reaction progressed. As soon as removed, these aliquots were cooled in an ice bath, neutralized with 15% aqueous sodium hydroxide, and extracted thoroughly with ether. The combined organic layers were then washed with saturated brine, and the solvent was removed by evaporation under reduced pressure. The residue was then diluted to a known volume with 95% ethanol, and the amount of 5-hexenyl *p*-nitrobenzenesulfonate was determined by ultraviolet spectroscopy. From these data the time required for 50% reaction was determined in this case to be approximately 40 min. In a similar manner the half-lives for the solvolysis of *n*-hexyl and of 6-heptenyl *p*-nitrobenzenesulfonates were found to be 85 and 100 min., respectively. In 80% formic acid the half-lives of 5-hexenyl and of *n*-hexyl *p*-nitrobenzenesulfonates were found to be 30 and 42 min., respectively.

Acknowledgments.—We wish to thank the U. S. Public Health Service and the National Science Foundation for assisting this study. B. J. wishes to express thanks to the Wellcome Foundation (London) for a travel grant.

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Cationic Cyclizations Involving Olefinic Bonds. III.[1] On the Mechanism of Formation of *trans*-Fused Rings

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RECEIVED DECEMBER 17, 1963

Evidence and arguments have been adduced to support the hypothesis that the 2-Δ^3-butenylcyclohexyl cation (formula D) and related systems will undergo ring closure stereoselectively to form preferentially the *trans*-decalin ring system (formula E). In accordance with this view, the cation D is not involved in the acid-catalyzed cyclization of Δ^3-butenylcyclohexene which, in contrast, gives mainly *cis*-decalin derivatives and is therefore regarded as a concerted protonation–cyclization (Fig. 2). The possible relationship of these considerations to the biosynthesis of polycycloisoprenoids is discussed.

The stereorational theory of Stork[2] and Eschenmoser[3] for the biogenesis of the polycyclotriterpenoids and steroids is based on the premise that the *trans*-fused ring systems are produced by what is in effect a synchronous process[4] initiated by electrophilic attack (*e.g.*, by ^+OH) on an all *trans*-fused polyene as represented in Fig. 1. If the nucleophile Y is an external species, such as the solvent, the cyclization process is interrupted with the formation of two *trans*-fused rings; on the other hand, if Y represents an appropriately juxtaposed olefinic bond in the side chain R, the cyclization process may continue further to give *trans-anti-trans*-fused rings. A corollary to this principle is that a synchronous[4] protonation and cyclization of a monocyclic diene, like Δ^3-butenyl-1-cyclohexene, will produce exclusively a *cis*-fused ring system as depicted in Fig. 2. The cyclization of butenylcyclohexene (Fig. 2, R = H) in a mixture of sulfuric and acetic acid has been examined by Linstead, *et al.*[5] After saponification, the crude *cis-syn*-β-decalol (I, R = H) was isolated in 12.5% yield. (A 25% yield of this decalol was obtained from the precursor of the diene, Δ^3-butenylcyclohexanol, with added acetic anhydride to assist dehydration.) Similarly the homologous diene, produced by dehydration of the tertiary alcohol *in situ*, afforded the *cis*-substance I (R = CH_3)[6] as the only bicyclic product that was identified. Now it is possible that in both of these cases the *cis*-decalin derivative did represent the major cyclization product; however, it was not demonstrated that the total reaction product did not contain significant amounts, or even possibly a preponderance, of the *trans* isomers. Therefore we have repeated the work of Linstead with butenylcyclohexene and, by taking advantage of vapor phase chromatographic techniques, have made a quantitative analysis of the product which in a typical experiment was found to have the following composition (compounds are given in the order of elution); about 16% of starting material, 13% of a cyclic ether (see below), 1–2% of two additional products neither of which was *trans*-Δ^2-octalin, 1.0% of Δ^3-butenylcyclohexanol, 1.8% of an unidentified unsaturated alcohol, 2.8% of an unidentified saturated alcohol which was not identical with any of the β-decalols, and 4.4% of *cis-syn*-2-decalol. The yield of *trans*-2-decalols was less than 0.3%. The remainder of the total reaction product evidently was water soluble (perhaps consisting of glycols or sulfate esters). The major products were separated by preparative vapor phase chromatography and identified with authentic materials by infrared spectroscopic comparison. The ether (see above) is tentatively assigned the structure 2-methyl-5,5-pentamethylenetetrahydrofuran on the basis of the following evidence: (1) the compositional analysis was compatible with the formula $C_{10}H_{18}O$; (2) the infrared spectrum failed to show absorption in the hydroxyl, carbonyl, or olefinic bond region; (3) the n.m.r. spectrum exhibited absorption for one (and only one) proton as a multiplet in the region indicative of the grouping ROCH; (4) the structure is a rational product of hydration, followed by ring closure involving the alcoholic oxygen as the nucleophile.

The possibility that the observation of the formation of a high ratio of *cis*- to *trans*-decalol was due to selective reaction of *trans-syn*-2-decalol (the more likely epimer of *trans* cyclization) to form water-soluble products was disproved by submitting a mixture of *cis-syn*-2-decalol and *trans-syn*-2-decalol to the cycli-

(1) (a) Paper 11 of this series: W. S. Johnson, D. M. Bailey, R. Owyang, R. A. Bell, B. Jaques, and J. K. Crandall, *J. Am. Chem. Soc.*, **86**, 1959 (1964); (b) a preliminary account of the work described in the present paper was reported at the I.U.P.A.C. Meeting in London, July 17, 1963; see W. S. Johnson, *Pure Appl. Chem.*, **7**, 317 (1963).

(2) G. Stork and A. W. Burgstahler, *J. Am. Chem. Soc.*, **77**, 5068 (1955).

(3) A. Eschenmoser, L. Ruzicka, O. Jeger, and D. Arigoni, *Helv. Chim. Acta*, **38**, 1890 (1955); see also L. Ruzicka in "Perspectives in Organic Chemistry," A. Todd, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, pp. 290–310.

(4) Nonclassical carbonium ion intermediates (see ref. 3) would serve as well to preserve the stereochemical integrity of the process, and this alternative possibility is recognized in using the term "synchronous."

(5) R. P. Linstead, A. B. L. Wang, J. H. Williams, and K. D. Errington, *J. Chem. Soc.*, 1136 (1937).

(6) R. P. Linstead, A. F. Millidge, and A. L. Walpole, *ibid.*, 1140 (1937).

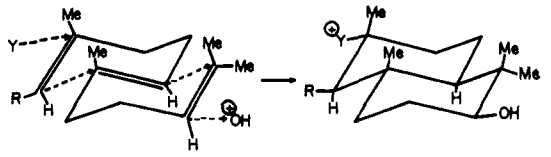
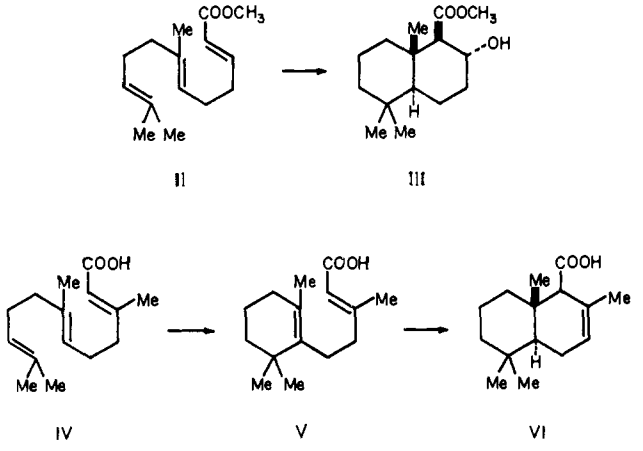


Figure 1.

zation conditions. The ratio of these products was not altered by this treatment.

The cyclization experiment was repeated a number of times, once at high dilution to minimize polymerization, but we never were able to realize as high a yield of the *cis*-decalol as reported by Linstead. Although we are not able to account for this discrepancy, it is clear from our study that the Linstead cyclization is highly stereoselective, if not stereospecific, and the mechanistic interpretation of Stork[2] may be regarded as reasonable.

Now to return to the major premise in the Stork–Eschenmoser theory: in paper II of this series we showed that the formolysis of *trans*-5,9-decadienyl *p*-nitrobenzenesulfonate gave bicyclic material, albeit in poor yield, which was exclusively *trans*-fused. Seemingly this constitutes an *in vitro* model for the Stork–Eschenmoser hypothesis.



There has been relatively little previous work that is pertinent.[7] Eschenmoser and his collaborators[8] have reported the acid-catalyzed cyclization of *trans*-desmethylfarnesic ester (II) to yield a single *trans*-fused decalin derivative III in 60–70% yield. Seemingly this is an example of the process in question; however, Stork and Burgstahler,[2] working in the farnesic acid (IV) series, showed that under mild conditions the process proceeded only to the monocyclic stage, formula V, and that the monocyclic diene on more vigorous treatment was converted into the *trans*-fused bicyclic substance VI.[9] This suggests that the Eschenmoser case is similarly a two-stage cyclization. Although Eschenmoser has not reported the isolation of monocyclic intermediates from cyclization of the diene II, he has shown that the monocyclic substances give essentially the same yield of *trans*-fused bicyclic material

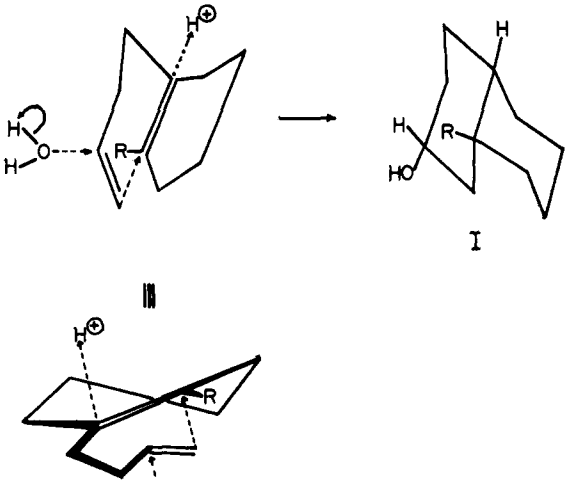
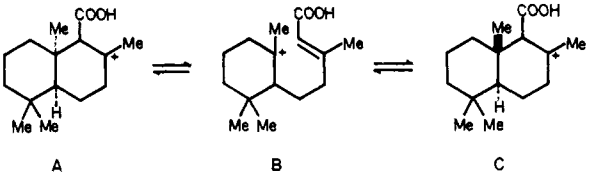


Figure 2.

as is produced from the acyclic substance,[10] and these observations are consistent with a two-stage cyclization process. The most striking feature of the work of Stork and of Eschenmoser is that the cyclization of the monocyclic diene proceeds stereochemically in a manner exactly *opposite* from that expected on the basis of Linstead's butenylcyclohexene case which gives only the *cis*-decalin derivative. A possible interpretation of this enigma is that the unknown *cis* product, shown in the protonated form in formula A, is



actually formed initially as in Linstead's case,[11] but that under the conditions of reaction the *cis* is converted to the more stable *trans* isomer C through an equilibrium established *via* the ring-opened carbonium ion B. Such a ring-opening process falls into the class of a well known type of cationic fragmentation reaction, and its activation energy might be lowered (with respect to the comparable ring opening in the Linstead case) because in the protonated forms A and C of the bicyclic acids there would be a stabilizing effect resulting from having the positive charge removed to a position that is more remote from the electron-deficient carbon of the carboxyl group. The *cis*-fused bicyclic acids were not found either by Eschenmoser or Stork so that there has up to now been no way of finding out if it was indeed convertible to the *trans* isomer by acid treatment.

In order to test this hypothesis, we undertook the preparation of the *cis* and *trans* bicyclic acids VII and VIII by an unequivocal synthesis from the known *cis*-

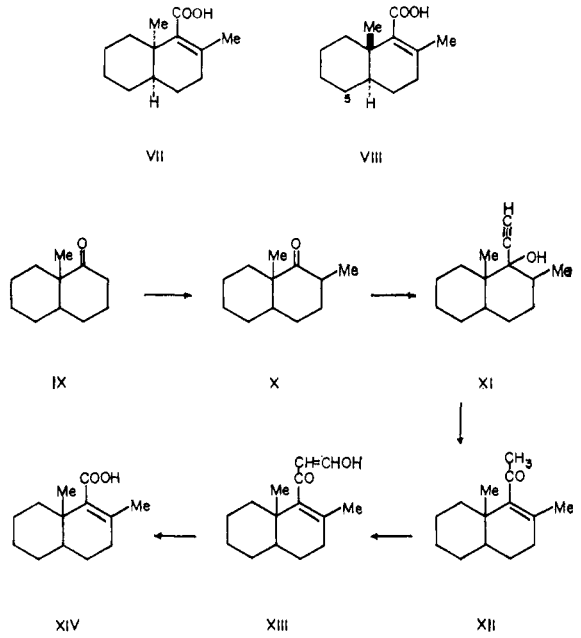
(7) The cyclization of farnesylacetic acid [P. Dietrich and E. Lederer, *Helv. Chim. Acta*, **35**, 1148 (1952)], for example, cannot be regarded as relevant, because the *trans*-fused product was isolated only in low (5%) yield, and it was not demonstrated that the remainder of the reaction product did not contain significant amounts, or even a preponderance, of the *cis* material.

(8) P. A. Stadler, A. Nechvatal, A. J. Frey, and A. Eschenmoser, *ibid.*, **40**, 1373 (1957).

(9) P. A. Stadler, A. Eschenmoser, H. Schinz, and G. Stork, *ibid.*, **40**, 2191 (1957).

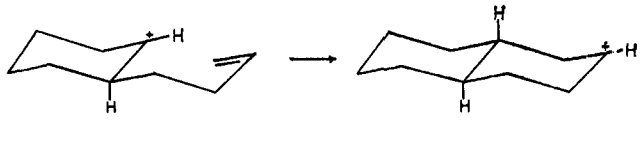
(10) A. Eschenmoser, D. Felix, M. Gut, J. Meier, and P. Stadler, "Ciba Foundation Symposiun on the Biosynthesis of Terpenes and Sterols," J. and A. Churchill, Ltd., London, 1959, pp. 221–223.

(11) Note that in the case of the cyclization of Eschenmoser's monocyclic acids (ref. 10) this interpretation would require initial isomerization of the olefinic bonds of his substances X and X1 (p. 222, ref. 10), which is consistent with the results obtained with the optically active form of the latter substance. Also the interpretation under consideration would require that the desmethylfarnesic acid having the *cis* configuration of the internal olefinic bond (formula 1Xa, p. 222, ref. 10) undergo isomerization to the *trans* isomer prior to cyclization, which is an entirely reasonable possibility.



and *trans*-9-methyldecalones. The steps were the same for both series and are summarized in the accompanying flow sheet with nonstereochemical formulas. The methyldecalone IX was converted, by alkoxide-catalyzed condensation with ethyl formate, into the hydroxymethylene derivative which, on catalytic hydrogenation in ethanol over palladium-on-carbon in the presence of hydrochloric acid, was transformed into the 2,9-dimethyldecalone (X). In both the *cis* and *trans* series this ketone failed to react with cyanide to form the cyanohydrin. However, it did react smoothly with ethynylmagnesium bromide to give the acetylenic alcohol XI which, on treatment with 90% formic acid, was transformed readily into the unsaturated ketone XII. A number of attempts to degrade the ketone to the acid, for example by alkaline hypobromite, failed. Finally it was discovered that the ketone XII would undergo condensation with ethyl formate to produce the hydroxymethylene derivative XIII. Ozonolysis of this derivative followed by treatment with periodic acid afforded the desired unsaturated acid XIV.

The acids VII, m.p. 100–102°, and VIII, m.p. 108–109°, were thus in hand for testing the interconversion hypothesis. Each was treated with boron trifluoride etherate in benzene under the conditions reported by Stork for conversion of monocyclic to bicyclic material. After esterification with diazomethane, the products were analyzed by vapor phase chromatography, and it was found that there had been no interconversion. If it is assumed that the acid VIII constitutes a satisfactory model of Stork's acid, then the interconversion hypothesis is invalidated.



In view of these findings we are forced to adopt an alternative interpretation of the stereochemical course of the cyclization of acids related to V, namely, that the conjugated olefinic bond, because of delocalization of the π-electrons by the carboxyl group, is such a poor nucleophile that it does not react synchronously, *i.e.*, the process occurs in steps with the intermediacy of the tertiary carbonium ion B.[12] If this interpretation is correct, it follows that a free monocyclic carbonium ion, like B, will undergo an irreversible cyclization so as to produce preferentially a *trans*-fused ring system. Although it has been suggested[2] that this type of cyclization will not be stereoselective, it is not unreasonable to expect that a nucleophile would prefer to make an equatorial rather than axial attack on a cyclohexyl cation. Indeed such a process has considerable geometrical similarity to the case of the protonation of the enolate of 2-phenylbenzoylcyclohexane to give the (less stable) *cis* isomer,[13] which constitutes an example of a rate-controlled reaction involving a single sp^2-carbon in the cyclohexane ring where the attacking group prefers the equatorial approach. Similarly, in the hypothetical carbonium ion D an equatorial attack by the olefinic bond would give the *trans*-fused system E.[14] If the carbonium ion D is actually an intermediate in the solvolysis of the decadienyl *p*-nitrobenzenesulfonate[1a]—a hypothesis which we regard as less attractive, but plan to put to test—then the ring closure process D $\rightarrow$ E is absolutely stereospecific. Should this prove to be the case, then the mechanism of the biosynthesis of natural products from squalene is again open to question, as it could be equally satisfactorily rationalized as occurring in steps rather than by a concerted pathway.[15] These steps would involve intermediary tertiary cations which, however, could not be long lived enough to suffer reversible deprotonation; otherwise *cis* ring-fused products would result as well as deuterium incorporation from deuterium oxide. Although less attractive than the concerted picture, this hypothesis cannot be excluded without further experimentation.

Experimental[16]

cis- and *trans*-9-methyldecalone-1 were prepared by a modification of a previously reported procedure[17] for the alkaline hydroly-

(12) This possibility has already been suggested by Eschenmoser (ref. 10). It is to be noted that the cyclization experiments with the isomer of desmethylfarnesic acid having the internal olefinic bond in the *cis* configuration does not prove the case because of the reasonable possibility that geometric isomerization occurs prior to cyclization.

(13) H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

(14) It is to be noted, however, that there are additional factors, involving nonbonded interactions of substituents, that would favor the formation of the *trans* bicyclic product from the carbonium ion B (see ref. 10). The formation of the *cis*-decalol from butenylcyclohexene could also be rationalized as proceeding through the flipped form of carbonium ion D with the side chain in the axial conformation. The preference for reaction in this less stable form would have to be rationalized as being due to more favorable geometry for overlap of the π-orbital of the olefinic bond with the cationic center in the transition state.

(15) Similar stereochemical arguments are applicable if the biosynthesis is a free-radical process as suggested by R. Breslow, E. Barrett, and E. Mohacsi, *Tetrahedron Letters*, 1207 (1962).

(16) (a) The prefix "DL" is omitted from the names of all racemic compounds described in this section. (b) Melting points were determined on a Kofler hotstage microscope. (c) N.m.r. spectra were determined under the supervision of Dr. L. J. Durham on a Varian Associates A-60 n.m.r. spectrometer. Deuteriochloroform was employed as the solvent with tetramethylsilane as the internal reference. The chemical shifts are reported as δ-values in p.p.m. relative to tetramethylsilane = 0. (d) Vapor phase chromatographic analyses were performed on an Aerograph Hy-Fi vapor chromatographic apparatus (Model A-550). Analyses were carried out on a 7.5-ft. × 1/8-in. column packed with 15% Craig succinate on Chromosorb W, referred to as the "Craig succinate" column, or on a 7.5-ft. × 1/8-in. column packed with 20% UCON polar on a Chromosorb P base, referred to as the "UCON polar" column. (e) The elution order used in column chromatography was petroleum ether (b.p. 60–68°), ether, ethyl acetate, and acetone. (f) Thin

sis of the furfurylidene derivatives. The new procedure involves the addition of water in order to lower the alkoxide (from diethylene glycol) concentration, thus minimizing the formation of decalol by hydride transfer to initially formed ketone. The oxidation step,[17] therefore, has been eliminated, and the yields have been improved.

To a solution of 150 ml. of diethylene glycol and 150 ml. of 25% aqueous potassium hydroxide solution was added 42.4 g. of oily 2-furfurylidene-*cis*-9-methyldecalone-1.[18] The mixture was heated under reflux for 20 hr., then submitted to steam distillation. The distillate (about 4 l.) was saturated with sodium chloride and the product was isolated by ether extraction.[16g] Distillation of the residue through a 4-in. Vigreux column yielded 7.85 g. (27%) of *cis*-9-methyldecalone-1, b.p. 85–87° (3 mm.) (reported[19] 116° (14–15 mm.)). The semicarbazone was obtained from 95% ethanol as long colorless rods, m.p. 223–225° (reported[19] 226–227°). When the alkaline cleavage was carried out on a 1.5-g. scale, yields as high as 52% were realized.

A 31.6-g. sample of 2-furfurylidene-*trans*-9-methyldecalone-1,[18] m.p. 109–111°, was treated as described above for the *cis* compound with 100 ml. of diethylene glycol and 100 ml. of 25% aqueous potassium hydroxide solution. The yield of *trans*-9-methyldecalone-1 was 6.4 g. (29%), b.p. 86–88° (3 mm.) (reported[19] 119–120° (14–15 mm.)). The semicarbazone was obtained from 95% ethanol as long colorless rods, m.p. 216–219° (reported[19] 219–220°).

cis-2,9-Dimethyldecalone-1.—2-Hydroxymethylene-*cis*-9-methyldecalone-1 was prepared by condensation of 0.57 g. of the aforementioned *cis*-9-methyldecalone-1 with 1.3 g. of ethyl formate and 2.1 g. of sodium methoxide in 22 ml. of benzene as previously described.[20] The crude product obtained by evaporation of the extraction solvent under reduced pressure amounted to 0.65 g. of a yellow liquid, $\lambda_{max}^{CHCl_3}$ 6.1 and 6.3 μ, which gave a violet color with a chloroform solution of ferric chloride. The product was used directly without further purification in the experiments described below.

(a) **Methylation of 2-Hydroxymethylene-*cis*-9-methyldecalone-1.**—The following procedure is an adaptation of a method of Cornforth and Robinson.[21] A mixture of 1.19 g. of the crude hydroxymethylene ketone prepared as described above, 8.5 ml. of anhydrous acetone, and 1.0 g. of ignited potassium carbonate was heated at reflux with stirring for 10 min.; then 3.1 g. of methyl iodide was added slowly and the heating was continued for 20 hr. The reaction mixture was diluted with water and extracted with ether. The combined organic layers were washed with 5% sodium hydroxide solution, then with water, followed by saturated brine, and dried over anhydrous sodium sulfate. The yellow oily residue obtained upon removal of the solvent under reduced pressure was heated on the steam bath with 12 ml. of methanol, 8 ml. of water, and 4 ml. of concentrated hydrochloric acid for 10 min. The mixture was cooled, diluted with water, extracted with ether, washed, and isolated as described directly above. The residue obtained upon evaporation of the solvent was heated on the steam bath with 10 ml. of 10% methanolic potassium hydroxide for 10 min. The cooled mixture was diluted with water, and the product was isolated by ether extraction[16g] to give 0.43 g. (39% yield) of a colorless oil. The infrared spectrum of this material was identical with that of the analytical specimen described below.

(b) **Hydrogenation of 2-Hydroxymethylene-*cis*-9-methyldecalone-1.**[22]—A solution of 3.35 g. of the crude hydroxymethylene ketone in 70 ml. of 95% ethanol containing 2 ml. of 10% aqueous hydrochloric acid was hydrogenated over 2 g. of 5% palladium-on-carbon catalyst (Davison Chemical Co.) at atmospheric pressure and 22°. After 2.5 hr. about 89% of the calculated amount of hydrogen had been absorbed and reaction had essentially ceased. The mixture was filtered, and the combined filtrate and washings were concentrated under reduced pressure. Ether was added to the yellow oily residue, and the solution was washed with 5% aqueous sodium hydroxide, then with water, followed by saturated brine, and finally dried over anhydrous sodium sulfate. The colorless oily residue (3 g.) obtained on evaporation of the solvent under reduced pressure was filtered through 150 g. of basic alumina with 1.5 l. of petroleum ether. The residue obtained on evaporation of the solvent under reduced pressure amounted to 2.6 g. (83% yield) of a colorless oil which was evaporatively distilled at 76° (2–3 mm.), $n^{25}D$ 1.476, $\lambda_{max}^{CHCl_3}$ 5.90 μ (C=O).

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.9; H, 11.3.

The oxime crystallized from ether–petroleum ether as colorless prisms, m.p. 175–176°.

Anal. Calcd. for $C_{12}H_{21}ON$: C, 73.79; H, 10.84; N, 7.17. Found: C, 73.7; H, 10.7; N, 6.85.

One attempt was made to hydrogenate an ethanolic solution of the potassium salt of the hydroxymethylene ketone over palladium-on-carbon. There was no apparent uptake of hydrogen and only the starting hydroxymethylene ketone was isolated.

Attempts to convert *cis*-2,9-dimethyldecalone-1 into its cyanohydrin by treatment with potassium cyanide and acetic acid in ethanol,[23] with acetone cyanohydrin[24] or with liquid hydrogen cyanide[23] failed. Only the starting ketone was obtained.

trans-2,9-Dimethyldecalone-1.—2-Hydroxymethylene-*trans*-9-methyldecalone-1 was prepared from 0.92 g. of the aforementioned *trans*-9-methyldecalone-1 using 35 ml. of benzene, 2.25 ml. of ethyl formate, and 3.3 g. of sodium methoxide (see above). The crude product amounted to 1.1 g. of a yellow oil which gave a violet color with a chloroform solution of ferric chloride and was used as described below without further purification.

A solution of 3.2 g. of the hydroxymethylene ketone, prepared as described directly above, in 50 ml. of 95% ethanol containing 2 ml. of 10% hydrochloric acid was hydrogenated at atmospheric pressure and 10° over 1.1 g. of 5% palladium-on-carbon catalyst (Davison Chemical Co.). The product, which was isolated as described above for the *cis* series, amounted to 1.81 g. (60% yield) of a colorless oil which was evaporatively distilled at 76° (2–3 mm.), $n^{25}D$ 1.480, $\lambda_{max}^{CHCl_3}$ 5.90 μ (C=O).

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.3; H, 11.4.

The oxime crystallized from ether–petroleum ether as long colorless rods, m.p. 158–160°.

Anal. Calcd. for $C_{12}H_{21}ON$: C, 73.79; H, 10.84; N, 7.17. Found: C, 73.65; H, 10.85; N, 6.9.

cis-2,9-Dimethyl-1-ethynyldecalol-1.—An attempt to effect ethynylation of *cis*-2,9-dimethyldecalone-1 with sodium acetylide by the procedure of Sondheimer and Elad[25] gave a mixture of ill-defined products; therefore we turned to the use of ethynylmagnesium bromide.[26]

A solution of 1.62 g. of the aforementioned *cis*-2,9-dimethyldecalone-1 in 40 ml. of anhydrous tetrahydrofuran was added dropwise with stirring at 25° over a 0.5-hr. period to a solution of a Grignard reagent prepared[26] from 2.5 g. of magnesium, 9.1 ml. of ethyl bromide, and excess acetylene in 120 ml. of tetrahydrofuran. After the addition was complete, the mixture was heated under reflux with stirring (atmosphere of nitrogen) for 24 hr. The mixture was cooled and 10 ml. of a saturated solution of ammonium chloride which had been adjusted to pH 7 by the addition of ammonium hydroxide was added dropwise. The yellow solution was decanted and the granular precipitate was washed thoroughly with ether. The combined organic layers were dried over anhydrous sodium sulfate, and the solvent was removed at reduced pressure to yield 2.28 g. of a brown oil which was chromatographed on 140 g. of Florisil. The product eluted with petroleum ether (6 l.) amounted to 1.05 g. of a colorless oil which was homogeneous to thin layer chromatography,[16f]

layer chromatography experiments were performed according to E. Stahl, "Dünnschicht-Chromatographie, Ein Laboratoriumshandbuch," Springer-Verlag, Berlin, 1962. Silica Gel G (E. Merck A.G.) was employed as the adsorbent and 10% ether in benzene as the eluent. (g) The isolation procedure normally followed consisted of extraction of the product with the solvent indicated. The organic phase was washed thoroughly with water, followed by saturated salt solution, then dried over anhydrous sodium sulfate. The solvent was then removed under reduced pressure (water aspirator) at about 50°.

(17) W. S. Johnson, 1. A. David, H. C. Dehm, R. J. Highet, E. W. Warnhoff, W. D. Wood, and E. T. Jones, *J. Am. Chem. Soc.*, **80**, 661 (1958).

(18) W. S. Johnson, B. Bannister, and R. Pappo, *ibid.*, **78**, 6331 (1956).

(19) W. S. Johnson, *ibid.*, **65**, 1317 (1943).

(20) W. S. Johnson and H. Posvic, *ibid.*, **69**, 1361 (1947).

(21) J. W. Cornforth and R. Robinson, *J. Chem. Soc.*, 1855 (1949).

(22) *Cf.*, *inter alia*, Y. Abe, T. Harukawa, H. Ishikawa, T. Miki, M. Sumi, and T. Toga, *J. Am. Chem. Soc.*, **75**, 2567 (1953); M. Yanagita and R. Futak, *J. Org. Chem.*, **21**, 949 (1956); H. J. Ringold, E. Batres, O. Halpern, and E. Necoechea, *J. Am. Chem. Soc.*, **81**, 427 (1959); and C. Djerassi, N. Finch, R. C. Cookson, and C. W. Bird, *ibid.*, **82**, 5488 (1960).

(23) S. Swaminathan and M. S. Newman, *Tetrahedron*, **2**, 88 (1958).

(24) H. J. Ringold, *J. Am. Chem. Soc.*, **82**, 961 (1960).

(25) F. Sondheimer and D. Elad, *ibid.*, **80**, 1967 (1958).

(26) E. R. H. Jones, L. Skattebol, and M. C. Whiting, *J. Chem. Soc.*, 4765 (1956).

R_f 0.570, $n^{25}D$ 1.503; $\lambda_{max}^{CHCl_3}$ 2.74 μ (OH), 3.00 (C≡CH), and 10.23. The fraction eluted with 1% ether in petroleum ether (2 l.) amounted to 0.33 g. of colorless oil, evidently the epimeric (at C-1) *cis*-acetylenic alcohol, R_f 0.457, $n^{25}D$ 1.512; $\lambda_{max}^{CHCl_3}$ 2.75 μ (OH), 3.00 (C≡CH), and 9.88. The total yield of crude ethynylation product was 75%. The ratio of epimer a (eluted with petroleum ether) to epimer b (eluted with 1% ether in petroleum ether) was 3:1. Epimer a was prepared for analysis by drying to constant weight at 25° (0.02 mm.).

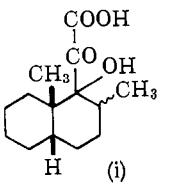
Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.65; H, 10.8.

***trans*-2,9-Dimethyl-1-ethynyldecalol-1** was prepared, as described above for the *cis* isomer, from 0.29 g. of the aforementioned *trans*-2,9-dimethyldecalone-1 in 5 ml. of tetrahydrofuran and a solution of Grignard reagent prepared from 0.61 g. of magnesium, 2.3 ml. of ethyl bromide, and excess acetylene in 32 ml. of tetrahydrofuran. The crude product (0.37 g.) was chromatographed on 40 g. of Florisil. Elution with 1% ether in petroleum ether gave 0.18 g. (55% yield) of a colorless oil which was homogeneous by thin layer chromatography,[16f] R_f 0.460, $n^{25}D$ 1.506, $\lambda_{max}^{CHCl_3}$ 2.75 μ (OH) and 3.0 (C≡CH). This product was prepared for analysis by drying to constant weight at 25° (0.02 mm.).

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 80.8; H, 10.7.

Oxidation of *cis*-2,9-Dimethyl-1-ethynyldecalol-1 with Potassium Permanganate.—To a solution of 0.22 g. of the *cis*-acetylenic alcohol (preponderant epimer) in 10 ml. of acetone was added 0.42 g. of potassium permanganate in 11 ml. of water containing 0.2 ml. of 5% aqueous sodium hydroxide. The mixture was stirred at 25° for 2 hr., sodium sulfite was added to decolorize the supernatant liquid, and the manganese dioxide was removed by filtration. Ether was added to the filtrate and the solution was extracted with 10% aqueous potassium hydroxide solution. The combined alkaline aqueous extracts were acidified to pH 2 with cold concentrated hydrochloric acid, and the product was isolated by extraction with ethyl acetate.[16g] The yellow oily acidic product which amounted to 0.12 g. was chromatographed on 7 g. of silicic acid. The fraction eluted with 10% ether in petroleum ether amounted to 0.024 g. (9% yield) of a substance that is provisionally assigned the structure ***cis*-2,9-dimethyl-1-hydroxydecalin-1-glyoxylic acid** (i). Repeated recrystallizations from ether–petroleum ether afforded colorless prisms, m.p. 155–160°. The mass spectrum exhibited no molecular ion peak, but had strong peaks at M − 18 (loss of H_2O) and M − 44 (loss of CO_2).

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 65.9; H, 8.9.



(i)

***cis*-1-Acetyl-2,9-dimethyl-Δ¹-octalin.**—A solution of 0.36 g. of the aforementioned epimer a of the *cis*-acetylenic alcohol in 4 ml. of 90% formic acid was heated under reflux with stirring in an atmosphere of nitrogen for 2 hr.[27] The dark brown solution was added to ice and the mixture was extracted with ether. The combined organic layers were washed thoroughly with 10% potassium hydroxide solution, then with water, followed by saturated brine, and finally dried over anhydrous sodium sulfate. The brown residue obtained on evaporation of the solvent under reduced pressure was evaporatively distilled at 85° (0.4 mm.) to give 0.29 g. (81% yield) of a colorless oil, $n^{25}D$ 1.506; $\lambda_{max}^{CHCl_3}$ 5.94 μ (conjugated C=O), 6.00 (C=C); $\lambda_{max}^{95\%\ EtOH}$ 244 mμ (ϵ 1540). The n.m.r. spectrum[16c] exhibited absorption for 3 protons as a singlet at 2.26 p.p.m. (CH_3CO), 3 protons as a singlet at 1.57 (CH_3 at C-2), and 3 protons as a singlet at 1.17 (CH_3 at C-9).

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.4; H, 10.8.

Attempts to prepare an oxime failed. Starting ketone was recovered. An attempt to oxidize this unsaturated ketone with hypobromite according to the procedure of Djerassi and Staunton[28] gave what appeared to be a complex mixture of products from which no crystalline material could be isolated.

When a 0.19-g. sample of the aforementioned epimer b of the *cis*-acetylenic alcohol was stirred at reflux for 1.5 hr. in 2 ml. of 90% formic acid, and the mixture processed as described above, 0.125 g. (67% yield) of *cis*-1-acetyl-2,9-dimethyl-Δ¹-octalin was obtained after evaporative distillation at 90° (0.15 mm.). The infrared spectrum of this product was identical with that of the material prepared from epimer a (see above).

***trans*-1-Acetyl-2,9-dimethyl-Δ¹-octalin.**—A 0.13-g. sample of the *trans*-acetylenic alcohol was treated just as described above for the *cis* compound with 2 ml. of 90% formic acid. The crude product, which was a yellow oil, was chromatographed on 30 g. of basic alumina. Elution with 1% ether in petroleum ether gave 0.07 g. of a yellow liquid which was evaporatively distilled at 85° (0.4 mm.). The distillate amounted to 0.05 g. (36% yield) of a colorless liquid; $\lambda_{max}^{CHCl_3}$ 5.94 μ (conjugated C=O), 6.04 (C=C); $\lambda_{max}^{95\%\ EtOH}$ 242 mμ (ϵ 1480). The n.m.r. spectrum[16c] exhibited absorption for 3 protons as a singlet at 2.26 p.p.m. (CH_3CO), 3 protons as a singlet at 1.57 (CH_3 at C-2), and 3 protons as a singlet at 1.12 (CH_3 at C-9).

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.2; H, 10.7.

***cis*-2,9-Dimethyl-Δ¹-octalin-1-carboxylic Acid (VII).**—A 0.15-g. sample of the aforementioned *cis*-1-acetyl-2,9-dimethyl-Δ¹-octalin was allowed to condense with 6.2 g. of ethyl formate in the presence of 0.52 g. of sodium methoxide and 5.2 ml. of benzene according to a previously described procedure.[29] The crude alkali-soluble hydroxymethylene ketone amounted to 0.155 g. of a yellow oil which gave a dark red color with a chloroform solution of ferric chloride and was used as described below without further purification.

Oxidation of a specimen of this hydroxymethylene ketone with sodium metaperiodate according to the procedure of Cornforth, Cornforth, and Popjak[29] gave a very complex mixture of acidic material which was not examined further.

Ozonization of the hydroxymethylene ketone was carried out according to a previously described procedure.[30] A saturated solution of ozone in 45.4 ml. of anhydrous methylene chloride at −70° was added slowly with stirring at −70° to a solution of 0.26 g. of the *cis*-hydroxymethylene ketone, prepared as described directly above, in 5 ml. of methylene chloride. The resulting yellow solution was allowed to warm to ice bath temperature; then 15 ml. of 0.33 *M* aqueous periodic acid was added, followed by sufficient acetic acid (55 ml.) to produce a homogeneous solution. The mixture was then allowed to come to room temperature and to stand for 24 hr.

The above reaction mixture was combined with a second identical one. Water and ether were added, and the organic layer was washed thoroughly with water, then with 10% aqueous potassium bicarbonate, followed by 10% potassium hydroxide solution. The combined potassium hydroxide extracts were acidified at 0° with hydrochloric acid, and the product was isolated by ether extraction.[16g] The crude product amounted to 0.32 g. of a cream-colored solid. Crystallization from dilute methanol afforded 0.25 g. of colorless needles, m.p. 96–100°. Chromatography of the residues from the mother liquors on 7 g. of silicic acid yielded, on elution with petroleum ether, an additional 0.03 g., m.p. 96–100°, making the total yield 0.28 g. (60%). Repeated recrystallizations from dilute methanol gave colorless needles, m.p. 100–102°, $\lambda_{max}^{CHCl_3}$ 5.92 μ (acid C=O) and 6.05 (C=C).

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.25; H, 9.7.

The ultraviolet absorption spectrum showed no maxima; however, a continuously increasing absorption was observed between 265 and 210 mμ with an extinction of 2400 at 220 mμ. The n.m.r. spectrum[16c] exhibited absorption for 3 protons as a singlet at 1.77 p.p.m. (CH_3 at C-2) and 3 protons as a singlet at 1.22 (CH_3 at C-9). **The methyl ester**, prepared with diazomethane, was obtained, after drying to constant weight at 25° (0.1 mm.), as a colorless oil, $\lambda_{max}^{CHCl_3}$ 5.86 μ (ester C=O), 6.05 (C=C). The ultraviolet absorption spectrum was identical with that of the corresponding acid. The n.m.r. spectrum[16c] exhibited ab-

(27) *Cf.* M. S. Newman and P. H. Goble, *J. Am. Chem. Soc.*, **82**, 4098 (1960).

(28) C. Djerassi and J. Staunton, *ibid.*, **83**, 736 (1961).

(29) R. H. Cornforth, J. W. Cornforth, and G. Popjak, *Tetrahedron*, **18**, 1351 (1962).

(30) W. L. Meyer, D. D. Cameron, and W. S. Johnson, *J. Org. Chem.*, **27**, 1130 (1962).

sorption for 3 protons as a singlet at 3.73 p.p.m. ($COOCH_3$), 3 protons as a singlet at 1.66 (CH_3 at C-2), and 3 protons as a singlet at 1.19 (CH_3 at C-9).

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.4; H, 10.0.

trans-2,9-Dimethyl-Δ^1-octalin-1-carboxylic Acid (VIII).—Condensation of 0.04 g. of *trans*-1-acetyl-2,9-dimethyl-Δ^1-octalin with ethyl formate as described above for the *cis* series gave 0.04 g. of crude hydroxymethylene ketone as a yellow oil, which gave a dark red color with a chloroform solution of ferric chloride. A 0.17-g. sample of the hydroxymethylene ketone in 1 ml. of methylene chloride was treated at −70° with 29 ml. of methylene chloride saturated with ozone at −70°. The mixture was then treated with periodic acid as described above in the *cis* series to give 0.08 g. of a cream-colored oil which crystallized with some difficulty on trituration with petroleum ether. Crystallization from dilute methanol yielded 0.04 g. of colorless crystals, m.p. 105–108°. Chromatography of the residue from the mother liquors on 5 g. of silicic acid afforded, on elution with 5% ether in petroleum ether, an additional 0.01 g. of material, m.p. 104–108°, making the total yield 33%. Repeated recrystallizations from dilute methanol gave colorless needles, m.p. 108–109°, $\lambda_{max}^{CHCl_3}$ 5.94 μ (acid C=O), 6.05 (C=C). As in the *cis* series, the ultraviolet spectrum showed continuously increasing absorption from 265–210 mμ. The extinction at 220 mμ was 2300. The n.m.r. spectrum[16c] exhibited absorption for 3 protons as a singlet at 1.73 p.p.m. (CH_3 at C-2) and 3 protons as a singlet at 1.14 (CH_3 at C-9).

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.7; H, 9.55.

The methyl ester, prepared with diazomethane, was obtained, after drying to constant weight at 25° (0.1 mm.), as a colorless oil, $\lambda_{max}^{CHCl_3}$ 5.84 μ (ester C=O), 6.04 (C=C). The ultraviolet spectrum was identical with that of the corresponding acid. The n.m.r. spectrum[16c] exhibited absorption for 3 protons as a singlet at 3.72 p.p.m. ($COOCH_3$), 3 protons as a singlet at 1.65 (CH_3 at C-2), and 3 protons as a singlet at 1.12 (CH_3 at C-9).

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.4; H, 9.9.

Attempted Equilibration of the *cis*- and *trans*-Acids VII and VIII. (a) **With Boron Trifluoride Etherate.**—The conditions of Stork and Burgstahler[2] were used. To a solution of 0.012 g. of the *cis*-acid VII, m.p. 98–100°, in 2 ml. of benzene was added 0.5 ml. of freshly distilled boron trifluoride etherate. The mixture was immersed in an oil bath preheated to 43° and maintained at this temperature with stirring under nitrogen for 7 hr. The solution was then added slowly to ice and the mixture extracted with ether. The combined organic layers were washed thoroughly with 10% aqueous potassium bicarbonate, then with water, followed by saturated salt solution, and finally dried over anhydrous sodium sulfate. The colorless solid residue obtained on removal of the solvent under reduced pressure amounted to 0.013 g. This product was esterified with an ethereal solution of diazomethane. Vapor phase chromatography on the UCON polar column[16d] at 132° and a flow rate of about 2.5 ml./min. gave two peaks: one corresponding to (as shown by peak enhancement) the ester of the *cis*-acid VII, R_t 7.9 min.; and the other (unidentified material), R_t 11.0 min. The relative areas of the two peaks, determined by the triangulation method, were 92 and 8%, respectively.

Another vapor phase chromatography on the Craig succinate column[16d] at 182.5° and a flow rate of about 25 ml./min. gave peaks for the *cis*-ester, R_t 24.8 min. (95%), and for the unidentified material, R_t 27.2 min. (5%).

When the *trans*-acid VIII, m.p. 105–108°, was treated exactly as described above for the *cis* isomer, the esterified product on vapor phase chromatography gave only one peak corresponding to (as shown by peak enhancement) the methyl ester of the *trans*-acid VIII, R_t 12.5 min. Chromatography on the Craig succinate column at 182.5° gave a single peak corresponding to that for the *trans*-ester, R_t 32.0 min.

A specimen of the *cis*-acid VII, m.p. 98–100°, was treated with boron trifluoride etherate as described above except that the reaction mixture was heated at reflux for 5 hr., then allowed to stand for 17 hr. at 25°. The esterified product, on vapor phase chromatography over the UCON polar column[16d] at 132° and a flow rate of about 2.5 ml./min., showed the presence of the *cis*-ester, R_t 7.9 min. (92%), and the unidentified substance, R_t 11.0 min. (8%). The same vigorous boron trifluoride etherate treatment of the methyl ester of the *cis*-acid VIII gave a product which was submitted to vapor phase chromatography on the UCON polar column as described directly above. Three peaks were obtained, one corresponding to the *cis*-ester, R_t 7.8 min. (81%), and two peaks (unidentified substances) with R_t 6.2 min. (10%) and R_t 10.8 min. (9%).

(b) **With Formic–Sulfuric Acid.**—The cyclization conditions of Eschenmoser, *et al.*,[8] were used. To a cooled (ice bath) solution of 0.03 g. of the *cis*-acid VII, m.p. 101–103.5°, in 2.5 ml. of formic acid (97–100%) was added 0.25 ml. of concentrated sulfuric acid. The mixture was allowed to warm to room temperature, then maintained at 23° for 7 hr. Ice was added, and the mixture was extracted with ether. The combined organic layers were washed with water until neutral, then with saturated brine, and dried over anhydrous sodium sulfate. The residue obtained upon evaporation at reduced pressure amounted to 0.03 g. of a colorless solid, the infrared spectrum of which was identical with that of the starting acid. The product was esterified with an ethereal solution of diazomethane, and the resulting colorless oil was submitted to vapor phase chromatography on the Craig succinate column[16d] at 190° and a flow rate of about 25 ml./min. Only one peak was observed, corresponding to that of the *cis*-ester, R_t 26.1 min.

When a specimen of the methyl ester of the *cis*-acid VII was treated with formic–sulfuric acid exactly as described above, a colorless solid was obtained, the infrared spectrum of which was identical with that of the starting material. This product was esterified with an ethereal solution of diazomethane. Vapor phase chromatography on the Craig succinate column[16d] at 187° and a flow rate of about 25 ml./min. gave only one peak corresponding to that for the *cis*-ester, R_t 30.6 min.

Cyclization of Δ^3-Butenyl-1-cyclohexene.—Several experiments were performed in which an effort was made to duplicate exactly the reported procedure[5] except that instead of distilling, the product was submitted directly to vapor phase chromatographic analysis. Since in all of these experiments the reaction mixture became extremely dark, presumably due to polymerization, a cyclization was carried out at higher dilution. The reaction mixture was considerably cleaner, but the yields of products were not changed significantly. This last experiment is described below.

One gram of Δ^3-butenyl-1-cyclohexene[31] was added to 30 ml. of ice-cold 5% sulfuric acid in acetic acid (prepared by mixing 5 g. of concentrated sulfuric acid with 95 g. of glacial acetic acid). The mixture was stirred (nitrogen atmosphere) at 24° for 24 hr., then heated at 75° for 1 hr., cooled with an ice bath, and cautiously poured into 200 ml. of cold saturated sodium bicarbonate solution. This partially neutralized mixture was extracted thoroughly with pentane. The combined organic layers were washed with saturated sodium bicarbonate solution, followed by saturated brine, and then dried over anhydrous magnesium sulfate. The oily residue obtained on removal of the solvent by distillation through a 30-in. Podbielniak-type column was dissolved in 20 ml. of anhydrous ether and added dropwise to a cooled slurry of 0.5 g. of lithium aluminum hydride in 20 ml. of anhydrous ether. The mixture was stirred for 1 hr. at 0°, then 2 ml. of water was added dropwise with cooling, followed by sufficient dilute sulfuric acid to dissolve the inorganic solids. The aqueous layer was extracted with ether, and the combined organic layers were washed with saturated sodium bicarbonate solution, followed by saturated brine, and finally dried over anhydrous magnesium sulfate. The oily residue obtained on removal of the solvent by distillation as described above was diluted to exactly 10 ml. with carbon disulfide.

The quantitative vapor phase chromatographic analysis of this product was carried out similarly to the analysis of the product of solvolysis of *trans*-5,9-decadienyl *p*-nitrobenzenesulfonate.[1a] The specimens of authentic comparison substances were those previously described.[1a] *trans-syn*-2-Decalol, which was shown to be absent by qualitative analysis, was used as the internal standard for analysis of the alcohols which were all assumed to have the same detector response. A 7.5-ft. × 1/8-in. 15% Craig succinate column and a flow rate of 25 ml./min. were used. The absolute yields (with retention times at 174°) were: 1.0% of 1-Δ^3-butenylcyclohexanol (10.1 min.); 1.8% of an unidentified unsaturated alcohol (12.7 min.), $\lambda_{max}^{CHCl_3}$ 6.10 μ, 10.00, 10.90; 2.8% of an unidentified saturated alcohol (14.9 min.), λ_{max}^{film} 2.98 μ; and 4.4% of *cis-syn*-2-decalol (27.2 min.).

(31) This material was prepared as described in ref. 5. Vapor phase chromatography on a 15% Carbowax 20M column indicated the presence of about 2% impurity.

The volatile components of the cyclization mixture were analyzed by using Δ^3-butenyl-1-cyclohexene as the internal standard. A 5-ft. × 1/8-in. 15% Carbowax 20M column and a flow rate of 25 ml./min. were used. The absolute yields (with retention times at 101°) were: 16% of Δ^3-butenyl-1-cyclohexene (8.1 min.); 13% of the cyclic ether (11.2 min.), the properties of which are described below; 1–2% of two additional unidentified substances (11.8 and 13.3 min.) which were not identical with *trans*-Δ^2-octalin (10.3 min.).

The major components of the mixture were isolated by preparative vapor phase chromatography on a 20-ft. × 3/8-in. 20% Carbowax 20M column. The infrared spectra of the products named in the yield summaries above were identical with those of authentic specimens.[1a]

The substance referred to above as the cyclic ether was a colorless liquid, $n^{27}D$ 1.4593, and is tentatively regarded as **2-methyl-5,5-pentamethylenetetrahydrofuran.**[32] The infrared spectrum showed no absorption in the hydroxyl or carbonyl region, or for an olefinic bond. The n.m.r. spectrum, determined at 60 Mc. with tetramethylsilane as an internal standard (carbon tetrachloride solution) exhibited absorption for 1 proton as a multiplet centered at δ *ca.* 4.1 p.p.m. (R–O–CH); 17 protons, unresolved between 1–2 p.p.m., including what appears to be a doublet centered at 1.14 p.p.m. (*J* 6 c.p.s.) (CH_3CH).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.6; H, 11.5.

(32) *Cf.* C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1597 (1963).

Acknowledgment.—The n.m.r. and mass spectral determinations were carried out under the supervision of Dr. L. J. Durham and H. Budzikiewicz, respectively, to whom we express our thanks. We wish to thank also the U. S. Public Health Service and the National Science Foundation for assisting this study.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

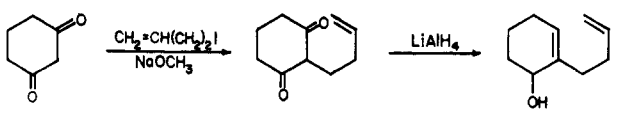
Cationic Cyclizations Involving Olefinic Bonds. IV.[1] The Butenylcyclohexenol System

BY WILLIAM S. JOHNSON, WILLIAM H. LUNN, AND KONRAD FITZI

RECEIVED DECEMBER 17, 1963

The dienol II has been prepared from 2-butenylcyclohexane-1,3-dione (I). On treatment with formic acid it underwent facile stereoselective cyclization to give *syn*-$\Delta^{1,9}$-6-octalol. The dienols VI and VII were prepared from 6-butenyl-Δ^2-cyclohexenone (X) (obtained by Birch reduction of 2-butenylanisole, VIII). Hydride reduction of X gave VI, and VII was obtained by the Wharton rearrangement of the epoxide XI of X. Formic acid cyclization of the dienols VI and VII proceeded stereoselectively to give $\Delta^{7,8}$-*cis-anti*-2-octalol (XV) as the major product. Consideration is given to the mechanistic pathway of the cyclization of the dienols II, VI, and VII.

In a previous report[2] we described a study of the use of the solvolysis of primary *p*-nitrobenzenesulfonates in order to generate incipient cationic sites for promoting cyclization into an appropriately juxtaposed olefinic bond. The formolysis of 5-hexenyl *p*-nitrobenzenesulfonate thus yielded cyclohexyl formate. This approach, at least in the simple cases that were examined, leaves something to be desired, because the conditions for effecting the anchimerically assisted solvolysis are strenuous enough to promote some undesirable side reactions.[2] We therefore decided to examine systems which are intrinsically more susceptible to ionization, thus permitting the use of milder reaction conditions. One of a number of potential candidates is the allylic system which was expected to serve as a progenitor of relatively stable (allylic), and hence easily generated, cationic sites. One further advantage of the allylic system is that the competing direct substitution reaction promoted by attack of solvent on the allylic cation is potentially (under appropriate conditions) reversible. Instead of being irreversibly eliminated by direct substitution, as in the solvolysis of the primary *p*-nitrobenzenesulfonates,[2] this cationic site thus may be continuously regenerated until it finally reacts essentially completely with the olefinic bond. These objectives of promoting ionization under relatively mild conditions to give good yields of cyclic product have been realized with the butenylcyclohexenol system which represents the subject of the present paper. A precedent for this type of cyclization is found in the conversion of *S*-(−)linalool into *R*-(+)terpineol.[3]



I II

The first, and simplest, system to be examined was 2-(Δ^3-butenyl)-Δ^2-cyclohexenol (II) which was readily prepared by alkylation of dihydroresorcinol with butenyl iodide, followed by reduction with lithium aluminum hydride.[4] The product appeared to be contaminated with butenylcyclohexanol; therefore it was converted into the crystalline 3,5-dinitrobenzoate. Recrystallization gave material, m.p. 62.5–64°, which was saponified to afford dienol II which was 93% pure as shown by vapor phase chromatography. This substance proved to be extremely susceptible to cyclization. Indeed, on dissolution in anhydrous formic acid at room temperature, essentially all of the starting material had reacted in less than 5 min. as estimated by thin layer chromatography. After 5.5 min., the reaction mixture was made alkaline so as to convert any formates into the corresponding alcohols, and the product was then analyzed by vapor phase chromatography on a Craig succinate column which indi-

(1) (a) Paper III of this series: W. S. Johnson, S. L. Gray, J. K. Crandall, and D. M. Bailey, *J. Am. Chem. Soc.*, **86**, 1966 (1964); (b) a preliminary account of the work described in the present paper was reported at the I.U.P.-A.C. Meeting in London, July 17, 1963; see W. S. Johnson, *Pure Appl. Chem.*, **7**, 317 (1963).

(2) W. S. Johnson, D. M. Bailey, R. Owyang, R. A. Bell, B. Jaques, and J. K. Crandall, *J. Am. Chem. Soc.*, **86**, 1959 (1964).

(3) K. Stephan, *J. Prakt. Chem.*, **58**, 109 (1898); V. Prelog and E. Watanabe, *Ann.*, **603**, 1 (1957).

(4) A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 3723 (1953).