

AN INVESTIGATION OF THE UNCATALYZED
ALKYLATION OF PHENOL WITH
1-CHLORO-4-METHYL-3-PENTENE

Thesis for the Degree of Ph. D.
MICHIGAN STATE COLLEGE
Charles Roe Wagner
1955



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AN INVESTIGATION OF THE UNCATALYZED ALKYLATION
OF PHENOL WITH 1-CHLORO-4-METHYL-3-PENTENE

By

Charles Roe Wagner

AN ABSTRACT

Submitted to the School of Graduate Studies of Michigan
State College of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

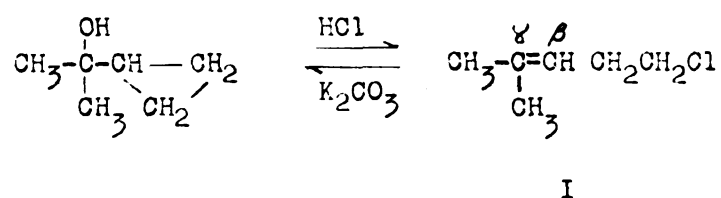
Department of Chemistry

1955

Approved Harold Hawk

ABSTRACT

Bruylants and Dewael¹ and later Favorskaya and Fridman² reported that 1-chloro-4-methyl-3-pentene (I) which was the product obtained when dimethylcyclopropylcarbinol was treated with hydrochloric acid, was converted back to dimethylcyclopropylcarbinol on treatment with base. It appeared that the β , γ -double bond participated in the

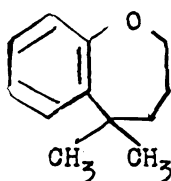


solvolysis reaction. One would conclude that I should be more reactive than most primary halides, being a potential source of a tertiary carbonium ion. It had previously been shown³ that tertiary halides, or other unusual reactive halides, such as allyl or benzyl halides, alkylate the aromatic nucleus of phenol without the need of the usual Friedel-Crafts type of catalyst. Primary halides (other than allyl or benzyl) do not alkylate phenols without such a catalyst.

It was the object of this research, then, to determine whether the primary chloroolefin, 1-chloro-4-methyl-3-pentene, was sufficiently reactive to alkylate the nucleus of phenol without a catalyst, and if so, to determine the structure of the product; that is, to determine whether the alkyl group reverted to the dimethylcyclopropylcarbinyl form.

When I was heated with phenol at 150°, hydrogen chloride was evolved and two isomeric crystalline products were isolated. Neither

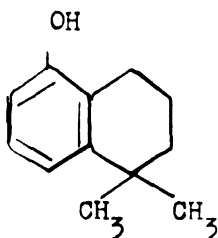
of these was the expected *p*-dimethylcyclopropylcarbonyl phenol. One was an ether, to which the structure 5,5-dimethylhomochroman (II) was assigned. The elemental analysis and infrared and ultraviolet absorption spectra were consistent with this structure.



II

Furthermore, this ether was obtained when an authentic sample of 5-phenoxy-2-methyl-2-pentene, was treated with a few drops of sulfuric acid.

The second crystalline product was an alkylated phenol. A number of structures were considered and the one which was most consistent with the chemical and physical data was 1,1-dimethyl-5-tetralol (III). Further work is needed, before this structure assignment can be considered unequivocal.



III

When the ether (II) was refluxed with hydrobromic acid and acetic acid, a second crystalline alkylated phenol was obtained. The structure of this compound is not clear but it appears to be alkylated para to the hydroxyl group.

Since saturated primary alkyl halides did not evolve hydrogen chloride when heated with phenol at 150° , it can be concluded that the double bond of I is involved in this reaction, but from the structure of the products, it is likely that the mechanism is quite different from the hydrolysis of I to dimethylcyclopropylcarbinol.

During the course of these studies, several new compounds were synthesized, mainly for the purposes of comparison with the observed alkylation products. 2-Isopropylchroman was prepared by treating 1-(o-hydroxyphenyl)-4-methyl-3-pentanone with zinc dust and sulfuric acid. 5-Phenoxy-2-methyl-2-pentene was obtained by refluxing a mixture of phenol, 1-chloro-4-methyl-3-pentene, acetone and potassium carbonate. The structure of 5-phenoxy-2-methyl-2-pentene was proved by degradation to known compounds.

1-(o-Methoxyphenyl)-4-methyl-3-pentanone was prepared by the catalytic reduction of the known compound, o-methoxystyryl isopropyl ketone. Reduction of 1-(o-methoxyphenyl)-4-methyl-3-pentanone with lithium aluminum hydride gave 1-(o-methoxyphenyl)-4-methyl-3-pentanol. 1-(p-Methoxyphenyl)-4-methyl-3-pentanone was prepared by the catalytic reduction of the known compound p-methoxystyryl isopropyl ketone. Reduction of 1-(p-methoxyphenyl)-4-methyl-3-pentanone with lithium aluminum hydride gave 1-(p-methoxyphenyl)-4-methyl-3-pentanol. Derivatives of the new ketones and alcohols were made.

Dimethylcyclopropylcarbonylbenzene was prepared by the following series of reactions. Reduction of the known compound, ethyl

2-carbethoxy-3-methyl-3-phenylbutanoate, with lithium aluminum hydride gave 2-hydroxymethyl-3-methyl-3-phenyl-1-butanol. Treatment of the diol with phosphorus tribromide gave 2-bromomethyl-3-methyl-3-phenyl-1-bromobutane. Ring closure with zinc dust gave dimethylcyclopropylcarbonylbenzene.

t-Butyl phenyl ether prepared from phenol and isobutylene, was split readily in benzene solution at 50° with hydrogen chloride. Cleavage, rather than rearrangement products were obtained.

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- 1 P. Bruylants and A. Dewael, Bull. Sci. Acad., Belg., (v), 14, 140 (1928).
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- 3 J. H. Simons and H. Hert, J. Am. Chem. Soc., 66, 1309 (1944).

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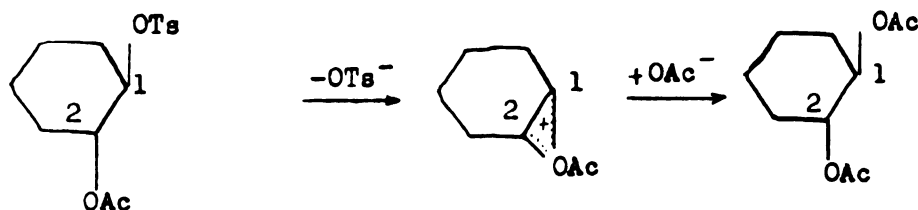
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INTRODUCTION AND HISTORICAL

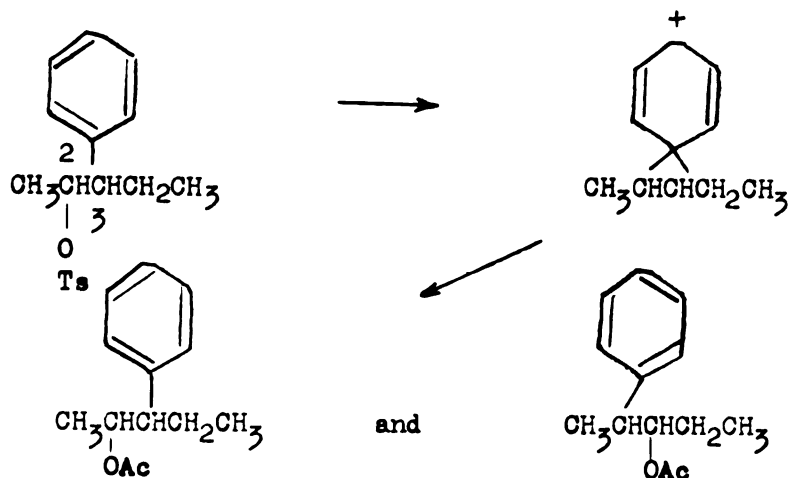
It has long been known that the reactivity of a functional group in an organic molecule is influenced by other groups in its immediate environment. In particular, a functional group on a carbon atom adjacent to a moiety which is undergoing chemical reaction may influence both the rate at which the process occurs, and its stereochemical course. This phenomenon, known as neighboring group participation, was first investigated in a systematic way with particular reference to displacement reactions by Winstein and his co-workers (1).

The normal stereochemical result of a bimolecular displacement process is inversion at the carbon holding the displaced group. Retention of configuration often occurs, however, in the course of a displacement reaction in which participation is possible. Thus, the acetolysis of trans 2-acetoxycyclohexyl p-toluenesulfonate proceeds with retention of configuration (1). The retention of configuration is ascribed to the participation of the trans 2-acetoxy



group on the reverse side of C₁ as the p-toluenesulfonate group ionizes. This gives one inversion at C₁. The second inversion at C₁, which produces overall retention of configuration, occurs as the entering acetate ion attacks C₁ from the opposite side of the participating group.

Isomerization through participation is also possible. Gram (2) studied in detail the acetolysis of the *p*-toluenesulfonate of 3-phenyl-2-pentanol, which gave a mixture of 3-phenyl-2-acetoxypentane and 2-phenyl-3-acetoxypentane. The isomerization occurs by

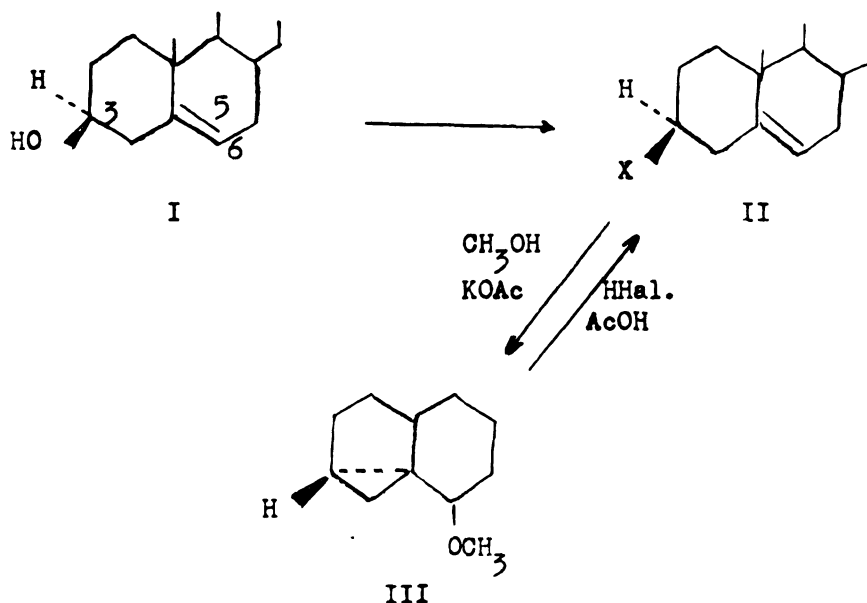


participation of the phenyl group with C_2 as the *p*-toluenesulfonate group ionizes, followed by attack of acetate at C_2 or C_3 .

The concept of participation is not restricted only to stereochemical control of a reaction path; a neighboring group also influences the rate of a chemical reaction. Thus, the acetolysis of trans 2-iodocyclohexyl *p*-bromobenzenesulfonate is 1800 times the rate for cyclohexyl *p*-bromobenzenesulfonate itself (3). In general Winstein and Grunwald (3) observed that the trans 2-substituted cyclohexyl *p*-bromobenzenesulfonates react faster than the corresponding cis isomers. This can be attributed to the favorable position of a trans substituent, which may participate by a back-side attack during the ionization at an adjacent carbon. In the cis isomer, however, a substituent is not favorably located for participation in this manner, and consequently it is less reactive.

Non-functional groups such as the phenyl (2), the carbon double bond (4), and carbon and hydrogen atoms (5) may also participate in organic displacements.

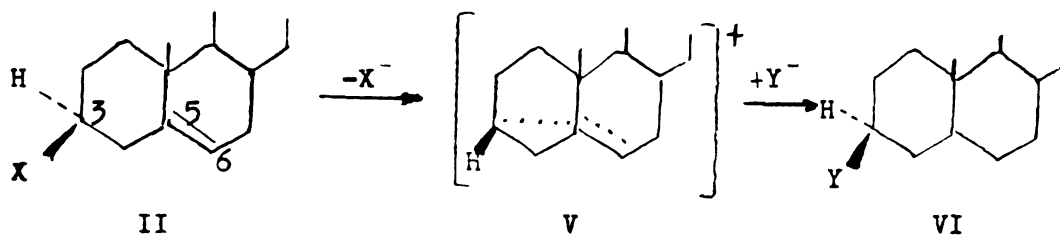
The i-steroid rearrangement in the cholesteryl system involves double bond participation in which all three aspects of neighboring groups are exemplified; i.e., stereochemical control, isomerization, and influence on reaction rate. Shoppee (4) has reviewed the i-steroid rearrangement, which can best be discussed with the aid of the following flow sheet.



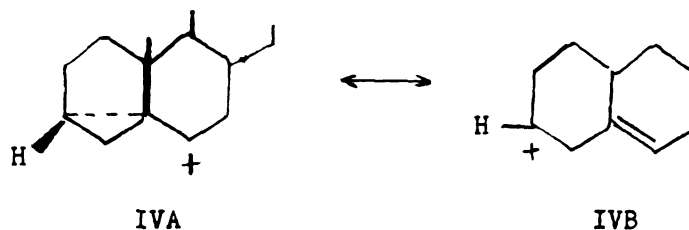
The reaction of cholesterol (I) with thionyl chloride or phosphorus pentachloride leads to cholesteryl chloride (II; X equals Cl) with retention of configuration at C₃. Treatment of cholesteryl chloride (II; X equals Cl) with methyl alcohol and potassium acetate forms the methyl ether of i-cholestanol (III) in which the configuration at C₃ is inverted. The methyl ether of i-cholestanol is unstable

in the presence of acid and rearranges to the methyl ether of cholesterol (II; X equals OCH_3); the potassium acetate apparently acts as a buffer preventing rearrangement of the initial product. The reverse reaction, from the methyl ether of i-cholestanol (III) to cholesteryl chloride (II; X equals Cl), leads to a second inversion at C_3 , giving the original configuration.

A mechanism (4) which satisfactorily explains the retention of configuration at C_3 involves the back-side participation of the π -electrons from the double bond as ionization occurs. This leads to one inversion at C_3 when the intermediate ion (V) is formed. The



or

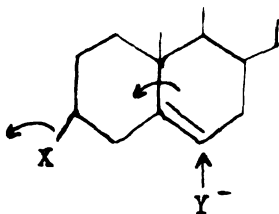


attacking nucleophilic group would then enter on the opposite side from the participating π -electrons, consequently leading to a second

inversion and overall retention of configuration at C_3 . On the other hand, the entering group may attack C_6 , whereupon the i-cholestanol system would be obtained.

When i-cholestanyl compounds are subjected to ionizing conditions, rearrangement to the cholesteryl system occurs. The C_3 - C_5 distance in cholesterol is 2.5 Å., and in i-cholestanol it must approach bonding distance, or approximately 1.5 Å., which involves considerable strain; hence, a driving force in the opposite direction from IVA to IVB should exist.

An alternative mechanism, referred to as S_N2' , for the i-steroid rearrangement can be pictured as a simultaneous attack of Y^- at C_6 , a shift of the double bond to the 3-5 position, with expulsion of X^- . This mechanism has been tentatively ruled out by Winstein and Adams (5). Their argument is based on the fact that the rate of acetolysis

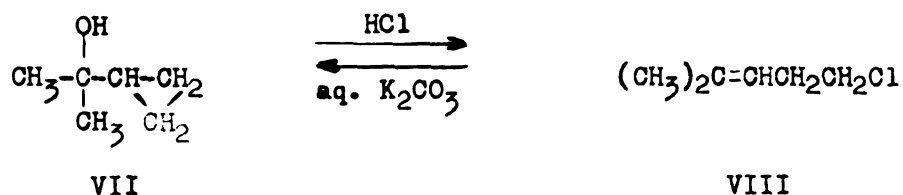


of cholesteryl p-toluenesulfonate in acetic acid is not affected by potassium acetate except for salt effects. If an S_N2' mechanism were operative, the rate of acetolysis should have been dependent upon the concentration of potassium acetate.

The cholesteryl system also shows an increase in chemical reactivity due to participation of a double bond. Winstein and Adams (5) studied

the acetolysis of cholesteryl *p*-toluenesulfonate (II; X equals TsO) and cyclohexyl *p*-toluenesulfonate. The former was found to react at a rate approximately one hundred times the latter. The reaction was kinetically first order in the tosylate and essentially independent of acetate ion concentration; therefore, the rate controlling step must have been the ionization of the tosylate. The increased reactivity in the cholesteryl system is ascribed to the participation of the unshared electron pair from the C₅-C₆ double bond which would furnish a driving force not possible in the cyclohexyl system.

It was of interest to examine the literature for analogs of the *i*-steroid rearrangement in simple acyclic systems. Bruylants and Dewael (7) and later Favorskaya and Fridman (8) reported that 1-chloro-4-methyl-3-pentene (VIII) is the product obtained from dimethylcyclopropylcarbinol (VII) and hydrochloric acid. This is not too unusual, for if one considers the cyclopropane ring as having properties similar to the carbon - carbon double bond, then this is simply an extension of ordinary allylic rearrangements to the cyclopropane system. It is similar to the conversion of the methyl ether of

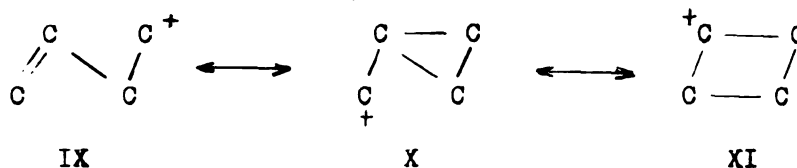


i-cholestanol (III) to cholesteryl chloride (II; X equals Cl) in the presence of hydrochloric acid. What is more surprising, is the conversion of the chloroölefin back to dimethylcyclopropylcarbinol on

treatment with base. This is an acyclic analog of the i-steroid rearrangement, but because of the greater flexibility of the system, the double bond need not be fixed in a position favorable for participation. Possibly the driving force is the opportunity of forming a tertiary carbonium ion.

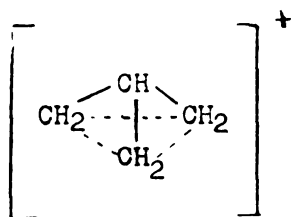
If the double bond in 1-chloro-4-methyl-3-pentene does indeed participate in the solvolysis reaction, then this compound should be more reactive than most primary halides. It has been shown (9) that tertiary halides, or other halides which are unusually reactive, such as those of the allyl or benzyl type, can alkylate the aromatic nucleus of phenol without need for the usual Friedel-Crafts type catalyst. Primary alkyl halides (other than allyl or benzyl) do not alkylate phenols without a catalyst. It was the object of this research, then, to determine whether the primary chloroölefin, 1-chloro-4-methyl-3-pentene, would alkylate the nucleus of phenols without a catalyst, and if so, to establish the nature of the products; that is, to determine whether the chloroölefin reverted to the dimethylcyclopropylcarbinyll derivative.

In this latter connection, it is important to note that often the cyclopropylcarbinyll and cyclobutyl systems are interconvertible.



Reactions which involve the cyclopropylcarbinyll ion (X) may yield

rearranged products of the structure IX or XI. Roberts and Mazur (10) reported that treatment of cyclobutylamine or cyclopropylcarbinylamine with nitrous acid gave approximately identical mixtures of alcohols, consisting of 47% cyclobutanol, 48% cyclopropylcarbinol and 5% allylcarbinol. They postulated that the interconversion of X and XI occurred with a minimum of energy, because both cyclobutylamine and cyclopropylcarbinylamine gave mixtures with nearly identical amounts of the isomeric alcohols. In a later paper, Roberts and Mazur (11) noted that the three methylene groups in cyclopropylcarbinylamine achieved some degree of equivalence in the course of the reaction with nitrous acid. This was established using C_{14} . The intermediate ion XII was postulated as a possible explanation for the apparent equivalence of three methylene groups



XII

The first part of the present work dealt with attempts to prepare dimethylcyclopropylcarbinyl chloride from the corresponding alcohol. This would be the tertiary chloride isomeric with the homoallylic chloride, 1-chloro-4-methyl-3-pentene. These attempts were unsuccessful.

The uncatalyzed reaction of 1-chloro-4-methyl-3-pentene with phenol was then examined, to determine whether aromatic alkylation

could be included among those reactions which are facilitated by a homoallylic system. Two crystalline products were obtained from the reaction, and the major body of the thesis is concerned with the determination of their structure.

It was hoped that the present work would also include kinetic data on the reactions of acyclic homoallylic systems with phenols, but since the reaction took an unexpected course, the major task became one of establishing the identity of the reaction products.

EXPERIMENTAL

5-Chloro-2-pentanone

The procedure in Organic Syntheses (12) was followed. To a solution of 450 ml. of concentrated hydrochloric acid in 525 ml. of water was added 384 g. (3.0 moles) of α -acetyl- γ -butyrolactone. The mixture was heated cautiously until the carbon dioxide evolution abated. The mixture was steam distilled until a total of 1.2 l. of distillate was collected. The organic layer was separated and the aqueous layer was extracted with three 150 ml. portions of ether. The combined organic extracts were dried over calcium chloride. The reaction was repeated using 136 ml. of concentrated hydrochloric acid, 158 ml. of water, and 116 g. (0.91 mole) of α -acetyl- γ -butyrolactone. The ether solutions from both runs were combined, the solvent removed, and the residue distilled in vacuo. Three hundred and sixty-six grams (75%) of 5-chloro-2-pentanone, b.p. 70°-72° at 20 mm., was obtained.

Methyl Cyclopropyl Ketone

The procedure was taken from Organic Syntheses (12). To a solution of 183 g. (4.57 moles) sodium hydroxide in 180 ml. of water in a 2 l. round-bottomed, three-necked flask equipped with a motor-driven iron stirrer, a reflux condenser, and an addition funnel, was added 366 g. (3.04 moles) of 5-chloro-2-pentanone during a twenty minute period. While being stirred, the solution was heated cautiously for one hour. To the refluxing solution was slowly added 375 ml. of water. The solution was refluxed an additional hour, then

steam distilled. The distillate was saturated with potassium carbonate and extracted with two 150 ml. portions of ether. The combined ether extracts were dried over calcium chloride. The solvent was removed through a 30 cm. glass packed column and the residue distilled through a short Vigreux column. Three hundred and sixty-six grams (78%) of methyl cyclopropyl ketone, b.p. 109° - 111° , was obtained.

A similar experiment using 1.57 moles of 5-chloro-3-pentanone yielded 79.5% of the theoretical amount of methyl cyclopropyl ketone.

Dimethylcyclopropylcarbinol

Method 1. In a typical preparation, 292 g. (2.06 moles) of methyl iodide in 950 ml. of anhydrous ethyl ether was slowly added to 64 g. (2.5 moles) of magnesium turnings in a 3 l. round-bottomed flask equipped with a Friedrichs condenser, a mercury-sealed stirrer, and an addition funnel. The resulting solution was refluxed for one-half hour. One hundred and seventy-two grams (2.06 moles) of methyl cyclopropyl ketone dissolved in 550 ml. of anhydrous ethyl ether was added dropwise to the stirred, cooled reaction mixture. The mixture was allowed to stand for 12 hours, then hydrolyzed by pouring into a solution of 214 g. (4.0 moles) of ammonium chloride in 1 l. of water and 400 g. of ice. The ether layer was separated and the aqueous layer extracted with three 150 ml. portions of ether. The combined ether extracts were dried over potassium carbonate and the solvent was then removed through a Vigreux column. The residue was distilled through a Claisen head and the fraction boiling from 115° to 122° was redistilled under reduced pressure using a Stedman

packed column. One hundred and fifty-three grams (74%) of dimethylcyclopropylcarbinol, b.p. 51.5° - 53° at 40 mm., n_D^{20} 1.4310 was obtained. Volkenburgh et al. (13) report for dimethylcyclopropylcarbinol, n_D^{20} 1.4337.

Method 2. The modified Grignard method of Swain and Boyles (14) was used in one preparation. To 64.5 g. (2.69 moles) magnesium turnings and 800 ml. of anhydrous ethyl ether, 400 g. (2.5 moles) of bromine was added slowly with stirring. After stirring the mixture for 3 hours, 100 g. (1.19 moles) methyl cyclopropyl ketone was added to the stirred mixture. To the reaction was added, dropwise, 800 ml. of ethyl ether containing 2.28 moles of methyl magnesium iodide. The resulting mixture was hydrolyzed by pouring it into a cold 10% sodium carbonate solution. The ether layer was separated and the aqueous layer extracted with ethyl ether. The combined ether extracts were dried over potassium carbonate, the solvent removed, and the residue distilled. Twenty-one grams (18%) of dimethylcyclopropylcarbinol, b.p. 119.1° - 121° , was obtained. Fifty-three milliliters of a dark red residue remained.

Attempted Preparation of Dimethylcyclopropylcarbiny l Hydrogen Tetrachlorophthalate

The general procedure of Fensler and Shriner (15) was followed. To 1.21 g. (0.05 mole) of magnesium turnings, in a 500 ml. round-bottomed flask equipped with a stirrer, condenser, and addition funnel was added 4 ml. (0.05 mole) ethyl bromide in 75 ml. of anhydrous ether. Five grams (0.05 mole) of dimethylcyclopropylcarbinol dissolved in 25 ml. of ether was added, dropwise, to the ethyl

magnesium bromide solution. When the evolution of ethane abated 100 ml. of anhydrous dioxane was added. A white precipitate formed. The temperature of the mixture was increased to 60° and 14.3 g. of tetrachlorophthalic anhydride was added. After stirring for one hour at 60° the contents of the flask were cooled and poured into 625 ml. of 2 N hydrochloric acid and 250 g. of ice. The hydrolyzed mixture was filtered to remove unreacted tetrachlorophthalic acid. The ether layer was separated and washed with water and then extracted with one 100 ml. portion and one 25 ml. portion of 5% sodium hydroxide solution. The combined alkaline extracts were acidified with 6 N hydrochloric acid, and the precipitate which formed was removed by filtration. After recrystallization from a mixture of petroleum ether and ethyl ether the solid melted with decomposition at 250° . The melting point of tetrachlorophthalic acid is 250° with decomposition.

1-Chloro-4-methyl-3-pentene

The procedure of Favorskaya and Fridman (8) was used. Sixty grams (0.5 mole) of dimethylcyclopropylcarbinol was stirred vigorously with a solution of 130 ml. of concentrated hydrochloric acid (d. 1.19) and 130 ml. of water for 2.5 hours. The organic layer was separated, washed with 200 ml. of water, and dried over calcium chloride. The crude 1-chloro-4-methyl-3-pentene, b.p. 129° - 134° , after a simple distillation, was redistilled through a glass-packed column. Forty-nine grams (57.1%) of 1-chloro-4-methyl-3-pentene, b.p. 131.6° - 133° , n_D^{25} 1.4444, was obtained. Favorskaya and

Fridman (8) reported a 76% yield of 1-chloro-4-methyl-3-pentene, b.p. 131° - 133° , $n_D^{13.5}$ 1.44485.

The reaction was repeated several times and the yield of the crude 1-chloro-4-methyl-3-pentene, b.p. 130° - 133° , varied from 71% to 80% of the theoretical.

Reaction of 1-Chloro-4-methyl-3-pentene with Aqueous Potassium Carbonate

The procedure of Favorskaya and Fridman (8) was followed. Nineteen and four-tenths grams (0.16 mole) of 1-chloro-4-methyl-3-pentene was refluxed with 200 ml. of 10% potassium carbonate solution for 9.5 hours. The mixture was refluxed with stirring for an additional six hours. The reaction mixture was cooled and the organic layer separated. The aqueous layer was extracted with three portions of ether. The combined organic extracts were dried over magnesium sulfate. The solvent was distilled through a short Vigreux column and the residue distilled in a semi-micro distillation apparatus. Eleven and four-tenths grams (70%) of dimethylcyclopropylcarbinol was obtained.

Favorskaya and Fridman (8) reported a 60 per cent yield of the product. A 2 ml. center cut was taken for the infrared spectrum. The spectrum was identical with that of an authentic sample of dimethylcyclopropylcarbinol.

Reaction of Dimethylcyclopropylcarbinol and Phosphorus Trichloride

The general experimental conditions of Hatch and Nesbitt (16) were used. Ten grams (0.1 mole) of dimethylcyclopropylcarbinol and 2.2 g. (0.028 mole) of pyridine were added over a twenty minute

period to a 5.5 g. (0.04 mole) of phosphorus trichloride with cooling. The mixture was allowed to stand at 0° for forty minutes. The mixture was washed with two portions of 10% sulfuric acid and four portions of 10% sodium carbonate and dried over sodium sulfate. The material was distilled through a modified Claisen head. Two fractions were collected: fraction 1, b.p. 70° - 73° , n_D^{20} 1.4260, 0.5 g.; fraction 2, b.p. 119° , n_D^{20} 1.4330, 5.0 g. Volkenburgh, et al. (13) report for isopropenylcyclopropane, b.p. 70.41° , n_D^{20} 1.4254. Fraction 2 was recovered dimethylcyclopropylcarbinol.

Reaction of Dimethylcyclopropylcarbinol and Phosphorus Pentachloride

The general procedure of Gerrard (17) was followed. A suspension of 10.4 g. (0.05 mole) phosphorus pentachloride in 40 ml. ethyl ether was added slowly to a solution of 31.6 g. (0.4 mole) pyridine and 10 g. (0.1 mole) dimethylcyclopropylcarbinol in 30 ml. of ethyl ether at -10° . The mixture was allowed to react for sixteen hours at 15° and then filtered.

The filtrate was washed with 10% sulfuric acid, then 10% sodium carbonate, and dried over sodium sulphate. The solvent was removed and the residue distilled through a modified Claisen head in vacuo.

Sixty-one and six-tenths per cent (6.16 g.) of dimethylcyclopropylcarbinol, b.p. 86° at 145 mm., n_D^{20} 1.4340, was recovered.

The experiment was repeated four times varying the solvent and mode of addition. Dimethylcyclopropylcarbinol or 1-chloro-4-methyl-3-pentene were obtained in these experiments.

Reaction of Dimethylcyclopropylcarbinol and Thionyl Chloride

The general procedure of Gilman and Harris (18) was followed.

A solution of 14.3 g. (0.12 mole) thionyl chloride, 10.3 g. (0.13 mole) of pyridine and 10 ml. chloroform was added slowly at 0° to 10 g. (0.1 mole) dimethylcyclopropylcarbinol in 10 ml. chloroform. After the addition the mixture was allowed to stand at room temperature for one and one-half hours. The mixture was washed thoroughly with water, dried over potassium carbonate, and then the solvent was removed. The residue was distilled under reduced pressure. Six and eight-tenths grams (58%) 1-chloro-4-methyl-3-pentene, b.p. 52° at 55 mm., n_D^{22} 1.4440 was obtained.

Reaction of 1-Chloro-4-methyl-3-pentene and Potassium Acetate

The procedure of Bruylants and Dewael (7) was followed. A mixture of 16.5 g. (0.169 mole) of potassium acetate, 20 g. (0.169 mole) of 1-chloro-4-methyl-3-pentene, and 2 ml. of acetic acid were refluxed for thirty hours. The cooled mixture was poured into water. The organic layer was separated, dried over potassium carbonate, and distilled. Three and six-tenths grams (15%) of 1-acetoxy-4-methyl-3-pentene, b.p. 155° - 175° , n_D^{20} 1.4331, was obtained. Bruylants and Dewael (7) reported for 1-acetoxy-4-methyl-3-pentene, b.p. 170° - 171° , n_D^{20} 1.43107.

Reaction of 1-Chlorohexane and Phenol at 150°

The apparatus described by Bordeaux (19) was used. A mixture of 6.03 g. (0.05 mole) of 1-chlorohexane and 18.8 g. (0.2 mole) of phenol was heated at 150° in an oil bath while a stream of dry nitrogen was bubbled through the mixture. The nitrogen was used to sweep the hydrogen chloride, which would be formed if alkylation did occur, from the reaction mixture into a potassium carbonate adsorption tube.

The reaction was followed by determining the amount of hydrogen chloride adsorbed by the potassium carbonate at various intervals. (The per cent of the theoretical amount of hydrogen chloride which would have been evolved, if complete alkylation occurred, was calculated and recorded in Table I.) The chloride was determined by the Volhard procedure. The reaction mixture remained clear

TABLE I.

Time - Hours	0	1.0	2.5	5.0	8.0
Per Cent HCl Evolved	0	0	0	3.0	5.7

throughout the heating period.

The cooled mixture was dissolved in 20 ml. of benzene, extracted with three 15 ml. portions of 10% sodium hydroxide, and dried over potassium carbonate. The solvent was removed and the residue distilled. Seventy-one per cent (4.28 g.) of 1-chlorohexane, b.p. 130°, was recovered. One milliliter of 1-chlorohexane remained as hold-up in the distillation apparatus.

The alkaline extracts were acidified with acetic acid and extracted with four 20 ml. portions of benzene. The combined benzene extracts were dried over sodium sulfate, the solvent removed, and the residue distilled in vacuo. Sixteen grams (85%) of phenol, b.p. 67°-70° at 3 mm., was recovered. One and one-half grams of phenol remained as hold-up in the distillation apparatus.

Reaction of 1-Chloro-4-methyl-3-pentene and p-Cresol

Twenty-one and two-tenths grams (0.2 mole) of p-cresol and 5.94

g. (0.05 mole) 1-chloro-4-methyl-3-pentene were placed in the apparatus described by Bordeaux (19). The mixture was heated at 150° while nitrogen was bubbled through it. The hydrogen chloride was determined as previously described. The mixture became dark after heating for five minutes.

TABLE II.

Time - Hours	0	1	2	3	4	5	7	9	11
Per Cent HCl Evolved	0	4.1	17.1	30.9	38.6	41.9	50.5	56.1	60.1

The mixture was cooled, dissolved in 50 ml. of benzene, extracted with two 20 ml. portions of 20% sodium hydroxide and 20 ml. of Claisen's alkali, and dried over potassium carbonate. The solvent was removed and the residue was distilled in vacuo using a semi-micro distillation apparatus. Two and seven-tenths grams of material, b.p. 85° - 95° at 1.5 mm., was obtained. A dark residue (2.7 g.) remained.

The alkaline extracts were acidified and extracted with three 50 ml. portions of benzene. The combined benzene extracts were dried over sodium sulphate, the solvent removed, and the residue distilled in vacuo using the semi-micro distillation apparatus. Fourteen and one-tenth grams (66.6%) of *p*-cresol, b.p. 70° - 75° at 1.5 mm., was recovered. The residue (2.6 g.) would not distill and when cooled became very hard.

The reaction was repeated using 42.4 g. (0.4 mole) of *p*-cresol and 11.8 g. (0.1 mole) of 1-chloro-4-methyl-3-pentene. The mixture was heated thirteen hours at 150° and treated as described above. Four grams of neutral material, b.p. 90° - 95° at 1.5 mm., was obtained.

The benzene was removed from the alkali soluble material and the residue distilled in vacuo. Twenty-five grams (60%) of p-cresol, b.p. 83° - 86° at 2.0 mm., was recovered. The residue (9.7 g.) would not distill.

Reaction of 1-Chloro-4-methyl-3-pentene and Phenol at 150°

The apparatus described by Bordeaux (19) was used. A mixture of 5.95 g. (0.05 mole) of 1-chloro-4-methyl-3-pentene and 18.8 g. (0.20 mole) of phenol were placed in the reaction flask. The temperature for the reaction was 150° . Dry nitrogen was bubbled through the mixture and the amount of hydrogen chloride evolved determined as previously described.

TABLE III.

Time - Hours	0	1.5	3.	5.	7.	9.	11.
Per Cent HCl	0	21.8	34.6	41.8	46.8	51.6	54.4

The mixture, which had darkened within ten minutes at 150° , was cooled, dissolved in benzene, extracted with 10% sodium hydroxide, and dried over sodium sulfate. The solvent was removed and the residue, which was distilled in vacuo, gave 2.13 g. of material, b.p. 125° - 161° at 3 mm. One-half gram of a dark viscous residue remained.

The alkaline extracts were acidified, extracted with benzene and dried over sodium sulfate. The solvent was removed and the residue distilled in vacuo. Eight and four-tenths gram of phenol, b.p. 64° - 68° at 3 mm., and 1.6 g. of material, b.p. 79° - 151° at 3 mm.,

were obtained. One gram of a dark viscous residue remained.

The reaction was repeated using 149 g. (1.58 moles) of phenol and 37.5 g. (0.317 mole) of 1-chloro-4-methyl-3-pentene. The mixture was stirred and heated at 150° for twelve and one-half hours. The mixture was treated as previously described. After the benzene was removed from the neutral portion the residue was distilled in vacuo and the following fractions were obtained: fraction 1, b.p. 80°-92° at 1 mm., 9 g.; fraction 2, b.p. 92°-116° at 1 mm., 3.5 g.; fraction 3, b.p. 116°-140° at 1 mm., 7.0 g.; fraction 4, b.p. 140°-195° at 0.5 mm., 7.5 g. One gram of a dark viscous residue remained. Fraction 1 crystallized at room temperature. After recrystallization from petroleum ether, fraction 1 melted at 47°-48°. The remaining fractions were viscous liquids which did not solidify.

The benzene was removed from the alkali soluble portion and the residue distilled in vacuo. The following fractions were obtained: fraction 1a, b.p. 54°-60° at 5 mm., 95.5 g.; fraction 2a b.p. 60°-64° at 2 mm., 6 g.; fraction 3a, b.p. 110°-115° at 2 mm., 15.4 g.; fraction 4a, b.p. 116°-185° at 1.5 mm., 8.0 g. Five grams of a dark residue remained. Fractions 1a and 2a were recovered phenol. Fraction 3a solidified and after recrystallization from petroleum ether melted at 113°-114°. Fraction 4a was a viscous oil which did not solidify. Fraction 1 will be referred to as compound "A" and fraction 3a will be referred to as compound "B".

Anal.¹ Calcd. for "A", C₁₂H₁₆O: C, 81.77; H, 9.15. Found C, 81.99; H, 9.10.

¹ Analyses were performed by the Clark Microanalytical Laboratory, Urbana, Illinois.

Calcd. for "B", $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.73; H, 9.32.

Experiments Concerning Neutral Product "A"

Attempted Thermal Rearrangement of the Neutral Product "A"

Four and one-tenths grams of "A" was placed in a 50 ml. round-bottomed flask equipped with a reflux condenser. The flask was heated in a sand bath until "A" refluxed. It was allowed to reflux at 234° for three and one-half hours. The cooled material was dissolved in petroleum ether and washed with two 8 ml. portions of 20% sodium hydroxide, dried over sodium sulfate, and part of the solvent removed. Ninety-one per cent (3.75 g.) of "A", m.p. 47° - 48° , was recovered.

The alkaline extracts were acidified and treated with an aqueous bromine solution. Only a trace of phenolic material was present as indicated by the slight loss of color of bromine.

Reaction of Phenol, "A" and Hydrogen Chloride at 150°

Seven grams (0.075 mole) of phenol and 6.6 g. (0.037 mole) of "A" were placed in the apparatus described by Bordeaux (19). Hydrogen chloride gas was bubbled through the solution for five and one-half hours at 150° . The mixture remained clear. The cooled mixture was dissolved in 50 ml. of benzene, extracted with two 20 ml. portions and one 10 ml. portion of 20% sodium hydroxide, dried over magnesium sulfate, and the solvent removed. The residue was distilled in vacuo. Four and one-half grams (70%) of "A", b.p. 75° - 80° at 1 mm., was recovered. One gram of "A" remained as residue from hold-up in the distillation apparatus.

The alkaline extracts were acidified and extracted with four 15 ml. portions of benzene. The combined benzene extracts were dried over magnesium sulfate, the solvent removed and the residue distilled in vacuo. Six and two-tenths grams (88%) of phenol, b.p. 58° - 62° at 1 mm., was recovered.

Attempted Nitration of "A"

Method 1. A solution of 3 ml. acetic acid and 1 ml. of nitric acid (d. 1.42) was added slowly to 1.4 g. of "A" dissolved in 5 ml. of acetic acid. The temperature was 15° - 20° . The mixture was allowed to react at room temperature for forty-five minutes and then poured into ice. The solid which separated was recrystallized from petroleum ether. Ninety-six per cent (1.35 g.) of "A", m.p. 46° - 47° , was recovered.

The nitration was repeated at higher concentrations of nitric acid and higher temperatures. Again the starting material was recovered in a seventy-one per cent yield.

Method 2. One gram of "A" was dissolved in 4 ml. of concentrated sulfuric acid. A light red colored solution was obtained. Upon the addition of one drop of nitric acid (d. 1.42) the solution became black. The mixture was poured onto ice. The solid which separated was filtered, dissolved in petroleum ether and dried over potassium carbonate.

Part of the petroleum ether was removed and the dissolved solid allowed to crystallize. Sixty-five per cent (0.65 g.) of "A", m.p. 47° - 48° , was recovered.

Reaction of "A", Hydrobromic Acid, and Acetic Acid

Method 1. A solution of 3 ml. of 48% hydrobromic acid, 10 ml. of glacial acetic acid, and 1.2 g. (0.0067 mole) of "A" was refluxed for twenty-four hours. The solution was cooled, treated with 10% sodium bicarbonate and extracted with two 20 ml. portions of ethyl ether. The combined ether extracts were washed with two 10 ml. portions of sodium hydroxide. The alkaline extracts were acidified and treated with aqueous brominating solution. Eight-tenths gram (35%) of tribromophenol was obtained.

Method 2. The experiment was repeated. Four grams of "A", 33 ml. of acetic acid, and 18 ml. of 48% hydrobromic acid were refluxed for thirty hours. The solution was cooled, treated with 10% sodium bicarbonate and extracted with ethyl ether. The ether extracts were dried over magnesium sulfate, the solvent removed, and the residue distilled in vacuo.

One and two-tenths grams of material, b.p. 114° - 128° at 1.5 mm., was obtained. A residue of 2.14 g. remained. The distillate solidified, and after several recrystallizations from petroleum ether melted at 84.5° - 85.5° . This solid will be referred to as "C". The infrared spectrum of "C" had a strong band at $2.76\ \mu$ indicating the material was phenolic even though it was isolated from the alkali insoluble fraction.

Anal. Calcd. for "C", $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.43; H, 9.40.

The alkaline extracts were acidified, extracted with ethyl ether and dried over magnesium sulfate. The solvent was removed and the

residue treated with aqueous brominating solution. Less than 0.1 g. of tribromophenol was obtained.

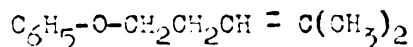
The experiment was repeated using 7.7 g. of "A" and the milder conditions found in Method 1. Product "C", m.p. 84° - 85° , was obtained from the neutral fraction and 1 g. of phenol from the alkali soluble fractions.

Attempted Reduction of "A"

Ten grams (0.057 mole) of "A" was dissolved in 130 ml. of absolute ethyl alcohol. Platinum oxide (0.1 g.) catalyst was added and the mixture was shaken while under a hydrogen pressure of 3 atmospheres. No hydrogen was absorbed after one-half hour. An additional 0.1 g. of platinum oxide was added, and the mixture again was shaken while under a hydrogen pressure of 3 atmospheres. No hydrogen was absorbed.

The mixture was transferred to a high pressure bomb and subjected to a hydrogen pressure of 500 p.s.i. The mixture was shaken for four hours with no hydrogen absorbed. The mixture was filtered, the solvent removed, and the starting material, b.p. 81° - 84° at 1 mm., was recovered.

5-Phenoxy-2-methyl-2-pentene



A mixture of 96.7 g. (0.7 mole) of potassium carbonate, 47 g. (0.5 mole) of 1-chloro-4-methyl-3-pentene, and 140 ml. of acetone were placed in a two-necked flask equipped with a Friedrichs condenser and a mercury-sealed, motor driven stirrer. The mixture

was refluxed on a steam bath for four days. Two gram portions of potassium carbonate were added periodically.

The cooled mixture was poured into 200 ml. of water and the organic layer separated. The aqueous layer was extracted with three 100 ml. portions of ethyl ether. The combined organic extracts were washed with 20% sodium hydroxide, dried over sodium sulfate, and the solvent removed through a glass packed column. The residue was distilled in vacuo.

Twenty-eight and six-tenths grams (48%) of 1-chloro-4-methyl-3-pentene, b.p. 45° - 50° at 20 mm., was recovered. Thirty-three and five-tenths grams (79% based on used 1-chloro-4-methyl-3-pentene) of material, which was shown to be 5-phenoxy-2-methyl-2-pentene, b.p. 85° - 90° at 1 mm., n_D^{20} 1.5112, was obtained. The experiment was repeated using the same quantities of reagents except that 20 ml. of acetone was added every twenty-four hours during the refluxing period. Thirty and nine-tenths grams (52.2%) of 1-chloro-4-methyl-3-pentene was recovered and 20 g. (47.6% based on used 1-chloro-4-methyl-3-pentene) of 5-phenoxy-2-methyl-2-pentene was obtained.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.76; H, 9.09.

Proof of Structure of 5-Phenoxy-2-methyl-2-pentene

Hydrogenation of 5-phenoxy-2-methyl-2-pentene. A mixture of 15.2 g. (0.087 mole) of 5-phenoxy-2-methyl-2-pentene, 170 ml. of absolute ethanol, and 0.2 g. of platinum oxide were placed in a 500 ml. low-pressure reduction bomb. Approximately 0.1 mole of

hydrogen reacted within a period of fifteen minutes. The initial hydrogen pressure was 12 p.s.i.

The catalyst was removed by filtration and the ethyl alcohol was removed through a short Vigreux column. Twelve and two-tenths grams (80%) of a material which was shown to be isohexyl phenyl ether, b.p. 77° - 80° at 1 mm., $n_D^{24.9}$ 1.4883, was obtained.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.17. Found: C, 79.98; H, 10.25.

Although the carbon analysis of isohexyl phenyl ether was low, the subsequent series of experiments confirmed the compound as isohexyl phenyl ether.

Cleavage of isohexyl phenyl ether. Twelve and one-tenth grams (0.067 mole) of isohexyl phenyl ether obtained by the reduction of 1-phenoxy-4-methyl-3-pentene, 100 ml. of glacial acetic acid, and 25 ml. of 48% hydrobromic acid were refluxed for nine hours. The mixture was cooled and extracted with six 40 ml. portions of ether. The combined ether extracts were washed with saturated sodium bicarbonate, extracted with 10% sodium hydroxide and dried over magnesium sulfate. The solvent was removed and the residue distilled in vacuo. Seven and one-half grams (68%) of isohexyl bromide, b.p. 55° - 60° at 41 mm., $n_D^{24.9}$ 1.4412 and 1.3 g. (10%) of recovered isohexyl phenyl ether were obtained.

The sodium hydroxide extracts were acidified and extracted with ether. The ether extracts were dried over magnesium sulfate, the solvent removed and the residue distilled in vacuo. Three and

eight-tenths grams (50%) of phenol, b.p. 85° at 20 mm., was obtained. Bromination gave 2,4,6-tribromophenol, m.p. 92° - 93.5° .

5-Methylhexanamide. Six and one-half grams (0.039 mole) of isohexyl bromide obtained from the cleavage of isohexyl phenyl ether, in 25 ml. of anhydrous ethyl ether was added slowly to 1.3 g. (0.054 mole) of magnesium turnings in a round-bottomed three neck flask equipped with a Friedrichs condenser, mercury-sealed, motor-driven stirrer, and an addition funnel. The mixture was refluxed and stirred for two hours. The mixture was cooled to -8° and while being stirred a stream of carbon dioxide gas was passed over the solution until no more white precipitate formed.

The mixture was hydrolyzed by slowly adding 100 ml. of 10% sulfuric acid. The ether layer was separated and the aqueous phase extracted with three 30 ml. portions of ether. The combined organic layers were extracted with three 25 ml. portions of 10% sodium hydroxide. The alkaline extracts were acidified and extracted with ether. The ether extracts were dried over magnesium sulfate and the solvent removed. The residue (3 g.) was refluxed with 5 ml. of thionyl chloride for forty-five minutes and then poured into 35 ml. of cold concentrated ammonium hydroxide. The solid which formed was removed by suction filtration, recrystallized from a mixture of ethyl alcohol and water, and dried. The melting point was 101° - 102° . The melting point of 5-methylhexanamide as reported by Levene and Allen (20) is 102° - 103° .

Reaction of 5-Phenoxy-2-methyl-2-pentene, Phenol, and Hydrogen Chloride at 150°

A mixture of 37.6 g. (0.4 mole) of phenol and 17.4 g. (0.1 mole) of 5-phenoxy-2-methyl-2-pentene was heated at 150° while hydrogen chloride was slowly bubbled through the mixture during a seven hour period. The mixture was cooled and dissolved in 100 ml. of benzene. The benzene solution was extracted with three 20 ml. portions of 20% sodium hydroxide, three 20 ml. portions of Claisen's alkali, and dried over potassium carbonate. The solvent was removed and the residue distilled in vacuo. Two and seven-tenths grams of material, b.p. 85°-89° at 1 mm., was obtained, which solidified. The material, after recrystallizing from petroleum ether, melted at 47° to 48°. The infrared spectrum was identical with that of the neutral product "A".

The alkaline extracts were acidified and extracted with three 50 ml. portions of benzene. The combined benzene extracts were dried over sodium sulfate, the solvent removed and the residue was distilled in vacuo.

The following fractions were obtained: fraction 1, b.p. 65°-70° at 1 mm., 29.7 g.; fraction 2, b.p. 70°-110° at 1 mm., 0.4 g.; fraction 3, b.p. 110°-120° at 1 mm., 2.54 g.; fraction 4, b.p. 120°-150° at 1 mm., 4.47 g. A black residue of 4.38 g. remained. Fraction 1 was recovered phenol (79%). Fraction 3 solidified and after recrystallization from petroleum ether melted at 112°. The infrared spectrum of fraction 3 was identical with "B".

Reaction of 5-Phenoxy-2-methyl-2-pentene and Hydrogen Chloride at 150°

Ten grams (0.057 mole) of 5-phenoxy-2-methyl-2-pentene was heated at 150° for five hours as hydrogen chloride was bubbled through the liquid.

The mixture was cooled, dissolved in 40 ml. of benzene, and extracted with two 20 ml. portions of 20% sodium hydroxide and one 15 ml. portion of Claisen's alkali.

The benzene extract was dried over potassium carbonate, the solvent was removed, and the residue distilled in vacuo. Nine and seven-tenths grams (97%) of 5-phenoxy-2-methyl-2-pentene, b.p. 90°-97° at 2 mm., n_D^{25} 1.5085, was recovered.

The alkaline extracts were acidified and extracted with four 25 ml. portions of benzene. The combined benzene extracts were dried over sodium sulfate and the solvent removed. A small amount of residue remained which did react with aqueous bromine. The residue was too small to obtain a derivative.

Reaction of 5-Phenoxy-2-methyl-2-pentene with Sulfuric Acid

To 2 ml. of concentrated sulfuric (95%) was added with shaking 0.45 g. (0.0025 mole) of 5-phenoxy-2-methyl-2-pentene. The reaction was exothermic and a red color developed. The mixture stood three minutes and was poured onto 5 g. of ice. A white solid (0.28 g.) separated. It was filtered, dried, and recrystallized from petroleum ether.

The melting point was 45°-47°; mixed melting point of the product with "A" was 47°-48°. The infrared absorption spectrum of the product was identical with that of "A".

Two drops of concentrated sulfuric acid was added to 0.5 ml. of 5-phenoxy-2-methyl-2-pentene. After shaking for approximately one minute, 10 ml. of water was added. "A" separated as white plates in a good yield.

Reaction of Isohexyl Phenyl Ether with Sulfuric Acid

One-half gram of isohexyl phenyl ether was dissolved in 2 ml. of sulfuric acid. A slight red color developed. The mixture was poured into 10 g. of ice, and an oil separated. The mixture was made alkaline with sodium hydroxide and then extracted with petroleum ether. The organic extracts were dried over potassium carbonate and the solvent removed. The residue (0.4 g.) was a clear liquid, n_D^{25} 1.4890 which was recovered (80%) isohexyl phenyl ether, $n_D^{24.9}$ 1.4883. The alkaline extracts were acidified and indicated no phenolic material present when tested with phosphomolybdate (22).

t-Butyl Phenyl Ether

The procedure of Stevens and Bowman (21) was followed. Ninety-four grams (1.0 mole) of phenol and 52 mg. of concentrated sulfuric acid were placed in a 500 ml. round-bottomed flask equipped with a gas inlet tube, a ground glass stirrer, and a dry ice condenser. The phenol was melted and a stream of isobutylene was passed through the stirred solution as it was quickly cooled to 5° to 8°.

The isobutylene was passed into the slurry only as rapidly as it was absorbed. Fifty-eight grams (1.04 moles) of isobutylene was absorbed in five hours.

Three hundred milliliters of 10% sodium hydroxide was added and the organic layer was dissolved in 150 ml. of ether. The organic

layer was separated, extracted with four 30 ml. portions of Claisen's alkali, and dried over sodium sulfate. The solvent was removed and the residue distilled in vacuo. Forty-six and four-tenths grams (56.9% based on used phenol) of t-butyl phenyl ether, b.p. 72° - 73° at 17 mm., n_D^{24} 1.4853, was obtained. This product gave a negative test with phosphomolybdate test, Platkovskaya and Vatkina (22). The infrared spectrum also showed no phenolic material being present. Forty-three grams (45.7%) of phenol, b.p. 85° - 90° at 20 mm., was recovered.

The experiment was repeated except that the product was washed with 10% sodium hydroxide only. The product obtained contained considerable amounts of phenol, and after extracting with Claisen's alkali 20 g. (13.3%) of t-butyl phenyl ether, b.p. 75° - 75° at 16 mm., n_D^{25} 1.4850, was obtained. Stevens and Bowman reported a yield of 59.2% based on phenol consumed.

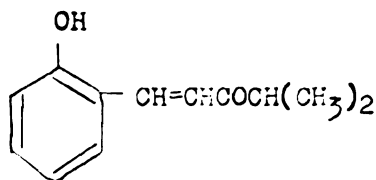
Reaction of t-Butyl Phenyl Ether and Hydrogen Chloride at 50°

Ten grams (0.067 mole) of t-butyl phenyl ether in 10 ml. of benzene was heated at 50° for forty-five minutes while hydrogen chloride gas was bubbled through the solution. The mixture was cooled, extracted with 20% sodium hydroxide, and dried over anhydrous potassium carbonate. The solvent was removed and the residue distilled in vacuo. Three and three-tenths grams (33%) of t-butyl phenyl ether, b.p. 72° - 73° at 16 mm., n_D^{25} 1.4851, was recovered.

The alkaline extracts were acidified and extracted with four 20 ml. portions of benzene. The combined benzene extracts were dried over sodium sulfate, the solvent removed, and the residue recrystallized

from petroleum ether. Two and two-tenths grams (24%) of phenol, m.p. 39° - 40° , was obtained. The tribromo derivative melted at 93° - 94° .

o-Hydroxystyryl Isopropyl Ketone

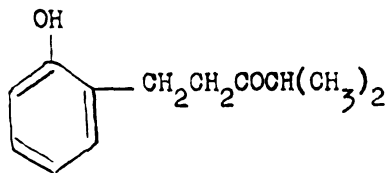


The general experimental conditions of Harries and Busse (23) were used. Fifty grams (0.41 mole) of salicylaldehyde was dissolved in a solution of 50 ml. of ethyl alcohol and 140 ml. of 10% sodium hydroxide. Fifty grams (0.58 mole) of methyl isopropyl ketone and 250 ml. of 10% sodium hydroxide was added. The solution was diluted with water to 2 l. and allowed to stand in the dark for eight days.

The solution was acidified with dilute hydrochloric acid and the precipitate was removed by filtration. The solid was dissolved in hot benzene and the solution decolorized with Norite. Upon cooling the benzene solution, 35 g. (45%) of o-hydroxystyryl isopropyl ketone, m.p. 104.5° - 105.5° was obtained. McGookin and Sinclair (24) report for o-hydroxystyryl isopropyl ketone, m.p. 107° .

The experiment was repeated four times using the same amounts of starting materials. The yields of o-hydroxystyryl isopropyl ketone varied from 38.4% to 51.3%.

1-(o-Hydroxyphenyl)-4-methyl-3-pentanone



Nineteen grams (0.1 mole) of o-hydroxystyryl isopropyl ketone was dissolved in 70 ml. of absolute ethanol. Two tenths gram of platinum oxide was added and the mixture reduced with hydrogen under a pressure of approximately two atmospheres. One-tenth mole of hydrogen was absorbed within forty minutes.

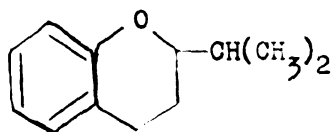
The catalyst was removed by filtration, the solvent was distilled, and the residue distilled in vacuo. Fifteen grams (70%) of 1-(o-hydroxyphenyl)-4-methyl-3-pentanone, b.p. 121° - 123° at 1 mm., was obtained. The 1-(o-hydroxyphenyl)-4-methyl-3-pentanone crystallized slowly, and after several recrystallizations from petroleum ether melted at 45° - 47° ; 2,4-dinitrophenylhydrazone, m.p. 146° - 147° .

Anal. Calcd. for $C_{12}H_{16}O$: C, 74.95; H, 8.39. Found: C, 73.39; H, 9.5. Calcd. for $C_8H_{20}N_4O_5$: C, 58.06; H, 5.41; N, 15.04. Found: C, 58.54; H, 5.86; N, 14.78.

Since the analyses were not too satisfactory, the methyl ether was prepared and the dinitrophenylhydrazone derivative made. The melting point of the dinitrophenylhydrazone was 115.5° - 116.5° ; mixed melting point with a known sample was 115.5° - 116.5° , (see page 41, Method 1.)

The experiment was repeated two times using 17 g. and 30 g. of o-hydroxystyryl isopropyl ketone. Seventy per cent yields of 1-(o-hydroxyphenyl)-4-methyl-3-pentanone were obtained in each experiment.

2-Isopropylchroman



Eighteen grams (0.094 mole) of 1-(o-hydroxyphenyl)-4-methyl-3-pentanone was dissolved in 250 ml. of ethyl alcohol in a 1 l. round-bottomed flask equipped with a motor-driven stirrer, a reflux condenser, and an addition funnel. Sixty grams (0.94 mole) of zinc dust was added and then 80 ml. of concentrated hydrochloric acid was added slowly with stirring. An additional 20 g. (0.31 mole) of zinc dust and 30 ml. of concentrated hydrochloric acid was added. The mixture was refluxed for twenty-four hours.

The mixture was cooled, filtered, and water was added. The solution was extracted with six 50 ml. portions of benzene. The combined benzene extracts were washed with 20% sodium hydroxide, dried over potassium carbonate, and the solvent removed.

The residue was distilled in vacuo, and 7 g. (42.4%) of 2-isopropylchroman, b.p. 95° - 105° at 1 mm., was obtained. The product was redistilled and 5.5 g. of 2-isopropylchroman, b.p. 95° - 98° at 1 mm., n_D^{25} 1.5155 was obtained.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.76; H, 9.15. Found: C, 81.38; H, 9.16.

Experiments Concerning Phenolic Product "B"

Derivatives of "B"

Phenoxyacetic acid derivative of "B". The procedure of Koelsch (25) was followed. One gram of "B" was dissolved in 3.5 ml. of 33% sodium hydroxide. Four milliliters of water was added to completely dissolve "B". Two and one-half milliliters of 50% chloroacetic acid in water was added and the mixture heated for two hours on a steam

bath. The mixture was cooled and acidified with dilute nitric acid to the congo-red end point and extracted with ether. The ether extracts were washed with water and then extracted with 20% sodium carbonate. The sodium carbonate extracts were acidified and the solid removed by filtration. The crude acid was recrystallized from water and dried. The melting point of the phenoxyacetic acid (0.9 g.) was 141° to 142° .

A weighed sample (0.2814 g.) of the phenoxyacetic acid was dissolved in 100 ml. of 50% ethyl alcohol and water. One-half aliquot portions were titrated with 0.0353 N sodium hydroxide, using a Beckmann pH meter. The neutralization equivalents found were 236.2 and 236.7. The neutralization equivalent calculated for $\text{C}_6\text{H}_{11}\text{C}_6\text{H}_4\text{OCH}_2\text{CO}_2\text{H}$ is 234.1.

β -Naphthyl urethan of "B". The procedure of Shriner and Fuson (26) was followed. One-half gram of "B", 0.5 g. of β -naphthyl isocyanate and 2 drops of pyridine were dissolved in 10 ml. of benzene. The mixture was refluxed overnight. The benzene was removed and the residue treated with petroleum ether. The white solid was recrystallized from ethyl alcohol five times. The melting point of the β -naphthyl urethan of "B" remained constant at 164° - 165° after the fourth recrystallization.

Anal. Calcd. for $\text{C}_{23}\text{H}_{23}\text{NO}_2$: C, 79.95; H, 6.71. Found: C, 79.48; H, 6.99.

Benzoate of "B". One gram of benzoyl chloride was heated cautiously with 1 g. of "B". The mixture was poured into water. The oil which formed was treated with 5% sodium carbonate. The solid

which slowly separated was recrystallized from water and ethyl alcohol four times. The melting point of the benzoate of "B" was 84° to 85° .

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.13; H, 7.27.

Oxidation of "B" with Permanganate

The general procedure of Eleuterio (27) was followed. To a solution of 8.7 g. (0.05 mole) of "B" in 250 ml. of acetone was added dropwise and with stirring a solution of 71.1 g. (0.45 mole) of potassium permanganate in 1.2 l. of water. The temperature was kept at 10° to 15° . The mixture was stirred forty-five minutes and then acidified with 6 N sulfuric acid. Sodium bisulfite was added to decompose the manganese dioxide. The mixture was extracted with five 100 ml. portions of benzene. The combined benzene solutions were extracted with five 30 ml. portions of 10% sodium bicarbonate. The combined sodium bicarbonate extracts were acidified with 6 N sulfuric acid and extracted with five 40 ml. portions of benzene. The combined benzene extracts were dried over sodium sulfate and the solvent removed through a Vigreux column.

The residue could not be distilled without decomposition. The reaction was repeated using the same quantities. One milliliter of an oil remained after removing the benzene. The oil was refluxed with 4 ml. of thionyl chloride for twenty minutes and then poured into 20 ml. of cold concentrated ammonium hydroxide. A brown solid with some oil formed. The crude solid, m.p. 115° to 120° , would not recrystallize from a mixture of ethyl alcohol and water. The

material normally separated as a very fine solid which would not filter readily or separated as an oil. Chloroform and petroleum ether were tried as solvents. The crude solid was too soluble in chloroform and insoluble in petroleum ether. The mixture of chloroform and petroleum, also, was unsuccessful.

Nitrosation of "B"

Method 1. The general procedure of Hodgson and Nicholson (28) was followed. One and one-tenth grams of "B" was dissolved in a mixture of 12 ml. of water and 20 ml. of acetic acid. A solution of 2.5 g. of sodium nitrite in 10 ml. of water was added slowly at -2° to the solution of "B", acetic acid, and water. The solution became reddish brown immediately. The mixture was allowed to stand for three hours in an ice bath. The red solid which separated was removed by filtration. The solid was recrystallized from acetic to give red crystals, m.p. 185° with decomposition.

Anal. Calcd. for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.36; N, 6.82. Found: C, 77.35; H, 7.36; N, 2.10.

The unsatisfactory analyses of the product was not entirely unexpected in view of the results obtained in attempted nitrosations on m-t-butylphenol which are described below.

Method 2. The general procedure found in Organic Syntheses (29) was followed. Eight grams of "B" was dissolved in 80 ml. of ethyl alcohol. Forty milliliters of concentrated hydrochloric acid was added to the stirred solution. Four and seven-tenths grams of sodium nitrite was added slowly to the stirred ice cold solution. The mixture was then stirred for twenty-four hours.

The mixture was poured into 500 ml. of water. A viscous oil separated. The water was decanted and the oil dissolved in acetic acid. Two grams of a black hard crystalline solid separated. After the second recrystallization from acetic acid the color of the crystals became dark red brown, m.p. 114° - 150° . Attempts at further purification were unsuccessful.

Attempted Nitrosation of m-t-Butylphenol

Method 1. One gram of m-t-butylphenol was dissolved in 5 ml. of 95% ethyl alcohol. The solution was stirred and cooled to 0° and 5 ml. of concentrated hydrochloric acid was added. Sodium nitrite (0.72 g.) was added to the cooled solution and the mixture allowed to stand overnight.

The mixture was poured into water. An oil separated which solidified after cooling for four days. The solid was removed by filtration and recrystallized from acetic acid. The solid, when dried in a vacuum desiccator over calcium oxide, slowly turned to an oil.

Method 2. The general procedure of Hodgson and Nicholson (28) was followed. A solution of 2 g. of sodium nitrite in 5 ml. of water was added dropwise to a solution of 1 g. of m-t-butylphenol, 21 ml. of acetic acid, and 12 ml. of water at -2° .

The mixture was stirred at room temperature for twenty hours. Approximately 0.3 ml. of a dark oil separated which did not solidify.

Methylation of "B"

To a stirred solution of 9.65 g. (0.055 mole) of "B", 3.4 g. (0.085 mole) of sodium hydroxide, and 25 ml. of water was added,

slowly, 8.2 g. (0.055 mole) of methyl sulfate. The mixture was heated with stirring on a steam bath for three hours and forty-five minutes.

The mixture was cooled, 30 ml. of 10% sodium hydroxide was added, and the whole then extracted with ether. The combined ether extracts were washed with 5 ml. portions of 10% sodium hydroxide until no further phenolic material was removed. The ether extracts were dried over magnesium sulfate, the solvent removed, and the residue distilled in vacuo. Four and eight-tenths grams (46%) of the methyl ether of "B", b.p. 81° - 92° at 1 mm., n_D^{25} 1.5315, was obtained.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.10; H, 9.53. Found: C, 82.01; H, 9.41.

The reaction was repeated using 22.3 g. (0.126 mole) of "B". The yield of product was 10.75 g. (45%).

Oxidation of the Methyl Ether of "B"

Five grams (0.024 mole) of the methyl ether of "B" was dissolved in a mixture of 35 ml. of acetone and 50 ml. of water. The solution was stirred and cooled to 10° . Twenty and two-tenths grams (0.128 mole) of potassium permanganate was added during a six hour period. The temperature was allowed to increase to 25° during the addition. The mixture was allowed to stand overnight.

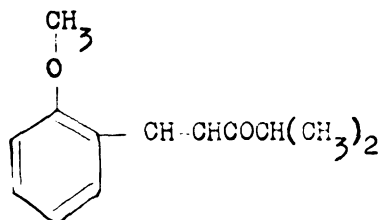
The mixture was filtered and the manganese dioxide cake was washed with water and then acetone. Part of the acetone was distilled from the filtrate; then the filtrate was acidified and extracted with three portions of benzene. The combined benzene extracts were

extracted with 20% sodium hydroxide, dried over sodium sulfate, and the solvent removed. One and three-tenths grams of an oil residue remained.

The sodium hydroxide extracts were acidified and extracted with ether. The ether extracts were dried over magnesium sulfate and the solvent removed. Approximately 1 ml. of an oily residue remained. The residue did not crystallize.

The reaction was repeated using 4.82 g. (0.023 mole) of "B" and 19.9 g. (0.125 mole) of potassium permanganate. The same type of residues were obtained. The residue from the alkali soluble fraction was a viscous oil which did not crystallize. The residues in each instance were dark colored.

o-Methoxystyryl Isopropyl Ketone



A solution of 23.9 g. (0.125 mole) of o-hydroxystyryl isopropyl ketone, 50 ml. of methyl alcohol, and 16 g. (0.13 mole) of methyl sulfate was stirred and cooled to -3° . A cold solution of 11.25 g. (0.2 mole) of potassium hydroxide in 25 ml. of water was added in one portion. The temperature increased to 34° . The mixture was stirred at room temperature for two and one-half hours.

One hundred milliliters of water was added and the mixture extracted with three 50 ml. portions of benzene. The combined

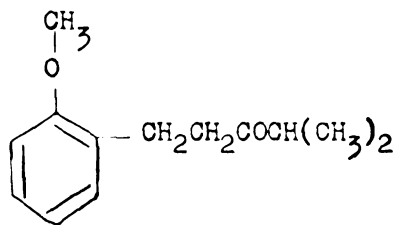
benzene extracts were washed with 20% sodium hydroxide, dried over potassium carbonate, the solvent removed, and the residue distilled in vacuo. Eleven and eight-tenths grams (75% based on starting material consumed) of o-methoxystyryl isopropyl ketone, b.p. 155°-161° at 1.8 mm., n_D^{25} 1.5768, was obtained.

The alkaline extracts were acidified, and 7.3 g. (33.8%) of o-hydroxystyryl isopropyl ketone was recovered.

The semicarbazone of o-methoxystyryl isopropyl ketone was prepared by the procedure of Gheorghiu (30), m.p. 182° to 183°. Gheorghiu reported the melting point was 179° to 181°.

The experiment was repeated two times using 48 g. (0.25 mole) of o-hydroxystyryl isopropyl ketone. The yields varied from 76% to 95% based on the amount of starting material consumed.

1-(o-Methoxyphenyl)-4-methyl-3-pentanone



Method 1. The general procedure of Perkin and Weizmann (31) was followed. Sixteen grams (0.082 mole) of 1-(o-hydroxyphenyl)-4-methyl-3-pentanone, 50 ml. of methyl alcohol, and 10.1 g. (0.082 mole) of dimethyl sulfate were stirred and cooled to -5°. Nine and two-tenths grams (0.164 mole) of potassium hydroxide dissolved in 21 ml. of water was added in one portion. The temperature increased to 28°. The mixture was stirred for two hours at room temperature.

Fifty milliliters of water was added and the mixture was extracted with three 30 ml. portions of benzene. The combined benzene extracts were washed with 20% sodium hydroxide, then Claisen's alkali, and dried over potassium carbonate. The solvent was removed and the residue distilled in vacuo. Seven and four-tenths grams (43.8%) of 1-(o-methoxyphenyl)-4-methyl-3-pentanone, b.p. 120° - 122° at 2 mm., was obtained. The melting point of its 2,4-dinitrophenylhydrazone was 115.5° to 116.5° . The mixed melting point with an analyzed sample was 115.5° to 116.5° .

Method 2. Twenty grams (0.1 mole) of o-methoxystyryl isopropyl ketone, 80 ml. of ethyl alcohol, and 0.2970 g. of 5% palladium on carbon were placed in a 500 ml. low-pressure hydrogenation bomb. One-tenth mole of hydrogen was absorbed in thirty-five minutes.

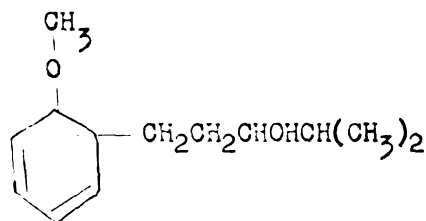
The catalyst was removed by filtration and the solvent distilled. The residue was distilled in vacuo. Nineteen and one-tenths grams (92.7%) of 1-(o-methoxyphenyl)-4-methyl-3-pentanone, b.p. 135° - 143° at 2 mm., was obtained. The reduction was repeated using 41 g. (0.2 mole) of o-methoxystyryl isopropyl ketone. Forty grams (97%) of 1-(o-methoxyphenyl)-4-methyl-3-pentanone was obtained.

The product was redistilled through an 8 inch heated Vigreux column. The pure product had the following physical constants; b.p. 121° - 123° at 2 mm., n_D^{25} 1.5082. The dinitrophenylhydrazone, after several recrystallizations from ethyl alcohol, melted at 115.5° to 116.5° .

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.70; H, 8.79. Found: C, 75.56; H, 8.74. Calcd. for $C_{19}H_{22}N_4O_5$: C, 59.05; H, 5.74; N, 14.50. Found: C, 58.66; H, 6.68; N, 14.25.

The unsatisfactory hydrogen analysis of the dinitrophenylhydrazine derivative could not be explained since the parent ketone analyzed correctly. After reduction of the carbonyl group to the alcohol in the following experiment, the analysis of the alcohol and the phenyl urethan derivative were satisfactory.

1-(o-Methoxyphenyl)-4-methyl-3-pentanol



Four grams (0.106 mole) of lithium aluminum hydride was dissolved in 300 ml. of anhydrous ether in a 1 l. flask equipped with a Friedrichs condenser, a mercury-sealed motor stirrer, and an addition funnel. Forty-nine grams (0.25 mole) of 1-(o-methoxyphenyl)-4-methyl-3-pentanone in 300 ml. of anhydrous ether was added during a period of one hour. The mixture was allowed to stand overnight.

The mixture was hydrolyzed by the cautious addition of 30 ml. of water and then 200 ml. of 10% sulfuric acid. The organic layer was separated, and the aqueous layer extracted with two 100 ml. portions of ether. The combined organic extracts were dried over sodium sulfate, the solvent removed, and the residue distilled in vacuo through an 8 inch heated Vigreux column. Eighty-two and

one-half per cent (42.85 g.) of 1-(o-methoxyphenyl)-4-methyl-3-pentanol, b.p. 119° - 123° at 1 mm., $n_D^{24.5}$ 1.5151, was obtained.

The phenyl urethan was made by the general procedure of Shriner and Fuson (26), m.p. 75° to 76° .

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.97; H, 9.83. Calcd. for $C_{20}H_{25}NO_3$: C, 73.36; H, 7.70; N, 4.28. Found: C, 73.56; H, 7.66; N, 4.32.

Dehydration of 1-(o-Methoxyphenyl)-4-methyl-3-pentanol

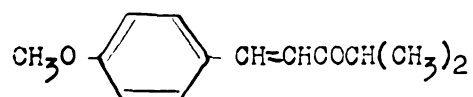
A mixture of 1 g. of concentrated sulfuric acid and 21.55 g. (0.108 mole) of 1-(o-methoxyphenyl)-4-methyl-3-pentanol was placed in a 50 ml. round-bottomed flask. The mixture was distilled slowly through an eight inch heated Vigreux column. Fourteen and eight-tenths grams (72%) of material, b.p. 95° - 105° at 1 mm., was obtained. The experiment was repeated twice using a total of 17.7 g. of alcohol and 13.58 g. (84%) of material, b.p. 95° - 105° at 1 mm., was obtained. The products were combined, dissolved in ethyl ether, extracted with sodium bicarbonate, dried over anhydrous potassium carbonate, and the solvent removed. The residue was distilled in vacuo in a semi-micro distillation apparatus. The following fractions of 4 ml. each were obtained: fraction 1, b.p. 88° - 90° at 1 mm., n_D^{25} 1.5232; fraction 2, b.p. 90° - 94° at 1 mm., n_D^{25} 1.5248; fraction 3, b.p. 92° at 0.9 mm., n_D^{25} 1.5270; fraction 4, b.p. 92° - 93° at 1 mm., n_D^{25} 1.5290; fraction 5, b.p. 93° - 98° at 1 mm., n_D^{25} 1.5320. The constant increase of the refractive index indicated the unsaturated material was a mixture of isomers. The bromine number of fractions 2 and 4 was obtained

by the procedure of Johnson and Clark (32). The calculated bromine number for 5-(o-methoxyphenyl)-2-methyl-2-pentene or an isomer is 84.1

Found for fraction 2: 78.6; 79.4.

Found for fraction 4: 83.9; 85.4.

p-Methoxystyryl Isopropyl Ketone



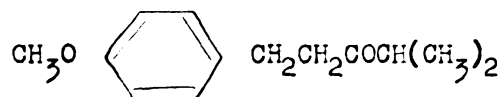
Forty-seven grams (0.35 mole) of anisaldehyde and 25 g. (0.35 mole) of methyl isopropyl ketone, and 250 ml. of ethyl alcohol were placed in a 500 ml. flask. Fifteen milliliters of 10% sodium hydroxide was added with shaking and the mixture was allowed to stand for one day.

Two hundred milliliters of water was added and the oil extracted with benzene. The benzene extracts were dried over potassium carbonate, the solvent removed and the residue distilled in vacuo through a Claisen head. Thirty-seven and four-tenths grams (60%) of p-methoxystyryl isopropyl ketone, b.p. 120°-150° at 2 mm., was obtained. The experiment was repeated using 42 g. (0.307 mole) of anisaldehyde and 37 g. (59%) of the product was obtained. One run using 68 g. (0.5 mole) of anisaldehyde gave only 17.7 g. (17.4%) of the product when the reaction time was decreased to three hours. The combined product from the three experiments (92 g.) was redistilled through an eight inch heated Vigreux column. Sixty-nine grams of

product, b.p. 155° - 160° at 2 mm., m.p. 28° to 30° was obtained.

Vorlander and Knotzsch (33) reported for p-methoxystyryl isopropyl ketone, b.p. 217° - 219° at 40 mm., m.p. 28° .

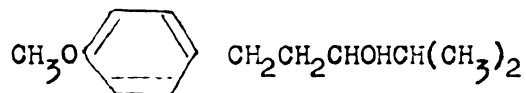
1-(p-Methoxyphenyl)-4-methyl-3-pentanone



Sixty-nine grams (0.335 mole) of p-methoxystyryl isopropyl ketone, 200 ml. of ethyl alcohol, and 0.50 g. of platinum oxide were placed in a 500 ml. low pressure hydrogenation bomb. The mixture was shaken at an initial hydrogen pressure of 49.5 p.s.i. The reduction was stopped when approximately 0.34 mole of hydrogen had been absorbed (one hour). The catalyst was removed by filtration, the solvent removed, and the residue distilled in vacuo through an eight inch Vigreux column. Sixty-five grams (95%) of 1-(p-methoxyphenyl)-4-methyl-3-pentanone, b.p. 128° - 129° at 1 mm., n_D^{24} 1.5082, was obtained.

Anal. Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 75.69; H, 8.79. Found: C, 76.17, 76.41; H, 9.30, 9.25.

The discrepancies in the analyses cannot be explained by incomplete reduction occurring or by reduction of the carbonyl as well as reduction of the carbon double bond. The alcohol obtained by reducing the above ketone with lithium aluminum hydride had a satisfactory analysis (see page 47).

1-(p-Methoxyphenyl)-4-methyl-3-pentanol

Sixty-three grams (0.306 mole) of 1-(p-methoxyphenyl)-4-methyl-3-pentanone in 150 ml. of anhydrous ether was added slowly to a stirred solution of 5.7 g. (0.15 mole) of lithium aluminum hydride in 250 ml. of anhydrous ether. The mixture was stirred at room temperature for four hours and then heated for one hour.

The excess lithium aluminum hydride was destroyed by the addition of 5 ml. of ethyl acetate and then 50 ml. of water. The mixture was hydrolyzed with 200 ml. of 10% sulfuric acid. The organic layer was separated, and the aqueous layer extracted with two 100 ml. portions of ether.

The combined organic extracts were dried over potassium carbonate, the solvent removed, and the residue distilled through an eight inch heated Vigreux column in vacuo. Fifty and four-tenths grams (80.8%) of 1-(p-methoxyphenyl)-4-methyl-3-pentanol, b.p. 125°-127° at 0.6 mm., $n_D^{23.8}$ 1.5151, was obtained. The phenyl urethan, m.p. 66.5° to 67.5°, was prepared by the general procedure of Shriner and Fuson (26).

Anal. Calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_2$: C, 74.96; H, 9.68. Found: C, 74.68; H, 9.50. Calcd. for $\text{C}_{20}\text{H}_{25}\text{NO}_3$: C, 73.36; H, 7.70; N, 4.28. Found: C, 73.63; H, 7.46; N, 4.18.

Dehydration of 1-(p-Methoxyphenyl)-4-methyl-3-pentanol

The general experimental condition of Whitmore and Simpson (34)

were used. Fifty grams (0.24 mole) of the alcohol was dissolved in 140 ml. of anhydrous ether were placed in a 500 ml. round-bottomed flask equipped with a reflux condenser, a motor stirrer, and an addition funnel. The condenser was fitted with a calcium chloride drying tube. A slurry of 10 g. (0.25 mole) of powdered sodium hydroxide and 12 ml. of carbon tetrachloride was added, and the mixture was stirred for forty minutes.

Eighteen and two-tenths grams (0.24 mole) of carbon bisulfide was added over a period of twenty minutes, and the mixture was stirred an additional five hours. A pink precipitate formed. Thirty-four grams (0.24 mole) of methyl iodide was added slowly and the mixture was stirred overnight and then refluxed for eight hours.

The inorganic salts were removed by filtration and the solvent removed. The methyl xanthate decomposed when distillation was attempted at 1 mm. The residue was then heated at 170° - 180° at 20 mm. until the vigorous evolution of gases ceased (one hour). The residue was then distilled, b.p. 175° - 180° at 18 mm.

The distillate was dissolved in 50 ml. of benzene, washed with two 30 ml. portions of 40% potassium hydroxide, one 30 ml. portion of water, and with a saturated mercuric chloride solution. It was then washed with 20 ml. of water, dried over sodium sulfate, filtered, and redried over sodium sulfate. The solvent was removed and the residue distilled through a heated Vigreux column in vacuo. The following fractions were obtained: fraction 1, b.p. 103° - 105° at 2 mm., $n_D^{24.5}$ 1.5160, 1 g.; fraction 2, b.p. 105° - 106° at 2 mm., $n_D^{24.5}$ 1.5086, 3.04 g.; fraction 3, b.p. 105° - 106° at 2 mm., $n_D^{24.5}$

1.5090, 2.24 g.; fraction 4, b.p. 105° - 139° at 2 mm., $n_D^{24.5}$ 1.5442, 3.8 g.; fraction 5, b.p. 139° - 140° at 2 mm., $n_D^{24.5}$ 1.5148, 22 g.

Fractions 4 and 5 (51.5%) were essentially pure recovered alcohol, $n_D^{23.8}$ 1.5151. Fractions 2 and 3 (28.3% based on alcohol used) were later shown to be the unsaturated material.

The reaction was repeated using 25 g. (0.12 mole) of the 1-(p-methoxyphenyl)-4-methyl-2-pentanol. After the addition of carbon bisulfide the mixture was stirred overnight instead of only five hours. The reaction was treated as previously described. Seven and one-half grams of material, b.p. 100° - 110° at 2 mm., was obtained. This material was redistilled and 3 g. (21.9% based on alcohol used) of unsaturated material, b.p. 90° - 100° at 0.7 mm., $n_D^{24.6}$ 1.5090 was obtained. Ten gram (40%) of crude alcohol was recovered. In the distillations small foreruns were obtained which were consistently yellow and decomposed to give a yellow inorganic precipitate.

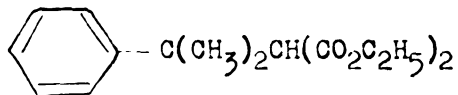
The products were combined and redistilled through the semi-micro distillation apparatus in vacuo. The following fractions were obtained: fraction 1, b.p. 85° - 90° at 0.9 mm., n_D^{25} 1.5098, 1.28 g.; fraction 2, b.p. 90° - 95° at 1 mm., n_D^{25} 1.5092, 1.05 g.; fraction 3, b.p. 95° at 1 mm., n_D^{25} 1.5095, 2 g.; fraction 4, b.p. 95° - 97° at 1 mm., n_D^{25} 1.5097, 0.75 g.

All fractions had a small amount of suspended solid in them. Since the refractive index was not constant a mixture of the unsaturated compounds, 5-(p-methoxyphenyl)-2-methyl-2-pentene and 1-(p-methoxyphenyl)-4-methyl-3-pentene, was apparently obtained.

The bromine number was obtained by the procedure of Johnson and Clark (32). The calculated bromine number for $C_{17}H_{18}O$ is 84.1.

Bromine number found: 83.7, 83.5.

Ethyl 2-Carbethoxy-3-methyl-3-phenylbutanoate



One hundred and fifty-six and nine-tenths grams (1 mole) of bromobenzene in 300 ml. of anhydrous ether was added dropwise to 25.3 g. (1.04 moles) of magnesium turnings in a 2 l. round-bottomed flask equipped with a Friedrichs condenser, mercury-sealed motor stirrer, and addition funnel. The mixture was stirred for one hour at room temperature and then one hour with refluxing on a steam bath. The mixture was cooled in an ice bath and 190 g. (0.95 mole) of ethyl isopropylidene malonate [prepared from acetone, malonic ester and zinc chloride (35)] in 200 ml. of anhydrous ether was added over a two hour period. The mixture was stirred at room temperature for two and one-half hours.

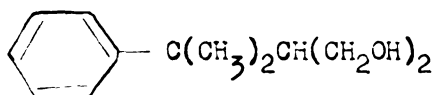
The mixture was hydrolyzed by the addition of 400 ml. of 10% sulfuric acid. The organic layer was separated and the aqueous layer extracted with three 100 ml. portions of ether. The combined organic extracts were dried over sodium sulfate, the solvent removed, and the residue distilled through a Claisen head in vacuo.

Ninety and two-tenths grams (30%) of the ethyl 2-carbethoxy-3-methyl-3-phenylbutanoate, b.p. 145° - 150° at 0.5 mm., $n_D^{25.5}$ 1.4982, was obtained. A forerun of 74.1 g., b.p. 102° - 145° at 0.5 mm., was

obtained also. Prout, et al. (36), report for the product, b.p. 177° - 178° at 18 mm., n_D^{25} 1.4939, and obtained an average yield of 40% based on two runs.

The experiment was repeated using the same quantities and 55 g. (21%) of the product obtained.

2-Hydroxymethyl-3-methyl-3-phenyl-1-butanol



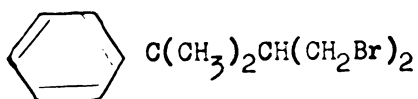
The general procedure of Pines, et al. (37) was used. Ninety grams (0.32 mole) of ethyl 2-carbethoxy-3-methyl-3-phenylbutanoate in 150 ml. of anhydrous ether was added slowly to a stirred solution of 18.95 g. (0.5 mole) of lithium aluminum hydride in 650 ml. of ether. The mixture was stirred seven hours. Ethyl acetate was added to decompose the excess lithium aluminum hydride. The mixture was hydrolyzed by the addition of 400 ml. of 10% sulfuric acid.

The organic layer was separated and the aqueous phase extracted with two 100 ml. portions of ether. The combined organic extracts were dried over magnesium sulfate, the solvent removed, and the residue distilled in vacuo through a Claisen head. Fifty-one grams (82%) of 2-hydroxymethyl-3-methyl-3-phenyl-1-butanol, b.p. 165° - 174° at 0.9 mm., was obtained. The product, which slowly crystallized, was recrystallized twice from petroleum ether, m.p. 62.5° to 64° .

The experiment was repeated using 52 g. (0.18 mole) of the malonic ester and 11.27 g. (0.3 mole) of lithium aluminum hydride. Twenty-eight grams (81%) of the diol was obtained.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.43; H, 9.25.

2-Bromomethyl-3-methyl-3-phenyl-1-bromobutane



The general procedure of Pines, et al. (37) was followed. Eighteen and four-tenths gram (0.1 mole) of 2-hydroxymethyl-3-methyl-3-phenyl-1-butanol was heated to 70° in a 500 ml. round-bottomed flask equipped with a Friedrichs condenser, a motor stirrer, and an addition funnel. With vigorous stirring 19.76 g. (0.073 mole) of phosphorus tribromide was added at such a rate that the temperature of the mixture remained at 70° . The mixture was then stirred at 70° for one hour and then heated on the steam bath overnight.

The cooled mixture was poured into a slurry of ice and water. The mixture was extracted with two 60 ml. portions of benzene. The combined benzene extracts were washed successively with water, 10% potassium carbonate, and then water until the aqueous washings were neutral to litmus. The benzene extracts were dried over calcium chloride, the solvent removed, and the residue distilled in vacuo.

Nineteen and six-tenths grams (63%) of the product, b.p. 150° - 160° at 1 mm., n_D^{26} 1.5672, was obtained. One gram of a viscous residue remained.

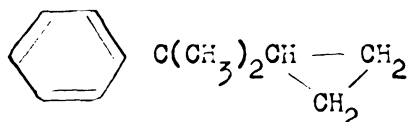
The experiment was repeated using 32 g. (0.174 mole) of the diol and 34.7 g. (0.128 mole) of phosphorus tribromide. The yield was 24.7 g. (46%) of dibromide, b.p. 160° - 162° at 1.6 mm. Five

grams of a viscous residue remained. The product was analyzed for bromine by the method of Umhoefer (36).

Anal. Calcd. for $C_{12}H_{18}Br_2$: Br, 49.63. Found: Br, 49.2;

48.7.

Dimethylcyclopropylcarbinybenzene



The general experimental conditions of Shortridge, et al. (39) were used. Thirty-two grams (0.48 mole) of zinc dust and 500 ml. of 80% ethyl alcohol were placed in a 500 ml. round-bottomed flask equipped with a Friedrichs condenser, a mercury-sealed motor stirrer, and an addition funnel. The mixture was brought to reflux and with vigorous stirring 32 g. (0.1 mole) of 2-bromomethyl-3-methyl-3-phenyl-1-bromobutane was added over a period of one and one-quarter hours. The heating and stirring was continued for twenty-four hours.

The mixture was cooled and filtered. The excess zinc and zinc bromide was washed with benzene. The benzene washes and filtrate were combined, and the organic layer separated. The aqueous layer was then extracted with benzene. The combined organic extracts were dried over calcium chloride, the solvent removed through a Vigreux column, and the residue distilled in vacuo through a semi-micro distillation apparatus. Eleven and three-tenths grams (71%) of dimethylcyclopropylcarbinybenzene, b.p. 95° - 98° at 12 mm., $n_D^{24.8}$ 1.5135, was obtained. One and one-half grams of material,

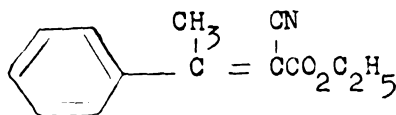
b.p. 98° - 150° at 12 mm., was obtained and a residue of 1.4 g. remained which did not distill.

The experiment was repeated using 43.7 g. (0.137 mole) of the dibromide. Nineteen and two-tenths grams (87%) of the product, b.p. 92° - 98° at 12 mm., was obtained. This material was redistilled through a small Vigreux column yielding 15.5 ml. of product, b.p. 94° at 12 mm., $n_D^{24.5}$ 1.5130. A forerun of 1.4 ml., b.p. 92° - 94° at 12 mm., $n_D^{24.5}$ 1.5103, was obtained. A residue of 1.5 g. remained which was distilled in the semi-micro distillation apparatus; approximately 0.5 g. of material, b.p. 94° - 98° at 12 mm., $n_D^{24.5}$ 1.5151, was collected before the residue in the distilling flask became colored and viscous.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.93; H, 10.06. Found: C, 90.22; H, 9.75.

The infrared spectrum had absorption band at 1018 cm.^{-1} , for the cyclopropane ring, absorption bands at 1446, 1388, 1368, 1209, and 1186 cm.^{-1} for the $C(CH_3)_2$ and the characteristic spectrum for monosubstituted benzene in the 5 to $6\text{ }\mu$ region and the strong absorption bands at 699 cm.^{-1} and 760 cm.^{-1}

Ethyl 1-Phenylethylidene Cyanoacetate



The procedure of Cope, et al. (40) was followed. Twenty-eight and five-tenths grams (0.25 mole) of ethyl cyanoacetate, 30 g. (0.25 mole) of acetophenone, 50 ml. of benzene, 12 g. (0.2 mole) of acetic

acid and 3.85 g. (0.05 mole) of ammonium acetate were placed in a 500 ml. round-bottomed flask equipped with a constant water remover and reflux condenser. The mixture was refluxed for twelve hours. Eight milliliters (0.5 mole) of water was removed.

The mixture was cooled and washed with three 50 ml. portions of water. The combined aqueous extracts were extracted with two 30 ml. portions of benzene. The combined organic extracts were dried over sodium sulfate, the solvent removed, and the residue distilled in vacuo.

Nine and two-tenths grams of a mixture of starting materials, b.p. 94° - 154° at 15 mm., was recovered. Twenty-six grams (48.5%) of ethyl 1-phenylethylidene cyanoacetate, b.p. 137° - 140° at 1.9 mm., was obtained. Ten grams of residue remained. Cope, et al. (40) report the boiling point is 136° - 137° at 2 mm.

The experiment was repeated using twice the quantities as described above. Forty-seven grams (44%) of product, b.p. 137° - 140° at 2.2 mm., n_D^{25} 1.5480 was obtained.

Reaction of Acetophenone and Ethyl Malonate

The general procedure of Cope, et al. (40) was followed. Forty grams (0.25 mole) of ethyl malonate, 30 g. (0.25 mole) of acetophenone, 50 ml. of benzene, and 3.85 g. of ammonium acetate were placed in a 500 ml. round-bottomed flask equipped with reflux condenser and constant water remover.

The mixture was refluxed for 13 hours. Three and three-tenths milliliters (0.18 mole) of water was removed. The mixture was cooled and extracted with three 50 ml. portions of water. The combined

aqueous layers were extracted with two 25 ml. portions of benzene. The combined organic extracts were dried over sodium sulfate, the solvent removed, and the residue distilled in vacuo. Fifty-three grams of a mixture of acetophenone and ethyl malonate, b.p. 93° - 100° at 20 mm. was recovered. Six and two-tenths grams of a yellow liquid, b.p. 140° - 170° at 1.8 mm., n_D^{25} 1.5804 was obtained. Two and six-tenths grams of residue remained.

Reaction of Ethyl 1-Phenylethylidene Cyanoacetate and Ethyl Alcohol

Method 1. Twenty-six grams (0.12 mole) of ethyl 1-phenylethylidene cyanoacetate, 55.2 g. of absolute ethyl alcohol and 12.5 g. (0.12 mole) of sulfuric acid were placed in a 250 ml. round-bottomed flask equipped with a water cooled condenser. The mixture was heated in an oil bath at 130° to 135° for three hours. The excess ethyl alcohol was distilled and the residue poured into 150 ml. of water.

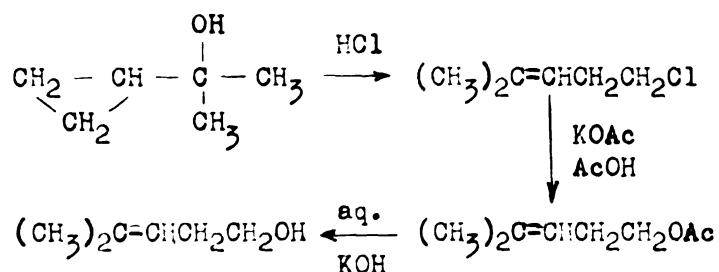
The mixture was extracted with four 50 ml. portions of ether. The combined ether extracts were dried over sodium sulfate, the solvent removed, and the residue distilled in vacuo. Four grams of material, b.p. 130° - 135° at 1.8 mm., n_D^{25} 1.5388, was obtained. Fourteen and one-half grams (56%) of starting material, b.p. 136° - 138° at 1.8 mm., n_D^{25} 1.5478 was recovered. Two grams of a residue remained which was hold-up in the distillation apparatus.

Method 2. Fourteen grams (0.065 mole) of ethyl 1-phenylethylidene cyanoacetate, 6.5 g. (0.065 mole) of sulfuric acid and 30 g. (0.65 mole) of absolute ethyl alcohol were placed in a pyrex tube. The tube was sealed and heated at 130° to 140° for three hours.

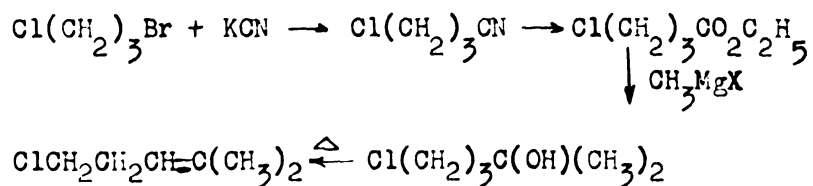
The tube was cooled, opened, and the contents washed out with ethyl alcohol. The excess ethyl alcohol was distilled and the residue poured into 100 ml. of water. The mixture was extracted with three 30 ml. portions of benzene. The combined benzene extracts were dried over sodium sulfate, the solvent removed, and the residue distilled through the semi-micro distillation apparatus in vacuo. The following fractions were obtained: fraction 1, b.p. 60° - 65° at 1.8 mm., n_D^{25} 1.4845, 1 g.; fraction 2, b.p. 65° - 145° at 1.8 mm., n_D^{25} 1.5382, 2.7 g.; fraction 3, b.p. 145° - 164° at 1.8 mm., n_D^{25} 1.5460, 6.2 g. An elemental analysis of fraction 3 indicated nitrogen was present. The refractive index of ethyl 1-phenylethylidene cyanoacetate is 1.5480. Consequently fraction 3 appeared to be mainly starting material.

DISCUSSION

In 1928 Bruylants and Dewael (7) reported the formation of 1-chloro-4-methyl-3-pentene from dimethylcyclopropylcarbinol and hydrochloric acid. The 'proof' of structure of the chloroolefin, as shown below, involved the formation of the acetate followed by hydrolysis to 1-hydroxy-4-methyl-3-pentene, which had previously been prepared by Van Aerde (41).



Although Van Aerde (41) prepared 1-chloro-4-methyl-3-pentene by a different procedure, as shown in the following sequence of reactions,



he obtained the unsaturated alcohol from the chloroolefin by the same sequence of reactions used by Bruylants and Dewael (7). Thus, this does not constitute a rigorous proof of structure of the compounds involved.

Bruylants and Dewael (7) and later Favorskaya and Fridman (8) reported that hydrolysis of 1-chloro-4-methyl-3-pentene gave dimethylcyclopropylcarbinol.

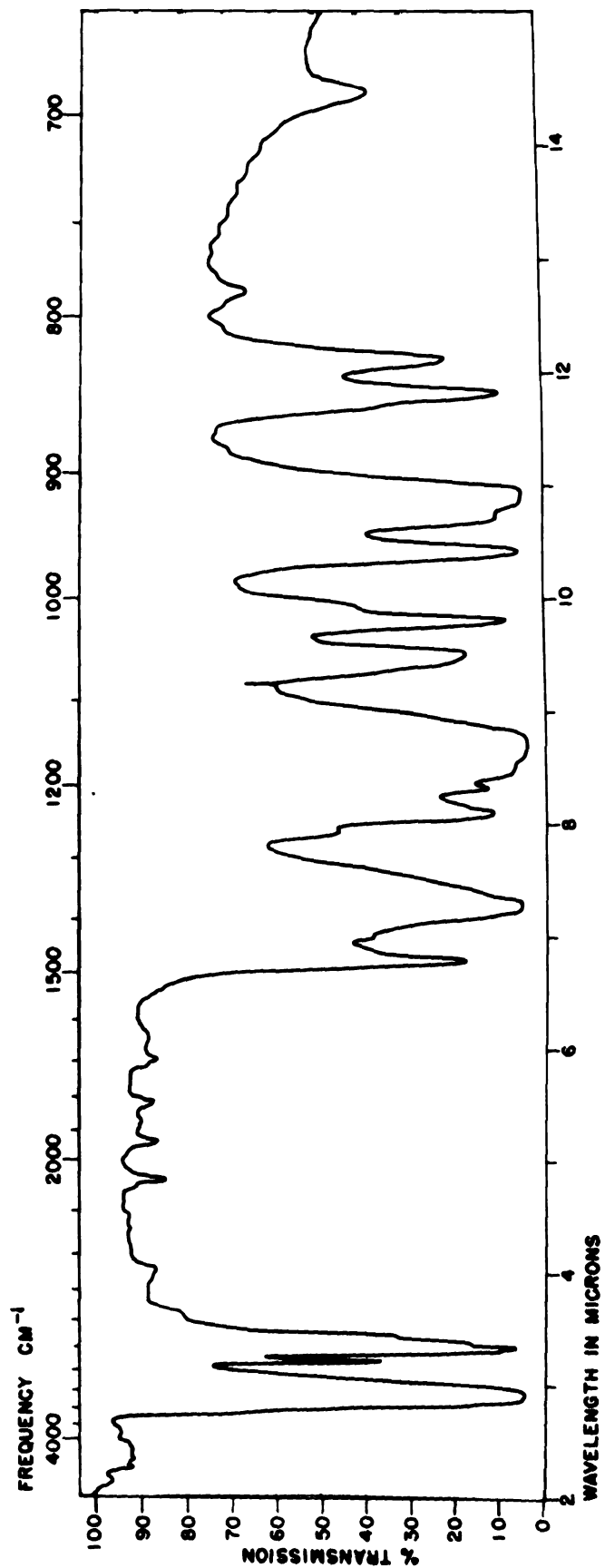


PLATE 1. Infrared Absorption Spectrum of Dimethylcyclopropylcarbinol (neat). Cell thickness 0.031 mm.

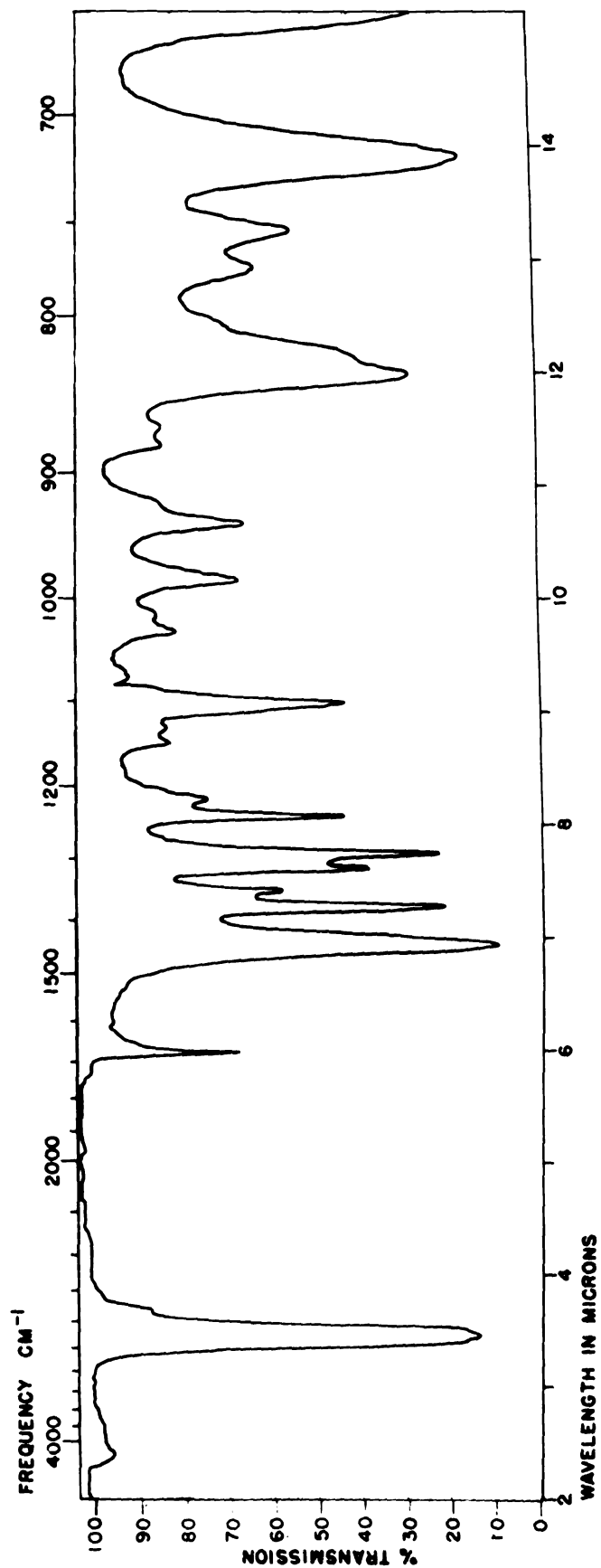


PLATE 2. Infrared Absorption Spectrum of 1-Chloro-4-methyl-3-pentene (neat). Cell Thickness 0.031 mm.

potassium carbonate, and the infrared absorption spectrum of the product was identical with that of a known sample of dimethylcyclopropylcarbinol. Thus, the rearrangements in the reaction of hydrochloric acid with dimethylcyclopropylcarbinol and the hydrolysis of 1-chloro-4-methyl-3-pentene were confirmed.

Several attempts were made to prepare dimethylcyclopropylcarbinyl chloride from the alcohol. Experimental conditions were used which had previously been successful in preventing racemization or isomerization in preparing alkyl halides from the corresponding alcohols. Thus Gerrard (17) had found that active 2-octanol was converted to the chloride without loss of optical activity using phosphorus pentachloride at low temperatures. Consequently, the reaction apparently did not proceed via a carbonium ion intermediate which would have given racemization. Dimethylcyclopropylcarbinol, however, under the same conditions, gave no reaction (starting material recovered) or rearranged product (1-chloro-4-methyl-3-pentene).

Gilman and Harris (18) used thionyl chloride and pyridine in chloroform in preparing cinnamyl chloride from cinnamyl alcohol. Other reagents, such as hydrochloric acid, gave an unsatisfactory product. Using the cyclopropylcarbinol, however, rearranged product or recovered alcohol were obtained.

Hatch and Nesbitt (16) found that cis or trans-crotyl alcohol with phosphorus trichloride and pyridine gave respectively cis or trans-crotyl chloride. By using these conditions, isomerization was avoided. The reaction of dimethylcyclopropylcarbinol under

identical conditions, however, gave isopropenylcyclopropane and recovered alcohol.

In as much as the hydrolysis of 1-chloro-4-methyl-3-pentene involved rearrangement from a primary chloride to a tertiary alcohol, it appeared that this chloroölefin might be a potential source of a tertiary carbonium ion, or something akin to one. In order to determine whether this was indeed the case, the uncatalyzed reaction of 1-chloro-4-methyl-3-pentene with phenol was examined. It has previously been shown (9) that tertiary alkyl halides alkylate the aromatic nucleus of phenols without the usual Friedel-Crafts type of catalyst; primary halides, on the other hand, unless unusually reactive (such as allyl or benzyl) do not give this reaction. The anticipated product was p-dimethylcyclopropylcarbiny phenol, but as shall be seen below, the reaction took a rather different course.

When the chloroölefin was heated with phenol at 150° in a molar ratio of one to four, hydrogen chloride was evolved, indicating that a reaction occurred. The chloroölefin also reacted with p-cresol at approximately the same rate as with phenol. Under identical conditions, 1-chlorohexane and phenol did not react. Consequently, the carbon-carbon double in 1-chloro-4-methyl-3-pentene must have provided a driving force in the alkylation.

The product from the alkylation of phenol with 1-chloro-4-methyl-3-pentene was investigated in detail. The reaction mixture was separated into a neutral fraction and a fraction which was soluble in 20% alkali. A crystalline compound, m.p. 47°-48°,

was isolated from the neutral product in 16% yield. This substance will be referred to as "A" for the remainder of the discussion. Another crystalline product, m.p. 113° - 114° , was isolated from the alkali-soluble (phenolic) fraction in 29% yield. It will be referred to as "B" for the remainder of the discussion. In addition, high boiling viscous liquids were obtained which were not further characterized.

Neutral Product "A"

"A" analyzed for $C_{12}H_{16}O$ which corresponded to a monoalkylation product, as, for example $C_6H_5OC_6H_{11}$. An analysis of the infrared absorption spectrum (see plate 3.) indicated that the following groups or type of substitution might be present:

$C(CH_3)_2$ ¹ 1322, 1368, 1448, 1203, 1189 $cm.^{-1}$

Aromatic ether² 1285, 1225 $cm.^{-1}$

ortho-disubstitution^{3,4} 1980, 1945, 1910, 751 $cm.^{-1}$

The absence of a strong band at 700 $cm.^{-1}$ also supports ortho-disubstitution on the benzene ring.³

The ultraviolet absorption spectrum of "A" (see plate 4.),

1 Bellamy, Chp. 2.

2 Ibid., p. 102.

3 Ibid., pp. 65, 66.

4 These bands were obtained from the infrared absorption spectrum in mineral oil mull, which was made available by Dr. J. L. Johnson, Upjohn Company, Kalamazoo, Michigan. The 751 $cm.^{-1}$ absorption band was obtained using carbon disulfide as the solvent for "A".

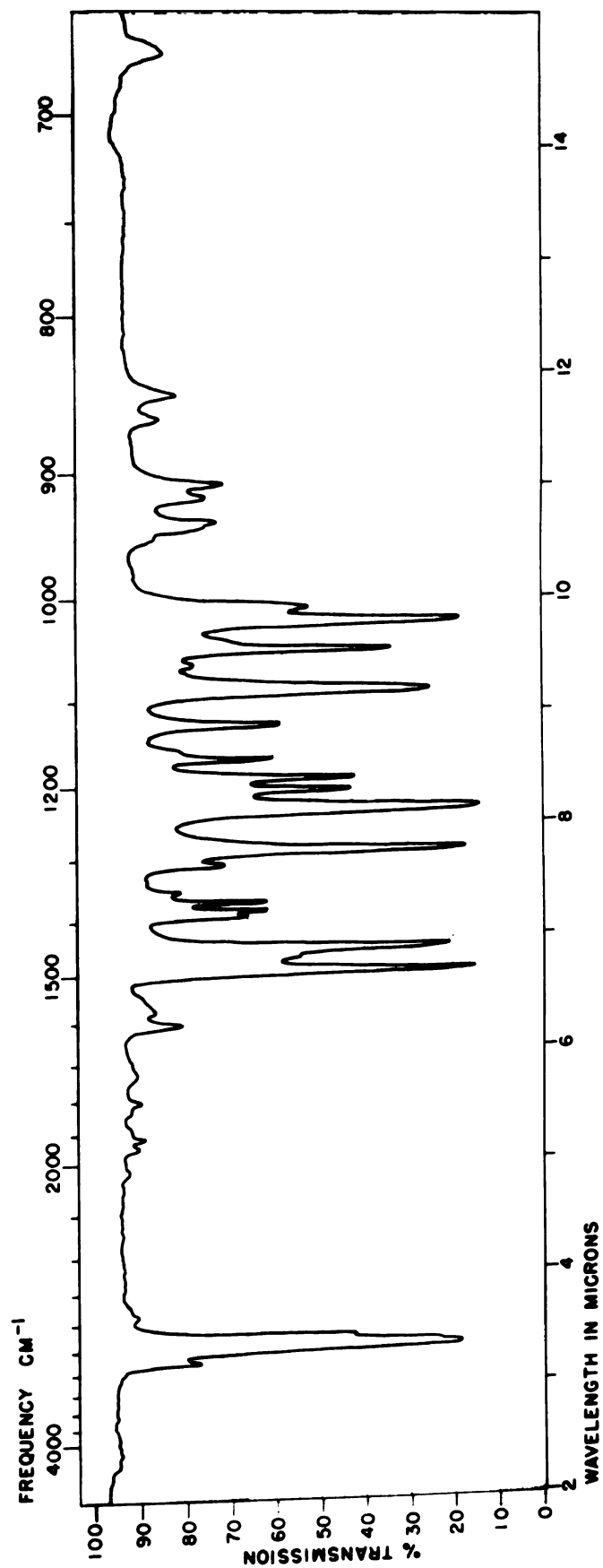


PLATE 3. Infrared Absorption Spectrum of Neutral Product "A" in Carbon Tetrachloride Solution. Cell thickness 0.5 mm.

C

X
Y
C
E
P

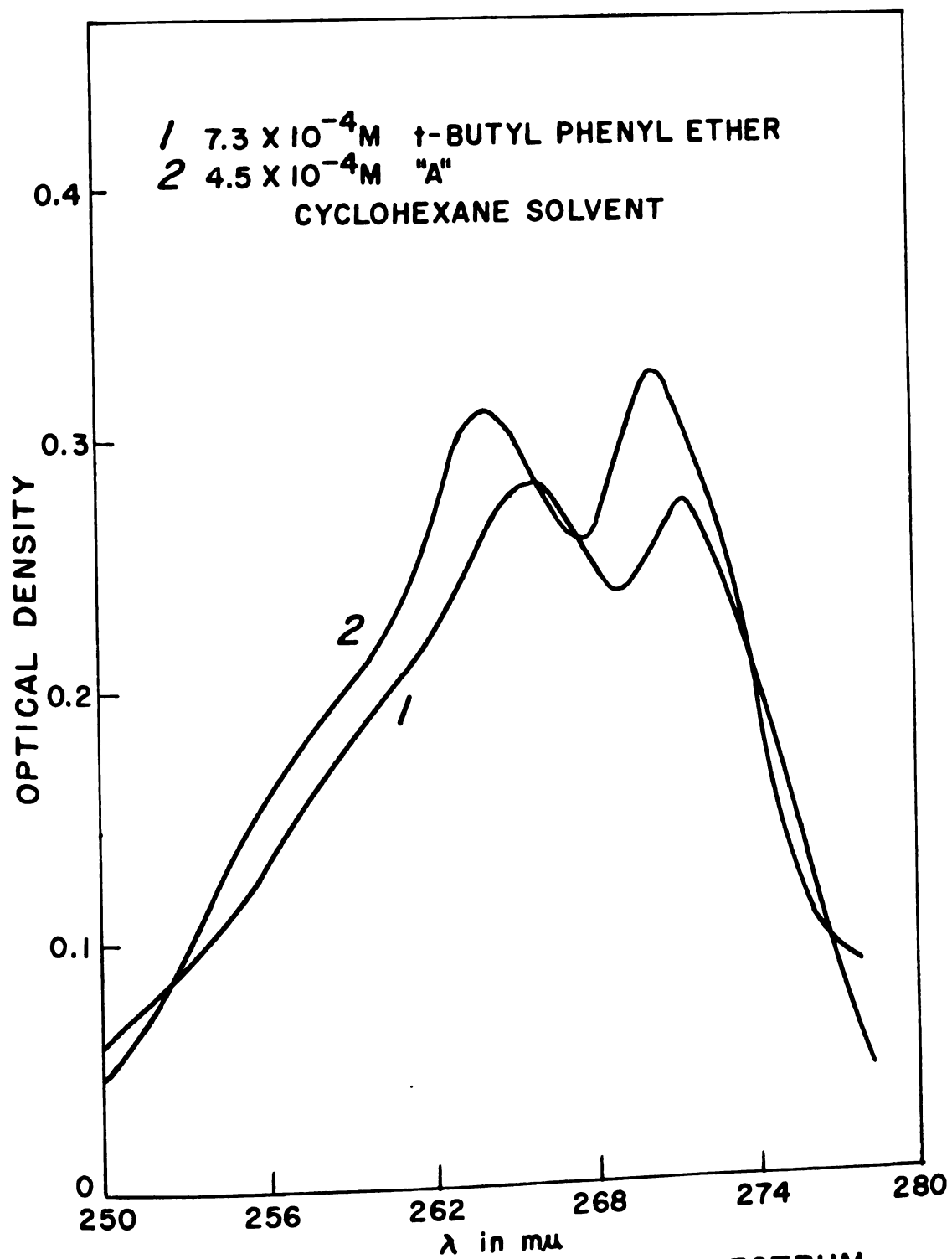
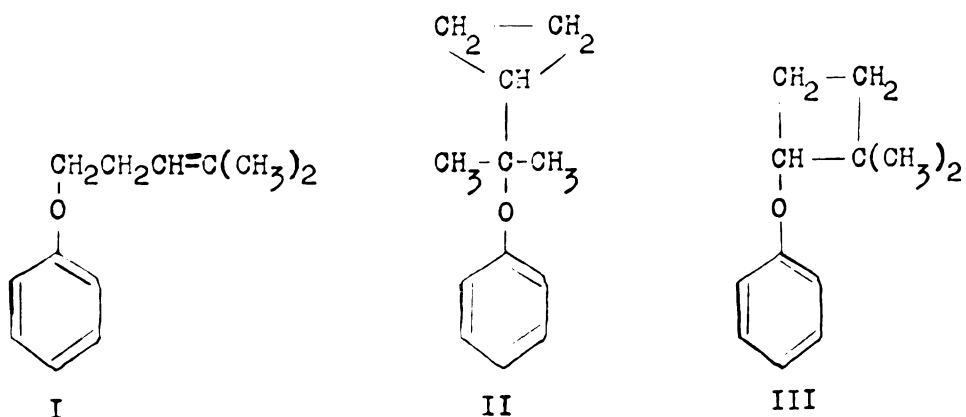
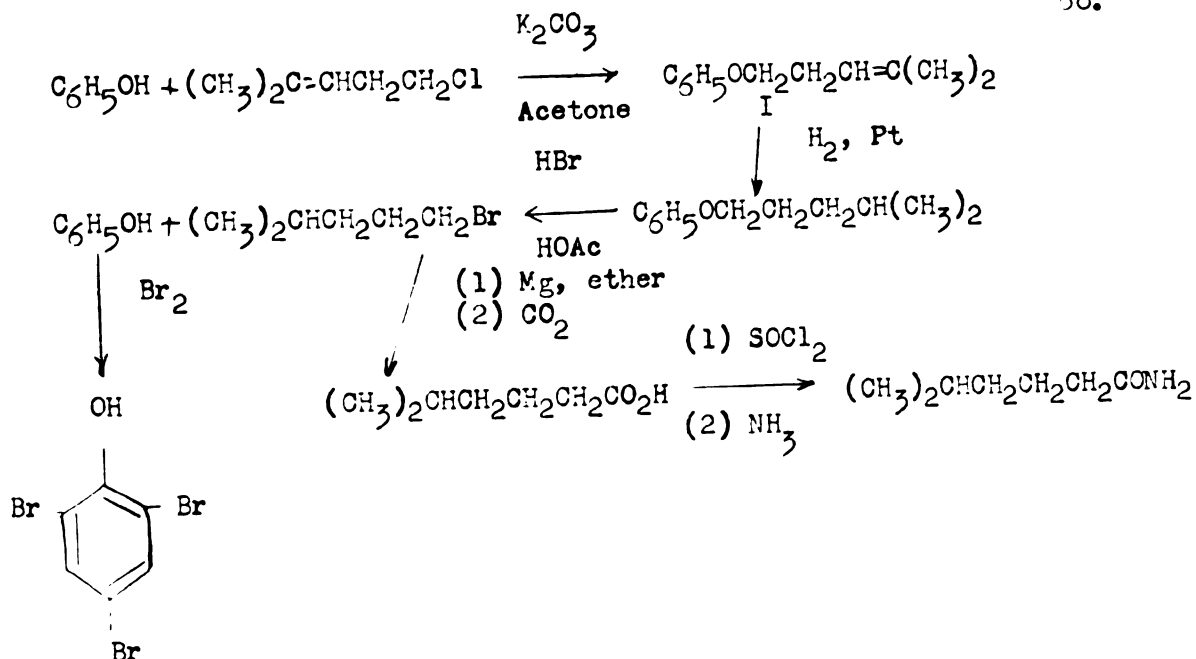


PLATE 4. ULTRAVIOLET ABSORPTION SPECTRUM
OF NEUTRAL PRODUCT

however, was comparable to that of t-butyl phenyl ether, which indicated that "A" might be a simple phenyl alkyl ether. Three structures of this type appeared possible since the ion from the homoallylic system of 1-chloro-4-methyl-3-pentene has three contributing forms.



Neutral product "A" resisted hydrogenation under conditions which normally caused reduction of the carbon-carbon double bond. Furthermore, there was no evidence for the carbon-carbon double bond in the infrared spectrum. Consequently, structure I for "A" was doubtful. Nevertheless, an authentic sample of 5-phenoxy-2-methyl-2-pentene (I) was prepared and its structure proven by the following sequence of reactions:

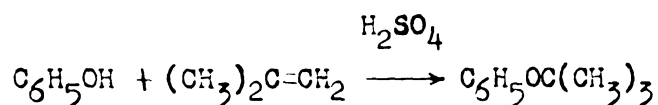


Since the preparation may have involved rearrangement, the product was degraded to the known compounds, tribromophenol and 5-methylhexanamide, to prove the structure of I.

The physical and chemical properties of 5-phenoxy-2-methyl-2-pentene (I) were not consistent with "A" and thus eliminated structure I for "A". Furthermore, 5-phenoxy-2-methyl-2-pentene was probably not an intermediate in the formation of "A". When I was treated with hydrogen chloride at temperatures used in the alkylation, no reaction occurred. When I was heated with an excess of phenol and hydrogen chloride at 150° some "A" and "B" were formed; this may have been due, however, to initial cleavage of the ether, followed by alkylation of the phenol which was present in a large amount.

Structure II was rather unlikely, because of the known lability of tertiary alkyl phenyl ethers in the presence of acids (43). That is, II ought not to be stable under the conditions of the formation

of "A". In order to emphasize this conclusion, t-butyl phenyl ether was prepared and compared with "A". Isobutylene and phenol gave a good yield of t-butyl phenyl ether when the concentration of sulfuric acid was carefully controlled. Stevens and Bowman (21) found that 0.050 mole of sulfuric acid per mole of phenol gave good



conversion to the ether. Larger amounts of sulfuric acid gave alkylated phenols.

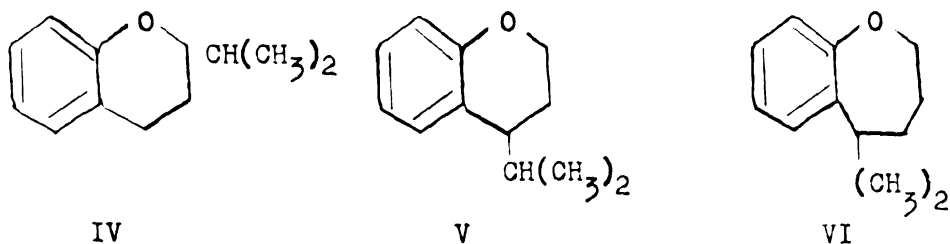
At 50°, t-butyl phenyl ether in benzene solution was cleaved rapidly by hydrogen chloride. Neutral product "A", by refluxing with acetic acid and hydrobromic acid, gave a mixture of phenol and another alkylated phenol, "C". "C" will be discussed later.

"A" was soluble in concentrated sulfuric acid and could be recovered from it unchanged, in direct contrast to t-butyl phenyl ether. "A" was also thermally stable; after refluxing at 232° for three and one-half hours, "A" was recovered unchanged. Under these conditions t-butyl phenyl ether rearranges to p-t-butylphenol (43). Thus, by comparing the chemical properties of "A" with t-butyl phenyl ether, structure II was eliminated.

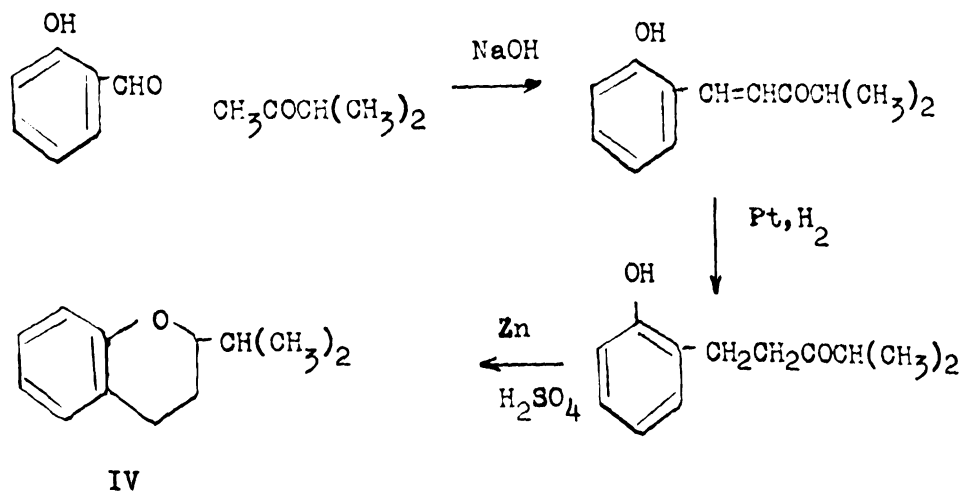
Structure III remains as a possibility for "A". As in the case of neopentyl compounds, a difficult cleavage would be predicted. Once the cleavage had occurred the active carbonium ion formed would be expected to realkylate the phenol. Although not eliminated conclusively by chemical evidence, it should be emphasized that III is

inconsistent with the infrared spectrum of "A" which indicates ortho-disubstitution. Further chemical evidence antagonistic to III is given below.

Among the possible structures of "A" involving ortho-disubstitution, the most likely would be the following:



When "A" was dissolved in sulfuric acid, a red color typical of chromans was observed. Also, the chroman structures (IV and V) would be consistent with ortho-disubstitution indicated by the infrared spectrum. Accordingly 2-isopropylchroman was prepared by an unambiguous route. The ultraviolet absorption spectrum of



2-isopropylchroman (see plate 5.), with bands at 274.5 μ and 284 μ , indicated that "A" did not have the chroman structure (IV and V). The ultraviolet absorption spectrum of 2-isopropylchroman was compatible with 2,2-dimethylchroman which absorbs at 278 μ and 284 μ (45). Further chemical evidence is given below for eliminating the chroman structure.

Structure VI remains as a possible structure of "A". The infrared spectrum of "A" is compatible with the groups present; i.e., the $\text{C}-(\text{CH}_3)_2$ group, an aromatic ether, and ortho-disubstitution on the benzene ring. The predicted chemical properties are also consistent. The ether linkage would be resistant to cleavage, such as, a primary alkyl phenyl ether. The cleavage of structure III could occur with complete loss of the alkyl group from the phenyl ring to give phenol, which was found in the cleavage of "A". Instances are found in the literature where tertiary alkyl groups have been removed by acids, as in the nitration of 1,1,2-trimethyl-5-indanol (44).

Structure VI appears to be the most probable. The most compelling evidence for structure VI is the formation of "A" from 5-phenoxy-2-methyl-2-pentene when the latter was treated with a few drops of concentrated sulfuric acid. This can best be formulated as follows:

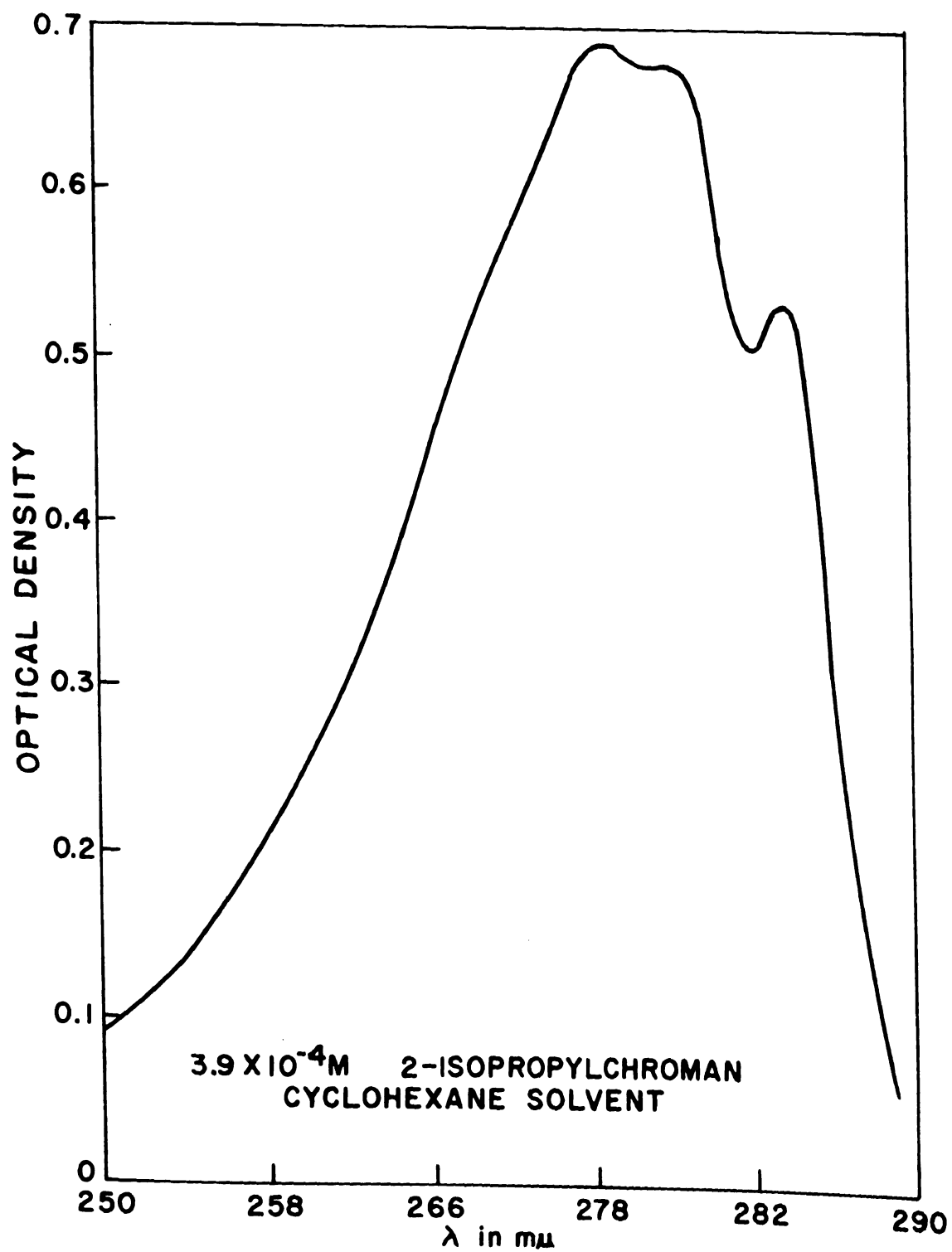
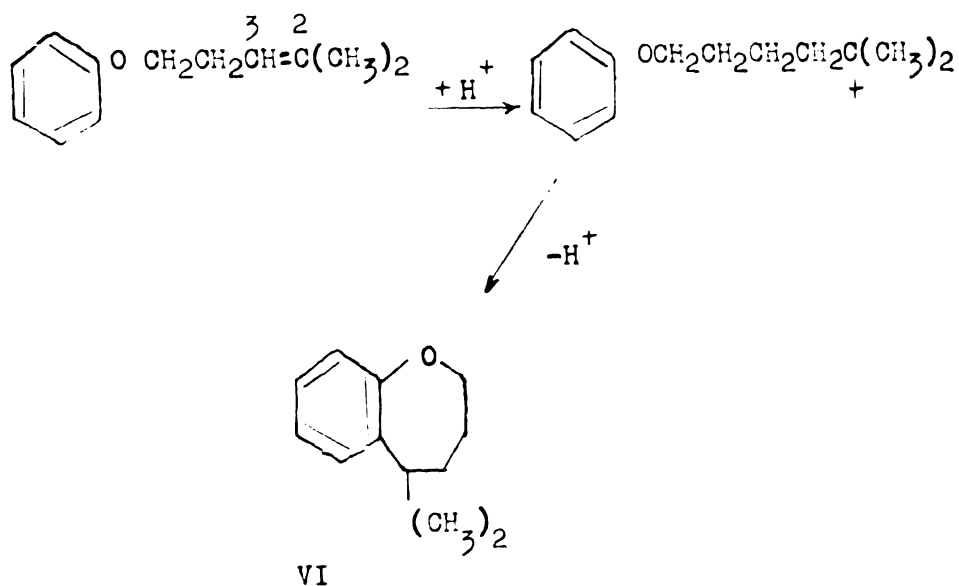


PLATE 5. ULTRAVIOLET ABSORPTION SPECTRUM
OF 2-ISOPROPYLCHROMAN

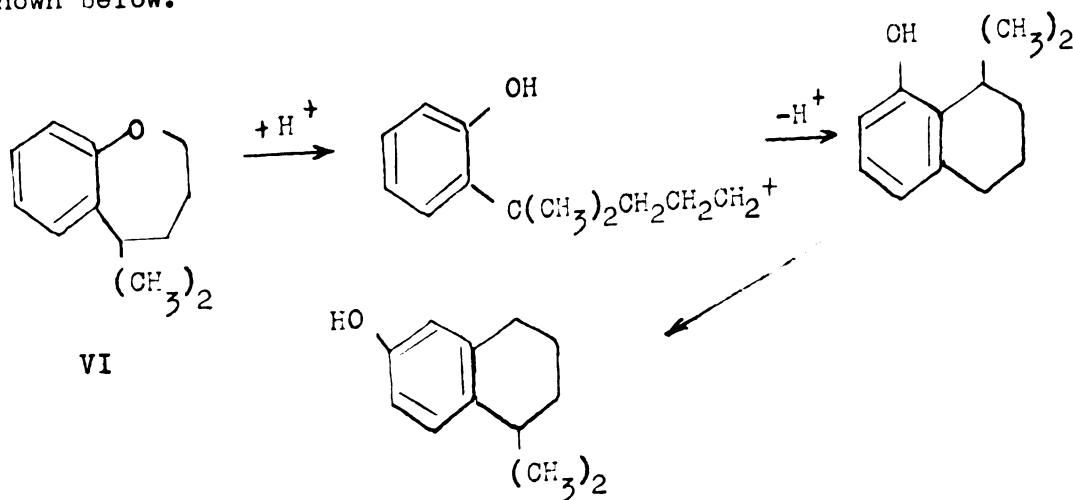


The tertiary alkyl ion formed by protonation of C₃ in the first step would be very reactive and alkylation would be anticipated. The fact that only "A" was isolated also indicates that there was not an initial cleavage and then realkylation. Furthermore, 1-phenoxy-4-methylpentane (isohexyl phenyl ether) was not cleaved under identical conditions; hence, the formation of "A" from I proceeds intramolecularly. In order to form 4-isopropylchroman (V) from I, doubtful reverse addition of sulfuric acid to the double bond would be required. The formation of structure III from I by sulfuric acid seems very improbable, especially, considering that cleavage of the ether linkage does not occur.

The possible exception for structure VI is the ultraviolet absorption spectrum. The ultraviolet absorption spectrum can be rationalized for this type of structure in the following manner: 2-methylcoumaran absorbs at 281 mμ and 269 mμ (45); 2-isopropylchroman

absorbs at 274.5 μ and 284 μ (see plate 5); 2,2-dimethylchroman absorbs at 278 μ and 284 μ (45); and *t*-butyl phenyl ether absorbs at 264 μ and 270 μ (see plate 4). The absorption bands are shifted progressively to shorter wavelengths as the heterocyclic ring is increased from five in coumaran, to six in chroman, to the complete open chain in *t*-butyl phenyl ether. The seven membered ring in structure VI would then be expected to have absorption bands between those of *t*-butyl phenyl ether and chroman. "A" absorbs at 266 μ and 271.5 μ which is in the predicted range for structure VI. From the chemical and spectral evidence it seems very probable that VI is the correct structure for "A".

Structure VI could also explain the formation of an alkylated phenol, "C", from "A". The ultraviolet absorption spectrum of "C" (see plate 5) has bands at 279 μ (broad band) and 288 μ which is typical of a *p*-alkylated phenol or 5-tetralol, the latter of which has absorption bands at 279 μ , 281.5 μ , and 289 μ (45). Thus one possible structure for "C" which could be postulated from the reaction of structure VI in refluxing acetic acid and hydrobromic acid is shown below.

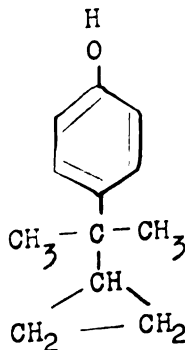


The initial cleavage of VI is followed by alkylation in the meta position. The tertiary alkyl group on the ortho position could then rearrange to the para position giving the 6-tetralol type of structure. This mechanism is not unique for the formation of an alkylated phenol from "A"; the tertiary alkyl group could possibly be displaced prior to the cleavage of the ether linkage. On the whole, this series of transformations is not too satisfactory. The structure of "C" is not established and it requires further work.

Phenolic Product "B"

The phenolic product "B" analyzed for $C_{12}H_{16}O$ which corresponded to monoalkylation of phenol with the chloroolefin. The neutralization equivalent of the phenoxyacetic acid derivative, and the elemental analyses of the β -naphthyl urethan, benzoate, and methyl ether derivatives of "B" gave further evidence that "B" was a monoalkylated phenol, such as, $C_6H_{11}C_6H_4OH$.

The ultraviolet absorption spectrum of "B" (see plate 6) was similar to that normally obtained from ortho or meta alkylated phenols (see Table IV). The position of the absorption bands were considerably different from that of a *p*-alkylated phenol. This seems to eliminate the anticipated structure, *p*-dimethylcyclopropylcarbinyphenol.



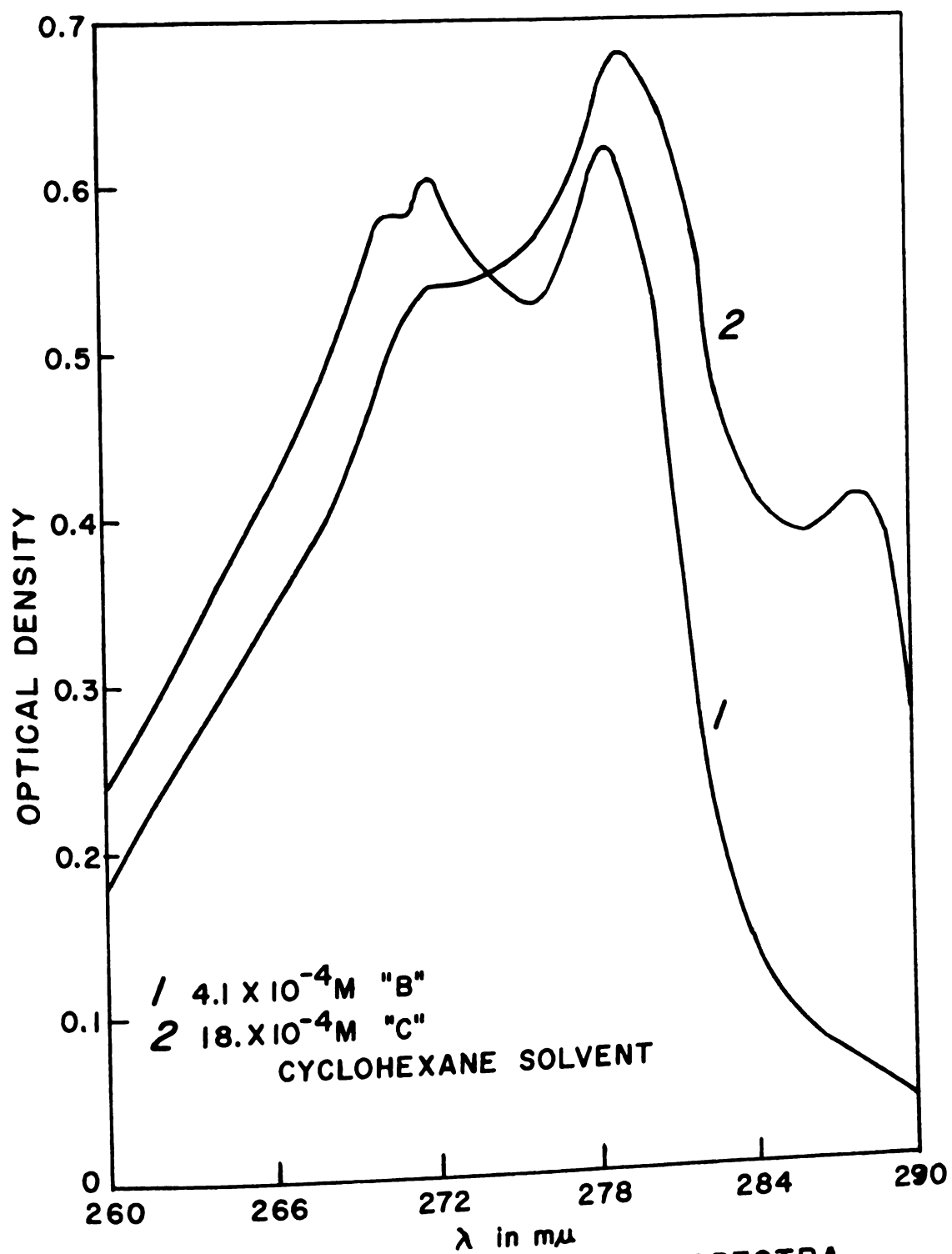


PLATE 6. ULTRAVIOLET ABSORPTION SPECTRA
OF PHENOLIC PRODUCTS

TABLE IV. ULTRAVIOLET ABSORPTION BANDS OF VARIOUS ALKYLATED PHENOLS.

Compound	Absorption bands (mμ)		Reference
<u>o</u> -ethylphenol	272	276	(46)
<u>o</u> -cresol	272	278	(46)
<u>o</u> - <u>t</u> -butylphenol	271	278	(47)
<u>m</u> -ethylphenol	272	279	(46)
<u>m</u> -cresol	272	279	(46)
<u>p</u> -cresol	279	287	(46)
<u>p</u> - <u>t</u> -butylphenol	277	283	(47)
<u>p</u> -ethylphenol	278	285	(46)
"B"	272	279	

Coggeshall and Glessner (48) reported for various alkylated phenols that a shift of the ultraviolet absorption spectrum to higher wavelengths was found for unhindered phenols in 0.1 M sodium hydroxide solutions. They included ortho-substituted phenols, such as, 2,6-dimethylphenol in the class of unhindered phenols. The ultraviolet absorption spectrum of "B" in 0.1 M sodium hydroxide solution¹ showed such a shift to higher wave lengths; hence, "B" was either unsubstituted in the ortho position or the group, if present, did not sterically hinder the hydroxyl group. An ortho-substituted phenol structure for "B" appeared quite improbable,

¹ The ultraviolet absorption spectrum of "B" in 0.1 M sodium hydroxide solution was determined by Dr. R. B. Hannan, Standard Oil Company of Indiana, Whiting, Indiana.

since the possible alkyl groups would have six carbon atom, branched chain structures. Thus, from the ultraviolet spectrum "B" appeared to be a meta or an ortho substituted phenol (which was not hindered), or possibly alkylated in both positions.

An analysis of the infrared absorption spectrum (see plate 7,8) was complicated by the large number of absorption bands. The following groups were indicated:

phenolic C-OH¹ 3600, 1264 cm.⁻¹

C(CH₃)₂² 1462, 1442, 1389, 1368 cm.⁻¹

The 5 μ to 6 μ region in the mineral oil mull absorption spectrum³ showed 1,3 or 1,2,3 substitution on the benzene ring. Young, et al. (49) have shown that a characteristic absorption pattern is obtained in this region for variously substituted benzene rings. "B" absorbed at 5.2, 5.4, 5.7, 6.0 μ with approximately equal intensities. 1,3-substituted benzene compounds show bands at 5.2, 5.4, 5.7 and a weak band at 5.8 μ . 1,2,3-Substituted benzene compounds have bands at 5.2, 5.4, 5.6, and 6.0 μ . Other structures have different patterns. The position of absorption varies to a certain extent but the overall pattern, including relative intensities, remains independent of the type of groups on the benzene ring.

1 Bellamy, p. 84.

2 Ibid., Chp. 2.

3 The infrared absorption spectrum of "B" in mineral oil mull was supplied by Dr. J. L. Johnson, Upjohn Company, Kalamazoo, Michigan.

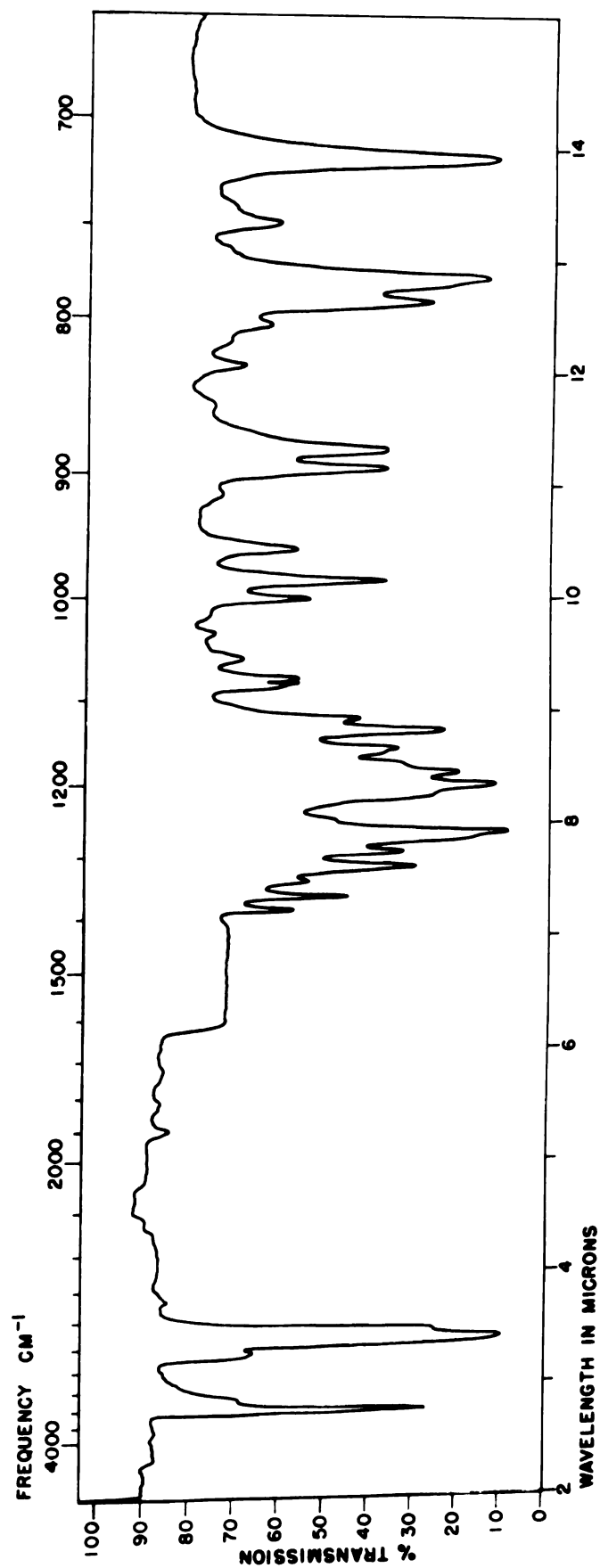


PLATE 7. Infrared Absorption Spectrum of "B" in Carbon Disulfide.
Cell thickness 0.5 mm.

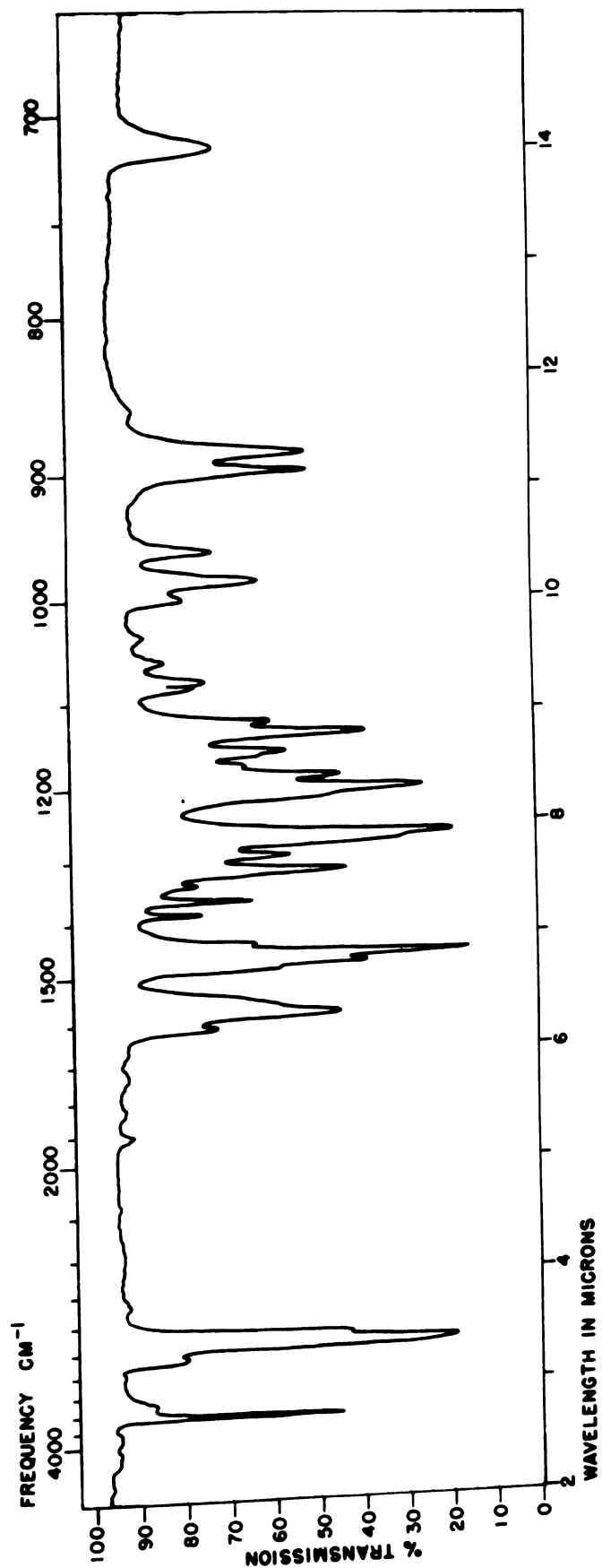
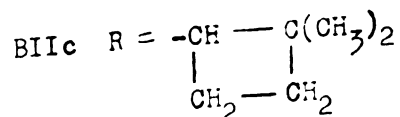
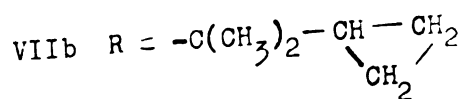
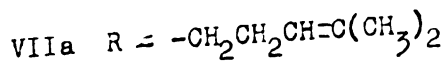
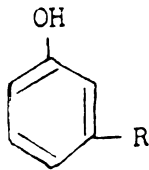


PLATE 8. Infrared Absorption Spectrum of "g" in Carbon Tetrachloride
Cell thickness 0.5 mm.

1,3- and 1,2,3-substitution¹ was also supported by the bands at 717 cm^{-1} and 778 cm^{-1} . Unfortunately, the phenolic C-O absorbs in the 1200-1300 cm^{-1} region eliminating use of this region for assignment of type of substitution. There was no band near 1025 cm^{-1} , which would have been evidence for the cyclopropane ring². Also, there was no sharp band present for the carbon-carbon double bond³ at 1680-1620 cm^{-1} .

Hence, from the ultraviolet and infrared absorption spectra one would conclude that "B" was a phenol which was either meta-alkylated, or ortho-meta dialkylated, with the latter formulation fitting the spectra somewhat more closely than the former. Although it seemed most unusual that phenol should have been mono-alkylated in the meta position, our initial efforts were directed toward proving or eliminating structures of this type. At this stage of the problem, the interpretation of the infrared spectrum in detail, as above, was not possible.

For a 1,3 disubstituted benzene ring the following structures of "B" were possible. The three structures of R in VII are derived

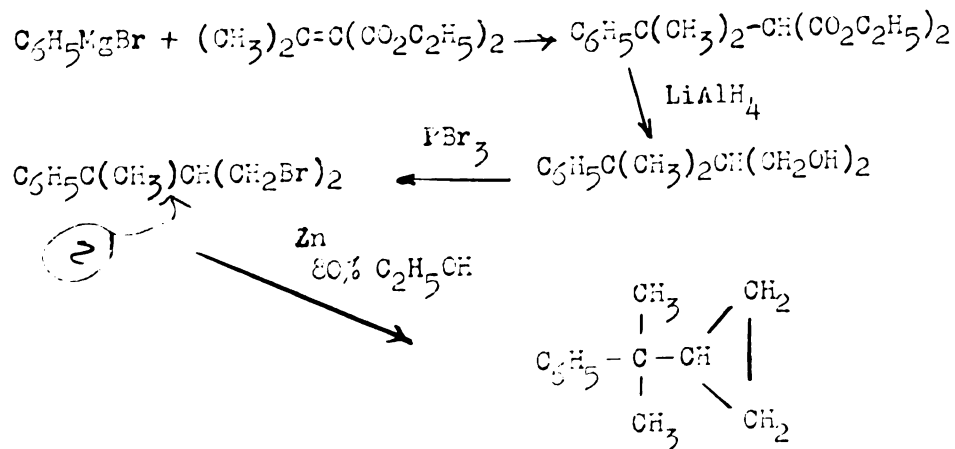


1 Bellamy, p. 66.

2 Ibid., p. 28.

3 Ibid., p. 32.

from the three contributing forms of the homoallylic ion of 1-chloro-4-methyl-3-pentene. Certain of the structures postulated for "B" can be tentatively eliminated from the absence of certain bands in the infrared absorption spectrum. Thus, the absence of a medium intensity absorption band from 1680-1620 cm^{-1} indicated the absence of a carbon-carbon double¹ bond, eliminating structure VIIa. There was no evidence for the cyclopropane ring² by the absence of a band near 1025 cm^{-1} which should probably have been present if VIIb were the correct structure. To further verify this, dimethylcyclopropylcarbonylbenzene was prepared by methods previously used to prepare alkyl cyclopropanes (37, 39), and its infrared absorption spectrum was analyzed (see Plate 9).



The structure of the product was supported by the infrared absorption spectrum with absorption bands at 1017 cm^{-1} for the

1 Bellamy, p. 32.

2 Ibid., p. 28.

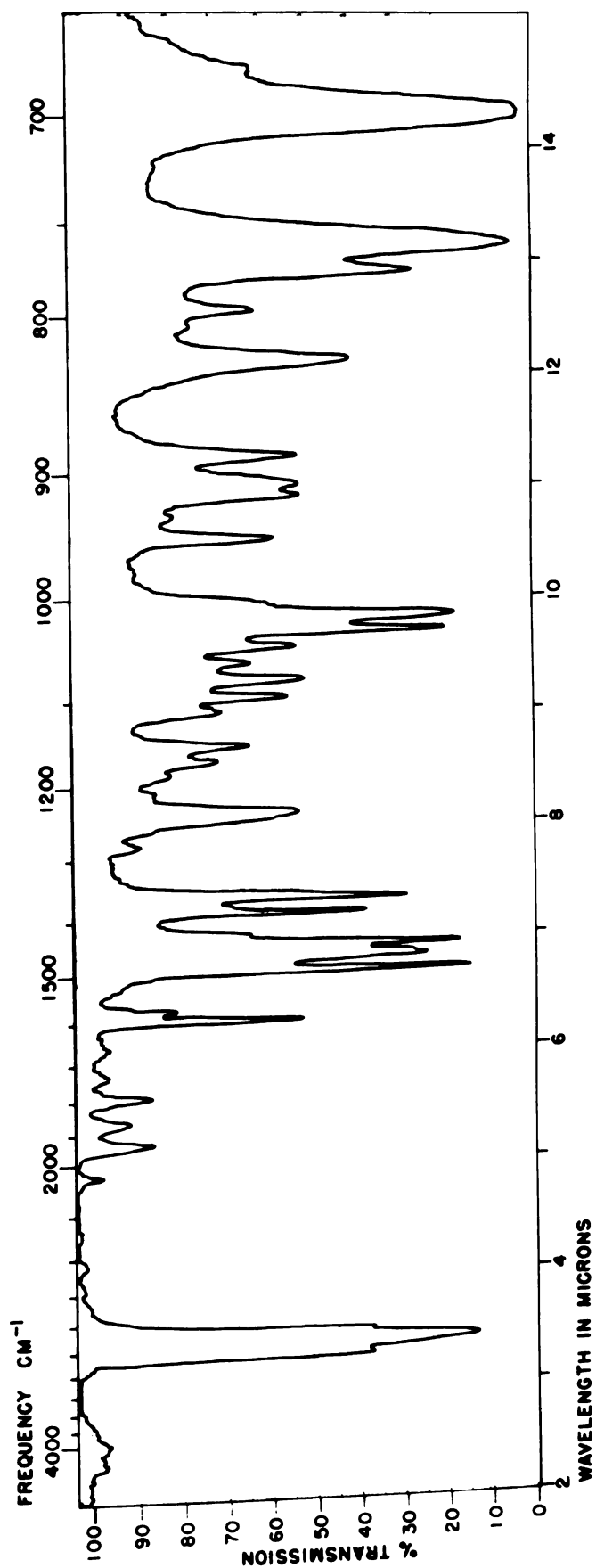
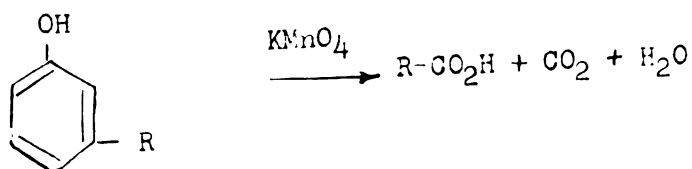


PLATE 9. Infrared Absorption Spectrum of Dimethylcyclopropylcarbinylbenzene (neat). Cell thickness 0.031 mm.

cyclopropane ring, bands at 1446, 1388, 1368 cm^{-1} for $\text{C}(\text{CH}_3)_2$ and the pattern in the 5 μ to 6 μ region was similar to that found by Young, et al. (49) for monosubstituted benzene ring. Dimethylcyclopropylcarbinylbenzene had four typical bands at 5.16, 5.36, 5.48, and 5.78 μ which were similar to those for a monosubstituted benzene ring. Monosubstitution¹ was also further verified by the absorption bands at 766 cm^{-1} and 699 cm^{-1} . The presence of a sharp cyclopropyl band at 1017 cm^{-1} in dimethylcyclopropylcarbinylbenzene indicated if VIIb were the correct structure, the 1017 cm^{-1} should have appeared in the spectrum of "B".

Oxidation of "B" with potassium permanganate was attempted several times following a procedure (27) which had previously been used successfully on monoalkylated phenols. The purpose was to



obtain the alkyl group as an acid which could be converted to an amide and eventually characterize the alkyl group. Unfortunately the "acid" obtained decomposed on distillation under reduced pressures; yet monocarboxylic acids as isomylacetic acid, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, can be distilled at atmospheric pressures without decomposition.

1 Bellamy, p. 55.

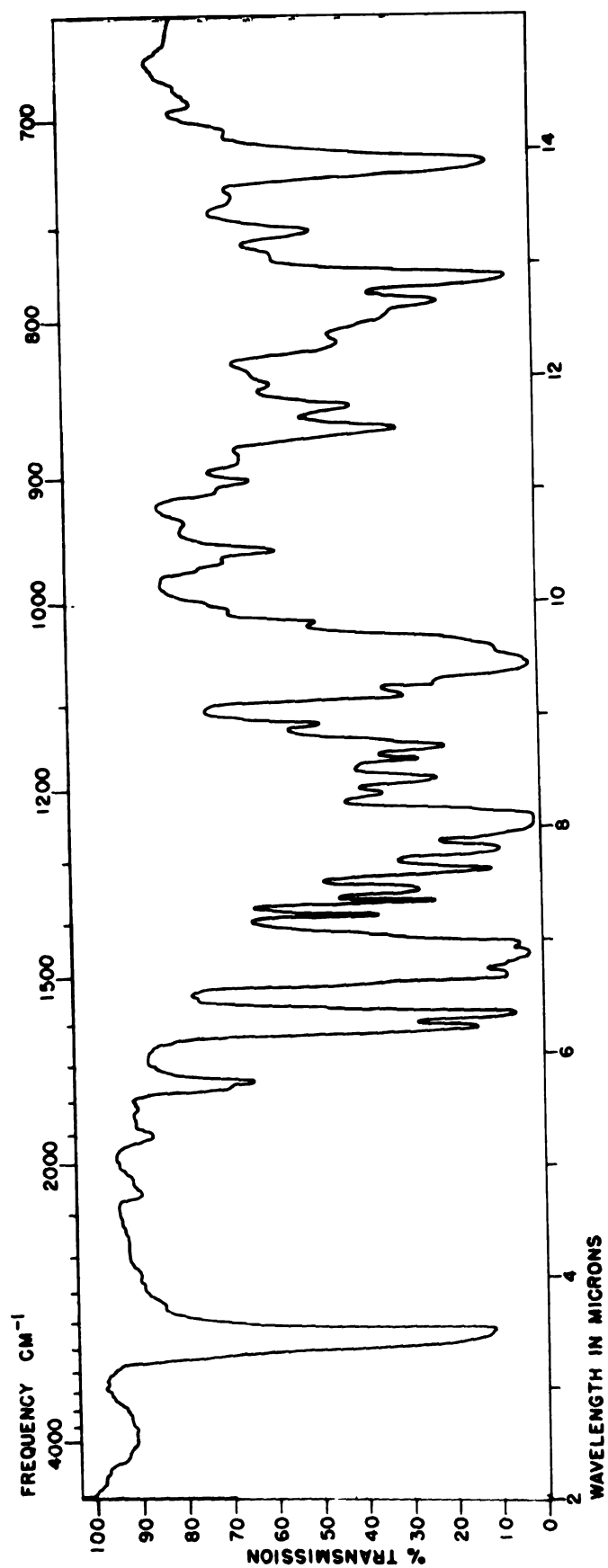
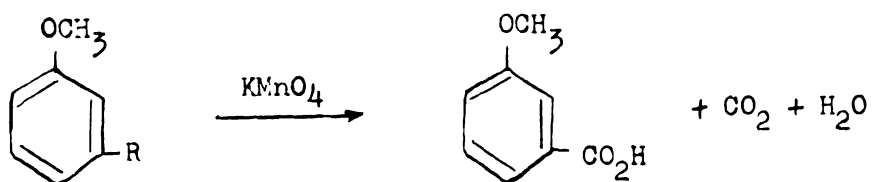


PLATE 10. Infrared Absorption Spectrum of the Methyl Ether of "B" (neat). Cell thickness 0.031 mm.

The methyl ether of "B" (infrared absorption spectrum given in Plate 10) was then oxidized with potassium permanganate to determine the position of alkylation. It was hoped to isolate a methoxybenzoic acid; however, the mixture isolated was a dark oil which did not solidify. If VII were the correct structure, an R group as in VIIb would not be expected to give a benzoic acid

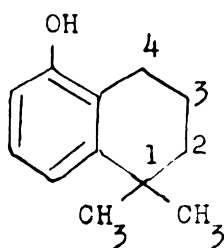


because of the tertiary alkyl group adjacent to the ring. VIIa and VIIc would be expected to give the acid more easily. Additional structures of "B" will be postulated later which also would not be anticipated to oxidize completely because of a tertiary alkyl group adjacent to the benzene ring.

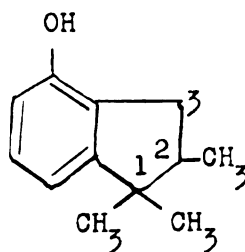
A further experiment designed to show the alkylation of "B" was not para, was the attempted nitrosation of "B". The experimental procedures used (28, 29) gave good results with m-cresol. Nitrosation of m-t-butylphenol using the same conditions, however, gave inconclusive results. A dark colored material was obtained. A solid product was obtained from the nitrosation of "B"; the analysis of the nitrosated product gave a very low analysis for nitrogen and high analysis for carbon. Thus "B" acted similar to m-t-butylphenol in not giving the appropriate nitrosophenol. The unreactivity may be attributed to the steric hindrance of a large group present in the meta position.

In summary, then, oxidation and nitrosation experiments are not consistent with structures VIIa or VIIc, but indicate that a large group may be present in the position meta to the hydroxyl.

Other structures for "B" were possible which could fit the spectral and chemical evidence; i.e., the trisubstituted benzene ring. Any trisubstituted benzene ring would require that group occupying the ortho position to the hydroxyl group be small. 1,2,3-Trisubstituted benzene structures for "B" involved bicyclic structures as VIII and IX.



VIII

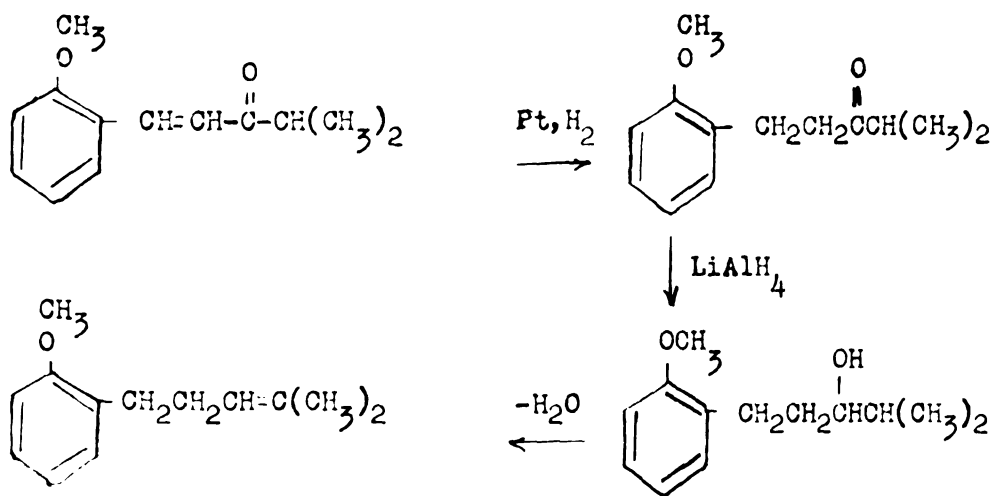


IX

Both structures VIII and IX were compatible with the infrared absorption spectrum of "B", with the group $C(CH_3)_2$ present and 1,2,3 trisubstitution. The ultraviolet absorption spectrum of "B" was similar to 5-tetralol which absorbs at 271, 272 and 279 $m\mu$ (46), but dissimilar to 4-indanol which absorbs at 269, 270 and 275 $m\mu$ (46). "B" absorbed at 272 $m\mu$ and 279 $m\mu$. Either VIII and IX were also compatible with the ultraviolet absorption spectrum of "B" in alkaline solution on the condition that position 4 in VIII and 3 in IX were unsubstituted. The methylene group should offer no more and probably less hindrance than the methyl group in 2,6-dimethylphenol.

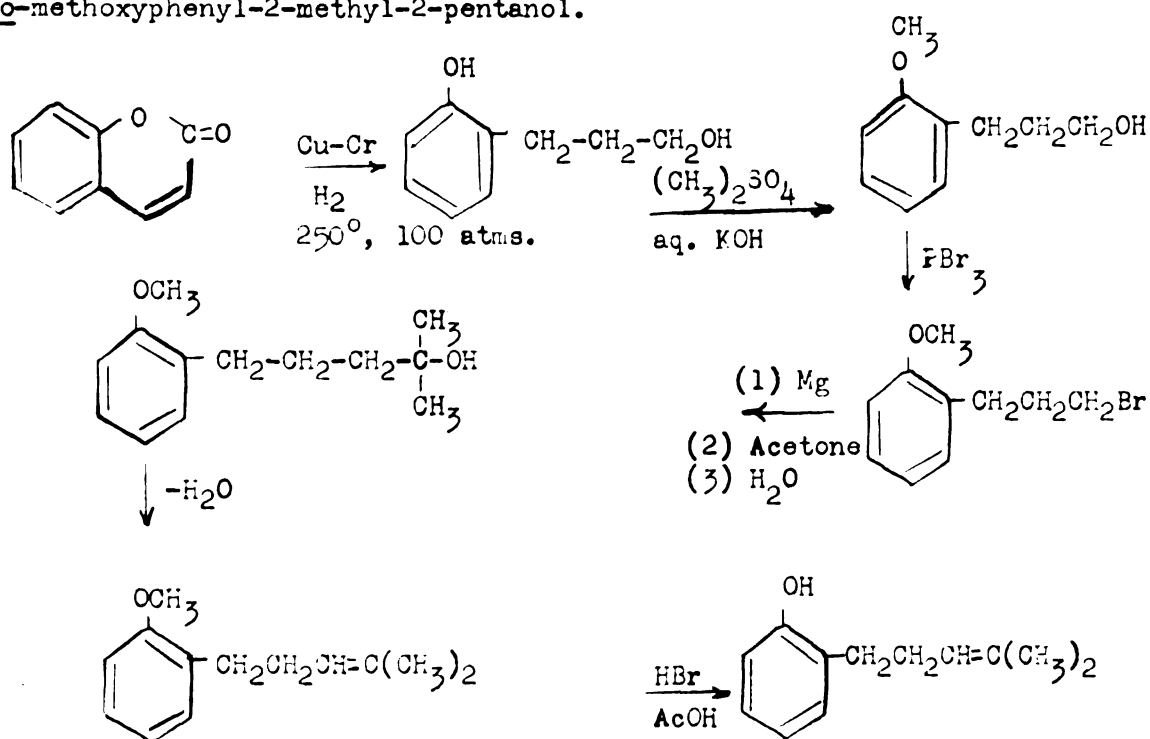
Structures VIII and IX are also consistent with the chemical evidence. The relative ease of formation of derivatives of "B", such as the benzoate, indicate that the phenolic hydroxyl group was unhindered. The tertiary alkyl group would prevent oxidation of the methyl ether of "B" to 3-methoxyphthalic acid. The experimental conditions used in the oxidation of "B" itself were not suited to the isolation of a dicarboxylic acid. Dicarboxylic acids, such as adipic acid, are not readily extracted from aqueous solutions by benzene. The meta tertiary alkyl group would also be consistent with the lack of formation of a nitroso derivative from "B". Furthermore, the bicyclic structure would eliminate the need for a mechanism to explain meta substitution in phenol, which normally substitutes in the ortho or para positions.

The preparation of 5-(o-hydroxyphenyl)-2-methyl-2-pentene and the corresponding para isomer was attempted to see if they were intermediates in the formation of "A" and "B".



Unfortunately, the dehydration of 1-(o-methoxyphenyl)-4-methyl-3-pentanol with sulfuric acid gave a mixture. The dehydration of 1-(p-methoxyphenyl)-4-methyl-3-pentanol using Whitmore's (34) modification of the Tschugaeff reaction also gave a mixture.

A better procedure for preparing 5-(o-methoxyphenyl)-2-methyl-2-pentene would be by the dehydration of the tertiary alcohol, 5-(o-methoxyphenyl)-2-methyl-2-pentanol.

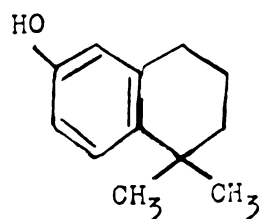


This proposed series of reactions leading to the tertiary alcohol starts with the reduction of coumarin. Unfortunately it was not possible to carry out this reduction because adequate hydrogenation apparatus was not available.

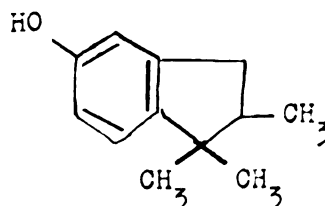
Phenolic Product "C"

"C" analyzed for C₁₂H₁₅O. The infrared absorption spectrum (see Plates 11 and 12) were very similar to "B" with the differences

occurring from 1200 cm.^{-1} to the lower frequencies. The infrared absorption spectrum appears to support the same type of substitution on the benzene ring as "B". The ultraviolet absorption spectrum (see plate 5) indicates that "C" is a para substituted phenol with bands at $279\text{ m}\mu$ and $288\text{ m}\mu$. (Cf. with the *p*-alkylated phenols in Table IV). A 3,4-disubstituted phenol as shown in structures XI and XII is possible. The ultraviolet absorption spectrum of "C" is more consistent with that of 6-tetralol (45) with absorption bands



XI



XII

at 279 , 281.5 and $289\text{ m}\mu$ than with 5-indanol which has absorption bands at 282 and $285\text{ m}\mu$. Thus XI seems the more probable structure for "C".

Since "C" was isolated in small quantities, no chemical degradation or reactions were attempted. It was hoped that the eventual determination of the structure of "B" would indicate the possible structure of "C". More of "C" will be available from the reaction of "A" with hydrobromic acid and acetic acid, since "A" can be made in larger quantities from 5-phenoxy-2-methyl-2-pentene and sulfuric acid, than from the direct reaction of 1-chloro-4-methyl-3-pentene with phenol.

The formation of compounds of structures similar to XI and XII have been reported by Bruson and Kroeger (50). They alkylated phenol

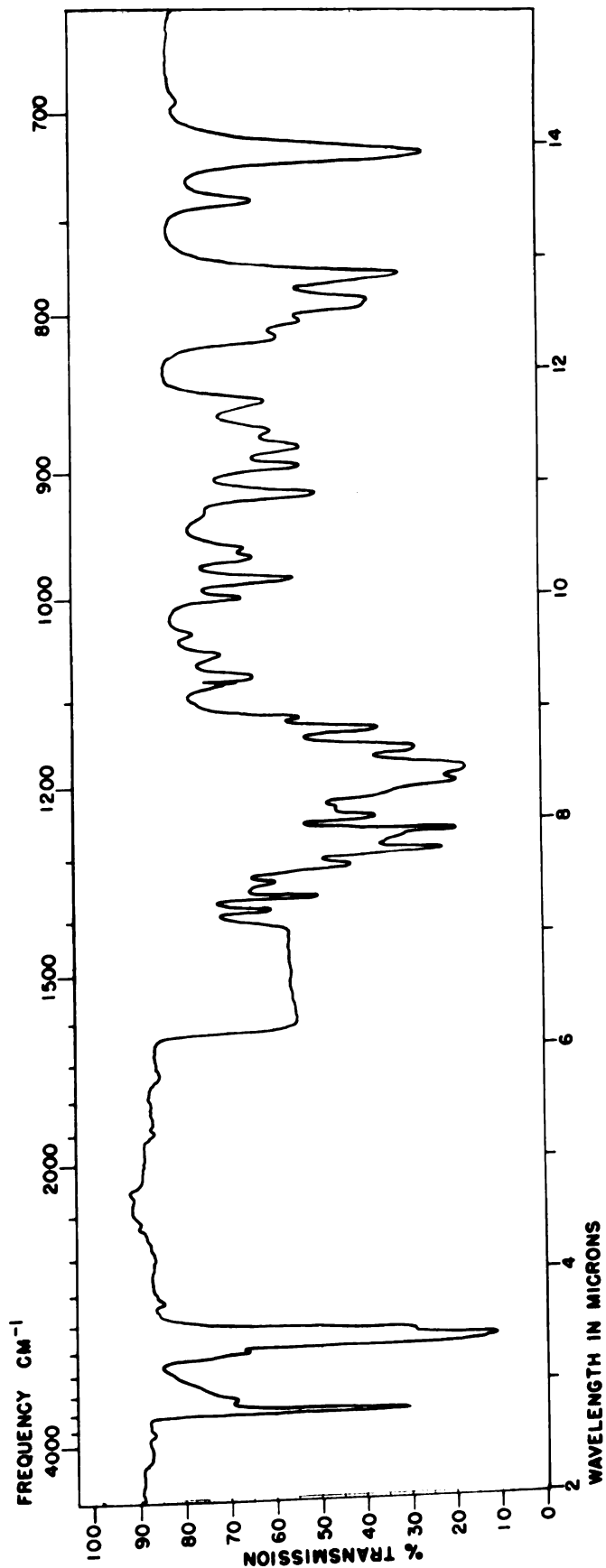


PLATE 11. Infrared Absorption Spectrum of "¹³C" in Carbon Disulfide.
Cell thickness 0.5 mm.

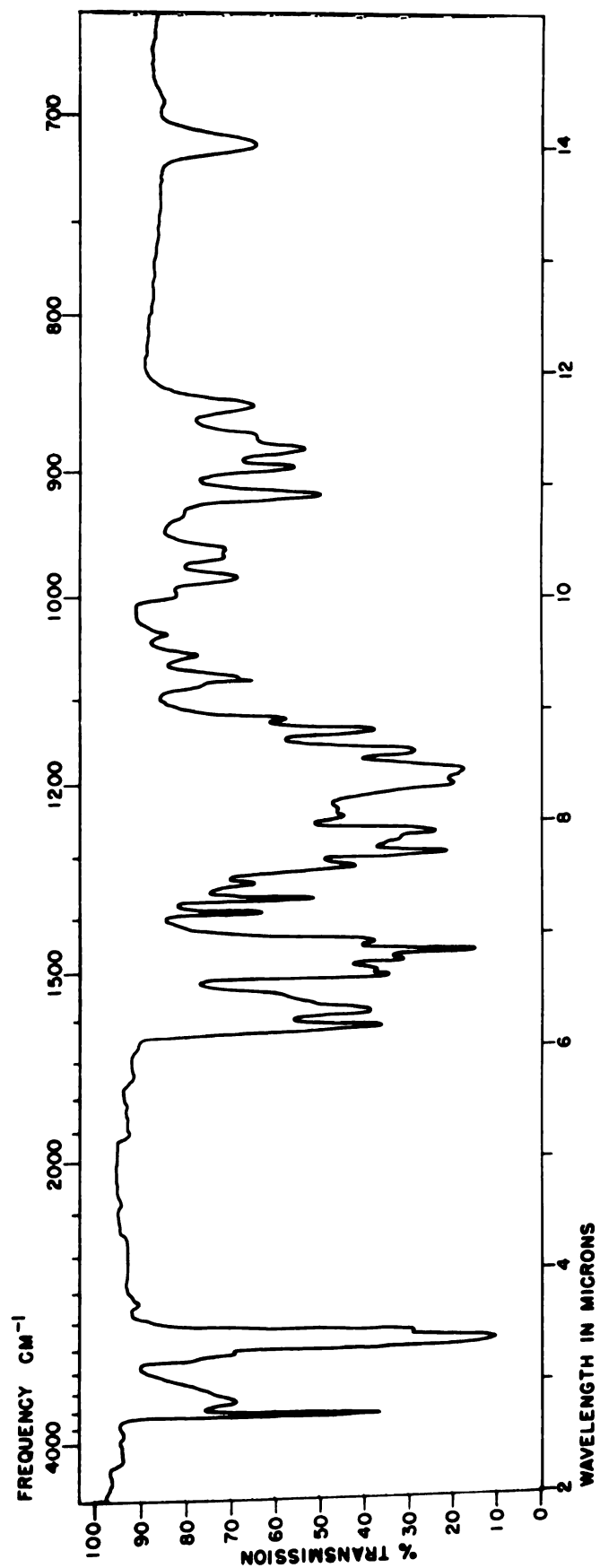
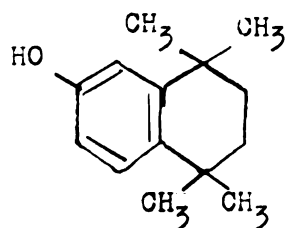


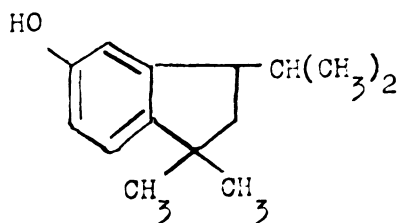
PLATE 12. Infrared Absorption Spectrum of ¹³C in Carbon Tetrachloride.
Cell thickness 0.5 mm.

with 2,4-dimethyl-2,4-hexandiol, 2,4-dimethyl-2,4-dichlorohexane, and 2,4-dimethyl-2,4-hexadiene using aluminum chloride as a catalyst and in each case isolated the same alkylated phenol to which they gave the structure XIII (1,1,4,4-tetramethyl-6-tetralol). However,



XIII

the proof of structure was not rigorous. Bruson and Kroeger (50) also found that alkylation using sulfuric acid as the catalyst gave an isomeric alkylated phenol for which they postulated structure XIV (1,1-dimethyl-3-isopropyl-5-indanol).



XIV

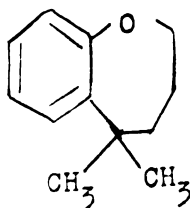
The products, then, of the reaction between 1-chloro-4-methyl-3-pentene and phenol are an ether of structure VI and a phenol with the probable structure VIII. These are not the anticipated products, had the double bond participated in the reaction analogously to its role in the formation dimethylcyclopropylcarbinol from the chloroolefin.

There is no doubt, however, that the β,γ -double bond has been effective in activating the primary carbon to chloride bond. The mechanism by which this activation occurs is not clear, and it requires further study. In addition to the need for more evidence on the structure of the products described in this thesis, it would also be advantageous to study the effect of structure of the chloro-olefin and the phenol on the course of the reaction. Other experiments with 1,4-dichloro-4-methylpentane, 5-chloro-2-methyl-2-pentanol, and 4-methyl-1,3-pentadiene and phenol might also be helpful.

SUMMARY

The rearrangement of dimethylcyclopropylcarbinol with hydrochloric acid, to 1-chloro-4-methyl-3-pentene, and the hydrolysis of the latter back to dimethylcyclopropylcarbinol was reinvestigated using infrared absorption spectra. The rearrangement and the assigned structures were confirmed. Several attempts were made to prepare dimethylcyclopropylcarbiny chloride from the corresponding alcohol by methods which were known to produce alkyl halides from alcohols without rearrangement. These methods were unsuccessful; in each case, dimethylcyclopropylcarbinol either did not react or the rearranged chloride, 1-chloro-4-methyl-3-pentene, was obtained.

1-Chloro-4-methyl-3-pentene, when heated with phenol at 150° , gave two isomeric crystalline products. One was an ether to which structure VI was tentatively assigned. The elemental analysis and infrared and ultraviolet absorption spectra were consistent with this structure. Furthermore, the ether was synthesized from 5-phenoxy-2-methyl-2-pentene, by treatment with concentrated sulfuric

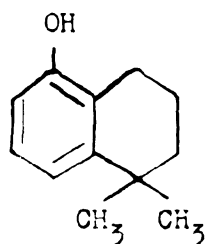


VI

acid. A number of likely alternative structures for this ether were examined and discarded.

The second product was an alkylated phenol. The anticipated

product of the reaction was p-dimethylcyclopropylcarbinylphenol. Infrared and ultraviolet absorption spectra quickly demonstrated that the anticipated product was not obtained. A number of possible structures were considered, and the one which is most consistent with the chemical and physical evidence is 1,1-dimethyl-5-tetralol



VIII

(structure VIII), but further work is necessary to establish this structure conclusively.

When the ether, 5,5-dimethylhomochroman, was treated with hydrobromic acid and glacial acetic acid, another isomeric phenol was obtained. The structure of this compound is not clear, but it probably has alkyl substitution para to the hydroxyl group.

During the course of these studies several new compounds were prepared. These compounds were: 2-isopropylchroman, 5-phenoxy-2-methyl-2-pentene, 5-(o-methoxyphenyl)-2-methyl-3-pentanol, 5-(o-methoxyphenyl)-2-methyl-3-pentanone, 5-(p-methoxyphenyl)-2-methyl-3-pentanol, 5-(p-methoxyphenyl)-2-methyl-3-pentanone and dimethylcyclopropylcarbinylbenzene. Some reactions of t-butyl phenyl ether were also examined.

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