and, with vigorous stirring, 0.01 mol of acyl chloride dissolved in 3 g of solvent was added at a constant rate over a period of 5 min. The reaction was allowed to proceed an additional 10 min after the additions were complete. The solution was then washed with ice water and extracted with ether. The organic layer was separated, dried (Na_2SO_4), condensed on a water bath, and analyzed by gas–liquid chromatography. The data obtained are summarized in Tables I and II.

(b) Without Solvent. To a solution of 0.1 mol each of benzene and toluene in a reaction flask fitted with a thermometer, reflux condenser, and gas inlet tube, was introduced 0.04 mol of formyl (or acetyl) fluoride at −30°. Stirring was begun and 0.04 mol of boron trifluoride gas was introduced into the solution at −30° over a period of 3 min. The reaction system was then allowed to warm to 25° and stirring was continued for another 10 min. The solution was then washed three times with water. The organic layer was extracted with ether, separated, dried (Na_2SO_4), and analyzed by gas–liquid chromatography. The data obtained are shown in Table I.

Determination of Kinetic Hydrogen Isotope Effect. Benzene-d_6 (0.02 mol) and toluene (0.02 mol) were used to obtain $k_H:k_D$ values for formylation and acetylation. The reaction conditions, work-up procedures, and gas–liquid chromatographic analyses were followed as described above (b). For formylation, $k_T:k_{B-d_6}$ was found to be 92.7. Calculations gave a $k_H:k_D$ value for benzene of 2.68 (92.7/34.6). For acetylation, $k_T:k_{B-d_6}$ was found to be 318; calculation gave a $k_H:k_D$ value for benzene of 2.45 (318/130).

Conversion of Nitro-Substituted Benzophenones to Benzophenones (Replacement of NO_2 by H). Competitive reaction products of *p*-nitrobenzoyl, 3,5-dinitrobenzoyl, and 2,4-dinitrobenzoyl chlorides were converted to the corresponding benzophenones and analyzed as such by gas–liquid chromatography. A typical experiment was as follows. A mixture of 0.005 mol of competitive reaction products, 0.03 mol of stannous chloride crystals,[11] and 10 g of concentrated hydrochloric acid was placed at 0° in a flask equipped with a thermometer and reflux condenser, then warmed up to 80° and kept for 30 min. The solution was cooled in an ice water bath, neutralized with 30% sodium hydroxide solution, and extracted three times with ether. Evaporation of ether gave the corresponding anilines whose analysis by ir and nmr spectroscopy confirmed the conversion of the nitro groups to amino groups. The aminobenzophenones were diazotized at 5–10° by treating a mixture of 0.003 mol of amines, 0.9 g of concentrated hydrochloric acid, and 10 g of water with 0.009 mol of sodium nitrite in 2 g of water. The solution was then added to 30 g of 30% hypophosphorous acid solution[12] and placed in a refrigerator overnight. The reaction mixture was extracted with ether, dried over Na_2SO_4, concentrated, and analyzed by gas–liquid chromatography.

Gas–Liquid Chromatographic Analysis. The analyses of all products were carried out by gas–liquid chromatography on a Perkin-Elmer Model 226 gas chromatograph equipped with a hydrogen flame ionization detector system and open tubular capillary columns. Characteristic retention time of benzaldehyde, acetophenone, and benzophenone derivatives along with Golay-type capillary columns employed and column temperatures are listed in Table III. Peak areas were determined with an Infotronics Model CRS-1 electronic integrator. Products were identified by comparison with authentic samples.

Acknowledgment. Partial support of our work by the Petroleum Research Fund, administered by the American Chemical Society, and the C. F. Mabery Fund of Case Western Reserve University is gratefully acknowledged. Esso Research and Engineering Company is also thanked for their help.

(11) J. S. Buck and W. S. Ide, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 130.

(12) N. Kornblum, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 295.

Participation of Acetylenic Bonds in Pericyclic Reactions. Thermal Cleavage of β-Hydroxyacetylenes

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Abstract: The ability of acetylenic systems to participate in intramolecular reactions proceeding *via* six-membered cyclic transition states has been established by thermolyses of a number of substituted β-hydroxyacetylenes, in both the vapor and the liquid states. Thermolyses products consisted solely of those allenes and carbonyl compounds derivable from a 1,5-hydrogen transfer. The homogeneous reactions followed the first-order rate law. Activation energies with a variety of alkyl substituents were essentially within experimental error. The activation parameters, $E_a \sim 40$ kcal/mol and $\Delta S^{\ddagger} \sim -10$ eu, are indicative of a cyclic transition state and closely parallel the parameters for the cleavages of those analogous olefins whose data are available. However, the acetylenic compounds utilized reacted at rates varying from 1.3 to 7 times as fast as those of their olefinic analogs. The effects of alkyl, phenyl, and vinyl substituents, and relative rate comparisons with the reaction of analogous olefins, are in accord with a planar transition state for the participation of the triple bond.

The investigation reported herein concerns the participation of acetylenes in reactions whose olefinic analogs normally proceed *via* six-membered cyclic transition states. Although the acetylenic bond is considered to be linear in the ground state in acyclic molecules, the existence of cyclooctyne and the transitory formation of smaller cycloalkynes, down to cyclopentyne,[2] suggest that deviation from linearity is not improbable.[3]

Among the recent reports of reactions of acetylenes which fall into the above category are the following: thermolyses of vinyl propargyl ethers to yield 3,4-pentadienals[4] in the vapor as well as in the liquid phase

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(1) (a) Northeastern University; (b) Universidad del Valle.

(2) L. K. Montgomery and L. E. Applegate, *J. Amer. Chem. Soc.*, **89**, 5305 (1967), and references cited therein.

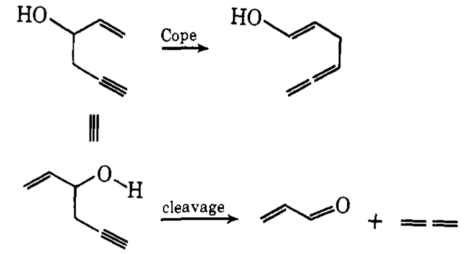
(3) There is a low energy bending mode for propyne at 336 cm^{-1}. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1951.

(4) D. K. Black and S. R. Landor, *J. Chem. Soc.*, 6784 (1965); J. K. Crandall and G. L. Tindell, *Chem. Commun.*, 1411 (1970). For a recent review of triple bond participation in Claisen rearrangements, see A.

including one example of stereospecificity;[5] the aromatic Claisen rearrangement of substituted phenyl propargyl ethers;[6] the thio-Claisen rearrangement in aromatic[7] as well as acyclic[8] systems; a nitrogen analog of the acyclic Claisen rearrangement;[9] an enolyne rearrangement;[10] a stereospecific S_Ni' reaction;[11] the rearrangement of a propargylic to an allenic acetate with migration of the acetoxy group;[12] Cope rearrangements;[4,13] and oxy-Cope rearrangements.[14–17] There have also been several reports of Cope-type rearrangements of various 1,5-hexadiynes in which both acetylenic systems appear to participate in the same six-membered transition state, although the mechanism of these reactions is still uncertain.[16,18–20] Finally, there have been several reports of thermal cleavages of β-hydroxyacetylenes.[14–16]

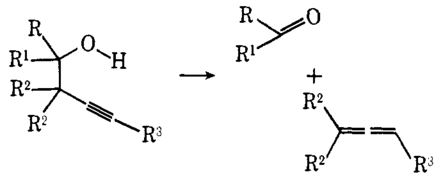
Despite the analogy to the corresponding olefinic reactions, only in a few of the above examples is there evidence for the participation of cyclic transition states. Only a few involve vapor state rearrangements and most of the reactions cited occurred in the liquid state, accompanied by extensive polymerization, under conditions favoring intermolecular reactions. Only in two cases does the observation of stereospecificity implicate a concerted intramolecular rearrangement.[5,11] However, in all of the few instances where activation parameters have been determined,[7b,17,18] the low Arrhenius energy implicates energetic assistance of bond-forming steps in the bond-breaking process and the large negative entropies of activation imply rigid transition states.

Thermal cleavage of β-hydroxy olefins has been shown to be a homogeneous, unimolecular, first-order reaction,[21] which apparently proceeds through a six-membered cyclic transition state.[22] This process constitutes a competing reaction in the oxy-Cope rearrangement.[23] Similarly, the acetylenic oxy-Cope rearrangement of 1-hexen-5-yn-3-ol[14] and its 3-methyl derivative[15,16] appears to be a process competing with β-hydroxyacetylene cleavage. Although activation parameters for either competitive process could not be determined, both processes occurred at a faster rate than the corresponding reactions of their olefinic analogs in 1,5-hexadien-3-ol.[24] In addition, we have reported that the β-hydroxyacetylene cleavage is not restricted to the oxy-Cope systems, in that 5-hexyn-3-ol is quantitatively converted to propionaldehyde and allene at 350°.[25] Therefore, thermal cleavage of β-hydroxyacetylenes appeared to represent an ideal system for a study of the participation of acetylenes in cyclic six-membered transition states.



Results

Thermolyses of all β-hydroxyacetylenes, which were found or have been reported to undergo a thermal cleavage reaction, result in the formation of the carbonyl and allenic compounds expected on the basis of a 1,5 sigmatropic hydrogen shift. In no case has there been any evidence for the formation of acetylenic products.



The nine β-hydroxyacetylenes, **1–9**, listed in Chart I, were thermolyzed in static systems which permitted the determination of reaction kinetics. In addition, most of these compounds were also thermolyzed in a vapor state flow system, on a preparative scale. In all cases the reaction appeared homogeneous and no other primary products were detectable. As indicated in Chart I, the strutures of a sufficient number of the products were verified to establish the generality of the reaction. Included in Chart I are the three previously reported examples of β-hydroxyacetylene cleavage in oxy-Cope systems **10–12**.

Rates of the vapor phase thermolytic cleavage of acetylenic compounds **1–9** and of 1-phenyl-3-buten-3-ol, **13**, were determined in static system A and are listed in the Experimental Section, Table V. Visual observation of the hot tubes confirmed that the sample was completely vaporized, except in the case of the 1-phenyl 3-buten-1-ol, **13**, and 1-phenyl-3-butyn-1-ol, **9**. These latter compounds pyrolyzed at too low a temperature

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(11) R. J. D. Evans, S. R. Landor, and R. Taylor-Smith, *J. Chem. Soc.*, 1506 (1963).

(12) P. D. Landor and S. R. Landor, *ibid.*, 1015 (1956); Hoffman-LaRoche and Co., Akt.-Ges., Belgian Patent 617,174; *Chem. Abstr.*, **59**, 1540 (1963).

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(19) B. A. W. Coller, M. L. Hefferman, and A. J. Jones, *Aust. J. Chem.*, 21, 1807 (1968); M. B. D'Amore and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 5694 (1969).

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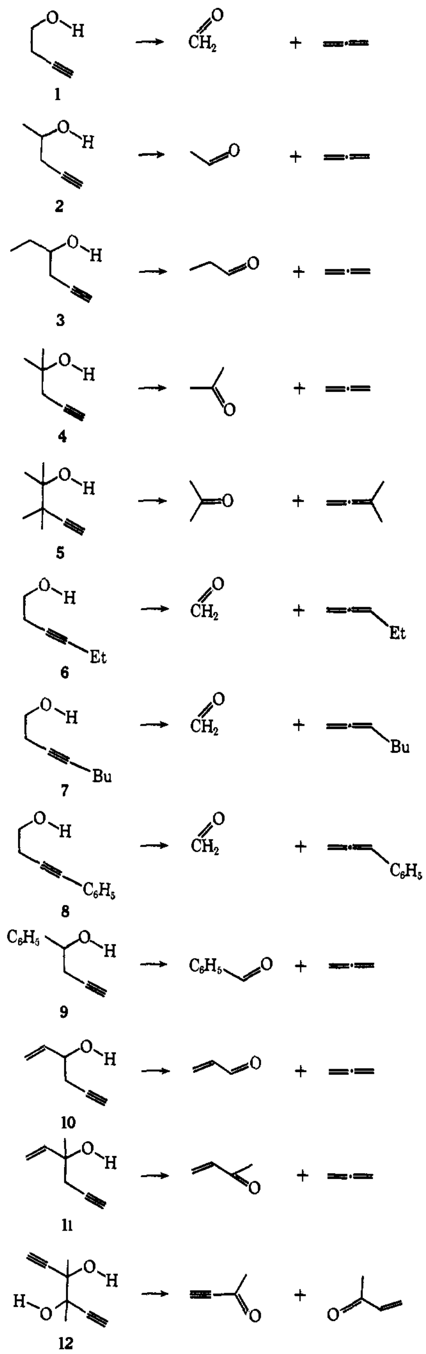
(24) A. Viola, J. H. MacMillan, R. J. Proverb, and B. L. Yates, *Chem. Commun.*, 936 (1971).

(25) See footnote 15, ref 14.

Chart I



	Method[a]	Structure[b]
1	V, L, F	C A
2	V	C
3	V, L, F	C
4	V, L, F	C A
5	V, F	C
6	V	
7	V, F	A
8	V, F	A
9	V_l, F	C
10	ref 14	
11	ref 15, 16	
12	ref 16	

[a] V, static system A, vapor phase; L, static system B, liquid phase; V_l, static system A, liquid phase; F, flow system. [b] Components of product mixtures which were identified, as detailed in the Experimental Section. C, carbonyl component; A, allenic component.

to be vaporized and hence their rates of pyrolysis were determined in dilute solution, by sealing in the capillaries a sample of sufficient size (100–150 μl) so that all remained in the liquid state. The validity of this method is verified by the excellent agreement of the results described herein with the kinetic parameters recently reported for **13**.[26]

Reaction homogeneity was established by packing some tubes with glass capillaries, which increased the area by a factor of five. No change in the rate of pyrolysis was observed. Also no change in the rate of pyrolysis was observed on using different concentrations of the alcohol nor on using different sample sizes, as long as the sample size was small enough so that all was vaporized.

The rates of the thermolytic cleavage of compounds **1**, **3**, and **4** were also determined in the liquid state in static system B and are listed in the Experimental Section. The fact that random variation of sample size and length of capillary still gave linear first-order kinetic plots indicated that the free space in the capillaries was not a factor.

In all cases the plots of log C_0/C against time were linear for at least two half-lives. Rate constants were found to be reproducible to within ±5%. Equal rate constants were obtained when the reaction was followed by the rate of appearance of the products as by the rate of disappearance of alcohol. All Arrhenius plots showed excellent linearity.[27] The calculated energies and entropies of activation,[28] listed in Table I, are estimated[27] to be accurate to within ±1.5 kcal and ±2 eu, respectively.

Discussion

Thermolyses of all β-hydroxyacetylenes studied, in both vapor and liquid phases, followed the first-order rate equation and afforded the Arrhenius parameters summarized in Table I. The data suggest a concerted 1,5 sigmatropic rearrangement. The low activation energies, from 36 to 41 kcal/mol, indicate energetic assistance in the C–C bond breaking process and the large negative entropies of activation are in accord with a cyclic transition state. Moreover, as shown in Table II, there is a close relationship in the kinetic parameters of the thermal cleavages of similarly substituted olefinic and acetylenic alcohols,[29] and the reaction of the olefinic analogs has been rigorously established as a homogeneous, unimolecular, first-order process.[21,22] In the following discussion, the emphasis has been placed on the small but real differences in reaction rates, rather than activation energies, since the latter for the most part are within experimental error of each other.

Transition State Geometry. Due to the cylindrical symmetry of the acetylenic system, a π lobe can become available in any direction for the approaching hydroxyl proton and the least deformation of the linear acetylenic system occurs in a planar structure. In such a structure there is also a maximum overlap of participating orbitals, centered in the plane of the transition state. However, such a transition state, **14**, requires eclipsing of the remaining σ bonds at C_1 and C_2. The rotatory motion usually associated with developing sp^2 carbons in pericyclic reactions is replaced by a 60° swinging motion of each of the two planes defined by these σ bonds at C_1 and C_2, respectively, toward one another while the C_1–C_2 bond is breaking.

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[26] The thermolysis of **13** has recently been reported: E_a 36.2 kcal/mole, log A 10.8: G. G. Smith and K. J. Voorhees, *J. Org. Chem.*, **35**, 2182 (1970).

[27] In all Arrhenius plots, the standard deviations of individual points from the "least squares" straight line were less than 0.2% of the slope and standard deviations of ln A were less than 0.05. Error limits were assigned as described in S. W Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 86.

[28] All $\Delta S^{\ddagger}$ values reported herein are based on the formula $A = e(K/h)T_m e^{\Delta S^{\ddagger}/R}$, as urged by H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1968).

[29] For the purpose of emphasis, the various compounds discussed in this section will be named as derivatives of the parent alcohols.

Table I. Kinetic Parameters of the Thermolysis of β-Hydroxyacetylenes

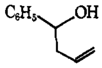
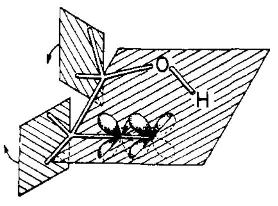
	Gas phase			Liquid phase		
Alcohol	E_a, kcal/mol	log A	$\Delta S_{300}^{\ddagger}$, eu	E_a, kcal/mol	log A	$\Delta S_{300}^{\ddagger}$, eu
1	39.9	11.2	−10.7	37.0	10.6	−13.2
2	39.4	11.3	−10.1			
3	41.0	12.1	−6.9	36.8	11.1	−10.9
4	39.9	11.6	−9.0	37.5	11.1	−10.9
5	40.6	12.4	−5.2			
6	41.7	11.2	−10.7			
7	40.4	10.7	−13.0			
8	41.6	11.5	−9.2			
9				36.3	11.2	−10.7
 **13**				36.1	10.9	−11.8

Table II. Kinetic Parameters of 1-Substituted 3-Buten-1-ols and 3-Butyn-1-ols[a] at 350°

	Olefin			Acetylene		
Compound	E_a	$\Delta S^{\ddagger}$	Relative rate	E_a	$\Delta S^{\ddagger}$	Relative rate
Parent β-hydroxy compound	40.7[b]	−11.4	1	39.9	−10.7	1
1-Me	40.2[b]	−10.5	2.9	39.4	−10.1	2.0
1,1-Dimethyl	40.5[b]	−8.6	5.5	39.9	−9.0	2.5
1-Phenyl	36.1	−11.8	33	36.3	−10.7	19
1-Vinyl[c]			22			20

[a] See ref 29. [b] Calculated by the method of least squares from the data in ref 21. $\Delta S^{\ddagger}$ calculated according to ref 28. [c] From ref 24. For internal consistency, these relative rates have been recalculated on the basis of the rate constant for 1-phenyl-3-buten-1-ol reported herein.

By contrast, the transition state for the analogous olefinic cleavage cannot be planar. Not only would the terminal vinylic protons interfere with the approaching hydroxyl proton, but the available π lobes are centered in a plane orthogonal to the potential transition plane. It is therefore necessary for the hydroxyl proton to approach C_4 from a direction orthogonal to the plane of the olefinic system and consequently the most likely transition state is chair-like **15**, in which the remaining σ bonds at C_1 and C_2 are in a staggered conformation. The geometry suggested is in accord with the Woodward–Hoffmann rules for orbital symmetry conservation in a 1,5-sigmatropic hydrogen shift, which necessitates a suprafacial process.



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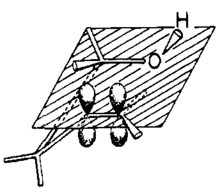

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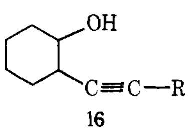
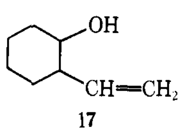
This situation accounts for the earlier reported[30] lack of reactivity in **16**, as opposed to its olefinic analog, **17**. The mode of preparation probably afforded trans 1,2-disubstituted cyclohexane derivatives, which can attain the geometry requisite for **15**, in the case of **17**, but not as required for **14**, in the case of **16**.



16



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A consequence of conformational differences between **14** and **15** is the effect of substitution on the respective thermolysis rates. Although substitution at C_1 or C_2 weakens the C_1–C_2 bond and thereby decreases the activation energy required for both olefinic and acetylenic cleavages, eclipsing in the acetylenic case partially counteracts this effect. In all cases where comparable data are available, there is a decrease in rate enhancement for the acetylenic case when compared with its olefinic analog. This factor is shown in Table II by a comparison of the relative rates for any particular mode of substitution. It is also apparent in Table III in the decrease of the ratio, $k_{\text{acet}}/k_{\text{olef}}$, for any substitution at C_1, in an amount paralleling the degree of repulsion of eclipsed substituents.

Within the series of acetylenic compounds, differences in activation energies appear to be within experimental error for alkyl substituted compounds, **1**–**7**. In compounds **1**–**5** a balance can be expected between additional energy required for bond eclipsing in the planar transition state and the bond weakening effect of these same substituents.[31] The degree of substitution, however, affects the entropy factor, and despite the fact that $\Delta S^{\ddagger}$ values are subject to considerable uncertainties, the values obtained indicate a definite trend of smaller entropy differences between the ground and transition states with increasing substitution at C_1 and C_2 (see **1**, **2**, **4**, and **5**, Table I). This trend is in

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(30) R. T. Arnold and G. Smolinsky, *J. Amer. Chem. Soc.*, **82**, 4918 (1960).

(31) For example, in **5** eclipsing is expected to add 5–8 kcal/mol for normal bond length, since each Me–Me interaction adds 2.4–4.1 kcal to the rotational barrier as opposed to H–H eclipsing (ref 32, p 125 ff). On the other hand, two methyl substituents decrease the bond dissociation energy of an adjacent C–C bond by 5–7 kcal, as exemplified by comparing CH_3–C_2H_5, 85 kcal (ref 33), with CH_3–$C(CH_3)_3$, 78 kcal (ref 34) and C_2H_5–C_2H_5, 83 kcal (ref 34), with $(CH_3)_2CH$–$CH(CH_3)_2$, 78 kcal (ref 33).

(32) E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962.

(33) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(34) J. J. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1967.

Table III. Vapor Phase Thermolysis Rates of 3-Butyn-1-ols and Some Analogous Olefinic Alcohols[a] at 350°

Substituent	Acetylenic 10^3k, sec^{-1}	Acetylenic Relative rate	Olefinic 10^3k, sec^{-1}	k_{acet}/k_{olef}
None	1.78	1.0	0.640[b]	2.8
1-Methyl	3.61	2.0	1.88[b]	1.9
1,1-Dimethyl	4.55	2.5	3.50[b]	1.3
1-Ethyl	4.69	2.6		
1,1,2,2-Tetramethyl	12.8	7.2		
4-Ethyl	0.442	0.25		
4-Butyl	0.378	0.21		
4-Phenyl	0.891	0.5	0.129[b]	6.9
1-Phenyl[c]	34.1	19	21.7	1.4
1-Vinyl[d]	36	20	14	2.5

[a] See ref 29. [b] Calculated from the data in ref 21. [c] Extrapolated from data obtained from dilute solutions at lower temperatures. [d] From ref 24. For internal consistency, these rates have been recalculated relative to the rate constant for 1-phenyl-3-buten-1-ol reported herein.

accord with the calculations of Allinger and Zalkow[35] who have explained the rate enhancement due to *gem*-dimethyl substituents in cyclization reactions by a more restricted ground state which is a consequence of increased rotational barriers. The same argument predicts a somewhat smaller entropy difference between the two states for the 1-ethyl, **3**, as compared with the 1-methyl derivative, **2**.

In general, substitution in the 4 position decreases the rate of thermolysis, as shown in Table III. The reason for this effect is probably steric, as previously observed in olefins,[23] and may also reflect the motion required of these substituents as C_4 changes from sp to sp^2. Unlike the reaction of the corresponding olefin, the 4-phenyl substituent does not resonance destabilize the transition state since the phenyl group remains conjugated with the nonreacting component of the acetylenic π system, *i.e.*, the plane of the phenyl ring remains coplanar to the transition plane. By contrast, in the olefinic case the π bond must move out of conjugation.[21] As a result of this factor, the ratio of k_{acet}/k_{olef} is the largest of any observed in this study.

Substitution of phenyl or vinyl groups in the 1 position leads to more substantial rate increases in both the acetylenic and the olefinic systems. Both groups aid π bond formation at the site of the incipient carbonyl, but the phenyl group is estimated to have a slightly greater effect, by 2.5 kcal, on weakening the C_1–C_2 bond than does the vinyl substituent.[36] However, the greater bulk of the phenyl group requires a larger energy increment for swinging or rotatory motion as C_1 changes from sp^3 to sp^2. These partially offsetting factors result in a slightly faster rate for the phenyl derivative in the olefinic series. However, there is an unequal rate enhancement of olefinic as opposed to acetylenic cleavages. The data in Table II indicate that the effect of the vinyl group is virtually the same in both systems, but that the phenyl enhancement is less in the acetylenic series. This fact again points toward a planar transition state for the acetylenic cleavage wherein bond eclipsing with the large phenyl group hinders the acetylenic transition state more than is the case for the staggered conformation in the olefinic analog. The vinyl group represents the smallest rotational barrier of any substituent utilized in this study[32] and can assume a position either cisoid or transoid in relation to the incipient carbonyl. There appears to be considerably less overlap with the eclipsed proton on C_2 in the cisoid conformation than is the case with the phenyl group. The ratio of k_{acet}/k_{olef} for the vinyl group is closest to that of the parent system for any substituent.

Transition State Polarity. The term "no mechanism reaction" has been coined for rearrangements such as the Cope types because of the small substituent or medium effects which have rendered difficult the mechanistic delineation of these reactions,[37] This situation may not apply equally to reactions such as β-hydroxy olefin or β-hydroxyacetylene cleavages. Here the transition state is such that a hydrogen atom has transferred, at least partially, from an oxygen to a carbon and hence the transition state must *per se* exhibit polar characteristics. In this connection, the rate-accelerating influence of substituents, which stabilize a partial positive charge at C_3 in the olefinic series, has been shown[21,23] and a Hammett study of cleavage rates of 1-aryl-3-buten-1-ols has indicated a small negative ρ for substituents at the 1 position.[26] By comparison, no polarity should be exhibited by a Cope system where no heteroatoms are directly involved. The data of Table IV give an indication of the medium effects in the acetylenic cleavage. The rate enhancement observed parallels the H-bonding ability of the medium, *i.e.*, increasing concentrations of starting alcohol. Increased association weakens the O–H bond and thereby enhances proton transfer as evidenced by a decreased E_a in the liquid phase, Table I. At the same time, association in the liquid state can be expected to result in greater stabilization of the more polar transition state, relative to the ground state, and greater solvation requires a more negative $\Delta S^{\ddagger}$ (compare parameters in Table I).[38] It is also of interest to

Table IV. Medium Effects on Thermolysis Rates, $10^5k_{260°}$

	Gas phase (extrapolated)	Liquid phase (extrapolated)	Xylene (dil soln)
3-Butyn-1-ol, **1**	0.818	2.86	1.88
5-Hexyn-3-ol, **3**	1.80	9.4	
2-Methyl-4-pentyn-2-ol, **4**	2.03	5.3	3.42

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(35) N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960). See also the "gem-dialkyl effect," ref 32, p 197.

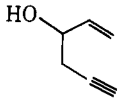
(36) The bond dissociation energies of $CH_2{=}CHCH_2{-}CH_3$ and $C_6H_5{-}CH_2{-}CH_3$ are given as 74.5 and 72 kcal, respectively: S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 215.

(37) S. J. Rhoads, in "Molecular Rearrangements," P. de Mayo, Ed., Wiley, New York, N. Y., 1963, Chapter 11.

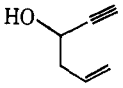
(38) In light of this analysis, the strict first-order rate relationships observed in the liquid state might be surprising. However, although the

note that gas phase reactivities of primary, secondary, and tertiary alcohols, in both acetylenic and olefinic series, increase in the same order as the gas-phase acidities of such alcohols.[39] Further consideration of charge separation in the transition state must await the results of a Hammett study which is in progress.

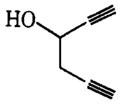
Reactivity of Acetylenes. Contrary to our original expectations, the participation of an acetylenic bond in a six-membered transition state invariably has lead to higher reaction rates than the corresponding olefinic compound, as shown in Table III. Similarly, the intramolecular ene reaction of 6-octen-1-yne has also been found to proceed more rapidly than the corresponding reaction of 1,6-octadiene.[40] Furthermore, the cleavage reaction and Cope process in **10**, wherein both involve the acetylenic bond, are competitive.[14] By contrast, no cleavage was observable[17] in **18**, where only the Cope process involves acetylene participation and the slower olefinic cleavage cannot compete successfully. It is of interest to note that no cleavage reaction, even an acetylenic one, was observed[20] in **19** wherein the competing Cope process is enhanced by two acetylenic systems.



10



18



19

Not only must the activation energy for the acetylenic process include a contribution for bending the linear acetylenic system to accommodate the six-membered ring, but evidence has been presented above which indicates a planar transition state, with increased repulsion of eclipsed substitutents, for the acetylenic reaction as opposed to the corresponding olefin. Furthermore, the C_1–C_2 bond dissociation is expected to be 3–4 kcal/mol less in the case of the olefinic system.[41] Since all of these factors argue for an increase in activation energy, the reason for the observed rate increases must lie in the reactivity of the triple bond. The acetylenic system represents a paradoxical situation wherein effects of a greater electron deficiency are counterbalanced by an increased electron density.[42] However, in direct competition experiments involving the addition of HX to nonconjugated enynes, the triple bond has been found to coordinate the proton more readily than a double bond with an equal number of alkyl substituents.[43] Consequently, we attribute the increased rate of reaction of the β-hydroxyacetylenes, in comparison with their olefinic analogs, to the greater nucleophilicity of the triple bond toward the hydroxyl proton. Analogous considerations may account for the reactivities of the other acetylenic substances cited above, in intramolecular cyclic processes.

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-5A spectrophotometer on neat liquid or gas phase samples. Nmr spectra were determined with a Varian A-60A spectrometer in deuterated chloroform solutions with an internal tetramethylsilane standard. Elementary analyses were performed by Dr. Stephen M. Nagy, Belmont, Mass. Vapor phase chromatographic analyses were obtained either with a F & M Model 500, equipped with a disc integrator for determination of relative peak areas and using 2-ft columns packed with 10% silicone grease or 20% Triton X-305 on Chromosorb P, or with a Varian-Aerograph Model 90 using 5-ft columns packed with SE-30.

Sources of β-Hydroxyacetylenes. The various alcohols utilized in this study were either purified commercial compounds or were prepared as described below. 3-Butyn-1-ol, **1**, was obtained from Farchan Research Labs. 4-Phenyl-3-butyn-1-ol, **8**, 3-hexyn-1-ol, **6**, and 3-octyn-1-ol, **7**, were obtained from Chemical Samples Co. 4-Pentyn-2-ol, **2**, was obtained from K & K Ltd. The remaining alcohols were prepared as follows.[44]

Preparation of 5-Hexyn-3-ol, 3. This compound was prepared *via* Sondheimer's[45] low temperature modification of the Barbier reaction in order to minimize rearrangements leading to internal acetylenic bonds.

Into a 1-l. three-necked flask equipped with an internal thermometer, mechanical stirrer and a "Y" tube leading to a condenser and a dropping funnel were placed 4.0 g (0.03 mole) of propargyl bromide, 24.0 g (1.0 g-atom) of magnesium turnings, 0.1 g of mercuric chloride, and 200 ml of anhydrous diethyl ether. The mixture was stirred and heated gently until the reaction became exothermic. The flask was then cooled by means of a Dry Ice–acetone bath until the contents were at a temperature of −20° to −25°.

A solution of 67.0 g (0.56 mole) of 3-bromopropyne and 26.5 g (0.49 mol) of propionaldehyde in 300 ml of anhydrous ether was then added dropwise over a 10-hr period, with continuous stirring, such that the internal temperature did not exceed −20° during the addition period. After the addition was completed, the mixture was cooled to −30°, stirred for 1 hr, and was then allowed to warm up to room temperature. The mixture was then decomposed with ammonium chloride and ice water, the ether layer was separated, washed with water, and dried with anhydrous magnesium sulfate. Distillation afforded 19.8 g (0.202 mole) of the desired 5-hexyn-3-ol (45% yield): bp 138–139°, bp 44° (10 mm), $n^{23}\mathrm{D}$ 1.4435, d_4^{25} 0.8555 (lit.[46] bp 58–59° (25 mm), $n^{20}\mathrm{D}$ 1.4437, d_{20} 0.8918). *Anal.* Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.48; H, 10.25.

The infrared spectrum contained pertinent bands at 3400 (OH), 3300 ($\equiv$CH), and 2120 (terminal C$\equiv$C) cm^{-1}. There was no absorption in the internal acetylenic or allenic region; nmr spectrum ($CDCl_3$) δ 0.93 (3 H, t, methyl), 1.55 (2 H, m, methylene), 2.05 (1 H, t, acetylenic), 2.4 (3 H, m, methylene and OH—collapsed to doublet of doublets, 2 H, on D_2O exchange), and 3.67 (1 H, quintet, methine).

Hydrogenation of a small sample of this alcohol with Pd/C afforded a mixture whose major constituent (65%) had a vpc retention time equal to that of authentic 3-hexanol. The remaining constituent was shown to be 3-hexanone by conversion to its 2,4-dinitrophenylhydrazone, mp 129–133° (lit.[47] mp 130°), which showed no depression on admixture with an authentic sample.

Preparation of 2-Methyl-4-pentyn-2-ol, 4. The low temperature Barbier reaction of 3-bromopropyne and acetone, by a procedure entirely analogous to that described above for the preparation of 5-hexyn-3-ol, afforded a 52% yield of this alcohol: bp 124°, $n^{24}\mathrm{D}$ 1.4375, d_4^{25} 0.8729 (lit.[48] bp 124–127°, $n^{21}\mathrm{D}$ 1.4381).

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concentration of alcohol decreases as the reaction proceeds, medium polarity increases with the production of the more polar carbonyl component. The two effects on the observed rates are cancelled within the limits of experimental error.

(39) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970).

(40) W. D. Huntsman and R. P. Hall, *J. Org. Chem.*, 27, 1988 (1962).

(41) M. M. Martin and E. B. Sanders, *J. Amer. Chem. Soc.*, **89**, 3777 (1967), and references cited therein.

(42) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, p 575, and references cited therein. In general, ionization potentials for olefins are about 0.5 eV lower than those of corresponding acetylenes [K. Watanabe, T. Nakayama, and J. R. Mottl, *J. Quant. Spectrosc., Radiat. Transfer*, 2, 369 (1962)].

(43) A. A. Petrov and Yu. I. Porfir'eva, *J. Gen. Chem. USSR*, **33**, 3142 (1963).

(44) Only those preparations of aceylenic alcohols found to be free of internal acetylenic or allenic links are reported in this section.

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

(46) M. Bertrand, *C. R. Acad. Sci.*, **244**, 1790 (1957).

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

(48) H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 2696 (1949).

The infrared spectrum contained pertinent bands at 3400 (OH), 3300 ($\equiv$CH), and 2120 (terminal acetylene) cm^{-1} but showed no absorption in the internal acetylene or allene regions; nmr (neat) δ 1.25 (6 H, s, methyl), 2.05 (1 H, t, J = 2.5 cps, acetylenic), 2.25 (2 H, d, J = 2.5 cps, methylene), and 3.35 (1 H, s, hydroxyl).

Preparation of 1-Phenyl-3-butyn-1-ol, 9. The attempted low temperature Barbier reaction of benzaldehyde and 3-bromopropyne gave mainly high-boiling substances. Therefore a Grignard procedure was utilized.

Into a 1-l. three-neck flask equipped with condenser, mechanical stirrer, and dropping funnel, were placed 24 g (1 g-atom) of magnesium turnings, 0.1 g of mercuric chloride, 200 ml of anhydrous ether, and 1 g of 3-bromopropyne. The mixture was warmed, with stirring, until the reaction commenced as evidenced by vigorous ether reflux. The flask was then immersed in a Dry Ice–acetone bath whose temperature was maintained at about −20°. A solution of 46 g (total 0.4 mol) of freshly distilled 3-bromopropyne in 150 ml of anhydrous ether was then added dropwise over a 3-hr period. After the addition was complete, the mixture was stirred for another hour before the bath temperature was allowed to increase to −10°. A solution of 26 g (0.25 mol) of freshly distilled benzaldehyde in 150 ml of anhydrous ether was then added over a period of 2 hr while the bath was maintained between −10° and 0°. The mixture was then allowed to warm up to room temperature and decomposed with ice–ammonium chloride. The ether layer was separated, the aqueous layer was extracted with two 50-ml portions of ether, and the combined ether layers were washed with water and then dried with anhydrous magnesium sulfate. Reduced pressure fractionation of the residual oil after evaporation of the ether afforded 28 g (77% yield) of the desired alcohol: bp 80° (0.5 mm), n^{26}D 1.5457, d_4^{29} 1.0265 (lit.[49] bp 89° (1 mm), n^{20}D 1.5470). *Anal.* Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.10; H, 6.92.

The infrared spectrum contained pertinent bands at 3400 (OH), 3300 ($\equiv$CH), and 2120 cm^{-1} (terminal acetylene). There was no absorption in the internal acetylene or allene region; nmr spectrum δ 1.95 (1 H, t, acetylenic), 2.50 (2 H, doublet of doublets, methylene), 3.50 (1 H, s, hydroxyl), 4.70 (1 H, t, methine), and 7.25 (5 H, s, phenyl).

Catalytic hydrogenation of a small sample of this alcohol with Pd/C led to the absorption of 105% of the amount of hydrogen theoretically required to saturate one triple bond. Dichromate oxidation of the saturated alcohol gave a ketone whose 2,4-dinitrophenylhydrazone, mp 189–191°, gave no depression on admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of *n*-propyl phenyl ketone (lit.[50] mp 190°).

Preparation of 2,3,3-Trimethyl-4-pentyn-2-ol, 5. This compound was prepared in a manner analogous to the one above. The requisite bromo compound, obtained from the reaction of 2-methyl-3-butyn-2-ol with PBr_3, had physical constants in accord with those in the literature.[51] From 8 g (0.33 g-atom) of magnesium, 0.1 g of $HgCl_2$, 29.5 g (0.2 mol) of 3-methyl-3-bromo-1-butyne, and 10 g (0.17 mol) of acetone, in appropriate amounts of anhydrous ether, a yield of 4.9 g (20%) of the desired alcohol was obtained: bp 50° (18 mm), n^{23}D 1.444. *Anal.* Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.30; H, 11.10.

The infrared spectrum contained pertinent bands at 3500 (OH), 3300 ($\equiv$CH), 2970 (CH), 2120 (weak, C$\equiv$CH), 1460 (CH_3), 1380 (CH_3), 1145 (OH), and 630 (C$\equiv$C) cm^{-1}. The nmr spectrum consisted of singlets at δ 1.25 (6 H), 1.30 (6 H), 2.05 (1 H, hydroxyl), and 2.28 (1 H, acetylenic).

1-Phenyl-3-buten-1-ol, 13. This compound was prepared by the reaction of allylmagnesium bromide with benzaldehyde in the usual manner: bp 83° (2 mm), n^{20}D 1.5308 (lit.[52] bp 119° (12 mm), n^{23}D 1.5303).

Flow System Thermolyses. For preparative scale thermolysis studies, the system previously described was utilized.[23] The products isolated were identified as follows.

Thermolysis of 3-Butyn-1-ol, 1. Approximately 20 ml of ethanol was placed into each of the two product traps which were then connected in series and cooled with Dry Ice–acetone baths before evacuation of the system. A 6.5 g sample of 3-butyn-1-ol was then thermolyzed at 370° and a pressure of 20 mm. After the thermolysis, the traps were removed, about 20 ml of dilute 2,4-dinitrophenylhydrazine solution was added to each trap, and the contents were then allowed to warm up to room temperature. The copious yellow precipitates which formed in both traps were recrystallized from ethanol–ethyl acetate to give yellow crystals, mp 166–168°, which gave no depression on admixture with authentic formaldehyde 2,4-dinitrophenylhydrazone (lit.[47] mp 167°). The allene component in this thermolysis mixture was isolated from a static system thermolysis, by means of vpc, and its infrared spectrum, determined in a gas cell, was identical with that of allene. It showed no bands attributable to propyne.[53]

Thermolysis of 5-Hexyn-3-ol, 3. This compound was thermolyzed at 350° and at 370° under various pressures. The only products detectable by vpc were unreacted starting alcohol, propionaldehyde, and a low boiling component believed to be allene. In a typical experiment, 1.53 g of 5-hexyn-3-ol was thermolyzed at 370° and 30 mm with a constant rate of 3 drops/min. Analysis (vpc) of the condensed product, 0.94 g (60% recovery), indicated it to consist of 75% propionaldehyde, 21% starting alcohol, and 4% of the low boiling constituent believed to be allene. The propionaldehyde was identified by its vpc retention time, characteristic odor, and its 2,4-dinitrophenylhydrazone derivative, mp 149–153° (lit.[47] mp 154°), which gave no depression on admixture with an authentic sample.

Thermolysis of 2-Methyl-4-pentyn-2-ol, 4. A 1.04-g sample of this alcohol was thermolyzed at 375° and a pressure of 10 mm. Analysis (vpc) of the condensed product, 0.64 g (62% recovery), indicated it to consist of 40% acetone and 60% starting material. The acetone was identified by its vpc retention time, characteristic odor, and its 2,4-dinitrophenylhydrazone derivative, mp 124–126° (lit.[47] mp 126°), which gave no depression on admixture with an authentic sample. Allene was identified as described in the thermolysis of **1**.

Thermolysis of 2,3,3-Trimethyl-4-pentyn-2-ol, 5. Thermolysis of a 0.70-g sample of this alcohol at 370° and 70 mm afforded a condensed product mixture weighing 0.45 g (65% recovery). Treatment of the crude product with 2,4-dinitrophenylhydrazine reagent gave the DNPH of acetone, mp 123–126° (lit.[47] 126°), which showed no depression on admixture with an authentic sample.

Thermolysis of 3-Octyn-1-ol, 7. A sample of this alcohol was thermolyzed at 410° and 20 mm. Since the condensed product still contained 48% starting alcohol, along with 52% 1,2-heptadiene, the material was passed through the column a second time. After the second thermolysis, the first product trap was allowed to warm up to room temperature while the second trap was kept in its Dry Ice–acetone bath. Pure 1,2-heptadiene was collected in the second trap.

Physical constants of 1,2-heptadiene were in good agreement with the literature: bp 105–106°, n^{20}D 1.4364, d_4^{23} 0.7354 (lit.[54] bp 105–106°, n^{18}D 1.4322, d_{18} 0.7306).

The infrared spectrum contained strong allenic bands at 1950 cm^{-1} (unsym stretch)[53] and 840 cm^{-1} (=CH_2 wagging).[53] The nmr spectrum consisted of bands at δ 0.9 (3 H, filled-in distorted triplet, methyl), 1.2–1.6 (4 H, aliphatic methylenes), 1.8–2.2 (2 H, m, α methylene), 4.3–4.6 (2, H, m, terminal methylene), and 4.9 (1 H, distorted quintet, internal allenic).

Thermolysis of 4-Phenyl-3-butyn-1-ol, 8. A 3-g sample of this alcohol was thermolyzed at 420° and 15 mm. After the reaction was completed, the Dry Ice–acetone bath around the first trap was replaced by a hot water bath and the system was evacuated to 2 mm. A small amount of pure phenylallene collected in the second trap.

The structure assignment of phenylallene is based solely on its ir and nmr spectra. The infrared spectrum contained strong allenic bands at 1950 cm^{-1} (unsym stretch)[53] and 850 cm^{-1} (=CH_2 wagging).[53] The nmr spectrum contained bands centered at δ 4.92 (2 H, d, terminal methylene), 5.91 (1 H, t, internal allenic), and 7.0 (5 H, s, phenyl). This spectrum was identical with that of an authentic sample, kindly supplied to us by Professor Maitland Jones, Jr.

Thermolysis of 1-Phenyl-3-butyn-1-ol, 9. This compound was thermolyzed at temperatures from 370 to 430°. Analysis (vpc) of the condensed product always showed a very low boiling constituent, believed to be allene, and a single higher boiling constituent shown to be benzaldehyde. In a typical experiment, 12.16 g of this alcohol was thermolyzed at 430° and 10 mm. The con-

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Table V. Thermolysis Rates, System A

Compound	Temp, °C	10^4k, sec^{-1}	Compound	Temp, °C	10^4k, sec^{-1}
3-Butyn-1-ol, **1**[a]	336.4	8.71	4-Pentyn-2-ol, **2**[a]	324.5	9.38
	324.1	4.50		314.8	5.30
	314.7	2.52		307.0	3.50
	297.9	0.981		290.9	1.28
5-Hexyn-3-ol, **3**[b]	330.0	15.6	2-Methyl-4-pentyn-2-ol, **4**[a]	321.5	9.80
	320.0	8.77		315.0	6.82
	310.0	4.94		308.0	4.50
	300.0	2.69		288.9	1.39
2,3,3-Trimethyl-4-pentyn-2-ol, **5**[c]	320.0	24.0	3-Hexyn-1-ol, **6**[c]	360.0	7.64
	310.0	13.2		350.0	4.42
	300.0	7.37		340.0	2.56
	290.0	3.93		325.0	1.10
3-Octyn-1-ol, **7**[d]	360.0	6.48	4-Phenyl-3-butyn-1-ol, **8**[d]	360.0	15.0
	350.0	3.78		350.0	8.91
	340.0	2.16		345.0	6.78
	325.0	0.944		340.0	5.15
				335.0	3.87
1-Phenyl-3-butyn-1-ol, **9**[e]	280.0	8.54	1-Phenyl-3-buten-1-ol, **13**[e]	285.0	7.44
	270.0	4.53		280.0	5.50
	260.0	2.48		270.0	2.97
	250.0	1.28		250.0	0.846

[a] Using xylene as the solvent and toluene as the internal standard. [b] Using benzene as the internal standard. Under these conditions 2-methyl-4-pentyn-2-ol gave a rate of 6.92×10^{-4} at 315°. [c] Using toluene as the solvent and mesitylene as the internal standard. Under these same conditions 3-butyn-1-ol gave a rate of 4.64×10^{-4} at 325°. [d] Using decalin as the internal standard. Under these conditions 2-methyl-4-pentyn-2-ol gave a rate of 6.88×10^{-4} at 315°. [e] In solution using xylene as the solvent and decalin as the standard.

densed product, 8.69 g (72% recovery), was found to consist of 3% of a very low boiling component and 97% benzaldehyde. The low boiling ingredient was removed by bubbling a nitrogen stream through the mixture and the remaining benzaldehyde was identified by its vpc retention time, ir spectrum, and 2,4-dinitrophenylhydrazone derivative, mp 238–240° (lit.[47] 237°), which showed no depression on admixture with an authentic sample.

Kinetic Procedures.[55] **Method A.** Pyrolyses were carried out in a heated aluminium block 14 in. long by 8 in. in diameter, insulated by glass wool. The block was heated by a resistance coil and its temperature controlled to ±0.2° by a Fielden type TCB2 temperature controller, calibrated with a chromel alumel thermocouple. Approximately 10–15 μl of a solution of the alcohol (4% v/v) and toluene (2% v/v) in xylene were placed in a capillary 2.5 mm ID and 40–50 mm length. ACS reagent grade toluene and xylene were used without further purification. Because of problems with retention times, in some cases decalin was used as the internal standard in place of toluene, and in other cases toluene was used as the solvent and mesitylene as the internal standard. In all of these cases, runs were carried out with standard compounds to make sure that the changes of conditions did not change the rate of pyrolysis (see Table V).

The contents of the tube were then frozen in Dry Ice–isopropyl alcohol, evacuated to pressures of 2 mm or less, and sealed while frozen. No differences in the rate constants were observed if the tubes were sealed without prior freezing and evacuation. Five sealed capillaries were placed in holes drilled in the block, the holes being of such a diameter that the tubes fitted precisely, and at determined intervals the tubes were withdrawn and the reaction was quenched by plunging them into cold water. The contents of the tubes were analyzed by glc. The areas of the starting alcohol and the standard, toluene, were compared using a photovolt Model 49 integrator. The rate constants determined are listed in Table V. The validity of this method was demonstrated by a determination of the cleavage rates of 2-methyl-4-penten-2-ol, 10^4k = 10.5 (330°) and 6.20 (320°). Corresponding values calculated from data in the literature[21] are 11.1 and 6.31, respectively.

Method B. The procedure used for liquid phase determinations utilized a Colora HT-13 constant temperature bath with Dow-Corning 210-H Fluid as the bath oil. Temperature accuracy with a calibrated thermometer is estimated as ±0.3°. The rates of disappearance of starting materials were determined in sealed 1 mm ID capillary tubes, 30–50 mm in length, containing approximately 5–10 μl of a solution of the alcohol in nonane. The contents of the tubes were then frozen in Dry Ice–acetone, evacuated to pressures of 1 mm or less, and sealed off while frozen. After measured intervals, (Precision Scientific Co. timer) the reactions were quenched by plunging the tubes into ice water. The contents of each tube were then analyzed by vpc to determine the ratio of nonane to remaining starting material. A calibration curve was used to correct for nonlinearity in thermal conductivity response. Variations in sample and capillary sizes and random use of base-washed capillaries did not affect plot linearity. For the rate study on 3-butynol, cyclohexanol was used as the internal standard with benzene as solvent, since 3-butynol and nonane showed insufficient miscibility and also since the formaldehyde polymers rendered the solution too viscous in the absence of a suitable solvent. Estimated error limits of vpc peak areas are ±3%. Estimated precision of rate constants is ±8% and error limits of the calculated kinetic parameters were assigned accordingly.[27]

Under the conditions of temperature and available volume, as indicated above, the bulk of the sample in each tube appears to remain in the liquid state. The validity of this method was demonstrated by a determination[56] of the cleavage rates of 2-methyl-4-penten-2-ol: 10^6k = 10.0 (257°), 8.60 (254°), 5.96 (249°), and 3.84 244°). Corresponding values calculated from data in the literature[21] are 10.2, 8.16, 5.67, and 3.84, respectively. The rate constants determined follow ($\times 10^5$): 3-butyn-1-ol (**1**), 2.35 (257°), 1.29 (248°), 0.804 (241°), and 0.522 (236°); 5-hexyn-3-ol (**3**), 8.59 (257°), 6.13 (252.5°), 4.78 (247°), 2.92 (241°), 2.09 (236°), and 1.14 (228.5°); 2-methyl-4-pentyn-2-ol (**4**), 4.66 (257°), 3.15 (252°), 2.46 (247°), 1.43 (241°), and 1.00 (235°).

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[55] All needed slopes and intercepts were calculated by the method of least squares.

[56] We wish to thank Mr. Fred Garafolo, an undergraduate research participant, for this determination.