

THE RUPE AND MEYER-SCHUSTER REARRANGEMENTS

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I. Introduction

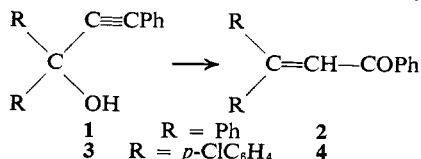
A. DEFINITION

The Rupe rearrangement is the acid-catalyzed rearrangement of tertiary α -acetylenic alcohols leading to the formation, predominantly, of α,β -unsaturated ketones.

The Meyer-Schuster rearrangement is the isomerization, by a 1,3 shift, of secondary and tertiary α -acetylenic alcohols to α,β -unsaturated carbonyl compounds. When the acetylenic group is terminal, the products are aldehydes; otherwise, they are ketones.

B. BACKGROUND

Meyer and Schuster¹ reported the first example of a Meyer-Schuster rearrangement when they obtained the ketones **2** and **4** by treating the carbinols **1** and **3** with a variety of acidic catalysts like acetic acid-concentrated sulfuric acid, ether saturated with dry hydrogen chloride, acetic anhydride, and



(1) K. H. Meyer and K. Schuster, *Chem. Ber.*, **55**, 819 (1922).

acetyl chloride. An attempt² at converting compound **1** to its ethyl ether with concentrated sulfuric acid and ethanol also gave the α,β -unsaturated ketone **2**. Rupe and colleagues then effected the acid-catalyzed isomerization of a large number of α -acetylenic alcohols.³⁻¹⁵ The color tests answered by the (presumably impure) products led them to conclude that they were aldehydes.^{4,6-8} Repetition of these experiments later¹⁶⁻²⁰ showed that the main products of Rupe rearrangements are ketones and that the aldehydes reported were probably impurities. More recently, carefully performed experiments by Chanley²¹ and others²²⁻²⁵ have confirmed the observation that aldehydes are at best only minor products in Rupe rearrangements.

II. Scope of This Review

A search of the literature shows that two reviews^{26,27} on the Meyer-Schuster and Rupe rearrangements have appeared

- (2) C. Moureu, C. Dufraisse, and C. Mackall, *Bull. Soc. Chim. Fr.*, 934 (1923).
- (3) H. Rupe and K. Glenz, *Justus Liebigs Ann. Chem.*, **436**, 195 (1924).
- (4) H. Rupe and E. Kambli, *Helv. Chim. Acta*, **9**, 672 (1926).
- (5) H. Rupe and E. Kambli, *Justus Liebigs Ann. Chem.*, **459**, 215 (1927).
- (6) H. Rupe and L. Giesler, *Helv. Chim. Acta*, **11**, 656 (1928).
- (7) H. Rupe, W. Messner, and E. Kambli, *ibid.*, **11**, 449 (1928).
- (8) H. Rupe, A. Wirz, and P. Lotter, *ibid.*, **11**, 965 (1928).
- (9) H. Rupe and A. Gassmann, *ibid.*, **12**, 193 (1929).
- (10) H. Rupe and H. Hirschmann, *ibid.*, **14**, 687 (1931).
- (11) H. Rupe and F. Kuenzy, *ibid.*, **14**, 701 (1931).
- (12) H. Rupe and F. Kuenzy, *ibid.*, **14**, 708 (1931).
- (13) H. Rupe, R. Haecker, E. Kambli, and N. Wassieleff, *ibid.*, **16**, 685 (1933).
- (14) H. Rupe and A. Gassmann, *ibid.*, **17**, 283 (1934).
- (15) H. Rupe and H. Werdnberg, *ibid.*, **18**, 542 (1935).
- (16) F. G. Fischer and K. Lowenberg, *Justus Liebigs Ann. Chem.*, **475**, 184, 199, 203 (1929).
- (17) C. D. Hurd and R. E. Christ, *J. Amer. Chem. Soc.*, **59**, 118 (1937).
- (18) C. D. Hurd and R. N. Jones, *ibid.*, **56**, 1924 (1934).
- (19) C. D. Hurd and W. D. McPhee, *ibid.*, **71**, 398 (1949).
- (20) C. C. Price and S. L. Meisel, *ibid.*, **69**, 1497 (1947).
- (21) J. D. Chanley, *ibid.*, **70**, 244 (1948).
- (22) H. B. Henbest and G. Woods, *J. Chem. Soc.*, 1150 (1952).
- (23) K. Suga and S. Watanabe, *Chiba Daigaku Kogakubu Kenkyu Hokoku*, **9**, 67 (1958); *Chem. Abstr.*, **54**, 5432 (1960).
- (24) T. Takeshima, *J. Sci. Res. Inst., Tokyo*, **45**, 103 (1951); *Chem. Abstr.*, **46**, 4477 (1952).
- (25) T. Takeshima, *J. Amer. Chem. Soc.*, **75**, 3309 (1953).
- (26) R. Heilmann and R. Glenat, *Ann. Chim. (Paris)*, **8**, 178 (1963).
- (27) G. Kugatova-Shemyakina, H. Laumenskase, G. K. Krasil'nikova, V. Mezolis, and V. Kaloelite, *Vop. Khim. Terpenov Terpenoidov, Akad. Nauk Lit. SSR, Tr. Vses. Soveshch., Vilnyus*, **65** (1959).

recently, both of them relatively short. These isomerizations are also discussed briefly²⁸ in a review on rearrangements of acetylenic compounds involving π electrons of the triple bond.

This review therefore covers in detail the literature appearing in *Chemical Abstracts* up to the end of June 1968 and in about 20 selected journals up to the end of June 1970. Base-catalyzed and vapor-phase transformations of acetylenic alcohols have also been included, but the reactions of acetylenic glycols have been left out.

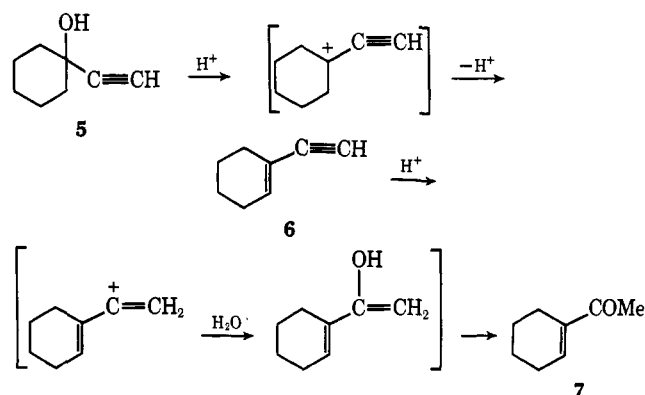
III. Liquid-Phase Acid-Catalyzed Rearrangements

A. MECHANISM

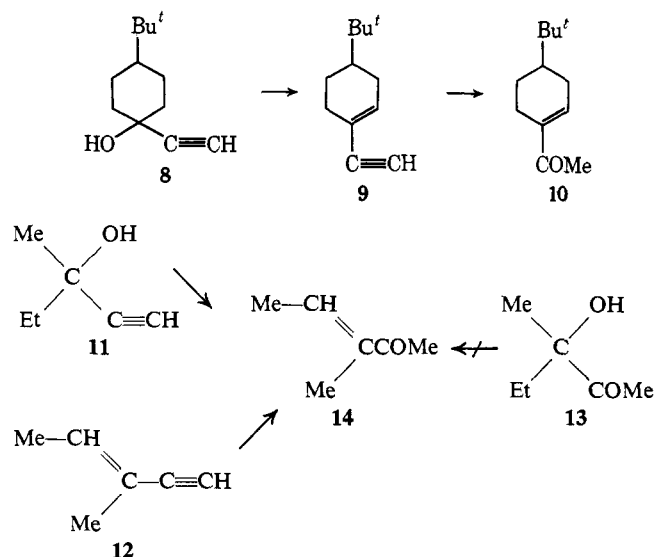
1. The Rupe Rearrangement

It is now generally agreed that the Rupe rearrangement of tertiary α -acetylenic alcohols to α,β -unsaturated ketones proceeds through a dehydration-hydration sequence, with enynes as intermediates.

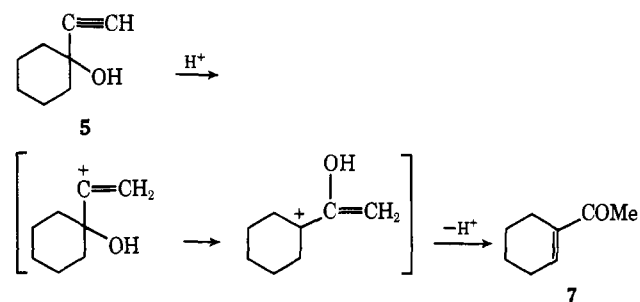
Electrophilic attack by protons from the catalyst results in the formation of a tertiary carbonium ion which then expels a proton from an adjacent carbon atom, giving a



vinylacetylene like 6. Further electrophilic attack gives a secondary carbonium ion, which on work-up furnishes eventually the α,β -unsaturated ketone 7. Such enyne intermediates have been detected spectroscopically²⁹ and even isolated^{18,30-34} on several occasions. The quicker conversion³⁵ under identical conditions of the vinylacetylene 9 than the ethynyl carbinol 8 to the product 10 has been interpreted as evidence favoring the intermediacy of 9 in the rearrangement of 8 to 10. The observation³⁶ that compounds 11 and 12 are converted by formic acid to 14, while the alcohol 13 is not, rules out a hydration-dehydration sequence for the Rupe rearrangement.



It was observed that ethynylcyclohexene (6) was transformed much slower than ethynylcyclohexanol (5) to acetylcyclohexene (7) by the acid form of the cation-exchange resin Dowex 50 in acetic acid, and therefore a mechanism not invoking an enyne as intermediate was proposed.³⁷ This mechanism was accepted by Ansell, Hancock, and Hickinbottom³⁰ who were attempting hydration of terminal vinylacetylenes with formic acid. The need for such a mechanism



has recently been questioned by Apparū and Glenat³⁸ who observed enynes as well as ketonic products during the isomerization of a few ethynyl carbinols with Dowex 50 in acetic acid. Contrary to earlier reports,^{30,37} they were able to effect quick and complete hydration of vinylacetylenes with Dowex 50 in acetic acid. They also observed that enynes with terminal vinyl groups were hydrated much slower and that sulfuric acid in acetic acid brought about isomerization faster.

2. The Meyer-Schuster Rearrangement

In the acid-catalyzed rearrangement of an acetylenic alcohol of the general formula 15, the intermediate alkynyl cation 16a cannot expel a proton from an adjacent carbon atom and therefore isomerizes to the allenyl cation 16b which on work-up furnishes the carbonyl compound 18. When $R''' = H$, the product is an aldehyde. In effect, the hydroxyl group undergoes a 1,3 or "propargylic"³⁹ shift across the triple bond. Such isomerizations occur when $R', R'' = Me$ also.

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(31) L. E. Coles, W. H. Linnell, D. W. Mathieson, and A. S. Shoukri, *ibid.*, 2617 (1954).

(32) J. C. Hamlet, H. B. Henbest, and E. R. H. Jones, *ibid.*, 2652 (1951).

(33) H. H. Inhoffen, W. Logemann, W. Hohlweg, and A. Serini, *Chem. Ber.*, **71**, 1029 (1938).

(34) E. E. Smisssmann, R. H. Johnson, A. W. Carlson, and B. F. Aycock, *J. Amer. Chem. Soc.*, **78**, 3395 (1956).

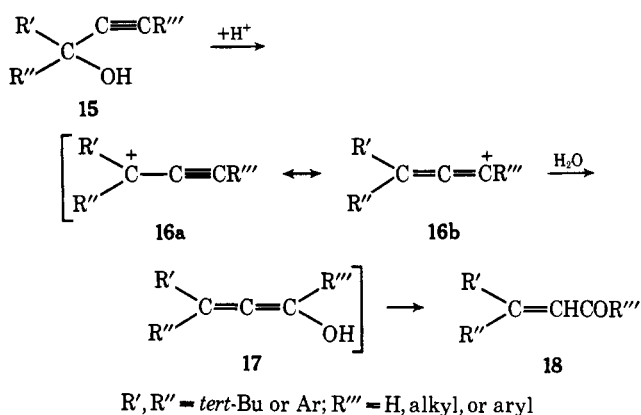
(35) M. S. Newman and P. H. Goble, *ibid.*, **82**, 4098 (1960).

(36) G. F. Hennion, R. B. Davis, and D. E. Maloney, *ibid.*, **71**, 2813 (1949).

(37) M. S. Newman, *ibid.*, **75**, 4740 (1953).

(38) M. Apparū and R. Glenat, *Bull. Soc. Chim. Fr.*, 1113 (1968).

(39) J. H. Wotiz in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, pp 365-424.



Alkynyl cations like **16a** have been recently detected⁴⁰ by nmr and uv spectroscopy. The formation³⁸ of allenyl acetates in some reactions performed in acetic acid is evidence for the (transient) existence of allenyl cations like **16b**. The isolation¹ of 4,4'-dichlorobenzophenone from the acid-catalyzed isomerization of **3** and oxidative degradation is another item of evidence corroborating the above mechanism.

The driving force for both the Rupe and the Meyer-Schuster rearrangements appears to be the irreversible processes involved in the formation of unsaturated carbonyl compounds from the intermediate carbonium ions.

B. SUBSTRATES

The types of products obtained by the action of acidic catalysts on a variety of ethynyl carbinols are indicated in Table I.

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 (44) N. Hagihara and I. Hirao, *Mem. Inst. Sci. Ind. Res. Osaka Univ.*, **7**, 133 (1950); *Chem. Abstr.*, **45**, 8997 (1951).
 (45) W. S. MacGregor, *J. Amer. Chem. Soc.*, **70**, 3953 (1948).
 (46) J. Jadot and N. Doyen, *Bull. Soc. Roy. Sci. Liege*, **24**, 2 (1955); *Chem. Abstr.*, **50**, 3993 (1956).
 (47) I. Ichikizaki and M. Kindaichi, *J. Chem. Soc. Jap., Pure Chem. Sect.*, **71**, 409 (1950); *Chem. Abstr.*, **45**, 9458 (1951).
 (48) E. R. H. Jones and J. T. MacCombie, *J. Chem. Soc.*, 261 (1943).
 (49) Y. Okajima, *Yakugaku Zasshi*, **79**, 1288 (1959); *Chem. Abstr.*, **54**, 4475 (1960).
 (50) M. Julia and J. Bullot, *C. R. Acad. Sci.*, **247**, 474 (1958).
 (51) J. Issei, and O. Yakutaro, *J. Pharm. Soc. Jap.*, **79**, 1288 (1959).
 (52) I. M. Heilbron, E. R. H. Jones, and R. A. Raphael, *J. Chem. Soc.*, 264 (1943).
 (53) I. M. Heilbron, A. W. Johnson, E. R. H. Jones, and R. A. Raphael, *ibid.*, 265 (1943).
 (54) I. Iwai and Y. Okajima, *Yakugaku Zasshi*, **79**, 1284 (1959); *Chem. Abstr.*, **54**, 4474 (1960).
 (55) H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, **91**, 2375 (1969).
 (56) M. S. Newman, S. Ramachandran, S. K. Sankarappa, and S. Swaminathan, *J. Org. Chem.*, **26**, 727 (1961).
 (57) V. T. Ramakrishnan and S. Swaminathan, unpublished results.
 (58) P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 1015 (1956).
 (59) H. P. W. Huggill and J. D. Rose, *ibid.*, 335 (1950).
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 (61) J. Cymerman, I. M. Heilbron, and E. R. H. Jones, *ibid.*, 90 (1945).
 (62) N. A. Preobrazhenskii and I. A. Rubtsov, *Zh. Obshch. Khim.*, **18**, 1719 (1948).
 (63) I. Heilbron, E. R. H. Jones, M. Julia, and B. C. L. Weedon, *J. Chem. Soc.*, 1823 (1949).

C. CATALYSTS

A wide variety of acidic materials catalyzes the Rupe and the Meyer-Schuster rearrangements. The commonest of these is formic acid, in concentrations from 70%⁷⁹ to 97%⁷⁸ for periods ranging from 3 min⁷⁸ to 100 hr²⁹ at different temperatures. Formic acid usually serves as the solvent also,⁷⁹ but in some instances it has been used in methanol solution.⁸⁰ It has been claimed that formic acid is not strong enough an acid to bring about rearrangements of all acetylenic carbinols, while stronger mineral acids are generally not miscible with the carbinols used. Better results have therefore been reported⁸¹ with a mixture of sulfuric acid and acetic acid as catalyst, or, alternatively, a cation exchanger like Dowex 50 in acetic acid. Aqueous sulfuric acid of various strengths,^{2, 3, 2, 4, 3, 4, 5, 5, 5, 9} sulfuric acid diluted with solvents like ethanol,^{9, 8, 2-84} 2-propanol,⁸ *n*-butyl ether,⁸⁵ and acetic acid,^{1, 86-88} and phosphoric acid diluted with acetic acid^{89, 90} also bring about isomerization. Improved yields of aldehydes are claimed when some hydroquinone is added^{84, 91} to the catalyst and when a mixture of water and a miscible nonhydroxylic solvent like dioxane or acetic acid is used.⁴⁴ Phenol, malic, maleic, malonic, chloroacetic, trichloroacetic, and benzenesulfonic acids and zinc chloride have also been observed⁸⁹ to catalyze the isomerization; the evidence indicates that the rearrangement is appreciable with acids stronger than formic acid and that the nature

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 (65) W. H. Davies, I. M. Heilbron, W. E. Jones, and A. Lowe, *J. Chem. Soc.*, 584 (1935).
 (66) W. Chodkiewicz, P. Cadiot, and A. Willemart, *C. R. Acad. Sci.*, **250**, 150 (1960).
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 (77) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and G. K. I. Magomedov, *Dokl. Akad. Nauk SSSR*, **163**, 1159 (1965); *Engl. Trans.*, **163**, 768 (1965).
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 (81) M. Appar and R. Glenat, *Bull. Soc. Chim. Fr.*, 1106 (1968).
 (82) M. Badoche, *ibid.*, 337 (1928).
 (83) G. F. Hennion and B. R. Fleck, *J. Amer. Chem. Soc.*, **77**, 3253 (1955).
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 (90) T. Takeshima, *J. Amer. Chem. Soc.*, **75**, 4107 (1953).
 (91) T. Takeshima, *J. Sci. Res. Inst., Tokyo*, **45**, 211 (1951); *Chem. Abstr.*, **47**, 6864 (1953).

Table I

| Substrates | Remarks | Ref |
|--|--|------------|
| 1. α -Acetylenic alcohols | | |
| (a) Primary $\text{CH}\equiv\text{CCH}_2\text{OH}$ | They undergo no rearrangement, giving only formates with 99% formic acid | 41 |
| (b) Secondary | They take part in Meyer-Schuster rearrangements | 34, 42-45 |
| (i) Saturated aliphatic | Conflicting claims have appeared on their ability to undergo Rupe rearrangements | |
| $\begin{array}{c} \text{OH} \\ \\ \text{RCH} \\ \\ \text{C}\equiv\text{CH} \end{array}$ R = saturated alkyl | Reactions in formic acid and acetic acid have been claimed to yield only formates and acetates, respectively | 42 |
| | Loss of acetylene to give starting aldehydes and their self-condensation products has been reported. | 46 |
| | Hot, concentrated sulfuric acid has been reported to yield Rupe-type products | 47 |
| (ii) α' -Vinyl | It is unaffected by 25% sulfuric acid | 48 |
| $\begin{array}{c} \text{CH}=\text{CH}_2 \\ \\ \text{HOCH} \\ \\ \text{C}\equiv\text{CH} \end{array}$ | | |
| (iii) Substituted α' -vinyl | When R = R' = Cl | 50 |
| $\begin{array}{c} \text{CH}=\text{CHR} \\ \\ \text{HOCH} \\ \\ \text{C}\equiv\text{CR}' \end{array}$ | R = R' = Ph | 51 |
| | R = Ph, R' = H or Me propargylic shifts to Meyer-Schuster products take place | 43, 49, 51 |
| | In other cases, products arising from allylic shifts of OH group are obtained | 48, 52 |
| (iv) α',γ -Divinyl | The OH group undergoes a 1,3 allylic shift; this is accompanied at times by dehydration | 42, 49, 53 |
| $\begin{array}{c} \text{CH}=\text{CHR} \\ \\ \text{HOCH} \\ \\ \text{C}\equiv\text{C}(\text{R}')=\text{CHR}' \end{array}$ | | |
| (v) α' -Acetylenic | They rearrange to Meyer-Schuster products | 54 |
| $\begin{array}{c} \text{C}\equiv\text{CAr} \\ \\ \text{HOCH} \\ \\ \text{C}\equiv\text{CAr} \end{array}$ | | |
| (c) Tertiary | They undergo Rupe or Meyer-Schuster rearrangement, depending on whether a proton can be ejected or not from an α -carbon atom | |
| | Ethynylcyclopropanol, however, is unaffected by aqueous hydrochloric acid | 55 |
| (i) Acetates of | Rupe rearrangement products are obtained | 56, 57 |
| | Pyrolysis gives allenyl acetates | 58 |
| (ii) ω -Dialkylaminoalkyl | Meyer-Schuster products are formed | 59 |
| $\begin{array}{c} \text{Ar} \quad \text{C}\equiv\text{CCHNMe}_2 \\ \diagdown \quad / \\ \text{C} \\ / \quad \backslash \\ \text{Ar} \quad \text{OH} \\ \\ \text{Me} \end{array}$ | | |

Table I (Continued)

| Substrates | Remarks | Ref |
|--|--|------------------------------------|
| (iii) α' -Substituted vinyl $\begin{array}{c} \text{HO} \quad \text{C}\equiv\text{CR}'' \\ \diagdown \quad / \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R}'' \quad \text{CH}=\text{CRR}' \end{array}$ | The OH group undergoes an allylic shift; this is accompanied by dehydration sometimes When R''' = OEt, the Meyer-Schuster product is an ester | 43, 48, 52, 53, 60, 61 62 |
| (iv) α' -Butadienyl. $\begin{array}{c} \text{Me} \quad \text{C}\equiv\text{CR}'' \\ \diagdown \quad / \\ \text{C} \\ \diagup \quad \diagdown \\ \text{HO} \quad \text{CH}=\text{CHCH}=\text{CR}_2 \end{array}$ | The OH group migrates to the end of the butadienyl system. | 65 |
| (v) γ -Vinyl $\begin{array}{c} \text{R} \quad \text{C}\equiv\text{CCH}=\text{CHR}' \\ \diagdown \quad / \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{OH} \end{array}$ | Meyer-Schuster products are formed. Formation of ethers (by loss of water from 2 mol of carbinol) has also been noted Dehydration to dienyne occurs at times When R' = OMe, the OH group migrates across the triple and then the double bond to yield R ₂ C=C=C=CHCHO | 66 67 32 68 |
| (vi) Conjugated polyacetylenic $\begin{array}{c} \text{Ar} \quad (\text{C}\equiv\text{C})_n\text{Ar} \\ \diagdown \quad / \\ \text{C} \\ \diagup \quad \diagdown \\ \text{Ar} \quad \text{OH} \end{array}$ | They undergo Meyer-Schuster rearrangements, but more slowly | 66, 69 |
| (vii) Miscellaneous ^a $\begin{array}{c} \text{Ar} \quad \text{C}\equiv\text{CX} \\ \diagdown \quad / \\ \text{C} \\ \diagup \quad \diagdown \\ \text{Ar} \quad \text{OH} \end{array}$ | When X = Br or Cl, acid chlorides or carboxylic acids are obtained by Meyer-Schuster isomerizations When X = OEt or SEt, the corresponding α,β unsaturated esters are formed by Meyer-Schuster rearrangements | 66, 69 63, 64, 70-73 |
| 2. β -Acetylenic tertiary alcohols $\begin{array}{c} \text{R} \quad \text{OH} \\ \diagdown \quad / \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R}' \quad \text{CH}_2\text{C}\equiv\text{CH} \end{array}$ | When R, R' = Me, <i>tert</i> -Bu, or Ar, α,β -unsaturated ketones are formed by a dehydration-hydration sequence When R, R' = other aliphatic groups, both α,β - and β,γ -unsaturated ketones are formed, the former in larger amounts When R, R' = part of an alicyclic ring, the mixture of α,β - and β,γ -unsaturated ketones is richer in the latter By using different catalysts, the <i>cis</i> and <i>trans</i> forms of the α,β -unsaturated ketone have been obtained separately | 74, 75 75 75 76, 77 |

^a A few other examples are given in ref 28.

of the acidic catalyst does not affect the course of the rearrangement.

Other effective catalysts are cation exchangers like Dowex 50 in formic acid⁹² and acetic acid,^{37,93} anhydrous oxalic acid,^{94,95} hydrochloric acid in 2-propanol,⁹⁶ hydrochloric acid

and mercuric chloride,⁹⁷ dry ether saturated with hydrogen chloride,¹ *p*-toluenesulfonic acid,⁸⁰ phosphorus pentoxide in dry benzene,^{80,98} potassium bisulfate,⁴³ sodium or magnesium sulfate under vacuum,⁷⁶ sulfuric acid and mercuric

(92) M. E. McEntee, A. R. Pinder, H. Smith, and R. E. Thornton, *J. Chem. Soc.*, 4699 (1956).

(93) R. Heilmann and R. Glenat, *C. R. Acad. Sci.*, **240**, 2317 (1955).

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sulfate,⁹⁹⁻¹⁰² ethanol and mercuric sulfate,⁷⁷ phosphorus oxychloride-pyridine,⁸⁰ acetyl chloride,¹ acetic anhydride-acetyl chloride,⁸⁰ acetic anhydride-sodium acetate,⁸⁰ acetyl chloride-pyridine,⁸⁰ acetic anhydride,^{1,7,103} 2,4-dinitrophenylhydrazine reagent,^{101,104-106} and thionyl chloride.^{1,107}

Phosphorus and thionyl halides generally convert ethynyl alcohols to mixtures of acetylenic and allenic products. These mixtures arise from "acetylene-allene" or "propargylic"³⁹ rearrangements, which have been reviewed^{28,39,108,109} recently. The types of products obtained by reaction of ethynyl carbinols with these reagents are outlined in Table II. R represents the propargyl ($-C\equiv C<$) group, R' the isomeric allenyl ($>C=C<$) group, and R'' the alkynyl group ($>CC\equiv C-$) obtained from R'.

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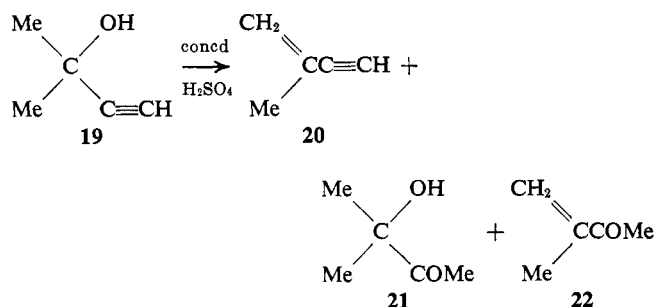
D. REACTION PRODUCTS

The separation and identification of the reaction products and the minor modifications observed in them are discussed here.

Mixtures of aldehydes and ketones are separated from each other through bisulfite addition compounds,^{10,15} column chromatography,^{28,78} distillation through a fractionating column,¹³⁹ or by fractional crystallization of the semicarbazones.^{6,13}

The structures of the products are established by ozonolysis^{13,15,19} oxidative degradation,¹ hydration of the appropriate enynes⁹⁵ (prepared from the starting ethynyl carbinols by treatment with phosphorus oxychloride and pyridine³²), comparison of melting points of reaction products and their derivatives with those of authentic specimens,^{10,11,16,25,35} air oxidation,¹⁴⁰ reduction to saturated alcohols and reoxidation to acids and ketones,⁸⁰ and spectroscopically.^{29,35,78}

Cis-trans isomerism in the reaction products has been detected only in a few instances,^{76,141-143} although it would be expected to be more prevalent. Polymorphic modifications of reactions products^{144,145} have been reported. In addition to α,β -unsaturated ketones, β,γ -unsaturated ketones are also formed at times.^{13,25,31,75,146} The sulfuric acid catalyzed rearrangement of the carbinol **19** yields the enyne **20**, the keto alcohol **21**, and the Rupe product **22**, but none of



the expected aldehyde.

Even carbinols which can undergo Rupe rearrangement quite often give^{25,30} low yields of Meyer-Schuster products (α,β -unsaturated aldehydes). The low yields have been attributed to their easy oxidation and self-condensation. Attempts to inhibit polymerization by adding hydroquinone^{54,91} have not been very successful. Other attempts to improve the yields of aldehydes (by trapping them^{26,106} with carbonyl reagents as soon as they are formed and by sweeping the reaction products away from the catalyst, as by steam distillation⁴⁵ or passage over a catalyst in the vapor phase^{139,147-148}) have been more successful.

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 (144) C. Dufraisse and A. Gillet, *Ann. Chim. (Paris)*, 6, 295 (1925).
 (145) C. Dufraisse and H. Moureu, *Bull. Soc. Chim. Fr.*, 676 (1924).
 (146) E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer, and J. B. Toogood, *J. Chem. Soc.*, 1890 (1949).
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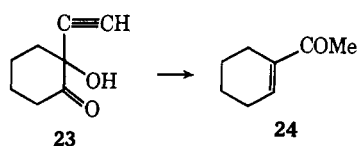
Table II

| Halide | Reaction conditions | Products | Ref |
|--------------------------------------|--|---|------------------|
| PBr ₃ ^a | Py, 0°, <i>i</i> -Pr ₂ O | (RO) ₃ P + (RO) ₂ POR' | 110 |
| PBr ₃ ^a | Py, higher temp | (R'Br) ₂ | 110 |
| PBr ₃ ^a | 0°, Py or no Py | RBr | 111 |
| PBr ₃ ^a | No Py | RBr + the two products from addition of HBr to each of the two double bonds in R'Br | 112 |
| PBr ₃ ^a | No Py | R'Br | 113 |
| PBr ₃ ^a | No Py, HOAc | R'Br + product from addition of HBr to R'Br | 114 |
| PBr ₃ ^a excess | No Py | (R'POBr ₂) ₂ + (the product from addition of HBr to R'Br) ₂ | 110 |
| PBr ₅ ^b | 0°, Et ₂ O, no Py | RBr + R'Br + ROEt + product from addition of HBr to R'Br | 115 |
| PBr ₅ ^b | Et ₂ O, 0°, Py | RBr + R'Br + products from addition of bromine to ROH, RBr, and R'Br | 115 |
| SOBr ₂ ^c | Et ₂ O, no Py | R'Br + products formed by addition of HBr to R'Br and addition of bromine to R'Br | 115 |
| SOBr ₂ ^c | No Py, pentane | RBr | 111 |
| SOBr ₂ ^c | Py, 0° | R'Br | 115 |
| HBr aq | | No reaction; incomplete formation of R'Br | 116, 117 |
| HBr aq | NH ₄ Br + Cu ₂ Br ₂ | RBr | 118 |
| HBr aq | | R'Br | 117, 119, 120 |
| PCl ₃ | Py, low temp | (RO) ₃ P + (RO) ₂ POR' | 110 |
| PCl ₃ | Py, low temp | (RO) ₂ POR' | 121-123 |
| PCl ₃ | Py, higher temp | RCI | 110 |
| PCl ₃ excess | Et ₃ N, Et ₂ O, -20° | (RO) ₂ POR' | 122 |
| PCl ₃ excess | No Py | R'POCl ₂ → R''POCl ₂ | 124-126 |
| PCl ₃ excess | No Py | RCI + addition product of HCl to R'Cl + (addition product of HCl to R'POCl ₂) + R'POCl ₂ | 110, 113 |
| PCl ₅ | No Py, 0°, ether | RCI | 112 |
| PCl ₅ | 0°, no Py, Et ₂ O | ROEt + R'Cl | 116 |
| SOCl ₂ | Py | RCI (with primary and secondary carbinols) + R'Cl | 112, 127 |
| SOCl ₂ | Py | R'Cl | 128, 129 |
| SOCl ₂ | Py | R'Cl + (RO) ₃ S | 116 |
| SOCl ₂ | No Py | RCI | 112 |
| SOCl ₂ | No Py | R'Cl | 113, 116 |
| HCl | CaCl ₂ | RCI | 130 |
| HCl aq | CuCl + NH ₄ Cl | RCI + R'Cl | 131-133 |
| HCl aq | CuCl + NH ₄ Cl | RCI + R'Cl + conjugated chlorodienes | 19, 99, 134, 135 |
| SF ₄ ^d | | R'F | 135 |

^a The products of these reactions were earlier thought to be propargyl bromides, but later^{113, 119, 136-138} it was recognized that many of them were partly, if not wholly, allenic bromides. ^b The decomposition $PBr_5 \rightarrow PBr_3 + Br_2$ accounts for the presence of free bromine and consequent reactions. ^c The reaction $2SOBr_2 \rightarrow S + SO_2 + 2Br_2$ liberates free bromine. ^d The alcohols used were tertiary and liberally substituted with chlorine and fluorine.

E. ABNORMAL PRODUCTS

Deoxygenation has been observed, the keto carbinol **23** giving **24**.⁹²

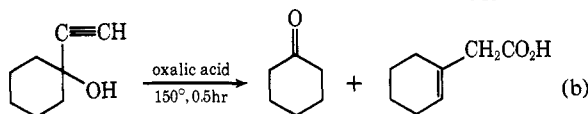
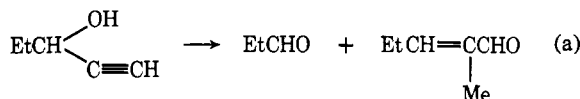
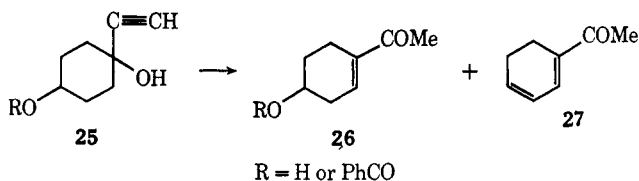


The isomerization of the alcohol **25** gives the normal product **26** and the abnormal product **27**.¹⁴⁹

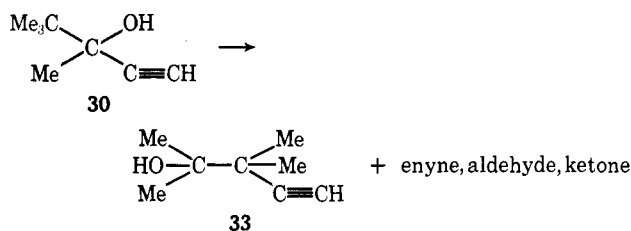
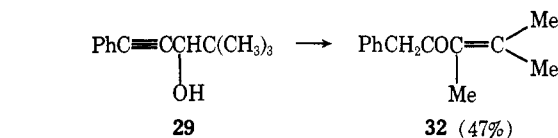
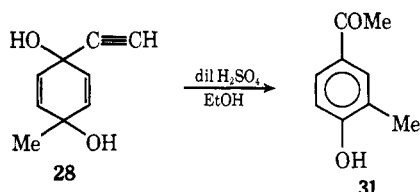
Dismutation of ethynyl carbinols to starting aldehydes or ketones followed by self-condensation or rearrangement and oxidation are also known (eq a and b).^{46, 150}

(149) E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).

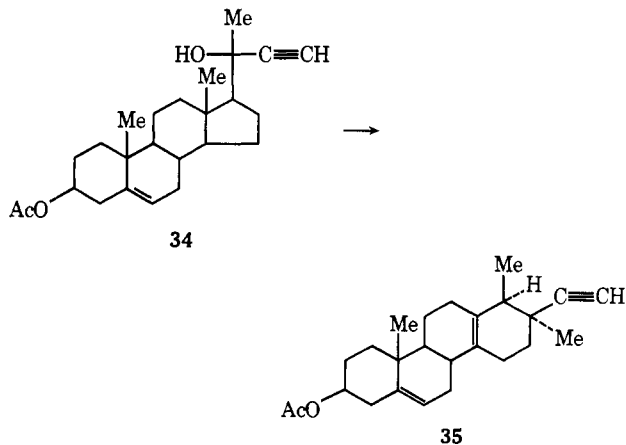
(150) E. Bergmann and F. Bergmann, *J. Amer. Chem. Soc.*, **59**, 1449 (1937).



Methyl group migrations, with^{34,151} or without⁸¹ subsequent ejection of a proton, explain the formation of compounds **31**, **32**, and **33** from **28**, **29**, and **30**, respectively.



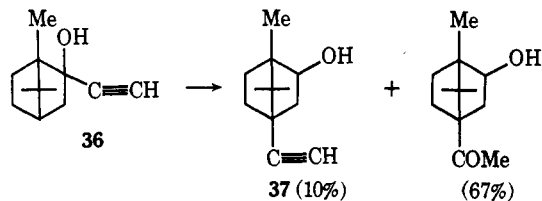
A Wagner–Meerwein rearrangement⁷⁸ converts the ethynyl alcohol **34** to **35** and a Wagner–Nametkin rearrangement¹⁵²



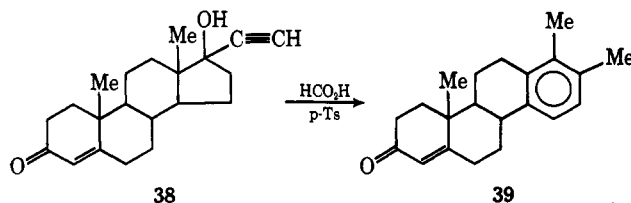
converts the carbinol **36** to **37**.

(151) F. Wessely, E. Zbiral, and E. Lahrman, *Chem. Ber.*, **92**, 2141 (1949).

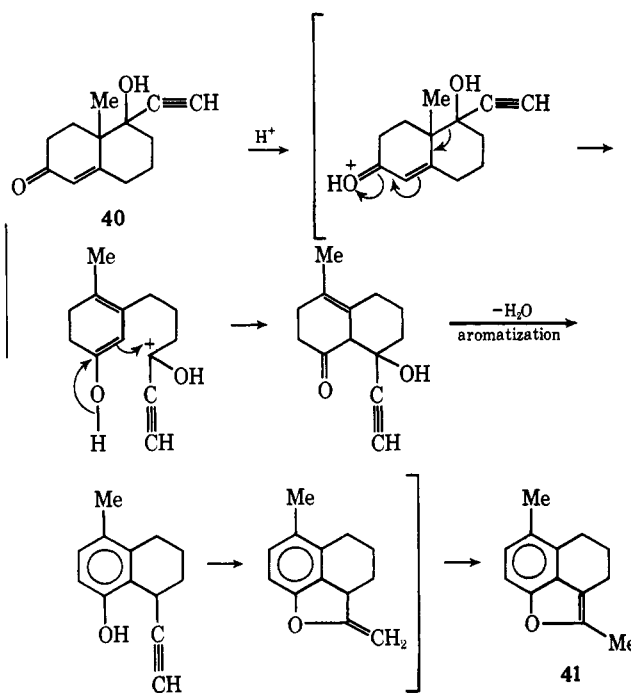
(152) M. Kagawa, *Chem. Pharm. Bull. Jap.*, **7**, 306, 751 (1959); *Chem. Abstr.*, **55**, 1682 (1961).



The transformation of 17-ethynyltestosterone **38** to the ring D homo aromatic product **39** is explained by a Wagner–Meerwein shift and internal Prins rearrangement, followed by isomerization.^{153–156}



The δ -hydroxy- δ -ethynyl α,β -enone **40** is rearranged to the benzofuran **41** by the mechanism shown below when



refluxed with *p*-toluenesulfonic acid in chloroform for 2 hr.¹⁵⁷

The thionyl chloride–pyridine catalyzed reaction¹⁵⁸ of the ethynyl alcohol **1** leads to the tetracyclic compound **42** in addition to the expected product **2**. The corresponding reaction with compound **43** gave three compounds assigned¹⁵⁸ structures **44–46**.

(153) J. Canceill, M. Dvolaitzky, and J. Jacques, *Bull. Soc. Chim. Fr.*, 336 (1963).

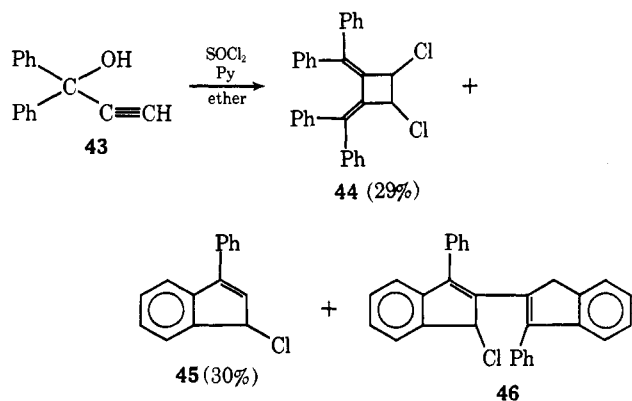
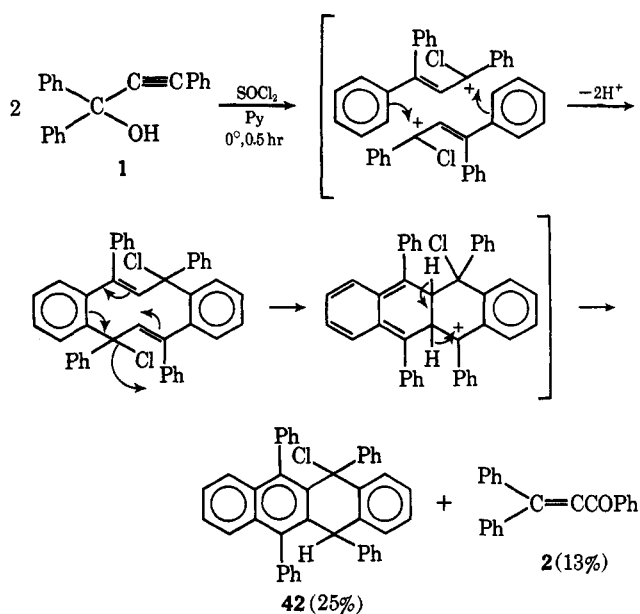
(154) M. Dvolaitzky, A. M. Giroud, and J. Jacques, *ibid.*, 62 (1963).

(155) E. Hardegger and C. Scholz, *Helv. Chim. Acta*, **28**, 1355 (1945).

(156) C. Ouannes, M. Dvolaitzky, and J. Jacques, *Bull. Soc. Chim. Fr.*, 776 (1964).

(157) S. Swaminathan, R. K. Natarajan, S. Ramachandran, and S. K. Sankarappa, *J. Org. Chem.*, **31**, 656 (1966).

(158) P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 2707 (1963).

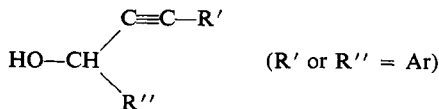


IV. Liquid-Phase Base-Catalyzed Rearrangements

The literature on this aspect of the Rupe and Meyer-Schuster rearrangements is meager, but, nevertheless, some generalizations can be made.

A. MECHANISM

The base-catalyzed rearrangements of α -acetylenic carbinols like^{159,160}

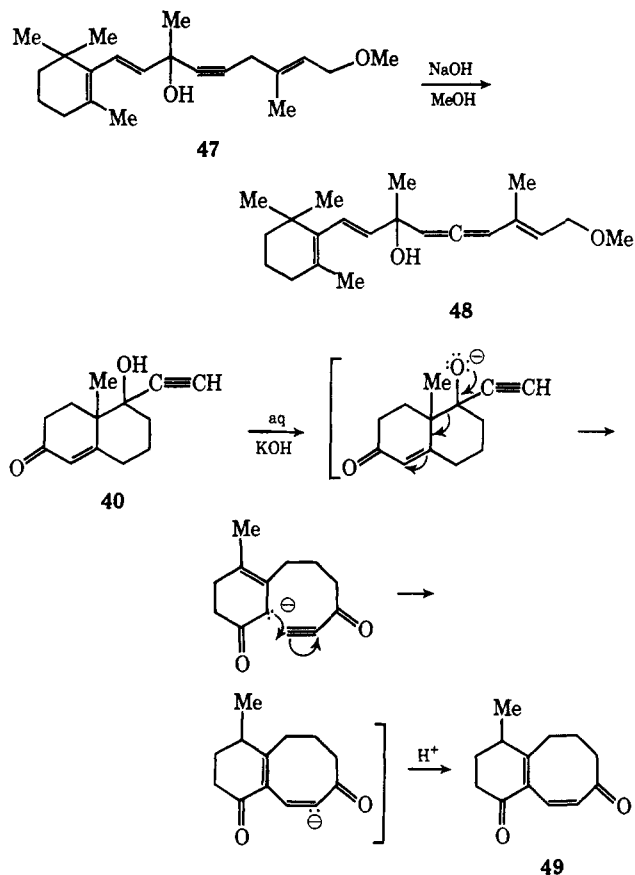


lead to products of the Meyer-Schuster type. Isomerizations to Rupe-type products seem to be unknown. The base-catalyzed isomerizations appear to proceed with propargylic shift of the α -acetylenic hydrogen.

B. SUBSTRATES

Secondary α -acetylenic alcohols like the one above isomerize as expected, but tertiary alcohols appear to yield other

products.¹⁶¹⁻¹⁶⁴ Thus the alcohol 47 is isomerized¹⁶⁵ to 48 while 40 is rearranged¹⁶⁶ to 49.



C. CATALYSTS

Alkalis like aqueous alcoholic potassium hydroxide^{159,165,167,168} and organic bases (amines) like pyridine,¹⁵⁹ diethylamine, and triethylamine¹⁶⁰ have been employed. The more potent inorganic catalysts degrade the rearrangement products further unless they are trapped with carbonyl reagents like hydrazine.¹⁶⁸ It is not known definitely whether pyridine causes rearrangements.¹⁵⁹

Sodium and potassium amides in liquid ammonia react with terminal α -acetylenic carbinols replacing the hydroxylic and acetylenic hydrogens and subsequently forming *C*- and *O*-monoalkyl and *C,O*-dialkyl compounds with alkyl halides.¹⁶⁹⁻¹⁷¹ Lithium amide in liquid ammonia also forms

(161) P. Rona and P. Crabbe, *J. Amer. Chem. Soc.*, **91**, 3289 (1969).

(162) S. A. Vartanyan and Sh. O. Babanyan, *Izv. Akad. Nauk Arm. SSR, Khim. Nauki*, **12**, 37 (1959); *Chem. Abstr.*, **54**, 6538 (1960).

(163) S. A. Vartanyan, S. A. Melkonyan, and Sh. O. Badanyan, *Zh. Org. Khim.*, **3**, 671 (1967).

(164) V. Wolf, W. Block, and H. Piater, *Justus Liebig's Ann. Chem.*, **682**, 112 (1965).

(165) S. Swaminathan, K. G. Srinivasan, and P. S. Venkataramani, *Tetrahedron*, **26**, 1453 (1970).

(166) W. Orosnik, A. D. Mebane, and G. Karmas, *J. Amer. Chem. Soc.*, **75**, 1050 (1953).

(167) M. Bertrand, *C. R. Acad. Sci.*, **247**, 824 (1958).

(168) R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworths, London, 1955, p 79.

(169) M. Barrelle, D. Plouin, and R. Glenat, *Bull. Soc. Chim. Fr.*, 449 (1967).

(170) M. D. d'Engenieres, M. Miocque, and J. A. Gautier, *ibid.*, 2477 (1964).

(171) M. D. d'Engenieres, M. Miocque, and J. A. Gautier, *ibid.*, 2480 (1964).

(159) G. R. Lappin, *J. Org. Chem.*, **16**, 419 (1951).

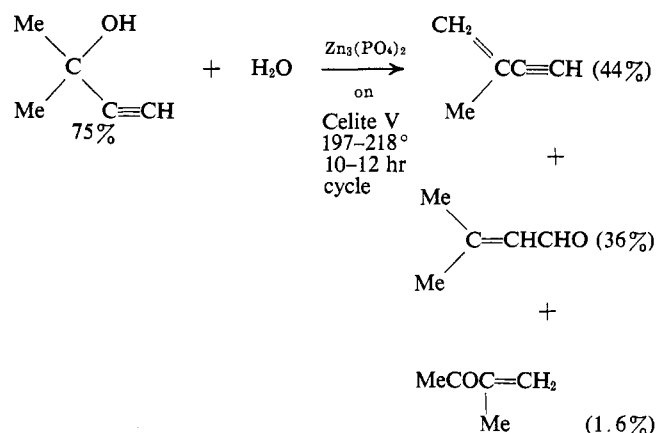
(160) A. W. Nineham and R. A. Raphael, *J. Chem. Soc.*, 118 (1949).

C,O-dilithio compounds, but only C-alkylation occurs with alkyl halides.¹⁷⁰⁻¹⁷² Alkylating agents like 1-bromo-3-chloropropane are extensively dehydrohalogenated by sodium and potassium amides.¹⁷¹ The allylethynyl compounds thus formed are rearranged to propenylethynyl compounds *via* vinylallenyl intermediates.¹⁷³ Methylacetylenic alcohols are isomerized to terminal acetylenic alcohols¹⁷⁴ by potassium amide in liquid ammonia.

V. Vapor-Phase Rearrangements

Reactions of ethynyl alcohols with catalysts in the vapor phase are primarily processes¹⁷⁵⁻¹⁷⁷ for preparing vinylacetylenes.^{80,139,147,148,178} In addition, Rupe as well as Meyer-Schuster types of products^{147,148} are also obtained; since the aldehydes formed are swept away from the catalyst continu-

ously, self-condensation is not possible and so they are isolated in significantly higher yields than in the liquid phase.^{179,180}



The thermolysis of α -ethynyl- α' -allyl¹⁸¹ and α' -propargyl- α -vinyl^{182,183} carbinols results in products arising from an oxy-Cope rearrangement.

(172) M. D. d'Engenieres, M. Miocque, and J. A. Gautier, *Bull. Soc. Chim. Fr.*, 201 (1968).

(173) J. Blanc Guenee, M. D. d'Engenieres, and M. Miocque, *ibid.*, 603 (1964).

(174) J. H. Van Boom, P. P. Montijn, M. H. Berg, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **84**, 813 (1965).

(175) I. M. Heilbron, E. R. H. Jones, J. B. Toogood, and B. C. L. Weedon, *J. Chem. Soc.*, 1827 (1949).

(176) T. H. Vaughn (to Union Carbide and Carbon Research Laboratories, Inc.), U. S. Patent 2,250,558 (1941); *Chem. Abstr.*, **35**, 7070 (1941).

(177) T. H. Vaughn (to Union Carbide and Carbon Research Laboratories, Inc.), U. S. Patent 2,197,956 (1940); *Chem. Abstr.*, **34**, 5461 (1940).

(178) C. Weizmann (to Percy May), British Patent 569,373 (1944); *Chem. Abstr.*, **41**, 5545 (1947).

(179) K. Suga and S. Watanabe, *Nippon Kagaku Zasshi*, **79**, 1167 (1958); *Chem. Abstr.*, **54**, 5505 (1960).

(180) T. Takeshima, K. Wakamatsu, and A. Furuhashi, *Bull. Chem. Soc. Jap.*, **31**, 640 (1958).

(181) A. Viola and J. H. MacMillan, *J. Amer. Chem. Soc.*, **92**, 2404 (1970).

(182) J. Chucho and N. Manisse, *C. R. Acad. Sci.*, **267**, 78 (1968).

(183) A. Viola and J. H. MacMillan, *J. Amer. Chem. Soc.*, **90**, 6141 (1968).