

The volatile components of the cyclization mixture were analyzed by using Δ^3 -butenyl-1-cyclohexene as the internal standard. A 5-ft. \times $1/8$ -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. \times $3/8$ -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_D^{20} 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,

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

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 $\text{C}_{10}\text{H}_{18}\text{O}$: C, 77.86; H, 11.76. Found: C, 77.6; H, 11.5.

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.

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

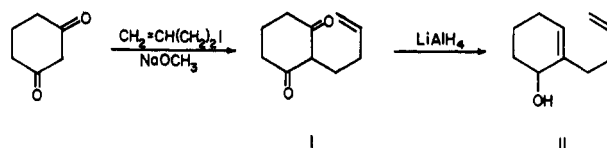
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The dienol II has been prepared from 2-butenylcyclohexane-1,3-dione (I). On treatment with formic acid it underwent facile stereoselective cyclization to give *syn*- Δ^1 ,⁹-6-octalol. The dienols VI and VII were prepared from 6-butenyl- Δ^2 -cyclohexenone (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 report² 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



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-

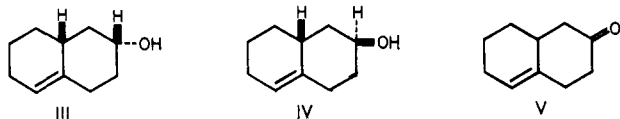
(1) (a) Paper III of this series: W. S. Johnson, S. L. Gray, J. K. Crandall, and D. M. Bailey, *J. Am. Chem. Soc.*, **86**, 1966 (1964); (b) a preliminary account of the work described in the present paper was reported at the I.U.P.-A.C. Meeting in London, July 17, 1963; see W. S. Johnson, *Pure Appl.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

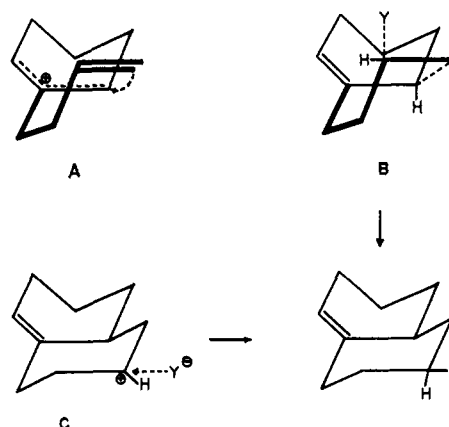
cated the composition: 92% *syn*⁵- $\Delta^{1,9}$ -6-octalol (III), 6% *anti*⁵- $\Delta^{1,9}$ -6-octalol (IV), and 2% olefins. The absolute yield of the octalol III, determined by quantitative peak area comparison experiments and corrected for the purity of dienol II, was 80%. The actual yield therefore is between 80 and 92%. In these simple model series we have not endeavored to obtain more precise information on the actual yield, since we were more concerned about the specificity of the process as reflected by relative yields.



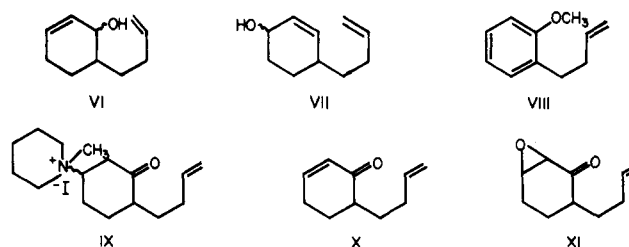
Evidence for the structure and configuration of the *syn* and *anti* octalols III and IV was provided as follows. The fraction containing a mixture of these alcohols was separated by preparative gas chromatography, and one of the components was isolated as the crystalline 3,5-dinitrobenzoate, m.p. 118–119.5°, the compositional analysis of which was compatible with the formula $C_{17}H_{18}O_6N_2$. Oxidation of the alcohol mixture with Jones reagent gave a single (by gas chromatography) ketone, namely $\Delta^{1,9}$ -6-octalone (V), characterized as the 2,4-dinitrophenylhydrazone, m.p. 172–174°. The n.m.r. spectrum of this derivative was entirely consistent with the presumed structure. Since there was absorption for one, and only one, vinylic proton, and since the double bond did not move into conjugation with the hydrazone residue, the structure of the octalone must be that represented by V. Reduction of the octalone V with lithium aluminum hydride gave a mixture of epimeric alcohols which exhibited gas chromatographic behavior identical with that of the alcohols produced in the cyclization reaction. The preponderant epimer obtained in the reduction corresponded to that in the cyclization, and it showed a higher retention time on gas chromatography than the less preponderant isomer. The former alcohol is therefore considered to be the substance III with a pseudo-equatorial hydroxyl group, and the latter isomer is regarded as the epimer IV. Confirmation of the configurational assignments was obtained by examination of the n.m.r. spectrum of the epimeric mixture of alcohols from the cyclization. The band width of the resonance corresponding to the proton on the carbon holding the hydroxyl group was about 30 c.p.s., which indicates that the proton in the major component is axial.⁶

Some other cyclization conditions were examined. With 0.08 *N* perchloric acid in 80% aqueous acetone at 75°, the reaction was about 90% complete in 4.5 hr. The product composition was almost the same as that obtained in the experiment described above. Solvolysis of the 3,5-dinitrobenzoate of II either in perchloric acid–aqueous acetone at 75° or in formic–acetic acid at room temperature was considerably slower than that of the free alcohol. Thus solvolysis of the ester in the former solvent required 29 hr. and,

in the latter, 8 hr. for about 90% completion. In both experiments the absolute yields of the octalols III and IV, determined by vapor phase chromatography, were 65 and 4–5%, respectively. When the solvolysis of the ester in formic–acetic acid was conducted at 75° for 2.3 hr., the gas chromatogram exhibited a new peak. After a reaction period of 4.7 hr., none of the $\Delta^{1,9}$ -octalols remained, and only the peak corresponding to the new substance was present. This new product, therefore, is derived from both of the octalols. Since it showed no resonance for a vinylic proton in the n.m.r. spectrum, it is tentatively regarded as the product resulting from migration of the olefinic bond of III and IV into the 9,10-position. When the product of cyclization of the dienol II with perchloric acid (see above) was heated with formic–acetic acid containing sodium formate for 4.7 hr. at 76°, isomerization to the presumed 9,10-octalol was complete.



The stereoselective formation of the *syn* isomer III in the cyclization may be rationalized as a rapid ionization to the allylic cation A followed by a synchronous ring closure and attack by nucleophile as suggested by formula B. Alternatively the process could be stepwise, giving the intermediary cyclic secondary cation C which undergoes preferential equatorial attack by the nucleophile.^{1a} It is, on the other hand, possible that the cyclization occurs synchronously with the ionization of the allylic system, as is evidently the case in the linalool \rightarrow terpineol conversion.³ However, in the systems VI and VII described below, evidence has been obtained which suggests (but does not prove) that the ionization step precedes cyclization.



We next undertook the examination of the cyclization of the butenylcyclohexenols VI and VII. This pair is of interest because, if ionization precedes cyclization, these substances would afford a common intermediate. *A priori* these are more complex systems than the case of II, treated above, because there is an additional problem of stereoisomers in both re-

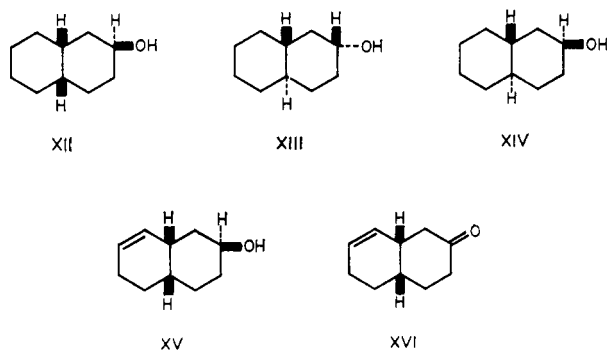
(5) The terms *syn* and *anti* are used here to designate the stereochemical relationship between the hydrogen atom on the carbon bearing the substituent (usually hydroxyl) and the angular hydrogen atom in the nearest angular position.

(6) Cf. R. V. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).

actants (VI and VII) as well as in the expected products. The alcohols VI and VII were prepared as follows. *o*-(Δ^3 -Butenyl)anisole (VIII), obtained by coupling allylmagnesium bromide with *o*-methoxybenzyl bromide, was submitted to Birch reduction with lithium and ethanol in ammonia at -78° .⁷ Mild acid hydrolysis of the resulting enol ether, followed by treatment with piperidine,⁸ gave the piperidyl ketone which was converted to the methiodide IX, m.p. 162.5–164° dec. On warming with pyridine this quaternary salt decomposed to give 6-(Δ^3 -butenyl)- Δ^2 -cyclohexenone (X). Quantitative analysis of this product by n.m.r. spectroscopy demonstrated that the terminal vinyl group was intact to the extent of 87%. The remainder of the material was undoubtedly the dihydro compound resulting from partial reduction of the vinyl group. This contaminant evidently was not eliminated on recrystallization of the quaternary salt IX. It was therefore carried all the way through the series, as it was not expected to interfere with the cyclization experiments.

Treatment of the unsaturated ketone X with lithium aluminum hydride under conventional conditions resulted in considerable reduction of the conjugated olefinic bond as well as of the carbonyl group.⁹ After considerable experimentation, a low temperature procedure was finally developed which, as shown by quantitative vapor phase chromatography, gave a product consisting of 81% of a 2.3 to 1 epimeric mixture of the desired butenylcyclohexenol VI.

For the preparation of the isomeric butenylcyclohexenol VII, the dienone X was converted, by the action of alkaline hydrogen peroxide, into the epoxy ketone XI (undoubtedly a mixture of epimers), which was submitted to the Wharton rearrangement.¹⁰ Thus treatment with hydrazine and acetic acid gave a product which, by quantitative vapor phase chromatographic analysis, was shown to contain 70% of the desired dienol VII as a 2.1 to 1 epimeric mixture. This material was also used directly in the cyclization studies.



When the dienols VI and VII were treated with the formic-acetic acid (82:18) at room temperature, the

(7) Bryan Roberts, of our laboratory, has demonstrated that these mild conditions are required in order to minimize reduction of the terminal vinyl group.

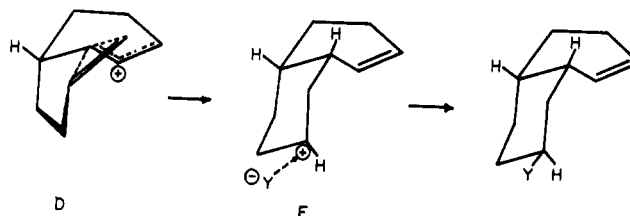
(8) The method of G. Stork and W. N. White, *J. Am. Chem. Soc.*, **78**, 4604 (1956).

(9) Cf., *inter alia*, R. Albrecht and Ch. Tamm, *Helv. Chim. Acta*, **40**, 2216 (1957); D. Kupfer, *Tetrahedron*, **15**, 193 (1961); C. Djerassi and W. Rittel, *J. Am. Chem. Soc.*, **79**, 3528 (1957); A. Akisanya, C. W. L. Bevan, T. G. Halsall, J. W. Powell, and D. A. H. Taylor, *J. Chem. Soc.*, 3705 (1961); M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdoun, *Bull. soc. chim. France*, [5] **19**, 1042 (1952).

(10) P. S. Wharton and D. H. Bohlen, *J. Org. Chem.*, **26**, 3615 (1961).

reaction was about 90% complete after 5 min. After 18 min. the reaction mixture was neutralized, and the product was treated with excess lithium aluminum hydride in order to cleave the esters. Vapor phase chromatography showed one major alcohol peak corresponding to a relative yield of 92% of the same octalol from both dienols. This crude product was hydrogenated over palladium-on-carbon in order to saturate the olefinic bonds and analyzed by vapor phase chromatography by a technique which is known to separate all of the four β -decalols.² By quantitative peak enhancement and area comparison experiments with *trans-syn*- β -decalol, it was possible to show that the absolute yield (corrected for the state of purity of starting material) of alcohols from the dienol VII was: 56% of *cis-anti*-2-decalol (XII), 5% of *trans-syn*-2-decalol (XIII), and 0% of *trans-anti*-2-decalol (XIV). The yields from the dienol VI were: 68% of XII, 10% of XIII, and 3% of XIV. The deduction that the principal primary product of cyclization was $\Delta^{7,8}$ -*cis-anti*-2-octalol (XV) was confirmed by isolation of the octalol fraction *via* preparative gas phase chromatography. The n.m.r. spectrum of this fraction indicated absorption for two vinylic protons, showing that the double bond did not involve one of the bridgehead carbons. Oxidation of the octalol fraction with Jones reagent gave a ketone XVI which was converted to a yellow (unconjugated) unsaturated 2,4-dinitrophenylhydrazone, m.p. 167–168°. The n.m.r. spectrum of this derivative also exhibited absorption for two vinylic protons. The small yields of *trans*-decalols XIII and XIV found after hydrogenation may indicate the formation of traces of the corresponding $\Delta^{7,8}$ -octalols in the cyclization; however, since there seemed to be only a single octalol produced on cyclization (see above), the *trans*-decalols might be artifacts due to bond migration or to isomerization at the allylic position during hydrogenation.¹¹

Considering the state of purity of the starting dienols, and the number of operations involved before an analysis of products could be made, the yields of cyclic products are, within experimental error, the same from each isomeric dienol. This result constitutes suggestive evidence¹² for a common intermediate, namely the allylic cation D.



Of special interest is the high degree of stereoselectivity of the cyclization to give, unexpectedly, the *cis-anti*-octalol XV in good yield. Formation of the *cis-anti* isomer precludes a concerted *trans*-addition of nucleophile to the olefinic bond which would lead to the *syn* series. The results, on the contrary, suggest a stepwise process with the intermediacy of a secondary bicyclic cation like E. Examination of

(11) Cf. D. K. Fukushima and T. F. Gallagher, *J. Am. Chem. Soc.*, **77**, 139 (1955).

(12) Note that the result is a necessary, but not sufficient, condition for proof of the intermediacy of the allylic cation.

Dreiding models suggests that when the allylic cation is in a conformation that would lead to a *cis*-fused product, *e.g.*, that represented by formula D, the bond angles permit better overlap of the empty orbital of the allylic cation with the π -orbital of the terminal olefinic bond than with conformations which would lead to *trans* ring fusion. Perhaps it is this stereo-electronic factor which is responsible for the preference of cyclization to form a *cis*-fused product, $D \rightarrow E$. If the nucleophile makes a preferential equatorial attack on the intermediary bicyclic secondary cation,^{1a} the latter must react in the conformation E, rather than in its flipped version, in order to yield the product found.

Experimental

2-(Δ^3 -Butenyl)cyclohexane-1,3-dione (I).—A previously described¹³ method was followed. To a solution of 110 g. of cyclohexane-1,3-dione¹⁴ and 56.8 g. of sodium methoxide in 290 ml. of anhydrous methanol was added 179 g. of Δ^3 -butenyl iodide.¹⁵ The mixture was heated under reflux for 3 hr., then concentrated by distillation at reduced pressure. The residue was treated with excess 3% aqueous sodium hydroxide and washed with ether to remove nonacidic O-alkylated material. The aqueous layer, after removal of dissolved ether in a stream of air, was cooled in an ice-salt bath, then carefully acidified with hydrochloric acid while the walls of the flask were scratched. The crystalline product was collected by filtration, washed well with water, dried, and recrystallized from aqueous methanol to give 16.3 g. of colorless needles, m.p. 95–97.5°. An additional 1.0 g. (second crop), m.p. 94.5–97.5°, and 0.4 g. (third crop), m.p. 93–97.3°, were obtained by concentration of the mother liquors. The first-crop material was analyzed.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.1; H, 8.55.

2-(Δ^3 -Butenyl)- Δ^2 -cyclohexenol (II).³—To a stirred solution of 30 g. of lithium aluminum hydride in 1350 ml. of anhydrous ether was added 19.1 g. of the solid diketone I. The mixture was heated under reflux for 5 hr., then cooled in an ice-salt bath while 69 ml. of water was added, followed by 61.5 ml. of 10% sodium hydroxide solution. The mixture was filtered; the inorganic salts were washed with ether and the combined filtrates evaporated. The residue was distilled through a 24-in. spinning band column to give 13.2 g. of the dienol as a colorless liquid, b.p. 75–76.5° (1.6 mm.). Vapor phase chromatography on a silicone-rubber column indicated the presence of up to 10% of a contaminant with a retention time close to that of the principal product. The material was therefore purified by conversion to the 3,5-dinitrobenzoate as described below.

To a solution of 7.7 g. of the aforementioned dienol in 92 ml. of anhydrous pyridine was added, in portions over a period of 10 min., 19.5 g. of 3,5-dinitrobenzoyl chloride. During the addition the mixture was stirred vigorously and was maintained at a temperature of 0–5°. The mixture was allowed to stand at room temperature for 35 min., then water was added with stirring and cooling so that the temperature did not exceed 10°. After the exothermic reaction was over, the mixture was diluted further with 200 ml. of water. The crystalline precipitate that was formed was collected by filtration, washed thoroughly with water, and dried. Three recrystallizations from petroleum ether gave 12.55 g. of the 3,5-dinitrobenzoate as colorless plates, m.p. 62.6–64.2°.

Anal. Calcd. for $C_{17}H_{18}O_6N_2$: C, 58.95; H, 5.24; N, 8.09. Found: C, 59.1; H, 5.43; N, 8.13.

The dienol was regenerated by distilling a mixture of 8 g. of the aforementioned 3,5-dinitrobenzoate and 350 ml. of 3 *N* aqueous sodium hydroxide, the volume being maintained constant by the dropwise addition of water. The dienol, which steam distilled, was isolated by saturating the distillate with sodium chloride and extracting the mixture with ether. The combined ether layers

were dried over anhydrous magnesium sulfate, and the residue obtained on evaporation of the solvent was distilled through a 24-in. Podbielniak column to give 3.4 g. of colorless liquid, which was 93% pure as indicated by vapor phase chromatography over a 15% Craig succinate column.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.7; H, 10.6.

The *p*-nitrobenzoate was prepared by reaction with *p*-nitrobenzoyl chloride in pyridine. The product could not be crystallized even after chromatography on Florisil. The chromatographically homogeneous material was analyzed.

Anal. Calcd. for $C_{17}H_{18}O_4N$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.9; H, 6.48; N, 4.88.

***o*-(Δ^3 -Butenyl)anisole (VIII).**—Allylmagnesium bromide was prepared¹⁶ from 310 g. of allyl bromide, and titration indicated it to contain 74% of the Grignard reagent. To this reagent was added a solution of 169.5 g. of *o*-methoxybenzyl bromide,¹⁷ b.p. 75–77° (0.5 mm.), in an equal volume of dry benzene over a period of 45 min. with stirring and cooling. The mixture was allowed to stir for 15 hr. at room temperature, then for 1 hr. at the boiling point. The mixture was cooled (ice-salt bath), and 80 ml. of water was added slowly with stirring. The inorganic precipitate was removed by filtration, and the combined filtrates and ether washings were concentrated by distillation through a 18-in. saddle-packed column. The residue, which contained solid material, was again filtered, the filter cake washed with benzene, and the combined filtrates and washings were distilled through a 24-in. spinning band column. The fraction boiling at 95.8–96.1° (7 mm.) amounted to 84 g. (61% yield).

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.7; H, 8.79.

6-(Δ^3 -Butenyl)- Δ^2 -cyclohexenone (X).—A solution of 22 g. of the aforementioned butenylanisole in 410 ml. of liquid ammonia and 220 ml. of 1,2-dimethoxyethane was cooled with a Dry Ice-acetone bath, then 6.6 g. of lithium wire was added. The mixture was vigorously stirred while 5 g. of absolute ethanol was added over a 15-min. period, after which time the bronze phase had disappeared. An additional 19.9 g. of ethanol was added over a 6-min. period. Excess ammonium chloride was then added rapidly until the blue color of the solution disappeared. The ammonia was allowed to evaporate at room temperature, then sufficient water was added to dissolve the inorganic material, and the whole was extracted with ether. The combined ether extracts were washed with water, then with saturated brine, and dried over anhydrous magnesium sulfate. The residue obtained after removal of the solvent through a 24-in. spinning band column was mixed with 68 ml. of 5% aqueous oxalic acid and 32 ml. of 1,2-dimethoxyethane and allowed to stir for 4 hr. in an atmosphere of nitrogen. The product was extracted with ether, and the combined ether extracts were washed with water, saturated brine, 5% sodium bicarbonate solution, again with saturated brine, and finally dried over anhydrous magnesium sulfate. The residue obtained on removal of the solvent through a 24-in. spinning band column was refluxed gently with 69.5 g. of piperidine for 4 hr. under an atmosphere of nitrogen, and the mixture was processed according to the procedure already described.⁸ The product was distilled through a 6-in. Vigreux column, and the fraction boiling at 135–139° (0.035 mm.) amounted to 23.6 g. The infrared spectrum showed a major band at 5.85 μ , indicating that the product consisted primarily of the piperidyl ketone contaminated with the unsaturated ketone. The crude product (23.9 g.) was treated with 115 g. of methyl iodide as previously described.⁸ Recrystallization of the crude product three times from isopropyl alcohol gave 31.5 g. of 2-*N*-piperidyl-6-(Δ^3 -butenyl)-cyclohexenone methiodide, m.p. 162.5–164° dec.

Anal. Calcd. for $C_{16}H_{28}ONI$: C, 50.94; H, 7.48; N, 3.72. Found: C, 50.7; H, 7.73; N, 3.52.¹⁸

The aforementioned methiodide was treated with 20.1 g. of pyridine as previously described.⁸ Distillation of the crude product through a 24-in. spinning band column gave 11.4 g., b.p. 55–56° (0.35 mm.), of the α,β -unsaturated ketone X, $\lambda_{\max}^{5.95} \mu$ (conj. C=O).

(13) H. Stetter and W. Dierichs, *Ber.*, **85**, 61 (1952).

(14) R. B. Thompson, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 278.

(15) Prepared from Δ^2 -butenyl alcohol (R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, 1995 (1934)) by displacement of the tosylate with iodide according to the procedure of M. F. Ansell and S. S. Brown, *ibid.*, 1788 (1957).

(16) O. Grummitt, E. P. Budewitz, and C. C. Chudd, *Org. Syn.*, **36**, 60 (1956).

(17) Prepared from *o*-methoxybenzyl alcohol by the method of A. Lapworth and J. B. Shoesmith, *J. Chem. Soc.*, 1391 (1922).

(18) Note that this product contains about 13% of dihydro material as shown by quantitative n.m.r. spectroscopic analysis of the vinyl proton absorption of the product described as 6-(Δ^3 -butenyl)- Δ^2 -cyclohexenone (X).

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.0; H, 9.56.

2,3-Oxido-6-(Δ^3 -butenyl)cyclohexanone (XI).—The method of Wharton and Bohlen¹⁰ was used. A solution of 7.5 g. of the aforementioned butenylcyclohexenone X, 50 ml. of methanol, and 14.4 ml. of 30% hydrogen peroxide was cooled to 15°, then 4.1 ml. of 6 *N* sodium hydroxide solution was added slowly with stirring over a period of 40 min. while the temperature was maintained at 15–20°. The mixture was stirred for 3.25 hr. while the temperature was maintained at 20–25°. Water was then added and the whole extracted with ether. The combined ether layers were washed with saturated brine and dried over anhydrous magnesium sulfate. The residue obtained on distillation of the solvent through a spinning band column was distilled through a 24-in. Podbielniak column to give 3.43 g. of colorless liquid, b.p. 71–73° (0.20 mm.), $\lambda_{\text{max}}^{\text{film}}$ 5.82 μ ($C=O$).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.5; H, 8.99.¹⁸

4-(Δ^3 -Butenyl)- Δ^2 -cyclohexenol (VII).—The procedure of Wharton and Bohlen¹⁰ was used. To a cooled solution of 3 g. of the aforementioned epoxy ketone XI in 3.6 ml. of absolute ethanol was added 1.52 ml. of 95+ % hydrazine followed by 0.22 ml. of glacial acetic acid with stirring and cooling. On removal of the cooling bath, the mixture became quite warm with a vigorous evolution of gas which was complete in less than 5 min. After standing for 10 min. the solution was diluted with water, saturated with sodium chloride, and extracted with ether. The combined ether layers were washed with saturated brine and dried over anhydrous magnesium sulfate. The yellow oily residue obtained on removal of the solvent through a Podbielniak column was distilled through a 15-in. Vigreux column to give 1.44 g. of colorless liquid, b.p. 95.2–97° (2 mm.). The infrared spectrum showed no absorption in the carbonyl region.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.2; H, 10.47.¹⁸

6-(Δ^3 -Butenyl)- Δ^2 -cyclohexenol (VI).—A mixture of 8.2 g. of lithium aluminum hydride and 170 ml. of anhydrous ether was cooled with Dry Ice–acetone, and a solution of 1.70 g. of the unsaturated ketone X in 25 ml. of anhydrous ether was added slowly with vigorous stirring at a rate such that the temperature remained below –60°. After the addition was complete, the temperature was allowed to rise to –40° where it was maintained for 45 min. by means of an alcohol–ice bath. The mixture was then permitted to warm to 5° over a period of 1.75 hr., and after 5 min. at this temperature the mixture was again cooled to below –60°; then 21.7 ml. of water, followed by 10 ml. of 15% aqueous sodium hydroxide, was added slowly while the temperature was maintained below –50°. The mixture was then allowed to stir overnight at room temperature. The solids were removed by filtration, and the filtrate was concentrated by distillation through a 24-in. spinning band column. The residue was evaporatively distilled twice at 85–86° (0.6 mm.) to give 1.49 g. of colorless product.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.2; H, 10.7.

Determination of Purity of the Dienols VI and VII.—The dienols were analyzed on an Aerograph gas chromatograph equipped with a hydrogen flame ionizer detector and a 7.5-ft. 15% Craig succinate column operated at 177–185°. The peak areas were estimated by triangular approximation and those corresponding to olefins (retention time 1.4–4.7 min.) were corrected for relative peak response by the factor 0.47 which was obtained by comparing the areas obtained on analysis under the same conditions of a mixture of known concentration of pure *trans*- Δ^2 -octalin and *trans*-syn- β -decalol. The product VI was thus shown to contain: 4.5% olefins (retention time at 185°, 1.4–4.7 min.), 14.5% dihydro impurity (10.8–11.8 min.), 24.2% dienol-epimer a (13.9 min.), and 56.8% dienol-epimer b (15.3 min.). Similarly the product VII was shown to contain: 9.4% olefins (retention time at 185°, 1.4–4.7 min.), 19.6% dihydro impurity (12.7–14.0 min.), 22.4% dienol-epimer a (16.5 min.), and 47.6% dienol-epimer b (18.1 min.). The dihydro impurities in VI and VII appeared in the chromatograms as characteristic doublets. (When either of the dienols VI or VII was cyclized as described below, both of these doublets appeared in the same ratio in the chromatograms of the products, suggesting simple allylic rearrangement of the dihydro impurities.) Further evidence for the presence of these dihydro impurities was provided by n.m.r. spectroscopy of the dienols. Integration of the spectrum of

dienol VI indicated 86 \pm 3% of the absorption was due to the protons on the terminal olefinic bond.

Cyclizations. 1. **2-(Δ^3 -Butenyl)- Δ^2 -cyclohexenol (II) with Formic Acid.**—A small glass tube containing 106.7 mg. of the dienol II (93% pure as determined by vapor phase chromatography) was dropped into a flask containing 35 ml. of anhydrous¹⁹ formic acid (substrate, 0.02 *M*). The mixture was swirled and allowed to stand at 25°. After 5 min., thin layer chromatography as described below (experiment 2) indicated that only a trace of dienol remained. After 5.5 min., the mixture was added slowly to a slurry of 140 ml. of 30% sodium hydroxide solution and 200 g. of ice. The temperature was not allowed to exceed 18°. The mixture was saturated with sodium chloride, stirred for 1 hr. at 24° and then extracted with ten 6-ml. portions of carbon disulfide, each portion being washed once with saturated brine. The combined organic layers were dried over anhydrous sodium sulfate, diluted to exactly 100 ml., and analyzed by vapor phase chromatography as described above for determining the purity of the dienols VI and VII. The relative yields of products thus obtained were: hydrocarbons: 0.86% (retention time at 178°, 3.8 min.), 1.39% (4.2 min.), 2.45% (5.0 min.); impurity also found in starting material: 4.03% (11.9 min.), 2.47% (12.6 min.); *anti*-octalol IV: 5.47% (26.3 min.); *syn*-octalol III: 83.3% (28.7 min.). This last peak corresponded to the major product obtained in the cyclization described below (experiment 2). The evidence for the constitution of this major product is also given below. The relative yield of the octalol III, corrected for impurity in the starting material, is therefore 92%. The absolute yield was determined by adding exactly 1 ml. of a standard 3.78×10^{-3} *M* solution of *trans*-syn-2-decalol²⁰ in benzene to a 1-ml. aliquot of the 100-ml. carbon disulfide solution of the cyclization product. The area of the octalol peak was then compared with that of the decalol. The relative peak areas were 1:1.40; therefore the concentration of the octalol was 5.29×10^{-3} *M*, it being reasonable to assume that the peak responses of the two substances are the same. Thus the absolute yield of the octalol III was 80%, corrected for the impurities in the starting material.

2. **2-(Δ^3 -Butenyl)- Δ^2 -cyclohexenyl 3,5-Dinitrobenzoate with Perchloric Acid.**—A 3.46-g. sample of the aforementioned 3,5-dinitrobenzoate was dissolved with stirring in 200 ml. of the perchloric acid reagent²¹ maintained at $75 \pm 1^\circ$ (substrate, 0.05 *M*). The progress of the reaction was followed by thin layer chromatography on Merck and Co. Silica Gel G. With 30% ethyl acetate in benzene as the mobile phase, the starting material exhibited R_f 0.75. After 29 hr. the major component appeared as a single spot, R_f 0.35, with only traces of materials with R_f 0.75 and 0.24. The reaction mixture was cooled and 50 ml. of water was added, followed by enough 3 *N* sodium hydroxide solution, added in drops, so that the mixture was only slightly acidic (pH 5–6). The bulk of the acetone was then removed by distillation through a 24-in. Podbielniak column. The aqueous residue, containing droplets of separated oil, was saturated with sodium chloride and extracted with ether. The combined ether layers were washed with saturated sodium bicarbonate solution, then concentrated by distillation as described above. The residue was diluted with 200 ml. of water and the mixture submitted to steam distillation until about 400 ml. of distillate was collected. The distillate was saturated with sodium chloride, extracted with ether, and the combined ether layers were dried over anhydrous magnesium sulfate. The residue obtained on distillation of the solvent through a 24-in. Podbielniak column amounted to 1.38 g. of pale brown oil. (A total of 0.16 g. of crude semicrystalline 3,5-dinitrobenzoate was removed from the residue from the steam distillation.)

An accurately weighed specimen of the crude solvolysis product was dissolved in carbon disulfide and diluted to an appropriate volume for vapor phase chromatographic analysis as described above in experiment 1. The absolute yields (with retention times at 184°) were: 5% *anti*-octalol IV (24.8 min.) and 65% *syn*-octalol III (27.0 min.).

Structure and Configuration of the $\Delta^{1,9}$ -6-Octalols (III and IV).—A 0.488-g. portion of the crude cyclization product from cycl-

(19) Distilled from boric anhydride.

(20) We are indebted to Prof. W. G. Dauben for providing us with the pure comparison material.

(21) This reagent was prepared by mixing four volumes of acetone with one of water containing the calculated amount of perchloric acid (reagent grade) so that the final solution was 0.08 *N* in acid; cf. H. L. Goering and E. F. Silversmith, *J. Am. Chem. Soc.*, **77**, 6249 (1955).

ization experiment 2 described above was submitted to preparative vapor phase chromatography over a silicone-rubber column, and the octalol fraction was collected. A 39-mg. portion of the material was converted into the 3,5-dinitrobenzoate (as described above). Four recrystallizations from hexane afforded 16 mg. of pale yellow needles, m.p. 118–119.5°.

Anal. Calcd. for $C_{17}H_{18}O_6N_2$: C, 58.95; H, 5.24; N, 8.09. Found: C, 59.1; H, 5.32; N, 8.19.

A 0.143-g. portion of the octalol fraction in 2.5 ml. of acetone was titrated slowly (with stirring and cooling) with Jones reagent²² until an excess of the oxidant was present. Isopropyl alcohol was added to destroy the excess oxidant, and the mixture was saturated with sodium chloride. A little potassium carbonate was added to neutralize the acid, and the mixture was extracted with ether. The combined ether layers were washed thoroughly with saturated brine and dried over anhydrous magnesium sulfate. The residue obtained on removal of the solvent through a 24-in. Podbielniak column exhibited a single peak on gas chromatography over a UCON polar 20% column at 126°.

The 2,4-dinitrophenylhydrazone of $\Delta^{1,9}$ -6-octalolone crystallized from isopropyl alcohol as dense orange microcrystals, m.p. 172–174°, $\lambda_{\text{max}}^{\text{CHCl}_3}$ 367 m μ (ϵ 26,400). The n.m.r. spectrum exhibited absorption for 1 proton as a singlet at 5.63 p.p.m. (C=CH).

Anal. Calcd. for $C_{16}H_{18}O_4N_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.0; H, 5.59; N, 16.90.

A sample of the octalene prepared as described in the preceding experiment was reduced with excess lithium aluminum hydride as described below for reducing the formates. Vapor phase chromatography of the product as described above in cyclization experiment 1 gave two peaks with retention times that were identical with those of the presumed octalols in the cyclization experiment 1. The major peak from the lithium aluminum hydride reduction product corresponded with the major octalol peak in the cyclization experiment.

3. 2-(Δ^3 -Butenyl)- Δ^2 -cyclohexenyl 3,5-Dinitrobenzoate with Formic-Acetic Acid.—A 3.46-g. sample of the aforementioned 3,5-dinitrobenzoate was dissolved in 500 ml. of formic-acetic acid reagent²³ containing 1.36 g. (2 moles per mole of substrate) of sodium formate. After 8 hr. at room temperature, thin layer chromatography (see cyclization experiment 2) indicated that the reaction was essentially complete. (In this case benzene was used as the mobile phase and the R_f values were 0.54 for the starting material and 0.41 for the cyclization product.) The mixture was diluted with saturated brine and extracted with ether. The combined ether layers were washed thoroughly with saturated brine, then with sodium bicarbonate to remove residual formic acid. The combined ether layers (including those from back-extractions) were dried over anhydrous magnesium sulfate and concentrated by distillation through a 24-in. Podbielniak column.

Water was added to the residue which was then steam distilled as described above (cyclization experiment 2). The product, isolated from the distillate as described above, in 40 ml. of ether was treated with 0.87 g. of lithium aluminum hydride which was added with stirring and cooling. The mixture was then refluxed for 1 hr., then, with stirring and cooling, diluted with 2.1 ml. of water, followed by 1.8 ml. of 10% sodium hydroxide solution. After stirring for 3 hr. at room temperature, the mixture was filtered and the inorganic salts were washed well with ether. The combined filtrates and washings were concentrated by distillation through a 24-in. Podbielniak column, and the residue analyzed by vapor phase chromatography as described above (cyclization experiments 1 and 2). The absolute yields (with retention times at 184°) were: 4% *anti*-octalol IV (24.9 min.) and 65% *syn*-octalol III (26.9 min.).

A total of 0.3 g. of semicrystalline dinitrobenzoate was recovered from the residue from the steam distillation (*cf.* experiment 2).

When the cyclization described above was repeated at $75 \pm 1^\circ$ for 2.3 hr., the gas chromatogram of the product over an SE 30/5% column at 150° exhibited a new peak with retention time

6.9 min., and the peaks corresponding to the $\Delta^{1,9}$ -octalols III and IV (at 6.2 and 6.3 min. respectively) were diminished. When the reaction period was extended to 4.7 hr., the peaks corresponding to the $\Delta^{1,9}$ -octalols III and IV had disappeared completely, and only the new peak was present. The fraction corresponding to this new peak was isolated by preparative chromatography. The n.m.r. spectrum showed no absorption for a vinylic proton in the region between 4.1 and 7.3 p.p.m.

4. 2-(Δ^3 -Butenyl)- Δ^2 -cyclohexenol (II) with Perchloric Acid.—A 1.01-g. sample of the alcohol II, purified by saponification of the 3,5-dinitrobenzoate (see above), was dissolved in 132 ml. of the perchloric acid reagent.²¹ After 4.5 hr. at $75 \pm 1^\circ$, the reaction was estimated to be more than 90% complete as determined by thin layer chromatography with 30% ethyl acetate in benzene as the mobile phase (R_f starting material, 0.50; product, 0.34). The reaction mixture was treated as described above for experiment 1 except that the steam distillation was omitted. The vapor phase analysis indicated that the absolute yields of the octalols III and IV were 66 and 5%, respectively.

A solution of 18 mg. of the crude cyclization product described directly above in 5.5 ml. of formic-acetic acid²³ containing 15 mg. of sodium formate was heated at 76° for 4.7 hr. The product was isolated as described below (experiment 5). Vapor phase chromatography over an SE 30/5% column indicated no peaks for the octalols III and IV, but only a single peak for the presumed $\Delta^{9,10}$ -octalol (see preceding experiment).

5. 4-(Δ^3 -Butenyl)- Δ^2 -cyclohexenol (VII) with Formic-Acetic Acid.—A 0.76-g. sample of the dienol VII (see above) was dissolved in 250 ml. of the formic-acetic acid reagent²³ and allowed to stand at room temperature. After 5 min. the reaction appeared to be essentially complete as estimated by thin layer chromatography with 30% ethyl acetate in benzene as the mobile phase (R_f starting material, 0.37; product, 0.32). After 18 min. the mixture was processed as described in cyclization experiment 3 except that the steam distillation step was omitted and a 24-in. spinning band column was used in place of the Podbielniak column. Vapor phase chromatographic analysis, carried out as described in cyclization experiment 1, indicated the following relative yields (and retention times at 183°): 10% olefins (1.7–4.7 min.), 2.8% unidentified material (7.7 and 8.8 min.), 19.0% impurities also found in starting material (11.1–14.3 min.), and 65.5% octalol XV (28.0 min.).

The crude cyclization product was dissolved in 20 ml. of methanol and hydrogenated over 115 mg. of 10% palladium-on-carbon catalyst at room temperature and atmospheric pressure. The major hydrogen uptake occurred during the first hour. After 18 hr. the mixture was filtered and the filtrate including washings was concentrated by distillation through a 24-in. Podbielniak column. The residue was diluted with carbon disulfide and submitted to vapor phase chromatographic analysis as described above in cyclization experiment 1. The relative yields (with retention times at 177°) were: 15.4% hydrocarbons (1.5–4.0 min.), 18.1% dihydro alcohol derived from impurities present in starting material (8.9–11.0 min.), 0% *trans-anti*-2-decalol²⁰ (XIV) (15.9 min.), 5.9% *trans-syn*-2-decalol²⁰ (XIII) (18.2 min.), and 60.5% *cis-anti*-2-decalol²⁰ (XII) (22.6 min.). By a quantitative peak enhancement experiment carried out as described above (cyclization experiment 1), the absolute yields of the decalols (corrected for the purity of the starting dienol) were found to be 56% of XII, 5% of XIII, and 0% of XIV.

6. 6-(Δ^3 -Butenyl)- Δ^2 -cyclohexenol (VI) with Formic-Acetic Acid.—A 0.76-g. sample of the dienol VI (see above) was treated exactly as described above (cyclization experiment 5) for the isomer VII. Note that the R_f values in the thin layer chromatography (30% ethyl acetate in benzene) were 0.49 for starting material and 0.32 for product. Vapor phase chromatographic analysis of the crude cyclization product indicated the following yields (and retention times at 184°): 6.5% olefins (1.4–3.8 min.), 1.2% unidentified material (7.5–8.6 min.), 16.2% impurities also present in starting material (10.8–14.0 min.), and 74.2% octalol XV (27.6 min.). Analysis of the hydrogenated material gave the following relative yields (and retention times at 177°): 10.7% hydrocarbons (1.5–4.0 min.), 13.9% dihydro alcohols derived from impurities present in starting material (6.2–11.0 min.), 2.6% XIV (15.9 min.), 10.3% XIII (18.2 min.), and 62.5% XII (22.6 min.). A quantitative peak enhancement experiment gave the absolute yields (corrected for the purity of the starting dienol): 68% of XII, 10% of XIII, and 3% of XIV.

Isolation and Oxidation of $\Delta^{1,9}$ -*cis-anti*-2-Octalol (XV).—A 0.186-g. sample of the dienol VI was treated with 60.5 ml. of

(22) *Cf.* C. C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

(23) A reagent containing 82 parts (by weight) of formic acid and 18 parts of acetic acid was prepared as follows. Commercial 97–100% formic acid was assayed by titration, and the required amount of water was added to make the concentration 97.0%. Acetic anhydride, equivalent to the water, was then added.

anhydrous¹⁹ formic acid for 18 min. at 24°. The red solution was then added slowly with stirring to a mixture of 77 ml. of 50% sodium hydroxide solution and 150 g. of ice. After the addition was complete, the mixture was saturated with sodium chloride, stirred for 2 hr. at 24°, and extracted thoroughly with ether. The organic layers were washed with saturated brine and dried over anhydrous sodium sulfate. The residue obtained on evaporation of the ether by distillation through a 24-in. Podbielniak column was diluted with 10 ml. of carbon disulfide and a portion was submitted to vapor phase chromatography through a preparative Craig succinate column at 190°. The fraction corresponding to the major peak (see above) was collected. The n.m.r. spectrum of this fraction (CDCl₃ solution) showed absorption for 2 protons as a multiplet centered at δ 5.55 p.p.m. (vinylic protons), 1 proton as a broad multiplet at 3.2–3.8 p.p.m., 1 proton as a singlet at 2.67 p.p.m. (–OH), and 12 protons at 1.0–2.3 p.p.m. (CH and CH₂). A 67-mg. sample of this octalol fraction was dissolved in 5 ml. of acetone and titrated with Jones reagent²² at 0° until the color of the reagent persisted. The mixture was

then stirred for 10 min. at 0°, then diluted with 10 ml. of saturated brine, and extracted with ether. The ether layers were washed with saturated brine and dried over anhydrous sodium sulfate. The residue obtained upon evaporation of the ether amounted to 59 mg. of a colorless oil, $\lambda_{\text{max}}^{\text{nm}}$ 5.83 μ (C=O). The 2,4-dinitrophenylhydrazone was obtained from ethanol-ethyl acetate as yellow plates, m.p. 167–168°, $\lambda_{\text{max}}^{\text{CHCl}_3}$ 367 m μ (ϵ 25,410).

Anal. Calcd. for C₁₅H₁₈O₄N₄: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.0; H, 5.65; N, 16.9.

The n.m.r. spectrum of the 2,4-dinitrophenylhydrazone in CDCl₃ solution exhibited absorption for 2 protons as a singlet at δ 5.65 p.p.m. (vinylic protons).

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF., AND THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Thermal Rearrangements of the 7-Carbomethoxy- Δ^2 -norcarenes¹

By JEROME A. BERSON² AND ELLI S. HAND

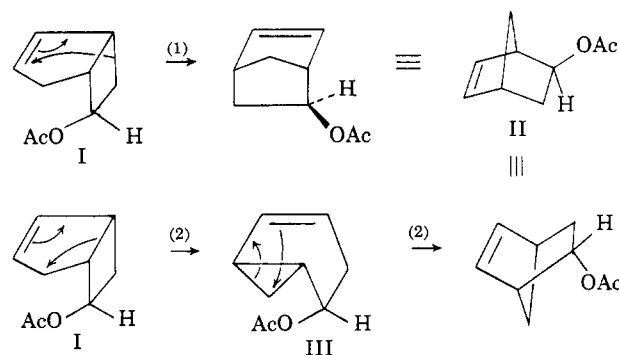
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Pyrolysis of the epimeric esters of the title compound at 425° leads to three sets of products: (i) dihydrophenylacetic ester derivatives and the corresponding aromatic; (ii) cyclopentadienecarboxylic ester and ethylene; (iii) *o*- and *p*-toluic esters and their dihydro analogs (but no *m*-toluic ester). The most likely mechanisms for these processes are, respectively: (i) C₁–C₇ cleavage to a diradical; (ii) vinylcyclopropane rearrangement followed by fragmentation; (iii) a new type of cleavage, leading to an open-chain heptatrienecarboxylic ester, followed by hydrogen shifts and cyclizations. The latter cleavage of the bicyclo[4.1.0]heptene-2 system to a 1,4,6-heptatriene is accompanied by at most a trace of the type of 1,5-hydrogen shift observed by Doering and Grimme in the higher homologs, bicyclo[5.1.0]octene-2 and bicyclo[6.1.0]nonene-2.

In molecular rearrangements that pass over carbonium ion, carbanion, or free radical intermediates, those sites of the reactant at which bonds are broken and new bonds are formed are usually obvious by inspection. Many thermal rearrangements (including some of the so-called "valence isomerizations"), however, are ambiguous in this respect, since the over-all structural change frequently can be formulated as proceeding by way of any of a number of different hypothetical bond reorganization paths. Thus, even the most rudimentary prerequisite for the specification of mechanism is missing. Although it usually is difficult to devise experiments that distinguish cleanly among the various possibilities, the feasibility or likelihood of the proposed component steps can sometimes be tested on independently prepared samples of the hypothetical intermediates or related model substances.

The stereospecific intramolecular thermal isomerization of *syn-cis*-bicyclo[3.2.0]hept-2-enyl-6 acetate (I) to *exo*-5-norbornenyl-2 acetate (II) provides an example of this kind of ambiguity. The rearrangement can be described by at least two paths which have not yet been distinguished from each other.³ One of these is a one-step formal allylic rearrangement of carbon (path 1); the other (path 2) is a two-step process, a preliminary cyclopentene \rightarrow vinylcyclopropane isomerization (I \rightarrow III) followed by conversion

of the intermediate vinylcyclopropane III to a new cyclopentene II. The original object of the present work was to test the feasibility of the hypothetical second step of path 2 by an investigation of the thermal behavior of readily accessible models of III.



For this purpose we prepared *endo*- and *exo*-7-carboethoxy- Δ^2 -norcarenes (IVb and Vb). The action of ethyl diazoacetate on 1,3-cyclohexadiene in the presence of powdered copper^{4,5} gives, in addition to diethyl fumarate and diethyl maleate, at least one 2:1 adduct VIb and the two 1:1 adducts IVb and Vb. Two other 1:1 adducts are formed in minute yields. Saponification and methylation converts these two minor adducts to methyl esters which have vapor chromatographic (v.p.c.) retention times identical with those of au-

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