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Rearrangement of allylic alcohols

Herbert Barbehenn

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REARRANGEMENT OF ALLYLIC ALCOHOLS

HERBERT S. BARBEHENN

JANUARY, 1971

THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

APPROVED:

Dr. Jerry Adduci
Project Adviser

Illegible Signature
Department Head

Library

Rochester Institute of Technology
Rochester, New York
To Kath, my wife — —
for the many lonely nights, for the many
unfinished chores and for being herself.
Acknowledgements

Grateful appreciation is tendered to the many faculty members with whom it has been my pleasure to be associated with during the past eleven years at Rochester Institute of Technology.

Special thanks are expressed to Dr. Jerry Adduci for his guidance and patience in seeing this endeavor to its conclusion. While it may have taken a little longer than the norm, much of the credit for this thesis must be ascribed to his dedication to complete and conclusive research.

I also wish to thank Dr. Earl Krakower for the many nuclear magnetic resonance spectra he so graciously completed in the course of elucidating the many structures formed and to Dr. Jonas of the University of Illinois and the National Science Foundation.
ABSTRACT

Three allylic type alcohols were rearranged in sulfuric acid (1, 10 and 50%) at 25 and 100°C and their products identified. Specifically, 2-phenyl-1-propen-3-ol, 2-methyl-1-phenyl-1-propen-3-ol and 2-methyl-3-phenyl-1-propen-3-ol were studied.

2-Phenyl-1-propen-3-ol was found to rearrange to 2-phenylpropionaldehyde while 2-methyl-1-phenyl-1-propen-3-ol formed 2-methyl-2-phenylpropanal, isobutyrophenone and 2-methyl-3-phenyl-1-propen-3-ol. The final rearrangement of the 2-methyl-3-phenyl-1-propen-3-ol allylic alcohol produced 2-methyl-2-phenylpropanal, isobutyrophenone, 2-methyl-1-phenyl-1-propen-3-ol and 2-(2-phenylisopropyl)-4-phenyl-5-methyl-1,3-dioxane.
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INTRODUCTION

**Definition of Allylic Alcohols**

Allylic alcohols are those organic alcohols having an ethylenic linkage \( \text{C} = \text{C} \) to the carbon atom bearing the highly electronegative hydroxyl group:

\[
\begin{align*}
\text{R} & \quad \text{R}^2 \text{R}^3 \\
\text{R}^4 & \quad \text{C} = \text{C} - \text{O} - \text{OH}
\end{align*}
\]

The R groups may be saturated or unsaturated organic radicals, or they may be other functional groups.\(^1,2\)

**Preparation of Allylic Alcohols**

A brief outline of the more important methods for synthesizing this family of alcohols is an appropriate way to begin a discussion of the rearrangements of these allylic alcohols. Consider first, their preparation from non-allylic starting compounds. The addition of hydrogen halides, halogens and α-halo ethers to conjugated dienes followed by hydrolysis to the alcohol can be utilized. As a result of the occurrence of 1,4-addition and the isomerization of the initially formed allylic halides, the following mixtures are usually obtained:\(^3,4\)

\[
\begin{align*}
\text{HX} & \rightarrow \text{C} = \text{C} - \text{CX} - \text{CH} & + & \text{CH} - \text{C} = \text{C} - \text{CX} \\
\text{C} = \text{C} - \text{C} - \text{C} & \rightarrow \text{CX} - \text{CX} - \text{C} = \text{C} & + & \text{CX} - \text{C} = \text{C} - \text{CX} \\
\text{RCHX} & \rightarrow \text{R}' \text{OCHRC} - \text{C} = \text{C} - \text{CX} & + & \text{R}' \text{OCHRC} - \text{CX} - \text{C} = \text{C}
\end{align*}
\]

However, the more widely used method of direct preparation
is the addition of Grignard reagents to \( \alpha,\beta \)-unsaturated carbonyl compounds such as acrolein, crotonaldehyde and cinnamaldehyde:

\[
C=\mathbf{C}-\mathbf{C} + \mathbf{R}\mathbf{MgX} \rightarrow C=\mathbf{C}-\mathbf{C}\mathbf{R}
\]

Reactions of this type are carried out by using ordinary procedures and usually give normal products.\(^5\)

Braude and coworkers\(^6,7,8,9,10\) developed a useful and direct method for synthesizing allylic alcohols from carbonyl compounds and lithium alkenyls:

\[
C=\mathbf{C}-\mathbf{L}i + \mathbf{RCR}\mathbf{R}' \rightarrow C=\mathbf{C}-\mathbf{CRR}'
\]

Vinyl Grignard reagents have also been used to prepare these allylic alcohols from ketones.\(^10,11\)

Acetylenic Grignard reagents also react with carbonyl compounds to yield substituted propargyl alcohols. The acetylenic bond of the propargyl alcohol can be partially reduced, yielding an allylic alcohol:

\[
\mathbf{RCOR}' + \mathbf{R''C=CMgX} \rightarrow \mathbf{RR'CC=CR''} \xrightarrow{2\mathbf{H}} \mathbf{RR'CCH=CHR''}
\]

Such reductions are usually carried out catalytically, using a catalyst such as palladium on barium sulfate\(^12\) though lithium aluminum hydride has also been used.\(^13\)

Catalytic reduction yields cis-alcohols, while hydride
reduction yields trans-alcohols.

Alkali or quinoline treatment of 1,2 and 1,3-dihalides yields mixtures of dehydrohalogenation products which contain allylic compounds:\(^{14}\):

\[
\text{XC-CX-CH} \xrightarrow{-HX} \text{XC-C=C}
\]
\[
\text{XC-C-CX} \xrightarrow{-HX} \text{XC-C=C}
\]

These again could be converted to their respective alcohols.

Other allylic compounds can be prepared by a variety of methods including carbonyl replacement and ester formation, olefinic oxidations and anionotropic rearrangements.

Rearrangements of Allylic Alcohols (Three Carbon Oxotropy)

Reactions of allylic alcohols are important from both a practical and theoretical standpoint.

Since allylic alcohols are both unsaturated compounds and alcohols, they are a highly reactive and versatile family which react to form a wide variety of compounds. Additions to the olefinic bond, as well as formation of esters, ethers, acetals, ketals and other alcohol derivatives, are characteristic reactions of this family. The ethylenic bond of the allylic system activates
the hydroxyl group, so that allylic alcohols undergo displacement reactions much more readily than analogous saturated alcohols.

Theoretical interest in allylic alcohols has centered mainly around their high reactivity and the ease with which they undergo rearrangement reactions. Migration of the electronegative groups from one end of the allylic system to the other are well known, and rearrangement frequently accompanies replacement reactions in these systems.

Rearrangements of this type are conveniently classified as anionotropic rearrangements. Anionotropy includes all rearrangements in which the migrating or the departing group or groups retain the electron pairs by which they were originally linked to the rest of the molecule.\(^1\)

**Pinacol - Pinacolone Rearrangement.**

Diad anionotropy involves a two carbon system and because of the retention of complete electron octets, includes such well known reactions as the oxime-amide (Beckmann) and the pinacol-pinacolone rearrangements.\(^2\)

Specifically, because of its historical and
theoretical importance in this investigation, consider the pinacol - pinacolone rearrangement. The reaction is facilitated by electron-donating substituents. The rearrangement of benzopinacol in aqueous media is a first order reaction, and the rate constant is dependent on the acidity function.$^{17}$

The accepted mechanism for the pinacolic transformation involves the prior formation of a carbonium ion intermediate. Shown below, this is formally written as a simple shift of an alkyl group or hydrogen atom from an adjacent atom to the electron deficient carbon atom.

\[
\begin{align*}
\text{R}_2\text{C}-\text{CR}_2 & \xrightarrow{\text{H}^+} \text{R}_2\text{C}-\text{CR}_2 \\
\text{OH} \quad \Theta \text{H}_2\text{O} \quad \text{OH} & \quad \left[ \begin{array}{c} \\ \text{R} \quad \text{R} \\
\text{OH}_2 \quad \Theta \\
\text{OH} \end{array} \right] \\
\left[ \begin{array}{c} \\ \text{R} \quad \text{R} \\
\text{OH}_2 \quad \Theta \\
\text{OH} \end{array} \right] & \xrightarrow{\text{R}_3\text{C}-\text{OH} \xrightarrow{-\text{H}^+} \text{R}_3\text{C}-\text{CR}} \\
\left[ \begin{array}{c} \\ \text{R} \\
\text{OH}_2 \Theta \\
\text{OH} \end{array} \right] & \xrightarrow{-\text{H}_2\text{O}} \\
\end{align*}
\]

It is evident that if we consider the pinacolic rearrangement, one has, neglecting conformation isomers, five possible carbonium ion intermediates (RR'C(OH)C(OH)RR').
Pinacol (2,3-dimethyl-2,3-butanediol) (VII) itself has only three structurally different carbonium ions:

Evidence points however, to an intermediate (I & IX) in which the rearrangement takes place in the oxonium ion formed by the addition of a proton to one of the hydroxyl
groups. In an asymmetrical glycol, the direction of the rearrangement will be determined by the relative basicities of the two hydroxyl groups, and the ease of separation of the migrating group. It is therefore not surprising that no simple generalization can be made concerning the "relative migratory aptitudes" of different groups.\textsuperscript{15,18}

**Oxotropic Rearrangements.**

There is a close resemblance between these diad systems and triad aniontropy, in which a hydroxyl or similar group exchanges positions intra-molecularly with an electron pair:

\[ \text{RC} - \text{C} = \text{CR}' \xrightarrow{\text{OH}, \text{H}^+} \text{RC} - \text{C} = \text{CR}' \xrightarrow{\text{OH}_2^+, \text{OH}_2^+} \text{RC} - \text{C} = \text{CR}' \]

The majority are rearrangements involving unsymmetrically substituted allyl alcohols. The special term "oxotropy"\textsuperscript{19} is used for such anionotropic rearrangements involving only the migration of a hydroxyl group.
Oxotopic rearrangements are catalyzed by proton donating species, i.e., acidic reagents. With simple allyl alcohols containing only alkyl substituents, oxototropic mobility is low and prolonged reactions at elevated temperatures are required. Thus, 1-methylallyl alcohol (XI) and 3-methylallyl alcohol (crotyl alcohol) (XII) are interconverted by 1% sulfuric acid in 5 hours at 95°C.20

\[
\text{HOCH(CH}_3\text{-CH=CH}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{CH(CH}_3\text{)=CH-CH}_2\text{OH}}
\]

XI  \hspace{2cm} XII

The next higher homologues, 1,1-dimethylallyl alcohol and 3,3-dimethylallyl alcohol, are similarly interconverted by treatment with 1% sulfuric acid at room temperature for 60 hours,21 with equal proportions of both isomers found in the equilibrium mixture.

In aryl-substituted allyl alcohols, oxotopic mobility is considerably enhanced. Valeur and Luce21 showed that 1-phenylallyl alcohol (XIII) is converted into 3-phenylallyl alcohol (cinnamyl alcohol) (XIV) by dilute sulfuric acid, whereas 1-cyclohexylallyl alcohol remains unchanged under similar conditions.22,23,24

\[
\text{HOCHPh-CH=CH}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{PhCH=CH-CH}_2\text{OH}}
\]

XIII  \hspace{2cm} XIV (92% at equilibrium)

This reaction can be followed quantitatively by the
ultra-violet absorption\textsuperscript{8} of the band near 2510 Å corresponding to the conjugated (styryl) system in the cinnamyl derivative (XIV).

The rearrangement rate and mechanism depend on both the acid concentration and the reaction media. Reactions in solution are invariably found to be simple first-order reactions. The oxonium ion of the alcohol (XV) is formed first while subsequent migration may be intra-molecular, as shown previously; or it may take place inter-molecularly through an attack by water at C\textsubscript{3} as shown below (XVI):

\[
\begin{align*}
C\equiv C&=C \xrightarrow{\text{fast}} C\equiv C=\overset{\text{OH}}{\overset{\text{H}^+}{\text{H}_2\text{O}}}^+ \xrightarrow{\text{slow}} [C\equiv C\equiv C\overset{\text{OH}_2}{\overset{\text{H}_2\text{O}}{\text{OH}_2}}^+] \xrightarrow{-\text{H}_2\text{O}} C=\overset{\text{OH}\text{H}}{\text{C}=\overset{\text{OH}}{\text{C}}}
\end{align*}
\]

(XV) \hspace{1cm} (XVI) \hspace{1cm} (XVII)

Inter- and intra-molecular rearrangements probably occur side by side. In anhydrous dioxane, the intra- would be favored while the inter- is favored under aqueous conditions. Evidence for inter- is given for the XIII to XIV reaction. It was found that (a) 1-phenylallyl alcohol (XIII), recovered after interruption of the rearrangement reaction, has partially exchanged its oxygen atoms with the solvent
water (b) 3-phenylallyl alcohol (XIV), recovered after complete rearrangement, has the $^{18}O$ abundance of the enriched solvent, and that (c) oxygen exchange between 3-phenylallyl alcohol is considerably slower than the rates of oxygen exchange and of rearrangement of 1-phenylallyl alcohol. $^{25,26}$

The function of the hydrogen ion catalyst is to weaken the existing carbon-oxygen bond of the alcohol. Instead of the separation of a charged hydroxyl anion during the rearrangement, the migration then involves the energetically favored separation of a neutral water molecule, XVI to XVII, formed by protonation of the hydroxyl group (XV) and the addition of a water molecule to C$_3$ (XVI). The rate determining step involves the continuous transfer of the positive charge from the departing oxygen atom via the allyl group to the entering oxygen atom, while a continuous electron displacement takes place simultaneously in the opposite direction. Both the formation of the oxonium ion and the fission of the carbon-oxygen bond are facilitated by electron accession at the reaction center and oxotropic mobility is therefore increased by electron-donating substituents, and decreased by electron-attracting substituents in the allyl groups. The effect of these substituents is exerted mainly through changes in the
energy of activation.

The rate of any allylic rearrangement will also depend on the location and size of substituents on the allylic backbone. This steric effect or hindrance may be demonstrated in two ways:

1), spatial resistance exerted by the molecule undergoing change as a result of the approach of the reagent ("kinetic" effects) and

2), an increase or decrease in steric strain in going from reactant to product ("thermodynamic" effects).\textsuperscript{27}

As the above scale projections show, $R^1$ & $R^2$ will not interfere with the approach of a solvent water molecule to the carbon atom bearing $R^3$ & $R^4$. However, they will interfere in the formation of a uniplanar styrene system conformation. The effect of group size has been established by Braude, et.al.\textsuperscript{27}

Current Investigation.

This study is based on work first reported by Hearne, Tamele and Converse.\textsuperscript{28} Their findings
established that in 12% sulfuric acid, 2-methylallyl alcohol (XII) can be converted to isobutyraldehyde (XVIII) provided the reaction mixture is distilled at reflux for one hour. If distillation is not employed, the acetal, 2-isopropyl-4,4-dimethyl-1,3-dioxolane (XXI), is formed as the principal product with XVIII as the by-product.

Additional experimentation showed that the isobutylene glycol (XIX) is formed during the treatment of XII with acid. It therefore appears that the hydration of XII to XIX is the first step in the rearrangement to the
aldehyde. The acetal is then formed from a reversible reaction between the final (XVIII) and intermediate (XIX) products. An intermediate of structure (XX) is proposed.

As might be expected, other unsaturated alcohols possessing a tertiary carbon atom attached to both the carbinol group and the double bond, rearrange in a similar manner when treated with dilute acid. When 2-methyl-2-buten-1-ol (XXII) was distilled in 12% sulfuric acid, it rearranged to a mixture of 72% 3-methyl-2-butanone (XXIII) and 28% 2-methylbutanal (XXXIV).²⁸

\[
\text{HOCH}_2\text{C(CH}_3\text{)=CHCH}_3\xrightarrow{\text{H}_2\text{O} / \text{H}^+} \text{CH}_3\text{COCH(CH}_3\text{)}_2 + \text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)}\text{CHO} \\
\text{XXII} \quad \text{XXIII} \quad \text{XXIV}
\]

An isomeric alcohol, 3-methyl-3-buten-2-ol (XXV) formed a mixture of 88% 3-methyl-2-butanone (XXIII) and 12% 2-methylbutanal (XXXIV).²⁸

\[
\text{CH}_2\text{=C(CH}_3\text{)CHOHCH}_3\xrightarrow{\text{H}_2\text{O} / \text{H}^+} \text{CH}_3\text{COCH(CH}_3\text{)}_2 + \text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)}\text{CHO} \\
\text{XXV} \quad \text{XXIII} \quad \text{XXIV}
\]

In both cases, the various possible acetals were formed if distillation was not utilized.²⁸ Further rearrangement to carbonylic compounds was accompanied by an allylic rearrangement between alcohols.

\[
\text{HOCH}_2\text{C(CH}_3\text{)=CHCH}_3\xrightarrow{\text{H}_2\text{O} / \text{H}^+} \text{CH}_2\text{=C(CH}_3\text{)CHOHCH}_3 \\
\text{XXII} \quad \text{XXV}
\]
Green and Hickenbottom\textsuperscript{29}, during their studies concerning the acid catalyzed rearrangements of $\alpha\beta$-unsaturated alcohols, also established the formation of dienes, carbonyl compounds, glycols and cyclic acetics as well as unidentified high boiling products. Principally, they demonstrated that a $\text{C}_\beta$-alkyl group has considerable effect in promoting anionotropic change. Allyl alcohol and its linear homologues undergo anionotropic change only with difficulty; the $\beta$-substituted allyl alcohols do so readily and practically quantitatively. Additionally their data indicated that if, however, the unsaturated 2-carbon of the allyl alcohol carries an alkyl group, oxotropy is the predominate reaction. The anionotropic change mentioned previously was explained by the formation of a glycol from the unsaturated alcohol and from this, excellent yields of cyclic acetics or ketals was observed.

Traditionally, however, acetics of allylic based structures have been prepared by reacting 1,2-glycols with carbonyl compounds under acid conditions. The parent acetal, 1,3-dioxolane, was first prepared by Trielat & Camber\textsuperscript{30} by reacting equimolar quantities of trioxymethylene and ethylene glycol at $100^\circ\text{C}$ with 2\% ferric chloride. The preferential method, however, is the acid catalyzed reaction of a carbonyl with a
1,2-glycol. A hemiacetal is proposed as a probable intermediate:

\[
\begin{align*}
R^1\text{COH} + R^2\text{COH} + O=\text{C} & \rightarrow \text{R}^1\text{C} - \text{O} - \text{C} - \text{R}^3 \\
& \qquad \text{R}^2\text{C} - \text{O} - \text{C} - \text{R}^4 \\
\end{align*}
\]

As might be expected, water removal favors dioxolane (XXVI) formation\textsuperscript{31}.

To date, a relatively small amount of work has been done in this area of ring formation\textsuperscript{32}. A typical example of this type of reaction, is the reaction between crotonic aldehyde (XXVII) and ethylene glycol (XXVIII) to form 2-(1-propenyl)-1,3-dioxolane (XXIX).

\[
\begin{align*}
\text{CH}_3\text{CH}=\text{CHCHO} + \text{HOCH}_2\text{CH}_2\text{OH} & \xrightarrow{\text{H}^+} \text{CH}_2\text{O} - \text{C} - \text{CH} - \text{CH}_3 \\
\text{XXVII} & \qquad \text{XXVIII} & \qquad \text{XXIX}
\end{align*}
\]

As cyclic acetals and ketals, the 1,3-dioxolanes are readily hydrolyzed to their components by dilute acids. They are, however, stable to alkali. Two hydrolysis mechanisms have been proposed by Ceder\textsuperscript{33} of which the second is preferred.
This hydrolysis is proportional to the hydronium ion concentration in 0.001-0.005 N perchloric acid$^{34}$. It is also possible for 1,3-dioxolanes to undergo exchange of the acetal group with other acetals in the presence of acid. A patent$^{35}$ covers this type of reaction.

It becomes obvious that the treatment of allylic alcohols under varying conditions of acid and temperature may produce unique effects. For example, at lower acid concentrations and temperatures, allylic rearrangement of the hydroxyl group would be expected. At higher temperatures and acid conditions, carbonyl compounds and eventually dioxolane ring structures might be formed.
Our objective was to study the products resulting when various substituted allyl alcohols are treated in acid conditions under ambient and refluxing temperatures. The alcohols in this study included 2-phenyl-1-propen-3-ol (XXX), 2-methyl-1-phenyl-1-propen-3-ol (XXXI) and 2-methyl-3-phenyl-1-propen-3-ol (XXXII).

\[
\begin{align*}
\text{XXX} & : \quad \text{CH}_2=\text{CCH}_2\text{OH} \\
\text{XXXI} & : \quad \text{HOCH}_2\text{C}=\text{CHPh} \\
\text{XXXII} & : \quad \text{OH} \quad \text{CH}_2=\text{CCHPh} \quad \text{CH}_3
\end{align*}
\]
EXPERIMENTAL

I. General Information

Derivative Techniques

The semicarbazone and 2,4-dinitrophenyl hydrazone derivatives of carbonyl compounds were synthesized according to the method of Shriner, Fuson and Curtin^41.

Hydrolysis Procedure

Compounds were added to 10 ml of 10% sulfuric acid and distilled for 4 hours with the volume in the pot held constant by the addition of water. The distillate was then collected and the organic products extracted with ether and isolated by glpc.

The pot liquor was then neutralized with an iced, saturated solution of sodium bicarbonate and the products isolated by ether extractions. It was then concentrated and tested for the presence of 1,2-glycol by using periodic acid reagent.

Identification and Purification of Reagents

All solvents, inorganic salts and acids were reagent grade and utilized as supplied.
2-Phenylallyl alcohol was utilized as received from Sinclair Petrochemicals (#SC-6032).

Bromobenzene, Eastman Organic Chemical #43, bp 154-5°C and magnesium turnings, Eastman #761, were reagent chemicals.

Methacrolein (Matheson, Coleman and Bell #T7491) was vacuum distilled and the center fraction, bp 33-5°C/1.8 mm (bp 67-9°C/760 mm) reserved for investigations.

2,4-Dinitrophenylhydrazine, Eastman #1866 (mp 192°C dec.); 3,5-dinitrobenzoyl chloride, Eastman #2654; semicarbazide hydrochloride, Eastman #226; α-methyl cinnamaldehyde, Eastman #P7322 and boron fluoride, Eastman #4272 were used without additional purification.

Sodium borohydride was supplied by Metal Hydrides, Inc.

Instrumentation

All gas liquid phase chromatographic separations were performed on an F & M Model 720 gas chromatograph equipped with ¼ inch x 4 foot 20% FFAP (free fatty acid phase -- reaction between 2-nitroterephthalic acid and Carbowax 20M) on 60/80 mesh acid washed Chromosorb W column for all rearrangement reactions. Conditions used for the purification and collection of products are shown in the Appendix (Tables IA & B).
Yields were established by condensing the various fractions directly from the chromatograph into tared U-tubes. Accuracy, as established by duplicate and controlled separations was ± 2%.

Infrared spectra were recorded on a Perkin Elmer model 257 (sodium chloride) spectrophotometer (letters s, m, and w in parentheses correspond to a strong, medium or weak absorption band respectively).

Refractive indices were obtained at either 20° or 25°C on a Bausch & Lomb model 352 refractometer.

Nuclear magnetic resonance spectra were recorded on a Hitachi Perkin-Elmer High Resolution Nuclear Magnetic Resonance spectrometer, model R-20, frequency 60 MHz for hydrogen. The solvent was deuterochloroform (CDCl₃) and chemical shifts (δ) are expressed in parts per million downfield from internal tetramethysilane.

Mass spectral analyses were obtained on an A.E.I. MS902 double-focusing high resolution mass spectrometer. The heated inlet temperature was maintained at 210°C and the ion source equilibrium at 235°C with an electron beam energy of 70 eV.
Vapor phase osmometry measurements were carried out in the Kodak Park Micro-analytical Lab, elemental analyses were done by Baron Consulting Co, and melting points were obtained on a Fisher-John melting point apparatus. All melting points as well as boiling points are uncorrected.

**Rearrangements**

The alcohol, 0.05 mole, was placed in 30 ml of sulfuric acid (1, 10 or 50 weight percent) for 24 hours at the indicated temperature (25° or 100°C). The addition of the alcohol resulted in a heterogeneous mixture. The reaction mixtures were stirred under nitrogen.

At the end of the reaction period, the acid solution, if required, was rapidly cooled to room temperature and neutralized with an iced, saturated solution of sodium bicarbonate. Rearrangement products of XXX were isolated using chloroform extractions (four-10ml portions) while ether was used for XXXI and XXXII. The extracted layers were washed twice with 10 ml of a saturated sodium bicarbonate solution. Two additional 10 ml water washes were then employed and the combined organic layers dried over sodium sulfate. The solvent was evaporated using dry air and the resulting residue fractionated in a micro-distillation apparatus.
II. Synthesis & Characterization of Alcohols

2-Phenyl-l-Propen-3-ol (XXX, 2-phenyl allyl alcohol) had a bp of 105°C/4mm and a \( N_D^{25} \) of 1.5688, and exhibited a retention time of 30 mins. (Table IA) on chromatographic analysis 36,37. It also exhibited: ir absorption (Fig.1) at 3420-3280 (s) (-OH), 1605 (m) and 1500 (s) (C\(_6\)H\(_5\)) and at 1580 (m) and 1450 (m) cm\(^{-1}\) (C\(_6\)H\(_5\), conjugated); nmr (Fig. 2), 3.70 (1H, singlet, -OH), 4.35 (2H, singlet, -CH\(_2\)), 5.34 (2H, doublet, =CH\(_2\)) and 7.28 ppm (5H, singlet, -C\(_6\)H\(_5\)).

Anal. Calculated for C\(_9\)H\(_{10}\)O: C, 80.56; H, 7.51. Found : C, 80.63; H, 7.46.

2-Methyl-l-Phenyl-l-Propen-3-ol (XXXI). The Goering and Dilgren method was employed\(^{39}\). 2-Methyl-3-phenyl-l-propen-3-ol (XXXII), 2 g (0.014 mole), was refluxed for 24 hours in 100 ml of a 60% aqueous acetone solution of 0.1 M hydrochloric acid. The reaction mixture was neutralized with an aqueous saturated solution of sodium bicarbonate and extracted with two 50 ml volumes of ethyl ether. A vacuum distillation gave 1.14 g of XXXI (0.008 mole, 57.0% yield): bp 77-78/0.1 mm; \( N_D^{25} \) 1.5675; ir absorption (Fig. 3) at 3480-3300 (s) (-OH), 1605 (m) and 1495 (s) (C\(_6\)H\(_5\)), 1580 (w) and 1450 cm\(^{-1}\) (s) (C\(_6\)H\(_5\), conjugated); nmr (Fig.4), 1.80 (3H, singlet, -CH\(_3\)), 2.62 (1H, singlet, -OH), 4.05 (2H, singlet, -CH\(_2\)), 6.44 (1H, singlet, =CH).
and 7.20 ppm (5H, singlet, -C₆H₅).

**Anal.** Calculated for C₁₀H₁₂O: C, 81.04; H, 8.16.

**Found** : C, 80.93; H, 8.20.

XXXI can also be prepared by an easier and more direct method, i.e. the sodium borohydride reduction of α-methyl cinnamaldehyde. To 150 ml of tetrahydrofuran was added 14.6 g (0.1 mole) of α-methyl cinnamaldehyde. This was then added dropwise over a one hour period, to a mixture consisting of 3.8 g (0.1 mole) of NaBH₄ in 50 ml tetrahydrofuran. After reduction, 400 ml of water was added and the alcohol extracted with ether. Subsequent vacuum distillation, isolated 10.2 g (0.08 mole, 69.9% yield) of pure XXXI.

**2-Methyl-3-Phenyl-1-Propen-3-ol (XXXII).** Bromobenzene, 4 g (0.025 mole), in 100 ml dry ethyl ether was added to 80 g of magnesium turnings at 25°C. Reaction occurred spontaneously. An ethereal solution of bromobenzene, 310 g (1.975 moles), in 770 ml ether was then added dropwise over a two hour period under reflux conditions. Refluxing was continued for an additional hour with the resulting solution cooled to -10°C.

Methacrolein, 35.1 g (0.5 mole), was added
dropwise, with vigorous stirring, to the phenyl-
magnesium bromide Grignard reagent over a two hour
period at -10°C. An amorphous precipitate formed
immediately but redissolved when the solution was
stirred. After the addition period, the reaction
vessel was removed from the freezing mixture and
allowed to warm to 25°C for 16 hrs.

Excess Grignard reagent was destroyed by
the addition of an iced saturated solution of ammonium
chloride in water. The ether layer was then isolated
and washed with two 250 ml portions of a saturated
sodium bicarbonate solution followed by two 250 ml water
washes. The ether layer was then dried over sodium
sulfate. Vacuum distillation yielded 56.0 g (75.6% yield)
of 2-methyl-3-phenyl-1-propen-3-ol\(^3\). On GLPC analysis,
the presence of biphenyl was established. Redistillation
resulted in pure alcohol. The product (XXXII) had: bp
55-56°C/0.1 mm\(^3\); \(N_D^{20} \) 1.5350; ir absorption (Fig. 5)
at 3400-3360 (s) (-OH) and 1610 (w) and 1500 cm\(^{-1}\) (s)
(-C\(_6\)H\(_5\)); nmr (Fig. 6), 1.53 (3H, singlet, -CH\(_3\)), 2.26
(1H, singlet, -OH), 4.84 (1H, singlet, CH-OH), 5.04
(2H, doublet, =CH\(_2\)) and 7.22 ppm (5H, singlet, -C\(_6\)H\(_5\)).

\textbf{Anal.} Calculated for C\(_{10}\)H\(_{12}\)O: C, 81.04; H, 8.16.

\textbf{Found} : C, 80.93; H, 8.20.
2-Methyl-1-Phenyl-1,3-Propanediol (XXXIII).\(^{40}\)
\(-\text{Methyl cinnamyl alcohol (XXXI. 11g or 0.065 mole)}\)
in 45 ml of the tetrahydrofuran was mixed with 4.5g
pulverized NaBH\(_4\). This mixture was stirred while
being treated dropwise with a solution of 22.7g of
ethereal boron trifluoride in 20 ml of THF. The
addition period was 1.5 hours. This was allowed to
stand overnight, hydrolyzed with 45 ml of 30% hydrogen
peroxide and extracted with ether. This ether extract
was washed with water, dried and distilled to give 9.2 g
of 2-methyl-1 phenyl-1,3-propanediol. On redistillation
6.2 g (0.037 mole -57% yield) resulted: bp 165°C/5.5 mm,
ir absorption (Fig.7) at 3700-3100 (s) (-OH) and 1610 (w)
and 1500 cm\(^{-1}\) (s) (-C\(_6\)H\(_5\)); nmr (Fig.8) 0.68
(3H, doublet, -CH\(_3\)), 2.04(1H, septet, CH\(_3\) - CH),
3.38 (2H, singlet, -CH\(_2\)), 3.70 (2H, doublet, -OH),
4.50 (1H, doublet, \(\phi\) - CH) and 7.33 ppm (5H,
singlet, -C\(_6\)H\(_5\))

**Anal.** Calculated for C\(_{10}\)H\(_{14}\)O\(_2\): C, 72.30; H, 8.43.
Found : C, 72.24; H, 8.30.

**III. Rearrangements**

2-Phenyl-1-Propen-3-ol (XXX). Treatment with 10%
sulfuric acid at 100°C for 24 hrs. afforded the following
fractions on distillation.

(a) Fraction distilled over from 25-100°C/1 mm\(^{42}\).
After glpc analysis, the following were isolated:

(i.) Retention time of 10 mins. - colorless liquid; \( \text{ND}_{25}^2 = 1.5142 \) (lit. \( \text{ND}_{25}^2 = 1.513843 \)); ir absorption (Fig. 9) at 2710 (w) and 2815 (w) (C-H of aldehyde) and 1725 cm\(^{-1}\) (s) (C=O) (lit.\(^{43}\) 2710 and 2815 (C-H of aldehyde) and 1720 cm\(^{-1}\) (C=O); nmr (Fig. 10), 1.43 (3H, doublet, -CH\(_3\)), 3.58 \(^1\)H, quartet, -CH), 7.22 (5H, multiplet, -C\(_6\)H\(_5\)) and 9.6 ppm (1H, doublet, HC=O); semicarbazone deriv. mp 153° C (lit.\(^{44}\) 152° C); and 2,4 dinitrophenylhydrazone deriv. mp 135° C (lit.\(^{44}\) 134° C).

\textit{Anal.} Calculated for C\(_9\)H\(_{10}\)O: C, 80.56; H, 7.51.

\textit{Found} : C, 80.62; H, 7.51.

This corresponded to 2-phenylpropanal (XXXV).

(i.i.) Retention time of 30 mins - colorless liquid; ir and nmr spectra corresponded to Figs. 1 and 2 respectively. This corresponds to starting alcohol XXX.

(b) Fraction retained in distillation pot - brown and very viscous oil (XXXVI). By VPO* in acetone, it had an average molecular weight of 450 ±20. On glpc analysis, retention times in excess of 2 hrs. were obtained with a multitude of over-lapping peaks. The

*Vapor Phase Osmometry.
ir and nmr spectra provided no useful information.

Product distribution formed under each set of reaction conditions is summarized in Table II, p33.

2-Methyl-1-Phenyl-1-Propen-3-ol (XXXI). Treatment with 10% sulfuric acid at 100°C for 24 hrs. afforded the following fractions upon vacuum distillation and subsequent glpc separation. Listings are in order of increasing retention times:

(a) Retention time of 17.2 mins. (bp 70°C/2.5mm) - colorless liquid; ir absorption (Fig. 11) at 2805 (m) and 2705 (m) (C-H of aldehyde) and 1730 cm⁻¹ (s) (C=O) (lit.45 1725 cm⁻¹ (C=O)); nmr (Fig. 12), 1.45 (6H, singlet, (-CH₃)₂), 7.35 (5H, singlet, -C₆H₅) and 9.55 ppm (1H, singlet, -CH(=0)); semicarbazone deriv. mp 170-2°C (lit.46 172°C); and did not form bisulfite addition compound (lit.46 no bisulfite add'n).

Anal. Calculated for C₁₀H₁₂O: C, 81.04; H, 8.16
Found : C, 81.01; H, 8.19.

This corresponded to 2-methyl-2-phenylpropanal (XXXVII).

(b) Retention time of 23.6 mins. (bp 70°C/25mm)
- colorless liquid, $N_D^{20}$ 1.5192 (lit. 1.5192); ir absorption (Fig. 13) at 1695-1682 (s) (C=O) and 1586 (m) and $1452$ cm$^{-1}$ (s) ($C_6H_5$, conjugated); nmr (Fig. 14), 3.5 (1H, quintet, -CH) 1.18 (6H, doublet, -(CH$_3$)$_2$) and 7.3 - 8.0 (5H, double multiplet, -C$_6$H$_5$); semicarbazone deriv. mp $182^\circ C$ (lit. 181°C); and 2,4-dinitrophenylhydrazone deriv. mp $162^\circ C$ (lit. 162°C).

Anal. Calculated for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.98; H, 8.20.

This corresponded to isobutyrophenone (XXXVIII).

(c) Retention time of 59.0 mins. (bp 64°C/1.3 mm) - colorless liquid; $N_D^{20}$ 1.5350; ir and nmr spectrums identical to Figs. 5 & 6 respectively. This data corresponded to alcohol XXXII.

(d) Retention time of 118.2 mins. (bp 100°C/1.2mm) - colorless liquid; $N_D^{25}$ 1.5674; ir and nmr spectrums identical to Figs. 3 & 4 respectively, and corresponds to starting alcohol XXXI.

(e) Retention time in excess of 120 mins. (bp 118-165°C/1.1 mm) with several overlapping peaks - very viscous brown oil (XXXIX) having a molecular weight of 524 as determined by VPO. The ir and nmr spectra
provided no useful structural information.

The summary of products formed under each set of reaction conditions is contained in Table III, p36.

2-Methyl-3-Phenyl-1-Propen-3-ol (XXXII). Treatment with 10% sulfuric acid at 100°C for 24 hrs. afforded the following compounds; listed in order of increasing glpc retention times:

(a) Retention time of 17.2 mins. (bp 70°C/2.5mm) - colorless liquid; ir and nmr spectra were identical to Figs. 11 and 12 respectively, and corresponds to compound XXXVII.

(b) Retention time of 23.6 mins. (bp 70°C/2.5mm) - colorless liquid; ir and nmr spectra corresponded to Figs. 13 and 14 respectively. This corresponded to compound XXXVIII.

(c) Retention time of 59.0 mins. (bp 64°C/1.3mm) - colorless liquid; Np20 1.5350; ir and nmr spectrums identical to Figs. 5 and 6 respectively. This data corresponded to alcohol XXXII.

(d) Retention time of 118.2 mins. (bp 100°C/1.2mm) - colorless liquid; Np25 1.5674; ir and nmr
spectrums identical to Figs. 3 & 4 respectively, and corresponds to starting alcohol XXXI.

(e) Retention time of 24.2 mins. (bp 100°C/1.2mm) - colorless liquid; N\textsubscript{D}\textsuperscript{20} 1.5206, ir absorption (Fig. 15) at 1180 (m), 1145 (m) and 1090 (m) (C-0-C-0-C)\textsuperscript{49} and 1112 cm\textsuperscript{-1} (s) (acetal C-H)\textsuperscript{50}; nmr (Figs. 16 A and B; 60 and 220 MHz respectively) 0.7-2.0 (10H, multiplet, aliphatic H's), 4.6 and 5.3-5.5 (4H, multiplet, \textgamma-mono and disubstituted aliphatic H's) and 7.3 ppm (10H, multiplet, aromatic H's) however this actually integrated to a ratio of 16:2:8; mass spectral analysis (Table V in Appendix) showed a molecular weight of 296.177 (C\textsubscript{20}H\textsubscript{24}O\textsubscript{2} - calculated 296.412) with intense peaks at 177 and 149 a.m.u.\textsuperscript{51}

Anal. Calculated for C\textsubscript{20}H\textsubscript{24}O\textsubscript{2}: C, 81.04; H, 8.16.

Found : C, 81.00; H, 8.18.

This compound (0.1g) was hydrolyzed in 10% sulfuric acid for a period of four hours at distillation temperatures (see p.18). A total distillate of 20 ml was collected and extracted with ether. Isolation by glpc, (Table IA) followed by ir analysis showed this to be compound XXXVII. The reaction mixture in the pot gave a negative periodic acid test; this indicating no 1,2-glycol structures. Glpc (Table IB) and ir analysis
identified compound XXXIII as a hydrolysis product.

This data is consistent with the structure of 2-(2-phenylisopropyl)-4-phenyl-5-methyl-1,3-dioxane (XL).

(f) Retention time in excess of 120 mins. (bp 118-165°C/1.1mm) - several overlapping peaks - very brown viscous oil (XLI) having a molecular weight of 574 as determined by VPO. The ir and nmr spectra were of no value in identification.

The summary of reaction products under each set of reaction conditions is contained in Table IV, p39.
RESULTS AND DISCUSSION

Although investigations\textsuperscript{20,29} have been carried out to differentiate effects of alkyl substitution on the acid catalyzed rearrangements of allyl alcohols, to date, no work has been reported on effects of phenyl substitution. Therefore, three phenyl substituted allyl alcohols, 2-phenyl-1-propen-3-ol (XXX), 2-methyl-1-phenyl-1-propen-3-ol (XXXI) and 2-methyl-3-phenyl-1-propen-3-ol (XXXII) were treated with 1, 10 and 50\% sulfuric acid, by weight, under ambient and refluxing conditions.

\begin{align}
\begin{array}{ccc}
\text{XXX} & \text{XXXI} & \text{XXXII} \\
\end{array}
\end{align}

Under these conditions, one might expect to observe the following characteristic reactions: reversible oxotrophic change, anionotropic change with the formation of a saturated aldehyde or ketone (pinacol-pinacolone rearrangement), polymerization, dehydration to dienes, and either, acetal or ketal formation. Each alcohol is capable of undergoing one or more of these reactions. With the exception of dehydration, we have observed all these reactions or the products derived from them.

\textsuperscript{32}

The isolation and identification of the various reaction products are described in the Experimental section. It should be noted that since reactions were heterogeneous, the percentages of products in any one rearrangement may vary from one replicate run to another. The reactions of each alcohol are discussed separately with mechanisms postulated to account for the observed products.

2-Phenyl-1-Propen-3-ol (XXX).

Treatment of 2-phenyl-1-propen-3-ol with 10% sulfuric acid at 100°C resulted in the formation of 2-phenylpropanal (XXV, hydatropaldehyde). An oil of unknown composition was also formed. The distribution of products formed under different conditions is summarized in Table II.

\[
\begin{align*}
\text{OH} & \quad \rightarrow \quad \text{H} + \text{Oligomers} \\
\text{XXX} & \quad \rightarrow \quad \text{XXXV} \quad \text{XXXVI}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Table II</th>
<th>Distribution of Products Formed in Acid Catalyzed Rearrangement of 2-Phenyl-1-Propen-3-ol (XXX).</th>
</tr>
</thead>
<tbody>
<tr>
<td>([H_2SO_4] ), wt %</td>
<td>Temperature ( ^\circ \text{C} )</td>
</tr>
<tr>
<td>(1 )</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td>(10 )</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td>(50 )</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>

33
Increasing acid concentration and temperature resulted in high yields, up to 90%, of 2-phenylpropanal. However, when the acid concentration was increased to 50%, an oil was the predominate product at 100°C. Vapor phase osmometry (VPO) has shown these oils to have a molecular weight of approximately 450. These oils are oligomers or low molecular weight polymers of the starting alcohol, probably resulting from the cationic polymerization of the styryl grouping present in XXX. One would expect the formation of only low molecular weight oligomers from the polymerization of monomers containing allylic hydrogen atoms since they serve as chain terminators.\(^{52}\) We have also observed the formation of an oil from the starting alcohol XXX which had stood on a laboratory shelf for over a year. A white solid polymer was extracted from this oil, but this material was not characterized.

The rearrangement mechanism for the formation of the aldehyde is postulated as a simple protonation of the double bond to give a stable phenyl carbonium ion (XXXa), followed by a hydride shift and proton loss (eq 1).\(^{20}\) Because of the preferential stability of the benzyl cation ion \(^{16,19}\) and the driving force for carbonyl formation, this reaction proceeds rapidly to completion. Simultaneously, an oxotropic rearrangement
can be taking place (eq 2). However, since a symmetrical cation intermediate (XXXb) is involved, one would have to use a labeling device, eg. \( \text{H}_2\text{O}^{18} \), to show that this rearrangement was occurring.

\[
\begin{align*}
\text{XXX} & \xrightarrow{\text{H}^+} \text{XXXa} \\
\text{XXX} & \xrightarrow{\text{H}_2\text{O}^+} \text{XXXb} \\
\end{align*}
\]

2-Methyl-1-Phenyl-1-Propen-3-ol (XXXI).

When alcohol XXXI was treated with 10% sulfuric acid at 100°C, the following products were observed: 2-methyl-3-phenyl-1-propen-3-ol (XXXII), 2-methyl-2-phenylpropanal (XXXVII), isobutyrophenone (XXXVIII) and an oil. The results of these reactions are summarized in Table III.
Table III.
Distribution of Products Formed in Acid Catalyzed Rearrangement of 2-Methyl-1-Phenyl-1-Propen-3-ol (XXXI).

<table>
<thead>
<tr>
<th>[H₂SO₄], wt. %</th>
<th>Temperature</th>
<th>Products, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>XXXI</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>91</td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>27</td>
</tr>
<tr>
<td>50*</td>
<td>25</td>
<td>11</td>
</tr>
</tbody>
</table>

*100°C reaction not carried out

The formation of small amounts of rearrangement products at low acid concentrations and ambient temperature show alcohol XXXI to be extremely stable to oxotropic and anionotropic change. Stability can be attributed to the presence of the styryl system (Ø-C=C-). At higher acid concentrations and temperature, oil formation predominates. Correspondingly the alcohol concentration decreased. Oil formation is probably due to the styryl grouping which can be readily polymerized either thermally or cationically. However, due to the presence of allylic hydrogens⁵², only formation of low molecular weight oligomers would be expected. The oil was shown to have an average molecular weight of 574 by vapor phase osmometry.

The following mechanisms are postulated to
account for the observed products:

\[
\begin{align*}
\text{XXXI} & \quad \text{XXXIa} & \quad \text{XXXII} \\
\text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

(eq.3)

Alcohol XXXII is formed via an oxotropic reaction (Eq.3) involving the formation of the unsymmetrical allyl cation, XXXIa. Although the equilibrium favors the thermodynamically more stable XXXI, alcohol XXXII is considered extremely important to the formation of carbonyl compounds XXXVII and XXXVIII. An anionotropic mechanism (Eq.4) involves the protonation of the double bond in alcohol XXXII to give a tertiary carbonium ion, XXXIIa, which can undergo a 1,2-phenyl and/or a hydride shift resulting in the formation of XXXVII and XXXVIII respectively.

The phenyl shift should be preferred because of the intermediate phenonium ion, XXXIIb. This type of rearrangement very closely resembles the pinacol-pinacolone rearrangement\textsuperscript{15-18} in which migration takes place according to the following
sequence, Ar- \rightarrow -H, -R.

Alcohol XXXI can be also protonated to give the phenyl carbonium ion XXXIb, which apparently is stable to anionotropic rearrangement but reactive enough to initiate a polymerization reaction\(^5\). We believe species XXXIb and XXXIIa to be involved in the formation of the low molecular weight oligomers.

2-Methyl-3-Phenyl-1-Propen-3-ol (XXXII).

The rearrangement of alcohol XXXII in 10\% sulfuric acid at 100° C gave the following: 2-methyl-1-phenyl-1-propen-3-ol (XXXI), 2-methyl-2-phenylpropanal (XXXVII), isobutyrophenone (XXXVIII), 2-(phenylisopropyl)-4-phenyl-5-methyl-1,3-dioxane (XL) and an oligomer (XLI).
The distribution of products formed under different conditions is summarized in Table IV.

**Table IV**

Distribution of Products From the Acid Catalyzed Rearrangement of 2-Methyl-3-Phenyl-1-Propen-3-ol (XXXII).

<table>
<thead>
<tr>
<th>[H₂SO₄], wt. %</th>
<th>Temperature</th>
<th>Products, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>XXXII</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>84</td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>4</td>
</tr>
<tr>
<td>50*</td>
<td>25</td>
<td>8</td>
</tr>
</tbody>
</table>

*100°C reaction not carried out

It shows that at a low acid concentration and 25°C, no oxotropic reaction takes place. We observe the formation of substantial amounts of oligomer at 50% acid concentration (25°C). If this same reaction were carried out at refluxing temperatures, one would certainly expect the polymerization reactions to predominate. If competing reactions were not taking place, alcohol XXXII would be converted almost entirely to alcohol XXXI at higher acid concentrations or temperatures.

The variety of products observed at 10% acid concentration and 100°C illustrates that at least four
competing reactions are taking place and that they are complex and interrelated. Three of these reactions have been discussed previously: the oxotropic rearrangement of XXXI to XXXII, the anionotropic rearrangement of XXXI to XXXVII and XXXVIII, and the polymerization reactions to give oligomers. The quantities of alcohol XXXI and XXXII present will determine the amount of carbonyl compounds and oligomer formed, respectively.

The fourth reaction involves the formation of a dimeric substance, either a 1,3-dioxane or 1,3-dioxolane, arising from the reaction of a carbonyl compound, either XXXVII or XXXVIII, with alcohol XXXI or XXXII, all of which are present in the mixture. Each carbonyl compound is capable of reaction with either alcohol to form an open-chain or cyclic acetal or ketal, with the cyclic structures preferred\(^5\). Four cyclic structures, XL, XLII, XLIII and XLIV, resulting from combinations of the above reactions, were considered before structure XL was chosen.

\[
\begin{align*}
\text{XL} & \quad \text{XLII} \\
\text{XLIII} & \quad \text{XLIV}
\end{align*}
\]
The mechanism (Eq. 5) we postulate for the formation of XL involves the formation of hemi-acetal XLa, protonation to form benzyl cation LXb and its subsequent ring closure to form a 1,3-dioxane structure. Similar mechanisms can be written for the reactions of XXXVII and XXXII, XXXVIII and XXXI, XXXVIII and XXXII to account for structures XLII, XLIII and XLIV, respectively.

\[
\begin{align*}
\text{XXXVII} & \quad \text{XXXI} \\
\text{XL} & \quad \text{XLa} \\
\text{XLb}
\end{align*}
\]

The infrared spectrum obtained for XL (Fig.15) showed that the compound was basically an ether with four absorptions at 1180, 1145, 1112 and 1090 cm\(^{-1}\) attributed to various vibration modes of a \(-\text{C-O-C-O-C-}\) structure.\(^{50,57}\) Multiple absorptions are generally observed in this area for acetals and ketals.

The nmr spectrum (60MHz, CDCl\(_3\)) obtained for XL (Fig.16a) was complex and provided limited information.
The spectrum showed three major signals at 0.7 - 2.0, 4.6 - 5.5, and 7.3 ppm which were attributed to aliphatic, \( \alpha \)-mono- and disubstituted aliphatic, and aromatic protons respectively. The complexity of the nmr spectrum can be attributed to the highly substituted heterocyclic system which can exist as cis, trans isomers and/or racemates of optically active isomers. Since we made no attempt to isolate stereoisomers and because chemical shifts are dependent on stereo-configurations, broadening and poor peak definition were expected.\(^{58-60}\) A 220 MHz nmr spectrum (CDCl\(_3\)) was recorded (Fig. 16b) and provided an expanded version of the 60 MHz spectrum. Although the spectrum was still complex and the integration inexact, the multiplicity of certain signals allowed us to make a structure correlation. The signals at 4.73 and 5.50 (ab quartet, \( J =10 \) cps), 4.85 (doublet) and 5.37 (singlet) are of particular interest (cf Fig. 17) because they can be attributed to the following structures \(-O-CH\(_2\)-CH\) and \(-O-\text{CH(O)}-\text{CH}\) and \(-O-\text{CH-CH-}\) respectively, and are consistent only with structures, XL. These assignments are in good agreement with literature values.\(^{58,59}\)

The mass spectrum obtained for compound XL (Table V) showed a parent ion of 296.177 m/e which is in excellent agreement with the calculated molecular
Figure 16A. Nuclear Magnetic Resonance Spectrum (60 MHz) of 2-(2-Phenylethynyl)Ethyl-5-Methyl-1,3-Dioxane (ELH).
Figure 16B. Nuclear Magnetic Resonance Spectrum (220 MHz) of 2-(2-Phenylisopropy1)-4-Phenyl-5-Methyl-1,3-Dioxane (XL).
weight of $296.412 \cdot C_{20}H_{24}O_2$, and a fragmentation pattern consistent with the proposed structure XL. A print-out of m/e and fragmentation data, which had been transcribed from a computer print-out which incorporated a 5% intensity cut-off, is listed in Table V. The principal fragments can be viewed as arising from the following fragmentation patterns (see also Figure 17; following page).

The initial fragmentation is illustrated as loss of an H· radical from XL, to produce the m/e 295 ion (a, M-H). Subsequent ring cleavage and loss of carbon monoxide resulted in ions m/e 147 and m/e 119 (species b and c). This type of fragmentation reaction is specific because the oxonium ion (species a) formed by loss of H· from the number 2 position, may be stabilized by delocalization of the positive charge between the two equivalent oxygen atoms and the intervening sp$^2$ hybridized carbon atom.
Figure 17. Mass Spectrum of 2-(2-Phenylisopropyl)-4-Phenyl-5-Methyl-1,3-Dioxane (XL).
The major loss at the number 2 position will be that which provides maximum release of steric strain in the ring. Hence, the major loss was that of the $\phi \rightarrow \cdot$ radical to produce the following species$^{61,62}$.

Since the predominate reaction is the one presented for the formation of species d, e and f, let's consider, in some detail, the subsequent fragmentation of the m/e 149 ions (species e and f). First let's examine species e.
The principal fragments resulted from the elimination of either a stable molecule (H₂, C₃H₈ or CH₄) or an atom of oxygen. The fragmentation of species f is similar to that presented above for the m/e 149 species e ion. It is postulated as the following.
The resemblance between the fragmentation patterns of both species, e and f, of the m/e 149 ion is obvious and expected as based on known alkyl fragmentations. Most certainly, it would be quite lengthy to outline schematics for each and every fragment listed in the fragmentation print-out (Table V), however each one listed in this abbreviated print-out is accountable. Besides the basic patterns outlined previously, we have possible fragmentation of (CH₃)₂ OCO (peaks at principally 119 through 116 m/e) plus possible form-
ation of meta-stable species of the following structures.\textsuperscript{64,65,66}

\[
\begin{array}{c}
\text{\textsuperscript{+}} \\
\text{H} \\
\text{H} \\
\text{CH}_2 \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\quad \text{\textsuperscript{+}} \quad \text{etc.}
\]

m/e 92 \quad m/e 91

Each are prominent in our spectrum.

The spectographic data, ir, nmr and mass spect., is not conclusive in itself although it is consistent with the proposed dioxane structure XL. To establish the structure conclusively, chemical data was provided by the acid hydrolysis of the dimeric substance. Acid hydrolysis\textsuperscript{34} would result in the regeneration of the carbonyl and glycol components of an acetal or ketal. Hydrolysis of a 1,3-dioxolane (XLII) or 1,3-dioxane (XL) would result in the formation of a 1,2- or a 1,3-glycol respectively.\textsuperscript{29,33} Glpc analysis of the distillate obtained from the hydrolysis mixture of the dimeric substance showed the presence of a component with the same retention time as XXXVII, 2-methyl-2-phenylpropanal. The infrared spectrum of a sample collected from the distillate corresponded to the known aldehyde.
The pot residue gave a negative periodic acid test indicating the absence of any 1,2-glycol structures. Glpc analysis of the extracts obtained from the pot residue showed the presence of XXXIII, 2-methyl-1-phenyl-1,3-propanediol (similar retention time and ir spectrum). In addition to chemical and spectroscopic evidence, the following points led us to favor XL as the dimeric structure:

1) Aldehydes are more reactive than ketones, especially with respect to acetal or ketal formation.

2) Dioxane structures have greater conformational stability than the five-membered dioxolane ring.\textsuperscript{55,56}

3) The concentration of aldehyde XXXVII is higher than ketone XXXVIII due to the preferential migration of phenyl in the anionotropic reaction.

4) The concentration of alcohol XXXI is higher because of its thermodynamic stability.

5) Because XXXVII and XXXI are present in higher concentration, the probability of their reacting to form XL is greater.

On the basis of the evidence, we propose the following structure and hydrolysis mechanism for

\[
\begin{array}{c}
\text{structure XL.} \\
H - O - H \quad \text{CH}_3 \\
\text{XL} \\
\text{CH}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{XXXVII} \\
\text{H} \quad \text{CH}_3 \\
\text{H} \\
\end{array}
\]

\[
\begin{array}{c}
\text{XXXIII} \\
\text{HO} \quad \text{H} \quad \text{CH}_3 \\
\text{HO} \\
\end{array}
\]
Thus structure XL, 2-(2-phenyl isopropyl)-4-phenyl-5-methyl-1,3-dioxane is consistent with all data.

One additional point which may be considered is the oligomer which has been present in each of the three rearrangement reactions. In this particular system, we have an added possible source of polymer formation; that of a polyether due to the dioxane ring.\textsuperscript{67,68} While, this is remote, it must be considered.
CONCLUSIONS

The acid catalyzed rearrangements of the phenyl substituted allylic alcohols were complex with many competing reactions occurring. We observed the formation of isomeric alcohols, aldehydes, ketones, a heterocyclic dioxane ring and polymers; these a result of both oxotropic and anionotropic rearrangements and acetal formation. Additionally, each rearrangement was found dependent on the carbonium ion stability during the transition states.

Direct comparisons between alkyl and phenyl substituted allyl alcohols are difficult because no significant differences were observed. If anything, the phenyl substituent appears to activate the molecule towards polymerization reactions. Specifically, 2-phenyl 1-propen-3-ol rearranged to 2-phenyl propanal while 2-methyl-1-phenyl-1-propen-3-ol formed 2-methyl-2-phenyl propanal, isobutyrophenone, and 2-methyl-3-phenyl-1-propen-3-ol. The final rearrangement of 2-methyl-3-phenyl-1-propen-3-ol produced 2-methyl-2-phenylpropanal, isobutyrophenone, 2-methyl-1-phenyl-1-propen-3-ol and 2(2-phenylisopropyl)-4-phenyl-5-methyl-1, 3-dioxane.
Bibliography

2. Allyl Alcohol, Shell Chemical Corporation, Cleveland, Ohio (1964).
15. E. A. Braude, Quarterly Reviews, 4, 404 (1950).
31. German pat. 253,083 (C.A., 7, 868 (1913)).
35. U. S. patent. 2,383,874 (C.A., 40, 592 (1946)).


64. R. I. Reed, *Quarterly Reviews*, XX, No. 4, 527 (1966).


Table IA  
Retention Times of Rearrangements Products

<table>
<thead>
<tr>
<th>Injector Temperature</th>
<th>Detector Temperature</th>
<th>Attenuation</th>
<th>Column</th>
<th>Sample Size</th>
<th>Gas Flow</th>
<th>Column Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>205°C</td>
<td>235°C</td>
<td>2</td>
<td>1/4&quot; x 4'</td>
<td>2 μl</td>
<td>30 ml/min</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>@ 150 ma</td>
<td>20% FFAP on acid washed Chromosor W, 60/80 mesh</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>XXX</td>
<td>30.0 mins.</td>
</tr>
<tr>
<td>XXXV</td>
<td>10.1</td>
</tr>
<tr>
<td>XXXI</td>
<td>118.2 26.2</td>
</tr>
<tr>
<td>XXXII</td>
<td>59.0</td>
</tr>
<tr>
<td>XXXVII</td>
<td>39.9 17.2</td>
</tr>
<tr>
<td>XXXVIII</td>
<td>58.4 23.6</td>
</tr>
<tr>
<td>XL</td>
<td>24.2</td>
</tr>
<tr>
<td>XLI</td>
<td>120+</td>
</tr>
</tbody>
</table>

Oligomers
### Table IB

Retention Times for Isolation of 2-Methyl-3-Phenyl-1, 3-Propanediol (XXXIII)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
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</thead>
<tbody>
<tr>
<td>Injector Temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Attenuation</td>
<td>2</td>
</tr>
<tr>
<td>Sample Size</td>
<td>2 µl</td>
</tr>
<tr>
<td>Column</td>
<td>15% ethylene glycol succinate on Acid washed Chromosorb W, 60/80 mesh</td>
</tr>
<tr>
<td>Column Temperature</td>
<td>180°C</td>
</tr>
<tr>
<td>Detector Temperature</td>
<td>220°C</td>
</tr>
<tr>
<td>Gas Flow</td>
<td>30 ml/min</td>
</tr>
<tr>
<td>Retention Times:</td>
<td></td>
</tr>
<tr>
<td>2-Methyl-1-Phenyl-1, 3-Propanediol (XXXIII)</td>
<td>54 mins.</td>
</tr>
<tr>
<td>2-(2-Phenylisopropyl) - 4 - Phenyl - 5 - Methyl - 1, 3-dioxane</td>
<td>32 mins.</td>
</tr>
</tbody>
</table>


### Table V

Computer Printout of the Mass Spectrum of 2-(2-Phenyl isopropyl)-4-Phenyl-5-Methyl-1,3-Dioxane (XL)*

<table>
<thead>
<tr>
<th>Measured Mass</th>
<th>Cl2/13</th>
<th>H</th>
<th>O</th>
<th>Intensity</th>
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</thead>
<tbody>
<tr>
<td>296.1777</td>
<td>20/0</td>
<td>24</td>
<td>2</td>
<td>0.13</td>
</tr>
<tr>
<td>295.1666</td>
<td>19/1</td>
<td>23</td>
<td>2</td>
<td>0.003</td>
</tr>
<tr>
<td>279.1718</td>
<td>19/1</td>
<td>22</td>
<td>1</td>
<td>0.14</td>
</tr>
<tr>
<td>278.1668</td>
<td>20/0</td>
<td>22</td>
<td>1</td>
<td>1.08</td>
</tr>
<tr>
<td>177.0913</td>
<td>11/0</td>
<td>13</td>
<td>2</td>
<td>11.34</td>
</tr>
<tr>
<td>149.0960</td>
<td>10/0</td>
<td>13</td>
<td>1</td>
<td>7.72</td>
</tr>
<tr>
<td>147.0815</td>
<td>10/0</td>
<td>11</td>
<td>1</td>
<td>9.19</td>
</tr>
<tr>
<td>132.0926</td>
<td>10/0</td>
<td>12</td>
<td>0</td>
<td>50.10</td>
</tr>
<tr>
<td>131.0841</td>
<td>10/0</td>
<td>11</td>
<td>0</td>
<td>100.00</td>
</tr>
<tr>
<td>130.0771</td>
<td>10/0</td>
<td>10</td>
<td>0</td>
<td>6.99</td>
</tr>
<tr>
<td>129.0699</td>
<td>10/0</td>
<td>9</td>
<td>0</td>
<td>13.63</td>
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<tr>
<td>128.0627</td>
<td>10/0</td>
<td>8</td>
<td>0</td>
<td>6.81</td>
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<tr>
<td>119.0854</td>
<td>9/0</td>
<td>11</td>
<td>0</td>
<td>9.84</td>
</tr>
<tr>
<td>118.0761</td>
<td>9/0</td>
<td>10</td>
<td>0</td>
<td>5.90</td>
</tr>
<tr>
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<td>8/1</td>
<td>9</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>116.0622</td>
<td>9/0</td>
<td>9</td>
<td>0</td>
<td>29.72</td>
</tr>
<tr>
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<td>9/0</td>
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<td>0</td>
<td>16.76</td>
</tr>
<tr>
<td>105.0347</td>
<td>7/0</td>
<td>5</td>
<td>1</td>
<td>7.87</td>
</tr>
<tr>
<td>97.0657</td>
<td>6/0</td>
<td>9</td>
<td>1</td>
<td>9.76</td>
</tr>
<tr>
<td>92.0596</td>
<td>7/0</td>
<td>8</td>
<td>0</td>
<td>6.45</td>
</tr>
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<td>91.0555</td>
<td>6/1</td>
<td>7</td>
<td>0</td>
<td></td>
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<tr>
<td>78.0462</td>
<td>6/0</td>
<td>6</td>
<td>0</td>
<td>7.52</td>
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<td>77.0395</td>
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<td>5</td>
<td>0</td>
<td>12.92</td>
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<tr>
<td>65.0399</td>
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<td>0</td>
<td>6.56</td>
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<tr>
<td>53.0401</td>
<td>4/0</td>
<td>5</td>
<td>0</td>
<td>5.51</td>
</tr>
<tr>
<td>51.0234</td>
<td>4/0</td>
<td>3</td>
<td>0</td>
<td>9.17</td>
</tr>
<tr>
<td>50.0156</td>
<td>4/0</td>
<td>2</td>
<td>0</td>
<td>6.55</td>
</tr>
</tbody>
</table>

*Except for the first four measured mass values, a 5% intensity cut-off was employed in the computer printout.
Figure 2. Nuclear Magnetic Resonance Spectrum of 2-Phenyl-1-Propen-3-ol (XXX).
Figure 4. Nuclear Magnetic Resonance Spectrum of 2-Methyl-1-Phenyl-Propan-3-ol (XXXI).
Figure 6. Nuclear Magnetic Resonance Spectrum of 2-Methyl-3-phenyl-1-propan-3-ol (XIII).
Figure 7. Infrared Spectrum of 2-Methyl-1-Phenyl-1,3-Propanediol (III).
Figure 8. Nuclear Magnetic Resonance Spectrum of 2-Methyl-1-Phenyl-1,3-Propanediol (XXXIII).

A: 1-2 drops trifluoromethic acid added

B: 5-6 drops trifluoromethic acid added
Figure 11. Infrared Spectrum of 2-Methyl-2-Phenyl Propanal (XXXVII).
Figure 13. Infrared Spectrum of Isobutyrophenone (XXXVIII).
Figure 14. Nuclear Magnetic Resonance Spectrum of isobutyrophenone (XXXVIII).
Figure 15. Infrared Spectrum of 2-(2-Phenylisopropyl)-4-Phenyl-5-Methyl-1,3-Dioxane (XL).