zenesulfenyl group in II is joined at the 5′-oxygen, is provided by the synthesis of thymidylyl-(3′–5′)-deoxyadenosine from compound IV and 5′-O-monomethoxytritylthymidine.[7] This compound was completely hydrolyzed by snake venom phosphodiesterase, an enzyme specific for oligonucleotides possessing a terminal 3′-hydroxyl group and 3′–5′ phospho diester links.

Experimental Section

Infrared spectra were determined in potassium bromide with a Baird recording spectrophotometer. Thin layer chromatography was performed on Eastman Chromagram sheets, 6060 silica gel, with ethyl acetate; R_f values are indicated in text. Elemental analyses were made by the Micro-Tech Laboratories, Skokie, Ill.

5′-O-(2,4-Dinitrobenzenesulfenyl)thymidine.—Thymidine (2.00 g, 8.28 mmol) was dissolved in 150 ml of anhydrous pyridine and cooled to 0°. 2,4-Dinitrobenzenesulfenyl chloride (1.94 g, 7.62 mmol) in 50 ml of anhydrous pyridine was added dropwise over a period of 1 hr with stirring; then, after the mixture had stood for 4 hr at 0°, it was allowed to warm to room temperature. The mixture was diluted with 1 l. of ice–water and extracted three times with $CHCl_3$. The organic layer was washed twice with water, dried with Na_2SO_4, and concentrated. The residue was taken up in warm methanol and the solution was filtered while hot. Methanol was then distilled off and the residue was dissolved in ethyl acetate and chromatographed on silica gel (12 × 50 cm) using ethyl acetate as an eluent. The first fraction yielded 0.19 g of a yellow solid, mp 122–128°, R_f 0.85, which is probably 3′,5′-bis-O-(2,4-dinitrobenzenesulfenyl)thymidine. The second fraction contained 0.35 g (10%) of 3′-O-(2,4-dinitrobenzenesulfenyl)thymidine,[5] mp 182–184° dec, R_f 0.62. Finally, elution with 50% ethyl acetate–acetone yielded 5′-O-(2,4-dinitrobenzenesulfenyl)thymidine, isolated by stripping off the solvent, dissolving the residue in ethyl acetate, and precipitation by addition of hexane: weight 1.25 g (37%); mp 102–110°; R_f 0.43; prominent infrared bands at 2.90, 5.95, 6.28, 6.60, 7.47, and 12.08 μ. The spectrum was very close to that of the 3′-O isomer, differing primarily by absence of a shoulder at 9.0 μ.

Anal. Calcd for $C_{16}H_{16}N_4O_9S$: C, 43.64; H, 3.66; N, 12.72; S, 7.28. Found: C, 43.65; H, 3.93; N, 11.78; S, 7.06.

5′-O-(2,4-Dinitrobenzenesulfenyl)-3′-O-(β-benzyoylpropionyl)-N⁶-benzoyldeoxyadenosine (III).—To 0.366 g (1.03 mmol) of dry N⁶-benzoyldeoxyadenosine in 10 ml of pyridine at 20° was added 0.350 g (1.49 mmol) of 2,4-dinitrobenzenesulfenyl chloride in 5 ml of pyridine. After 1.5 hr the mixture was poured over 300 g of ice and allowed to stand 1 hr. The insoluble material was extracted into chloroform which, after drying over Na_2SO_4, was stripped *in vacuo*. Ethanol was added and stripped to remove traces of pyridine, and the gummy residue was dissolved in hot $CHCl_3$. Column chromatography on silica gel with ethyl acetate yielded on concentration and precipitation with hexane 0.097 g of a yellow solid, mp 115–125°, R_f 0.85, which is probably the bis-2,4-dinitrobenzenesulfenyl derivative. From the second chromatographic fraction was obtained 0.066 g (12%) of 3′-O-(2,4-dinitrobenzenesulfenyl)-N⁶-benzoyldeoxyadenosine: mp 151–153°; R_f 0.66; prominent infrared bands at 2.93, 5.82, 6.24, 6.55, 7.44, and 11.96 μ.

Anal. Calcd for $C_{23}H_{19}N_7O_8S$: C, 49.90; H, 3.46; N, 17.72; S, 5.79. Found: C, 49.64; H, 3.80; N, 17.58; S, 5.61.

Continued elution of the column yielded 0.253 g (45%) of II: mp 115–125°; R_f 0.32; prominent infrared bands at 2.95, 5.84, 6.24, 6.55, 7.44, and 11.97 μ. A mixture of 0.244 g (0.44 mmol) of compound II, 0.451 g (2.53 mmol) of β-benzoylpropionic acid, and 0.6 g (3 mmol) of dicyclohexylcarbodiimide in 2 ml of pyridine was stirred for 2 hr at room temperature, diluted with 1 ml of water, and stirred an additional hour. The insoluble dicyclohexylurea was filtered off and washed with $CHCl_3$ (50 ml) and the combined filtrate and $CHCl_3$ washings were washed with saturated $NaHCO_3$. After drying over Na_2SO_4 the solution was stripped in a rotatory evaporator, diluted with ethanol, and stripped again to a gummy residue. This material was dissolved in hot ethyl acetate and, after standing overnight, was filtered to remove the crystalline acylurea. On chromatography on a silica gel column with ethyl acetate the filtrate yielded compound III: mp 94–96°; weight 0.170 g (54% from II); R_f 0.67; prominent infrared bands at 2.98, 3.48, 5.78 (s), 5.93, 6.27, 6.60, 7.48, and 12.00 μ (w).

Anal. Calcd for $C_{33}H_{27}N_7O_{10}S$: C, 55.53; H, 3.81; N, 13.74; S, 4.49. Found: C, 55.59; H, 4.12; N, 13.63; S, 4.41.

3′-O-(β-Benzoylpropionyl)-N⁶-benzoyldeoxyadenosine (IV).—The preparation of compound III was repeated on a fourfold scale to the point where the products were dissolved in ethyl acetate and separated by chromatography. In this case, in place of the chromatographic separation, the gummy products were dissolved in pyridine and H_2S was slowly bubbled through the solution for 16 hr. Following the usual work-up procedure (stripping of the solvent, addition of ethanol, stripping of the ethanol, etc.) the solid products were chromatographed on silica gel with ethyl acetate–methanol (90/10). Compound IV was recovered by concentrating the appropriate fraction and was recrystallized from ethyl acetate: mp 111–112.5°; weight 0.532 g (57%); R_f 0.57; prominent infrared bands at 2.96, 5.76, 5.93, 6.24, 6.87, and 8.63 μ. That the 2,4-dinitrobenzenesulfenyl group was absent was shown by absence of bands at ~6.6 and 7.4 (nitro groups) and 12.0 μ (characteristic for 2,4-dinitrobenzenesulfenyl derivatives).

Anal. Calcd for $C_{27}H_{25}N_5O_6$: C, 62.90; H, 4.89; N, 13.59. Found: C, 62.96; H, 4.99; N, 13.52.

Registry No.—5′-O-(2,4-Dinitrobenzenesulfenyl)thymidine, 16243-75-7; 3′-O-(2,4-dinitrobenzenesulfenyl)-N⁶-benzoyldeoxyadenosine, 16243-76-8; III, 16281-89-3; IV, 16243-74-6.

(7) Experiments of K. K. Ogilvie, Northwestern University, Evanston, Ill.

Reactions of Phosphorus Compounds. XVI. The Reaction of Several Hydroxyphosphonium Ylides

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The preparation of 2,3-dihydro-1-benzoxepin may be readily accomplished by treating 3(O-formylphenoxy)-propyltriphenylphosphonium bromide (I) in a nonprotonic solvent under basic conditions.[1] As an extension to this work, and due to the recent interest in the oxepin ring system,[2-7] we have first examined the feasibility of preparing 1-phenoxy-4-phenylbutadiene (VI) from 2-hydroxy-3-phenoxypropyltriphenylphosphonium bromide (III) and benzaldehyde. Finding this first reaction successful, we turned to the corresponding reaction of 2-hydroxy-3(2-formylphenoxy)propyltriphenylphosphonium bromide (XII) which we hoped would give 1-benzoxepin (XVII).

The salt III was allowed to react with base to form the ylide IV, and addition of benzaldehyde followed (Scheme I). The expected products of this reaction

(1) (a) E. E. Schweizer and R. Schepers, *Tetrahedron Lett.*, **15**, 979 (1963); (b) E. E. Schweizer, C. J. Berninger, D. M. Crouse, R. A. Davis, and R. Schepers, *Logothetis*, in press.

(2) (a) A. Shani and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 6310 (1967); (b) F. Sondheimer and A. Shani, *ibid.*, **86**, 3168 (1964).

(3) E. Vogel, M. Biskup, W. Pretzer, and W. A. Boll, *Angew. Chem. Intern. Ed. Engl.*, **3**, 642 (1964).

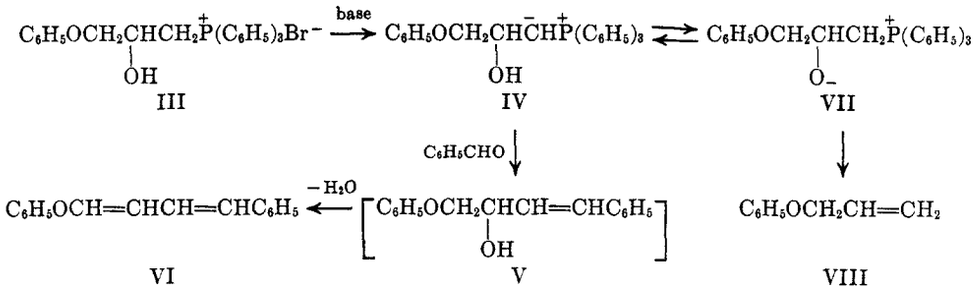
(4) H. Hoffman, *ibid.*, **4**, 872 (1965).

(5) E. Vogel, R. Schubart, and W. A. Boll, *ibid.*, **3**, 510 (1964).

(6) E. O. Fischer, C. G. Kreiter, H. Ruhle, and K. E. Schwarzhans, *Ber.*, **100**, 1905 (1967).

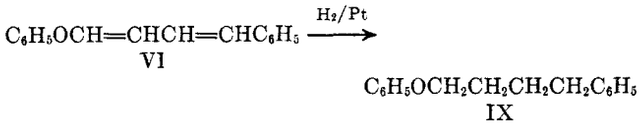
(7) E. Vogel, W. A. Boll, and H. Gunther, *Tetrahedron Lett.*, **10**, 609, (1965).

SCHEME I

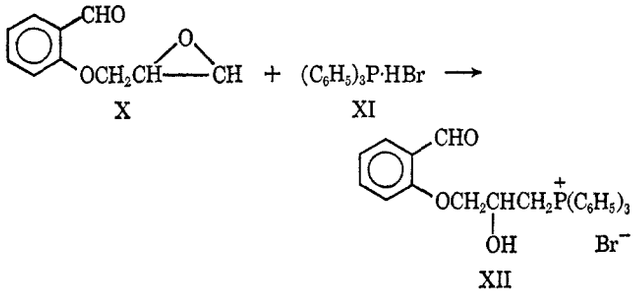


are 1-phenyl-3-hydroxy-4-phenoxy-1-butene (V) and allyl phenyl ether (VIII); however, it was found that under the reaction conditions employed most of V underwent dehydration to give 1-phenoxy-4-phenylbutadiene (VI). This reaction was carried out in two ways. If the base–solvent system used was ethoxide–ethanol, the yield of the butadiene VI was only 8.1%. If the base–solvent system used was *n*-butyllithium–benzene, the yield of the butadiene was increased to 25.5%. The major product of the reaction was allyl phenyl ether (VIII).

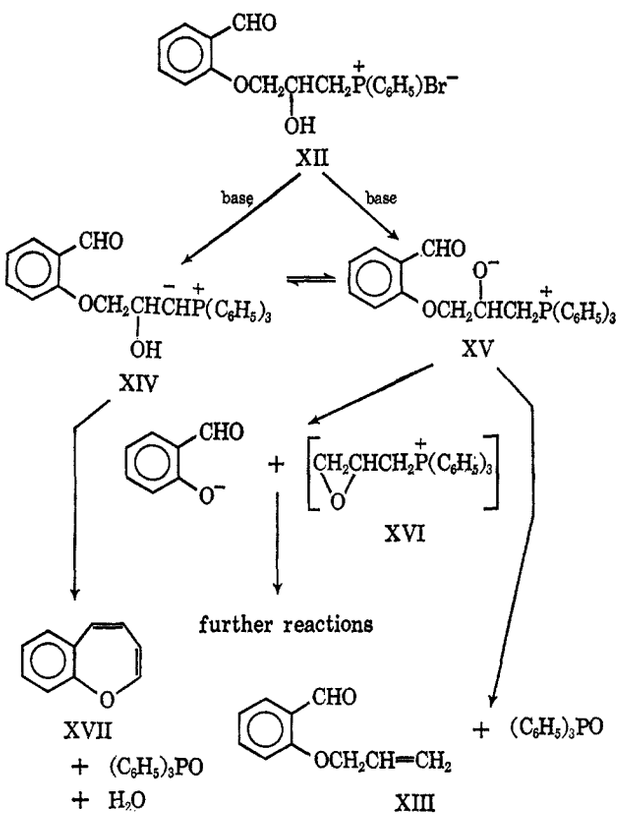
The butadiene VI was identified by its nmr and infrared spectra and by hydrogenation to 1-phenoxy-4-phenylbutane (IX) which was shown to be identical with an authentic sample.[8] Before the hydrogenation could be carried out, it was necessary to remove traces of codistilled triphenylphosphine which poisoned the



catalyst, by precipitating it as methyltriphenyl phosphonium iodide using methyl iodide in ether.



In order to prepare 1-benzoxepin (II) by an intramolecular Wittig reaction, the phosphonium salt (XII) was needed and was readily obtained by the reaction of 1,2-epoxy-3-(2-formylphenoxy)propane[9] (X) and triphenylphosphine hydrobromide (XI). The base–solvent system used to prepare the desired ylide from this salt was restricted to ethoxide–ethanol, since alkyllithium compounds would also react with the carbonyl moiety. When this reaction was carried out, 1-benzoxepin (XVII) was obtained in 5% yield. The oxepin XVII was identified on the basis of the nmr and ir spectra, which were identical with those in the literature.[2,3] The major by-products identified were *o*-allyloxybenzaldehyde (XIII) and salicylaldehyde. The reaction of ethoxide with the salt XII may be expected to initially produce either the ylide or the betaine XV. Intramolecular Wittig reaction of the ylide XIV followed by dehydration would yield 1-benzoxepine (XVII) and triphenylphosphine oxide. If the other intermediate XV were formed, decomposition of the betaine XV would give rise to *o*-allyloxybenzaldehyde (XIII); salicylaldehyde may be obtained by elimination, resulting in the salt XVI, which could undergo further reaction. The reactions of salts of type XVI have been studied by Bohlmann and Herbst.[10]



As to the possibility of interconversion between ylide XIV and betaine XV, the conversion of XV into XIV must be slower than the reactions just discussed, since we have found that reaction of 1,2-epoxy-3-(2-formylphenoxy)propane (X) with triphenylphosphine, which should proceed by way of XV, gave mainly *o*-allyloxybenzaldehyde (XIII) and absolutely no 1-benzoxepin XVII. The conversion of XIV into XV cannot be excluded, however.

(8) L. A. Walter and S. M. McElvain, *J. Amer. Chem. Soc.*, **56**, 1614 (1934).

(9) O. Stephenson, *J. Chem. Soc.*, 1571 (1954).

(10) F. Bohlmann and P. Herbst, *Ber.*, **92**, 1319 (1959).

Experimental Section[11]

Preparation of (2-Hydroxy-3-phenoxy)propyltriphenylphosphonium Bromide (III).—In a dry 50-ml, two-necked, round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet, and a reflux condenser with drying tube was placed 20 ml of anhydrous ethanol, 1.0 g (0.039 mol) of triphenylphosphine,[12] and 9.86 g (0.04 mol) of 2-hydroxy-3-bromo-1-phenoxypropane.[13] The reaction mixture was stirred and refluxed for 40 hr in a slow current of dry nitrogen. The resulting colorless oil was poured slowly into 150 ml of anhydrous ether, the solution being shaken after each addition. If the salt did not crystallize immediately, the ether was poured off and the remaining oil was let to stand in open air. The white crystals were filtered and washed twice with fresh anhydrous ether, then boiled for several minutes in anhydrous benzene and filtered while hot in order to remove any unreacted starting materials. After washing twice more with hot benzene, the salt was dried under vacuum at 100° for 48 hr. The product (15 g) was obtained with mp 207–209° (80% yield). The nmr spectrum ($DCCl_3$) showed bands at τ 6.2 (m, 2), 5.7 (m, 2), and 4.5 ppm (m, 1).

Anal. Calcd for $C_{27}H_{26}O_2BrP$: C, 67.72; H, 5.31. Found: C, 65.79; H, 5.53.

1-Phenoxy-4-phenylbutadiene (VI).—A dry 3 l., three-necked, round-bottomed flask was provided with a mercury-sealed stirrer, a reflux condenser with drying tube, a nitrogen inlet, and a Gooch tubing connected to an erlenmeyer flask. A gentle flow of dry nitrogen was maintained throughout the reaction. Anhydrous thiophene-free benzene (2300 ml) and 20.4 g (0.21 mol) of *n*-butyllithium were added to the flask. The solution was stirred and refluxed, and 104.6 g (0.21 mol) of (2-hydroxy-3-phenoxy)propyltriphenylphosphonium bromide (III) was added cautiously through the Gooch tubing as fast as possible. If the salt was added too rapidly, the evolution of butane caused excessive frothing of the solution. During the first additions of the salt, the reaction mixture became yellow and at the end it had changed to dark red. The reaction mixture was refluxed and stirred for several minutes after the salt addition was completed. The Gooch tubing was replaced by a dropping funnel and 22.26 g (0.21 mol) of freshly distilled benzaldehyde were added dropwise. After the addition of the benzaldehyde, the original color changed to light reddish brown. The reaction mixture was refluxed and stirred for 24 hr, allowed to cool to room temperature and then filtered. The solvent was evaporated and the remaining dark red liquid was distilled at reduced pressure. The first fraction obtained, weighing 8.3 g, had bp 50–89° (0.6 mm) and was composed of mostly benzene, phenol (37.7%), allyl phenyl ether (16%), and an unidentified alcohol, as determined by vpc. The second fraction, weighing 23 g, had bp 89–185° (0.6 mm). This fraction contained the diene VI and triphenylphosphine. The solution was seeded and cooled and the phosphine was removed by filtration. After recrystallization from ethanol, 4.2 g (7.6%) of triphenylphosphine was obtained and identified by a mixture melting point with an authentic sample. The filtrate was distilled under reduced pressure giving the butadiene VI, bp 120–122° (0.08 mm), which weighed 12.2 g or 25.5% of the theoretical amount. The nmr spectrum (CCl_4) showed bands at τ 2.9 (m, 10), 4.1 ppm (m, 4). The infrared spectrum was consistent with the structure assigned.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.34. Found: C, 86.33; H, 6.53.

Hydrogenation of 1-Phenoxy-4-phenylbutadiene (VI).—Several attempts were made to hydrogenate the diene VI, but they failed owing to catalyst poisoning by the presence of trace amounts of codistilled triphenylphosphine. All fractions containing the diene were combined and diluted with anhydrous ether, and 10 ml of methyl iodide was then added slowly with stirring. The triphenylphosphine came out of solution as triphenylmethylphosphonium iodide, which was identified by mixture melting point. After cooling, the salt was removed by filtration and the ether was removed by distillation. The residue was vacuum distilled yielding the diene VI, bp 114–120° (0.07 mm). The fraction boiling from 117 to 120° (0.70 g) was hydrogenated using Adams catalyst (PtO_2) with anhydrous ethanol as a solvent. An essentially quantitative uptake of 2 mol of hydrogen per mole of compound was obtained. The solution was filtered and the ethanol was evaporated. The remaining liquid was distilled at reduced pressure yielding 0.38 g of pure 1-phenoxy-4-phenylbutane: bp 113° (0.1 mm); $n^{24}D$ 1.5506 (lit.[8] bp 144–146° (1 mm); $n^{24}D$ 1.5504).

1,2-Epoxy-3(2-formylphenoxy)propane (X).—The sodium salt of salicylaldehyde 28.8 g (0.2 mol) and 300 ml of freshly distilled epichlorohydrin were allowed to react at 118° for 24 hr. After filtering the mixture, the epichlorohydrin was removed by distillation under vacuum until the temperature rose to 60° (1 mm). The residue was short-path distilled giving 31 g of the epoxide X, bp 118–120° (0.25 mm) (lit.[14] bp 118° (0.5 mm)) which was shown to be 93% pure by vpc for an 80% yield. The nmr spectrum (neat) showed signals at δ 2.5 (m, 2), 3.1 (m, 1), 4.1 (m, 2), 6.8–7.8 (m, 4, aromatic), and 10.3 ppm (S, 1, CHO).

2-Hydroxy-3(2-formylphenoxy)propyltriphenylphosphonium Bromide (XII).—Triphenylphosphine hydrobromide[15] (XI) 34.5 g (0.1 mol) and 20 g (0.1 mol) of 1,2-epoxy-3(2-formylphenoxy)propane (X) were thoroughly mixed in a beaker and allowed to stand overnight. The gummy viscous mixture was dissolved in a minimum amount of chloroform and slowly dropped into anhydrous ether (2 l.) with vigorous stirring. A white salt precipitated. Dissolving and reprecipitation gave 42 g (80%) of the salt XII, mp 198–203°. Recrystallization from acetonitrile gave an analytically pure sample, mp 214°.

Anal. Calcd for $C_{28}H_{26}BrO_3P$: C, 64.50; H, 5.03; Br, 15.33; P, 5.94. Found: C, 64.34; H, 4.89; Br, 15.19; P, 6.01.

The nmr spectrum ($CDCl_3$) showed signals at δ 10.3 (s, 1, CHO), 4.5 (s, 1, OH), 4.6 (m, 5), and 7.0–8.0 ppm (m, 19, aromatic). The ir spectrum showed absorptions at ν^{KBr} 3100, 2700, 1670, 1430, 1380, 1235, 1160, 1100, and 940 cm^{-1}.

Preparation of 1-Benzoxepin (XVII).—Into a 500-ml, two-necked flask fitted with a condenser and a calcium chloride tube was distilled directly 300 ml of absolute alcohol, prepared by the pthalate method.[16] In this was dissolved 0.7 g of sodium metal (0.031 g-atom). When the reaction was complete, 16.5 g of the salt XII (0.032 mol) was added at once. The solution was stirred and refluxed for 9 hr. The mixture was then cooled and filtered in order to remove the precipitated sodium bromide. The ethanol was removed by distillation, and some white crystals were separated. These were removed by filtration and were shown to be triphenylphosphine oxide by comparison with an authentic sample. The remaining liquid was short path distilled under vacuum yielding 2.70 g, shown by glpc analysis to be 25% 1-benzoxepin (XVII) and 72% *o*-allyloxybenzaldehyde (XVIII). Collection of the two major products and analysis by nmr spectroscopy showed one to be 1-benzoxepin (**XVII**) (5% yield as calculated from the vpc analysis), and the other was *o*-allyloxybenzaldehyde (XIII) (40% yield). The nmr spectrum (CCl_4) of the oxepin showed signals at τ 2.50–3.2 (m, 4, benzenoid), 3.37 (d, 1), 3.79 (m, 1), 4.03 (m, 1), and 4.60 ppm (m, 1). The product XIII was identified by ir and vpc comparison (DEGS, 170°) with an authentic sample.

Reaction of 1,2-Epoxy-3-(2-formylphenoxy)propane with Triphenylphosphine.—To a solution of 5.3 g of the epoxide (XIII, 0.0296 mol) in 50 ml of dry dimethylformamide in a 100-ml flask was added 7.8 g (0.0298 mol) of triphenylphosphine. The flask was fitted with a reflux condenser and a drying tube and was placed in a silicone oil bath at 110° for 13 hr. After this time the mixture was poured into 150 ml of water, and the aqueous mixture was extracted with five 50-ml portions of ether. The combined ether layers were extracted with two 25-ml portions of water. The ether was dried over magnesium sulfate and distilled. Vacuum distillation of the residue gave 3.0 g of a material, bp 80–120° (1 mm). Vpc analysis of the mixture (20% DEGS, 170°) showed that 86% of the product was *o*-allyloxybenzaldehyde (XIII), by comparison with an authentic sample, with no 1-benzoxepin being formed. Yield of the compound XIII was 2.58 g (54%).

(11) All melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Nmr spectra were obtained on a Varian A60-A spectrometer with a tetramethylsilane standard. Microanalyses were done by Micro Analysis, Inc., Wilmington, Del.

(12) Obtained from Metal and Thermit Co., Rahway, N. J.

(13) Prepared according to P. Pfeiffer and K. Bauer, *Ber.*, **80**, 7 (1947).

(14) O. Stephenson, *J. Chem. Soc.*, 1571 (1954).

(15) M. Akkar and F. Jellinck, *Rec. Trav. Chim. Pays-Bas*, **86**, 275 (1967).

(16) R. Adams and J. Johnson, "Laboratory Experiments in Organic Chemistry," The MacMillan Co., New York, N. Y., 4th ed, 1949, p 409.

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

Acknowledgment.—This investigation was supported in part by a Public Health Service Predoctoral Fellowship (to K. K. L.) for which we are most grateful.

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

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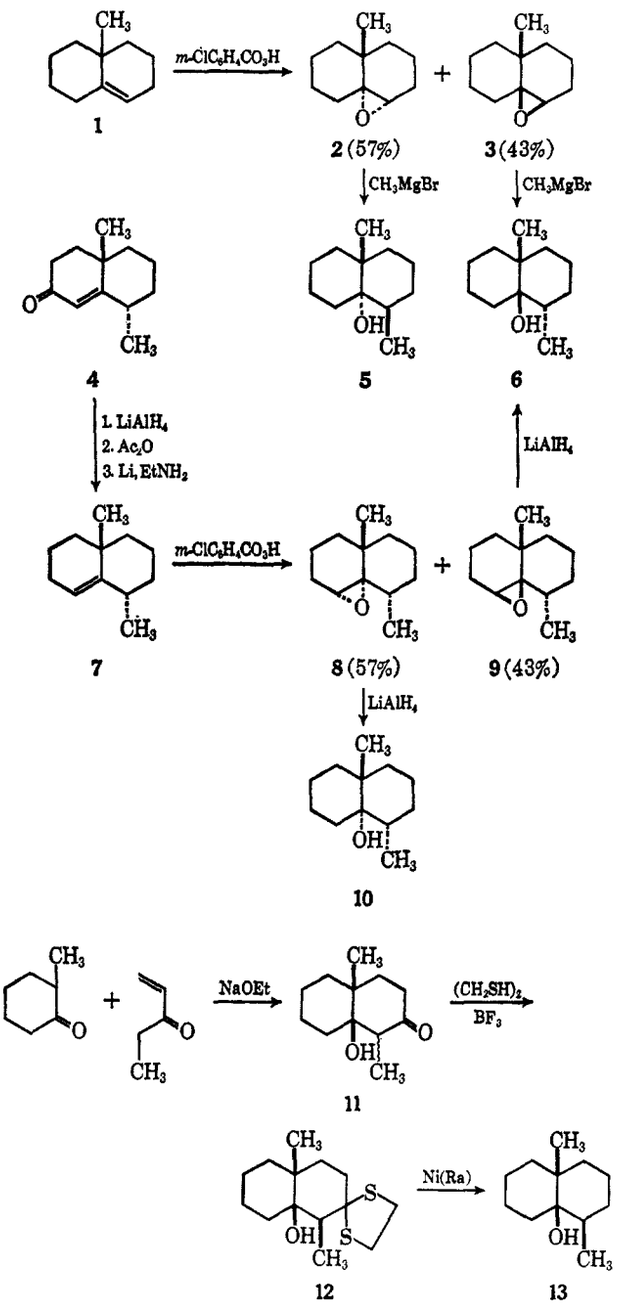
Received February 12, 1968

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

(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).