then removed. The acrylates were then distilled under vacuum, 0.3% hydroquinone was added, and the product was stored in a freezer until used. The following acrylates were prepared: (*R*)-(−)-menthyl acrylate, 85% yield, bp 102–104° (11 mm), $[\alpha]^{23}D$ −77.0° (*c* 8.4, dioxane), lit.[8] bp 78–80° (5 mm), $[\alpha]^{28}D$ −80.2° (*c* 10, dioxane); (*S*)-(+)-2-octyl acrylate, 78% yield, bp 73–75° (5 mm), $[\alpha]^{25}D$ +10.4° (*c* 3.3, dioxane), lit.[9] bp 79° (5.4 mm) for racemic ester; (*S*)-(+)-2-butyl acrylate, 73% yield, bp 54–56° (45 mm), $[\alpha]^{25}D$ +23.5° (*c* 2.0, dioxane), lit.[9] bp 60° for racemic ester (50 mm). All rotations were taken with a Gaertner polarimeter.

Reaction between Cyclopentadiene and Optically Active Acrylates.—To 0.05 mole of acrylate was added with stirring 0.06 mole of freshly distilled 1,3-cyclopentadiene. The reaction flask was immersed in a large water bath maintained at room temperature and allowed to sit for 6 hr. Yields were determined by diluting the reaction solution to a known volume with chloroform and comparing peak areas of gas chromatograms with that of a standard solution. The standard solutions were prepared by dilution of adducts previously isolated by fractional vacuum distillation. Boiling points of the ester adducts (*endo* and *exo* isomers inseparable without spinning column or preparative gc) are 1-menthyl, 134° (0.5 mm); 2-octyl, 112–114° (0.5 mm); 2-butyl, 72° (0.5 mm). Glpc measurements were made on a Perkin-Elmer Model 810 gas chromatograph equipped with hydrogen flame detector. Separation of *endo–exo* isomers was possible using a 6 ft × 1/8 in. column of 10% silicone DC-710 on 80–100 mesh Chromosorb W at temperatures of 200, 190, and 150°, respectively.

Lewis Acid Catalyzed Reaction between Cyclopentadiene and Optically Active Acrylates.—To a stirred solution of 0.06 mole of stannic chloride in 20 ml of dry toluene cooled to 3° was added dropwise a solution of 0.06 mole of acrylate in 30 ml of dry toluene. The temperature never rose above 8°. A change in color from clear to light yellow was noted. Then 0.10 mole of freshly distilled 1,3-cyclopentadiene in 40 ml of anhydrous toluene was added dropwise over 15 min so that the temperature never rose above 8°. The solution changed in color from yellow to red as the addition proceeded. The solution was allowed to react while stirred at 4° for 0.5 hr before 50 ml of dilute hydrochloric acid was added to hydrolyze the complex. The toluene layer was separated, washed with water, dried over sodium sulfate, and subjected to glpc analysis. The toluene was then distilled and the resulting solution was treated with lithium aluminum hydride without further isolation.

Reduction of Cyclopentadiene–Acrylate Adducts.—The products of the catalytic and noncatalytic reactions were taken up in 100 ml of anhydrous ether and added dropwise to a rapidly stirred solution of 2.5 g of lithium aluminum hydride (large excess) and stirred for 10 hr. The excess hydride was decomposed, the ether layer was separated and dried over sodium sulfate, and the ether was distilled. The resulting solution of isomeric bicyclo[2.2.1]-hept-2-enecarbinols was separated by preparative gas chromatography using an Aerograph Autoprep A-700 with a 3/8 in. × 10 ft 30% Carbowax 20M on 60–80 mesh Chromosorb W column maintained at 185°, He flow of 180 cc/min. The *endo* isomer was preferentially heart-cut for maximum purity and rotation measured in 95% ethanol. The *endo* isomer was characterized by its retention time being identical with the product obtained by reduction of the adduct of cyclopentadiene and acrylic acid (74% *endo*).[10]

(8) C. S. Marvel and Robert L. Frank, *J. Am. Chem. Soc.*, **64**, 1675 (1942).

(9) C. E. Rehberg, W. A. Faucette, and C. H. Fisher, *ibid.*, **66**, 1723 (1944).

(10) C. D. Ver Nooy and C. S. Rondestvedt, Jr., *ibid.*, **77**, 3583 (1955).

1(7)-Terpinen-4-ol

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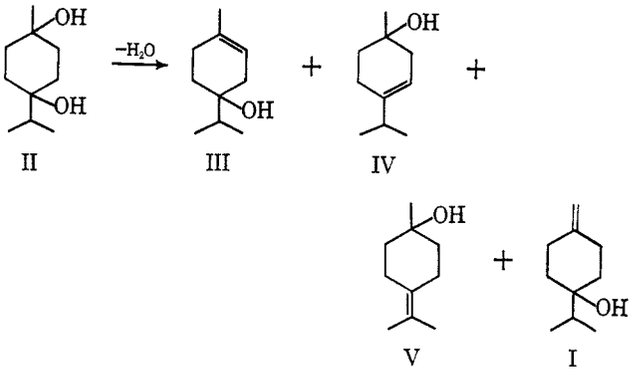
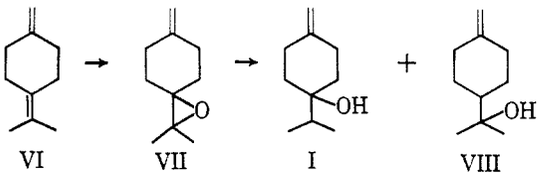
1(7)-Terpinen-4-ol (I) was previously unknown, but has been predicted to occur upon partial dehydration of terpinene terpin (II).[1] 1-Terpinen-4-ol (III), 3-terpinen-1-ol (IV), and 4(8)-terpinen-1-ol (γ-terpineol) (V) have been well documented.[1]



We were able to isolate the 1(7)-terpinen-4-ol from the dehydration products of terpinene terpin (approximately 0.3%) in an impure form and have also prepared it synthetically. We have also observed a peak in a capillary gas chromatogram of commercial terpineol that corresponds in elution time to 1(7)-terpinen-4-ol.

The attempted syntheses of 1(7)-terpinen-4-ol by conventional methods were unsuccessful owing to migration of the exocyclic double bond into the more stable internal position. The 1(7)-terpinen-4-ol was obtained from 1(7),4(8)-*p*-menthadiene VI[2] by conversion to the corresponding epoxide (VIII) which was reduced with lithium aluminum hydride to a mixture of 1(7)-terpinen-4-ol (I) and δ-terpinenol (VIII).[3] The exocyclic double bond was not epoxidized.



Proof of Structure.—The infrared spectrum (Figure 1) clearly shows the presence of the exocyclic double bond at 11.3 and 6.05 μ. The splitting pattern at 7.25 confirms the presence of a *gem*-dimethyl group.

The nmr spectrum (Figure 2) is self-explanatory.

Approximately 100 mg. of 1(7)-terpinen-4-ol was hydrogenated at atmospheric pressure using a 10% palladium-on-charcoal catalyst. A rearrangement to 1-terpinen-4-ol was observed prior to hydrogen uptake (indicating the facile isomerization of the exocyclic double bond to the internal position). Subsequently the *cis*- and *trans*-dihydroterpinenols were obtained. These were separated by gas chromatography and characterized by infrared analysis.

The mass spectrum of the 1(7)-terpinen-4-ol (I) indicated a molecular weight of 154 ($C_{10}H_{18}O$).

(1) J. L. Simonson and L. M. Owen, "The Terpenes," Vol. I, Cambridge University Press, London, 1947, p 274.

(2) B. M. Mitzner, E. T. Theimer, and S. Lemberg, *Can. J. Chem.*, **41**, 2097 (1963).

(3) B. M. Mitzner and S. Lemberg, *J. Org. Chem.*, **31**, 2022 (1966).

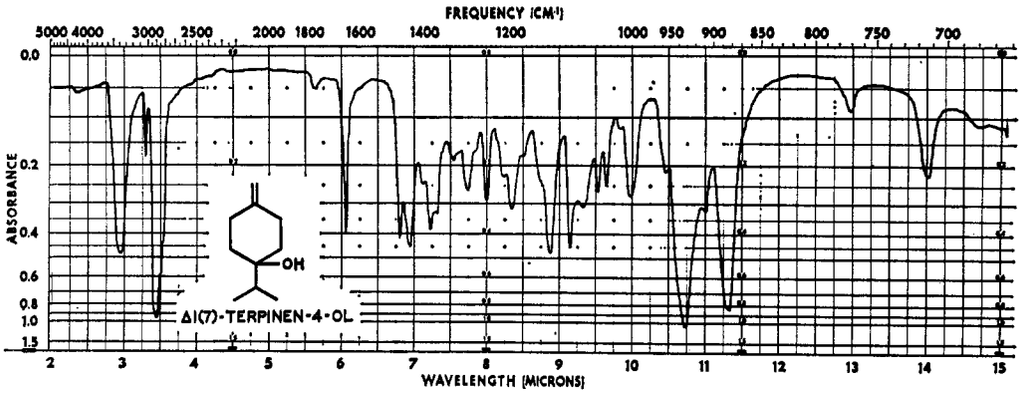


Figure 1.

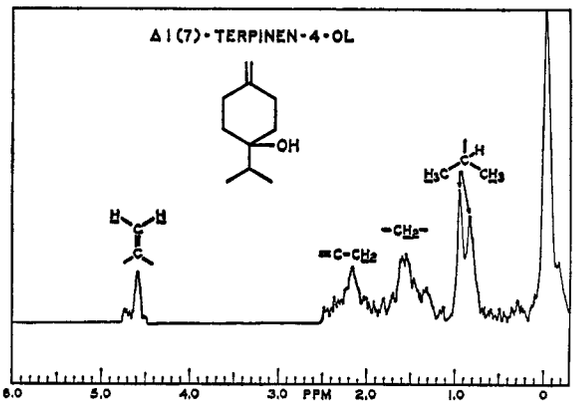


Figure 2.

Experimental Section

Approximately 7 g of 1(7),4(8)-*p*-methadiene was prepared as previously described.[2] This was placed into a 250-ml reaction flask equipped with a stirrer, thermometer, reflux condenser, dropping funnel, and Dry Ice bath. Anhydrous sodium acetate (8.2 g) and 40 ml of methylene chloride were added. The mixture was cooled to 0° and 10 g of 40% peracetic acid was added at 0–5° over a period of 2 hr. Stirring was continued at 0–5° for 3 hr. Water (30 ml) was added to the reaction mixture, and stirring was continued for 1 hr. The organic layer was washed with sodium bicarbonate and salt solutions and dried; the solvent was evaporated. The resulting 8 g of oil was then added (over a period of 1.25 hr) to 38 g of lithium aluminum hydride in 38 g of tetrahydrofuran in a 250-ml reaction flask, equipped with a stirrer, thermometer, reflux condenser, nitrogen purge, dropping funnel, and heating mantle.

The reaction mixture was then heated at reflux for 3 hr and cooled to 0–5°, and 20 ml of H_2O was added over a 1-hr period.

The product, isolated by extraction and solvent recovery, was passed through a preparative gas chromatograph which consisted of a 10 ft × 3/8 in. o.d. column containing 20% Carbowax 20M on silane-treated Celite at 150° with a helium flow rate of 250 cc/min. Successive 100-mg injections were made until 400 mg of 1(7)-terpinen-4-ol was obtained. Approximately 100 mg of δ terpinenol was also obtained which elutes after the 1(7)-terpinen-4-ol.

The product was then passed through a preparative gas chromatograph which consisted of a 10 ft × 0.25 in. o.d. column containing 20% Se-30 on 60–80 mesh silane-treated Chromosorb W, at 125° with a helium flow rate of 100 cc/min. Repeated 10-μl injections were employed and 200 mg of very pure product was thus obtained.

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The Shielding Effect of the Nitro Group

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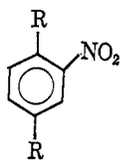
In recent years, the long-range shielding effect of the nitro group has been observed in *t*-butylnitrocyclohexanes,[1] nitrotestosterones,[2] nitrocholestenes,[3] nitroporphyrins,[4] nitronaphthalenes,[5] and nitromethylbenzenes.[6] We have examined the nmr spectra of the 2-nitro derivatives of *p*-xylene (**2**) and of the *p*-diethyl- (**3**), *p*-diisopropyl- (**4**), and *p*-di-*t*-butylbenzenes (**5**).



1, R = H
2, R = CH_3
3, R = CH_2CH_3
4, R = $CH(CH_3)_2$
5, R = $C(CH_3)_3$

In Table I there is presented the difference in chemical shift (downfield) (determined in two inert solvents) of the *ortho* proton in the nitro compound relative to the corresponding proton in the parent hydrocarbon. Also presented is the degree of twist φ of the nitro group from coplanarity with the aromatic ring as calculated by Wepster[7] from ultraviolet data. The corresponding shift difference of the *meta* and *para* protons is also tabulated. The observed signals in the nitro compounds are broad singlets (two unre-

(1) A. Huitric and W. F. Trager, *J. Org. Chem.*, **27**, 1926 (1962).
(2) K. Tori and K. Kuriyama, *Tetrahedron Letters*, 3939 (1964).
(3) J. McKenna, J. M. McKenna, and P. B. Smith, *Tetrahedron*, **21**, 2983 (1965).
(4) R. Bonnett and G. F. Stephenson, *J. Org. Chem.*, **30**, 2791 (1965).
(5) P. R. Wells, *Australian J. Chem.*, **17**, 967 (1964).
(6) I. Yamaguchi, *Mol. Phys.*, **6**, 105 (1963).
(7) B. M. Wepster, "Progress in Stereochemistry," W. Klyne and P. B. D. de la Mare, Ed., Academic Press, Inc., New York, N. Y., 1958, p 110. The angles are calculated from the equation $\epsilon/\epsilon_0 = \cos^2 \varphi$. ϵ is the extinction of the substituted nitro compound and ϵ_0 is the value for nitrobenzene.