positive. Recrystallization did not sharpen the melting point of this product which was concluded to be **anthracene 9-isothiocyanate.**

Anal. Calcd for $C_{15}H_9NS$: C, 76.7; H, 3.8; N, 5.96. Found: C, 76.0; H, 4.1; N, 5.95.

Asymmetric Induction in a 1,4-Cycloaddition Reaction. Influence of Variation of Configuration of the Asymmetric Center

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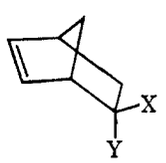
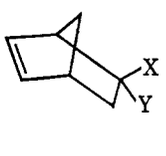
Partial asymmetric syntheses have been achieved in 1,4-cycloaddition reactions.[1-3] With the application of Lewis acid catalysis to promote reaction rate acceleration came the discovery of greatly enhanced asymmetric synthesis. Walborsky, Barash, and Davis presented an effective rationale for the steric course of a particular cycloaddition reaction and examined solvent, temperature, and catalyst effects.[2]

We wish to report our investigation of a system well suited for the study of the effect of variation of substituents about the influencing asymmetric center. This system consists of the reaction between 1,3-cyclopentadiene and acrylic acid esters. The four possible products are represented by I and II. In



Ia, X = H; Y = COOR
b, X = COOR; Y = H



IIa, X = H; Y = COOR
b, X = COOR; Y = H

particular the reaction of esters derived from (*R*)-(−)-menthol, (*S*)-(+)-2-octanol, and (*S*)-(+)-2-butanol were studied. Both catalytic and noncatalytic additions were run. Anhydrous stannic chloride was employed as the Lewis acid catalyst because homogeneous reaction solutions were obtained. The ester adducts were reduced with lithium aluminum hydride to the corresponding alcohols and their rotations were measured. The absolute rotations and configurations of the alcohols derived from the reduction of esters I and II have been assigned.[4] The alcohol obtained from Ia has the *S* configuration and in 95% alcohol the absolute $[\alpha]D$ −76.6°. Our results are summarized in Table I.

Reactions with stannic chloride catalysis were run at 4–8° because at much lower temperatures the catalytic effect on enhancement of optical purity appears to diminish. Walborsky[2] obtained a 75% optical yield for the reaction of 1,3-butadiene with (−)-dimenthyl fumarate using $SnCl_4$ catalysis in toluene at 25°, but at −70° the catalyst was ineffective.

TABLE I

REACTION OF CYCLOPENTADIENE WITH CH_2=CHCOOR

R	Solvent	Yield,[a] %	*endo*[a] %	*endo*[a] $[\alpha]^{25}D$, deg	Optical yield, %
(*R*)-(−)-Menthyl	0.6 *M* in toluene[b] and 1 equiv of $SnCl_4$	76	89	+31.4	41
(*S*)-(+)-2-Octyl		78	92	−11.1	15
(*S*)-(+)-2-Butyl		77	94	−18.4	24
(*R*)-(−)-Menthyl	Neat[c]	77	69	+6.1	8[d]
(*S*)-(+)-2-Octyl	Neat	77	71	−2.3	3
(*S*)-(+)-2-Butyl	Neat	70	74	−4.2	5

[a] Determined by glpc. [b] Temperature maintained at 4–8° for 0.5 hr. [c] Temperature maintained at 24–26° for 6 hr. [d] Agrees with ref 3.

It is noted that for a given acrylate there is a large difference in the amount of *endo* isomer formed in the catalytic and noncatalytic reactions. This gives further support to the contention[2] that the bulky Lewis acid catalyst participates in close coordination with the carboxyl group during cyclization as its steric requirement would result in a higher *endo* yield.[5a] Sauer and Kredel[5b] have reported similar results in a study of solvent and catalyst effects on the *endo–exo* product ratio of the (*R*)-(−)-menthyl acrylate reaction.

It is also seen that the (*R*)-acrylate gives an adduct with excess *R* configuration, and (*S*)-acrylates give adducts of excess *S* configuration. If one attempts to predict the configuration of the adducts from a consideration of diene steric approach control exerted by a dienophile of Cram–Prelog design, it is found that the (*R*)-acrylate should yield an excess of *S* isomer and the (*S*)-acrylate an excess of *R*. Walborsky[2] postulates that the (*R*)-(−)-methyl group exerts a steric control force in a manner deviating from that predicted because of the steric influence of substituents on the menthyl moiety which are not directly attached to the asymmetric carbon. The (*R*)-(−)-menthyl group, he argues, behaves as if the groups about the asymmetric carbon were of *S* configuration. Our data for the (*R*)-acrylate reactions are thus seen to agree with similar results obtained by Walborsky.[2] It is not feasible from the available evidence to rationalize the unexpected observations of the (*S*)-acrylates.

Experimental Section

Materials.—*l*-Menthol, *d*-2-octanol, and acrylyl chloride were purchased from Aldrich Chemical Co. Rotations of the alcohols conformed with literature values.[6] Optically pure *d*-2-butanol was prepared by brucine resolution of the acid phthalate.[7] Cyclopentadiene was freshly distilled before each use. Anhydrous stannic chloride employed was Baker Analyzed reagent. Boiling points are uncorrected.

Preparation of the Optically Active Acrylates.—To an ice-cooled solution of 19.0 g (0.21 mole) of acrylyl chloride and 21.3 g (0.21 mole) of triethylamine in 100 ml of anhydrous ether was added dropwise with stirring to a solution of 0.20 mole of alcohol in 100 ml of anhydrous ether. Triethylammonium hydrochloride precipitated. The addition was controlled to maintain mild reflux and then heated at reflux for an additional 0.5 hr. The ether solution was filtered from the hydrochloride precipitate and washed with 10% aqueous sodium bicarbonate. The ether layer was dried over anhydrous sodium sulfate and the ether was

(1) A. Korolev and V. Mur, *Dokl. Akad. Nauk SSSR*, **59**, 251 (1949).
(2) H. M. Walborsky, L. Barash, and T. C. Davis, *Tetrahedron*, **19**, 2333 (1963).
(3) J. Sauer and J. Kredel, *Angew. Chem. Intern. Ed. Engl.*, **4**, 989 (1965).
(4) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Am. Chem. Soc.*, **83**, 3989 (1961).
(5) (a) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961); (b) J. Sauer and K. Kredel, *Tetrahedron Letters*, **7**, 731 (1966).
(6) "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1964.
(7) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

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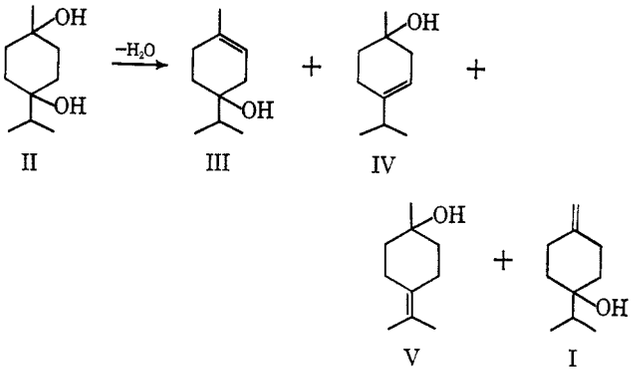
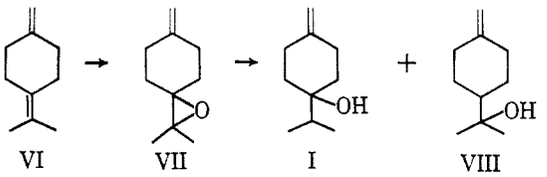
1(7)-Terpinen-4-ol (I) was previously unknown, but has been predicted to occur upon partial dehydration of terpinene terpin (II).[1] 1-Terpinen-4-ol (III), 3-terpinen-1-ol (IV), and 4(8)-terpinen-1-ol (γ-terpineol) (V) have been well documented.[1]



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).