Pseudo-first-order rate behavior was checked by the differential method.[13]

Kinetic Analysis of Data.—Conventional techniques for determining rate constants for first-order reactions require a measurement of the reaction variable at "infinite time," *i.e.*, after several half-lives. This infinite time reading is then used in the calculation of all data points so that the accuracy of the result depends almost entirely on the accuracy of this single measurement.

Swinbourne[14] has shown that this objection can be readily overcome. In order to take advantage of this little used but elegant method, a computer program was developed for the IBM 1620 which carries out a least-squares analysis of the data obtained in accordance with the Swinbourne method. Results were checked by comparison with conventional techniques using the infinite time technique.

Reactant Stability and Product Identification.—Solutions of the diols in the reaction medium lacking the oxidant were found to be stable throughout the reaction lifetime, ruling out the possibility of appreciable pinacol rearrangement.

The only products obtained from the oxidation were the expected acetophenone from I and *n*-butyrophenone from II, identified as their 2,4-dinitrophenylhydrazones by comparison with authentic samples.

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[13] K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 15.

[14] E. S. Swinbourne, *J. Chem. Soc.*, 2371 (1960).

Stereochemistry of Diels–Alder Adducts of Bi-1-cyclohexen-1-yl

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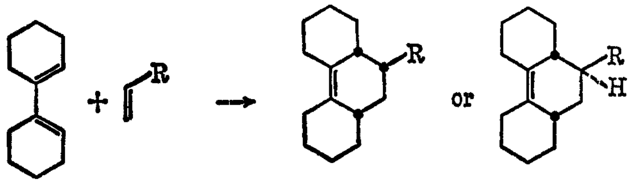
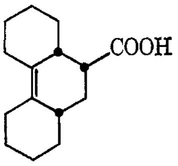
The most direct synthetic route to simple derivatives of the hydrophenanthrene skeleton involves Diels–Alder addition of dienophiles to bi-1-cyclohexen-1-yl.[2] When the dienophile is a monosubstituted olefin, two stereoisomeric adducts are possible, one resulting from *endo* orientation of the addends and one from *exo* addition.



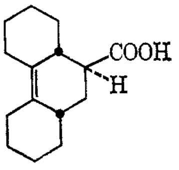
endo *exo*

Many of the reported additions do lead to a mixture of both isomeric adducts, whereas in other cases apparently only one isomer is formed. Alder's rule[3] of "maximum overlap of unsaturation" leads to the prediction that the *endo* isomer should predominate, although the possibility that steric interference in the transition state might favor *exo* addition[4] cannot be ruled out.

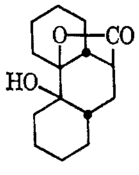
When this investigation was begun, no evidence was available for the configuration of any adducts of bi-1-cyclohexen-1-yl. Recently Christol and Levy[5] offered arguments favoring the *endo* configuration for the acrylic acid adduct (I). Diels–Alder addition furnishes a single product, mp 185°, although the epimeric acid (II), mp 130°, may be obtained by alkaline isomerization of I and its derivatives. The French workers oxidized both acids with osmium tetroxide; adduct I gave a nonlactonizable dihydroxy-acid, while II afforded, in addition to an isomeric dihydroxy acid, a 5% yield of the hydroxy lactone III. On the assumption that osmium tetroxide attacks exclusively from the less hindered side of the double bond, the 185° adduct was assigned the all-*cis* configuration I.



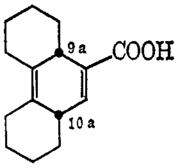
I



II



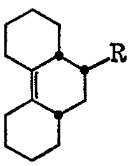
III



IV

To provide independent confirmation for this assignment, we have now been able to prepare acid I by partial hydrogenation of the propiolic acid adduct IV. At 5000 psi, over platinum at room temperature (conditions chosen to favor rapid, stereospecific reduction[6]), IV was hydrogenated cleanly to the acrylic acid adduct I. Since hydrogenation under these conditions should result in addition of hydrogen from the less hindered side of the double bond, in this case *cis* to the hydrogens at 9a and 10a, the product may be assigned the all-*cis* configuration.

Adducts in which the 9-substituent is cyano, formyl, carbomethoxy, carboxamido, and acetyl have all been related to the acrylic acid adduct I.[2,5] We have extended these stereochemical correlations to the nitroethylene adduct V. Reduction of V and acetylation gave amide VI. The same amide was produced by Beckmann rearrangement of the oxime (VII) of the methyl vinyl ketone adduct, as well as by acetylation of the amine formed by Curtius rearrangement of I. Addition of nitroethylene to bi-1-cyclohexen-1-yl is thus another Diels–Alder reaction which gives exclusively *endo* addition.



V, R = NO_2
VI, R = $NHCOCH_3$
VII, R = $C(CH_3)=NOH$

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[1] Acknowledgment is gratefully made to the American Machine and Foundry Co. and to the Proctor and Gamble Co. for fellowships to H. J. Barger, Jr.

[2] E. Bergmann, H. Davies, and R. Pappo, *J. Org. Chem.*, **17**, 1331 (1952).

[3] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

[4] For exceptions to the rule of *endo* addition, see J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

[5] H. Christol and M. Levy, *Bull. Soc. Chim. France*, 3056 (1964).

[6] R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

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 $C_{16}H_{25}NO$: 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 $C_{16}H_{25}NO$: 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.

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(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.

(9) J. A. Dixon and D. D. Neiswender, Jr., *J. Org. Chem.*, **25**, 499 (1960).

(10) N. L. Drake and C. M. Kraebel, *ibid.*, **26**, 41 (1961).

Δ-Terpineol

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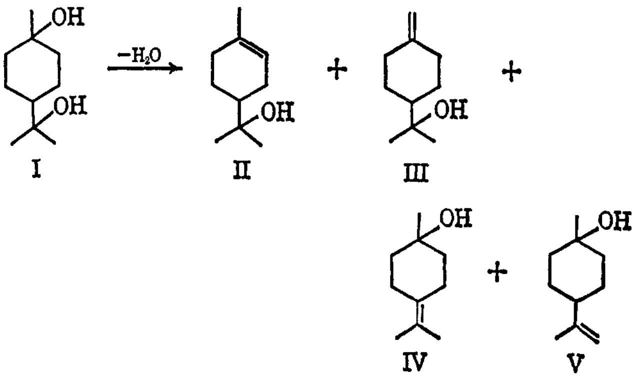
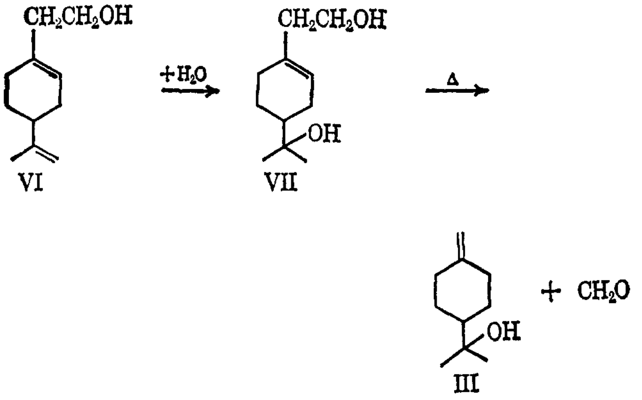
The formation of Δ-terpineol is anticipated as one of the dehydration products of terpin hydrate. This



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.