[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Addition of Ketenes to α,β -Unsaturated Ethers

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The structure of the adduct of diphenylketene and ethyl vinyl ether was shown to be 2,2-diphenyl-3-ethoxycyclobutanone (VI) rather than 2,2-diphenyl-4-ethoxycyclobutanone (V) as given in the literature, through the identification of the two compounds, 3-ethoxy-4,4-diphenylbutyric acid (VII) and 4,4-diphenyl-3-butenoic acid (VII), produced on basic hydrolysis of the adduct. Other adducts of diphenylketene and α,β -unsaturated ethers were prepared. The adduct of ketene and dihydropyran XI was synthesized and its structure was established by conversion of it to the γ -lactone XII, a known compound, with alkaline hydrogen peroxide.

Disubstituted ketenes add readily to compounds containing sufficiently active double bonds such as cyclic conjugated dienes, and less readily to simple olefins, such as an alkene or cyclohexene. The products of these reactions are substituted cyclobutanones. Staudinger² has reported the reaction of diphenylketene with styrene, cyclopentadiene, cyclohexene and ethyl vinyl ether.

Since the diphenylketene-styrene adduct gave neither the standard ketone reactions nor condensation at the α -carbon atom with benzaldehyde, Staudinger decided that the carbonyl group in the cyclobutanone was very hindered, that the methylene group was not alpha to the carbonyl, and that the structure of the adduct was 2,2,4-triphenylcyclobutanone (I) rather than 2,2,3-triphenylcyclobutanone (II).

$$\begin{array}{cccc} & & & O \\ Ph-CH-C & & CH_2-C \\ & & & \\ CH_2-C-Ph & Ph-CH-C -Ph \\ & & & \\ I & Ph & II & Ph \end{array}$$

Staudinger found that this adduct reacted with base to give an acyclic acid which he formulated as 2,2,4triphenylbutyric acid (III). Bergmann³ showed, however, that this compound was instead 3,4,4triphenylbutyric acid (IV), which meant that the

structure of the original adduct must have been II rather than I as postulated by Staudinger.

Staudinger formulated the adduct of dipheny ketene and ethyl vinyl ether as 2,2-diphenyl-4ethoxycyclobutanone (V), but he gave no supporting evidence for this structure as opposed to 2,2diphenyl-3-ethoxycyclobutanone (VI). Structure V would be analogous to the structure which he assigned to the diphenylketene-styrene adduct, but this was shown to be formulated incorrectly.

$$\begin{array}{cccc} & & & & O & & & O \\ EtO-CH-C & & & CH_2-C & \\ & & & & & \\ CH_2-C-Ph & & EtO-CH-C-Ph & \\ & & & & & \\ V & Ph & & VI & Ph \end{array}$$

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That diphenylketene and ethyl vinyl ether should react to give V is unlikely considering the bond polarizations of the two starting compounds.

EtO--CH
$$\delta^+$$

 \parallel δ^+C
 \parallel δ^+C
 \parallel \parallel \parallel \square
CH₂ $\delta^ \delta^-CPh_2$

Addition to form VI would be quite reasonable, for the positive end of each double bond would then react with the negative end of the other.

Staudinger reported that this adduct reacted with base to give an acidic product melting unsharply about 116°. This reaction has been confirmed, our acidic product melting between $110-130^{\circ}$. This was shown to be a mixture of two acids, separable by crystallization, which were identified as 3-ethoxy-4,4-diphenylbutyric acid (VII) and 4,4-diphenyl-3-butenoic acid (VIII).

$$\begin{array}{c} \text{OEt} \\ \downarrow \\ \text{Ph}_2\text{CH} - \begin{array}{c} \text{CH} - \begin{array}{c} \text{CH}_2 - \begin{array}{c} \text{COOH} \end{array} \end{array} \\ \text{Ph}_2\text{C} = \begin{array}{c} \text{CH} - \begin{array}{c} \text{CH}_2 - \begin{array}{c} \text{COOH} \end{array} \\ \text{VIII} \end{array} \\ \end{array}$$

The identities were established by synthesizing the two acids unambiguously and by showing them to have undepressed melting points when mixed with the compounds obtained from the cyclobutanone adduct, and also to have identical infrared spectra.

Since both of the hydrolysis products of the adduct of diphenylketene and ethyl vinyl ether have a methylene group attached to the carboxyl carbon atom, it follows that the methylene group in the original cyclobutanone derivative must have been attached to the carbonyl group rather than one removed from it as in V, the formula postulated by Staudinger. From this it is obvious that the structure of this adduct is VI not V.

To synthesize acid VII, ketene was added to 2,2-diphenyl-1-ethoxyethyl chloride and the resulting product was hydrolyzed.

$$PH_{2}CHCH(OEt)Cl + CH_{2} = C = O \xrightarrow[]{0^{\circ}} O^{\circ}$$

$$Ph_{2}CHCH(OEt)CH_{2}COCl \xrightarrow[]{H_{2}O} VII$$

The authentic sample of acid VIII was prepared by the method of Borsche⁴ from diphenylacetaldehyde and malonic acid

$$Ph_2CH-CHO + CH_2(COOH)_2 \xrightarrow{pyridine} VIII + H_2O$$

When the mechanism for the base-catalyzed hydrolytic ring opening of the cyclobutanone ad-(4) W. Borsche, Ann., **526**, 1 (1936).

⁽²⁾ H. Staudinger and E. Suter, Ber., 53, 1092 (1920).

⁽³⁾ E. Bergmann and O. Blum Bergmann, J. Chem. Soc., 727 (1938).

duct is considered, the formation of the two products isolated, VII and VIII, can be explained. The intermediate A formed by the addition of a hydroxyl ion to the carbonyl of the ketone can cleave into carbanion B which then reacts bidirectionally either to form the anion of VII by proton transfer or to eliminate ethoxide ion to form VIII. It is believed that VIII is not formed by elimination of the elements of ethanol from VII or its anion since VII is stable under the conditions employed.

$$\begin{array}{ccc} & & & & & \\ & & & & \\ VI & + & & \\ OH^- & & & \\ OH^- & & & \\ \end{array} \begin{array}{c} & & & \\ CH_2 - C - OH \\ + & & \\ OH^- & & \\ A \end{array} \begin{array}{c} & & & \\ CH_2 C - OH \\ + & & \\ CH_2 C - OH \\ + & \\ OH \\ + &$$

Diphenylketene formed similar adducts with other α,β -unsaturated ethers. When allowed to react with a slight excess of dihydropyran at room temperature for 48 hours, either without solvent or in a little hexane, an almost quantitative yield of crystalline adduct IX was obtained. This reaction was complete in about an hour at 100° . The product was assigned the structure 8,8diphenyl-2-oxabicyclo[4.0.2]octan-7-one because of the analysis and of the known structure of the analogous adduct of diphenylketene and ethyl vinyl ether. This adduct is completely stable in air at room temperature, unlike the adduct of diphenylketene and ethyl vinyl ether which decomposes over a period of several weeks at room temperature. Like the other 2,2-diphenylcyclobutanones reported by Staudinger,² this adduct fails to undergo the usual ketone reactions. It can be isolated unchanged in good yield after treatment with 2,4-dinitrophenylhydrazine, phenylhydrazine, semicarbazide and lithium aluminum hydride. This adduct dissolves slowly in alcoholic potassium hydroxide at room temperature and more rapidly when the mixture is refluxed, and then forms an insoluble semi-solid when the solution is acidified. This indicates that the product(s) of this reaction are acidic, but no further work has been done to characterize them.

Diphenylketene was also found to add to vinyl ether to give a crystalline product X. That the product represented addition of two molecules of diphenylketene was proved by the elementary analysis and by the molecular weight. Its structure as 3,3'-oxybis - (2,2-diphenylcyclobutanone) again was based on the known structure of the analogous adduct of diphenylketene and ethyl vinyl ether. Both racemic and meso forms of X are conceivable, but only one crystalline modification was isolated.



Ketene itself adds much less readily than the disubstituted ketenes to double bonds and only a few such reactions are known. These reactions

are all with compounds containing relatively reactive olefinic double bonds. Ketene adds 1,2 to one of the double bonds of cyclopentadiene⁵ or cyclohexadiene⁶ to give substituted cyclobutanones. Staudinger⁷ showed that ketene will also add to the carbon-to-nitrogen double bond in benzalanil to give a substituted β -lactam. Schenck⁸ added ketene to the nitrogen-to-nitrogen double bond of azobenzene in the presence of ultraviolet light.

It was found in the present work that ketene reacted with dihydropyran to form a liquid adduct XI when the reactants were heated in a steel bomb at 100°. The infrared absorption spectrum of this adduct showed the expected absorption for the cyclobutanone carbonyl at 5.58 μ . When this adduct was treated with 2,4-dinitrophenylhydrazine, a yellow crystalline 2,4-dinitrophenylhydrazone was formed. The adduct dissolved in aqueous base and from this solution an oil separated on acidification. This indicates that the product(s) of this reaction are acidic, but no further work has been done on this reaction.

The cyclobutanone ring of the adducts of diphenylketene and unsaturated compounds is known to be expanded to a γ -lactone by reaction with alkaline hydrogen peroxide.⁹



When the ketene-dihydropyran adduct was treated with alkaline methanolic hydrogen peroxide, a crystalline γ -lactone was isolated. This lactone (XII) was identical with the lactone formed by treatment of 3-acetoxytetrahydropyran-2-yl chloride with ketene in the presence of zinc chlo-

$$\bigcup_{O} \overset{OAc}{Cl} \rightarrow CH_2 = C = O \xrightarrow{ZnCl_2} \overset{distil.}{\longrightarrow} XII$$

ride. A mixture of these two samples showed no melting point depression and the infrared spectra were identical.

Since the methylene group must be attached to the carbon holding the ether oxygen in the lactone (the addition of ketene to hemiacetal chlorides is a reaction known to proceed in this way¹⁰), then in the ketene–dihydropyran adduct the methylene group must also be attached to the carbon holding the ether oxygen. This eliminates the possibility that this adduct has the alternate structure XIII.



(5) T. Brooks and G. Wilbert, THIS JOURNAL, 63, 870 (1941).

(6) A. T. Blomquist and J. Kwiatek, ibid., 73, 2098 (1951).

(7) H. Staudinger, Ber., 57, 1035 (1917).

(8) G. O. Schenck and N. Englehard, Angew. Chem., 68, 71 (1956).
(9) J. R. Lewis, G. R. Ramage, J. L. Simonsen and W. G. Wainwright, J. Chem. Soc., 1837 (1937).

(10) A. T. Blomquist, R. W. Holley and O. J. Sweeting, THIS JOURNAL, 69, 2356 (1947), The adduct, therefore, is 2-oxabicyclo[4.0.2]octan-7-one.

This formulation for the adduct of ketene and dihydropyran is consistent also with the polarizations of the double bonds involved in the formation of the cyclobutanone ring



As shown by these data, ketene adds to the double bond in the same manner as does diphenylketene.

This is the first example of the addition of ketene itself to the double bond of an α,β -unsaturated ether, and the third example of the 1,2-addition of ketene to an olefinic double bond, the other two being cyclopentadiene and cyclohexadiene.

Experimental

All microanalyses were performed by Miss H. Beck. Diphenylketene, b.p. range 110-130° at 1 mm., was prepared by pyrolyzing the diazo compound formed by reaction of benzil monohydrazone and freshly precipitated yellow mercuric oxide.11

Diphenylketene and Ethyl Vinyl Ether.-Two grams of diphenylketene was mixed with 3 g. of ethyl vinyl ether. The mixture became warm. It was stored for 16 hr. under nitrogen. The mixture solidified when cooled to -80° . The excess of ethyl vinyl ether was filtered from product VI. After one recrystallization from pentene it melted at 64-67°, yield 1.8 g. (67%). A second recrystallization brought the m.p. to $67-69^{\circ}$ (reported² 70-71°.)

Anal. Calcd. for C₁₈H₁₈O₂: C, 81.29; H, 6.76. Found: C, 81.56; H, 6.79.

Basic Hydrolysis of 2,2-Diphenyl-3-ethoxycyclobutanone $(\mathbf{VI}).-\mathbf{To}$ 50 ml. of 5% methanolic potassium hydroxide was added 1.0 g. of VI, and the yellow solution was left for two days. Two volumes of water was added and the solu-tion was acidified with coned. hydrochloric acid. After cooling to 0-3° the solid was filtered off and washed with 50 ml. of water; m.p. 110-130°. When it was recrystallized from warm 75% alcohol the first bit of solid melted at 144-147°; mixture melting point with authentic VII, 145–148°. Repeating this procedure of filtering off the first solid that separated from solution ultimately gave 0.48 g. (45%) of this product.

The remaining solid, m.p. 96-114°, was dissolved in isopropyl ether and allowed to evaporate to dryness at 25° during 24 hours. Large cubic crystals formed which were removed mechanically from the smaller, stickler ones and were recrystallized from dilute alcohol. The melting point was 114–117° and when mixed with VII the melting point was depressed to 104–109°. This second substance isolated was mixed with authentic VIII, m.p. 117–118°, and found to melt at 115-117°. The infrared absorption spectra of these two substances were identical. A total yield of 0.1 g. of this material was isolated from the original reaction mixture, 10% yield.

Diphenylacetaldehyde was prepared by a modification of the synthesis of Breuer.¹²

The meso-hydrobenzoin, m.p. 133–135°, prepared from 50 g. of benzil by the procedure of Fieser, ¹³ was added to 700 ml. of 20% sulfuric acid, and the mixture was refluxed for an hour. Steam was then passed through the mixture for 10 hours until the distillate (7.5 liters) came over clear. Each liter of distillate was extracted thrice with 50 ml. of chloroform and the combined chloroform extracts were dried with calcium chloride. The solution was distilled and the diphenylacetaldehyde was collected at 100-105° and 0.1 mm.; yield 1.6 g. (32% from benzil).
 1-Ethoxy-2,2-diphenylethyl Chloride.—Diphenylacetal-

dehyde (8.0 g., 0.04 mole), was mixed with 2.0 g. of absolute

ethanol (0.04 mole) and anhydrous hydrogen chloride gas was added until the reaction mixture at 0° had gained 1.6 g. in weight (0.045 mole of hydrogen chloride). The cloudy liquid product was added to 100 ml. of benzene. The few drops of water that had separated were drawn off and the benzene solution was dried with calcium chloride. No further isolation of this hemiacetal chloride was attempted. 3-Ethoxy-4,4-diphenylbutyric Acid (VII).—To half of the

above benzene solution of the hemiacetal chloride was added 1 g. of anhydrous zinc chloride and the mixture was cooled in ice-water. Ketene was bubbled into the mixture for 6 hr. at about 0.1 mole per hour. The benzene was distilled off under reduced pressure without heating the bath above Then 100 ml. of 5% potassium hydroxide in methanol 40°. was added and the mixture was left overnight. Then 200 ml. of water was added and the mixture was extracted with 50 ml. of chloroform. The water solution was acidified with concd. hydrochloric acid and then extracted three times with 50 ml. of chloroform. When the chloroform from these extractions had been evaporated off, the brown residue solidified. After two recrystallizations from dilute alcohol containing a pinch of Norite, white crystalline VII was obtained, m.p. $150-151^{\circ}$, yield 1.5 g. or 26% from the diphenylacet-aldehyde. This substance was not diphenylacetic acid since a mixture of this substance with diphenylacetic acid melted about 110-138°.

Anal. Caled. for $C_{18}H_{20}O_3;$ C, 76.12; H, 7.01. Found: C, 76.45; H, 6.83.

4,4-Diphenyl-3-butenoic acid (VIII) was prepared from diphenylacetaldehyde and malonic acid in pyridine at 100° by the method of Borsche.⁴ It melted at 117-118° after recrystallization from dilute alcohol.

Diphenylketene and Dihydropyran.—A solution of 4.0 g. of diphenylketene and 2.0 g. of dihydropyran in 20 ml. of hexane was kept at 20-25° for one week. During this time 5.0 g. (88%) of adduct IX separated as a pale yellow crystal-line solid, m.p. 145–150°. Pure, colorless, crystalline IX, m.p. 154–155°, was obtained by one recrystallization from ethyl acetate.

Anal. Caled. for C₁₉H₁₈O₂: C, 82.02; H, 6.47. Found: C, 82.04; H, 6.39.

Diphenylketene and Vinyl Ether .--- To a hexane solution of 2.0 g. of diphenylketene was added 0.7 g. of vinyl ether and the mixture was left for a week under nitrogen. Two grams (75%) of the adduct X separated as pale yellow crystals. After two recrystallizations from ethyl acetate, the yield was 1.3 g. (50%) of pure white crystals, m.p. 162-164°.

Anal. Calcd. for $C_{32}H_{36}O_3$: C, 83.79; H, 5.73; mol. wt., 458. Found: C, 83.52; H, 5.79; mol. wt. (cryoscopically in camphor), 418. Calcd. for $C_{18}H_{16}O_2$ (addition of only one molecule of diphenylketene to vinyl ether): C, 81.85; H, 6.10; mol. wt., 264.

Ketene and Dihydropyran.-One mole (84 g.) of dihydropyran, an equal volume of toluene, and a few crystals of hydroquinone were put in a steel bomb of capacity 1200 ml., and cooled to -80° in a mixture of Dry Ice and acetone. One mole of ketene was added during 90 minutes. (The mixture of ketene and methane came out of the ketene generator at a rate of about 0.75 liter per minute, and when it was passed through the reaction mixture first, about 0.5 liter per minute came out.).

The bomb then was sealed and heated for 2 hours at 100°. After it was cooled to 0° it was opened. A little gas escaped and the black liquid was distilled at reduced pressure. About 180 ml. was distilled between 35 and 45° (30 mm.) and about 15 ml. of XI at 50-55° (0.5 mm.); yield of XI, 14 g. (12%).

Anal. Caled. for $C_7H_{10}O_2$: C, 66.67; H, 7.94. Found: C, 66.32; H, 7.89.

The 2,4-dinitrophenylhydrazone of XI was prepared by the procedure of Shriner and Fusion¹⁴ from an ethanol solution of the adduct and acidic ethanol-water solution of 2,4dinitrophenylhydrazine. From 0.5 g, of the adduct and 0.4 g, of the hydrazine, about 0.6 g, of the derivative was prepared. After recrystallization from 95% ethanol it melted at 118–119°.

⁽¹¹⁾ Org. Syntheses, 20, 47 (1940).

⁽¹²⁾ A. Breuer and T. Zincke, Ann., 198, 156 (1879).

⁽¹³⁾ L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1957, p. 175.

⁽¹⁴⁾ R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 129.

Anal. Caled. for $C_{13}H_{14}N_4O_6;\ C,\ 50.98;\ H,\ 4.58.$ Found: C, 51.32; H, 4.48.

Reaction of XI with Alkaline Hydrogen Peroxide .solution of 1 g. of potassium hydroxide (0.04 mole) and 8.5 ml. of 15% hydrogen peroxide (0.04 mole) in 50 ml. of methanol was added slowly to 2 g. (0.02 mole) of XI dissolved in 50 ml. of methanol cooled to -10° . The reaction mixture was kept at 0° for one hour and at 25° for 12 hr. It was then made acid to congo red paper (concd. HCl) and evaporated to a volume of 10 ml. at reduced pressure on a steam-bath. To the residue was added 10 ml. of water and the mixture was thrice extracted with 20 ml. of ether. The combined ether extracts were dried (MgSO₄) and the ether removed, whereupon the residue crystallized on cooling; crude yield of XII, 1 g. (40%). After one recrystal-lization from isopropyl ether it melted at 77-79° and showed no m.p. depression when mixed with the product (XII) prepared from the reaction of ketene with 3-acetoxytetrahydropyran-2-yl chloride, described below. spectra of the two samples were identical. Infrared

Tetrahydropyran-2,3-diol diacetate was prepared by the method of Hurd,¹⁵ in which dihydropyran is oxidized with hydrogen peroxide in *t*-butyl alcohol in the presence of osmium tetroxide followed by treatment with acetic anhydride. In this method 30% aqueous hydrogen peroxide is mixed with *t*-butyl alcohol and the water is removed with anhydrous sodium sulfate. Here the volume of the sodium sulfate and water mixture indicated that less than half of the

(15) C. D. Hurd and C. D. Kelso, THIS JOURNAL, 70, 1484 (1948);
 C. D. Hurd, J. Moffat and L. Rosnati, *ibid.*, 77, 2793 (1955).

water had been removed, but the results obtained were about the same as those described. Using the same amounts that were given in the literature, a yield of 115 g. of tetrahydropyran-2,3-diol diacetate, b.p. $100-120^{\circ}$ at 1-2 mm., was obtained, compared to the reported yield of 135 g. of b.p. $96-115^{\circ}$ at 1 mm.

3-Acetoxytetrahydropyran-2-yl Chloride.—To 10 g. of tetrahydropyran-2,3-diol diacetate was added 15 g. of a 25% hydrogen chloride in anhydrous ether solution. The mixture was stored at 0° and it turned light brown in a few minutes. After three days the mixture was distilled at reduced pressure, first at 20 mm. and finally at 0.2 mm. The distillate from 51-54° at 0.2 mm. was collected; yield 7.0 g. (77%).

Anal. Calcd. for $C_7H_{11}ClO_3$: C1, 19.9. Found: Cl, 17.7.

2-(3-Hydroxytetrahydropyran)-acetic γ -Lactone (XII).----Ketene was bubbled into 7 g. of 3-acetoxytetrahydropyran-2-yl chloride in 30 ml. of ethyl acetate containing 1 g. of zinc chloride at a rate of about 0.2 mole per hour for 4 hours at 0°. The entire mixture was distilled and the fraction boiling 70-90° at 0.2 mm. was collected. When 5 ml. of isopropyl ether was added to the distillate, it solidified and the solid was filtered off; yield 2.0 g. (43%). The material thus obtained melted at 77-79° and after recrystallization from isopropyl ether it melted at 79-80°.

Anal. Caled. for $C_7H_{10}O_3$: C, 59.01; H, 7.10. Found: C, 58.81; H, 7.31.

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Allylic Rearrangements. XLVII. The Silver Ion-assisted Hydrolysis of α - and γ -Methylallyl Chlorides. Preservation of Configuration in Allylic Cations¹

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The hydrolysis of *cis*- and *trans*-crotyl and α -methylallyl chlorides with aqueous silver nitrate is accompanied by structural isomerization, as well as formation of nixed butenyl nitrates. The compositions of the products from crotyl and α -methylallyl starting materials yield information on the degree of similarity of the respective cationic intermediates from which they arise. Evidence has been obtained in the present work that geometrical configuration of the allylic butenyl cation is preserved. Such preservation of configuration of allylic cations is expected on theoretical grounds, and recent related experiments and discussions are commented on.

In 1944, Young and Andrews⁸ reported the results of a brief investigation of the silver ionpromoted hydrolysis of crotyl and α -methylallyl chlorides IP and IS, which gave some indication of *cis-trans* isomerization within the allylic cationic intermediate IV. However, sufficiently accurate analytical methods were not available to settle the question.

On theoretical grounds, cis-trans isomerization within a short-lived allylic cationic intermediate IV would be rather surprising, as was pointed out some time ago.^{4,5} The bond order of the C₂-C₃ carbon– carbon bond and the expected barrier to rotation are still sufficiently high in a cation such as IV, that one would expect preservation of *cis* or *trans* configuration in the unrearranged product III even by way of a cationic intermediate.

With the recent introduction of vapor phase chromatography, it has become convenient to study isomerizations of the kind involved, and the hydrolysis of the butenyl chlorides has been studied further. The results of this study are reported and discussed in the present paper.

Results

Allylic Materials.—Methods of preparation were selected for the various allylic compounds necessary in the present study which would guarantee structural and geometric purity. a-Methylallyl and trans-crotyl alcohols IIIS and IIIPT were prepared by lithium aluminum hydride reduction of methyl vinyl ketone and trans-crotonaldehyde, respectively, in ether. As summarized in Table I, analysis by vapor phase chromatography (v.p.c.) indicated that the secondary alcohol IIIS contained none of its allylic isomer. Similar analysis indicated that the trans-primary compound IIIPT was not contaminated with the secondary isomer but contained $3.2 \pm 0.7\%$ cis-alcohol IJIPC. cis-Crotyl alcohol resulted from the semi-hydrogenation of 2-butyne-1-ol. It contained no secondary alcohol IIIS and $0.3 \pm 0.2\%$ of the corresponding *trans* isomer IIIPT. Due to the shape of the curves

⁽¹⁾ This work was supported in part by a grant from the National Science Foundation.

⁽²⁾ Standard Oil Co. of California Research Fellow, 1956-1957.

⁽³⁾ W. G. Young and L. J. Andrews, THIS JOURNAL, 66, 421 (1944).

⁽⁴⁾ S. Winstein, Bull. soc. chim. France, 18, C43 (1951).

⁽⁵⁾ M. Daudel, *ibid.*, **18**, C8, 42 (1951).