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Vapor Phase Thermolysis of 1-Hexen-5-yn-3-ol. An Acetylenic Oxy-Cope Reaction

Alfred Viola and John H. MacMillan

Vapor Phase Thermolysis of 1-Hexen-5-yn-3-ol. An Acetylenic Oxy-Cope Reaction¹

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Abstract: 1-Hexen-5-yn-3-ol, shown to be free of the internal acetylenic isomer, was subjected to vapor phase thermolysis in a flow system over the range of 350–390° and under various pressures. The extent of β -hydroxy-olefin cleavage, which leads to formation of acrolein and allene, was independent of residence time in the thermolysis zone but increased with temperature, indicative of a higher activation energy than the competing rearrangement processes. One of these processes affords 4,5-hexadienal *via* an acetylenic analog of the oxy-Cope reaction. Also produced is 3-cyclopentenecarboxaldehyde in amounts increasing with increasing temperature and/or increasing residence time. The data are consistent with an electrocyclic reaction involving the enol progenitor of the Cope product, which ketonizes only upon condensation in the product trap.

As a part of our investigation of the thermolytic behavior of 3-hydroxy-1,5-hexadienes,² the effects due to the presence of an acetylenic bond have been studied. Only a few examples of the participation of triple bonds in Cope-type rearrangements have been reported. Black and Landor³ found several propargyl

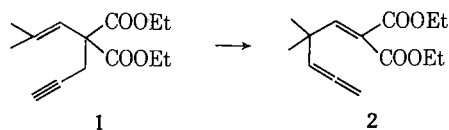
vinyl ethers to undergo thermal rearrangements to 3,4-pentadienals in a manner entirely analogous to that reported earlier⁴ in the case of allyl vinyl ethers. Also reported³ was the classical liquid-phase Cope reaction of **1**, although the formation of **2**, which occurred only to the extent of 20%, was accompanied by extensive polymerization. Huntsman has reported the thermal rearrangement of 1-alken-5-yne to give 1,2,5-

(1) Paper III in series entitled "Vapor Phase Thermolyses of 3-Hydroxy-1,5-hexadienes." For paper II see ref 2.

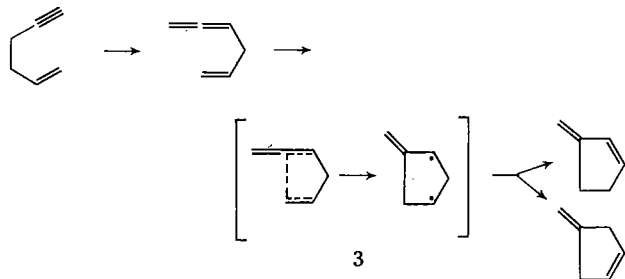
(2) A. Viola, E. J. Iorio, K. K. Chen, G. M. Glover, U. Nayak, and P. J. Kocienski, *J. Amer. Chem. Soc.*, **89**, 3462 (1967).

(3) D. K. Black and S. R. Landor, *J. Chem. Soc.*, 6784 (1965).

(4) C. D. Hurd and M. A. Pollack, *J. Amer. Chem. Soc.*, **60**, 1905 (1938).

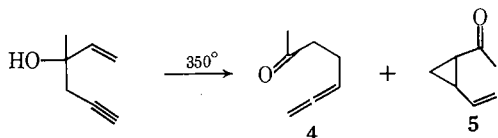


alkatrienes, followed by partial cyclization of the allenic products.⁵ A diradical pathway was proposed for the formation of the observed methylenecyclopentenes.



That the alkatrienes result from a Cope process and not from a thermal acetylene-allene isomerization was demonstrated by thermolysis of several methyl-substituted compounds such as 1-heptene-5-yne which afforded 3-methyl-1,2,5-hexatriene and not a heptatriene.

Recently, Wilson and Sherrod have reported⁶ that the thermal gas phase rearrangement of 3-methyl-1-hexen-5-yn-3-ol results in the formation of 5,6-heptadien-2-one, **4**, and 1-acetyl-2-vinylcyclopropane, **5**.



Since the pyrolysis products also contained methyl vinyl ketone, a stepwise mechanism for the formation of 5,6-heptadien-2-one was proposed. It was also suggested that the concerted formation of **5** from the enol of **4** constituted the first example of the isolation of the cyclopropane intermediate of an "enolene" rearrangement.⁷

Results

Although the addition of propargylmagnesium^{8,9} halide to carbonyls has been reported to give exclusively propargyl carbinols,⁹ we found the reaction of propargyl bromide with magnesium, followed by acrolein addition under normal Grignard conditions, resulted in extensive polymer formation and afforded a poor yield of a 50:50 mixture of the desired 1-hexen-5-yn-3-ol, **6**, and the internal acetylenic compound **7**. The

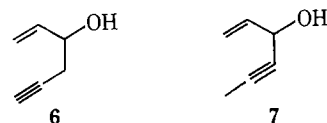
(5) W. D. Huntsman, J. A. DeBoer, and M. H. Woosley, *J. Amer. Chem. Soc.*, **88**, 5846 (1966).

(6) J. W. Wilson and S. A. Sherrod, *Chem. Commun.*, 143 (1968).

(7) R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967).

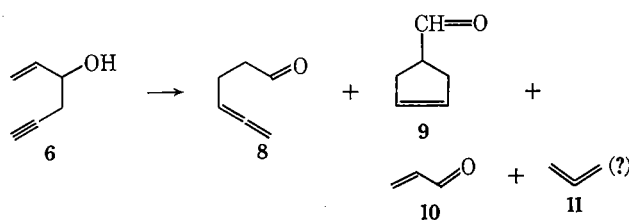
(8) The term propargylmagnesium as used herein is only a procedural one and has no structural connotation. The reagent may well have the allenylmagnesium structure or may represent a complex equilibrium system (see ref 9). We assume the claim of exclusive propargyl carbinol formation refers only to the possibility of allene formation and not to internal decomposition and rearrangement of the reagent by the acetylenic hydrogen. At no time did we find any evidence for the production of allenes during our syntheses of 1-hexen-5-yn-3-ol.

(9) T. L. Jacobs and T. L. Moore, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962, p 19-O; M. Gaudemar, *Ann. Chim. (Paris)*, [13] **1**, 161 (1956).



two carbinols were readily resolved by vpc and could be easily differentiated by the characteristic ir bands associated with the position of the acetylenic link. The structure of **6** was verified by chemical and spectral means as detailed in the Experimental Section. Far better yields of **6** were obtained from the low-temperature Barbier synthesis of propargylic alcohols developed by Sondheimer, *et al.*¹⁰ Under these conditions there was no contamination of **6** by the isomeric **7** and only isomer free **6** was utilized for all thermolyses reported herein.

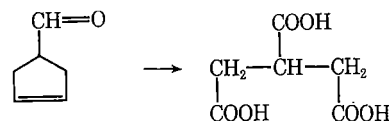
Thermolysis of **6** produced four products, **8-11**, whose relative amounts depended upon temperature and residence time in the thermolysis column.



Under the conditions employed in this study, **11** was only partially retained in the product trap and since the allene structure is known only by inference, the possibility of propyne formation cannot be excluded. The presence of acrolein, **10**, was unequivocally established by its odor, vpc retention time, ir spectrum, and formation of its 2,4-dinitrophenylhydrazone derivative. The mass balance of the reaction indicates formation of **10** and **11** in equimolar quantities under all conditions employed.

The carbon skeleton of **8** was determined by hydrogenation to hexanal and the location of the unsaturation was based upon ir and nmr spectra as detailed in the Experimental Section.

The carbon skeleton of **9** was similarly established by quantitative hydrogenation followed by oxidation to give cyclopentanecarboxylic acid. Although both ir and nmr spectra of **9** were consistent with the above structure, the lack of a proper model for comparison of the nmr spectrum did not permit assignment of double-bond location on this basis alone. Oxidation of **9**, however, afforded tricarballylic acid which unequivocally establishes the structure of **9** as 3-cyclopentene-carboxaldehyde.

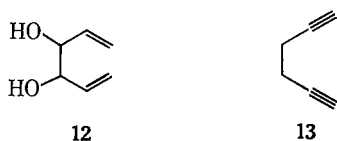


Discussion

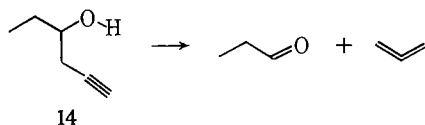
The data summarized in Table I indicate that the extent of cleavage product formation is solely a function of temperature. This observation is in line with our previously reported² findings in the 1,5-hexadien-3-ol series wherein β -hydroxyolefin cleavage¹¹ and oxy-

(10) F. Sondheimer, Y. Amiel, and Y. Gaoni, *J. Amer. Chem. Soc.*, **84**, 272 (1962).

Cope rearrangement¹² were found to be competitive concerted reactions. If such were to be the case here, then the presence of the initial acetylenic system and the subsequent formation of an allenic structure could not interfere in the formation of the requisite six-membered cyclic transition state. That the presence of such structures does not rule out their transient formation in six-membered rings has recently been illustrated for both acetylenes¹³ and allenes.¹⁴ The intermediacy of stabilized radicals which may lead to the observed cleavage products can be ruled out on the basis of the complete absence of any intermolecular coupling products, such as **12** or **13**, or products de-



rivable therefrom, in the thermolysis condensate, and by the fact that 5-hexyn-3-ol, **14**, is transformed



smoothly and quantitatively into propanal and allene at 350°.¹⁵

Table I. Effect of Temperature and Residence Time^a on Product Composition (%)^b

Run	<i>t</i> , °C	<i>P</i> , ^a mm	Rearrangement			Ratios ^b	
			Cleavage, ^b 10 + 11	Cope	Cyclic	8 / 9	(8 + 9)/(10 + 11)
1	350	1	39	46	12	3.8	1.5
2	370	1	48	36	15	2.4	1.1
3	370	8	49	28	23	1.2	1.1
4 ^c	390	1	50 ^c	28	22	1.3	1.0 ^c
5	390	8	54	20	26	0.77	0.85
6	390	15	54	7	38	0.18	0.83

^a Pressure was regulated at the trap end of the flow system and is not, therefore, a true measure of pressure within the thermolysis zone but, at constant drop rate, reflects the relative residence time.

^b Percentages are based on integrated vpc peak areas of condensed products and the weight loss. The assumption that noncondensation of the more volatile cleavage products accounts for all weight losses may lead to a small error in the ratio of rearrangement to cleavage products. ^c Run 4 represents a single small sample. Cleavage percentage is therefore not reliable since mechanical losses were not negligible.

A comparison of the rearrangement to cleavage ratio of **6** with that previously reported² for 1,5-hexadien-3-ol indicates a relatively higher activation energy for the rearrangement process involving the triple bond compared with the activation energy of the corresponding

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

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

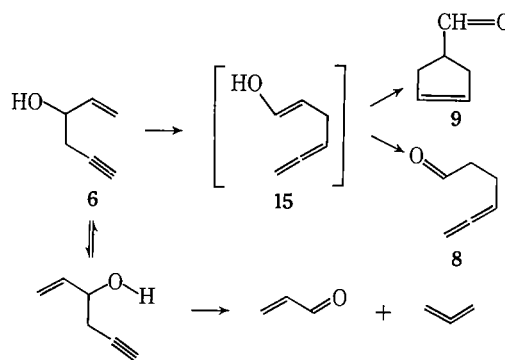
(13) L. K. Montgomery and L. E. Applegate, *ibid.*, **89**, 5305 (1967).

(14) G. Wittig and P. Fritze, *Angew. Chem. Intern. Ed. Engl.*, **5**, 846 (1966).

(15) R. Proverb, unpublished results, this laboratory. The kinetics of this acetylenic analog of β -hydroxyolefin cleavage are currently under investigation.

cleavage reactions in the two systems. While it is necessary to bend¹⁶ the C—C≡C system to accommodate both cyclic transition states, presumably less distortion is required in the cleavage reaction due to the mobility of the hydroxyl proton.

4,5-Hexadienal, **8**, is the anticipated oxy-Cope product from 1-hexen-5-yn-3-ol, **6**. Since residence time in the thermolysis zone is a function of pressure, a comparison of the ratio of **8** to 3-cyclopentenecarboxaldehyde, **9**, in the condensate (*i.e.*, compares runs 2 and 3 and runs 4, 5, and 6 in Table I) indicates the probable formation of **9** from **8** or from a common precursor. The former possibility was ruled out by the thermolysis of a 1:1 mixture of **8** and **9**, at 395–400°, from which **9** was recovered quantitatively whereas about 40% of **8** was converted to fragmentation products, none of which were noted in any other thermolyses. It therefore appears that **8** is formed only after condensation, presumably from its enol precursor **15**, which also serves as the precursor to the formation of **9**.

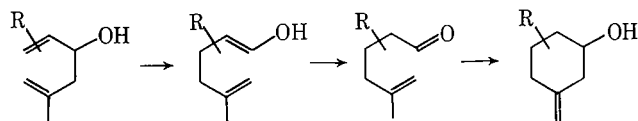


The absence of a **15** → **8** conversion in the vapor phase is in accord with the Woodward–Hoffman rules forbidding a thermal, concerted, uncatalyzed 1,3 shift¹⁷ and our previous experience involving secondary cyclization of oxy-Cope products.¹⁸ Additional evidence that wall reactions do not lead to the ketonization of the enol **15** is provided by the data of runs 1, 2, and 4, Table I. If it is assumed that contact time under these different temperature conditions is approximately constant and that reaction **6** → **15** is fast compared with **15** → **9**,¹⁹ then a modified Arrhenius plot for the latter

(16) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., Nov 1956, p 338. The C—C≡C bending mode for propyne is listed at 336 cm⁻¹. At the prevailing temperature, higher vibrational states will therefore be substantially populated.

(17) R. Woodward and R. Hoffman, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

(18) We have reported² that 5-methyl substitution in 5-hexenals invariably led to the formation of 3-methylenecyclohexanols. Such

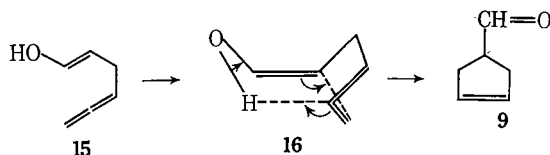


observations, however, occurred only on attempted redistillation or preparative vpc of thermolysis products and no 3-methylenecyclohexanols were ever observed as primary products. This cyclization therefore appears to be a reaction depending upon the free aldehydic group and not the enol precursor.

(19) This assumption appears valid since even at 350°, run 1, only trace amounts of starting alcohol **6** survived while about 80% of the six carbon species present must be the enolic progenitor of hexadienal.

process affords a straight line only if no $15 \rightarrow 8$ occurs within the thermolysis zone.²⁰

We favor a concerted 1,5 hydrogen shift, involving the bicyclic transition state **16**, for the transformation $15 \rightarrow 9$. This process is in accord with the crude



activation parameters derivable from the above Arrhenius plot,^{21,22} and is analogous to other examples of [3.2.1]bicyclic intermediates which have recently been reported,²³ although without activation parameters. Also, in the thermolysis of 1-hexen-5-yn-3-ol-*O-d*, all the deuterium label found in **9** appeared to be exclusively in the 3 position, as evidenced by the nmr spectrum. The intermediacy of **16** seems more favorable than any of the other apparent alternate pathways. Thus a diradical corresponding to **3** is inconsistent with the above kinetic parameters and also does not lead to the structure **9** observed in this system. Similarly, a vinylcyclopropane intermediate can be ruled out since no cyclopropanes were found in any of our product mixtures, whereas in the vinylcyclopropane rearrangement even at 510–515° nearly 20% of vinylcyclopropane survived.²⁴ The formation of the cyclopropane structure, **5**, reported⁸ for the thermolysis of 3-methyl-1-hexen-5-yn-3-ol can be explained on the basis of the steric effect, resulting from the additional methyl group, upon the formation of **16**, which allows the [4.1.0]-bicyclic intermediate required for the enolene rearrangement to compete favorably with the [3.2.1] system required for cyclopentene formation.

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-5 spectrophotometer on neat liquid samples. Nmr spectra were determined with a Varian

(20) Under the above assumptions the integrated first-order rate equation becomes $\log k = \log (2.303/t) + \log [\log (9 + 8)/8]$. With t constant, the plot of the log-log term against $1/T$ gives an excellent straight line relationship which is not maintained if any arbitrary corrections are applied for the possible formation of **8** in the thermolysis zone.

(21) The slope corresponds to an activation energy of about 20 kcal/mol for the process $15 \rightarrow 9$. Although this value is based upon a rather indirect measurement at only three temperatures, it is considerably lower than the range of 23–36 kcal/mol reported for concerted Cope processes.²² Although preliminary investigations in this laboratory indicate that electrocyclic reactions involving acetylenic bonds may well proceed more readily than their olefinic analogs, it seems unlikely that the activation energy for such a process, as exemplified by $6 \rightarrow 15$ would be reduced much below the lower end in this range. The slower rate for $15 \rightarrow 9$, compared to its preceding oxy-Cope step, is then best explained on the basis of a larger negative activation entropy, in accord with the more rigid transition state **16**.

(22) (a) E. G. Foster, A. C. Cope, and F. Daniels, *J. Amer. Chem. Soc.*, **69**, 1893 (1947); (b) G. R. Aldridge and G. W. Murphy, *ibid.*, **73**, 1158 (1951); (c) G. S. Hammond and C. D. DeBoer, *ibid.*, **86**, 899 (1964). The low value of 23 kcal/mol reported herein reflects accompanying ring strain relief. (d) A value of 36 kcal/mol has been found by W. von E. Doering and V. Toscano for the pure unperturbed Cope rearrangement of 1,1-dideuterio- \rightarrow 3,3-dideuterio-1,5-hexadiene. See footnote 12 of W. von E. Doering, *et al.*, *Tetrahedron*, **23**, 3943 (1967). We would anticipate a considerable lowering of the activation energy from this value due to the perturbation effects of a hydroxyl group.

(23) M. S. Newman, *et al.*, *J. Amer. Chem. Soc.*, **88**, 781 (1966); *J. Org. Chem.*, **32**, 3225 (1967); **31**, 2713 (1966).

(24) C. G. Overberger and A. E. Borchert, *J. Amer. Chem. Soc.*, **82**, 4896 (1960); see also E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 6 (1963); for the thermal stability of 2-vinylcyclopropanecarboxaldehydes.

A-60A spectrometer in deuterated chloroform solutions with an internal tetramethylsilane standard. Elementary analyses were performed by Stephen M. Nagy, M.I.T., 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 and relative peak areas were determined with a disk integrator. Preparative vapor phase chromatography was accomplished with an F & M Model 776 using 8 ft \times 1 in. columns packed with Triton X.

Preparation of 1-Hexen-5-yn-3-ol (6). In order to avoid internal rearrangement of the propargyl Grignard reagent, a modification of the procedure reported by Sondheimer¹⁰ for the preparation of 1,5-hexadiyn-3-ol was utilized.

To 200 ml of absolute ether, in a 1-l. three-necked flask, was added 24 g of magnesium (1.0 g-atom), 4 g of freshly distilled propargyl bromide, and 0.1 g of mercuric chloride. The mixture was warmed, with stirring, until the reaction commenced as evidenced by vigorous boiling of the ether. The flask was then immersed in a Dry Ice-acetone bath and, over a 3-hr period, a solution of 67 g of freshly distilled propargyl bromide (total 0.60 mol) and 25 g of freshly distilled acrolein (0.45 mol) in 200 ml of absolute ether was added with vigorous stirring. During the addition the bath temperature was maintained at -25° . The flask was then allowed to warm to room temperature and the mixture was poured onto ice-ammonium chloride. The product was isolated in the usual manner to afford a crude distillate, 29.2 g, boiling at 53–54° (20 mm), and containing about 5% low-boiling impurities. Careful fractionation yielded 24 g of product (56% based on the amount of acrolein used) which was chromatographically homogeneous and contained none of the isomeric internal acetylene: bp 53–54° (20 mm); n_D^{25} 1.4670 (lit.²⁵ bp 49° (12 mm); n_D^{17} 1.4650).

Anal. Calcd for C_6H_8O : C, 74.97; H, 8.39. Found: C, 75.10; H, 8.61.

The ir spectrum contained pertinent bands at about 3400 (s), 3330 (spike), 3120 (w), 3070 (w), 2950 (m), 2140 (w), 1650 (m), 1440 (s), 1130 (s), 1040 (s), 990 (s), and 930 cm^{-1} (s).

Hydrogenation of a small sample of the alcohol over Pd-C led to the absorption of 97% of the amount of hydrogen required for saturation of three double bonds. The product was identified as 3-hexanol by its vpc retention time and by conversion to the acid phthalate, mp 74–75° (lit.²⁶ mp 76–77°), which showed no melting point depression on admixture with an authentic sample.

Attempted preparations of 1-hexen-5-yn-3-ol by the usual Grignard procedure in the absence of the cooling bath led to extensive polymer formation and gave a product which was a 50:50 mixture of the desired alcohol and the isomeric 1-hexen-4-yn-3-ol. The two alcohols were readily resolvable by vpc and could be easily identified by their different ir spectra. The spectrum of 1-hexen-4-yn-3-ol contained pertinent bands at 3300 (s), 3080 (m), 2970 (w), 2900 (m), 2220 (m), 1650 (m), 1400 (s), 1265 (s), 1150 (s), 1010 (s), 980 (s), 920 (s), and 800 cm^{-1} (m).

Thermal Vapor Phase Rearrangements. The rearrangements were performed in a flow system which has been described previously.² The condensed products, usually representing a recovery of 80–90%, were subjected to vpc analysis and consisted of mixtures of the following compounds in varying amounts which depended upon reaction conditions: unreacted starting material, acrolein, allene, 3-cyclopentenecarboxaldehyde, and 4,5-hexadienal. The component believed to be allene condensed only partially under these conditions and always appeared as a minor component in the appropriate region of the vapor phase chromatogram; it was not otherwise identified. Thermolyses were performed numerous times under each of the pressure and temperature conditions listed in Table I, which summarizes the analytical data. A typical experiment follows.

1-Hexen-5-yn-3-ol (24.9 g) was passed through the column at 390° and at a pressure of 15 mm. The same uniform drop rate of 4 drops per minute was always maintained. The condensed product, 21.1 g (85% recovery), consisted of 36% acrolein, 45% 3-cyclopentenecarboxaldehyde, 12% 4,5-hexadienal, and 7% of the low-boiling constituent believed to be allene. The three main constituent were identified as follows.

Acrolein. This component was isolated from the mixture by distillation and identified by its characteristic odor, vpc retention time, superimposability of its ir spectrum on that of an authentic sample of freshly distilled acrolein and by its 2,4-dinitrophenyl-

(25) M. Gaudemar, *C. R. Acad. Sci., Paris*, **233**, 64 (1951).

(26) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **103**, 1938 (1913).

hydrazone derivative, mp 164–166° (lit.²⁷ mp 165°), which showed no melting point depression on admixture with an authentic sample.

3-Cyclopentencarboxaldehyde (9). The two rearrangement products were not readily separable by distillation but were isolated by preparative vapor phase chromatography. The samples used for the following structure determinations showed only single peaks on vpc.

The component subsequently identified as 3-cyclopentencarboxaldehyde, bp 148–150°, gave an ir spectrum containing pertinent bands at 3020 (m), 2900 (s), 2800 (s), 2700 (m), 1720 (s), 1610 (w), 1440 (m), 1340 (m), 1270 (w), 1170 (m), 1070 (m), 895 (w), 805 (w), and 685 cm⁻¹ (s).

The nmr spectrum consisted of bands centered at δ 9.63 (d, 1 H, aldehydic), 5.67 (s, 2 H, olefinic), 3.05 (m, 1 H, methine), and 2.60 (m, 4 H). The spectrum parallels that reported for 3-cyclopentencarboxylic acid.²⁸

Attempted carbon–hydrogen analyses of the compound were unsatisfactory due to sensitivity to oxidation and explosive decomposition in the combustion tube. Consequently, a sample of the compound was converted into its semicarbazone and recrystallized from water to a constant melting point of 174–175°, which is not in accord with the reported²⁹ value of 213°.

Anal. Calcd for C₇H₁₁N₃O: C, 54.80; H, 7.25. Found: C, 54.40; H, 7.40.

Hydrogenation of a small sample of the aldehyde over Pd–C led to absorption of 98% of the theoretical amount required to saturate one double bond. The resulting saturated product proved sensitive to air oxidation and a stream of oxygen quantitatively converted it into the corresponding acid. The ir spectrum of the

acid was identical with that published for cyclopentencarboxylic acid.³⁰ The acid was converted into its amide derivative, mp 178° (lit.³¹ mp 178°).

Oxidation of a sample of the cyclopentencarboxaldehyde with alkaline permanganate gave tricarballic acid, mp 157–158° (lit.³² mp 160–161°).

4,5-Hexadienal (8). The component subsequently identified as 4,5-hexadienal, bp 156–169° dec, n_D^{25} 1.4727, gave an ir spectrum containing pertinent bands at 3050 (w), 2900 (m), 2800 (m), 2700 (m), 1950 (m), 1710 (s), 1440 (m), 1410 (m), 1395 (m), 1060 (m), and 850 cm⁻¹ (s). The nmr spectrum consisted of a triplet at δ 9.73 (1 H, aldehydic) and complex multiplets at 5.15 (1 H, internal allenic), 4.7 (2 H, terminal allenic), and 2.4 (4 H, aliphatic).

Since the compound was too sensitive to oxidation to afford reproducible carbon–hydrogen analyses, a sample was converted into the 2,4-dinitrophenylhydrazone derivative, mp 91–92°.

Anal. Calcd for C₁₂H₁₂O₄N₄: C, 52.17; H, 4.38. Found: C, 51.88; H, 4.67.

Hydrogenation of a small sample of this component led to absorption of 90% of the amount of hydrogen required to saturate two double bonds and gave a product whose vpc retention time and ir spectrum were identical with those of authentic hexanal. The hydrogenated product gave a 2,4-dinitrophenylhydrazone, mp 92–93°, in agreement with the literature value³³ of 93–94° for this derivative of hexanal.

(30) B. Trost, "Problems in Spectroscopy," W. A. Benjamin, Inc., New York, N. Y., 1967, Compound No. 111.

(31) N. Zelinsky, *Chem. Ber.*, **41**, 2627 (1908).

(32) K. C. Murdock and R. B. Angier, *J. Org. Chem.*, **27**, 2397 (1962). All conceivable oxidation products derivable from the other double bond isomers of **9** have considerably lower melting points.

(33) M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **18**, 1225 (1953).

(27) C. F. H. Allen, *J. Amer. Chem. Soc.*, **52**, 2958 (1930).

(28) G. S. Schmid and A. W. Wolkoff, *J. Org. Chem.*, **32**, 254 (1967).

(29) M. Tiffeneau and B. Tchoubar, *C. R. Acad. Sci., Paris*, **212**, 581 (1941).