

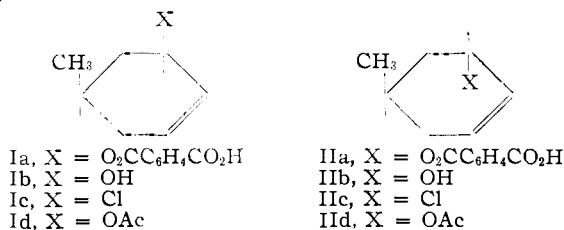
[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Stereochemistry of Allylic Rearrangements. IV. The Stereochemistry of the Conversion of *cis*- and *trans*-5-Methyl-2-cyclohexenol to 5-Methyl-2-cyclohexenyl Chloride¹BY HARLAN L. GOERING, THOMAS D. NEVITT AND ERNEST F. SILVERSMITH²

RECEIVED JANUARY 5, 1955

The reactions of *cis*-(Ib) and *trans*-5-methyl-2-cyclohexenol (IIb) with thionyl chloride, phosphorus trichloride and hydrogen chloride have been investigated in several solvents. The reaction of the isomeric alcohols with thionyl chloride in ether is stereospecific; the *cis*-alcohol Ib is converted to the *cis*-chloride Ic, and the *trans*-alcohol IIb is converted to the *trans*-chloride IId. Optically active chlorides are obtained from optically active alcohols by this method. The relative configurations of the optically active *cis*- and *trans*-alcohols and chlorides have been determined and these relationships show that the reaction of Ib and IIb with thionyl chloride in ether involves a stereospecific allylic rearrangement (*i.e.*, the chlorine atom becomes attached to the γ -carbon atom on the side of the ring originally occupied by the hydroxyl group). Binary mixtures of the isomeric chlorides Ic and IId are obtained from the reactions of the isomeric alcohols Ib and IIb with (1) thionyl chloride in hexane, (2) phosphorus trichloride in ether or hexane, and (3) hydrogen chloride in dioxane. In each case optically active products are obtained from optically active alcohols.

In previous papers in this series the isomeric anionotropic rearrangement of *cis*-(Ia) and *trans*-5-methyl-2-cyclohexenyl acid phthalate (IIa) in acetonitrile³ and the solvolysis of the isomeric acid phthalates in aqueous acetone⁴ have been described. We have now extended our studies to the chlorides and this paper describes the synthesis of racemic and optically active *cis*-(Ic) and *trans*-5-methyl-2-cyclohexenyl chloride (IId) and a stereochemical study of the replacement of the hydroxyl group by chlorine in the 5-methyl-2-cyclohexenyl system.



The isomeric 5-methyl-2-cyclohexenols⁵ were converted to the chlorides by reaction with: (1) thionyl chloride in ether and in hexane, (2) phosphorus trichloride in ether and in hexane, and (3) hydrogen chloride in dry dioxane. The results of these experiments are summarized in Table I, which shows the compositions of the isolated binary mixtures of *cis*-(Ic) and *trans*-5-methyl-2-cyclohexenyl chloride (IId) together with the optical activity of the products obtained from optically active alcohols. The compositions of the binary mixtures of Ic and IId were determined by infrared analysis and in every case the spectrum of the mixture was a composite of the spectra of the isomeric chlorides.

As shown by Table I (expt. 1 and 2) the reactions of the isomeric alcohols with thionyl chloride in ether are stereospecific. The 5-methyl-2-cyclohexenyl chloride (identified by its chemical composition and rates and products of solvolysis) obtained from *cis*-5-methyl-2-cyclohexenol (Ib) was fractionated with a short Vigreux column (the chlorides undergo *cis-trans* isomerization by pro-

longed heating required by more efficient columns) and the four fractions collected had physical properties, including infrared spectra, which were indistinguishable indicating the product to be homogeneous. The 5-methyl-2-cyclohexenyl chloride obtained from IIb was similarly found to be homogeneous and to have physical properties, including infrared spectra, differing from those of the chloride obtained from Ib. These results indicate that one of the isomeric chlorides (Ic or IId) is obtained from the *cis*-alcohol Ib and the other from the *trans*-alcohol IIb. This conclusion is supported by the fact that the infrared spectrum of each product has bands which are absent, weak or shifted in the spectrum of the other. The spectrum of the product from Ib has bands at 7.81, 10.93 and 13.03 μ , which are weak or absent in the spectrum of the product from IIb and the latter has bands at 8.00, 9.52 and 13.4 μ , which are absent or of lower intensity in the spectrum of the product from Ib. As little as 2% of one product in the other can be detected by these characteristic absorptions. It is noteworthy that the infrared spectra of all of the many preparations of each isomeric chloride (racemic and optically active) were indistinguishable. It is also significant that polarimetric and titrimetric first-order rate constants for acetolysis and ethanolysis (to be reported elsewhere) differ for the two products and do not show trends that would be expected if the products were binary mixtures of Ic and IId of different composition.

In order to determine the configurations of the isomeric chlorides they were related to the isomeric 5-methyl-2-cyclohexenols whose configurations have been unequivocally established.⁵ These relations are summarized in Chart I. The chlorides were converted to acetates by reaction with acetate ion (supplied as tetramethylammonium acetate) in acetone. It has been shown previously that under these conditions α -phenylethyl chloride is converted to the acetate with inversion of configuration⁶ and that α - and γ -methylallyl chlorides are cleanly converted to the corresponding acetates.⁷ The methylcyclohexenyl chloride obtained from the *cis*-alcohol (thionyl chloride in ether) was converted to a binary mixture of *cis*-(IId) and *trans*-5-methyl-2-cyclohexenyl acetate (IIId) consisting of 87% of the

(1) This work was supported by the Office of Ordnance Research.

(2) National Science Foundation Fellow, 1954-1955.

(3) H. L. Goering, J. P. Blanchard and E. F. Silversmith, THIS JOURNAL, **76**, 5409 (1954).(4) H. L. Goering and R. F. Silversmith, *ibid.*, **77**, 1129 (1955).(5) H. L. Goering and J. P. Blanchard, *ibid.*, **76**, 5405 (1954).(6) J. Steigman and L. P. Hammett, *ibid.*, **59**, 2536 (1937).(7) J. D. Roberts, W. G. Young and S. Winstein, *ibid.*, **64**, 2157 (1942).

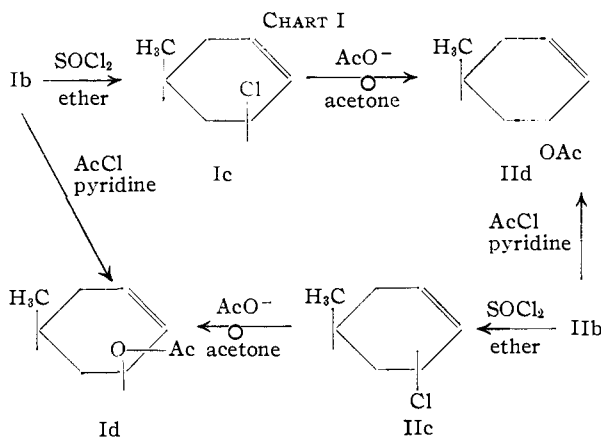
TABLE I

PRODUCTS ISOLATED FROM THE REACTIONS OF *cis*-(Ib) AND *trans*-5-METHYL-2-CYCLOHEXENOL (IIb) WITH THIONYL CHLORIDE, PHOSPHORUS TRICHLORIDE AND HYDROGEN CHLORIDE AT ROOM TEMPERATURE

Expt.	Alcohol	Reagent	Solvent	% Ic in binary mixt. of Ic and IIc ^a	$[\alpha]^{20D}$ of product
1	(-) <i>cis</i>	SOCl ₂	Ether	100	+32.3° (l 1 dm., neat) ^b
2	(-) <i>trans</i>	SOCl ₂	Ether	0	+32.4 (c 1.2, AcOH) ^c
3	(<i>dl</i>) <i>cis</i>	SOCl ₂	Hexane	59 ± 3	
4	(<i>dl</i>) <i>cis</i>	SOCl ₂ -Py	Hexane	39 ± 3	
5	(+) <i>cis</i>	PCl ₃	Hexane	32 ± 3	-65.0 (c 1, EtOH) ^b
6	(-) <i>cis</i>	PCl ₃	Hexane	32 ± 3	+71.0 (c 1, EtOH) ^b
7	(<i>dl</i>) <i>trans</i>	PCl ₃	Hexane	35 ± 3	
8	(+) <i>trans</i>	PCl ₃	Hexane	35 ± 3	-23.0 (c 1.5, AcOH) ^c
9	(<i>dl</i>) <i>cis</i>	PCl ₃	Ether	32 ± 3	
10	(<i>dl</i>) <i>cis</i>	PCl ₃ ^d	Ether	32 ± 3	
11	(<i>dl</i>) <i>cis</i>	PCl ₃ -Py	Ether	32 ± 3	
12	(-) <i>cis</i>	HCl	Dioxane	50 ± 3	+109.0 (c 3.7, dioxane) ^b

^a Determined by infrared analysis. ^b Calculated on the basis of optically pure Ib, $[\alpha]^{20D}$ 7.0° (l 1 dm., neat). ^c Calculated on the basis of optically pure IIb, $[\alpha]^{20D}$ 163.9° (l 1 dm., neat). ^d Run at -5°.

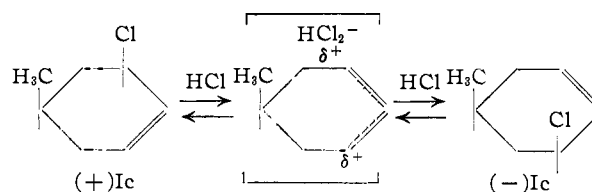
trans isomer (infrared analysis), and the chloride derived from the *trans*-alcohol was converted to a binary mixture of acetates consisting of 78% of the *cis* isomer Id. If it is assumed that this reaction involves predominating inversion, which seems very likely in view of the previous work referred to above, it follows that *cis*-5-methyl-2-cyclohexenyl chloride (Ic) is obtained from Ib, and *trans*-5-methyl-2-cyclohexenyl chloride (IIc) is obtained from IIb.



Unlike the reaction in ether, where clean retention of configuration is involved, the reaction of Ib with thionyl chloride in hexane gives rise to the isomeric chlorides (expt. 3). These results appear to be consistent with the observation of Boozer and Lewis⁸ that decompositions of secondary alkyl chlorosulfites, which are intermediates in the reactions of alcohols with thionyl chloride,⁹ proceed with predominating retention of configuration in dioxane and primarily with inversion of configuration in isoöctane, kerosene and toluene. The observation that the presence of pyridine increases the amount of inversion (expt. 4) also is consistent with previous findings.¹⁰

Optically active chlorides are obtained from the reaction of optically active Ib and IIb with thionyl

chloride in ether (expt. 1 and 2). In order to obtain active products it is necessary to isolate the chlorides without delay because they racemize rapidly in the reaction mixture. If the isolation of optically active Ic (or IIc) is delayed for over 15 minutes it is largely or completely racemic. The chlorides, however, do not undergo geometric isomerization to any detectable extent even if the product isolation is delayed for 2 hours. Indeed, geometric isomerization could not be detected (infrared analysis)¹¹ in any of the many preparations of optically active and racemic Ic and IIc, including completely racemic products from optically active alcohols. Preliminary experiments indicate that this racemization, which also occurs in dry dioxane containing hydrogen chloride (see below), is catalyzed by hydrogen chloride and probably involves "internal return"¹² from an ion-pair intermediate as illustrated below¹³ for the racemization of the *cis* isomer.¹⁴ Evidently the hydrogen chloride catalysis is similar to that which has been observed by Bartlett and Pöckel¹⁵ for the rearrangement of camphene hydrochloride to isobornyl chloride.



In order to further elucidate the stereochemistry of the reaction of the isomeric alcohols with thionyl chloride in ether the configurations of the reactant, (+)*cis*-5-methyl-2-cyclohexanol and product, (-)*cis*-5-methyl-2-cyclohexenyl chloride were related by

(11) As little as 2% of the geometric isomer can be detected in either Ic or IIc by the method of analysis.

(12) See previous papers in this series and references therein.

(13) The rotations have been arbitrarily assigned to the enantiomers in this illustration.

(14) It has been demonstrated previously that internal return in the 5-methyl-2-cyclohexenyl system is stereospecific in the sense that geometric isomerization does not occur (see ref. 3 and 4).

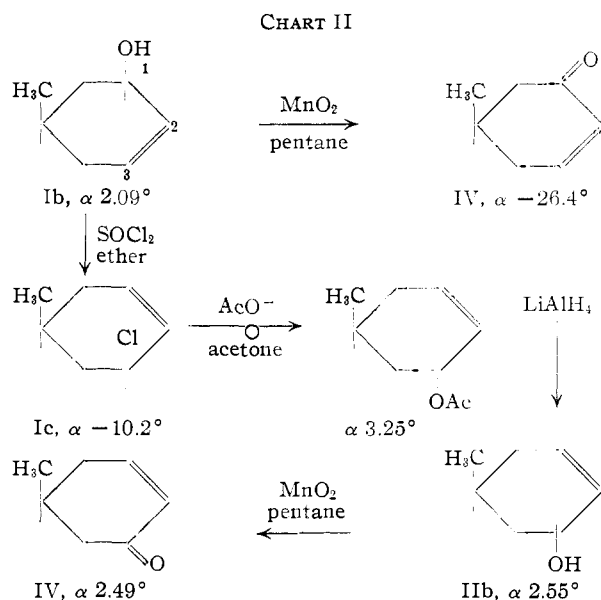
(15) P. D. Bartlett and T. Pöckel, *THIS JOURNAL*, **60**, 1585 (1938); see also P. D. Bartlett, "Organic Chemistry, An Advanced Treatise," Vol. III, H. Gilman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 66.

(8) C. E. Boozer and E. Lewis, *THIS JOURNAL*, **75**, 3182 (1953).

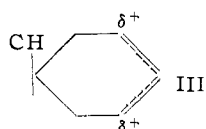
(9) E. S. Lewis and C. E. Boozer, *ibid.*, **74**, 308 (1952).

(10) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1252 (1937).

the series of reactions summarized in Chart II.^{13,16}



The reactions involving the conversion of the alcohol to the chloride and the chloride to the acetate have been discussed above. In the present case the isolated optically active acetate consisted of $83 \pm 2\%$ (infrared analysis) of the *trans* isomer (inversion). Since an optically active product is formed and since the conversion of both Ic and IIC to the acetates by this method results in predominating inversion of configuration it appears that an S_N2 type displacement is involved. The optically active *trans* isomer therefore is formed presumably without allylic rearrangement.⁷ The fact that the reaction does not result in complete inversion suggests that a simultaneous S_N1 displacement is involved.¹⁷ It seems likely that the *cis* isomer formed in the present reaction is optically inactive since it and indeed a part of the *trans* isomer probably are formed by an S_N1 process involving the symmetrical carbonium ion III.



The optically active alcohol isolated from the reduction of the acetate with lithium aluminum hydride consisted of $86 \pm 2\%$ of the *trans* isomer (infrared analysis). Since this reaction does not affect the configuration of the allylic asymmetric center (or that of C_5) the active alcohol has the same configuration as the active acetate as indicated in Chart II. Oxidation of the alcohol with manganese dioxide in pentane, a reaction which does not involve allylic rearrangement,¹⁸ gave (+)-5-methyl-

(16) The rotations reported in Chart II are observed rotations at 26° for pure liquid samples in a 1-dm. polarimeter tube.

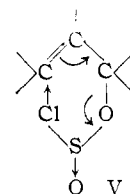
(17) The observation that the replacement is not cleanly bimolecular (S_N2) with Ic and IIC but appears to be with the butenyl chlorides (ref. 7) is not surprising since α, γ -dialkylallylic chlorides Ic and IIC are more susceptible to carbonium ion formation than the butenyl chlorides.

(18) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1430 (1952).

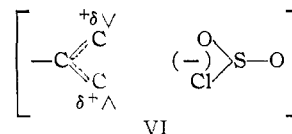
2-cyclohexenone (IV),¹⁹ the enantiomer of the ketone obtained by similar oxidation of (+)Ib. The active 5-methyl-2-cyclohexenones (IV) were identified by comparison of their infrared spectra, which showed the samples to be free of impurities, with that of authentic 5-methyl-2-cyclohexenone²⁰ and by chemical analysis.

Since the ketones obtained from the two methods are enantiomers, it is clear that a stereospecific allylic rearrangement has occurred in one of the steps. All of the reactions except one are known to proceed without allylic rearrangement in other systems and thus it follows that the rearrangement occurs in the conversion of the alcohol to the chloride, the chlorine becoming attached to C_3 . Comparison of the magnitudes of the rotations of the enantiomeric ketones (IV) shows that about 90% of the optical activity has been lost in the five-step process. As pointed out above, the chloride Ic racemizes rapidly under the conditions for its preparation and it is clear that considerable activity is lost in this step. Additional activity is undoubtedly lost in the conversion of the chloride to the acetate since part of the product probably is formed from a symmetrical carbonium ion intermediate (III).

The above stereochemical observations are consistent with the cyclic (S_N1') process (V) proposed by Roberts, Young and Winstein⁷ for the conversion of the intermediate chlorosulfite to product. There is evidence⁹ that ionic intermediates are in-



involved in the decomposition of alkyl chlorosulfites indicating that the cyclic process summarized by V may involve internal return from an ion-pair intermediate, VI.²¹ This interpretation, which is consistent with the experimental results providing that the ions in VI are rigidly oriented, is attractive because the present process appears to be similar to the intramolecular rearrangement of the isomeric 5-methyl-2-cyclohexenyl acid phthalates in which ion-pair intermediates evidently are involved.^{3,4}



As shown in Table I the reactions of the isomeric alcohols with phosphorus trichloride yield binary mixtures of Ic and IIC of similar composition and the composition is not affected by varying solvent or temperature or by the presence of pyridine.

(19) The fact that the sign of the rotation of the ketone (+IV) is the same as that of the alcohol IIB from which it is derived is consistent with the observation that (-)IIB (100% *trans*), $[\alpha]^{25D} -30.4^\circ$ (neat), is oxidized to (-)IV, $[\alpha]^{25D} -16.8^\circ$ (neat).

(20) J. P. Blanchard and H. L. Goering, *THIS JOURNAL*, **73**, 5863 (1951).

(21) A similar ion-pair intermediate has been suggested by D. J. Crain, *ibid.*, **75**, 332 (1953), for the decomposition of 3-phenylbut-2-yl chlorosulfite.

Control experiments show that Ic is isomerized under the conditions of the reactions; however, the isomerization is slow and it appears that the product composition is for the most part determined by kinetic control.

It has been proposed¹⁰ that the reaction of an alcohol with phosphorus trichloride involves the formation of an intermediate phosphorus ester chloride (ROPCl₂), with retention of configuration, followed by conversion of the intermediate to the chloride. Presumably the intermediate can be converted to product (chloride) by an S_N2 process (inversion), an S_N1 process (racemization) or an S_Ni (or S_Ni') process (retention) depending upon the conditions of the reaction and structure of the original alcohol.¹⁰ The formation of mixtures of Ic and Iic from the isomeric alcohols and the formation of optically active products from active alcohols can be explained by a combination of these processes but not by any one. The conversion of active Ib to chloride by either an S_N2 process with inversion or an S_Ni' process (similar to that illustrated by V) would give an active product with the sign of the rotation corresponding to that which is observed. In the case of the S_N2 process the rotation would be due to active Iic and for an S_Ni' process the rotation would be due to active Ic. It appears that the rotation of the product from active Ib is due to active Iic since the polarimetric solvolysis rate (to be reported in a future paper) of the product is indistinguishable from that of (-)Iic (100% *trans* isomer). Similarly, the product from (+)Iib (expt. 8) has a polarimetric rate indistinguishable from that of active Ic (100% *cis* isomer) indicating that the optical activity in this case is due to the formation of active Ic. The polarimetric rates for Ic and Iic differ by only about 10%, however, and thus this is not a sensitive method for determining the composition of the active component in the mixture. If indeed an intermediate phosphorus ester chloride is involved, the data in Table I indicate that it is converted to product by two simultaneous processes: an S_N2 process giving rise to optically active chloride from active alcohol with inversion of configuration, and an S_N1 process giving rise to a mixture of isomeric chlorides.²²

Our interest in the reaction of *cis*-5-methyl-2-cyclohexenol with hydrogen chloride in dry dioxane resulted from the unexpected observation²³ that under these conditions the alcohol is converted to chloride instead of undergoing the expected acid-catalyzed "oxotropic"²⁴ rearrangement. Braude and co-workers have reported²⁴ that under these conditions α -phenylallyl alcohols are rearranged (acid-catalyzed) to γ -phenylallyl alcohols.

When (-)Ib was treated with hydrogen chloride in dry dioxane an increase in the rotation was observed instead of the expected first-order loss of optical activity. In a typical experiment a dioxane solution 0.3 *M* in (-)Ib and 1 *M* in hydrogen chloride was thermostated at 30°. As illustrated by

(22) This explanation is similar to that proposed by W. G. Young and J. F. Lane, *THIS JOURNAL*, **59**, 2051 (1937), for the reaction of α - and γ -methylallyl alcohol with phosphorus tribromide.

(23) J. P. Blanchard, Ph.D. Thesis, University of Wisconsin, 1953.

(24) E. A. Braude, E. R. H. Jones and E. S. Stern, *J. Chem. Soc.*, 396 (1946).

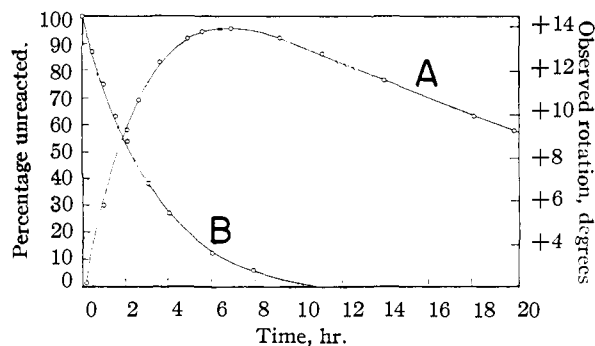
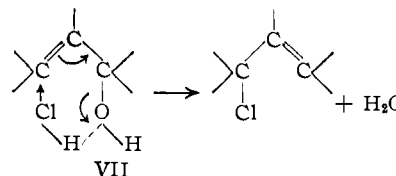


Fig. 1.—Rate of reaction of 0.3 *M cis*-5-methyl-2-cyclohexenol with 1 *M HCl* in anhydrous dioxane at 30°: A, observed rotation of the reaction mixture (right-hand scale); B, percentage *cis*-5-methyl-2-cyclohexenol unreacted (left-hand scale).

Fig. 1 (curve A)²⁵ the rotation increased rapidly until a maximum was reached (seven hours) and then decreased gradually.²³ When the concentrations of alcohol and hydrogen chloride were varied the rates of change in rotation (curve A) and consumption of alcohol (curve B)—measured by the consumption of acid—were changed, but the general picture was the same.²³ From the behavior of the optical activity and the consumption of alcohol it is obvious that alcohol is converted to chloride and in the present work this has been confirmed by isolation of the chloride (expt. 12, Table I). It is clear that the conversion of the alcohol to chloride is stereospecific in the sense that an active product is obtained and the data in Fig. 1 indicate that the initially formed active chloride is racemized slowly under the conditions of the reactions. It is significant that Ic is not appreciably isomerized to Iic under the conditions of the reaction, which indicates that the product composition (Table I) is determined by kinetic control and that the racemization must be of the same type that occurs in the thionyl chloride reaction. Because of the high activity of the product it appears that both of the isomeric chlorides formed in the reaction may be optically active.

The present results can be explained by two simultaneous processes. The S_N2 process which previously has been proposed to account for the conversion of an alcohol to chloride with inversion of configuration¹⁰ would in the present case result in the conversion of (-)Ib to (+)Iic. The *cis*-chloride may result from the S_N1 process previously suggested¹⁰ to account for racemization in the conversion of an alcohol to chloride with hydrogen chloride. However, this would give rise to racemic Ic (and require that part of the Iic be formed by this same process) and the magnitude of the rotation suggests that the *cis* isomer is contributing to the



(25) (-)Ib has a positive rotation in dioxane as illustrated by the initial value (+1.54°) in Fig. 1.

rotation. It is possible that a cyclic process VII involving the hydrogen-bonded complex of (-)Ib and hydrogen chloride may be involved. This process would convert (-)Ib to (+)Ic and thus a combination of the SN2 process and the cyclic process could account for the conversion of (-)Ib to a product (consisting of (+)Ic and (+)IIc) with a high positive rotation.

Acknowledgment.—We are indebted to Professor W. G. Young for disclosing the results of a study of the reactions of allylic alcohols with thionyl chloride prior to publication. This information was of considerable help in developing some of the experimental procedures used in the present work.

Experimental

Synthesis and Resolution of *cis*- and *trans*-5-Methyl-2-cyclohexenol.—The synthesis of *cis*- and *trans*-5-methyl-2-cyclohexenol and the resolution of the *cis* isomer have been described in an earlier paper.⁵ In the present work it was found that partially resolved (-)*cis*-5-methyl-2-cyclohexenol also can be obtained from the mixture of isomeric 5-methyl-2-cyclohexenols (95% of the *cis* and 5% of the *trans* isomer) which results from the reduction of 5-methyl-2-cyclohexenone with lithium aluminum hydride.⁶ This mixture of isomeric alcohols was converted to the cinchonidine salt of the acid phthalate by the same procedure⁵ that was used to convert *cis*-5-methyl-2-cyclohexenol to the cinchonidine salt of the acid phthalate. The portion of salt that precipitated from the solvent (dry acetone) was recrystallized twice from acetone and reconverted to (-)*cis*-5-methyl-2-cyclohexenol, b.p. 82° (25 mm.), $[\alpha]^{25}_D -2.75^\circ$ (*l* 1 dm., neat). From 168 g. of a mixture of 5-methyl-2-cyclohexenols, consisting of 95% of the *cis* isomer, 23.5 g. (14%) of partly resolved (-)*cis*-5-methyl-2-cyclohexenol was obtained in this way. The infrared spectrum of the optically active material was indistinguishable from that of authentic *cis*-5-methyl-2-cyclohexenol.

(+)*cis*-5-Methyl-2-cyclohexenol was obtained by resolving partly resolved (+)*cis*-5-methyl-2-cyclohexenyl acid phthalate, $[\alpha]^{25}_D 29^\circ$ (*c* 2, CHCl₃), and hydrolyzing the latter. The partly resolved acid phthalate was recovered from its cinchonidine salt which was obtained from mother liquors of resolutions which gave optically pure (-) acid phthalate.⁵ Equimolar amounts of the partly resolved acid phthalate and brucine were dissolved in dry acetone (3 ml. of solvent per gram of acid phthalate) at room temperature. Before the brucine was completely dissolved the brucine salt started to precipitate and in 20 minutes 60% of the salt had separated. A sample of this material was hydrolyzed to *cis*-acid phthalate having $[\alpha]^{25}_D 54.2^\circ$ (*c* 2, CHCl₃); when the brucine salt was recrystallized three times from acetone the (+)*cis*-5-methyl-2-cyclohexenyl acid phthalate had m.p. 50.0–50.6°, $[\alpha]^{25}_D 60.1^\circ$ (*c* 2, CHCl₃).

Anal. Calcd. for C₁₅H₁₆O₄: C, 69.21; H, 6.20. Found: C, 69.27; H, 6.18.

The acid phthalate was converted to (+)*cis*-5-methyl-2-cyclohexenol, b.p. 83° (25 mm.), $[\alpha]^{30}_D 6.95^\circ$ (*l* 1 dm., neat), in the usual manner.⁵ The infrared spectrum of this material was indistinguishable from that of authentic *cis*-5-methyl-2-cyclohexenol.

Anal. Calcd. for C₇H₁₂O: C, 74.95; H, 10.78. Found: C, 75.38; H, 10.83.

Optically active *trans*-5-methyl-2-cyclohexenols were obtained from the corresponding active acid phthalates. The partial resolution of *trans*-5-methyl-2-cyclohexenyl acid phthalate has been described previously.⁵ By the same method optically pure (-)*trans*-5-methyl-2-cyclohexenyl acid phthalate has been obtained which melts at 90–90.2° and has $[\alpha]^{25}_D -130.4^\circ$ (*c* 0.25, CHCl₃).

Anal. Calcd. for C₁₅H₁₆O₄: C, 69.21; H, 6.20. Found: C, 69.35; H, 6.22.

Optically pure (-)*trans*-5-methyl-2-cyclohexenol,²⁶ b.p. 82–83° (24 mm.), $[\alpha]^{27}_D -163.9^\circ$ (*l* 1 dm., neat), was ob-

tained from the corresponding acid phthalate in the usual manner.⁵

Anal. Calcd. for C₇H₁₂O: C, 74.95; H, 10.78. Found: C, 74.58; H, 10.83.

Partly resolved (+)*trans*-5-methyl-2-cyclohexenyl acid phthalate, m.p. 90.2–90.5° $[\alpha]^{27}_D 4.0^\circ$ (*c* 6.5, CHCl₃), was recovered from the mother liquors of the above resolution as described previously.⁵

Anal. Calcd. for C₁₅H₁₆O₄: C, 69.21; H, 6.20. Found: C, 69.11; H, 6.23.

A more highly resolved sample of this acid phthalate was converted to (+)*trans*-5-methyl-2-cyclohexenol,²⁶ b.p. 68–69° (24 mm.), $[\alpha]^{27}_D 127.0^\circ$ (*c* 19.4, acetone).

Anal. Calcd. for C₇H₁₂O: C, 74.95; H, 10.78. Found: C, 74.87; H, 10.84.

***cis*-5-Methyl-2-cyclohexenyl Chloride.**—Ten grams (89 mmoles) of *dl-cis*-5-methyl-2-cyclohexenol was added to a solution of 11 g. (93 mmoles) of thionyl chloride (Eastman Kodak Co. White Label grade) in 100 ml. of anhydrous ether at room temperature. In large-scale preparations (up to 50 g. of alcohol) the reaction flask was cooled in an ice-bath. After the effervescence had subsided, the ether and excess thionyl chloride were removed rapidly by distillation under reduced pressure and the residue was fractionated with a short Vigreux column under reduced pressure. The product, b.p. 60–62° (25 mm.), was collected in four fractions which totalled 8.3 g. (65% yield). The infrared spectra of the four fractions were indistinguishable and differed from that of *trans*-5-methyl-2-cyclohexenyl chloride obtained from *trans*-5-methyl-2-cyclohexenol by this same procedure. This product was shown (see below) to be *cis*-5-methyl-2-cyclohexenyl chloride and had b.p. 60–62° (25 mm.), $d^{25}_4 0.9952$, $n^{25}_D 1.4730$, $M_R 36.81$ (calcd. 36.84).

Anal. Calcd. for C₇H₁₁Cl: C, 64.37; H, 8.49; Cl, 27.15. Found: C, 64.63; H, 8.44; Cl, 27.17.

Optically active *cis*-5-methyl-2-cyclohexenyl chloride can be prepared from active *cis*-alcohol (see Table I) providing that the product is isolated rapidly from the reaction mixture. If the product is not isolated as soon as the addition of the alcohol is complete the product, which is the pure *cis* isomer, has little or no activity. For example, when the workup was delayed for 30 min. the product from active *cis*-alcohol was racemic *cis*-chloride. Speed in working up the product is required only when an active chloride is being prepared as it was found that delaying the workup for 2 hours did not cause detectable (infrared analysis) geometric isomerization.

When optically active 5-methyl-2-cyclohexenyl chloride was dissolved in a simulated reaction mixture (containing thionyl chloride and saturated with dry hydrogen chloride) and isolated by the above procedure about 50% of the optical activity was lost in one experiment, 75% in another and 35% in the third experiment. In each case the *cis-trans* isomer ratio of the product was identical with that of the original active chloride.

cis-5-Methyl-2-cyclohexenyl chloride slowly undergoes geometric isomerization at 60° and for this reason this compound could not be fractionated at 25 mm. with an efficient column. When *cis*-5-methyl-2-cyclohexenyl chloride, containing 5% of the *trans* isomer, was fractionated at 25 mm. with an efficient all-glass column all of the fractions obtained contained more than 5% of the *trans* isomer.

trans-5-Methyl-2-cyclohexenyl chloride was prepared from *trans*-5-methyl-2-cyclohexenol by the above procedure. The product distilled with constant physical properties including infrared spectrum (4 fractions were taken) indicating that it was homogeneous. *trans*-5-Methyl-2-cyclohexenyl chloride has b.p. 60–61° (25 mm.), $d^{25}_4 0.998$, $n^{25}_D 1.4778$, $M_R 37.03$ (calcd. 36.84).

Anal. Calcd. for C₇H₁₁Cl: C, 64.36; H, 8.49; Cl, 27.15. Found: C, 64.67; H, 8.79; Cl, 27.17.

Optically active *trans*-5-methyl-2-cyclohexenyl chloride is obtained from active alcohol providing the product is isolated immediately after the addition of the alcohol.

Conversion of 5-Methyl-2-cyclohexenols to 5-Methyl-2-cyclohexenyl Chlorides.—The results of these experiments are summarized in Table I. The procedure for the reaction of the alcohols with thionyl chloride in ether has been de-

(26) The infrared spectrum of this material was indistinguishable from that of authentic *trans*-5-methyl-2-cyclohexenol (ref. 5).

(27) Determined by Vollhard titration of completely solvolyzed solutions.

scribed above. The same procedure was used when freshly distilled hexane, b.p. 65°, was substituted for ether. Equimolar amounts of pyridine and thionyl chloride (1.05 moles of each per mole of alcohol) were used in expt. 4. In these runs the pyridine hydrochloride was removed by three extractions with cold water and the products were isolated from the dried organic solution as described above. All of the experiments involving thionyl chloride were carried out at approximately the same concentrations (100 ml. of solvent for 0.10 mole of 5-methyl-2-cyclohexenol). In all of the experiments the products were isolated by rapid distillation from a distilling flask so as to avoid fractionation.

The reactions involving phosphorus trichloride were carried out as follows: To a solution of 2.24 g. (20 mmoles) of *cis*- or *trans*-5-methyl-2-cyclohexenol in 10 ml. of solvent (ether or hexane) was added 2.88 g. (21 mmoles) of phosphorus trichloride (Eastman Kodak Co. White Label grade) and the resulting solution was allowed to stand at room temperature for about one hour. The solvent and excess phosphorus trichloride were taken from the reaction mixture under reduced pressure and the product was isolated by distillation at 25 mm. through a short Vigreux column. This distillation was carried out so as to avoid fractionation and the infrared spectrum of the product was found to be a composite of the spectra of the isomeric chlorides. The yield of the binary mixture of the isomeric chlorides was about 60% when the reaction was carried out in ether and 80% when hexane was used. In some experiments 0.007 ml. of pyridine was added to the reaction mixture prior to the addition of phosphorus trichloride. In these experiments the reaction mixtures were washed with water and dried before subsequent isolation of the product. The compositions of the binary mixtures of *cis*- and *trans*-5-methyl-2-cyclohexenyl chloride were determined by infrared analysis (see below) and are shown in Table I. When *cis*-5-methyl-2-cyclohexenyl chloride was mixed with an equimolar amount of *cis*-5-methyl-2-cyclohexenol and carried through the reaction sequence the product consisted of 29% of the *trans* and 71% of the *cis* isomer compared with 34% of the *trans* and 66% of the *cis* isomer expected had no isomerization of the added chloride occurred.

The reaction of the *cis*-alcohol with hydrogen chloride in dry dioxane was carried out as follows. A 1.25 *M* solution of hydrogen chloride in dioxane was prepared by passing dry hydrogen chloride into pure dioxane.²⁸ *cis*-5-Methyl-2-cyclohexenol, 5.6 g. (0.05 mole), was dissolved in 125 ml. of the dioxane solution and the resulting solution was thermostated at 30° for 14 hours. At this point the solution was 0.78 *M* in hydrogen chloride (determined by rapid titration of an aliquot with standard aqueous base) indicating that an equivalent amount of hydrogen chloride (0.05 mole) had been consumed. The reaction mixture was diluted with 150 ml. of freshly distilled pentane, b.p. 36°, and the resulting solution was extracted with four 100-ml. portions of water (to remove the dioxane) and dried over magnesium sulfate. After removal of the pentane by distillation the product was flash distilled. The product was shown to be a binary mixture (consisting of equal amounts of *cis*- and *trans*-5-methyl-2-cyclohexenyl chloride) by infrared analysis. In order to determine to what extent the chlorides isomerize under the conditions of the reaction the stability of *cis*-5-methyl-2-cyclohexenyl chloride was investigated in each of the following solvents: (1) dry dioxane, (2) dioxane 0.4 *M* in water, (3) dioxane 1.25 *M* in hydrogen chloride and (4) dioxane 1.25 *M* in hydrogen chloride and 0.4 *M* in water. Solutions of 3.9 g. (0.03 mole) of the *cis*-chloride in the above solvents were thermostated at 30° for 24 hours and the allylic chloride was isolated as described above. No isomerization occurred in dry dioxane; however, a small amount of isomerization occurred in the other solvents. Qualitatively the extent of *cis* to *trans* isomerization increased in the order in which the four solvents are listed above. However, even in dioxane containing both water and hydrogen chloride less than 10% of the *cis*-chloride was converted to the *trans* isomer.

***cis*- and *trans*-5-Methyl-2-cyclohexenyl Acetate.**—The isomeric acetates were prepared from the corresponding alcohols by adding the latter to cold solutions of stoichiometric amounts of acetyl chloride in pyridine. The reaction

mixtures were allowed to stand at room temperature for 1 hr. and then treated with excess 5% hydrochloric acid. The acetates were extracted from the reaction mixtures with pentane, b.p. 35°, and after drying the products were isolated from the pentane solutions by fractionation under reduced pressure.

cis-5-Methyl-2-cyclohexenyl acetate, b.p. 84° (25 mm.), d_{25}^{20} 0.9667, n_D^{25} 1.4508, $M_R D$ 42.93 (calcd. 42.76), was obtained in 87% yield. *Anal.* Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.82; H, 9.05.

trans-5-Methyl-2-cyclohexenyl acetate, b.p. 83° (25 mm.), d_{25}^{20} 0.979, n_D^{25} 1.4532, $M_R D$ 42.59 (calcd. 42.76), was obtained in 91% yield. *Anal.* Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.48; H, 9.23.

Assignment of Configuration of *cis*- and *trans*-5-Methyl-2-cyclohexenyl Chloride.—Two grams (0.0153 mole) of *cis*-5-methyl-2-cyclohexenyl chloride (prepared from *cis*-5-methyl-2-cyclohexenol and thionyl chloride) was added to a solution of 7 g. (0.0525 mole) of tetramethylammonium acetate²⁹ in 50 ml. of dry acetone. After the mixture was refluxed for 15 hours, 50 ml. of ether and 50 ml. of water were added and the organic layer was separated. After washing with 10% potassium carbonate and water the ether solution was dried (potassium carbonate) and the 5-methyl-2-cyclohexenyl acetate (76% yield) was isolated as described above. The infrared spectrum of the product showed that it was a binary mixture of *cis*- and *trans*-5-methyl-2-cyclohexenyl acetate consisting of 87% of the *trans* isomer.

When this experiment was repeated with *trans*-5-methyl-2-cyclohexenyl chloride (prepared from *trans*-5-methyl-2-cyclohexenol and thionyl chloride) a binary mixture of the isomeric 5-methyl-2-cyclohexenyl acetates was obtained which consisted of 78% of the *cis* isomer.

When optically active chloride was used in this experiment the resulting product was optically active (see below).

Relation of Configurations of (+)-*cis*-5-Methyl-2-cyclohexenol and (-)-*cis*-5-Methyl-2-cyclohexenyl Chloride.—The oxidation of (+)-*cis*-5-methyl-2-cyclohexenol to (-)-5-methyl-2-cyclohexenone was accomplished by the following modification of the method of Attenburrow, *et al.*³⁰ A solution of 3 g. of (+)-*cis*-5-methyl-2-cyclohexenol, $[\alpha]_D^{20}$ 2.09 (*l* 1 dm., neat), in 150 ml. of pentane was stirred with 30 g. of manganese dioxide for 19 hr. at room temperature. The manganese dioxide was removed by filtration and washed twice with pentane. The filtrate was concentrated under reduced pressure and the residual 5-methyl-2-cyclohexenone was purified by distillation, b.p. 54–55° (10 mm.). The infrared spectrum of the distilled product (70% yield) was indistinguishable from that of authentic 5-methyl-2-cyclohexenone,³⁰ and had $[\alpha]_D^{20}$ -26.4° (*l* 1 dm., neat).

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.97; H, 9.34.

The 2,4-dinitrophenylhydrazone melted at 150–150.5° (95% ethanol).

Anal. Calcd. for $C_{13}H_{14}O_4N_4$: C, 53.79; H, 4.86. Found: C, 53.74; H, 4.90.

The conversion of 11.3 g. of (+)-*cis*-5-methyl-2-cyclohexenol, $[\alpha]_D^{20}$ 2.09° (*l* 1 dm., neat), to 9.2 g. (70%) of (-)-*cis*-5-methyl-2-cyclohexenyl chloride, $[\alpha]_D^{20}$ -10.2° (*l* 1 dm., neat), with thionyl chloride in ether was accomplished as described above.

The (-)-*cis*-chloride (9.2 g.) was converted to 5-methyl-2-cyclohexenyl acetate by heating with tetramethylammonium acetate in dry acetone as described above. The distilled product (8.5 g., 78% yield) was shown by infrared analysis to consist of 83 ± 2% *trans*-5-methyl-2-cyclohexenyl acetate and 17 ± 2% of the *cis* isomer. It had $[\alpha]_D^{20}$ 3.25° (*l* 1 dm., neat).

The optically active acetate (8.5 g.) was converted to the corresponding 5-methyl-2-cyclohexenol by the following procedure. The acetate, dissolved in an equal volume of anhydrous ether, was slowly added to a stirred solution of 1.30 g. of lithium aluminum hydride in 100 ml. of anhydrous ether. After addition of water to decompose excess hydride,

(29) The tetramethylammonium acetate used in this work was prepared by neutralizing an aqueous solution of tetramethylammonium hydroxide with acetic acid and concentrating to dryness under reduced pressure. The solid residue was recrystallized from acetone and dried in a vacuum desiccator. The product obtained in this way did not contain silver or chloride ion.

(30) J. Attenburrow, *et al.*, *J. Chem. Soc.*, 1094 (1952).

(28) Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, 2nd ed., p. 369.

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 $[\alpha]^{25D} 2.55^\circ$ (1 l dm., neat).

The optically active alcohol was oxidized to (+)5-methyl-2-cyclohexenone, $[\alpha]^{25D} 2.49^\circ$ (1 l 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

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

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

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

$$D_{\text{mixture}}^{10.62\mu} = k_{\text{cis}}^{10.62\mu} [\text{cis}] + k_{\text{trans}}^{10.62\mu} [\text{trans}]$$

$$D_{\text{mixture}}^{11.42\mu} = k_{\text{cis}}^{11.42\mu} [\text{cis}] + k_{\text{trans}}^{11.42\mu} [\text{trans}]$$

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: $k_{\text{cis}}^{10.62}$, 0.277; $k_{\text{trans}}^{10.62}$, 0.288; $k_{\text{trans}}^{11.42}$, 0.762; $k_{\text{cis}}^{11.42}$, 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

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

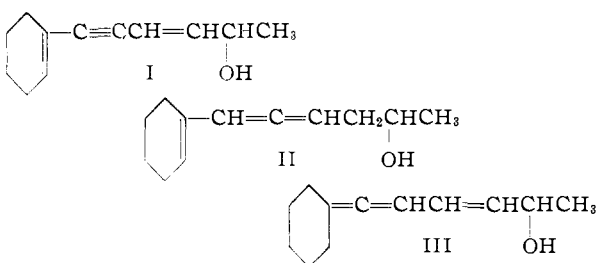
Synthesis of Polyenes. VII. The Formation of Allenes in the Reduction of Acetylenic Polyenes with Lithium Aluminum Hydride

By WILLIAM OROSHNIK

RECEIVED JANUARY 21, 1955

It has been shown that the grouping $-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-\text{C}-\text{OH}$ 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.

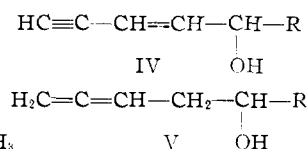
Recently Bharucha and Weedon reported the reduction of the conjugated divinylacetylene, I, with lithium aluminum hydride, and, on the basis of the diene band observed in the ultraviolet, λ_{max} 228 μ , provisionally assigned to the product the allenic structure II.¹ The formation of allenenes



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

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

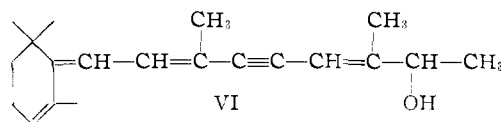
(2) F. B. Bates, E. R. H. Jones and M. C. Whiting, *ibid.*, 1854 (1954).



R = H or CH₃

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



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 C₂₀H₃₀O, showed only a very