Experimental Section

1,2,3,4,5,6,7,8,9a,10a-Decahydrophenanthrene-9-carboxylic Acid (IV).—A solution of 6.5 g of propiolic acid, 10 g of bi-1-cyclohexen-1-yl,[7] and a pinch of hydroquinone in 15 ml of benzene was refluxed for 12 hr. On cooling, 8.67 g of the adduct was obtained. Two recrystallizations from methanol gave colorless crystals, mp 193–195°.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.30; H, 8.80.

Hydrogenation of IV.—A solution of 1.0 g of IV in ethanol was hydrogenated[8] at 5000 psi over platinum catalyst at room temperature for 3 hr. After recrystallization from ethanol, the product melted at 180–182.5°, alone or admixed with the adduct (I)[5,9] of bi-1-cyclohexen-1-yl and acrylic acid. Infrared spectra of the two samples were identical.

N-Acetyl-9-amino-1,2,3,4,5,6,7,8,9,9a,10,10a-dodecahydrophenanthrene (VI). A. From the Nitroethylene Adduct (V).—A solution of 1.0 g of the nitroethylene adduct (V)[10] in ethanol was hydrogenated with 0.2 g of platinum oxide at 40 psi for 24 hr. The solution was filtered and concentrated, and the residue was taken up in ether and saturated with hydrogen chloride in the cold, precipitating 0.31 g of amine hydrochloride. Acetylation with acetic anhydride–pyridine gave the amide (VI), mp 197–199° after recrystallization from methanol.

Anal. Calcd for $C_{15}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.67; H, 10.26; N, 5.65.

B. From the Acrylic Acid Adduct (I).—To a solution of 6.42 g of I in 450 ml of 50% aqueous acetone at 0° was added 3.25 g of triethylamine and 4.0 g of ethyl chloroformate. After stirring the mixture for 30 min at 0°, sodium azide (2.75 g) in 15 ml of water was added dropwise, and stirring continued 1 hr. The mixture was poured into 6 l. of water and extracted with ether, and the extracts were dried and concentrated. The residue was taken up in 50 ml of toluene and heated at 100° until the evolution of gas was complete. After removal of the toluene at reduced pressure, the residue was treated with 50 ml of 20% hydrochloric acid and refluxed 12 hr. The mixture was evaporated to dryness, taken up in water, made alkaline with 40% sodium hydroxide, and extracted with ether. Hydrogen chloride was bubbled into the dried ether solution to precipitate the hydrochloride (1.17 g). Acetylated as above, it furnished the amide, mp 197–199°, shown identical with that obtained in part A by comparison of infrared spectra and mixture melting point determination.

C. From the Methyl Vinyl Ketone Adduct.—The adduct[2] (0.6 g) was converted to the oxime by heating 4 hr with 0.6 g of hydroxylamine hydrochloride, 5 ml of pyridine, and 5 ml of ethanol. The solution was decanted from precipitated salts and deposited the oxime (0.3 g), mp 201–203°, on cooling.

Anal. Calcd for $C_{15}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.70; H, 10.20; N, 5.44.

A chloroform solution of 1.0 g of the oxime was cooled in ice and treated with 1.25 g of phosphorus pentachloride in small portions. The solvent was removed in a stream of nitrogen and the residue decomposed with ice water, yielding 0.63 g of amide. Recrystallized from methanol, it melted at 197–199°, alone or admixed with the amide from part A.

(7) D. Ginsburg and D. S. Greidinger, *J. Org. Chem.*, **22**, 1406 (1957).

(8) We are grateful to Dr. B. Franko and Mr. W. McCarthy of the F. M. C. Corp., Princeton, N. J., for their aid in carrying out this hydrogenation.

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Δ-Terpineol

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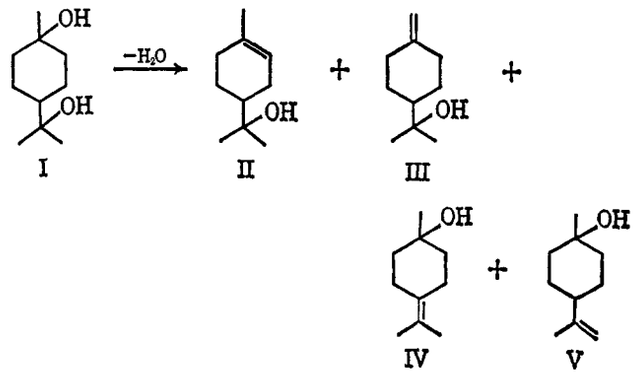
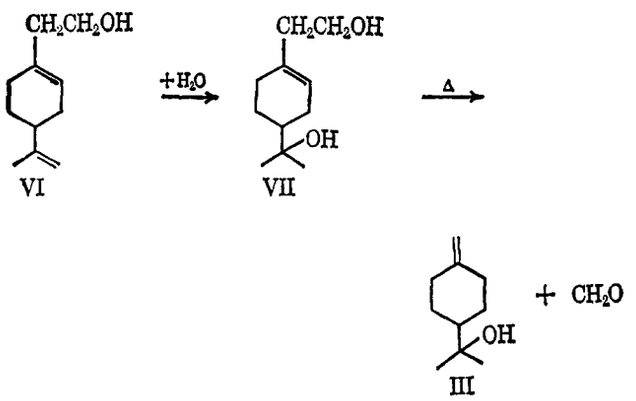
The formation of Δ-terpineol is anticipated as one of the dehydration products of terpin hydrate. This compound, however, has neither been prepared synthetically nor has it been reported as being present in nature. Conventional synthetic approaches in these laboratories toward the synthesis of III, *i.e.*, ionic elimination reactions on appropriate precursors, resulted only in the detection of II, IV, and V.



We have found that the pyrolysis of dipenol (1-[4-(1-hydroxy-1-methylethyl)cyclohexene]-2-ethanol) (VII), however, leads to the following. The structure of



Δ-terpineol (III) is firmly supported by the infrared and nmr spectra shown, respectively, in Figures 1 and 2. The salient infrared characteristics, *i.e.*, tertiary hydroxyl, 8.6 μ, and the exocyclic double bond, 11.30 and 6.05 μ, support the moieties requisite to the compound's structural identity. Nmr assignments are indicated on spectrum II. The mass spectrum (measured on a CEC 103-C mass spectrometer) indicated the proper molecular weight (154) with the base peak of 136 (M − 18), a characteristic phenomenon of tertiary terpenic alcohols.

The obtention of pure III aided us in establishing that Δ-terpineol is, in fact, present in commercial terpineol (*vide infra*) obtained from the dehydration of terpin hydrate in less than 0.5% concentration.

Experimental Section

Dipenol (25 g) was stirred with 100 ml of 25% sulfuric acid at 60° for 10 hr. The product was washed with two 100-ml portions of water and, after stirring with 100 ml of 25% sodium hydroxide for 1 hr at 25°, was washed with sodium bicarbonate until neutral; 8 g of the hydrated dipenol, VII, was obtained and passed through an 18-in. length of 1/8-in. stainless steel tubing heated to 350°. This pyrolysate was subjected to a preparative gas chromatograph fitted with an 8-ft, 3/8-in.-o.d. column packed with 20% Carbowax 20M on silane-treated Celite, maintained at 150°, with a helium flow rate of 200 cc/min. The peak ultimately corresponding to Δ-terpineol was trapped and *ca.* 1 g of the latter was passed through a column containing 20% SE30 on silane-treated Celite at 160° at a flow rate of 200 cc/min. Pure III (0.5 g) was obtained.

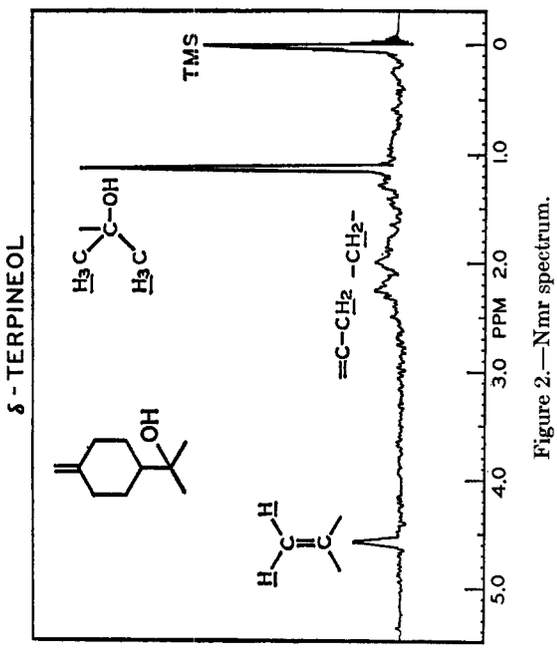


Figure 2.—Nmr spectrum.

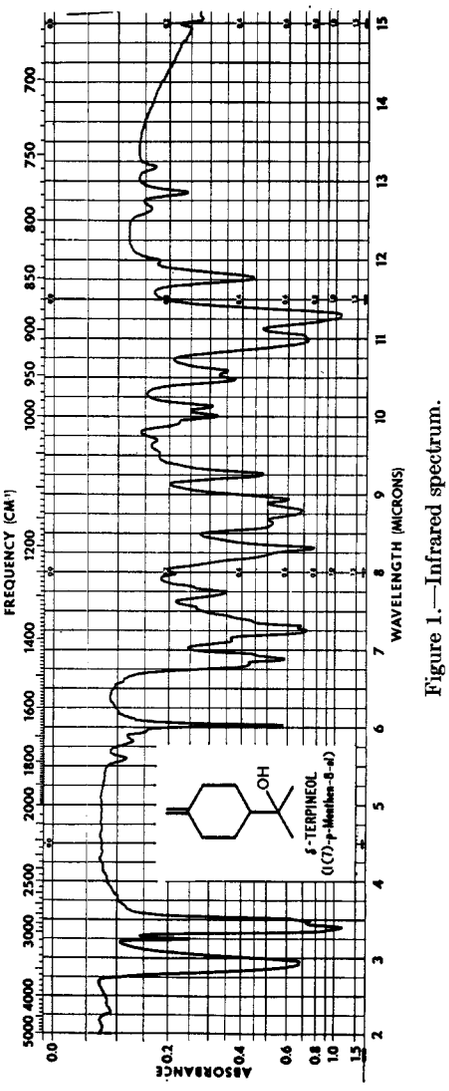


Figure 1.—Infrared spectrum.

Commercial terpineol was examined for Δ-terpineol content using a preparative gas chromatograph fitted with an 8-ft, $^3/_4$-in.-o.d. column containing Carbowax 20M on silane-treated Celite at 155° at a flow rate of 600 ml/min. *Ca.* 50 ml of the sample was passed through using 1-ml injections. That portion of the eluent was trapped where the Δ-terpineol was expected to elute; this is in the area just prior to where *trans*-β-terpineol emerges. *Ca.* 5 ml of material was thus obtained. Repeated injections, using identical experimental parameters, afforded 1 ml of material which, when passed through an 8-ft, $^3/_8$-in.-o.d. column containing 20% Carbowax 20M on silane-treated Celite at 150° with a flow rate of 200 ml/min, afforded 0.1 ml of material. Analysis on a 10-ft, $^1/_4$-in.-o.d., $^3/_{16}$-in.-i.d. column packed with 20% Carbowax 20M on silane-treated Celite at 150° at a flow rate of 60 cc/min gave a small amount of material consisting of *ca.* 60% Δ-terpineol and 40% *trans*-β-terpineol. Since it was fruitless to continue the attempted isolation of pure Δ-terpineol in the presence of β-terpineol, this method of isolating Δ-terpineol was abandoned. Calculations indicate that less than one-half of 1% of Δ-terpineol is present in commercial terpineol.

Pinacol Deamination Rearrangement of Dihydrosphingosine[1]

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The formation of an insoluble precipitate during the degradation of dihydrosphingosine with periodic acid was first observed by Carter and associates[2] in their classical studies of long-chain bases. A similar precipitate was formed when the radioactive long-chain bases from rat brain were degraded with periodate in aqueous methanol.[3] The use of various solvents during the oxidation appeared to have no effect on the formation of this precipitate. It was thought that quantitative degradation of the bases could be achieved if they were converted to the corresponding triols prior to treatment with periodate. The rearrangement of vicinal hydroxyamino compounds upon deamination with nitrous acid has been well documented,[4,5] but the nature and extent of a rearrangement in dihydrosphingosine has not been examined. The nitrite deamination of dihydrosphingosine in glacial acetic acid yielded <10% of 1,2,3-trihydroxyoctadecane. Although it was found, as this investigation was in progress, that dihydrosphingosine was easily degraded by lead tetraacetate in benzene–glacial acetic acid,[6] the study of the deamination of dihydrosphingosine was continued to determine the identity of the compounds formed in this reaction.

The deamination of the base was effected with $NaNO_2$ in glacial acetic acid and the products of the reaction

(1) This investigation was supported in part by Public Health Service Research Grant No. 03191-05 from the National Institute of Neurological Diseases and Blindness.

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(3) B. Weiss, *ibid.*, **238**, 1953 (1963).

(4) Y. Pocker, in "Molecular Rearrangements," P. De Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 1.

(5) P. W. Kent, and M. W. Whitehouse, "Biochemistry of the Aminosugars," Academic Press Inc., New York, N. Y., 1955, p 213.

(6) B. Weiss, *Biochemistry*, **4**, 1576 (1965).