

Acid Catalyzed Reactions of α -Allenic and α -Acetylenic Tertiary Alcohols*

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The acid catalyzed rearrangements of some isomeric α -allenic and α -acetylenic tertiary alcohols have been investigated with respect to the products formed and the reaction mechanisms. The allenic alcohols react to give α,β -unsaturated ketones in acidic aqueous solutions, allenyl ethers in methanol and dienol acetates in acetic acid. The reactions are proposed to proceed *via* an allenyl-vinyl cation. The formation of α,β -unsaturated ketones implies a 1,3-hydroxy shift, a reaction analogous to the Meyer-Schuster rearrangement of α -acetylenic alcohols. It is found that α -acetylenic tertiary alcohols having α -hydrogens can rearrange according to two different mechanisms. The course of the reaction depends on the chemical character of the substrate.

It is well known that the acid catalyzed rearrangement of α -acetylenic tertiary alcohols leads to α,β -unsaturated carbonyl compounds.¹ The reaction can proceed through a 1,2- or 1,3-hydroxy shift, depending on the structure of the starting acetylenic alcohol.

Only scant information is available in the literature about the behaviour of α -allenic alcohols towards acids.² During the course of the present study, a systematic investigation on the acid catalyzed rearrangements of different types of α -allenic alcohols was published,³ though only one tertiary derivative was included in that work.

α -Allenic tertiary alcohols occur in nature, *e.g.* among the carotenoids,⁴ and recently several 17α -propadienyl- 17β -hydroxy steroids⁵ and aliphatic alcohols⁶ have been prepared for pharmacological evaluations.

The aim of our study was to investigate the acid catalyzed isomerization of some allenic tertiary alcohols with respect to the products formed and the reaction mechanisms involved. As suitable substrates we chose the dimethyl and the cyclohexyl derivatives II and IV (*cf.* Table 1). These com-

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Table 1. Acid catalyzed reactions of α -allenic and α -acetylenic tertiary alcohols.

Substrate	Catalyst	Temp. °C	Reaction time	Products	Yield ^a % GLC
$\begin{array}{c} \text{CH}_3 \quad \text{OH} \\ \diagdown \quad / \\ \text{C} \\ / \quad \diagdown \\ \text{CH}_3 \quad \text{C}=\text{C}-\text{CH}_3 \\ \text{I}^{\text{p}} \end{array}$	5 % H_2SO_4 50 % HOAc	80	10 h	$\begin{array}{c} \text{CH}_3 \quad \text{O} \\ \diagdown \quad // \\ \text{C}=\text{CH}-\text{C}-\text{CH}_3 \\ / \\ \text{CH}_3 \\ \text{VI} \end{array}$	75
	5 % H_2SO_4 50 % HOAc	40	2 min	VI	95
	1 % H_2SO_4 CH_3OH	20	15 min	$\begin{array}{c} \text{CH}_3 \quad \text{OCH}_3 \\ \diagdown \quad / \\ \text{C} \\ / \quad \diagdown \\ \text{CH}_3 \quad \text{CH}=\text{C}=\text{CH}_2 \\ \text{VII} \\ + \\ \text{VI} \end{array}$	75 14
$\begin{array}{c} \text{CH}_3 \quad \text{OH} \\ \diagdown \quad / \\ \text{C} \\ / \quad \diagdown \\ \text{CH}_3 \quad \text{CH}=\text{C}=\text{CH}_2 \\ \text{II}^{\text{s}} \end{array}$	80 % HOAc	20	8 h	$\begin{array}{c} \text{CH}_3 \quad \text{O} \\ \diagdown \quad // \\ \text{C}=\text{CH}-\text{C}-\text{CH}_3 \\ / \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \\ \text{VIII} \\ + \\ \text{VI} \end{array}$	17 13
$\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_{10} \\ \\ \text{C}=\text{C}-\text{CH}_3 \\ \text{III}^{\text{p}} \end{array}$	5 % H_2SO_4 50 % HOAc	80	5 h	$\begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_9-\text{C}-\text{CH}_2-\text{CH}_3 \\ \text{IX} \end{array}$	95
	5 % H_2SO_4 50 % HOAc	80	2 min	$\begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_9-\text{CH}-\text{C}-\text{CH}_3 \\ \text{X} \\ + \\ \text{C}_6\text{H}_9-\text{CH}_2-\text{C}-\text{CH}_3 \\ \text{XI} \end{array}$	80 5
$\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_{10} \\ \\ \text{CH}=\text{C}=\text{CH}_2 \\ \text{IV}^{10} \end{array}$	1 % H_2SO_4 CH_3OH	20	15 min	$\begin{array}{c} \text{OCH}_3 \\ \\ \text{C}_6\text{H}_{10} \\ \\ \text{CH}=\text{C}=\text{CH}_2 \\ \text{XII} \\ + \\ \text{XI} \\ + \\ \text{X} \end{array}$	70 13 2

Table 1. Continued.

80 % HOAc	20	24 h	$\text{C}_6\text{H}_{11}=\text{CH}-\text{C}\equiv\text{CH}$	XIII	20	
				+		
			$\text{C}_6\text{H}_{11}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2$	XIV	20	
				+		
				X	30	
				+		
				XI	3	
<hr/>						
$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}-\text{OH} \\ \\ \text{C}_2\text{H}_5 \end{array} \text{CH}=\text{C} \begin{array}{c} \text{CH}_3 \\ \\ \text{C} \\ \\ \text{CH}_3 \end{array}$	5 % H ₂ SO ₄ 50 % HOAc	80	2 min	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH} \\ \qquad \\ \text{C}_2\text{H}_5 \qquad \text{CH}_3 \end{array}$	XV	70

^a The remaining part up to 100 % consists of unreacted substrates.

pounds can be considered to represent extreme cases with respect to the expulsion of protons from their carbonium ions, and we therefore suspected that they could react according to different reaction mechanisms. In the study we also included compound V which does not have a terminal allenic function.

There has been some controversy¹ regarding the mechanism of acid catalyzed rearrangement of α -acetylenic *t*-alcohols. We therefore considered it worthwhile to elucidate the isomerization of the acetylenic derivatives I and III. To our knowledge, this is the first comparative study concerning the reaction pathways of isomeric α -allenic and α -acetylenic alcohols in acidic media.

RESULTS

Many different acidic materials are known to act as useful catalysts for the rearrangement of α -acetylenic alcohols to α,β -unsaturated ketones. In the present study we mainly used 50 % acetic acid containing 5 % H₂SO₄, and in some experiments 80 % acetic acid or 1 % H₂SO₄ in methanol were also employed.

The experiments were run at different temperatures, the products being identified by GLC-MS or by preparative GLC and subsequent structure elucidation by spectroscopic methods (*cf.* Table 2). Representative results under conditions providing good yields of different products are summarized in Table 1.

The acetylenic alcohols I and III afforded different types of compounds in acidic aqueous solutions. The cyclohexyl derivative III, as expected, reacted solely according to a 1,2-hydroxy shift (Rupe rearrangement).¹ As indicated by

GLC-MS, 1-(1-propynyl) cyclohexene-1 (XVII) was rapidly formed (5 min) as an intermediate in 60 % yield at 80°C, whereafter it was transformed into the α,β -unsaturated ketone IX. In 80 % acetic acid, the enyne XVII was the only product formed, even at elevated temperature (80°C). 2-Methylpent-3-yn-2-ol (I) did not undergo the Rupe rearrangement, but reacted exclusively *via* a 1,3-hydroxy shift (Meyer-Schuster¹ rearrangement) to afford mesityl oxide (VI). During the experiments concerning the isomerization of compound I, 2-methylpent-1-en-3-one⁷ (XVIII) was used as a reference compound, but this product could not be detected in the reaction mixture (*cf.* Scheme 2).

The allenic alcohols II and IV rearranged rapidly through a 1,3-hydroxy shift producing the corresponding α,β -unsaturated ketones VI and X, respectively. This latter compound (X) isomerized further to the β,γ -unsaturated ketone XI at prolonged reaction times, and an equilibrium mixture of the two ketones was obtained after 1 h with a final composition of X:XI = 1:3.5. Compound V behaved in an analogous manner. After 2 min at 80°C the α,β -unsaturated ketone XV was formed in 70 % yield. An equilibrium was obtained after 2–3 h with approximately equal amounts of XV and the isomer XVI (5-ethyl-2-methyl-5-hepten-3-one) (*cf.* Scheme 1).

It is important to note the marked difference in reaction rate between the allenic and the acetylenic isomers II and I. While the conversion of II into mesityl oxide was rapid even at 0°C, compound I isomerized at a much slower rate. In the latter case, no reaction occurred at 0°C and some of the substrate still remained unchanged after 10 h at 80°C.

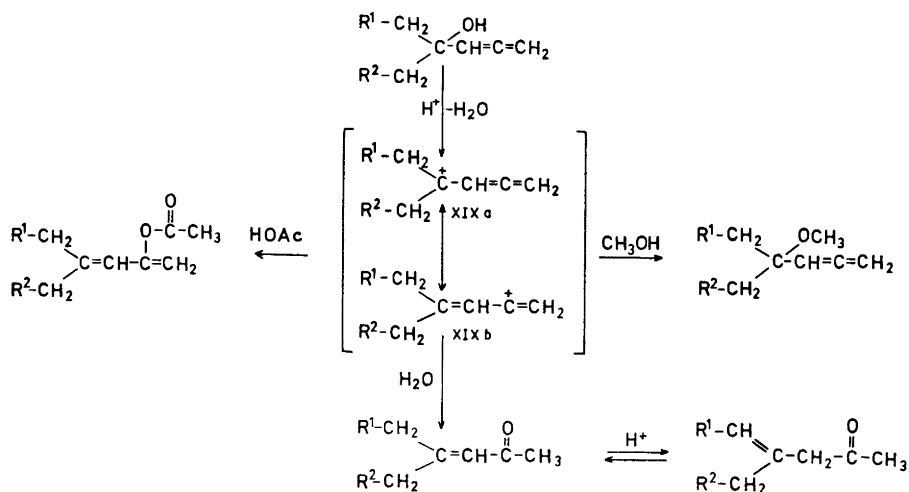
The allenic alcohols II and IV afforded good yields of the corresponding ethers VII and XII, respectively, when the reaction was performed in acidic methanol. This seems to be a useful synthetic procedure for allenic ethers from tertiary allenic alcohols.

Analysis of the reaction mixture obtained after treating IV with 80 % acetic acid revealed an unexpected product which was formed in 20 % yield. The IR (C=O: 1760 cm^{-1}) and NMR [(5.55–5.36 (m,1H), 4.80–4.57 (m,2H), 2.05 (s,3H)] spectra strongly suggest that this compound is represented by the unsaturated vinyl acetate structure XIV. MS-analysis at 10 eV with the ion source at 100°C gave an accurate molecular ion at m/e 180 supporting the structure deduced from IR and NMR data. Further evidence for the proposed structure XIV was obtained by hydrolysis in 10 % H_2SO_4 solution which yielded the ketone X. Analogous results were obtained with compound II. Compound XIV was formed in 50 % yield (GLC), when the reaction was carried out in 100 % acetic acid containing MgSO_4 at 80°C for $\frac{1}{2}$ h.

DISCUSSION

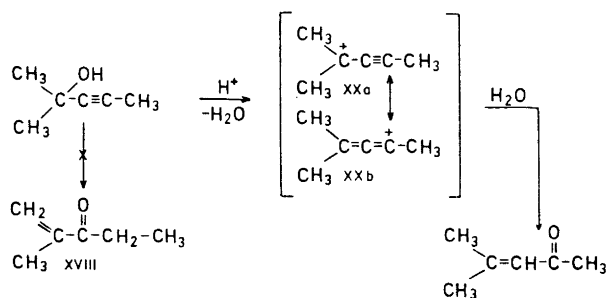
Acetylenic tert. alcohols. The results obtained show that α -acetylenic tertiary alcohols having α -hydrogens can rearrange according to two different mechanisms (*cf.* compounds I and III in Table 1). The course of the reaction seems to depend on the chemical character of the substrate. The detection of the enyne XVII as an intermediate in the transformation of III to IX supports earlier findings¹ that the Rupe rearrangement involves such a

compound. The reason why the dimethyl analogue I does not react (Scheme 2) in the same manner may be the low tendency of a carbonium ion to expel a proton to form a terminal double bond.



Scheme 1.

Allenic tert. alcohols. Our study indicates that compounds of this type react in acidic aqueous solutions according to a uniform mechanism involving a mesomeric allenyl-vinyl cation XIXa–XIXb, as outlined in Scheme 1. This isomerization implies a 1,3-hydroxy shift in analogy to the Meyer-Schuster¹ rearrangement. The proposed mechanism is supported by the formation of the allenic ethers VII and XII. Also the formation of the vinyl acetates VIII and XIV in acetic acid can be explained by this mechanism through the reaction of the carbonium ion involved with acetic acid.



Scheme 2.

Conclusion. We propose that the very pronounced difference in reaction rate between I and II may be explained on the basis of the mesomeric cations XIX and XX. To account for this assumption, we propose that the acetylenic cation is mainly represented by the mesomeric form XXa, while the allenyl-vinyl cation is advantageously represented by both mesomeric forms XIXa–XIXb, and the reaction pathway with nucleophiles depends on kinetic factors and the thermodynamic properties of the product. This type of cation has been found to be involved in the solvolysis of some 2-bromo-4-methyl-1,3-pentadiene derivatives.⁸ These compounds were solvolyzed with unexpected ease in dilute ethanol, the reaction being of first order. It was also shown that these bromodienes, which deviate from coplanarity already in the ground state, attain a conformation in the generated cation where the double bonds are perpendicular to each other (*cf.* XIXb, Scheme 1), allowing the positive charge to be delocalized over three carbon atoms. This favourable arrangement of the atoms is already present in the allenic alcohols, which constitutes a feasible explanation for their great reactivity.

EXPERIMENTAL

General. IR-spectra were run on a Perkin-Elmer Infracord 337 spectrophotometer using liquid film on NaCl discs. NMR spectra were obtained in CDCl_3 , using a Varian A 60 spectrometer and tetramethylsilane as internal standard. Mass spectra were run on an AEI MS-30 mass spectrometer connected to a Pye 104 gas chromatograph. Column: 1.5 m glass column packed with 3 % Carbowax 20 M on Chromosorb W (60–80 mesh). The ionizing energy was maintained at 70 eV, the accelerating energy at 4 kV, and the temperature of the source at 200°C.

GLC analyses were run on a Perkin-Elmer F 11 or a Varian 1700 instrument equipped with flame ionization detectors. Columns: 1.5 m columns packed with 5 % Carbowax 20 M. The preparative columns were of aluminium, $\varnothing = 3.8$ cm, 3 m long and packed with 20 % Carbowax 20 M or 20 % OV-25 on Chromosorb W (60–80 mesh).

Acid catalyzed rearrangements. General procedures. Method 1. One part of alcohol was allowed to react under stirring with 10 parts of an acid mixture (50 % HOAc + 5 % H_2SO_4 + 45 % H_2O) in a flask fitted with an efficient condenser. The flask was heated in an oil-bath, the temperature being controlled with a thermostat. Samples were withdrawn periodically and the reaction was stopped by cooling in ice and adding 5 M NaOH to slightly alkaline reaction. The solution was extracted with a known volume of ether, the extract was washed with water and dried with Na_2SO_4 . Samples of the dry ether extract were analyzed by GLC or GLC-MS. Preparative GLC or vacuum distillation was performed to isolate the products when necessary.

Method 2. One part of alcohol was allowed to react with ten parts of absolute methanol containing two parts of MgSO_4 and 1 % H_2SO_4 . The reaction was carried out in a sealed flask under magnetic stirring. Samples were withdrawn at intervals. The reaction was stopped by pouring the solution into a suspension of K_2CO_3 in light petroleum. After filtering, the samples were dried and analyzed as described in Method 1.

Method 3. One part of alcohol was treated with ten parts of 80 % acetic acid. Samples were withdrawn periodically. The reaction was stopped by neutralization in an ice bath with 5 M NaOH. The products were extracted with ether and analyzed as described in Method 1.

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Table 2. Physical data of compounds VII–XVII.

Compound	IR ^a (cm ⁻¹)	NMR (δ)	MS ^b [<i>m/e</i> (%)]
VII	1950	5.14–4.58 (m,3H) 3.12 (s,3H) 1.26 (s,6H)	112(0.1), 97(3), 83(6), 81(5) 79(5), 73(100), 67(6), 65(5), 55(28), 53(12), 45(6), 43(37) 41(32), 39(30)
VIII ¹¹	1760 1660 1645 1605	5.58–5.42 (m,1H) 4.75–4.57 (m,2H) 2.00 (s,3H) 1.84–1.67 (m,6H)	140(30), 99(7), 98(96), 84(9), 83(100), 82(9), 79(5), 60(5) 56(7), 55(13), 44(7), 43(24), 42(5), 41(6)
IX ¹²	1660 1620	6.90–6.65 (m,1H) 2.80–2.37 (q,2H) 2.37–2.00 (m,4H) 1.80–1.32 (m,4H) 1.20–0.85 (t,3H)	138(14), 110(7), 109(100), 82(6), 81(93), 79(30), 77(9), 57(9), 53(16), 45(7), 41(10), 39(7)
X ¹³	1680 1610	5.94–5.80 (m,1H) 2.95–2.50 (m,2H) 2.27–1.90 (m,2H) 2.05 (s,3H) 1.75–1.33 (m,6H)	139(7), 138(53), 123(33), 110(9), 109(13), 95(56), 93(7), 91(8), 81(18), 80(50), 79(21), 77(10), 67(48), 66(7), 65(8) 55(25), 53(15), 51(8), 43(100), 41(28), 39(31)
XI ¹⁴	1710 1610	5.48–5.27 (m,1H) 2.94–2.78 (m,2H) 2.18–1.70 (m,4H) 2.05 (s,3H) 1.70–1.33 (m,4H)	138(18), 123(6), 96(15), 95(100), 94(14), 93(10), 91(7), 81(27), 80(59), 79(27), 77(15), 73(8), 68(7), 67(63), 66(7), 65(11), 55(27), 53(22), 52(7), 51(12), 45(15), 44(7), 43(68), 41(57), 40(7), 39(51)
XII	1945	5.00–4.53 (m,3H) 3.05 (s,3H) 1.70–1.25 (m,10H)	152(1), 137(5), 114(8), 113(100), 109(11), 91(8), 81(50), 79(15), 77(9), 71(5), 67(6), 55(5), 53(7), 45(10), 41(10), 39(10)
XIII ¹⁴	3310 2090 1630	5.20–5.07 (m,1H) 2.94–2.80 (d,1H) 2.55–1.90 (m,4H) 1.90–1.35 (m,6H)	121(7), 120(55), 119(7), 105(42), 103(7), 92(63), 91(100), 81(55), 80(8), 79(55), 78(32), 77(37), 73(17), 68(22), 67(22), 66(15), 65(38), 63(20), 59(7), 55(17), 53(25), 52(24), 51(37), 50(16), 45(43), 43(12), 41(37), 39(72)
XIV	1760 1655 1640	5.55–5.36 (m,1H) 4.80–4.57 (m,2H) 2.47–1.80 (m,4H) 2.05 (s,3H) 1.80–1.32 (m,6H)	180(6), 139(8), 138(100), 137(5), 123(17), 122(7), 120(13), 110(7), 109(6), 105(7), 98(6), 96(14), 95(35), 94(10), 92(17), 91(10), 85(10), 84(5), 83(7), 82(8), 81(48), 80(85), 79(10), 78(8) 69(6), 67(12), 60(7), 59(8), 58(6), 55(8), 53(8), 44(13), 43(40), 42(12), 41(8)

Table 2. Continued.

XV	1685	6.05–5.93 (m,1H),	154(7), 112(5), 111(100), 69(12),
	1615	2.80–1.90 (m,5H) 1.20–0.80 (m,12H)	55(28), 53(6), 43(17), 41(25), 39(12)
XVI	1710	5.40–5.00 (m,1H)	154(10), 111(25), 83(19), 71(100),
		3.17–3.00	
	1620	(m,2H), 2.20–1.80	70(6), 69(9), 67(10), 55(43),
		(m,3H) 1.70–1.45 (m,3H) 1.20–0.70 (m,9H)	53(9), 43(12), 42(7), 41(43)
		39(22)	
XVII ^a	2230	5.90–5.64 (m,1H)	121(7), 120(100), 119(12),
		2.20–1.78 (m,4H)	
	1675	1.82 (s,3H)	106(9), 105(95), 103(12),
	1.67–1.30 (m,4H)		
	1630		92(37), 91(91), 79(28), 78(12), 77(40), 65(9), 63(9), 51(9), 41(6), 39(12)

^a Only important bonds of diagnostic value are listed.

^b Only peaks with a rel. int. >5 % of the base peak are listed.

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