposed by addition of 2 ml of saturated aqueous sodium sulfate. The semisolid total product, isolated as usual, gave four peaks upon gas chromatography, with the same retention times as diols **1**, **3**, **5**, and **7**. Diols **2**, **4**, **6**, and **8** were not detected. The gas chromatogram is consistent with the following diol composition: **1**, 1%; **3**, 47%; **5**, 33%; **7**, 19%.

(+)-*p*-Menthane-2,5-diol, mp 169° (7).—Three recrystallizations from hexane–ether of the above mixture of diols **1**, **3**, **5**, and **7**, gave thin white needle-like crystals of diol **7**: 20 mg (7%); mp 168.5–169.5°; uncontaminated by detectable amounts of diols **1–6** or **8** (gas chromatography); $[\alpha]^{25}\mathrm{D}$ $+65°$ (c 0.942, ethanol); ir (KBr) 1081, 1052, 1036, 1016 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.60; H, 11.75.

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[21] *Caution!* See *Org. Syn.*, **46**, 105 (1966).

[22] The authors are grateful to Mr. F. Porsch, Dragoco, Holzminden, Germany, for his kindness in supplying a generous sample of authentic (+)-neomenthol.

[23] H. Phillips, *J. Chem. Soc.*, **127**, 2584 (1925).

Reduction of (+)-*trans-p*-Menthane-2,5-dione (14) with Lithium Aluminum Hydride.—As above for **13**, 0.160 g (0.95 mmol) of (+)-*trans*-dione **14**, mp 56°, plus 0.150 g (4 mmol) of lithium aluminum hydride, gave a total product which showed three peaks upon gas chromatography, corresponding in retention time to a mixture of diols **2**, **4**, **6**, and **8**. Diols **1**, **3**, **5**, and **7** were not detected. The gas chromatogram is consistent with the following diol composition: **2**, plus **4**, 44%; **6**, 6%; **8**, 50%.

(+)-*p*-Menthane-2,5-diol, mp 144° (8).—Three recrystallizations from hexane–ether of the above mixture of diols **2**, **4**, **6**, and **8**, gave colorless needle-like crystals of diol **8**: 20 mg (12%); mp 144–144.5°; uncontaminated by detectable amounts of diols **1**–**7** (gas chromatography); $[\alpha]^{26}\mathrm{D}$ +20° (*c* 0.876, ethanol); ir (KBr) 1097, 1046, 1030 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.93; H, 11.80.

(+)-*p*-Menthane-2,5-diol, mp 169° (7), from Hydrogenation of Diol 12.—The hydrogenation product[2] of diol **12**, a mixture of diols **7** (59%) and **8** (41%, analysis by gas chromatography), mp 142–153°, 90 mg, was recrystallized five times from benzene–hexane–ether (5:3:2). The crystals, 11 mg, mp 169°, contained 96% diol **7** and 4% diol **8**. The mixture recovered from the combined filtrates was chromatographed on 20 g of alumina (Fisher A-540). Elution with benzene gave white solid. One crystallization from ether–hexane gave diol **8**, 20 mg, mp 142–144°, contaminated with 5% of diol **7**. Further elution with ether–benzene (1:9) gave fractions which after crystallization from hexane–ether yielded 13 mg of diol **7**, contaminated with 5% of diol **8**. The two fractions of impure diol **7**, totaling 24 mg, were combined and rechromatographed on 7 g of alumina. The last fraction obtained by elution with ether–benzene (1:9) was crystallized from hexane–ether to give 5 mg of diol **7**, mp 169°, of 99% purity, $[\alpha]^{26}\mathrm{D}$ +63° (*c* 0.302, ethanol).

(−)-Menthyl Tosylate (20).—(−)-Menthol (Aldrich) gave (−)-menthyl tosylate (**20**), mp 95–96° (reported[24] mp 94°).

Neomenthol from (−)-Menthyl Tosylate (20).—A solution of 1.03 g of (−)-menthyl tosylate (**20**) in 30 ml of dimethylformamide (Fisher reagent grade) was heated for 6 days at 75–80°. The reaction mixture, cooled to 25°, was diluted with 100 ml of water and was extracted with three 150-ml portions of ether. The ether extract was washed with two 50-ml portions of water and then was dried over anhydrous magnesium sulfate. Evaporation of the ether left 0.35 g of yellowish oil which showed a peak at 5.8 μ (presumably neomenthyl formate carbonyl absorption). Thin layer chromatography showed two major spots, one corresponding in R_f value to the starting tosylate **20**. To a stirred suspension of 0.305 g of lithium aluminum hydride in 100 ml of anhydrous ether was added slowly a solution of the above reaction product mixture in 10 ml of ether. After heating under reflux for 5 hr, excess hydride was decomposed by addition of 2 ml of saturated aqueous sodium sulfate solution. The product, isolated by ether extraction, yielded a yellowish oil which gave a gas chromatogram with two major peaks with the same retention times as neomenthol and menthol.[16] Two unidentified minor peaks were also detected.

Registry No.—**1**, 27525-51-5; **2**, 27525-52-6; **3**, 27525-53-7; **4**, 27525-54-8; **5**, 27525-55-9; **6**, 27525-56-0; **7**, 27525-57-1; **8**, 27525-58-2; **9**, 4031-55-4; **10**, 4031-54-3; **11**, 4031-53-2; **12**, 27570-89-4; **13**, 27525-61-7; **14**, 27525-62-8; **16**, 27570-90-7; **17**, 27570-91-8; **19**, 27525-63-9.

(24) W. Hückel and C.-M. Jennewein, *Justus Liebigs Ann. Chem.*, **683**, 100 (1965).

A New Synthesis of 7,12-Dimethylbenz[*a*]anthracene[1]

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A new synthesis, which may prove general for the synthesis of 7,12-dimethylbenz[*a*]anthracenes from the corresponding benz[*a*]anthracenes, is described. Benz[*a*]anthracene (II) was condensed with vinylene carbonate to yield 7,12-dihydro-7,12-ethanobenz[*a*]anthracene-13,14-diol cyclic carbonate (III). Hydrolysis yielded 7,12-dihydro-7,12-ethanobenz[*a*]anthracene-13,14-diol (IV) which on treatment with lead tetraacetate afforded 7,12-dialdehydo-7,12-dihydrobenz[*a*]anthracene (V). Reduction of V with lithium aluminum hydride yielded 7,12-bis(hydroxymethyl)-7,12-dihydrobenz[*a*]anthracene (VI), the bismethanesulfonyl derivative of which was reduced to 7,12-dihydro-7,12-dimethylbenz[*a*]anthracene (VIII) by lithium aluminum hydride. Aromatization of VIII by heating with sulfur afforded 7,12-dimethylbenz[*a*]anthracene (I). The yields in each step were high. Similarly, 5-fluoro-7,12-dimethylbenz[*a*]anthracene (I_F) was synthesized from 5-fluorobenz[*a*]anthracene (II_F) in high yield.

Three general syntheses of 7,12-dimethylbenz[*a*]anthracene (I) are known. One involves addition of methylmagnesium iodide to benz[*a*]anthraquinone followed by conversion of the resulting diol with acidic methanol to the corresponding dimethoxy derivative which is reduced with metallic sodium (or potassium) to I[3] or to 7,12-dihydro-7,12-dimethylbenz[*a*]anthracene. The latter is converted to I by heating with sulfur.[3] A second method involves treating the above-mentioned dimethyldiol with hydrogen iodide to yield 12-methyl-7-iodomethylbenz[*a*]anthracene which is reduced to I with stannous chloride.[4] The third method involves treatment of 12-methylbenz[*a*]anthrone (not isolated) with methylmagnesium bromide, followed by dehydration of the crude carbinol to I.[5]

Each of these methods has potential drawbacks if variously substituted 7,12-dimethylbenz[*a*]anthracenes are desired: the first two, because of possible difficulties in the synthesis of the desired quinones and in finding proper conditions for transforming the dimethyldiols to the desired analogs of I; and the third because benzanthrones are often too sensitive to give high yields on reaction with methylmagnesium halides. For these reasons a new synthesis was deemed desirable. In this paper, such a new route is illustrated in Scheme I.

Since anthracene was known to react with vinylene carbonate to give a Diels–Alder type addition product in good yield,[6] we heated benz[*a*]anthracene in excess vinylene carbonate to produce the adduct III[7] in high

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(3) W. E. Bachmann and J. M. Chermerda, *J. Amer. Chem. Soc.*, **60**, 1023 (1938). Similar reductions were carried out by B. M. Mikhailov and coworkers, *Chem. Abstr.*, 5842 (1939); 6350*i* (1948).

(4) R. B. Sandin and L. F. Fieser, *J. Amer. Chem. Soc.*, **62**, 3098 (1940).

(5) M. S. Newman, *ibid.*, **60**, 1141 (1938).

(6) M. S. Newman and R. W. Addor, *ibid.*, **77**, 3789 (1955).

(7) This product was probably a mixture of stereoisomers, but we made no attempts at separation or purification of individual isomers.