aration from the carbon by dissolving in sodium hydroxide, filtration, and regeneration.

Registry No.—IIb, 22946-47-0; IIc, 22946-48-1; IIIb, 22966-73-0; IIIc, 22966-74-1.

Acknowledgment.—The author is indebted to the Research and Development Department of American Oil Co. for aid, particularly to E. M. Banas for nmr determinations, T. L. Hunter and G. W. Powers for chromatographic separations, and S. Meyerson for mass spectral determinations.

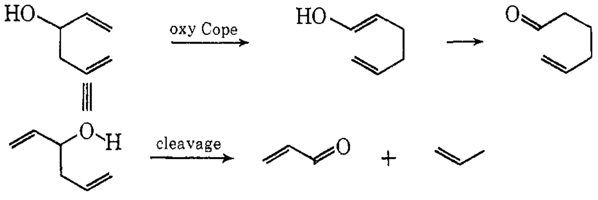
Vapor Phase Thermolyses of 3-Hydroxy-1,5-hexadienes. V. The Preparation of Allyl Vinyl Ketone[1]

ALFRED VIOLA AND E. JAMES IORIO

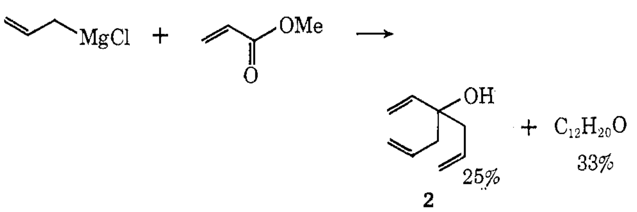
Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

Received June 2, 1969

The synthetic utility of the oxy-Cope reaction[2] thus far has consisted of a potential route to Δ^5-unsaturated carbonyl compounds or secondary products derived therefrom.[2-4] The oxy-Cope reaction, however, is almost invariably accompanied by a competing β-hydroxyolefin cleavage[5] which, in this system, may provide a facile route to α,β-unsaturated carbonyls.

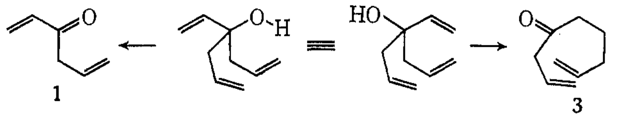


We have utilized this approach for the preparation of vinyl allyl ketone (1,5-hexadien-3-one) (1) in the following manner. The reaction of methyl acrylate with excess allylmagnesium chloride gave the expected 4-vinyl-1,6-heptadien-4-ol (2), albeit not as the major constituent of the product mixture.[6]



2

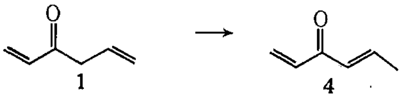
The structure of the previously reported[7] carbinol 2 was verified by its infrared spectrum and by quantitative hydrogenation to 4-ethyl-4-heptanol. The vapor phase thermolysis of 2 afforded the expected oxy-Cope product, 1,8-nonadien-4-one (3) and the desired cleavage product 1.



1 3

Under these conditions, there is no apparent tendency for double bond migrations. Thus, the structure of 3 was established by spectral data, by quantitative hydrogenation to 4-nonanone, and by oxidation which gave glutaric and succinic acids by cleavage of C_3–C_4 and C_4–C_5 bonds, respectively. The absence of any Δ^1 double bond rearrangement was established by the ultraviolet spectrum, which showed only end absorption above 220 mμ, except for the small n → π* band at 292 mμ, and by the nmr spectrum, which contains a two-proton doublet, with long range splitting, at δ 3.17, in agreement with a methylene group flanked by a carbonyl and a vinyl group.[8] Furthermore, the integrated areas of the nmr peaks clearly indicate the presence of six vinyl protons.

The structure assignment of 1 is based on spectral data and quantitative hydrogenation to 3-hexanone. Here again, the absence of any double bond migration is firmly established by the nmr spectrum, whose integrated peak areas indicate a 3:1 ratio of vinyl to aliphatic protons. The aliphatic doublet at δ 3.34 shows long range splitting and is in the region appropriate for its carbonyl and vinyl environment.[8] With prolonged standing, a small doublet gradually appeared at δ 2.1, indicative of the formation of a methyl group as in crotonaldehyde,[9] in accord with double bond migration to form vinyl propenyl ketone 4.



1 4

The characteristics of 1 prepared by this method are not in accord with those reported previously. The preparation of Nazarov and Zareteskaya,[10] consisting of hydration of divinylacetylene in strong acid media, is reported to polymerize rapidly, and the only structure proof appears to be acidcatalyzed cyclohydration to 2-methyltetrahydro-4-pyrone. These properties, as well as the physical constants given, appear more in accord with the vinyl propenyl ketone structure 4, and

---

(1) (a) Part IV: A. Viola and J. H. MacMillan, submitted for publication; (b) abstracted from part of the Ph.D. dissertation of E. J. I., Northeastern University, June 1968.

(2) J. A. Berson and M. Jones, Jr., *J. Amer. Chem. Soc.*, **86**, 5017, 5019 (1964); A. Viola and L. Levasseur, *ibid.*, **87**, 1150 (1965).

(3) A. Viola, E. J. Iorio, K. K. Chen, G. M. Glover, U. Nayak, and P. J. Kocienski, *ibid.*, **89**, 3462 (1967).

(4) J. Chuche and J. Wiemann, *Bull. Soc. Chim. Fr.*, 1491 (1968); J. W. Wilson and S. A. Sherrod, *Chem. Commun.*, 143 (1968); J. Chuche and N. Manisse, *C. R. Acad. Sci. Paris, Ser. C*, **267**, 78 (1968); A. Viola and J. H. MacMillan, *J. Amer. Chem. Soc.*, **90**, 6141 (1968).

(5) R. T. Arnold and G. Smolinsky, *ibid.*, **81**, 6443 (1959); *J. Org. Chem.*, **25**, 129 (1960); G. G. Smith and B. L. Yates, *J. Chem. Soc.*, 7242 (1965).

(6) The major $C_{12}H_{20}O$ component was shown to be 4-vinyl-1,9-decadien-4-ol, probably resulting from addition of the allyl Grignard reagent to one of the terminal allylic positions of 2. The structure proof of this compound has been described (R. Proverb, Annual Student Symposium of the Northeastern Section of the American Chemical Society, M.I.T., Cambridge, Mass., May 1968), and the reaction, of which the above constitutes one example, will be further discussed in a subsequent paper.

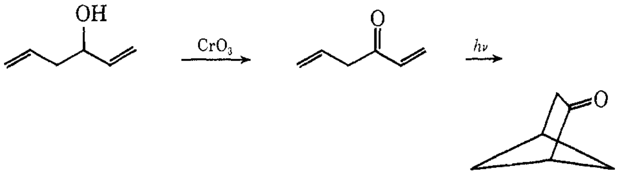
(7) I. N. Nazarov and A. I. Kakhniashvili, *Sb. Statei Obshch. Khim.*, **2**, 919 (1954); *Chem. Abstr.*, **49**, 6848 (1955).

(8) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.

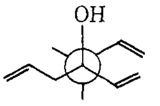
(9) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution Nmr Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.

(10) I. N. Nazarov and I. I. Zareteskaya, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 200 (1942); *Chem. Abstr.*, **39**, 1619 (1945).

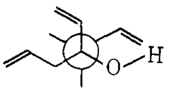
indeed a subsequent report[11] by the same authors establishes the formation of vinyl propenyl ketones by this method with several substituted derivatives. Bond, *et al.*, in a more recent publication,[12] have reported the chromic acid oxidation of 1,5-hexadien-3-ol followed by photolysis of the resultant product. The low yield of photoproduct formation, as well as the production of other unidentified products, may be an indication of substantial double bond migration during chromic acid oxidation. This possibility is further borne out by the ultraviolet spectrum reported by Bond, *et al.*, ϵ_{max} 11,000 at 212 mμ, whereas the spectrum obtained from this preparation, ϵ_{max} 6500 at 213 mμ, is more in agreement with the assigned structure.[13]



Our previous experiences with product distribution in the oxy-Cope reaction appeared in accord with the normally preferred chair forms of the transition states involved.[3] Accordingly, the preferred conformations for the Cope and cleavage reactions, **5** and **6**, respectively, require an axial hydroxyl in **5** as opposed to an axial vinyl group in **6**. This factor implies an even larger E_a difference between the two competing reactions in **2** compared with systems previously studied. Our experimental findings bear out this prediction. The yields of the two main products, resulting from 70% Cope and 30% cleavage at 370–375°, become 25% **3** and 75% **1** at 400–402°.



5



6

Experimental Section

General.—All melting points are uncorrected and were obtained on a Fisher-Johns melting point block. All boiling points are uncorrected and were obtained by distillation or by the micro boiling point technique.[14] Infrared spectra were determined with a Beckman IR-5A spectrophotometer on neat liquid samples. Ultraviolet spectra were determined with a Bausch and Lomb Spectronic 505 from Spectro Grade isooctane solutions. Nmr spectra were determined with a Varian A-60A spectrometer on deuteriochloroform solutions with a tetramethylsilane internal standard. Vapor phase chromatography (vpc) was accomplished with an F & M Model 500 using 2-ft columns packed with either 10% silicone grease or 20% Triton X-305 on Chromosorb P. Fractional distillations were accomplished on a Nester Faust Model NF-120 spinning band column. Microanalyses were performed by Dr. Stephen M. Nagy, Belmont, Mass.

4-Vinyl-1,6-heptadien-4-ol (2).—This compound was prepared essentially by the method of Nazarov and Kakhniashvili.[7] To an ethereal solution of allyl Grignard reagent, prepared from 195 g (8 g-atoms) of magnesium turnings, 2.5 l. of anhydrous ether, and 306 g (4 mol) of freshly distilled allyl chloride was added a solution of freshly distilled methyl acrylate, 86 g (1 mol), in 100 ml of anhydrous ether, at a drop rate sufficient to maintain moderate reflux. About 2 hr was required for the addition, after which stirring was continued for 2 additional hr. The reaction mixture was then poured onto a mixture of ice and excess ammonium chloride. The mixture was then worked up in the usual manner to yield 300 ml of a greenish yellow oil which was flash distilled, under reduced pressure, to remove nonvolatile impurities. Fraction of the distillate afforded 34.5 g (0.25 mol) of 4-vinyl-1,6-heptadien-4-ol, which corresponds to a 25% yield based on the amount of methyl acrylate used: bp 50° (6 mm), bp 167° (777 mm); $d^{26}{}_4$ 0.8737; $n^{20}{}_D$ 1.4645 (lit.[7] bp 57.5–58.5° (11 mm); d^{20} 0.8772; $n^{20}{}_D$ 1.467).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.31; H, 10.21.

The uv spectrum showed only end absorption above 230 mμ. Ir bands occurred at (cm^{-1}) 3450 (m), 3100 (m), 2970 (m), 2900 (m), 1830 (w), 1640 (m), 1435 (m), 1410 (m), 1335 (m), 990 (s), and 915 (s).

Hydrogenation of a small sample with Pd–C led to the absorption of 104% of the amount of hydrogen required to saturate three double bonds, and the hydrogenation product was shown to be 4-ethyl-4-heptanol, by comparison of its physical constants, vpc retention times, and ir spectrum with those of an authentic sample.

Vapor Phase Thermolysis of 4-Vinyl-1,6-heptadien-4-ol.—The apparatus used for the thermolyses has been previously described.[3] When 12.0 g of **2** was passed through the column, maintained at 400–402° and at a pressure of 17 mm, the condensed product weighed 11.1 g and contained[15] 8.0 g of **1** and 3.1 g of **3**, which corresponds to yields of 74 and 26%, respectively. With the column maintained at 370–375° at a pressure of 5 mm, thermolysis of 6.0 g of **2** resulted in the formation of 0.9 g of **1** and 3.8 g of **3**, and 0.4 g of starting material was recovered. Propylene was not condensed under the conditions used and its formation was indicated only by a small peak in the appropriate region of the vpc.

1,8-Nonadien-4-one (3).—The high boiling fraction of the thermolysis product consisted of the oxy-Cope product, which was isolated by fractional distillation under reduced pressure. The material obtained appeared homogeneous on vpc using both Triton X-305 and silicone grease columns: bp 67° (7 mm); $d^{24}{}_4$ 0.8668; $n^{23}{}_D$ 1.4482.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.49; H, 10.41.

The uv spectrum consisted only of end absorption (ϵ_{220} 250) and a small maximum, ϵ 54, at 292 mμ. The ir spectrum contained pertinent bands at (cm^{-1}) 3050 (w), 2930 (m), 1710 (s), 1640 (m), 1410 (m), 1360 (m), 990 (m), and 915 (s). The nmr spectrum consisted of a complex multiplet at δ 6.4–5.5, three complex multiplets between δ 5.3 and 4.8 (6 H, total vinyl region), a doublet at δ 3.17 (2 H), and a series of multiplets at δ 2.7–1.4 (6 H).

Hydrogenation of **3** with Pd–C led to the absorption of 103% of the amount of hydrogen required to saturated two double bonds. The hydrogenation product gave an ir spectrum and vpc retention time identical with those of an authentic sample of 4-nonanone and yielded a semicarbazone derivative, mp 58–59°, which gave no melting point depression on admixture with an authentic sample.

Oxidation of **3**, 0.9 g, with 6.9 g $KMnO_4$ in refluxing acetone for 12 hr was followed by addition of 200 ml of water, decomposition of the MnO_2 present with SO_2 gas, addition of 40% NaOH until basic, and continuous liquid–liquid extraction with ether for 24 hr. Acidification of the aqueous solution with 6 *N* HCl, followed by further ether extraction, afforded, upon evaporation of the ether, a white solid, which was extracted with warm petroleum ether (30–60°). The petroleum ether extract was evaporated to dryness and the residue extracted with hot benzene.

---

[11] I. N. Nazarov and I. I. Zareteskaya, *Zh. Obshch. Khim.*, **27**, 624 (1957); *Chem. Abstr.*, **51**, 16316 (1957).

[12] F. T. Bond, H. L. Jones, and L. Scerbo, *Tetrahedron Lett.*, 4685 (1965).

[13] For comparison, methyl vinyl ketone has ϵ_{max} 7000 at 212.5 mμ (ref 8). We considered the possibility of substantial enol content in **1** due to the potential stabilizing influence of the resulting conjugated linear triene system. However, lack of absorption in the 250–270-mμ region, absence of hydroxyl bands in the ir spectrum, a strict 1:3 ratio of aliphatic to vinylic protons in the nmr, and good gaussian vpc peaks all indicate the absence of any detectable amount of 3-hydroxy-1,3,5-hexatriene, the linear analog of phenol.

[14] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 5th ed, John Wiley & Sons, Inc., New York, N. Y., 1964.

[15] Amounts of **1** and **3** present in the thermolysis product were calculated from integrated vpc peak areas.

The remaining material was recrystallized from ether–benzene to yield succinic acid. The benzene-soluble fraction, upon removal of the benzene and recrystallization from petroleum ether, afforded glutaric acid. These acids gave no melting point depressions on admixture with authentic samples.

Vinyl Allyl Ketone (1,5-Hexadien-3-one) (1).—The lower boiling fraction of the thermolysis product mixture was isolated by fractional distillation under reduced pressure. The material obtained appeared homogeneous on vpc using both Triton X-305 and silicone grease columns: bp 125–126° (776 mm); $d^{23}{}_4$ 0.8717; $n^{20}{}_D$ 1.4460. Previously reported[10] literature values are bp 30–31° (8 mm), $d^{20}{}_4$ 0.8907, $n^{20}{}_D$ 1.4725. Spectral data follow: Uv max 337 mμ (ε 33), 213 (6500); ir bands at (cm^{-1}) 3080 (w), 3030 (w), 2960 (w), 2910 (w) 1700 (sh), 1680 (s), 1640 (m), 1620 (s), 1405 (s), 1330 (m), 1190 (m), 1075 (m) 995 (s), 965 (m), and 915 (s). The nmr spectrum is discussed above.

Anal. Calcd for C_6H_8O: C, 74.96; H, 8.39. Found: C, 74.65; H, 8.56.

Hydrogenation of **1** with Pd–C led to the absorption of 102% of the amount of hydrogen required to saturate two double bonds and afforded 3-hexanone, shown to be identical with an authentic sample by comparison of ir spectra, vpc retention times, and 2,4-dinitrophenylhydrazone derivatives.

Registry No.—**1,** 6857-93-8; **2,** 22922-45-8; **3,** 22922-46-9.

The Synthesis of Bicyclo[5.4.0]undecanones *via* Olefin Cyclization

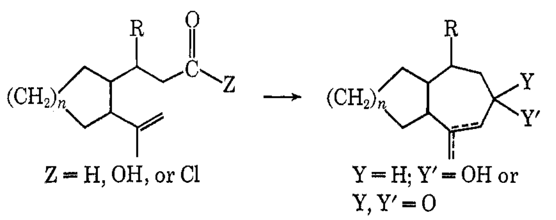
James A. Marshall, Niels H. Andersen,[1]
and John W. Schlicher[2]

*Department of Chemistry, Northwestern University,
Evanston, Illinois 60201*

Received July 25, 1969

During the course of a project aimed at the development of methods for the stereoselective synthesis of fused-ring cycloheptane derivatives, we examined a number of cyclization reactions of the type illustrated in Scheme I.[3] Our findings to date indicate that such

Scheme I



olefin cyclizations[4] can be usefully employed for the construction of cycloheptane rings.[5] This report summarizes our synthetic endeavors along these lines leading to bicyclo[5.4.0]undecanones.

Chart I

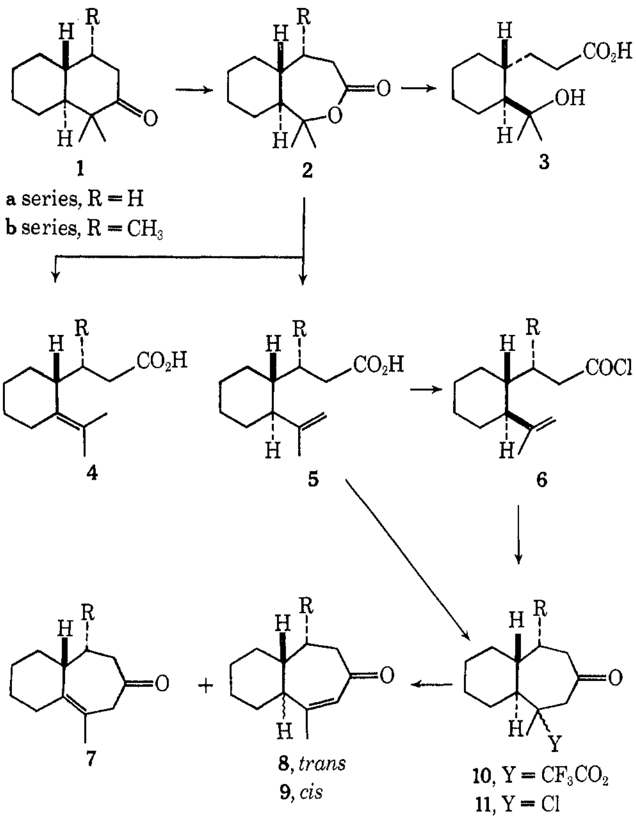
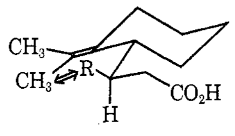
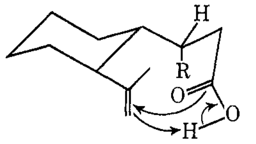


Chart I outlines our first approach starting with the known decalones **1a** and **1b**[6] which yielded the lactones **2a** and **2b**, respectively, upon treatment with *m*-chloroperoxybenzoic acid. Pyrolysis of these lactones gave the expected unsaturated acids **5a** and **5b** as the major products.[7] In the former case, a small amount of the isopropylidene isomer **4a** was also formed. The relative percentage of this isomer increased with reaction time at the expense of the isopropenyl isomer **5a** (see the Experimental Section) until an apparent equilibrium state of roughly 85% **5a** and 15% **4a** was reached. In the case of lactone **2b**, none of the isopropylidene acid **4b** could be detected, even after relatively prolonged reaction times. This trend may reflect increased steric strain[8] in the isopropylidene acid **4b** *vs.* **4a**, or may simply stem from an increased barrier to relactonization on the part of the acid **5b** *vs.* **5a** (see below).



4a, R = H
b, R = CH3



5a, R = H
b, R = CH3

The unsaturated acid **5a** cyclized upon treatment with trifluoroacetic anhydride affording the cycloheptanone derivative **10a** (presumably a mixture of

---

[1] Predoctoral Fellow of the National Institutes of Health, Institute of General Medical Sciences, 1966–1967.

[2] National Science Foundation Undergraduate Research Participant, 1968–1969.

[3] An application of this scheme to bicyclo[5.3.0]decanones led to a structure revision of the vetivane class of sesquiterpenes. For a preliminary report, see J. A. Marshall, N. H. Andersen, and P. C. Johnson, *J. Amer. Chem. Soc.*, **89**, 2748 (1967); J. A. Marshall and N. H. Andersen, *Tetrahedron Lett.*, 1219 (1967).

[4] For a recent review, see W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968).

[5] Prior to this work, results obtained with simple acyclic systems appeared unpromising. *Cf.* R. J. Ferrier and J. M. Tedder, *J. Chem. Soc.*, 1435 (1957). One report involving cyclization of a styrenyl nitrile leading to a benzocycloheptenone looked encouraging: R. Conley and R. Lange, *J. Org. Chem.*, **28**, 278, 210 (1963).

[6] J. A. Marshall and N. H. Andersen, *ibid.*, **31**, 667 (1966).

[7] *Cf.* D. Rosenthal, A. O. Niedermeyer, and J. Fried, *ibid.*, **30**, 510 (1965).

[8] *Cf.* F. Johnson, *Chem. Rev.*, **68**, 375 (1968).