Registry No.—III, 16315-61-0; VI, 16315-62-1; X, 16315-63-2; XII, 16315-64-3; XVII, 264-73-3.

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The Synthesis of (±)-Geosmin and the Other 1,10-Dimethyl-9-decalol Isomers

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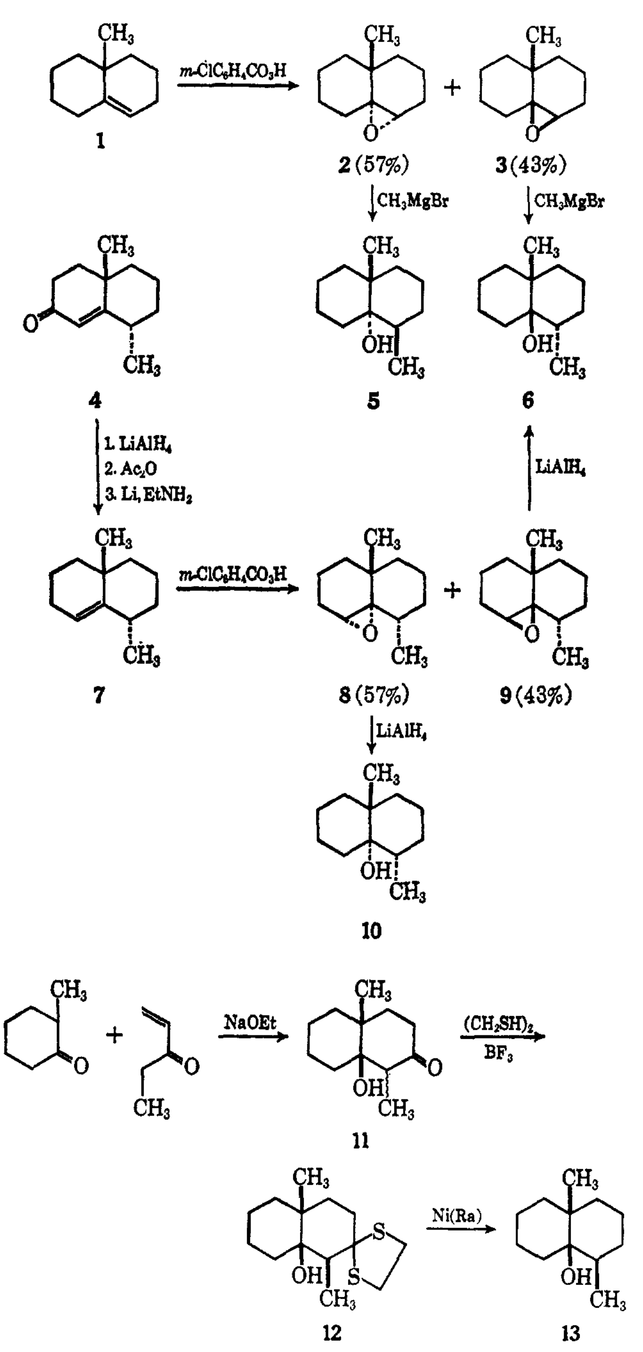
Recently, Gerber and Lechevalier[3] described the isolation of geosmin, the earthy smelling metabolite of actinomycetes microorganisms which is responsible for the characteristic odor of freshly plowed soil. Upon treatment with aqueous acid geosmin afforded a hydrocarbon[3] later identified[4] as a mixture of 1,10-dimethyl-1(9)-octalin[5] and an isomeric olefin. This finding coupled with nmr spectral evidence suggested that geosmin might be one of the isomeric 1,10-dimethyl-9-decalols.[4] In connection with some studies on olefin oxidations[5] we had prepared in racemic form decalols **5**, **6**, and **13**, three of the four possible isomers. The infrared spectra indicated that none of the three was geosmin. However, the spectra of geosmin and the *trans*-decalol **5** showed such striking similarities that we decided to attempt the synthesis of decalol **10**, the C-1 epimer of **5** and the remaining racemic 1,10-dimethyl-9-decalol isomer. In this note we describe synthetic work which pertains to these decalols and show that *trans*-1,10-dimethyl-*trans*-9-decalol (**10**) is the racemic modification of Gerber and Lechevalier's geosmin.

We previously found that the methyl octalin **1** affords a 57:43 mixture of the *trans* and *cis*-decalin oxiranes **2** and **3** upon treatment with *m*-chloroperoxybenzoic acid in benzene (Scheme I).[5] This mixture slowly reacted with methylmagnesium bromide in refluxing tetrahydrofuran to give decalols **5** and **6** which could be separated by careful chromatography on Florisil.[5] The dimethyloctalin **7** was prepared *via* reduction of octalone **4**[6] with lithium aluminum hydride, acetylation of the resulting epimeric alcohol mixture, and hydrogenolysis of the allylic acetate mixture with lithium in ethylamine, a sequence analogous to that employed for the synthesis of octalin **1**. Octalin **7**, like its desmethyl counterpart, gave a 57:43 mixture of *trans* and *cis* decalin oxiranes upon treatment with *m*-chloroperoxybenzoic acid in benzene. Reduction of this mixture with lithium aluminum hydride afforded the corresponding decalols **10** and **6** which were separated *via* careful chromatography on silica. The minor alcohol isomer was identified as *trans*-1,10-dimethyl-*cis*-9-decalol (**6**) by comparison of infrared and nmr spectra with those of an authentic sample.[5] The gas chromatographic retention times were likewise identical (peak enhancement) on several columns under a variety of conditions. This comparison defines the stereochemistry of decalol **10**, the reduction product of the predominant oxirane isomer **8**, since both oxiranes **8** and **9** originate from the same olefin. Decalol **10** was found to be identical with geosmin through spectral and chromatographic comparisons.

SCHEME I



The *cis,cis*-1,10-dimethyl-9-decalol **13** was prepared from ketol **11**, the condensation product of 2-methylcyclohexanone and ethyl vinyl ketone.[7] The crystalline thioketal derivative **12** upon desulfurization with

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[1] Fellow of the Alfred P. Sloan Foundation, 1966–1968.

[2] National Institutes of Health Predoctoral Fellow, 1965–1968.

[3] N. N. Gerber and H. A. Lechevalier, *Appl. Microbiol.* **13**, 935 (1965).

[4] N. N. Gerber, Institute of Microbiology, Rutgers University, personal communication, 1968.

[5] J. A. Marshall and A. R. Hochstetler, *J. Org. Chem.* **31**, 1020 (1966).

[6] J. A. Marshall and D. J. Schaeffer, *ibid.*, **30**, 3642 (1965).

[7] *Cf.* J. A. Marshall and W. I. Fanta, *ibid.*, **29**, 2501 (1964).

Raney nickel readily yielded decalol **13**. The stereochemistry of this decalol, which follows from its nonidentity with **5**, **6**, and **10**, must be preserved in the thioketal precursor **12**. Since epimerization of the C-1 methyl grouping could occur during formation of this derivative, an unequivocal stereochemical assignment to this center in ketol **11** cannot be made. However, conversion into decalol **13** does confirm the *cis* ring fusion of ketol **11** and thus supports our previous conclusions regarding the stereochemistry of aldol cyclizations leading to such ketols.[7]

The earthy odor referred to by Gerber and Lechevalier[3] is shared by all four decalols **5**, **6**, **10**, and **13**, but each is quite distinctive. The *cis*-fused isomers **6** and **13** have fragrances reminiscent of camphor and cedar and are thus somewhat more agreeable to the nose than their more pungent *trans* counterparts **5** and **10**.

Experimental Section[8]

***trans*-8,10-Dimethyl-1(9)-octalin (7).**—To a stirred solution containing 600 mg of lithium aluminum hydride in 60 ml of anhydrous ether was added 2.50 g of octalone **4** dissolved in 5 ml of ether. After 2 hr, the mixture was treated with 1.20 ml of water and 0.96 ml of 10% aqueous sodium hydroxide and allowed to stir overnight. The crude alcohol was obtained by filtration and distillation of the ether from the filtrate.

The resulting octalol mixture was dissolved in 15 ml of pyridine and treated with 4.0 ml of acetic anhydride. After 20 hr, water (60 ml) was added and the mixture was thoroughly extracted with hexane. The combined extracts were successively washed with water, 2% aqueous sulfuric acid, and water and dried over anhydrous magnesium sulfate.

The ether was removed from the above solution and the crude product was dissolved in 125 ml of ethylamine and treated with 950 mg of lithium wire according to the procedure of Hallsworth, Henbest, and Wrigley.[9] A deep blue color persisted after 1 hr and the solution was stirred for an additional 30 min. Solid ammonium chloride was then added to neutralize the salts and decompose the excess metal. Most of the ethylamine was allowed to evaporate, water was added, and the mixture was extracted thoroughly with hexane. The combined extracts were washed successively with water, 2% aqueous sulfuric acid, and water and dried over anhydrous magnesium sulfate. The solvent was carefully removed under reduced pressure and the residue was chromatographed on 70 ml of Florisil. Elution with hexane afforded 1.34 g (65%) of octalin **7**: $n^{26}\text{D}$ 1.4960; $\lambda_{\max}^{\text{film}}$ 6.05 (C=C), 8.30, 9.46, 10.03, 10.69, 11.47, 12.34, 12.61 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 5.32 (C-1 H, poorly resolved sextet, J = 1.8 Hz), 1.05 (C-10 CH_3), 0.96 ppm (C-8 CH_3, doublet, J = 6.5 Hz).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.9; H, 12.1.

Synthesis and Reduction of Oxiranes 8 and 9.—A solution of 200 mg of octalin **7** and 720 mg of *m*-chloroperoxybenzoic acid in 15 ml of benzene was stirred at 25° for 2.0 hr. The reaction mixture was washed with 10% aqueous sodium hydroxide and saturated aqueous sodium chloride, and the benzene solution was dried over anhydrous magnesium sulfate. The solvent was removed at reduced pressure affording 220 mg of a 57:43 mixture (by gas chromatography) of isomeric oxiranes **8** and **9**: $\lambda_{\max}^{\text{film}}$ 9.25, 9.70, 10.68, 11.06, 11.60, 12.82, 13.18 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 3.0–2.80 (C-1 H), 1.05 (C-10 CH_3 of **8**), 0.58 (C-8 CH_3 of **8**, doublet, J = 6.5 Hz), 1.01 (C-10 CH_3 of **9**), 0.63 ppm (C-8 CH_3 of **9**, doublet, J = 6.5 Hz).

The crude oxirane mixture dissolved in 5 ml of anhydrous 1,2-dimethoxyethane was added to a solution of 210 mg of lithium aluminum hydride dissolved in 15 ml of 1,2-dimethoxyethane and the mixture was maintained at reflux for 4 hr. The mixture was cooled and 50 ml of ether followed by 0.42 ml of water and 0.33 ml of 10% aqueous sodium hydroxide was added. The salts were filtered after stirring overnight, and the solvent was removed under reduced pressure affording 205 mg of crude decalols **6** and **10** which displayed peaks in the gas chromatogram[10] at 36.0 min (57%, **10**) and 40.4 min (43%, **6**).

***trans*-1,10-Dimethyl-*trans*-9-decalol (10). (±)-Geosmin.**—The crude decalol mixture described above was chromatographed on 40 ml of acid-washed silica. Elution with 2% ether–hexane (200 ml) afforded 82 mg of colorless oil (one peak on the gas chromatograph): bp 60° (bath temperature) at 0.3 mm; $\lambda_{\max}^{\text{film}}$ 2.83 (OH), 8.45, 9.42, 9.93, 10.52, 10.88, 11.29, 11.62, 12.47 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 1.01 (C-10 CH_3), 0.73 ppm (C-1 CH_3, doublet, J = 5.5 Hz). The infrared spectrum was identical with that of (−)-geosmin isolated by Gerber and Lechevalier.[3]

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.0; H, 12.2.

***trans*,1,10-Dimethyl-*cis*-9-decalol (6).**—Continued elution of the above column with 2% ether–hexane (200 ml) afforded 20 mg of a mixture of decalols **10** and **6**. Elution with 3% ether–hexane (200 ml) afforded 60 mg of colorless oil: bp 60° (bath temperature) at 0.3 mm; $\lambda_{\max}^{\text{film}}$ 2.85 (OH), 8.61, 9.32, 9.50, 9.99, 10.33, 10.53, 11.12, 11.97 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 0.95 (C-10 CH_3), 0.83 ppm (C-1 CH_3, doublet, J = 6.5 Hz). The infrared and nmr spectra of this decalol were identical with those of the minor decalol isomer formed upon treatment of oxirane mixture **2** and **3** with methylmagnesium bromide.[5] The gas chromatographic retention times were likewise identical (peak enhancement) under a variety of conditions.

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.0; H, 12.2.

1,10-Dimethyl-*cis*-9-hydroxy-2-decalone (11).[11]—A solution containing 7.8 g of 2-methylcyclohexanone and 0.85 ml of 3 *N* ethanolic sodium ethoxide was maintained at −10° and efficiently stirred while a solution of 5.9 g of ethyl vinyl ketone in 7.8 g of 2-methylcyclohexanone was added dropwise over a period of 5.5 hr. Stirring at −10° was continued for 6.5 hr after addition was complete and the organic material was isolated by extraction with ether. The combined extracts were dried and distilled affording 8.9 g (57% recovery) of 2-methylcyclohexanone, bp 55–58° (0.2 mm), and 9.3 g (68%) of ketol **11** and the corresponding conjugated ketone, bp 80–105° (0.1 mm). The higher boiling fraction was crystallized from hexane affording 4.9 g (36%) of ketol **11**, mp 70–77° (lit.[12] mp 88°). The analytical sample, mp 103°, was secured after several additional recrystallizations from hexane.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.4; H, 10.2.

Ethylene Thioketal Derivative of *cis*-1,10-Dimethyl-*cis*-9-hydroxy-2-decalone (12).—The procedure of Fieser was employed.[13] A solution of 1.50 g of ketol **11** in 27 ml of glacial acetic acid, 2.1 ml of 1,2-ethanedithiol, and 2.1 ml of boron trifluoride etherate was allowed to stand at ambient temperature for 2.2 hr. The solution was diluted with aqueous sodium chloride and extracted with ether. The combined extracts were washed with 10% aqueous sodium hydroxide and saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. The ether was distilled and the residue was crystallized from hexane affording 1.45 g (70%) of thioketal **12**, mp 119–120°. The analytical sample, mp 120.5–121°, was obtained after recrystallization from hexane and sublimation.

Anal. Calcd for $C_{14}H_{24}OS_2$: C, 61.71; H, 8.88; S, 23.54. Found: C, 61.7; H, 8.9; S, 23.4.

***cis*-1,10-Dimethyl-*cis*-9-decalol (13).**—A solution of 461 mg of thioketal **12** in 30 ml of absolute ethanol was efficiently stirred with 15 g of freshly prepared W-2 Raney nickel at 25° for 2 hr and at reflux for 4.5 hr. The cooled mixture was carefully filtered and the ethanol was removed under reduced pressure. The residue was dissolved in ether, washed with saturated aqueous sodium chloride, and dried over anhydrous magnesium sulfate. Removal of solvent and distillation afforded 262 mg (85%) of a colorless oil: bp 55–60° (0.25 mm); $\lambda_{\max}^{\text{film}}$ 2.86 (OH), 8.46,

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[8] (a) The apparatus described by W. S. Johnson and W. P. Schneider [*Org. Syn.*, **30**, 18 (1950)] was used to maintain a nitrogen atmosphere over reaction mixtures. (b) Melting points were determined on a Fisher-Johns hot stage. (c) An F & M Model 700 or Model 720 gas chromatograph was employed for analytical work (d) Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

[9] A. S. Hallsworth, H. B. Henbest, and T. I. Wrigley, *J. Chem. Soc.*, 1437 (1952).

[10] An 18 ft × 0.25 in. column containing 20% Carbowax 20M on Chromosorb W was employed at 146° with a helium flow rate of 100 cc/min.

[11] This experiment is abstracted from the Ph.D. Thesis of Wayne I. Fanta, Northwestern University, 1965.

[12] F. J. McQuillin, *J. Chem. Soc.*, 528 (1955).

[13] L. F. Fieser, *J. Amer. Chem. Soc.*, **76**, 1945 (1954).

9.33, 9.48, 9.88, 10.28, 10.46, 10.65, 11.18 μ; $\delta_{TMS}^{CCl_4}$ 0.96 (C-10 CH_3), 0.79 ppm (C-4 CH_3 doublet, J = 6.5 Hz).

The distillate solidified upon refrigeration, and the analytical sample, mp 40.5–41.5°, was obtained after two sublimations.

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.1; H, 12.0.

Registry No.—**6,** 16423-15-7; **7,** 16423-16-8; **8,** 16423-17-9; **9,** 16423-18-0; **10,** 16423-19-1; **12,** 16423-20-4; **13,** 16452-32-7.

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The Solvolysis of *p,p'*-Disubstituted Benzhydryl Halides

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The recent series of papers by Nishida on the additivity, or lack of additivity, in the alcoholysis of mono- and disubstituted benzhydryl halides[2] prompted us to report results of a similar, though less extensive study, which had similar objectives as its aim. Our data were obtained in aqueous acetone and therefore supplement the data of Nishida.

The problem of concern is whether two identical substituents in two different benzene rings act completely independently of each other in a reaction in which a carbonium ion is developed in the transition state, when both substituents are capable of interacting with the carbonium ion. Such a situation arises in the solvolysis of appropriately substituted benzhydryl halides. Although in most disubstituted chloro and methyl derivatives additivity occurs,[2,3] Nishida has demonstrated a characteristic deviation in the case of *p,p'*-dimethylbenzhydryl chloride, and it is this deviation from additivity which our data confirm for the acetone–water system. The problem has some added current interest because multiple methyl substitution has been utilized as a probe for the structure of carbonium ion transition states.[4]

Some of the required data have been in the literature for a long time. Ingold and coworkers, in the course of their study on mass law and salt effects, studied the solvolysis of *p*-methyl- and *p,p'*-dimethylbenzhydryl chloride in 80% aqueous acetone.[5] Their data show that one *p*-methyl group increases the reactivity by a factor of 29.6, but that *p,p'*-dimethylbenzhydryl chloride reacts only 567 times as fast as the parent compound, instead of 876 times, if additivity had strictly prevailed.

Our data are reported in Table I. Because of a slight difference in solvent composition (see Experimental Section) and the great sensitivity of the rates to water content,[6] our values for the rate constants differ slightly from those of Ingold, *et al.*, but the general pattern is the same. The solvolysis of *p,p'*-dimethylbenzhydryl chloride in aqueous acetone is not only very fast, but has a very strong mass law effect in the concentration range here used. The rate constants reported, ours, as well as the literature values, were obtained by extrapolation to 0% reaction, and our data for the dimethyl derivative are only approximate. However, in the alcoholysis (ethanolysis, 2-propanolysis) of the same compound, which is not beset by these difficulties, analogous results were obtained[2] which leaves no doubt as to the over-all validity of the results.

The *p,p'*-dimethyl compound does not react as fast as it should on the basis of additivity. This is also true of *p,p'*-di-*t*-butylbenzhydryl chloride, but with the less powerful electron-releasing effect of the *t*-butyl group, the difference between observed and calculated values is less than with methyl.

The situation is similar, although reversed in an absolute sense, when the substituents have an electron-attracting effect and therefore destabilize the carbonium ion. The chlorine atom in *p*-chlorobenzhydryl chloride lowers the rate of solvolysis, but the second chlorine hinders the reaction less than the first, and *p,p'*-dichlorobenzhydryl chloride does not solvolyze as slowly as calculated. This is true also of the bromine atom, but to a somewhat lesser extent. The deviations caused by the halogens are barely noticeable in the alcoholysis but the deviations become quite pronounced when more than two substituents are present.[2]

The results confirm that in this particular system characteristic deviations from additivity occur. Nishida has shown that this can formally be expressed by assigning two different ρ values to the reactions of mono- and disubstituted benzhydryl chlorides, or by modifying the Hammett equation by the inclusion of more parameters. But the physical meaning of the deviations must be that in a system such as the benzhydryl system, the second of two identical substituents does not affect the reaction to the same extent as the first, and that their effects appear to oppose each other. Consequently, both cannot interact with the developing carbonium ion as effectively as can one alone. The result which is noted in the rate studies is that the second substituent has less effect than the first, but, because of the complete symmetry of the system, the effect of both substituents must be diminished to the same extent.

This lack of additivity is not necessarily confined to transition states. It has also been noted in the dissociation of substituted triphenylmethyl halides in

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[1] Taken from the Ph.D. Thesis of M. Q. Malter, Bryn Mawr College, June, 1952.

[2] S. Nishida, *J. Org. Chem.*, **32**, 2692, 2695, 2697 (1967).

[3] Deviations from additivity in the solvolysis of benzhydryl chlorides have been observed and discussed by J. R. Fox and G. Kohnstam, *Proc. Chem. Soc.* (London), 115 (1964).

[4] P. D. Bartlett and G. D. Sargent, *J. Amer. Chem. Soc.*, **87**, 1297 (1965); P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

[5] E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 949 (1940); M. G. Church, E. D. Hughes, and C. K. Ingold, *ibid.*, 966 (1940); M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *ibid.*, 971 (1940); L. C. Bateman, E. D. Hughes, and C. K. Ingold, *ibid.*, 974 (1940); L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *ibid.*, 979 (1940).

[6] For instance, see V. J. Shiner, Jr., and C. J. Verbanic, *J. Amer. Chem. Soc.*, **79**, 369 (1957).