the mixture was poured into 50 ml. of ice-cold 10% sulfuric acid solution. The ether layer was separated, and the aqueous layer was washed twice with 50-ml. portions of ether. The ether layers were combined, washed with 5% sodium hydroxide solution, dried and the solvent was removed by distillation. A 75% yield of a mixture of 5-methyl-2-cyclohexenols consisting of 86% of the *trans* isomer (infrared analysis) was obtained. This alcohol mixture had $[\alpha]^{26}\text{D}$ 2.55° (*l* 1 dm., neat).

The optically active alcohol was oxidized to (+)5-methyl-2-cyclohexenone, $[\alpha]^{26}\text{D}$ 2.49° (*l* 1 dm., neat), with manganese dioxide as described above. The infrared spectrum of the optically active ketone was indistinguishable from that of authentic 5-methyl-2-cyclohexenone.

**Polarimetric Measurements.**—Optical rotations were measured with an O. C. Rudolph and Sons high precision model 80 polarimeter.

**Infrared Analyses.**—The *cis–trans* compositions of the binary mixtures were determined with a Baird Associates recording spectrophotometer. The mixtures of 5-methyl-2-cyclohexenyl chlorides were run as liquid films in a 0.025-mm. sodium chloride cell. The compositions of the binary mixtures were calculated from the optical densities at 7.84 μ (*cis* isomer) and 7.98 μ (*trans*-isomer) by solving the simultaneous equations

$$D^{7.84\mu}_{\text{mixture}} = (\%\ cis)D^{7.84\mu}_{cis} + (\%\ trans)D^{7.84\mu}_{trans}$$

$$D^{7.98\mu}_{\text{mixture}} = (\%\ cis)\ D^{7.98\mu}_{cis} + (\%\ trans)D^{7.98\mu}_{trans}$$

The optical densities of the pure isomers ($D$) were determined from the spectra of the pure isomers.

The spectra of the *cis–trans* mixtures of the acetates were run in approximately 3 *M* solutions in hexane, using a 0.025-mm. sodium chloride cell. Bands at 10.62 μ (present only in the spectrum of the *trans* isomer) and 11.42 μ (present only in the spectrum of the *cis* isomer) were used to calculate the *cis–trans* compositions using the equations

$$D^{10.62\mu}_{\text{mixture}} = k^{10.62\mu}_{cis}\ [cis] + k^{10.62\mu}_{trans}[trans]$$

$$D^{11.42\mu}_{\text{mixture}} = k^{11.42\mu}_{cis}\ [cis] + k^{11.42\mu}_{trans}[trans]$$

The $k$'s are constants (equal to the extinction coefficient times the cell thickness) determined from the spectra of the pure isomers. The $k$'s had the values: $k^{10.62}_{cis}$, 0.277, $k^{11.4}_{ci}$, 0.288; $k^{10.62}_{trans}$, 0.762; $k^{11.42}_{trans}$, 0.225.

The infrared analysis of mixtures of 5-methyl-2-cyclohexenols has been described previously.[5] In the present work, bands at 9.40 μ (present in the *trans* isomer) and 9.8 μ (present in the *cis* isomer) were used for the analysis.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE DIVISION OF ORGANIC CHEMISTRY OF THE ORTHO RESEARCH FOUNDATION]

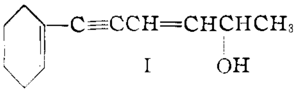
# Synthesis of Polyenes. VII. The Formation of Allenes in the Reduction of Acetylenic Polyenes with Lithium Aluminum Hydride

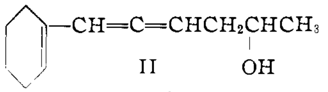
BY WILLIAM OROSHNIK

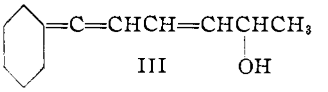
RECEIVED JANUARY 21, 1955

It has been shown that the grouping $-C{\equiv}C-CH{=}CH-\overset{\diagdown\diagup}{C}-OH$ is selectively reduced by lithium aluminum hydride to a β-hydroxyallene, the presence of conjugation on the other side of the acetylene group notwithstanding. Enyne glycols as well as their monoethers (allylic) also undergo this reaction to a minor extent, but the formation of the conjugated diene is the major reaction. Evidence is presented to show that an allylic hydroxyl group is vital for allene formation while a propargylic hydroxyl group is necessary for conjugated diene formation.

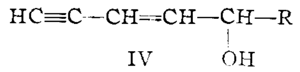
Recently Bharucha and Weedon reported the reduction of the conjugated divinylacetylene, I, with lithium aluminum hydride, and, on the basis of the diene band observed in the ultraviolet, $\lambda_{\max}$ 228 mμ, provisionally assigned to the product the allenic structure II.[1] The formation of allenes


I

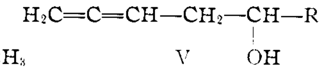

II


III

on reducing conjugated enynes with this reagent was subsequently confirmed by Bates, Jones and Whiting, who showed that simple acetylenylvinyl carbinols (IV) yield allenic alcohols V.[2] However, the structure of the product obtained from the divinylacetylene still remained in doubt since the 1:4 addition producing the allene group could conceivably have occurred on either side of the acetylene group, and each of the structures possible



$$\underset{\text{IV}}{HC{\equiv}C-CH{=}CH-\underset{\displaystyle OH}{\underset{|}{CH}}-R}$$

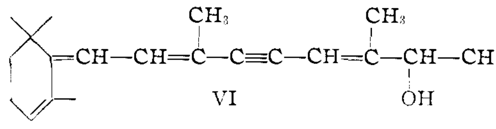


$$\underset{\text{V}}{H_2C{=}C{=}CH-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-R}$$

R = H or $CH_3$

thereby, II and III, would have satisfied the observed ultraviolet data. It appeared appropriate therefore to present data obtained in this Laboratory along similar lines which clearly define the course of the reaction in the longer polyenes, as well as the influence of hydroxyl groups on the extent of its occurrence.

Treatment of the acetylenic polyene VI, or its acetate, with lithium aluminum hydride yielded


VI

essentially a single product, which was shown by its infrared spectrum (Fig. 1) to be an allenic alcohol (strong bands at 2.98 and 5.15 μ). It proved to be a rather unstable material, oxidizing rapidly in air and rearranging and polymerizing extensively on heating or standing at room temperature. The small portion of distillate that could be obtained by rapid heating at 100–120° at $10^{-3}$ mm., although analyzing properly for $C_{20}H_{30}O$, showed only a very

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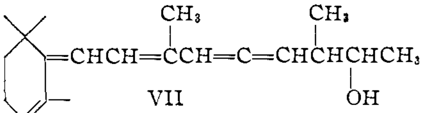
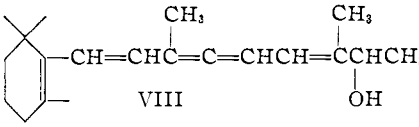
(1) K. R. Bharucha and B. C. L. Weedon, *J. Chem. Soc.*, 1584 (1953).

(2) E. B. Bates, E. R. H. Jones and M. C. Whiting, *ibid.*, 1854 (1954).

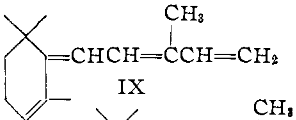
weak allene band (displaced now to 5.22 μ), as well as a considerably altered ultraviolet absorption spectrum. Chromatography of the undistilled product on neutralized alumina yielded a spectrally homogeneous product, but considerable polymerization occurred before it could be isolated from the eluate.

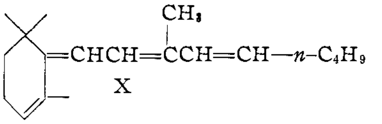
Although ultimate purification of the allenic alcohol was not accomplished, its structure nevertheless was deduced readily from its ultraviolet absorption curve. This showed $\lambda_{max}$ 312 mμ, which corresponds to a conjugated tetraene chromophore. Of the several possible allenes theoretically derivable from VI by a conjugate addition of hydrogen to the enyne or trienyne systems (*i.e.*, VII, by a 1:4 addition to the enyne; VIII, by a 1:8 addition to the trienyne; or the products of 1:6 or 1:4 addition to the trienyne), only structure VII is compatible with the ultraviolet data. In this compound, the last side-chain double bond would not participate in conjugation because of the non-planarity of the allene group.[3] The alternative possibilities would, for this reason, have shown only shorter chromophores, and no evidence for their presence was observed either in the crude product or among the impurities isolated on chromatography.

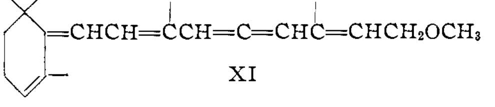

VII


VIII

In good agreement with the observed ultraviolet data and formulation VII, are the absorption properties of the compounds IX, X and XI, each of which contains the same conjugated tetraene chromophore shown for VII. These show $\lambda_{max}$ 310,[4] 315.5[5] and 317.5 mμ,[6] respectively, and their absorption curves very closely resemble that of the reduction product.[7]


IX


X


XI

An attempt was made to reduce the analogous non-allylic carbinol, 4,5-dehydro*retro*vitamin A (XII),[8] but this compound proved to be completely inert toward lithium aluminum hydride, even in the presence of a large excess of reagent.[13]

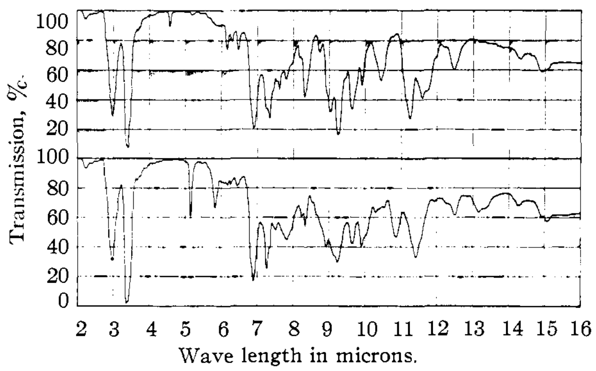
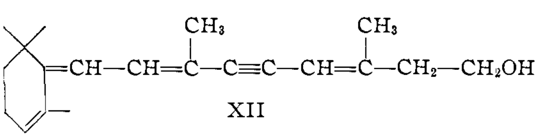
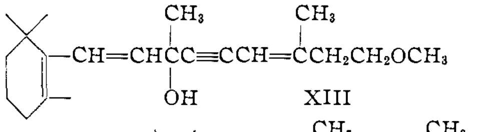


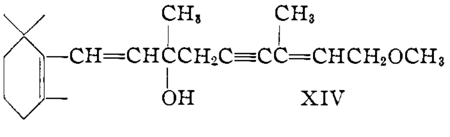
Fig. 1.—Infrared spectra: top curve, acetylenic polyene VI; bottom curve, allenic polyene VII (chromatographed product).[a]

[a] Although the 5.8 μ band would appear to suggest a carbonyl-containing impurity, its presence in the spectra of both the crude and the chromatographed products indicates it is an inherent vibrational mode of compound VII.


XII

These results and those of the British workers serve to establish this unique specificity of lithium aluminum hydride for the grouping $-C\equiv C-CH=CH-\overset{\diagdown\,\diagup}{C}-OH$, as a general reaction. Although the function of the *allylic* hydroxyl group here is at present obscure, it is obvious, from the negative results obtained with XII, that it plays a vital role in the reduction. A similar situation seems to prevail in the lithium aluminum hydride reduction of conjugated enynols to dienols discovered by Chanley and Sobotka,[9] and in the reduction of ethynylcarbinols to vinylcarbinols demonstrated by the British workers.[1,2] Experiments in this Laboratory have indicated that a *propargylic* hydroxyl group is necessary for such reductions to occur.[10,11] For example, compound XIII is converted readily to the corresponding dienol by


XIII


XIV

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[3] The spectral effects of an allene group in a conjugated polyene are discussed in part III[6] of this series.

[4] Unpublished observation in this Laboratory.

[5] W. Oroshnik and A. D. Mebane, THIS JOURNAL, **76**, 5719 (1954).

[6] W. Oroshnik, A. D. Mebane and G. Karmas, *ibid.*, **75**, 1050 (1953).

[7] It is interesting to note from this comparison that the bathochromic effect of a substituent group on a chromophore can operate through an allenic double bond as well as through the usual single bond.

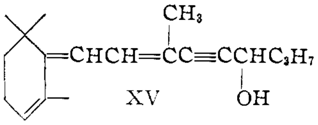
[8] The synthesis and properties of this compound will be described in a subsequent communication.

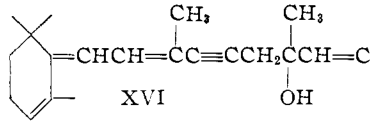
[9] J. D. Chanley and H. Sobotka, THIS JOURNAL, **71**, 4140 (1949).

[10] This principle also has been suggested by Bharucha and Weedon (ref. 1) but only on the basis of the results obtained with I.

[11] The ability of lithium aluminum hydride to reduce various α,β-acetylenic acids and esters to allylic alcohols [V. M. Mitchovitch and M. L. Mihailovic, *Compt. rend.*, **231**, 1238 (1950); G. E. Benedict and R. R. Russell, THIS JOURNAL, **73**, 5444 (1951); E. B. Bates, E. R. H. Jones and M. C. Whiting, ref. 2] is undoubtedly due to the initial reduction of the carboxyl to a hydroxyl group.

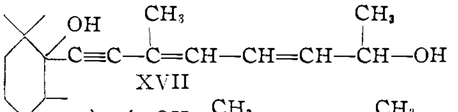
lithium aluminum hydride,[12] but the isomeric carbinol XIV[12] is unaffected. And similarly, the trienynol XV gives an excellent yield of the corresponding tetraenol,[5] while no reaction occurs with its desoxy analog.[5] The related trienynol XVI,[5]

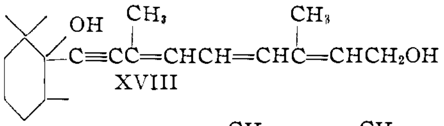

XV

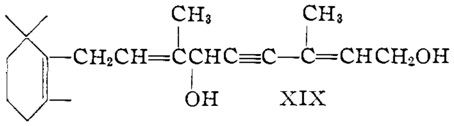

XVI

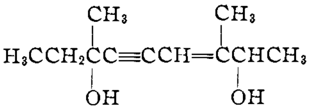
in which the hydroxyl group is not propargylic, likewise is unaffected by the reagent.[13]

When *both* allylic and propargylic hydroxyl groups are present in a conjugated enyne or polyenyne, it would now appear that allene as well as conjugated polyene formation should be possible on reduction with lithium aluminum hydride. Recent work with three such glycols, XVII,[14] XVIII[14] and XIX,[5] indicates that the formation of the conjugated polyene is the preferred reaction. However, the yields reported were far from satisfactory, and allenes may well have been present among the discarded by-products. This supposition is substantiated by the results obtained herein with the glycols XX and XXI. In both cases, appreciable amounts of allene were formed, and the yields of conjugated diene obtained were considerably lower than those from monohydroxy enynes.

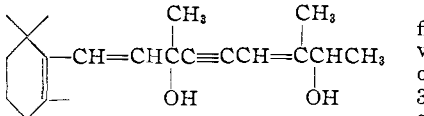

XVII


XVIII


XIX


$H_3CCH_2\overset{CH_3}{\underset{OH}{C}}C\equiv CCH=\overset{CH_3}{C}\underset{OH}{C}HCH_3$

XX


XXI

This side reaction was found to occur also with enyne glycols even when the allylic hydroxyl group is etherified. The successful reduction of such a compound, XIX monomethyl ether (primary), to the conjugated diene has been reported previously in part VI of this series.[5] An infrared examination of the distillation foreruns, which, fortunately, were still available at the time of this investigation, revealed considerable allene had been formed as a by-product. Similar results were obtained with the monoethyl ether (secondary) of XXI.

## Experimental[15]

**Absorption Spectra.**—The ultraviolet absorption spectra were determined in 95% ethanol with a Beckman DU spectrophotometer. The infrared spectra were determined on the neat compounds with a Baird double-beam spectrophotometer.

**Reduction of Compound VI.**—A solution of 20.4 g. of VI[5] in 50 ml. of dry ether was added, at 0°, to a stirred suspension of 2.0 g. of lithium aluminum hydride in one liter of dry ether. The mixture was refluxed for two hours, then cooled to −20° and hydrolyzed with 50% sodium potassium tartrate solution. The ether layer was filtered through anhydrous potassium carbonate and divided into two equal portions. One portion was set aside for chromatography and the other concentrated under vacuum. The latter after complete removal of volatiles at $10^{-3}$ mm. (24 hr. at room temperature), yielded 10.6 g. of a yellow viscous oil, $n^{25}D$ 1.5913.

*Anal.* Calcd. for $C_{20}H_{30}O$: C, 83.86; H, 10.56. Found: C, 82.51; H, 10.38.

Its ultraviolet absorption curve ($\lambda_{max}$ 312 mμ, $E^{1\%}_{1 cm.}$ 1,150; $\lambda\lambda_{infl.}$ 303, 325 mμ) was practically identical with that of the chromatographed product described below. Its infrared spectrum likewise showed no substantial difference from that of the chromatographed product (Fig. 1).

Rapid distillation of 5.0 g. of the above concentrate from a simple Claisen flask yielded 3.0 g. of distillate at 105–115° (0.001 mm.).

*Anal.* Found: C, 83.52; H, 10.43.

The ultraviolet absorption curve showed most of the original allene had isomerized ($\lambda\lambda_{max.}$ 275, 285, 310, 325 mμ; $E^{1\%}_{1 cm.}$ 525 at 285 mμ; $E^{1\%}_{1 cm.}$ 450 at 310 mμ). This was confirmed by the infrared spectrum in which the original strong allene band at 5.15 μ was now replaced by a very weak band at 5.22 μ. Also missing were the prominent bands appearing in Fig. 1 at 5.8, 10.85, 11.4 and 12.5 μ. This product was not further investigated.

The second half of the reduction product was freed of ether under vacuum, redissolved in petroleum ether, and chromatographed on a 3 × 65 cm. column of Alcoa F-20 alumina, deactivated with 10% of 1.5 *N* acetic acid. The first eluates (petroleum ether), contained chromatographic artifacts, $\lambda_{max.}$ 285 and 355 mμ. After a small intermediate fraction, elution with increasing proportions of ether in petroleum ether brought out the desired product, $\lambda_{max}$ 312 mμ, which continued, spectrally constant, until almost the entire chromatogram was eluted. A small final fraction (0.8 g. on concentration) showed $\lambda_{max}$ 300 mμ.

Concentration of the main fraction under vacuum and final removal of volatiles at 0.001 mm. yielded 8.5 g. of a very viscous, light yellow, but quite cloudy (polymer?) oil, $n^{18.5}D$ 1.5921, $\lambda_{max}$ 312 mμ, $E^{1\%}_{1 cm.}$ 1,240 (apparent ε 35,650); $\lambda\lambda_{infl.}$ 303, 325 mμ. Infrared absorption curve is given in Fig. 1.

*Anal.* Found: C, 82.74; H, 10.78.

The same results were obtained with the acetate[5] of VI, using the additional amount of lithium aluminum hydride required for the reduction of the ester group.

**Preparation of XX.**—A stirred solution of 11.0 g. of 4-methylhex-1-yn-3-en-5-ol[16] in 200 ml. of methylene dichloride was treated dropwise at 0° with 96 ml. of 2.1 *M* ethylmagnesium bromide and the mixture stirred for 48 hours at room temperature. A portion of the acetylenic Grignard reagent was deposited as a granular precipitate during this period. A solution of 11.0 g. of methyl ethyl ketone in 50

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[12] W. Oroshnik, G. Karmas and A. D. Mebane, This Journal, **74**, 3807 (1952).

[13] All of these comparisons refer to reactions in boiling ether.

[14] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen and T. Walker, *J. Chem. Soc.*, 1094 (1952).

[15] The lithium aluminum hydride used in this work was the commercial product supplied by Metal Hydrides, Inc., Beverly, Mass.

[16] E. R. H. Jones and J. T. McCombie, *J. Chem. Soc.*, 733 (1942), 261 (1943).

ml. of methylene dichloride was then added at room temperature and the mixture refluxed for six hours leaving a clear solution. Hydrolysis was effected at −20° with 30% ammonium acetate solution, and the methylene dichloride layer removed, washed with water, dried by filtering through anhydrous potassium carbonate and concentrated under vacuum. Distillation yielded 12.9 g. of product at 102–105° (0.12 mm.), $n^{20.5}\text{D}$ 1.5089, $\lambda_{\max}$ 231 m$\mu$, $\epsilon$ 15,200.

*Anal.* Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.29; H, 10.18.

The use of ether instead of methylene dichloride in the above reaction gave comparable yields, but both the acetylenic Grignard reagent and the addition product were gummy insoluble masses in ether and made stirring impossible.

**Reduction of XX.**—A mixture of 10.0 g. of XX, 3.1 g. of lithium aluminum hydride, and one liter of dry ether was stirred under reflux for three hours. The insoluble adduct which formed on mixing the reactants remained largely undissolved during this period. The crude reduction product, isolated as described in the reduction of VI, was distilled, cutting three fractions: (a) 1.8 g., b.p. 80–105° (0.65 mm.), $n^{18.5}\text{D}$ 1.5071; (b) 0.8 g., b.p. 105–109° (0.65 mm.), $n^{18.5}\text{D}$ 1.5093; (c) 7.1 g., b.p. 109–111° (0.65 mm.), $n^{18.5}\text{D}$ 1.5102, $\lambda_{\max}$ 237 m$\mu$, $E^{1\%}_{1\,\text{cm.}}$ 933.

All three fractions showed an allene band in the infrared at 5.10 $\mu$ accompanied by a very weak band at 4.85 $\mu$. Fraction c showed the characteristic strong *trans* —CH=CH— band at 10.35 $\mu$. This band was relatively weak in the other fractions.

Fraction c was redistilled, cutting two fractions. The first, 3.3 g., b.p. 106–110° (0.65 mm.), $n^{20}\text{D}$ 1.5119, $\lambda_{\max}$ 238 m$\mu$, $E^{1\%}_{1\,\text{cm.}}$ 785, showed the allene band at 5.10 $\mu$ as well as the accompanying 4.85 $\mu$ band; the *trans* —CH=CH— band at 10.35 $\mu$ was quite weak.

The second fraction, 3.3 g., b.p. 110–111° (0.65 mm.), $n^{20}\text{D}$ 1.5129, $\lambda_{\max}$ 238 m$\mu$, $E^{1\%}_{1\,\text{cm.}}$ 1,291, $\epsilon$ 23,800, showed the very strong *trans* —CH=CH— band but no allene or 4.85 $\mu$ band.

*Anal.* Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.78; H, 10.94.

**Preparation of XXI.**—The procedure described for XX was followed, substituting the equivalent amount of $\beta$-ionone for the methyl ethyl ketone and refluxing only a half-hour after the addition of the ketone. Distillation yielded 12.9 g. of a very viscous yellow liquid at 120–130° (0.002 mm.), $n^{20}\text{D}$ 1.5354, $\lambda_{\max}$ 233.5 m$\mu$, $\epsilon$ 19,500.

*Anal.* Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.44; H, 9.92.

**Reduction of XXI.**—A mixture of 12.6 g. of XXI, 2.0 g. of lithium aluminum hydride and 200 ml. of ether was stirred under reflux for three hours. The adduct in this case went into solution on heating. The crude product, isolated as described in the previous reductions, was distilled yielding 8.2 g. at 120–135° (0.001 mm.), $n^{22}\text{D}$ 1.5384; $\lambda_{\max}$ 240 m$\mu$, $E^{1\%}_{1\,\text{cm.}}$ 666. It showed the expected strong *trans* —CH=CH— band in the infrared at 10.35 $\mu$ and in addition a definite allene band at 5.10 $\mu$. The 4.85 $\mu$ band appearing in the reduction product of XX was not present here.

The product was redistilled at 0.001 mm., arbitrarily cutting three fractions: (a) 1.7 g., $n^{18.5}\text{D}$ 1.5353; (b) 2.9 g., $n^{19}\text{D}$ 1.5394, $\lambda_{\max}$ 240.5 m$\mu$, $E^{1\%}_{1\,\text{cm.}}$ 709; (c) 3.1 g., $n^{19}\text{D}$ 1.5426, $\lambda_{\max}$ 241 m$\mu$, $E^{1\%}_{1\,\text{cm.}}$ 801; apparent $\epsilon$ 24,400.

*Anal.* (fraction c) Calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.60. Found: C, 79.40; H, 10.72.

A little dehydration product ($\lambda\lambda$ 330, 348 and 367 m$\mu$) was now present in fraction c and is reflected in the somewhat high carbon values obtained. The allene band at 5.10 $\mu$ was present in all three fractions but was weakest in fraction c. This is in accord with the highest diene extinction (ultraviolet) recorded above for fraction c.

**4-Methyl-5-ethoxyhex-1-yn-3-ene.**—A solution of 44 g. of 4-methylhex-1-yn-4-ene-3-ol[16] and 30 ml. of boron trifluoride etherate in 450 ml. of absolute ethanol was allowed to stand at room temperature for 2.5 hours, at which time absorption spectral measurements indicated rearrangement was complete (*i.e.*, no further increase in extinction at 226 m$\mu$). The mixture was then made alkaline by the addition of ammonium hydroxide, diluted with a liter of water, and extracted five times with 100-ml. portions of petroleum ether. The combined extracts were filtered through anhydrous potassium carbonate and distilled, yielding 27.6 g. of product at 69–72° (30 mm.), $n^{20.5}\text{D}$ 1.4596, $\lambda_{\max}$ 226 m$\mu$, $\epsilon$ 13,000.

*Anal.* Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.65; H, 10.27.

**Preparation of XXI Monoethyl Ether.**—A solution of 22.6 g. of 4-methyl-5-ethoxyhex-1-yn-3-ene in 500 ml. of ether was treated at 0° with 81 ml. of 2.2 *M* ethylmagnesium bromide and the mixture stirred under gentle reflux for 18 hours. It was then cooled to 0°, 37.0 g. of $\beta$-ionone added, and, after a half-hour of refluxing, hydrolyzed at −20° with 30% ammonium acetate solution. The ether layer was separated, filtered through anhydrous potassium carbonate, and concentrated under vacuum. Distillation yielded 24.4 g. at 105–115° (0.001 mm.), $n^{22.5}\text{D}$ 1.5170, $\lambda_{\max}$ 232.5 m$\mu$, $\epsilon$ 20,000.

*Anal.* Calcd. for $C_{22}H_{34}O_2$: C, 79.95; H, 10.37. Found: C, 79.96; H, 10.48.

**Reduction of XXI Monoethyl Ether.**—A mixture of 28.4 g. of XXI monoethyl ether, 2.4 g. of lithium aluminum hydride and 500 ml. of dry ether was stirred at 5–10° for three hours. The crude reaction product, $\lambda_{\max}$ 238 m$\mu$, isolated as in the previous reductions, was dissolved in petroleum ether and chromatographed on a 3 × 90 cm. column of Alcoa F-20 alumina. Elution with increasing proportions of ether in petroleum ether gave three fractions: (a) 1.1 g., consisting of dehydration products and column artifacts; (b) 17.8 g. of the *bis* conjugated diene, $\lambda_{\max}$ 239–240 m$\mu$; (c) 6.5 g. of material showing $\lambda_{\max}$ 232–238 m$\mu$.

Fractions b and c showed an allene band at 5.15 $\mu$. Fraction b was distilled, yielding 15.6 g. of product at 117–119° (0.007 mm.), $n^{20.5}\text{D}$ 1.5247, $\lambda_{\max}$ 239 m$\mu$, $\epsilon$ 28,600. The infrared spectrum still showed the presence of some allene (very small band at 5.15 $\mu$).

*Anal.* Calcd. for $C_{22}H_{36}O_2$: C, 79.46; H, 10.91. Found: C, 79.94; H, 10.78.

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Raritan, New Jersey