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## Aromatic acetals : their synthesis and alkylation

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AROMATIC ACETALS, THEIR SYNTHESIS AND ALKYLATION

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A Thesis

Presented to

The Faculty of the Department of Chemistry

College of the Pacific

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In Partial Fulfillment

of the Requirements for the Degree

Master of Arts

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by

Robert Connor Gass

February 1952

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## TABLE OF CONTENTS

	PAGE
Introduction . . . . .	1
Acetals . . . . .	2
Lignin Intermediates . . . . .	15
Experimental Section . . . . .	17
Preparation of Acetals . . . . .	17
The Comparison of Sulfonic Acids to Hydrogen Chloride as Catalysts . . . . .	22
The Stability of Acetals under Alkylating Conditions . . . . .	25
Summary . . . . .	29
Bibliography . . . . .	30

## LIST OF TABLES AND FIGURES

TABLE	PAGE
I. Comparison of Equilibrium States of Beta Substituted Acetaldehydes and Their Respective Ethyl Acetals . . . . .	11
II. The Conversion of Selected Alcohols and Aldehydes to Acetals . . . . .	13
III. Variation of the Molar Ratio of Constituents in the Synthesis of the Butyl Acetal of Benzaldehyde . . . . .	20
IV. The Yield of the Butyl Acetal of Benzaldehyde Produced by Various Catalysts . . . . .	24
V. The Products of the Friedel Crafts Reaction on Acetals . . . . .	28
<b>FIGURE</b>	
I. Fractional Distillation Apparatus . . . . .	17

## FORWARD

Recent work in the field of natural products has developed an interest in further studies of the structure of lignin. Among the work done in this field is that of Russell, who found that a Fries rearrangement of the acetates of vanillin and salicylaldehyde produce a lignin like material. The intermediates in these reactions have not been isolated. It has been suggested that if it were possible to protect the aldehyde group from reacting during the Fries rearrangement by forming an acetal, the intermediate compound could be isolated and characterized.

The purpose of this investigation was to study the known methods of forming acetals and find one or several that could be used in preparing a variety of acetals to be used in further investigation. In connection with the reactions, the use of various catalysts was pertinent. Some of the catalysts used were hydrogen chloride, calcium chloride, ferric chloride, aromatic sulfonic acids, and others. There were no data available comparing the sulfonic acids with the inorganic salts and mineral acids. For that reason one of the subsidiary problems of this investigation was such a comparison.

In order to investigate stability, several acetals were subjected to conditions intended to produce ring acetylation. These conditions are the same imposed by a Friedel Crafts reaction or a Fries rearrangement.

## INTRODUCTION

One of the difficulties in the study of the products of the Fries rearrangement of acetoxybenzaldehydes is the extensive side reactions resulting in a polymer which has lignin like properties. It is known that aldehydes condense with groups containing a labile hydrogen atom in an aldol type of reaction. Russell (1948) suggests that the monomer of the above polymer is a formyl acetophenone. The monomer, containing an aldehyde and a methyl ketone on the same aromatic ring, would be unstable in the presence of the Lewis acid required to produce the Fries rearrangement.

The lignin like properties of the polymer are of special interest because the starting materials are similar to the degradation products of natural lignin and because of the abundance of lignin as a waste by-product. Thus any information as to the structure of lignin would be of importance.

It has been suggested in this laboratory that forming an acetal of the aldehyde group would protect it from condensing during the Fries rearrangement. The respective acetal of the monomer would be obtained as a product. The purposes of this investigation was to find a convenient method of preparing acetals, to study certain catalysts used in acetal formation, and to study the stability of the acetals in the presence of strong Lewis acids.

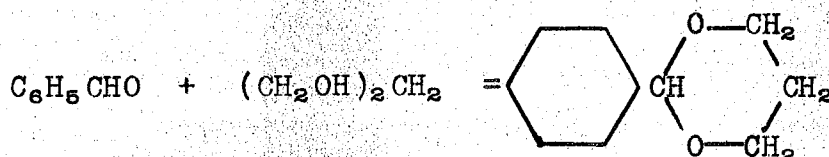
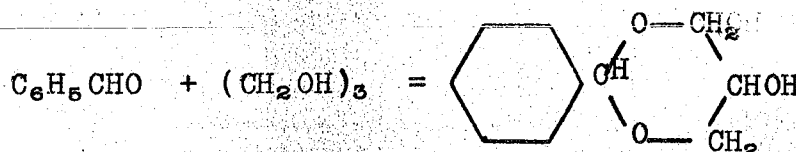
## ACETALS

Acetals were known early in the history of organic chemistry. Liebig reported, in 1835, (Abderhalden 1911) that the oxidation products of methyl and ethyl alcohol were their respective acetals. This was only eight years after Wohler synthesized urea to give birth to modern organic chemistry. The structure of these compounds however, was probably not known at this time. Wicke (Abderhalden 1911) prepared the ethyl, methyl, and iso-valeryl acetals of benzaldehyde in 1859 and in the same year Wurtz (Abderhalden 1911) reported the reaction of sodium ethoxide with alpha chloroether, obtaining acetal. The condensation of an alcohol with an aldehyde to obtain an acetal was first reported by Geuther in 1863 (Abderhalden 1911). This was achieved by combining acetaldehyde with ethyl alcohol in a bomb, first without a catalyst, and then with acetic acid as a catalyst. The fact that higher yields were obtained in less time with the catalyst present indicated the need for a catalyst in this type of reaction.

The active catalysts for acetal formation, listed in a work by Lellmann (1889), were acetic acid, dry hydrogen chloride, phosphine, and sulfur dioxide.



Fischer's work (Abderhalden 1911) with glycols and glycerol produced the cyclic acetals of benzaldehyde. The acetals were prepared by condensing benzaldehyde with 1,3-propylene glycol and glycerol.



## I

The method used principally at the present time for preparation of acetals was developed by Fischer and Giebe (1897 and 1898). It has been the standard method for many years because of its simplicity and applicability. The method consists of refluxing five parts of 1% alcoholic HCl and one part aldehyde, or allowing the mixture to stand for a period of time, neutralizing with potassium carbonate, and recovering the product by distillation. A relatively poor yield (36%) for the ethyl acetal of benzaldehyde was produced by this method. The yields obtained for aliphatic compounds were about 50%.

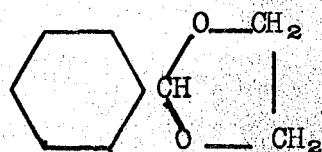
The modification used by Haworth and Lapworth (1922) was a marked improvement upon Fischer's method. Sodium ethoxide was used to neutralize the catalyst, thus increasing the yields of the aliphatic acetal to an average of 80%. They found that the benzaldehyde does not form acetals readily thus suggesting the need to shift the equilibrium by removing the water of reaction. This was accomplished by Young's process for dehydration of ethanol, a method using azeotropic distillation. Aromatic acetals were obtained in 74% yield employing such a method.

Benzene, ethanol, and water form a constant boiling mixture which cannot be separated even by fractional distillation (Morton 1938). Young's process takes advantage of the fact that the above constant boiling mixture upon cooling will separate into two phases. One phase rich in water can be separated and dried by appropriate agents. After the water rich layer is separated and dried, the entire distillate is returned to the distilling flask.

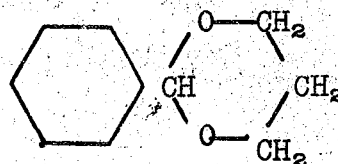
Benzene, many hydrocarbons, and halogenated hydrocarbons form binary mixtures with water and often ternary mixtures with water and alcohol (Horsley 1947). The azeotropic distillation method is applicable in removing the water of reaction in acetal formation and esterification reactions.

The azeotropic method had been selected as the most promising practical method for preparing acetals of aldehydes normally subject to side reactions. A part of the experimental section is concerned with the use of this method to obtain the butyl acetal of benzaldehyde, pure and in high yield.

The formation of cyclic acetals of substituted benzaldehydes has been achieved in high yield by the azeotropic method. These acetals are derivatives of the dioxane ring and are most often solid at room temperature (Salimi and Kurki 1948).



II

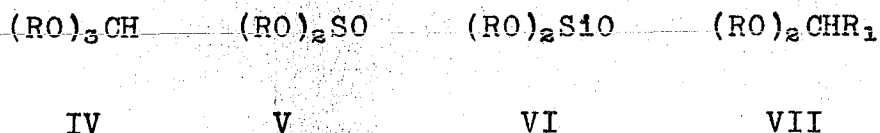


III

The yields reported vary according to the substituent groups, however no set pattern can be observed.

The carbonyl-carbon to oxygen linkage is the bond that is broken on hydrolysis of acetals as postulated by Hermans (1924). The alcoholate radical would be formed in accordance with this hypothesis and should exist in suitable media. Reagents that are known to exchange the

alcoholate radical are the orthoformic esters (IV), the sulfurous esters (V), the orthosilicic esters (VI), and the acetals (VII).



The orthoformic esters are prepared by adding sodium to a mixture of the alcohol and chloroform (Post 1940). The yields produced are approximately 40%. The acetal is obtained from the orthoformic ester in almost theoretical yield. The orthoformic ester is useful for preparing acetals of intermediates but it is not economical for starting compounds.



## VIII

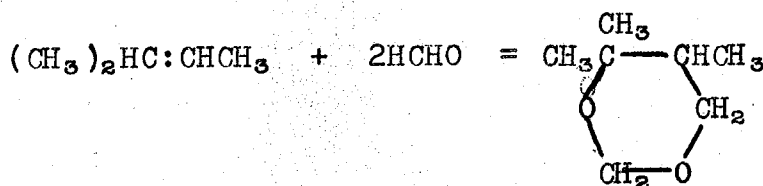
The sulfurous ester is produced by adding sulfonyl chloride to an alcohol (Voss and Banake 1931). This reagent, while an efficient alkylating agent, polymerizes unsaturated aldehydes. Sulfurous esters decompose in the presence of aldehydes and ketones and a catalyst of dry hydrogen chloride to produce acetals or ketals.



## IX

The alkoxy group of an acetal can be exchanged for that of an alcohol in the presence of an acid catalyst and in an alcoholic medium (Sussmann 1943). The exchange is brought rapidly to the point of equilibrium by heating the mixture. The alcohol of a low boiling acetal is replaced almost completely by a high boiling alcohol if the low boiling alcohol is distilled from the mixture.

Cyclic acetals are formed by the treatment of formaldehyde with a mono-olefinic hydrocarbon in the presence of catalysts such as zinc chloride, hydrochloric acid, sulfuric acid, and others (Fritzky 1944). The reaction extends the carbon chain and forms a 1,3-dioxane ring.



## X

Acetals of acetaldehyde are formed upon the reaction of acetylene with an alcohol in the presence of mercuric oxide-boron trifluoride catalyst (Hinton and Nieuwland 1930). This method is used commercially and is the subject of numerous patents.

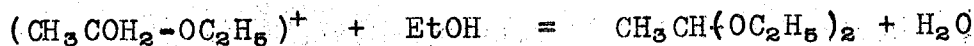
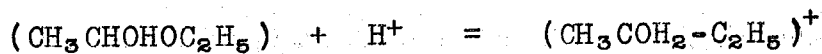
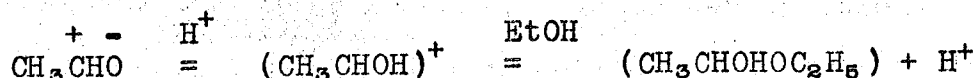
Vinyl ethers and an alcohol in the presence of an acid catalyst react exothermically to produce acetals (Farbenindustrie 1930). The vinyl ethers are formed from acetylene and an alcohol by use of an alkaline catalyst. Unsymmetrical acetals can be produced by this procedure. The vinyl ether synthesis does not differ extensively from the synthesis employing sodium alcoholate and the alpha chloroether.

Alkane oxides react vigorously with aldehydes in the presence of a trace of stannic chloride, (Bersin and Willfang 1937). The resulting product is a cyclic acetal. Epichlorohydrin reacts so vigorously that high dilution and a low temperature are necessary. Unstable aldehydes polymerize in the presence of the catalyst used in this reaction.

The behavior of alcohols and aldehydes in forming acetals, and the behavior of acetals themselves can be related to postulated mechanisms of reaction and to the structure of the reacting material.

The formation of acetals is a reversible process and is catalyzed by acids and certain salts. An intermediate in the process is thought to be a hemiacetal (Day 1950). Skrabal (1921) postulates that the formation

of the hemiacetal is the rate-determining step, and that the further reaction of the hemiacetal to form an acetal is rapid, the existence of the hemiacetal being transient, only. There are few cases in which the hemiacetal is known. The hydrolysis is thought to originate in the formation of an oxonium ion (Day 1950).



#### XI

The above mechanism is further verified by the observation that acetals are stable in base but hydrogen ion will readily catalyze the hydrolysis.

Adams and Adkins (1925) have made an extensive survey of inorganic salts as catalysts for acetal formation; many were found applicable, and some were inactive. Calcium chloride and ferric chloride were found to be especially good. The inorganic salts are objectionable in that they are known to catalyze the condensation of sensitive aldehydes (Bersin and Willfang 1937). It is believed that the

acetates of hydroxy-benzaldehydes will decompose in the presence of the active inorganic salts. Benzenesulfonic acid and p-toluenesulfonic acid have been used in many instances as catalysts for acetal formation. The experimental section compares the sulfonic acids to dry hydrogen chloride.

The affinity of aldehydes to form acetals is dependent upon their structure (Dunbar and Adams 1924). Substituents on the formyl group offer two types of influence, a steric effect and an alteration of the electronic configuration. Evidence for this is offered in Table I from the work of Hartung and Adkins (1927), and in Table II by Dunbar and Adkins (1934).

It may be tentatively concluded from the evidence cited in Table I that the beta substituents of negative character are the most active while the long chain is only slightly more active than the hydrogen. The di-methyl and beta hydroxy and beta unsaturation have a deactivating influence. The following paragraphs cite more recent work which should further explain the influence of substituent groups.



TABLE I  
 COMPARISON OF EQUILIBRIUM STATES OF  
 BETA SUBSTITUTED ACETALDEHYDES AND  
 THEIR RESPECTIVE ETHYL ACETALS

(Hartung & Adkins 1927)

Beta Substituent	Equilibrium Constant	Beta Substituent	Equilibrium Constant
NH <sub>2</sub> Cl	.134	CH <sub>3</sub> O <sub>2</sub>	.035
Br	.112	CH <sub>2</sub> Cl	.029
CN	.107	HO	.020
C <sub>5</sub> H <sub>11</sub>	.097	CH <sub>2</sub> :	.045
CH <sub>3</sub>	.078	Benz- Aldehyde	.0016
NHCl	.077	C <sub>6</sub> H <sub>5</sub> C:	.00089
H	.074	CH <sub>3</sub> CH:	.0006
C <sub>2</sub> H <sub>5</sub>	.069		

Table II gives the percent conversion obtained by using five parts alcohol to one part aldehyde. The results were determined by a titration method similar to the one described in the experimental section.

The figures for acetaldehyde, dimethylacetaldehyde and trimethylacetaldehyde show a progressive lowering of the extent of conversion to acetals. There exists evidence that the branched chain lowers affinity for acetal formation.

Cyclopentylaldehyde is rather similar to trimethylacetaldehyde in its affinity for acetal formation; however, it bears a closer resemblance to dimethylacetaldehyde. It is more nearly like benzaldehyde in acetal formation despite the difference in the degree of saturation.

The relationship of hexahydrobenzaldehyde to benzaldehyde in acetal formation is much the same as tetrahydrofurfural and furfural. The saturated compounds have a much higher affinity for acetal formation than the unsaturated; in fact, they are similar to straight chain compounds of similar carbon content.

It is noted that the two multiplanar cyclic aldehydes, hexahydrobenzaldehyde and tetrahydrofurfural, despite branching at the alpha carbon atom, have a high affinity for acetal formation. The monoplanar

TABLE II  
 THE CONVERSION OF SELECTED ALCOHOLS  
 AND ALDEHYDES OF ACETALS  
 (Dunbar & Adkins 1934)

Aldehyde Used	Alcohol Used			
	Ethanol	Cyclohexyl Carbinol	Iso Propyl	Octanol-2
Acetaldehyde	71%	56%	43%	46%
Dimethyl Acetaldehyde	56%	42%	23%	--
Trimethyl Acetaldehyde	45%	42%	11%	26%
Cyclopentyl- Acetaldehyde	39%	41%	13%	50%
Benzaldehyde	78%	35%	14%	49%
Hexahydro Benzaldehyde	31%	87%	29%	74%
Furfural	79%	--	17%	11%
Tetrahydro Furfural	--	--	49%	90%

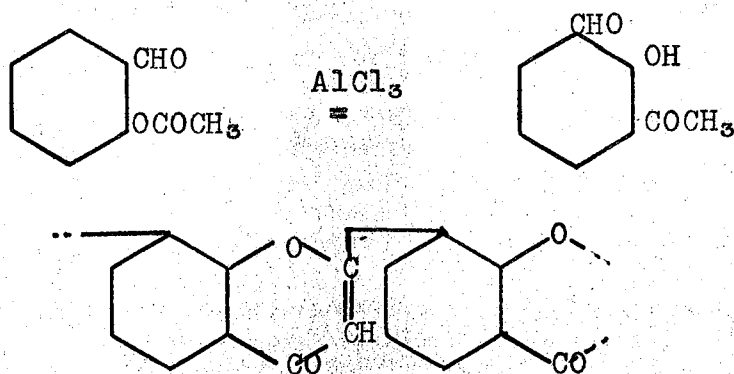
cyclopentylaldehyde has a low affinity value which is similar to two unsaturated monoplanar cyclic aldehydes, benzaldehyde and furfural.

This further indicates that the steric effect exerts a dominant force upon the affinity and it seems to have a positive effect in case of the multiplanar cyclic aldehydes.

The effect of ring substituted groups on the affinity of benzaldehyde to form acetals is in general positive, that is to say, the acetals form more readily. Extensive data are not available but Adams and Adkins (1924) reports the acetal of m-nitrobenzaldehyde in 15% higher yield than the same acetal of benzaldehyde. Other experimenters report high yields for the acetals of the ortho and para isomers of nitrobenzaldehyde (Salmi and Kyrki 1946). These cases are not on a comparable basis. There is a need for investigation in this field.

## LIGNIN INTERMEDIATES

Acetoxybenzaldehyde will produce a lignin like material when treated with aluminum chloride. This material was obtained by Russell (1946) as a result of a Fries rearrangement on the monoacetate of salicylaldehyde. Russell postulated that the reaction proceeds in a manner indicated by XII. The intermediate or monomer is a 2-hydroxy, 3-formylacetophenone, which will undergo an aldol condensation resulting in the indicated polymer. The experimental results of Russell show the polymer to be about 10% soluble in bisulfite solution which indicates free aldehyde groups available.



XII

This property is lost upon standing several days.

The above reaction is not established beyond reasonable doubt without the isolation of the intermediate

compound. It is hoped that masking the aldehyde by forming an acetal will provide enough stability during the Fries rearrangement to isolate and characterize the monomer.

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EXPERIMENTAL SECTION  
PREPARATION OF ACETALS

The preparation of acetals for this and the following experiments was achieved by condensing an aldehyde with an alcohol. The reaction was facilitated by the use of a catalyst and by removal of water.

The special equipment used in the reaction was a fractionating column and a vacuum distillation apparatus.

The fractionating column (see Figure 1) was designed to collect the distillate and allow the heavier portion of any two-phase system to be drawn off while the lighter portion was returned to the fractionating column as refluxate. It was discovered that the collection bulb required cooling if efficient phase separation was to be obtained. The lower layer was drawn off at convenient intervals and measured.

The vacuum system used was a standard type as described by Morton (1938) with the condenser altered to collect fractions without opening the system. The pump used was a Nelson type capable of evacuating to 3 mm.

The first step in the synthesis was to place the desired amounts of aldehyde and alcohol in a flask fitted with a thermometer and the fractionating column described above. The benzene or other entrant was added and the

17a

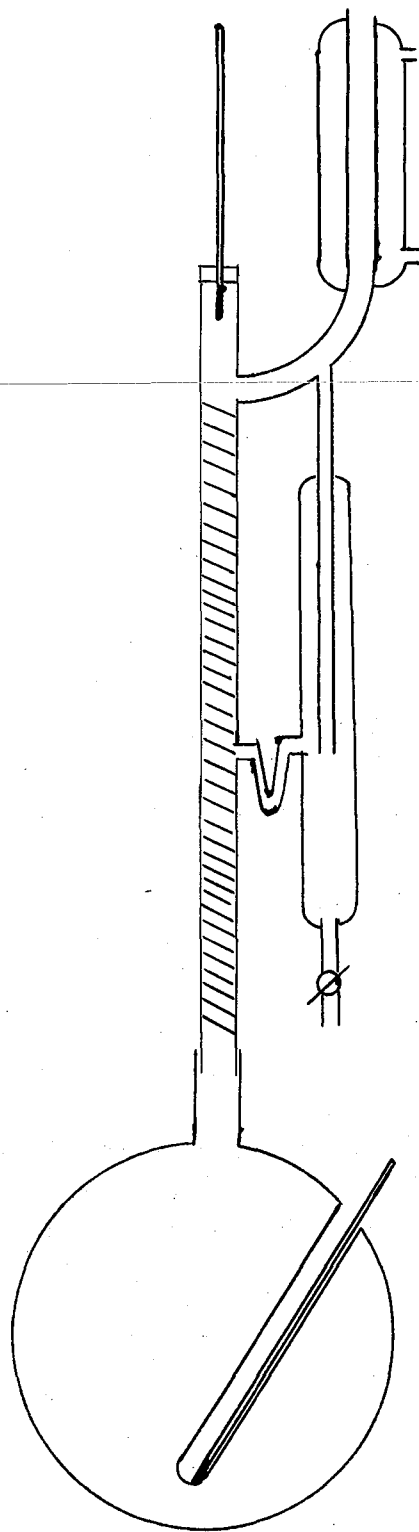


Figure 1



flask heated with an oil bath. The first distillate came over at  $69.3^{\circ}$  and was in two phases. The water phase (lower) was drawn off into a graduated cylinder at 15 minute intervals. The distilling temperature began to rise after about 50% of the theoretical amount of water was collected and eventually the distillate no longer separated into two phases, but a cloudy portion separated and was collected, dried over anhydrous magnesium sulfate, and returned through the reflux condenser. The drying was continued until the cloudiness of the distillate disappeared and the temperature was at  $79^{\circ}$ . The distillate was collected and set aside until the  $117^{\circ}$  fraction had partially distilled. The distillation was stopped and the material remaining in the distilling flask was washed with 20% sodium bisulfite and with water three times. The resulting organic layer was dried over anhydrous sodium carbonate. The liquid was decanted from the sodium carbonate and distilled under vacuum. The following distillation temperatures were observed:

120-5 at 4 mm.      142-3 at 10 mm.      152-4 at 18 mm.

Butyl alcohol is by no means an ideal alcohol for this method; the yields realized here can be equaled or

improved with other alcohols. The same is true for benzaldehyde. The above method of preparation seems to be simple and economical in that expensive alkylating agents are not used, and is mild in the treatment of sensitive aldehydes.

Complete removal of the water as a separate phase was not achieved in the case of butyl acetal. The fraction distilling from 69.3 to 79 degrees was a mixture water and benzene binary and benzene and butyl alcohol binary mixtures. There is no known ternary mixture of benzene, water and butanol (Horsley 1947). Reasonably improved yields were obtained on preliminary experiments by using magnesium sulfate as a drying agent.

The washing with sodium bisulfite removed free aldehyde but did not alter the acetal. The acid catalyst was also removed in this wash. Subsequent washings removed much of the butyl alcohol and any traces of salts. The use of sodium carbonate gives better yields than calcium chloride as a drying agent.

The preparation of acetals of glycols, ethylene and trimethylene, were prepared with about 90% removal of the water in four hours.

The butyl acetal of vanillin acetate was prepared

TABLE III  
VARIATION OF THE MOLAR RATIO OF  
CONSTITUENTS IN THE SYNTHESIS  
OF BUTYL ACETAL OF BENZALDEHYDE

Experiment	Moles of Alcohol	Moles of Aldehyde	Yield	Moles of Water Collected
1	1	1	66%*	--
2	2	1	51%	.5
3	3	1	73%	.75
4	4	1	71%	.60

\*Yield based on one-half mole of aldehyde.

by the azeotropic method. The method of synthesis was in general, the same as that of the benzaldehyde acetal, the purification steps were altered some.

There were placed in the flask, 21 grams of vanillin acetate and 35 grams of butanol (3 molar parts). Five hundred milliliters of benzene and 0.1 gram of benzene sulfonic acid was added and the flask was attached to the fractionating column. The procedure previously described was followed until 75% of the water was collected (1.8 grams). The mixture was extracted with 20% sodium bisulfite, with water once, with 10% sodium hydroxide and three times with water. The upper layer was collected and dried over anhydrous sodium carbonate. The benzene layer was distilled at standard pressure, using an oil bath at 120° for heating, followed by vacuum, and then distillation at 162-3° at 3 mm.; the yield being 25%.

Free aldehyde or phenolic hydroxy groups were found to be absent upon qualitative examination of the product. The resulting oil produces vanillin and butanol when boiled with mineral acid. Inconsistent results were obtained when a saponification number determination was attempted.

## THE COMPARISON OF SULFONIC ACIDS TO HYDROGEN CHLORIDE AS CATALYSTS

The benzenesulfonic acids were compared to hydrogen chloride by placing benzaldehyde, n-butanol, and a catalyst in a flask, and after a period of time, titrating the benzaldehyde using the method of Sigga and Maxcy (1947) with slight modifications. The end point can be determined in two ways, either at previously determined optimum pH values or a more accurate method of graphing the change in volume against the change in pH and selecting the point of inflection. The results in Table IV were determined by the former method.

The butanol used in the experiments was purified by fractionating in a 50 centimeter fractionating column. A small amount of benzene was added to remove any water. The fraction used was collected at  $117^{\circ}$  to  $117.5^{\circ}$  (corrected). The benzaldehyde was purified by washing it with sodium carbonate solution and distilling it from a standard distilling flask. The fraction collected at  $178-179.5$  was used.

The first step in the determination of benzaldehyde was to place 10 ml. of butanol in a 250 ml. ground glass stoppered Florence flask. If a catalyst was to be used, it was added, and then butanol was added to make up 10 ml.

The benzaldehyde was then pipetted into the flask (2 ml.) and the flask was placed in a water bath and shaken for five minutes, after which it was allowed to stand undisturbed. (This is a compromise between shaking the flask the full time thus allowing excessive oxidation to take place, or risking poor temperature distribution within the sample.) At the desired time, 100 ml. of 1. molar sodium sulfite was added to the flask from a graduated cylinder, quenching the reaction. Twenty five ml. of standard sulfuric acid, approximately 1 N., was pipetted into the flask and the flask was shaken by hand for five minutes. At this point, the mixture was clear except for the acetal present. The resultant mixture is next poured into a 600 ml. beaker equipped with a stirrer and pH meter electrodes and titrated with standard 1. normal base to a pH of 8.9.

Table IV is a result of experiments done in an attempt to compare the sulfonic acids to hydrogen chloride. All catalysts except dichloroacetic acid show about equal activity. The sulfonic acids were chosen in preference to hydrogen chloride because they produce less decomposition products, they are milder acids, and are easier to handle. The dichloroacetic acid is not considered to be useless as it shows mild activity.

TABLE IV  
THE YIELD OF BUTYL ACETAL OF  
BENZALDEHYDE PRODUCED BY VARIOUS CATALYSTS

Catalyst Used:	Milli- equivalents	Minutes of Reaction Time				
		2	15	30	60	540
No Catalyst	.013 . . . . .					17%
Dry HCl	1.3 . . . . .					42%
	.013 . . . . .					40%
Dichloro- acetic Acid	1.3 . . . . .					30%
p-Toluene Sulfonic Acid	.013 . . . . .	21%			39%	43%
Benzene Sulfonic Acid	1.3 . . . . .					44%
	.13 . . . . .			40%		41%
	.013 . . . . .	39%	40%	40%		

## THE STABILITY OF ACETALS UNDER ALKYLATING CONDITIONS

The intermediates formed when an aromatic aldehyde undergoes a ring acetylation was postulated by Russell (1947) to be a formal-acetophone. An attempt to show whether or not there is a possibility of protecting the aldehyde group by acetal formation was made in the following experiments.

All of the reactions cited in Table V were done in the presence of aluminum chloride catalyst and acetic anhydride was in most cases the alkylating agent.

The equipment used was a one liter three neck flask, a stirring motor, and a small propeller. Several speeds were tried but the high speed motor (2000 RPM) was found to be the most satisfactory when used with a small glass propeller.

The materials used were reagent grade and the acetals were prepared by the method described previously.

The first step in the experiment was to weigh the materials and place two components in the three neck flask which had been fitted with a reflux condenser and a stirrer. The third component was added over a 30 minute period in order not to induce excessive heating. The flask was cooled in a water bath except for the reactions



run at refluxing conditions. Whenever the acetic anhydride was added last, it was dropped from a separatory funnel through one of the necks. The aluminum chloride, when added last, was added in small portions through a small neck. A considerable amount of hydrogen chloride was given off and absorbed in sodium hydroxide solution. The reaction was stirred for 30 minutes after the addition was completed. The reaction mixture was poured into an ice and HCl mixture which had a layer of ether on top. Upon completion of the hydrolysis, the entire amount of material was poured into a separatory funnel and the ether layer recovered. The water phase was extracted once with ether and discarded. The entire ethereal fraction was washed once with dilute sodium hydroxide and twice with water and then dried over anhydrous sodium carbonate. The ethereal fraction was transferred to a distilling flask and the low boiling solvents were distilled over. The flask was heated by an oil bath at  $120^{\circ}$ . The residual material was distilled from a Claissen flask at from 8 to 3 mm.

Table V shows the results of the experiments done to test the stability of acetals in the presence of aluminum chloride and acetic anhydride. The molar ratios

of the reagents used were not considered important enough to include except in the cases of 2, 5 and 7. The molar ratio of aluminum chloride to the acetal in the case of 2 was 1.3, 5 was 3.0, and 7 was 2.5.

The reaction products were not characterized but they exhibit some interesting properties. They can be divided into three fractions, one distilling at  $124^{\circ}$  at 8 mm., another distilling at  $170^{\circ}$ - $220^{\circ}$  at 3 mm., and a third fraction, a solid when cool.

The low boiling fraction ( $124^{\circ}$  at 8 mm.) shows a positive ketone test but there appears to be no aldehyde present. The material is insoluble in bisulfite solution and no precipitate is formed with alcoholic sodium bisulfite. Schiff's reagent gives a negative aldehyde test. A precipitate is formed with 2,4-dinitrophenylhydrazine.

The high boiling liquid ( $175$ - $220^{\circ}$  at 3 mm.) gave no reaction to show free aldehyde or ketone but upon boiling with dilute HCl, a positive aldehyde test was given. This tends to show that there could be some acetals present.

TABLE V  
THE PRODUCTS OF FRIEDEL  
CRAFTS REACTION ON ACETALS

Aromatic Component	Reaction Conditions			Product	
	Temp.	Time	Solvent	Boiling Range	Yield
(1) 2-Phenyl dioxolane	25°	1 hr.	CS <sub>2</sub> 200 ml.	-	tars & solid
Butyl acetal of benzaldehyde	25°	1 hr.	CS <sub>2</sub> 100 ml.	b <sub>8</sub> 70 b <sub>6</sub> 115-25	butyl acetate 60 gms. unidentified water insol. ether insol. solid
Benzal chloride	at reflux	.5 hr.	CS <sub>2</sub> 200 ml.	-	benzaldehyde 27 gms. unidentified
2-Phenyl dioxolane	25°	1 hr.	CS <sub>2</sub> 200 ml.	b <sub>13</sub> 65 b <sub>13</sub> 135	butyl acetate 30 gms. 17 gms. 10 gms.
Butyl * acetal of benzaldehyde	at reflux	.5 hr.	CS <sub>2</sub> 200 ml.	b <sub>8</sub> 70 b <sub>8</sub> 124 b <sub>3</sub> 175-220	ether insol. solid and tars
Butyl (2)* acetal of benzaldehyde	25°	1 hr.	CS <sub>2</sub> 100 ml.	-	16 gms. 7 gms.
Butyl * acetal of benzaldehyde	at reflux	1 hr.	CS <sub>2</sub> 200 ml.	b <sub>4</sub> 120-5 b <sub>4</sub> 170-5	

(1) The ethylene glycol acetal of benzaldehyde.

(2) Acetyl chloride was used here in place of acetic anhydride.

\* Al Cl<sub>3</sub> added last.

## SUMMARY

Acetals can be obtained in high yield by removing water of reaction by azeotropic distillation. This is done with a minimum of effort using a modified fractionating column which returns the upper layer as refluxate. Neither expensive nor highly reactive reagents are used.

Benzenesulfonic acid and p-toluenesulfonic acid have been found to be approximately equal to dry hydrogen chloride in activity for acetal formation. A trace of the acid is sufficient for effective catalysts.

Acetals show definite possibilities of remaining stable during a Friedel-Crafts reaction. There was not sufficient time to characterize the products obtained.

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