same column at 0.5 mm. The first pure material collected was **3**, bp 65–70° (0.9 g), followed by a fraction contaminated with 3-acetoxymesityl oxide, bp 70–80° (1.3 g). The major component was 3,4-diacetoxy-4-methylpentan-2-one, bp 102–112° (9.9 g), purest fraction bp 108–112° (9.1 g).

A. **2,2-Dimethylacetoacetaldehyde** had the following properties: $n^{25}D$ 1.403; $\nu_{max}^{CCl_4}$ 2800, 2700, 1730, 1715, 1365, and 1135 cm^{-1}; λ_{max}^{EtOH} 283 mμ (log ε 1.60), shoulder 235 mμ (log ε 1.94); $\lambda_{max}^{n\text{-hex}}$ 292 mμ (log ε 1.66); nmr (CDCl$_3$): singlet 1.33 (6 H), singlet 2.17 (3 H), and singlet 9.58 ppm (1 H).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 63.38; H, 8.82.

B. **3-Acetoxy-4-methyl-4-penten-2-one (3)** was obtained in 13.5% yield; $n^{25}D$ 1.4335; $\nu_{max}^{CCl_4}$ 3065, 1735, 1725, 1640, 1365, 1225, 1060, and 915 cm^{-1}; λ_{max}^{EtOH} 287 mμ (log ε 2.23) and 241 mμ (log ε 2.45); $\lambda_{max}^{n\text{-hex}}$ 294 mμ (log ε 2.21) and 235 mμ (log ε 2.46); nmr (CDCl$_3$): broad singlet 1.68 (3 H), singlet 2.01 (6 H), quartet $J = 2$ cps, 4.96 (1 H), broad singlet 5.06 (1 H), and singlet 5.17 ppm (1 H).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.39; H, 7.96.

C. **3-Acetoxymesityl oxide** was collected by vpc from the aforementioned fractions; $n^{25}D$ 1.4533; $\nu_{max}^{CCl_4}$ 1755, 1700, 1630, 1375, 1280, 1235, and 1135 cm^{-1}; λ_{max}^{EtOH} 306 mμ (log ε 1.83) and 242 mμ (log ε 2.99); nmr (CDCl$_3$): singlet 1.75 (3 H), singlets 2.10 and 2.13 (6 H), and singlet 2.23 ppm (3 H).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.82; H, 7.89.

D. **3,4-Diacetoxy-4-methylpentan-2-one** showed $n^{35}D$ 1.4329 [lit.[20] bp 94° (0.1 mm) and 115–120° (0.3 mm); $n^{20}D$ 1.4384), and other spectral properties in accord with this assignment.

Acknowledgment. The investigation was aided by a Public Health Service Fellowship (Grant 5-Fl-GM 15,948-02) to R. M. W. for which we wish to express our appreciation.

(20) I. G. Tishchenko, *Uch. Zap. Belorussk. Gos. Univ., Ser. Khim.*, 42, 189 (1958); *Chem. Abstr.*, **55**, 4351*e* (1961); E. Detilleux and J. Jadot, *Bull. Soc. Roy. Sci. Liege*, **29**, 208 (1960;) *Chem. Abstr.*, **55**, 7276*e* (1961).

The Vapor-Phase Thermolyses of 3-Hydroxy-1,5-hexadienes. II. Effects of Methyl Substitution[1a]

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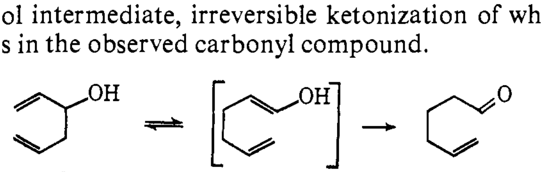
Abstract: The vapor-phase thermolyses of 3-hydroxy-1,5-hexadienes result in rearrangement to Δ⁵-unsaturated carbonyl compounds and in the formation of cleavage products. Based on a series of ten methyl-substituted compounds studied, the formation of these products is interpreted on the basis of two competing concerted bond reorganizations both of which proceed through a cyclic six-membered transition state. Production of cleavage products predominates at higher temperatures, whereas the rearrangement is favored at lower temperatures. The thermolysis presents a general method for the preparation of Δ⁵-unsaturated carbonyl compounds, although reaction yields are highly susceptible to substituent effects. Substitution in the 1 or 5 position favors the cleavage reaction due to steric and electronic factors, respectively.

We have previously reported[2] the thermal vapor-phase rearrangement of 1,5-hexadien-3-ol (**1**) to 5-hexenal (**2**), a process for which the term "oxy-Cope rearrangement" has been proposed.[3,4] This reaction may be considered a Cope rearrangement, leading to an enol intermediate, irreversible ketonization of which results in the observed carbonyl compound.



1 **2**

The occurrence of an analogous reaction involving two hydroxyl groups was suspected in 1934 in the catalytic pyrolysis of divinyl glycols,[5] although the purely thermal nature of the reaction has only recently been established.[4b,6]

In recent years there has been considerable interest in reactions involving bond reorganizations which are best interpreted on the basis of a cyclic transition state. The well-known Cope rearrangement falls into this category and has been described as an electrocyclic reaction.[7] This rearrangement is a typical "no-mechanism" reaction[8] which is brought about solely by thermal excitation either in solution or in the vapor state. The reaction usually appears as a unimolecular, homogeneous intramolecular process and only in rare instances have there been found intermolecular "crossover" products, resulting from fragmentation–recombination processes. Thus, Huntsman[9] has reported the formation of some 1,5-hexadiene and 2,5-dimethyl-

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(1) (a) Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966. (b) Taken in part from the M.S. Theses of K. K. C. and G. M. G., June 1966. (c) Undergraduate research participant.

(2) A. Viola and L. Levasseur, *J. Am. Chem. Soc.*, **87**, 1150 (1965).

(3) J. A. Berson and M. Jones, Jr., *ibid.*, **86**, 5017, 5019 (1964).

(4) (a) The name "enologenic Cope rearrangement" has now been suggested for this reaction.[4b] It would appear to us that it suffices to recognize the "Cope" rearrangement as a general reaction capable of occurring in a vast number of chemical environs. To attempt a definitive nomenclature for each variation of the reaction must of necessity lead to an undesirable profusion of adjectives. (b) E. Brown, P. Leriverend, and J. M. Conia, *Tetrahedron Letters*, 6115 (1966).

(5) M. Urion, *Compt. Rend.*, **190**, 1512 (1930); *Ann. Chim.*, [11] **1**, 5 (1934).

(6) J. Chuche and J. Wiemann, *Compt. Rend.*, **262**, 567 (1966).

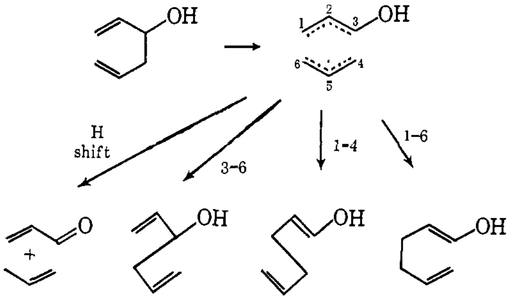
(7) R. B. Woodward and R. Hoffman, *J. Am. Chem. Soc.*, **87**, 395, 2511 (1965).

(8) For a review, see S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 11.

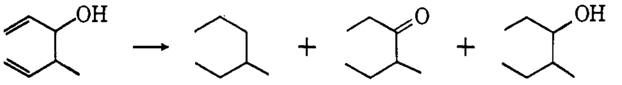
(9) W. D. Huntsman, *J. Am. Chem. Soc.*, **82**, 6389 (1960).

1,5-hexadiene from the high-temperature pyrolysis of 2-methyl-1,5-hexadiene, and Gibson and Pettit[10] have reported the thermolysis of 5,6-dimethyl-1,3,7,9-decatetraenes to give predominantly intermolecular reaction products.

It would appear, however, that the intramolecular reaction can proceed either by a concerted mechanism or by a two-step process consisting of scission of the bisallylic bond to form two stabilized allylic radicals, recombination of which affords the observed products.[11] Thus, Berson and Jones[3] have reported the thermal behavior of a series of compounds wherein the 3-hydroxy-1,5-hexadiene structure is incorporated within a bicyclic framework. The observed products were interpreted on the basis of competing reactions of a common diradical intermediate: double inversion (by C-1–C-6 bond formation), single inversion (by C-1–C-4 or C-3–C-6 bond formation), and hydrogen abstraction. The observed results are profoundly influenced by the steric requirement of the bicyclic skeleton, the remainder of which maintains the radicals in close proximity. We now report the thermolyses of ten methyl-substituted 3-hydroxy-1,5-hexadienes which were undertaken in order to further investigate the factors controlling the rearrangement and to evaluate the utility of the reaction as a general method for the preparation of Δ^5-unsaturated carbonyl compounds.



Preparation of Starting Materials. The various mono-, di-, and trimethyl-substituted 1,5-hexadien-3-ols were prepared *via* the reaction of the appropriate allylic Grignard reagent with the appropriate α,β-unsaturated carbonyl compound. Although eight of the ten compounds studied have been previously reported, we thought it desirous to affirm their structures to eliminate any possibility of allylic rearrangements during work-up of the Grignard mixtures, which would place the hydroxyl group on the site of the carbonyl function in the anticipated product, and also to eliminate any possibility of 1,4 Grignard addition which in all cases but one, the preparation of the 4-methylhexadienol, would give products corresponding to the anticipated rearrangements. The analyses and infrared spectra of all the dienols were in agreement with the desired structures, and hydrogenation afforded products consistent only with the assigned structures as, for example, with 4-methyl-1,5-hexadien-3-ol. Although hydrogen absorption was only about 80% of the theoretical amount[12] required for saturation of two double bonds, the products formed confirm the desired carbon skeleton and position of the oxygen function. We then assume the double-bond location follows from the mode of synthesis as confirmed by the infrared spectrum. Details of each structure verification are given in the Experimental Section.



Thermolysis Products. The thermolyses were conducted in a flow system, designed for preparative scale, at temperatures ranging from 340 to 390°. In all cases the products obtained consisted mainly of a mixture of the anticipated rearranged carbonyl compound, unreacted starting material, and cleavage products derived from scission of the C-3–C-4 bond. Only occasional trace amounts of other unidentified components were found, and usually these were due to trace impurities in the starting material. These reactions are outlined in Chart I.

The olefinic hydrocarbons produced were normally identified only by the appearance of a vpc peak in the appropriate region since most of the low-boiling constituents were not retained by the Dry Ice–acetone traps. In one case, the thermolysis of **17**, the suspected isobutylene was trapped in Br_2–CCl_4 and the bromination products were isolated to confirm the suspected olefin structure. The three- and four-carbon carbonyl compounds were readily separable from the less volatile methyl-substituted hexenals and were in all cases identified by their characteristic odor, vpc retention times, and suitable carbonyl derivatives.

$$CH_2{=}C(CH_3)_2 \longrightarrow CH_2BrCBr(CH_3)_2 + (CH_2Br)_2CBrCH_3 + CH_2{=}C(CH_3)CH_2Br \text{ (trace)}$$

The structures of the rearranged carbonyl compounds were all established in a similar manner. All gave C and H analyses and spectral data consistent with the assigned structures; all formed 2,4-dinitrophenylhydrazones or semicarbazones with consistent C and H analyses, and mass spectra of some of the 2,4-dinitrophenylhydrazones indicated consistent molecular weights. The carbon skeleton and location of the oxygen function were usually established by quantitative hydrogenation to saturated carbonyl compounds, most of which represented, or could readily be converted to, known compounds. The position of unsaturation was normally confirmed by means of oxidation as illustrated in Table I. The only compounds not subjected to oxidative degradation were the aldehydes **16** and **18**, due to their inherent chemical instability, and the ketone **22**, due to the small amount of material available and the absence of known derivatives of the potential oxidation product. It is assumed that the generality of the reaction reported herein, as evidenced by the other cases cited, would in itself serve to indicate the position of unsaturation. The details of each individual structure determination may be found in the Experimental Section.

The conversion of **9** → **10** is of special interest, since the alcohol is presumably a mixture of *threo* and *erythro* configurations, which might be anticipated to result in a mixture of *cis* and *trans* forms of the product. Either

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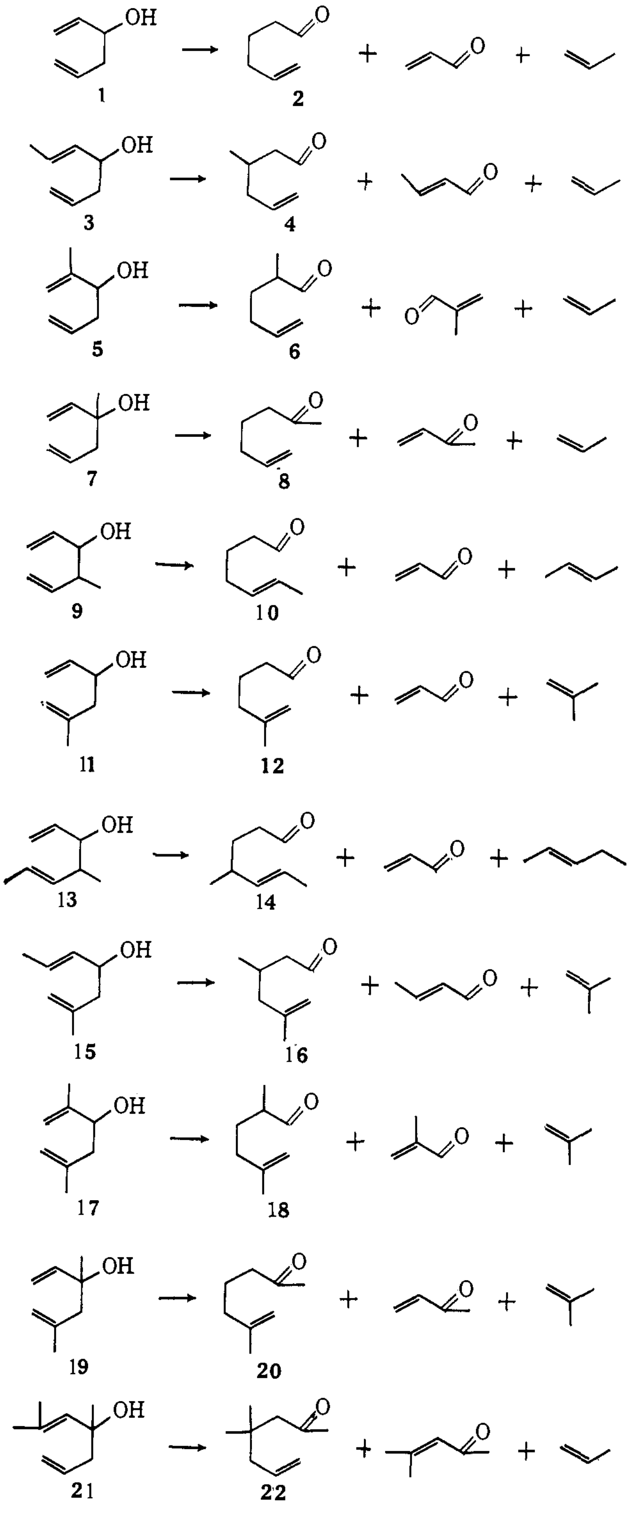
(10) D. Gibson and R. Pettit, *J. Am. Chem. Soc.*, **87**, 2620 (1965).

(11) G. S. Hammond and C. D. DeBoer, *ibid.*, **86**, 899 (1964); D. J. Trecker and J. P. Henry, *ibid.*, **86**, 902 (1964).

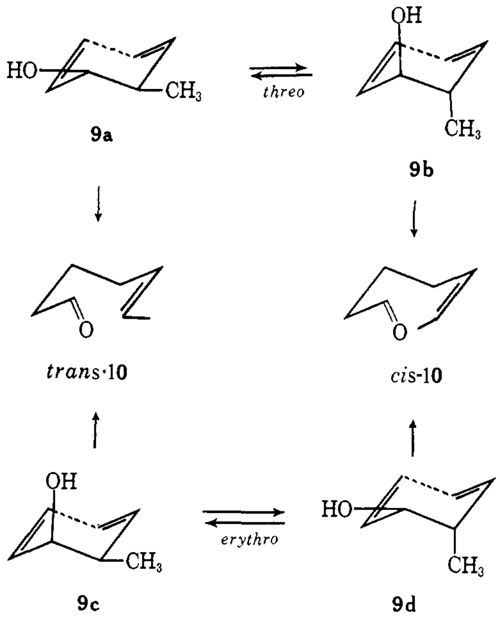
(12) The major product in this instance was the ketone, formed by the now well-documented[13] hydrogen transfer reaction of allylic alcohols in the presence of hydrogenation catalysts.

(13) J. Wiemann and G. Laude, *Compt. Rend.*, **226**, 345 (1948); R. G. Powell, *et al.*, *J. Org. Chem.*, 30, 610 (1965), and references cited therein.

Chart I



alcohol can by itself lead to a *cis–trans* mixture depending upon the conformational stabilities of the corresponding transition states as illustrated for the preferred four-center overlap.[14] Presumably an "equatorial" methyl substituent should lead to *trans*-**10** whereas an "axial" methyl substituent should result in *cis*-**10**. However, if an analogy to the cyclohexanol system is appropriate, then the preferred conformations are those with the equatorial alkyl group.[15] It is unlikely that



an axial hydroxyl can stabilize these transition states by hydrogen bonding to the π electrons, since such an event would result in the cleavage reaction. The aldehyde obtained appears to be a single entity as evidenced by its vpc behavior and its nmr and infrared spectra. Although our infrared spectrum appears somewhat simpler, it is in general agreement with that reported for *trans*-5-heptenal[16] and not that of the supposed *cis* isomer.[17] The nmr spectrum failed to offer conclusive evidence for the assignment of geometric structure, although the rather broad ethylenic multiplet is more in accord with a *trans* structure than a *cis*.[18] The conversion of **13** → **14** parallels the above situation, with the added complication of the presence of *cis*

Table I. Oxidation of Methyl-Substituted 5-Hexenals

Compd	Methyl position(s)	Product
2[a]	None	Glutaric acid
8	1	5-Oxohexanoic acid
6	2	α-Methylglutaric acid
4	3	β-Methylglutaric acid
12	5	5-Oxohexanoic acid
10	6	Glutaric acid
14	4,6	α-Methylglutaric acid
20	1,5	2,6-Heptanedione

[a] See ref 2.

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[14] W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

[15] M. Hanack, "Conformation Theory," Academic Press Inc., New York, N. Y., 1965, p 112 ff.

[16] R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 2601 (1959).

[17] P. W. Meyboom, Unilever Research Laboratorium, Holland; personal communication. This spectrum contains a strong broad band at 700 cm^{-1} which is totally absent in our case. However, Meyboom reports the 2,4-dinitrophenylhydrazone of *cis*-5-heptenal to melt at 85.5°, to which our melting point of 87–88° compares favorably, whereas the *trans* isomer is reported to melt at 105.8–106.3°.

[18] We wish to thank William Jankowski, Varian Associates, for the analysis of the nmr spectrum of 5-heptenal. Neither the resolutional capability of a 100-Mc spectrometer nor the application of double resonance techniques allowed a satisfactory interpretation of the exceedingly complex ethylenic region. A similar situation has been observed[19] in the case of 2-phenyl-2-methyl-4-hexenal, where both geometric configurations were assignable on the basis of infrared spectra and unambiguous syntheses but nmr spectra failed to provide corroborative evidence due to multiple coupling in the $CH_3CH{=}CHCH_2X$ system.

[19] R. K. Hill and N. W. Gilman, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p S104; R. K. Hill, personal communication.

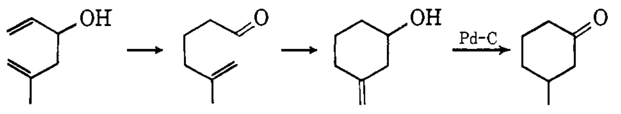
Table II. Effect of Substitution on Product Composition in Thermolysis of 3-Hydroxy-1,5-hexadienes at 370–375°[a]

Starting alcohol	1	3	5	7	9	11	13	15	17	19	21
Position of methyl groups	0	1	2	3	4	5	4,6	1,5	2,5	3,5	1,1,3
% rearrangement[b]	60	29	64	65	66	33	55	12[c]	25[c]	42	4
% cleavage[b]	40	70	36	35	33	67	45	88[c]	75[c]	58	96

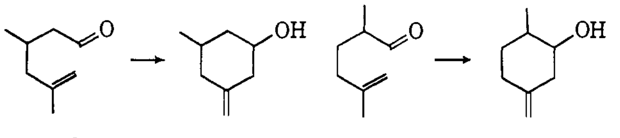
[a] Average results from numerous reactions. [b] These percentages have been corrected for recovered starting alcohol and do not represent yields. [c] Rearrangement may be somewhat more favorable than indicated due to uncertainty introduced by secondary reaction.

and *trans* forms in the alcohol, as evidenced by appropriate absorption bands in both infrared spectral regions. The aldehyde **14** also absorbed in both regions, indicating that temperature conditions during the reaction do not rule out formation of a *cis* product. Upon this consideration, it seems likely that the attainment of a single, presumably *trans*, 5-heptenal is indicative of highly favored transition states **9a** and **9c**.

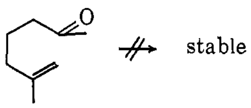
Thermolyses of 5-methyl-1,5-hexadienol (**11**) and of the dimethyl derivatives **15**, **17**, and **19** constitute another interesting series, since the aldehydic rearrangement products proved to be thermally labile, in agreement with the previously reported[20] cyclization of **12** to 3-methylenecyclohexanol (**23**). The structure assignment of **23** is based on analyses, spectral data, and disproportionation over palladium–charcoal to give 3-methylcyclohexanone. The aldehydes **16** and **18** proved to be labile to a degree which precluded their isolation from the reaction mixture and therefore were identified only in the form of various derivatives. The cyclohexanols **24** and **25** formed considerably more readily than **23**, a fact which introduces a larger degree of uncertainty in the figures pertaining to the thermolyses of **15** and **17** as given in Table II. The thermolysis of **19** proceeded smoothly to give the ketonic rearrangement product **20**. Despite the structural similarity of **20** to the 5-methyl-substituted 5-hexenals **12**, **16**, and **18**, no thermal instability was detected and no similar cyclization could be induced. Further investigations of this reaction are in progress.



11 12 23



16 24 18 25



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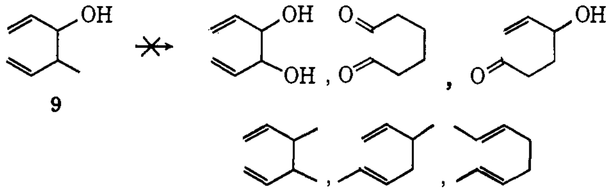
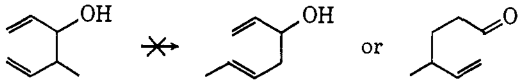
Discussion of Results. The thermolyses reported herein are best interpreted on the basis of a concerted reaction. It does not seem reasonable to expect the fragments required by the intermediacy of a diradical, in the absence of the constraint of a residual cyclic skeleton, to remain in sufficiently close proximity, at the prevailing temperatures, to afford solely intramolecular products. In no instance was there any evidence for products resulting from radical coupling of like fragments, such as might be expected, for example, in the thermolysis of **9**.

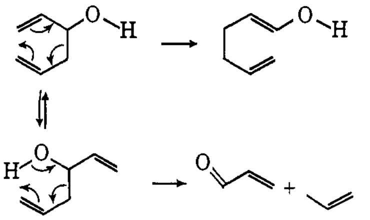


Furthermore, **9** also represents a case wherein both potential diradicals are unsymmetrical. No trace of either possible single inversion product could be detected in the product mixture. It is therefore apparent that only products derivable from a concerted reaction



are formed, with the complete exclusion of any anticipated by-products from possible diradical intermediates.

If a diradical mechanism is not operative, then a pathway other than radical hydrogen abstraction must be invoked for the formation of the observed fragmentation products. The cleavage of β-hydroxyolefins, as reported by Arnold and Smolinsky[21] and Smith, *et al.*,[22] constitutes an attractive alternate. Indeed, it would appear that a satisfactory explanation of the data, summarized in Table II, can be obtained on the basis of two competing concerted electrocyclic reactions, whose relative rates depend upon the stabilities of the corresponding conformers required for the formation of the favored four-centered quasi-six-membered cyclic transition state.



Under the conditions employed in this study, it was not feasible to reproduce residence times in the heated zone. However, pressures varying from 0.1 to 40 mm, variations in drop rate from 4 to 40 drops/min, and variations in carrier gas flow rate only affected the amount of recovered unreacted starting material; the ratio of rearrangement to cleavage products was

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(20) C. J. Albisetti, N. G. Fisher, M. J. Hagsed, and R. M. Joyce, *J. Am. Chem. Soc.*, 78, 2637 (1956).

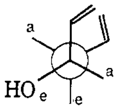
(21) R. T. Arnold and G. Smolinsky, *ibid.*, 81, 6443 (1959); *J. Org. Chem.*, 25, 129 (1960).

(22) (a) G. G. Smith and R. Taylor, *Chem. Ind.* (London), 949 (1961); (b) G. G. Smith and B. L. Yates, *J. Chem. Soc.*, 7242 (1965).

solely a function of temperature. In all cases, as reaction temperature increased, the production of cleavage products increased at the expense of rearrangement, which reflects the higher activation energy required by the less symmetrical transition state for β-hydroxyolefin cleavage. Although we were unable to obtain rate comparisons for different starting alcohols, the data, summarized in Table II, indicate the dependence of the relative rates of the two competing reactions upon the position of substitution.

Substitution in the 5 position stabilizes the formation of a transient positive charge, a factor which favors the more unsymmetrical transition state required by cleavage. Similarly, the substitution of a phenyl group in the appropriate position has been reported[22b] to increase the rate of β-hydroxyolefin cleavage. Consequently, in all cases of methyl substitution in the 5 position, a larger proportion of cleavage products is formed in comparison with the corresponding compound not bearing a 5-methyl substituent (*i.e.*, compare **11** and **1**, **15** and **3**, **17** and **5**, **19** and **7**).

Methyl substitution in the 3 and 4 positions, compounds **7** and **9**, leads to small changes in the product ratios, and although these effects are almost within experimental error of the ratio in the unsubstituted case, the changes are in the direction predictable from a consideration of the transition states involved. The conformations approaching the various chair-like four-centered transition states are represented by Newman projections **26** and **27**, for the Cope product, and **28** and **29**, for β-hydroxyolefin cleavage. In the simple unsubstituted compound **1**, the lower energy states for the respective processes are represented by **26** and **29**, by virtue of equatorial substituents as opposed to axial groups in **27** and **28**. Due to the smaller steric interaction of a hydroxyl group, the difference between states **26** and **27** is expected to be less than that between **28** and **29**. On this basis, introduction of a 3-methyl group results in a larger increase for the activation energy of the cleavage than for the Cope reaction, as the energetically favored transition states will now be **27**, with an axial hydroxyl, as opposed to **29**, with an axial methyl. In the case of 4-methyl substitution the unknown *threo–erythro* isomer ratio is an additional complication. The introduction of a substituent in the *threo* configuration clearly raises the energy of **29** (axial methyl) more than that of **26** (equatorial methyl), but in the *erythro* configuration the favored states are **27** and **29**, both with equatorial methyls. Undoubtedly, the two diastereomers react at different rates but the over-all effect of the 4-methyl substituent is to favor the transition states for rearrangement.



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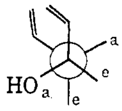

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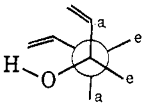

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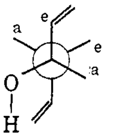

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Models indicate only a slight steric interference to rearrangement by a *trans*-1-methyl substituent, compound **3**, but a substantial one by the *cis* isomer. If a *cis* ⇄ *trans* thermal equilibrium is not excluded from consideration, a moderate concentration of the *cis* form easily accounts for the preponderance of cleavage products, since the energy barrier of isomerization is not small compared to that of rearrangement. In the absence of an actual *cis* ⇄ *trans* equilibrium, thermally increased excitation of the torsional vibration (methyl out-of-plane deformation) still results in steric inhibition of states **26** or **27**. With two 1-methyl substituents, as in compound **21**, the *cis* group destabilizes the requisite transition state considerably more and the rearrangement product is formed only in minute amounts. Although a similar situation arises in the case of **13**, a *cis–trans* mixture, the 6-methyl substituent interferes with *both* reactions; however, cleavage is less affected due to the smaller steric requirements of a proton.

Experimental Section[23]

Preparation of Starting Materials. All alcohols used were prepared by the addition of the appropriate Grignard reagent to the appropriate carbonyl compound. In each case, the product was purified by distillation, followed by preparative vapor phase chromatography when necessary. Each alcohol gave infrared and ultraviolet spectra consistent with the supposed structure and hydrogenation produced expected products.

1,5-Heptadien-4-ol (3). This compound was prepared *via* the reaction of allylmagnesium chloride with crotonaldehyde essentially according to the method of Kiun-Houo;[24] bp 151–152°, d^{24} 0.852, $n^{27}\text{D}$ 1.450 (lit.[21] bp 150–151°, $d^{20}{}_4$ 0.8598, $n^{20}\text{D}$ 1.4523).

2-Methyl-1,5-hexadien-3-ol (5). This compound was prepared according to the method of Fleischacker and Woods[25] by the reaction of allylmagnesium chloride with α-methylacrolein; bp 54–55° (11 mm), d^{20} 0.8393 $n^{24}\text{D}$ 1.452 [lit.[25] bp 48–49° (12 mm), $n^{26}\text{D}$ 1.449].

Hydrogenation of a small sample, with Pd–C catalyst, led to the absorption of 95% of the amount required for the saturation of two double bonds and gave 2-methyl-3-hexanol, isolated as the acid phthalate, mp 56–57° (lit.[26] 59–60°), which gave no depression on admixture with the same derivative prepared from an authentic sample.

3-Methyl-1,5-hexadien-3-ol (7). This compound was prepared according to the method of Fleischacker and Woods[25] by the reaction of allylmagnesium bromide with methyl vinyl ketone; bp 137°, $n^{25}\text{D}$ 1.444, $d^{22}{}_4$ 0.8613 (lit.[25] bp 137°, $n^{22}\text{D}$ 1.446).

Vpc indicated this substance to be a single entity. Hydrogenation of a small sample, with Pd–C catalyst, led to the absorption of 122% of the amount required for the saturation of two double bonds. Vpc of the hydrogenation product indicated a major component whose retention time was identical with that of the authentic saturated alcohol, while those of the other two components were in agreement with methylhexane and water (trace). Removal of the lower boiling constituents left a residue whose infrared spectrum was superimposable on that of authentic 3-methyl-3-hexanol.

4-Methyl-1,5-hexadien-3-ol (9). This compound was prepared essentially according to the method of Kiun-Houo[24] by the reaction of the Grignard reagent prepared from crotyl chloride on acrolein. Fractional distillation afforded a 42% yield, based on crotyl chloride, of 4-methyl-1,5-hexadien-3-ol; bp 142°, $d^{22}{}_4$ 0.8573, $n^{23}\text{D}$ 1.448 [lit.[24] bp 55–56° (14 mm), $d^{22}{}_4$ 0.863, $n^{22}\text{D}$ 1.4460]. The yield reported from the reaction using crotyl bromide is 25%.[24]

Since a mixture of 4-methyl-1,5-hexadien-3-ol and 1,5-heptadien-3-ol could be expected from the crotyl Grignard reagent, the prod-

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(23) Melting points and boiling points are uncorrected. Infrared spectra were determined with a Beckman IR-5 spectrophotometer on neat liquid samples. Ultraviolet spectra were determined with a Bausch and Lomb Spectronic 505 from spectro grade "isooctane" solutions. Elementary analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., or by Stephen M. Nagy, Massachusetts Institute of Technology, Cambridge, Mass. Vapor phase chromatographic analyses were obtained with a F & M Model 500 using 2-ft columns packed with 10% silicone grease on Chromosorb or with Triton X. Preparative vpc was accomplished with a Fisher Prep/Partitioner using four 2-ft columns packed with 10% silicone grease on Chromosorb.

(24) O. Kiun-Houo, *Ann. Chim.*, 13, 175 (1940).

(25) H. Fleischacker and G. F. Woods, *J. Am. Chem. Soc.*, 78, 3436 (1956).

(26) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 101, 633 (1912).

uct was examined carefully. Vpc indicated a single component, but this could be due to lack of resolution. Hydrogenation of samples of this compound over Pd–C led to the absorption of about 80% of the amount required to saturate two double bonds, and the product mixtures consisted of three components: a low-boiling component whose vpc retention time was in accord with a methylhexane, and two higher boiling components, isolated by preparative vpc, shown to be 4-methyl-3-hexanol and 4-methyl-3-hexanone. The ketone, which accounted for about 60% of the total, readily formed a 2,4-dinitrophenylhydrazone, mp 77.5–78.5° (lit.[27] mp 78°), which gave no melting point depression on admixture with the same derivative prepared from an authentic sample of 4-methyl-3-hexanone. The alcohol, a minor component of the hydrogenation mixture, had a vpc retention time and infrared spectrum identical with those of an authentic sample of 4-methyl-3-hexanol. Acid dichromate oxidation of this hydrogenation component afforded a ketone whose 2,4-dinitrophenylhydrazone also gave no mixture melting point depression on admixture with the same derivative prepared from an authentic sample of 4-methyl-3-hexanone. The ketone isolated from the hydrogenation mixture, the one obtained from the oxidation of the suspected 4-methyl-3-hexanol, and authentic 4-methyl-3-hexanone all had superimposable infrared spectra. At no time in this procedure was any evidence found for the formation of 1,5-heptadien-3-ol, or any compound derivable therefrom.

5-Methyl-1,5-hexadien-3-ol (11). This compound was prepared essentially according to the method of Spangler and Woods[28] by the reaction of methallylmagnesium chloride with acrolein; bp 145°, $n^{25}\text{D}$ 1.4505, d^{24} 0.867 (lit.[28] bp 145.5–146°, $n^{27}\text{D}$ 1.4498).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.15; H, 10.73.

Hydrogenation of a sample of the above compound over Pd–C led to the absorption of only 78% of the amount theoretically required for the saturation of two double bonds. Vpc of the hydrogenation product indicated two components, the major of which had a retention time identical with that of authentic 5-methyl-3-hexanol. A sample of the major component, isolated by preparative vpc, was converted into its 3,5-dinitrobenzoate, mp 71–72°, which showed no mixture melting point depression on admixture with the same derivative prepared from authentic 5-methyl-3-hexanol. The second component of the hydrogenation mixture was present in too small a quantity for isolation but is presumed to be 5-methyl-3-hexanone on the basis of its vpc retention time and a positive 2,4-dinitrophenylhydrazone test.

4-Methyl-1,5-heptadien-3-ol (13). This hitherto unreported compound was synthesized *via* the Grignard reagent prepared from 4-chloro-2-pentene (60 g, 0.57 mole) and magnesium (36 g, 1.5 g-atoms) in 900 ml of anhydrous ether, to which was added a solution of freshly distilled acrolein (25.5 g, 0.45 mole) dissolved in 90 ml of anhydrous ether. The gentle reflux which had been maintained by the heat of the reaction ceased after the addition of this quantity of the acrolein solution, and the addition was discontinued. The reaction mixture was decomposed with ice–ammonium chloride, and the product was then isolated in the usual manner. Distillation afforded a crude product [38 g, bp 70–80° (25 mm)] which consisted of 70% of the coupling product, 4,5-dimethyl-2,6-octadiene, and 30% of the expected alcohol.

The alcohol could not readily be separated from the contaminating coupling product by distillation and thus was isolated by preparative vpc which afforded a pure sample, bp 164–165°, $n^{27}\text{D}$ 1.455.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.10; H, 11.18.

Hydrogenation of small samples of the above alcohol with Pd–C led to the absorption of considerably more hydrogen than the amount theoretically required, and the amounts absorbed were not reproducible. The reaction mixtures were filtered to remove the catalyst, and the combined filtrates were subjected to preparative vpc. Of the three fractions obtained, the major one consisted of a compound whose infrared spectrum was superimposable on that of an authentic sample of 4-methyl-3-heptanol, $n^{26}\text{D}$ 1.4283 (lit.[29] 1.4260). One of the other fractions consisted of a compound whose infrared spectrum was superimposable on that of an authentic sample of 4-methyl-3-heptanone, $n^{26}\text{D}$ 1.4125 (lit. $n^{25}\text{D}$ 1.4137,[30a] 1.4109[30b]), prepared by acid dichromate oxidation of the above carbinol. The third fraction was not identified but its vpc retention time was consistent with that of the corresponding saturated hydrocarbon.

2-Methyl-1,5-heptadien-4-ol (15). This compound was prepared essentially according to the method of Sorenson[31] by the reaction of methallylmagnesium chloride with crotonaldehyde; bp 70–71° (12 mm), $n^{25}\text{D}$ 1.456, $d^{29}{}_4$ 0.8463 [lit.[31] bp 56–57.5° (6 mm), $n^{25}\text{D}$ 1.4559].

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.30; H, 11.42.

Hydrogenation of several samples of the above compound with palladium on charcoal led to the absorption of anywhere from 90 to 144% of the amount theoretically required for the saturation of two double bonds. Fractional distillation of the hydrogenation product gave mainly 2-methyl-4-heptanol, identified as its 3,5-dinitrobenzoate, which gave no melting point depression upon admixture with an authentic sample, mp 68–69°. The hydrogenation products also contained small amounts of a carbonyl compound as indicated by the formation of a 2,4-dinitrophenylhydrazone which was insufficient for isolation.

The hydrogenated alcohol gave a negative iodoform test, indicating the absence of 6-methyl-2-heptanol which would result from an allylic rearrangement of the original heptadienol.

2,5-Dimethyl-1,5-hexadien-3-ol (17). This compound, hitherto unreported, was prepared[32] from the Grignard reaction of methallylmagnesium chloride with 2-methacrolein. To the Grignard reagent prepared from methallyl chloride (109 g, 1.2 moles) and magnesium (60 g, 2.5 g-atoms) in 900 ml of anhydrous ether was added a solution of freshly distilled α-methacrolein (63 g, 0.90 mole) in 120 ml of anhydrous ether. After addition of this quantity of the methacrolein solution, the gentle reflux which had been maintained ceased, and the addition was discontinued. The reaction mixture was decomposed with an ice–ammonium chloride mixture, and the product was then isolated in the usual manner. Distillation afforded 2,5-dimethyl-1,5-hexadien-3-ol (85 g, 0.67 mole) in 75% yield based on the amount of α-methacrolein added. Redistillation afforded a center cut, bp 165–166°, $d^{22}{}_4$ 0.8699, $n^{25}\text{D}$ 1.456.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.19; H, 11.11.

Hydrogenation of a sample of the above compound with palladium on charcoal led to the absorption of 93% of the amount of hydrogen theoretically required for the saturation of two double bonds. The hydrogenation mixture was filtered to remove the catalyst and was then subjected to vpc which indicated three products, two of whose vpc retention times were identical with those of authentic samples of 2,5-dimethyl-3-hexanol and 2,5-dimethyl-3-hexanone. The third product, present only in small amount, was suspected to be 2,5-dimethylhexane. The suspected saturated alcohol and ketone were isolated by preparative vapor phase chromatography, and the alcohol was oxidized with acid dichromate to afford a ketone. Both of the ketones had infrared spectra superimposable with that of an authentic sample of 2,5-dimethylhexanone and both formed a 2,4-dinitrophenylhydrazone derivative, mp 66.5–68°, which gave no melting point depression on admixture with an authentic sample, mp 66.5–68° (lit.[33] mp 67–68°).

3,5-Dimethyl-1,5-hexadien-3-ol (19). This compound was prepared essentially according to the method of Woods and Viola[34] by the reaction of the Grignard reagent prepared from 2-methyl-3-chloropropene with methyl vinyl ketone. Fractional distillation of the product gave 3,5-dimethyl-1,5-hexadien-3-ol, which appeared to be a single entity by vpc; bp 146–147°, $n^{25}\text{D}$ 1.450, $d^{24}{}_4$ 0.856 [lit.[34] bp 46–47° (10 mm), $n^{26}\text{D}$ 1.449, $d^{25}{}_4$ 0.854].

A sample of the above compound absorbed 101% of the amount of hydrogen theoretically required to saturate two double bonds. The saturated alcohol had a vpc retention time equal to that of an authentic sample of 3,5-dimethyl-3-hexanol. The hydrogenated alcohol was converted to its 3,5-dinitrobenzoate, mp 88–90°, which

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(27) "Tables for Identification of Organic Compounds," compiled by M. Frankel and S. Patai, The Chemical Rubber Co., Cleveland, Ohio, 1960.

(28) C. W. Spangler and G. F. Woods, *J. Org. Chem.*, **28**, 2245 (1963).

(29) E. Bjelouss, *Ber.*, 45, 625 (1912).

(30) (a) J. Dubois and R. Luft, *Bull. Soc. Chim. France*, 1153 (1954); (b) P. Izzo and S. Safir, *J. Org. Chem.*, 24, 701 (1959).

(31) T. S. Sorenson, *Can. J. Chem.*, **42**, 2781 (1964).

(32) We wish to thank Mr. David Libby for the preparation of this compound.

(33) H. L. Herzog and E. R. Buchman, *J. Org. Chem.*, 16, 99 (1951).

(34) G. F. Woods and A. Viola, *J. Am. Chem. Soc.*, **78**, 4380 (1956).

gave no melting point depression upon admixture with an authentic sample of the same derivative of 3,5-dimethyl-3-hexanol.

4,6-Dimethyl-1,5-heptadien-4-ol (21). This compound was prepared essentially according to the method of Henze, *et al.*,[35] by the reaction of allylmagnesium chloride with mesityl oxide; bp 70–72° (18 mm), $n^{26}\mathrm{D}$ 1.4575 [lit.[35] bp 72° (18 mm), $n^{20}\mathrm{D}$ 1.4598].

A small sample of the above compound absorbed 104% of the amount of hydrogen required to saturate two double bonds. The small excess was probably accounted for by hydrogenolysis as evidenced by a small peak found in vpc in the region appropriate for the corresponding hydrocarbon.

Thermal Vapor-Phase Rearrangements. The apparatus used consisted of a vertical Pyrex column, 22 mm o.d., packed with $^1/_{16}$-in. i.d. Pyrex helices for a length of about 45 cm. The packed portion of the column was divided into three equal sections, each individually wrapped with resistance wire connected to a variac, and in the center of each section was a well containing a 500° thermometer. A dropping funnel attached to the top of the column admitted the sample, usually at a rate of about four to ten drops/min, and a capillary inlet just below the funnel maintained an atmosphere of dry nitrogen. The vapors were condensed at the bottom of the tube by means of two flasks connected in series and cooled in a Dry Ice–acetone bath. The system was evacuated by means of an aspirator through a drying tube in the vacuum line to protect the system from water vapor.

The condensed products, usually representing a recovery of 80–90%, were subjected to analysis by vpc and usually consisted of three main components: the rearrangement product, unreacted starting material, and the carbonyl component of the cleavage reaction (identical with the carbonyl compound used in the preparation of the particular alcohol). The hydrocarbon component derived from the cleavage reaction normally condensed only partially under these conditions and appeared as a minor peak in the appropriate region of the vapor phase chromatogram. The condensed products were separated by fractional distillation and, where necessary, by preparative vapor phase chromatography. Each of these thermolyses was performed numerous times and a typical experiment follows for each preparation.

3-Methyl-5-hexenal (4). 1,5-Heptadien-4-ol, 5.15 g, was passed through the column described above at a temperature of 370–380° and at a pressure of 28 mm. The condensed products, 4.10 g (80% recovery), consisted of 41% crotonaldehyde, 28% 3-methyl-5-hexenal, 30% starting material, and a small amount of a low-boiling constituent suspected to be propylene. The actual yield of 3-methyl-5-hexenal is therefore 22%. The crotonaldehyde was separated by distillation and identified as its 2,4-dinitrophenylhydrazone derivative, mp 188–189° (lit.[36] 190°). There was no depression on admixture with an authentic sample. 3-Methyl-5-hexenal was isolated by preparative vpc, d^{27} 0.8320, $n^{29}\mathrm{D}$ 1.4256.

Anal. Calcd for $C_7H_{12}O$: C, 74.94; H, 10.78. Found: C, 74.70; H, 10.74.

The ultraviolet spectrum consisted of only end absorption above 220 mμ and a small maximum, ϵ 15, at 280 mμ. The infrared spectrum showed pertinent bands at about 3400 (w), 3070 (m), 2900 (s), 1725 (s), 1650 (m), 1460 (w), 1450 (w), 1420 (w), 1380 (m), 1000 (s), and 915 (s) cm^{-1}.

On quantitative hydrogenation with Pd–C, a small sample of **4** absorbed 109% of the theoretical amount required for saturation of one double bond and gave 3-methylhexanal, identified as the 2,4-dinitrophenylhydrazone, mp 91–92° (lit.[37] 90–91°), and as the semicarbazone, mp 108–109.5° (lit.[37] 107–109°).

Oxidation of a small sample of **4** with potassium dichromate and sulfuric acid gave β-methylglutaric acid, mp 84–85° (lit.[38] 85–86°). Compound **4** readily formed a 2,4-dinitrophenylhydrazone, mp 65.5–66.5°, mol wt[39] 292.

Anal. Calcd for $C_{13}H_{16}N_4O_4$: C, 53.41; H, 5.52. Found: C, 53.55; H, 5.61.

2-Methyl-5-hexenal (6). 2-Methyl-1,5-hexadien-3-ol, 6.12 g, was dropped onto the column described above at 370–380° and under a pressure of 21 mm. The condensed products, 5.4 g (88% recovery), consisted of 73% 2-methyl-5-hexenal, 26% methacrolein, and a small amount of a low-boiling constituent believed to be propylene. The actual yield of 2-methyl-5-hexenal was therefore 64%.

The product was separated by fractional distillation, and the methacrolein was identified as its 2,4-dinitrophenylhydrazone derivative, mp 198–200° (lit.[36] 206°). There was no depression on admixture with an authentic sample. The higher boiling fraction was 2-methyl-5-hexenal, bp 140–141°, $n^{27}\mathrm{D}$ 1.4288.

Anal. Calcd for $C_7H_{12}O$: C, 74.94; H, 10.78. Found: C, 74.75; H, 10.78.

The 2,4-dinitrophenylhydrazone was prepared in the usual manner, mp 87–88°, mol wt 292.[39]

Anal. Calcd for $C_{13}H_{16}N_4O_4$: C, 53.41; H, 5.52. Found: C, 53.49; H, 5.65.

The ultraviolet spectrum consisted only of end absorption above 220 mμ and a small maximum, ϵ 88, at 284 mμ. The infrared spectrum showed pertinent bands at about 3500 (w), 3080 (m), 2950 (s), 2725 (m), 1830 (w), 1730 (s), 1650 (m), 1465 (s), 1430 (w), 1410 (w), 1385 (w), 1000 (s), and 915 (s) cm^{-1}.

On quantitative hydrogenation with Pd–C a small sample absorbed 104% of the theoretical amount required for saturation of one double bond and gave 2-methylhexanal, identified as the semicarbazone, mp 89–91° (lit.[40] 90–91°).

Oxidation of a small amount of the compound with permanganate in acetone according to the method of Nunn[41] gave α-methylglutaric acid, mp 71–74° (lit.[42] 75–77°).

6-Hepten-2-one (8). 3-Methyl-1,5-hexadien-3-ol, 7.96 g, was passed through the column described above at a temperature of 370–380° and a pressure of 13 mm. The condensed products, 7.15 g (90% recovery), consisted of 24% methyl vinyl ketone, 11% starting material, 64% 6-hepten-2-one, and a small amount of a low-boiling component believed to be propylene. The actual yield of 6-hepten-2-one was therefore 58%.

Methyl vinyl ketone was separated by distillation and identified by its vpc retention time and by quantitative hydrogenation (the sample absorbed 100% of the theoretical amount for saturation of one double bond) to 2-butanone, which readily formed a 2,4-dinitrophenylhydrazone, mp 116–117° (lit.[36] 117°). There was no depression on admixture with an authentic sample.

6-Hepten-2-one was obtained by fractional distillation, bp 149°, $n^{25}\mathrm{D}$ 1.4280, $d^{20}{}_4$ 0.8452 [lit.[43] bp 41–43° (10 mm), $n^{18}\mathrm{D}$ 1.4350].

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 74.85, 74.76; H, 10.99, 10.71.

The compound formed a 2,4-dinitrophenylhydrazone, mp 72.5–73.5 (lit.[44] 72.5–73.5°), mol wt 292.[39]

Anal. Calcd for $C_{13}H_{16}N_4O_4$: C, 53.41; H, 5.52. Found: C, 53.52; H, 5.38.

Compound **8** gave an iodoform test. Its ultraviolet spectrum showed only end absorption above 220 mμ and a small maximum, ϵ 25, at 277 mμ. The infrared spectrum showed pertinent bands at 3070 (m), 2930 (s), 1720 (s), 1640 (m), 1445 (w), 1420 (w), 1365 (s), 1228 (m), 1167 (s), 998 (m), and 915 (s) cm^{-1}. On quantitative hydrogenation, a small sample absorbed 101% of the theoretical amount required to saturate one double bond and gave 2-heptanone, whose 2,4-dinitrophenylhydrazone derivative, mp 76–78° (lit.[27] 74°), gave no depression on admixture with a nauthentic sample.

Oxidation with alkaline permanganate gave succinic acid, mp 183–185°, which showed no depression on admixture with an authentic sample. Oxidation with permanganate in the presence of excess magnesium sulfate afforded 5-oxohexanoic acid, identified as its semicarbazone derivative, mp 171–172° (lit.[45] 173°). This derivative gave no melting point depression on admixture with the same derivative prepared from the oxidation product of 5-methyl-5-hexenal (**12**).

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(36) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964.

(37) A. W. Burgstahler, *J. Am. Chem. Soc.*, **82**, 4681 (1960).

(38) R. E. Kent and S. M. McElvain, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p 591.

(39) We wish to thank Dr. R. J. C. Kleipool for the determination of the mass spectra of some of the 2,4-dinitrophenylhydrazones herein reported. The molecular weights stated represent the ion of largest *m/e* in the spectrum, neglecting isotopic contributions.

(40) G. Stork and S. R. Dowd, *J. Am. Chem. Soc.*, **85**, 2178 (1963).

(41) J. R. Nunn, *J. Chem. Soc.*, 313 (1952).

(42) J. C. Martin and J. P. Hawk, U. S. Patent 2,972,629 (Feb 21, 1961).

(43) B. Helferich and T. Malkomes, *Ber.*, **55B**, 705 (1922).

(44) H. E. DeLaMare, J. K. Kochi, and F. F. Rust, *J. Am. Chem. Soc.*, **85**, 1448 (1963).

(45) N. P. Shusherina, R. Ya Levina, and M. Yu Lure, *Zh. Obshch. Khim.*, **26**, 750 (1956).

5-Heptenal (10). 4-Methyl-1,5-hexadien-3-ol, 7.2 g, was passed through the column described above at 370–380° at a pressure of 13 mm. The condensed products, 5.8 g (81% recovery), consisted of 79% 5-heptenal, 15% acrolein, 4% starting material, and small amounts of low-boiling components believed to be butylenes. The actual yield of 5-heptenal is therefore 64%.

Acrolein was separated by distillation and identified by its characteristic odor, its vpc retention time, and its 2,4-dinitrophenylhydrazone derivative, mp 163–165° (lit.[36] 165°).

5-Heptenal was obtained by fractional distillation and purified by preparative vpc; bp 157°, n^{24}D 1.435.

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 74.99; H, 10.88.

The compound formed a 2,4-dinitrophenylhydrazone derivative, mp 87–88°.

Anal. Calcd for $C_{13}H_{16}N_4O_4$: C, 53.41; H, 5.52. Found: C, 53.37; H, 5.71.

Meyboom reports the melting points of the 2,4-dinitrophenylhydrazones of the *cis-* and *trans*-5-heptenal to be 85.5–86.5° and 105.8–106.3°, respectively.[17]

The ultraviolet spectrum of **10** showed only end absorption above 220 mμ and a small maximum, ϵ 24, at 295 mμ. The infrared spectrum showed pertinent bands at 3410 (w), 3040 (w), 2945 (s), 2720 (m), 1730 (s), 1460 (m), 1420 (w), 1400 (w), and 972 (s) cm^{-1}. This spectrum seems in general agreement with that reported by Srinivasan[16] for the isomer for which he favors the *trans* configuration. Meyboom[17] reports a strong broad band at 700 cm^{-1} in the supposed *cis* form.

On quantitative hydrogenation a small sample of **10** absorbed 101% of the theoretical amount required for the saturation of one double bond and gave heptanal, identified by its vpc retention time and its 2,4-dinitrophenylhydrazone derivative, mp 103–104° (lit.[36] mp 108°), which gave no depression on admixture with an authentic sample.

Oxidation of a sample of the heptenal with alkaline permanganate at room temperature gave succinic acid as the only isolable product, mp 187–188° (lit.[36] 188°), showing no depression on admixture with an authentic sample. If, however, the oxidation was carried out at 0° in neutral permanganate with a fourfold excess of magnesium sulfate over a period of several days, then the product was glutaric acid, mp 90–91° (lit.[36] 97°). On admixture with an authentic sample, mp 95–96°, a mixture melting point of 94–96° was obtained. Further recrystallization did not raise the melting point of the oxidation product.

5-Methyl-5-hexenal (12). 5-Methyl-1,5-hexadien-3-ol, 7.3 g, was passed through the column described above at 370–373° and at a pressure of 11 mm. The condensed products, 5.2 g (71% recovery), consisted of 36% acrolein, a trace of starting material, 49% 5-methyl-5-hexenal, 13% of a low-boiling component believed to be isobutylene, and traces of other low-boiling impurities. The actual yield of 5-methyl-5-hexenal was therefore 35%.

The above product was fractionally distilled and acrolein was identified in the forerun by its characteristic odor, its vpc retention time, and its 2,4-dinitrophenylhydrazone, mp 165–166° (lit.[36] 165°). The main fraction was 5-methyl-5-hexenal, bp 149°, n^{25}D 1.441, d^{27} 0.886 (lit.[20] bp 150°, n^{25}D 1.4350).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.03, 75.17; H, 10.76, 10.99.

The ultraviolet spectrum of this compound consisted of only end absorption above 220 mμ and a small maximum, ϵ 23, at 294 mμ. The infrared spectrum showed pertinent bands at 3050 (m), 2980 (s), 2700 (m), 1730 (s-overtone 3450), 1650 (m), 1460 (m), 1420 (w), 1400 (w), 1380 (w), and 892 (s) cm^{-1}.

The compound readily formed a 2,4-dinitrophenylhydrazone, mp 86–88°, mol wt 292.[39]

Anal. Calcd for $C_{13}H_{16}N_4O_4$: C, 53.41; H, 5.52. Found: C, 53.41; H, 5.45.

On quantiative hydrogenation, a small sample of **12** absorbed 103% of the amount required to saturate one double bond. Oxidation of 1.0 g of **12** with 2 g of potassium permanganate in 25 ml of water and 3 ml of concentrated sulfuric acid, followed by continuous liquid–liquid extraction with ether, afforded 5-oxohexanoic acid. The semicarbazone derivative, prepared in the usual manner, melted at 170–171° (lit.[45] 173°) and gave no depression on admixture with the same derivative prepared from the oxidation product of 6-hepten-2-one (**8**).

The attempted purification of 5-methyl-5-hexenal by preparative vpc failed as the compound was quantitatively transformed, under these conditions (100°, 30 min, silicone grease on Chromosorb), into 3-methylenecyclohexanol (**23**), bp 173°, n^{25}D 1.483 (lit.[20] bp 172–174°, n^{25}D 1.4797).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.17; H, 10.81.

This structure assignment is based on the following data. The infrared spectrum contains pertinent bands at 3350 (s), 3060 (m), 2950 (s), 1650 (s), 1460 (s), 1052 (s), and 890 (s-overtone 1770) cm^{-1}. A band at 1052 cm^{-1} has been reported for a secondary hydroxyl group in a six-membered ring β to an *exo*-methylene group.[46] The nmr spectrum,[47] relative to tetramethylsilane, consists of a two-proton singlet, δ 4.73 (ethylenic), a one-proton multiplet, 3.7 (tertiary H on carbinol carbon), a one-proton singlet, 3.3 (hydroxyl–D_2O exchange eliminates peak), and eight protons as a series of multiplets, 2.7–1.2. Attempted hydrogenation of the compound with Pd–C led to a disproportionation and afforded 3-methylcyclohexanone, isolated as the 2,4-dinitrophenylhydrazone, mp 153–155° (lit.[36] 155°).

4-Methyl-5-heptenal (14). 4-Methyl-1,5-heptadien-3-ol, 0.93 g, was passed through the column described above at a temperature of 370–375° and a pressure of 20 mm. The condensed product, 0.75 g (81% recovery), consisted of 22% unreacted starting alcohol, 57% 4-methyl-5-heptenal, and 22% low-boiling materials suspected to be acrolein and 2-pentene. The actual yield of 4-methyl-5-heptenal was therefore 45%. The 4-methyl-5-heptenal component in the above product was isolated by preparative vpc.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.09; H, 11.54.

The ultraviolet spectrum of **14** showed only end absorption above 230 mμ and a small maximum, ϵ 40, at 295 mμ. The infrared spectrum showed pertinent bands at 3020 (shoulder), 2950 (s), 2700 (m), 1730 (s-3400 overtone), 1480 (s), 975 (s), and 720 (w) cm^{-1}. The compound readily formed a 2,4-dinitrophenylhydrazone, mp 74–75°.

Anal. Calcd for $C_{14}H_{18}N_4O_4$: C, 54.89; H, 5.92. Found: C, 54.41; H, 5.71.

Oxidation of a small amount of the compound according to the method of Nunn[41] gave α-methylglutaric acid, mp 75° (lit.[42] 75–77°).

3,5-Dimethyl-5-hexenal (16). 2-Methyl-1,5-heptadien-4-ol, 34.8 g, was passed through the column described above at a temperature of 370–374° and a pressure of 9 mm. The condensed products, 25.2 g (72% recovery), consisted of 49% crotonaldehyde, 30% starting alcohol, 13% 3,5-dimethyl-5-hexenal, and 8% of a low-boiling component suspected to be isobutylene. The actual yield of 3,5-dimethyl-5-hexenal is therefore 9.5%.

Fractional distillation of the above product under reduced pressure afforded a forerun consisting mostly of crotonaldehyde, identified by its characteristic odor, vpc retention time, and 2,4-dinitrophenylhydrazone, mp 188–189° (lit.[36] 190°). The distillation did not afford a sample of the desired aldehyde since a new component appeared in the distillate. Attempted purification by preparative vpc also failed as the desired aldehyde was quantitatively transformed to the same compound observed in the distillation attempt. Consequently, a 4.0-g sample of the rearrangement mixture which contained about 25% of the desired aldehyde was treated with 2.5 ml of a saturated sodium bisulfite solution according to the method of Adams, Johnson, and Wilcox.[48] The bisulfite addition product was precipitated with 12.5 ml of ethanol, filtered, washed, and decomposed with dilute hydrochloric acid. Ether extraction followed by drying over anhydrous magnesium sulfate and evaporation of the ether gave a residue of about one drop, which consisted of about 40% water and 60% 3,5-dimethyl-5-hexenal, as indicated by their vpc retention times. The infrared spectrum of this mixture contained pertinent bands at 3450 (water), 3080 (w), 2980 (s), 2750 (w), 1740 (s), 1660 (s), 1480 (s), and 890 (s) cm^{-1}.

Since the attempts at isolation of the aldehyde were unsuccessful, a slow stream of nitrogen was passed through the rearrangement mixture until all crotonaldehyde had been removed. The semicarbazone derivative, prepared directly from the residue, melted at 106–108°.

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(46) A. R. H. Cole, R. N. Jones, and K. Dobriner, *J. Am. Chem. Soc.,* 74, 5571 (1952).

(47) We wish to thank the Monsanto Research Corp. for the use of their Varian A-60 nmr spectrometer.

(48) R. Adams, J. R. Johnson, and C. F. Wilcox, "Laboratory Experiments in Organic Chemistry," 5th ed, The Macmillan Co., New York, N. Y., 1963, p 217.

Anal. Calcd for $C_9H_{17}ON_3$: C, 58.98; H, 9.3. Found: C, 58.74; H, 8.8.

To the compound formed during distillation of the rearrangement product and to which 3,5-dimethyl-5-hexenal was quantitatively transformed during preparative vpc the 5-methyl-3-methylenecyclohexanol (**24**) structure was assigned on the basis of the following analysis and spectral data.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.80; H, 11.24.

The ultraviolet spectrum showed only end absorption above 230 mμ. The infrared spectrum contained pertinent bands at 3350 (s), 3060 (m), 2900 (s), 1770 (w), 1650 (s), 1460 (s), 1380 (s), 1052 (s), and 890 (s) cm^{-1}. Eglinton[49] lists bands at 3072, 1648, and 892 cm^{-1} for an *exo*-methylene group on a six-membered ring. A band at 1052 cm^{-1} has been reported in steroids for a secondary hydroxyl in a six-membered ring β to an *exo*-methylene group.[46] The nmr spectrum[47] consisted of the following, relative to tetramethylsilane: a two-proton singlet, δ 4.80 (ethylenic); a one-proton quintet, 4.05 (tertiary H on carbinol carbon); one-proton singlet, 2.7 (hydroxyl; peak disappears on D_2O exchange); two-proton doublet centered at 2.27; five protons as a series of multiplets at 2.5–1.1; three-proton doublet centered at 0.95 (methyl on tertiary carbon).

2,5-Dimethyl-5-hexenal (18). 2,5-Dimethyl-1,5-hexadien-3-ol, 34.4 g, was passed through the column described above at a temperature of 360–365° and a pressure of 8 mm. While the Dry Ice–acetone cooled trap was warming up to room temperature, the gas evolved was bubbled through a solution of bromine in carbon tetrachloride. Additional bromine was added as the color discharged. When gas evolution from the product mixture ceased the carbon tetrachloride solution was partially evaporated with a stream of nitrogen. Vpc of the residue indicated two main constituents in a ratio of 1:2 and a trace component. Preparative vpc afforded isobutylene dibromide, bp 149–149.5°, $n^{25}\mathrm{D}$ 1.5072, $d^{26}{}_4$ 1.755 (lit. bp 148–150°,[50] $n^{25}\mathrm{D}$ 1.5070,[51] $d^{20}{}_4$ 1.7595[50]), and 1,2,3-tribromo-2-methylpropane, bp 208°, $n^{25}\mathrm{D}$ 1.5575, $d^{26}{}_4$ 2.130 [lit. bp 102–105° (12 mm),[50] $d^{20}{}_4$ 2.1856,[50] $n^{25}\mathrm{D}$ 1.5587[51]].

The condensed product remaining after vaporization of the isobutylene, 23.2 g (67.5% recovery), consisted of 2.7 g of nonvolatile materials, and the 20.5-g volatile fraction was composed of 13% starting alcohol, 33% 2,5-dimethyl-5-hexenal, 46% methacrolein, 1% isobutylene, and five unidentified minor constituents totaling 7%. The actual yield of 2,5-dimethyl-5-hexenal was therefore 22%. The weight loss observed was due in part to the isobutylene vaporized out of the condensate and in part to polymerization in the cooler regions of the thermolysis column.

Fractional distillation of the reaction mixture gave a forerun from which the 2,4-dinitrophenylhydrazone of α-methacrolein was prepared, mp 204–205° (lit.[36] 206°). Further distillation was discontinued as the nature of the material changed rapidly during attempted fractionation as evidenced by the appearance of numerous new peaks in the vpc. Attempts at preparative vpc also resulted in substantial changes in the nature of the compounds present, but a small forerun appeared to be 2,5-dimethyl-5-hexenal in about 98% purity. This material, bp 152–153° dec, $n^{25}\mathrm{D}$ 1.454, $d^{26}{}_4$ 0.888, had an ultraviolet spectrum consisting only of end absorption above 230 mμ with a small maximum, ϵ 13, at 295 mμ. The infrared spectrum showed pertinent bands at 3050 (m), 2950 (s), 2700 (m), 1740 (s-overtone 3500), 1650 (s), 1460 (s), 1380 (s), and 890 (s) cm^{-1}.

The main fraction obtained by preparative vpc consisted of a different compound, in about 85% purity, to which the 6-methyl-3-methylenecyclohexanol (**25**) structure is tentatively assigned based solely on the infrared spectrum, which has pertinent bands at 3400 (s), 3050 (m), 2900 (s), 1640 (s), 1460 (s), 1380 (m), 1050 (s), and 890 (s) cm^{-1}.

Since it was not possible to obtain a pure sample of 2,5-dimethyl-5-hexenal of sufficient quantity for further work, the crude condensed product from a repeated thermolysis was subjected to hydrogenation. Preparative vpc afforded a sample of 2,5-dimethylhexanal, bp 161–161.5°, $n^{25}\mathrm{D}$ 1.4143, $d^{26}{}_4$ 0.8274.

Anal. Calcd for $C_8H_{16}O$: C, 74.95; H, 12.58. Found: C, 74.58; H, 12.46.

The 2,4-dinitrophenylhydrazone was prepared in the usual manner, mp 100–101°.

Anal. Calcd for $C_{14}H_{20}N_4O_4$: C, 54.53; H, 6.54. Found: C, 53.94; H, 6.19.

The remainder of the saturated aldehyde was oxidized with permanganate, and the resulting acid was isolated as the amide, mp 102–102.5°. Tiffenaeu[52] gives the melting point of 2,5-dimethylhexanamide as 103°.

6-Methyl-6-hepten-2-one (20). 3,5-Dimethyl-1,5-hexadien-3-ol, 6.2 g, was passed through the column described above at a temperature of 370–372° and a pressure of 11 mm. The condensed product, 5.0 g (80% recovery), consisted of 52% 6-methyl-6-hepten-2-one, 38% methyl vinyl ketone, 6% isobutylene, and 3% of an unidentified low-boiling constituent. The actual yield of 6-methyl-6-hepten-2-one was therefore 42%. The isobutylene was identified only by its vpc retention time. Preparative vpc of the product afforded a first fraction which was identified as methyl vinyl ketone by its vpc retention time, its characteristic odor, and its semicarbazone. The main fraction was 6-methyl-6-hepten-2-one, $n^{26}\mathrm{D}$ 1.432, $d^{24}{}_4$ 0.859 (lit.[20] $n^{25}\mathrm{D}$ 1.4358).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.84, 75.97; H, 11.43, 11.16.

The compound gave a positive iodoform test. The ultraviolet spectrum showed only end absorption above 230 mμ with a small maximum, ϵ 22, at 282 mμ. The infrared spectrum contained pertinent bands at 3060 (w), 2950 (s), 1720 (s), 1650 (m), 1475 (s), 1360 (s), and 888 (s-overtone 1770) cm^{-1}. The 2,4-dinitrophenylhydrazone was prepared in the usual manner, mp 76–78°, mol wt 306.[39]

Anal. Calcd for $C_{14}H_{18}N_4O_4$: C, 54.88; H, 5.93. Found: C, 54.83, 54.59; H, 6.30, 6.03.

Hydrogenation of a sample of 6-methyl-6-hepten-2-one with Pd–C in hexane led to the absorption of 102% of the amount theoretically required to saturate one double bond. Removal of the catalyst and solvent gave 6-methyl-2-heptanone, as evidenced by a positive iodoform test and the formation of its 2,4-dinitrophenylhydrazone, mp 75–77° (lit.[27] mp 77°).

Oxidation of a sample of 6-methyl-6-hepten-2-one with acid permanganate afforded 2,5-heptanedione, identified as the disemicarbazone, mp 214–215° (lit.[53] 213°).

4,4-Dimethyl-6-hepten-2-one (22). 4,6-Dimethyl-1,5-heptadien-4-ol, 19.9 g, was passed through the column described above at 370–380° (15 mm). The condensed products, 14.1 g (71% recovery), consisted of 74% mesityl oxide, 4.3% 4,4-dimethyl-6-hepten-2-one, 20% starting alcohol, and 1.4% low-boiling components. The actual yield of 4,4-dimethyl-6-hepten-2-one is therefore 3%. Mesityl oxide and the starting alcohol were identified only by their vpc retention times. 4,4-Dimethyl-6-hepten-2-one was isolated by preparative vpc, bp 167–168°, $n^{25}\mathrm{D}$ 1.4335.

Anal. Calcd for $C_9H_{16}O$: C, 77.15; H, 11.51. Found: C, 77.27; H, 11.39.

The ultraviolet spectrum showed only end absorption above 230 mμ with a small maximum, ϵ 40, at 268 mμ. The infrared spectrum contained pertinent bands at 3060 (m), 2950 (s), 1720 (s-overtone 3400), 1640 (m), 1470 (m), 1360 (s), 995 (s), and 915 (s-overtone 1840) cm^{-1}. The compound formed a semicarbazone derivative, mp 143°.

Anal. Calcd for $C_{10}H_{19}N_3O$: C, 60.88; H, 9.71. Found: C, 61.28; H, 9.92.

Hydrogenation of a small sample of the ketone with Pd–C led to the absorption of 96% of the amount theoretically required to saturate one double bond. The hydrogenation mixture was filtered to remove the catalyst; the solvent was evaporated and the residue treated with aqueous sodium hydroxide and iodine. The precipitation of iodoform confirmed the presence of a methyl ketone. Acidification of the aqueous medium followed by ether extraction afforded 3,3-dimethylhexanoic acid, isolated as the *p*-bromophenacyl ester, mp 64.5–65° (lit.[54] mp 66.2°).

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