

NEW CONDENSATIONS OF FORMALDEHYDE

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By

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A. COPOLYMERIZATION OF STYRENE AND FORMALDEHYDE

INTRODUCTION AND HISTORICAL

Styrene and formaldehyde are known to polymerize separately. The object of this study was to cause the copolymerization of styrene and formaldehyde to yield a product with the structure $(C_6H_5CH-CH_2-O-CH_2)_x$.

No reference to the copolymerization of styrene and formaldehyde or any copolymerization of an olefin with formaldehyde could be found in the literature.

STRATHMORE PARCHMENT

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EXPERIMENTAL

The attempted copolymerization of styrene and formaldehyde was carried out in an emulsion prepared as follows:

- 250 ml. distilled water
- 15 g. Aerosol OT
- 50 ml. 35% formalin solution
- 50 ml. distilled styrene
- 0.5 g. benzoyl peroxide

The Aerosol OT was added to the water, then the formalin solution and finally the styrene containing the benzoyl peroxide. The emulsified reaction mixture was stirred continuously for six hours while the temperature was held at 85-90°C. A similar mixture was prepared except that the formalin solution was excluded. This should yield polystyrene under the same conditions. The products obtained from both runs after addition of the emulsion to a saturated solution of sodium chloride were colorless and had identical softening points. Hence it is probable that copolymerization did not occur.

- 200 ml. distilled water
- 5 g. Aerosol OT
- 50 ml. distilled styrene
- 50 ml. 37% formalin solution
- 0.5 g. benzoyl peroxide
- 50 ml. conc. hydrochloric acid

The above mixture was prepared as before with the hydrochloric acid being added last. The mixture was heated at 80-85° for eight hours with stirring and then steam-distilled to remove all volatile materials. The water-insoluble residue was a light-brown, sticky mass. When this was washed with methanol, it became a powder. After washing with water and drying, the product was light-brown as

compared to the colorless styrene obtained in the previous run. A similar mixture was made except that the styrene and benzoyl peroxide were omitted. When this was subjected to the same treatment, no water-insoluble residue was obtained.

Since the copolymer should contain oxygen, the ferrox test for oxygenated compounds (1) was made. The test was inconclusive since only a very light color was noted. In order to test for the presence of a copolymer of the structure $(C_6H_5-CH-CH_2-CHOH)_x$, the dried solid was dissolved in thionyl chloride. Little reaction was noted. The addition of water to this solution caused a solid to precipitate. The solid gives only a slight Beilstein test for halogen (2) and therefore does not contain appreciable amounts of halogen. The suspected copolymer was refluxed with a dilute sulfuric acid solution. The mixture had a definite odor of formaldehyde and the physical appearance of the solid changed.

Reaction mixtures which included potassium hydroxide or stannic chloride failed to yield solid polymers of any sort.

DISCUSSION OF RESULTS

The attempted copolymerization of styrene and formaldehyde does not seem to occur under the given reaction conditions. The product obtained is probably a mixture of polystyrene and polymers of formaldehyde.

The characterization of such copolymers would be a difficult task. Moreover there is so much difference between the mechanisms of polymerization of formaldehyde (condensation-type) and styrene (addition-type) that a copolymerization is theoretically very improbable. Accordingly no further work on the project is advisable.

B. COPOLYMERIZATION OF ETHYLENE OXIDE AND FORMALDEHYDE

INTRODUCTION

Ethylene oxide may be polymerized to polyethylene oxide in the presence of dilute aqueous alkali as catalyst at room temperature (1). The degree of polymerization increases as the ratio of water/ethylene oxide decreases.

Formaldehyde may also be polymerized by addition of alkali to an aqueous solution of formaldehyde (2).

Since ethylene oxide and formaldehyde will thus polymerize individually in aqueous alkaline solutions, it seemed possible that a copolymerization could be effected and a product of the formula $(-O-CH_2-O-CH_2-CH_2)_x$ -- a 1,3-dioxolane-type polymer -- obtained. No mention of such a base-catalyzed copolymerization could be found in the literature.

HISTORICAL

1,3-Dioxolane is the cyclic formal of ethylene glycol. It may be prepared by heating ethylene glycol with paraformaldehyde (3) or formaldehyde solutions (4) with an acidic catalyst:



By causing ethylene glycol to react with formaldehyde in the presence of sulfuric acid under reflux conditions, a polymer of the general formula $(\text{HOCH}_2\text{CH}_2) - (\text{OCH}_2\text{OCH}_2\text{CH}_2)_x(\text{OCH}_2\text{OCH}_2\text{CH}_2\text{OH})$, where x is one or two, was produced (5). The viscous liquid polymer was removed from the reaction mixture by distillation under reduced pressure after the acid catalyst was neutralized.

1,3-Dioxolane may also be prepared by the reaction of ethylene oxide with formaldehyde in the presence of acidic catalysts, particularly boron trifluoride or its hydrates (6). Polymers of dioxolane are prepared by continuing the reaction beyond the formation of dioxolane under dehydrating conditions. The polymer is thought to have the structure $(-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-)_x$ (7), although the structure is not completely known and cross-linkages may be present. If x is less than 10, the polymer is a mobile to viscous liquid; if x is greater than 10, it is a solid; if the molecular weight is 10,000 or more, the polymers are solids that can be cold-drawn. Those of molecular weight 1,000 - 200,000 deteriorate when exposed to air and lose their elasticity and high tensile strength quite rapidly. The addition of a small amount of an antioxidant such as an amino or a hydroxy compound to the mixture in the final stage of polymerization stabilizes the solid polymer against oxidation (8).

EXPERIMENTAL

The concentrated methanol-free formaldehyde solutions used herein were obtained by concentration of 30% formalin solutions (from Tallant) via vacuum distillation.

The following reaction mixture was prepared:

20.1 g. ethylene oxide (0.46 mole)

9.3 g. 43% aqueous formaldehyde (0.13 mole)

0.1 g. potassium hydroxide

The ethylene oxide was condensed and collected by passing the gas into a container held at 0°C. The formalin solution was cooled and slowly added to the ethylene oxide with cooling. The potassium hydroxide was then added and the container -- a bottle -- sealed. The reaction mixture was held at room temperature for three days. At this point the mixture was a light-brown, viscous liquid. The reaction mixture was exactly neutralized and sodium sulfite solution was added to a small sample of it. No base was generated as determined with phenolphthalein indicator. Now the addition of a sodium sulfite solution to formaldehyde is known to generate sodium hydroxide (9) and it was found by experiment that ethylene oxide also yields sodium hydroxide upon addition of such a sulfite solution. Thus it was ascertained that no free ethylene oxide or formaldehyde existed in the reaction mixture. The neutralized mixture was distilled at atmospheric pressure; only water came over up to 100°C. Since 1,3-dioxolane boils at 76°C. (10), it was not present, at least not as the monomer. The residue (boiling point above 100°C.) was soluble in water and in 95% ethanol but insoluble in ethyl ether and in benzene.

Trial of the reaction was repeated with the following mixture, prepared as before:

90 g. ethylene oxide (2.04 moles)

80 g. 33% aqueous formaldehyde (0.88 moles)

0.75 g. potassium hydroxide

The container was sealed and the mixture allowed to remain at room temperature. After two days, a sample of the viscous liquid was added to a solution of 2,4-dinitrophenylhydrazine in 2N hydrochloric acid (11). A bright-yellow precipitate melting at 163-165° formed immediately; this melting point indicates (11) that free formaldehyde was present. After six days, another sample was withdrawn and added to the 2,4-dinitrophenylhydrazine reagent. The solution remained clear for 2-3 minutes but thereafter cloudiness and a yellow precipitate appeared. This solid melted at 165°. The mixture was now a light-yellow-brown viscous liquid without appreciable odor.

The liquid was distilled at 10 mm. Hg. pressure until the boiling point of the distillate reached 100°. The residue did not give an immediate test for aldehydes with fuchsin-aldehyde reagent (11) or with 2,4-dinitrophenylhydrazine but did so after a few minutes. A solution of the residue in dilute hydrochloric acid gave an immediate test for aldehyde with the same reagents.

Measurement of the depression of the freezing point of water was used to find the apparent molecular weight of the residue. The experimental value was 160, which corresponds to an average degree of polymerization of 2.4 if $\text{-(O-CH}_2\text{-O-CH}_2\text{-CH}_2\text{)-}$ is the repeating unit.

Attempts to increase the degree of polymerization by heating the residue to 110° and to 250° for a few hours in a sealed tube yielded a black liquid in each case.

The use of greater amounts of alkali as catalyst led to violent explosions due to uncontrollably rapid reaction.

Polyethylene oxide was prepared from the following reagents:

90 g. ethylene oxide (2.04 moles)

25 g. distilled water (1.4 moles)

0.7 g. potassium hydroxide

Liquid ethylene oxide was collected as before, the water and potassium hydroxide were carefully added with cooling, and the container was sealed. After standing at room temperature for a few days, the mixture was a yellow viscous liquid. Gaseous formaldehyde generated by heating paraformaldehyde was bubbled into the mixture. The formaldehyde was absorbed in appreciable amounts. The container was resealed and held at 40° for three weeks. The mixture was homogeneous at this point but gave a positive test for aldehyde with the 2,4-dinitrophenylhydrazine reagent, indicating that the formaldehyde had not completely polymerized.

The use of barium hydroxide as catalyst in the attempted copolymerization led to solutions which contained unreacted formaldehyde and ethylene oxide.

DISCUSSION

Ethylene oxide reacts with formaldehyde in the presence of dilute aqueous alkali to yield a viscous liquid which seems to be a copolymer. The liquid is very soluble in water and in 95% ethyl alcohol. Since alkali-precipitated para-formaldehyde is quite insoluble in these solvents, it is believed that the reaction is not a self-polymerization of the ethylene oxide and the formaldehyde separately. Formaldehyde did not polymerize completely in a solution of polyethylene oxide in dilute alkali which further indicates that the formaldehyde reacts with the unpolymersized ethylene oxide. Attempts to increase the degree of polymerization by increasing the amounts of alkali catalyst or heating the reaction mixture failed.

The structure of the copolymer has not been determined but the slow hydrolysis in dilute acid solution indicates an acetal structure, possibly $\text{-(O-CH}_2\text{-O-CH}_2\text{-CH}_2\text{)-}$.

The copolymer could possibly be polymerized further by a process in which all water would be removed from the completed reaction mixture followed by acidification and heat treatment. Further polymerization is necessary to make the product useful.

The difficulties encountered in characterization of the polymer and the inability to produce truly high polymers caused the discontinuance of experimental work on the ethylene oxide-formaldehyde reaction.

C. ADDITION OF FORMALDEHYDE INTO BUTADIENE

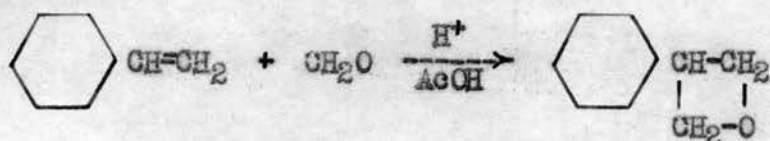
INTRODUCTION

The reaction between mono-olefins and formaldehyde in the presence of acid catalysts to yield 1,3-glycols and derivatives thereof is well known.

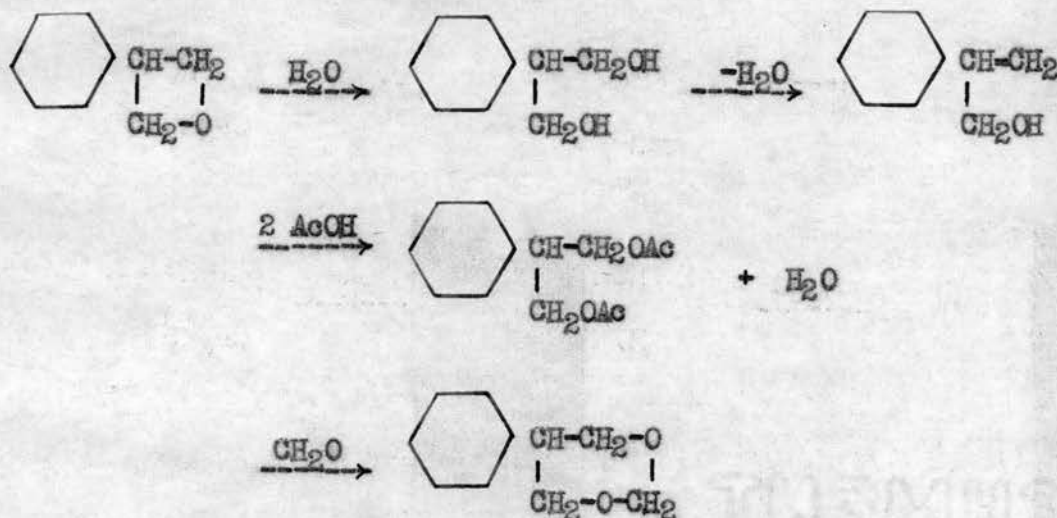
1,3-Butadiene and other diolefins would be expected to react with formaldehyde under similar conditions. The object of this investigation was to study such a reaction and its products.

HISTORICAL

The pioneer work on the addition of an aldehyde into the double bond of an unsaturated substance was made by Prins in 1919 (1,2,3). He found that formaldehyde adds at the double bond of such compounds as styrene, anethole, eugenol and some terpenes in the presence of glacial acetic acid with concentrated sulfuric acid catalyst to yield 1,3-glycols, formals, esters and unsaturated primary alcohols. He postulated the initial step in the reaction to be the addition of formaldehyde to the double bond to yield a four-membered ring, as illustrated in the case of styrene:

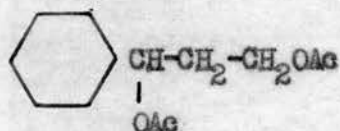


The ring may then open to absorb another molecule:



Fourneau, Benoit and Firmenich (4) caused styrene to react with formaldehyde in the presence of glacial acetic acid and concentrated sulfuric acid.

These workers proved the isolated diester to have the structure:



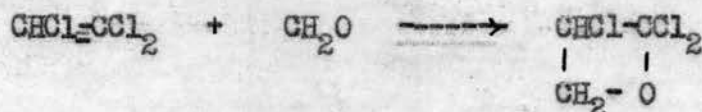
The ester was hydrolyzed to a 1,3-glycol:



The mechanism proposed by Prins is now considered to be extremely unlikely but it served as a foundation for subsequent investigations.

The initial industrial application of the reaction appeared in a French patent (5) (1930) in which the preparation of 1,3-glycols by reaction of olefins with formaldehyde in the presence of acetic and sulfuric acids followed by hydrolysis is described.

Prins (6) extended the reaction to chlorinated ethylenes. He postulated and experimentally verified the method of the addition of formaldehyde into substituted ethylenes. The carbon atom of the C=C group which contains the most electronegative substituents becomes linked to the oxygen atom of the formaldehyde:



Hydrolysis of the reaction product yields an acid:



This mechanism is untenable but it did serve to predict the exact products of the reaction. An interesting sequel to this particular addition is the dehydration of the product of hydrolysis to yield α -chloroacrylic acid.

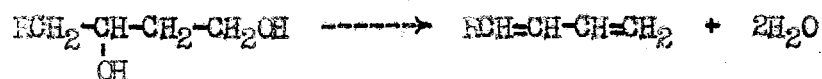
Matti (7) caused cyclohexene to react with formaldehyde in the presence of glacial acetic acid and concentrated sulfuric acid and isolated 1-methylol-2-cyclohexanol as the main product by hydrolysis of the mixture of mono- and diacetate esters produced. In addition, Matti found other materials which were not identified.

For the next ten years, published work on the addition of formaldehyde to double bonds was confined to industrial applications and recorded only in patents. The greatest number of patents was obtained on the preparation of 1,3-glycols and derivatives thereof such as meta-dioxanes, diolefins, chlorinated and unsaturated primary alcohols, and 1,3-dihalides.

The production of 1,3-glycols is described in a series of patents (9-16) dated from 1939-1947. The processes are essentially the same and may be represented by the equation:

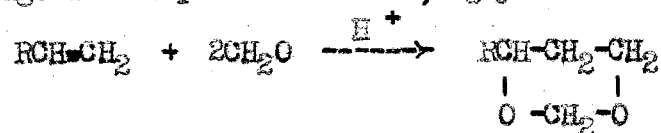


An olefinic hydrocarbon is made to combine with an aldehyde (usually formaldehyde) or aldehyde-yielding reagent (aqueous formalin, paraformaldehyde or methylal) in the presence of an acid catalyst such as hydrochloric acid, sulfuric acid, a metal halide, aqueous boron trifluoride, etc. The pressure and temperature vary but in general higher pressures and temperatures are required with the lower olefins. The glycols produced may be converted to diolefins (12, 17-20) by some method of complete dehydration:



In these processes, the 1,3-glycol is produced and the reaction mixture is passed over a dehydrating catalyst such as aluminum oxide (17,18) or through a dehydrating agent such as concentrated sulfuric acid (19,20) at high temperatures.

The production of formals and meta-dioxanes may be considered to be an intermediate stage in the production of 1,3-glycols:



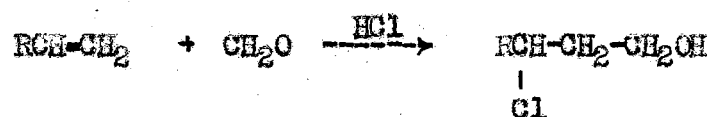
The starting materials are again an olefin, a source of an aldehyde and an acid

catalyst. As a rule, operating temperatures are lower and a non-reactive solvent may be used to increase solubility of the olefin in the reaction mixture.

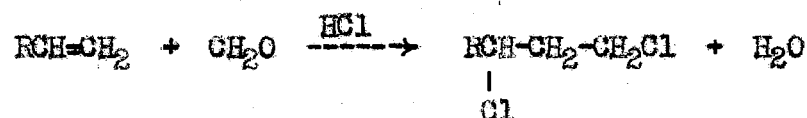
The use of highly unsymmetrical olefins such as trimethyl-ethylene, isobutylene, and diisobutylene as a source of the C=C group leads to the formation of unsaturated primary alcohols (32-37) under the usual reaction conditions:



Chlorinated alcohols (36-39) are produced by reaction of an olefin or an unsaturated alcohol with a source of formaldehyde and hydrochloric acid, usually at an elevated temperature and pressure:

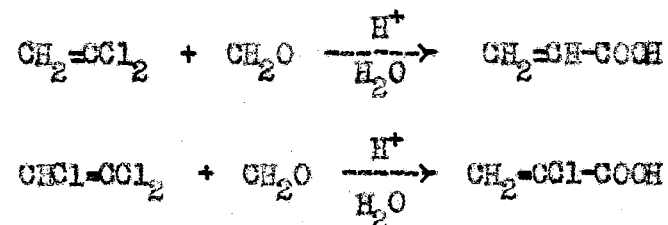


This process may be used to prepare 1,3-dihalides (40), even higher temperatures and pressures being required:



Terpene alcohols have been produced (41,42) by the use of terpenes as olefins together with a source of formaldehyde and an acid catalyst.

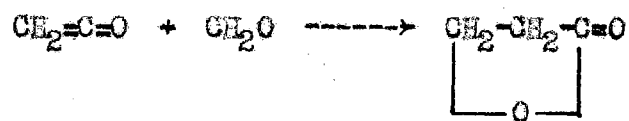
The addition reaction, as previously noted, may be used to produce acrylic and α -chloroacrylic acids (43-51):



The starting materials are di- and trichloroethylene, formaldehyde or a polymer

thereof and sulfuric acid. An alcohol may be added to the reaction mixture and the acrylic acid separated as its ester.

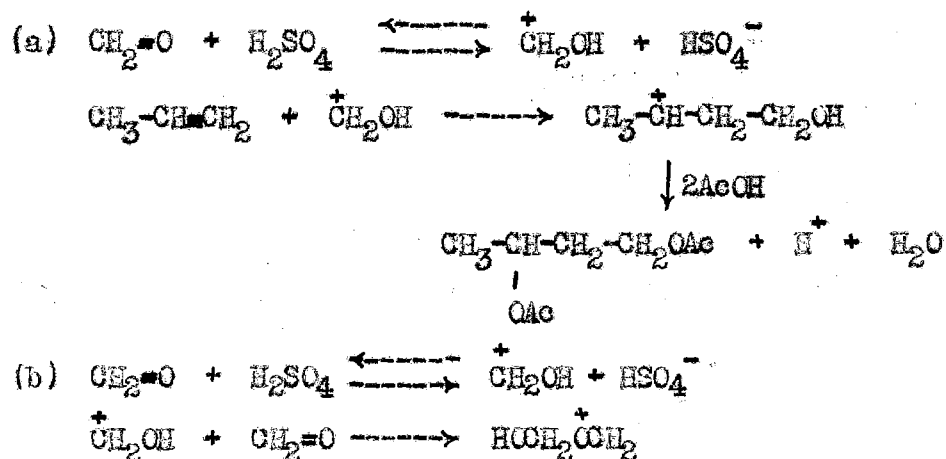
The addition of formaldehyde to the C=C group of ketene (52-54) in the presence of Friedel-Crafts catalysts yields β -lactones:

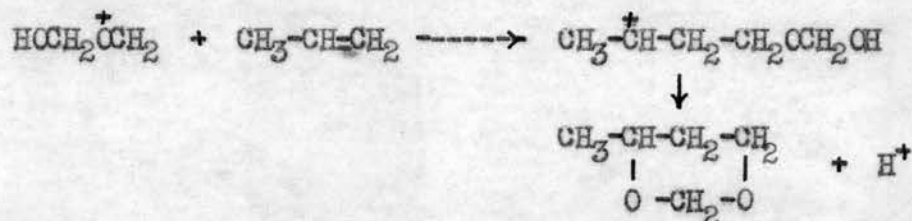


The industrial potentialities of the Prins reaction have stimulated research on the mechanism of the reaction. Baker (55) has investigated the reaction between propylene and formaldehyde (as paraformaldehyde) in 100% acetic acid using 100% sulfuric acid catalyst at 35°C. Increased yield is claimed by excluding all water from the reaction mixture. The main products isolated and characterized were:

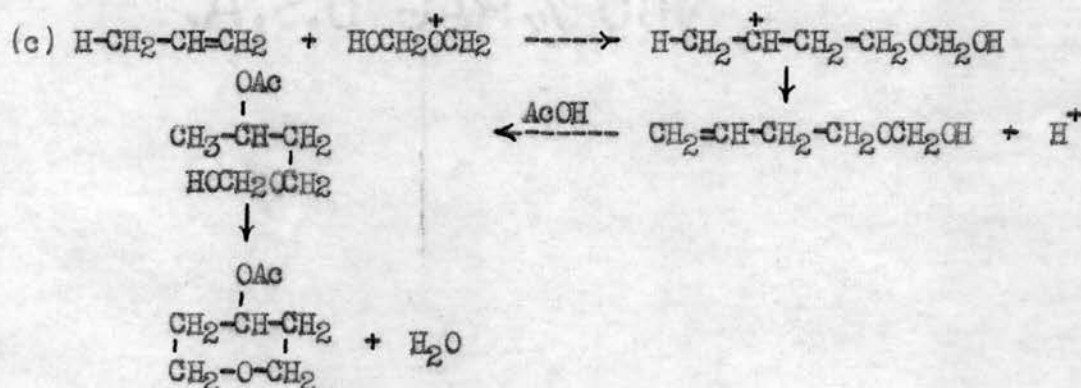
- (a) the diacetate of butane-1,3-diol (63%)
- (b) the cyclic formal of butane-1,3-diol (14%)
- (c) 4-acetoxytetrahydro- γ -pyran (23%)

Products (a) and (b) are believed to arise from an acid-catalyzed addition of formaldehyde into the double bond as follows:



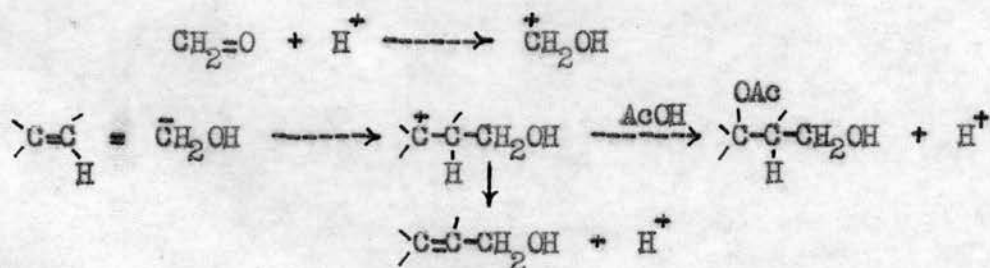


Baker contends that product (c) is formed by an entirely different mechanism: that of the direct reaction of the α -methylenic hydrogen activated by an adjacent olefinic linkage:



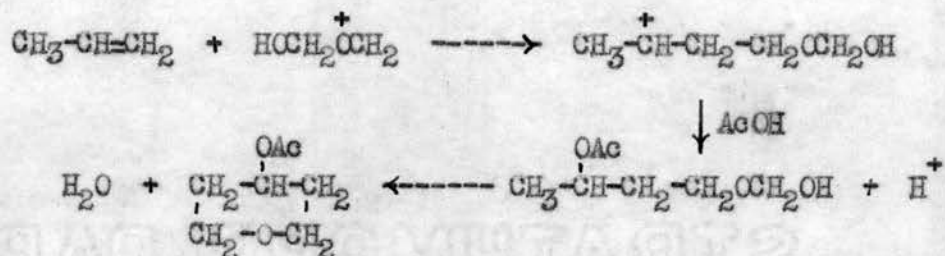
In addition to concentrated sulfuric acid, boron trifluoride was tested for catalytic action. Boron trifluoride in 100% acetic acid was found to be ineffective but it did increase the catalytic efficiency of lower concentrations of sulfuric acid.

In view of the difficulty in accounting for the catalytic effect of acids by such a mechanism, Price (56) has criticized the postulation of α -methylenic activity set forth by Baker. He claims that all observed reactions go through a common intermediate:

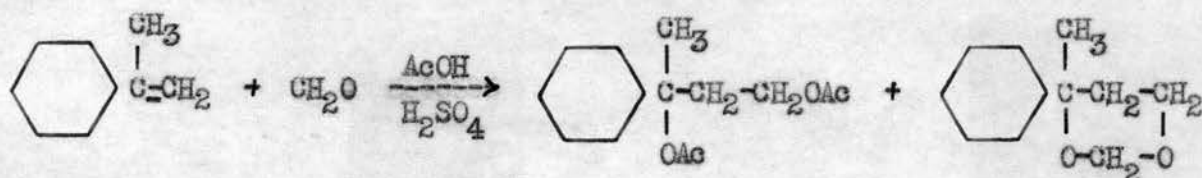


The 4-acetoxytetrahydro- γ -pyran found by Baker could be formed through such

an intermediate as:

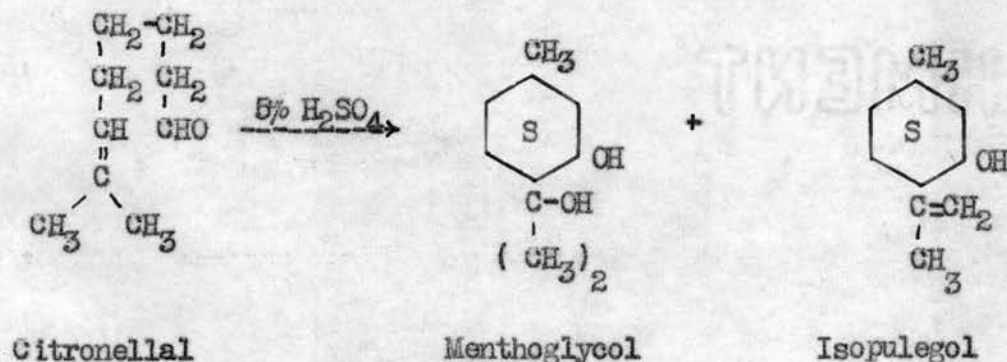


In a recently published work, Baker (57) used α -methylstyrene as the olefin in the Prins reaction. By combining this compound with paraformaldehyde in the presence of a mixture of 100% acetic acid-100% sulfuric acid, he obtained the formal of 3-phenylbutane-1,3-diol and the diacetate of 3-phenylbutane-1,3-diol:



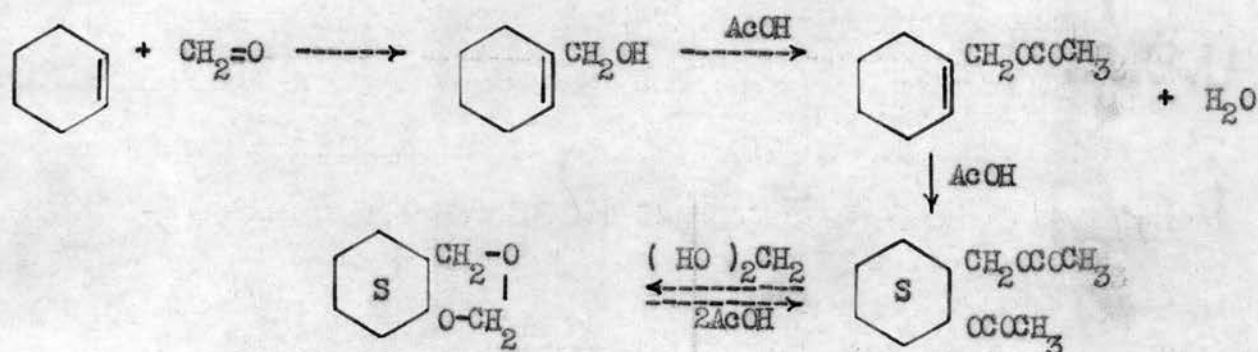
In addition to these compounds, appreciable polymers of the α -methylstyrene and unidentified substances were encountered. No product which could have been formed by a reaction involving α -methylenic activity was noted.

This mechanism is supported by the work of Barbier and Leser on the unsaturated aldehyde citronellal, as reported by Price and Dickman (58). This aldehyde undergoes an internal Prins reaction leading to ring closure and alcohol formation:



The most extensive investigation of the Prins reaction was carried out by

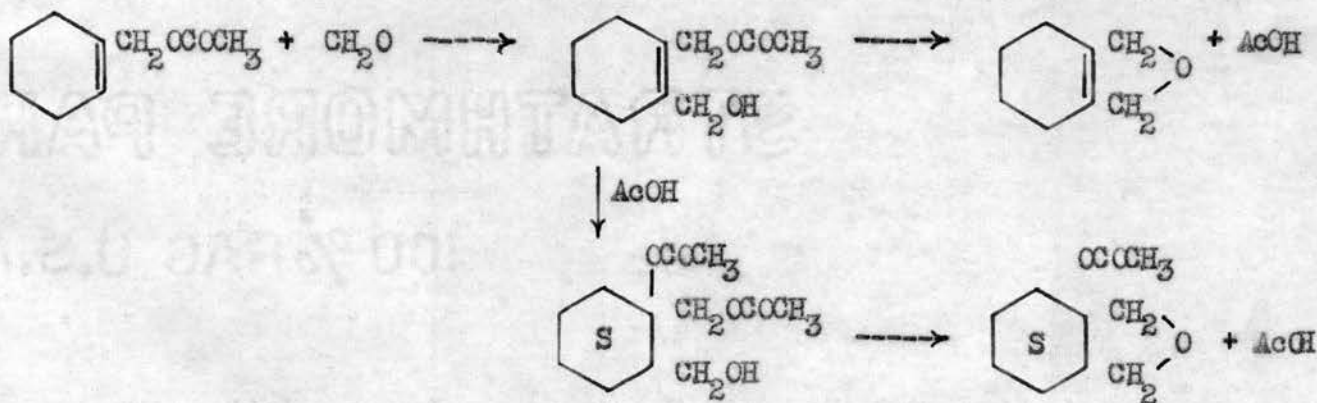
Olsen and Radberg (59,60). These workers, repeating the work of Matti (7), caused formaldehyde to react with cyclohexene in glacial acetic acid with concentrated sulfuric acid as catalyst. The products of the reaction were isolated and a reaction scheme was formulated. The chief products of the reaction are the acetates and formals of hexahydrosaligenin (o-hydroxyhexahydrobenzyl alcohol). These compounds result from the following reaction sequence:



One of the important side reactions is the acid-catalyzed addition of acetic acid into the double bond of cyclohexene:



Another important side reaction leads to the production of phthalan derivatives:

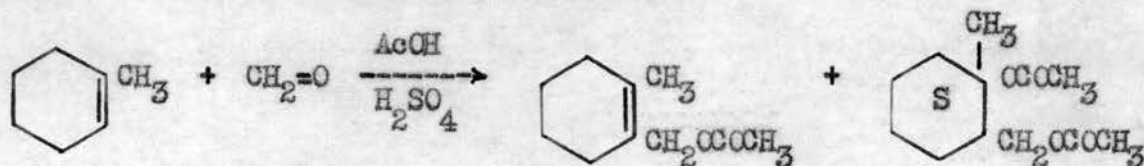


The overall reaction was shown to give a series of reaction products which are all in equilibrium with each other. The addition of any of the known inter-

mediates or side products to a mixture of formaldehyde, glacial acetic acid and concentrated sulfuric acid leads to the same reaction products.

Olsen and Radberg have not considered the mechanism of the reaction but it is of interest to note that all the products can be formed via the intermediate postulated by Price (56).

Nenitzescu and Przenetsky (61) caused 2-methylcyclohexene to react with paraformaldehyde in the presence of a glacial acetic acid-concentrated sulfuric acid mixture and isolated the acetate of 2-methyl-1-cyclohexene-1-methanol and the diacetate of 2-hydroxy-2-methylcyclohexanemethanol:

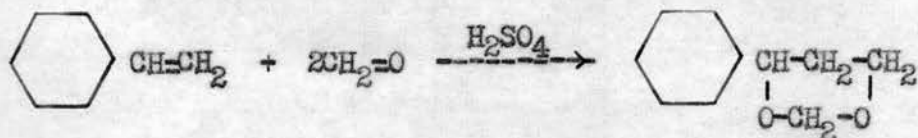


The presence of the methyl group on the C=C group leads to the formation of the unsaturated ester.

These workers caused cyclohexene to react with 35% formalin solution in the presence of sulfuric acid to yield small amounts of the formal $\text{o-CC}_6\text{H}_{10}\text{CH}_2\text{OCH}_2$.

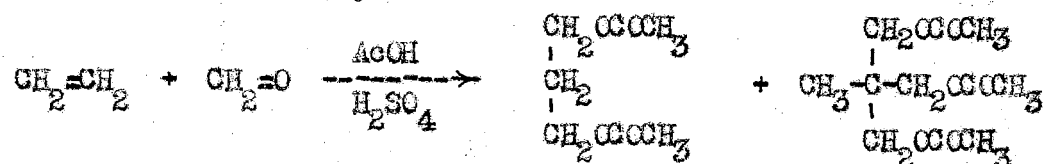
The scope of the reaction has been widened by Emerson (62). He effected the addition of acetaldehyde, propionaldehyde, n-butyraldehyde and isobutyraldehyde into the double bond of styrene in glacial acetic acid containing concentrated sulfuric acid. The main products were 1,3-dioxanes and acetates of 1,3-glycols. Acetaldehyde yielded diacetates while other aldehydes gave only monoacetates. All aldehydes except n-butyraldehyde produced dioxanes.

Shortridge (63) found that the reaction of formaldehyde and styrene with concentrated sulfuric acid catalyst in an inert solvent at room temperature gives a 78% yield of 4-phenyl-1,3-dioxane and no glycol:



The yield of the dioxane was increased to 88% by the use of styrene, 37% aqueous formalin and sulfuric acid under reflux temperatures.

The Prins reaction has been carried out at elevated temperatures and pressures with results similar to those obtained under less severe conditions. Reaction between gaseous olefins and aqueous formalin with a zinc chloride catalyst at high temperatures and pressures has been demonstrated (64). The chief product is the formal of a 1,3-glycol containing one more carbon atom than the original olefin. A water-immiscible solvent in which the olefins and formals are soluble was found to favor the formation of formals and to increase the overall yield. Aqueous hydrogen chloride solutions used as a catalyst in place of zinc chloride produces chlorinated alcohols instead of glycols. Ethylene caused to react with formaldehyde (65) under high temperature-high pressure conditions yielded trimethylene glycol diacetate and pentaglycerin diacetate:



The 1,3-dioxane was not found but Olsen believes it may have been lost by washing of the reaction mixture with water. This particular reaction is of interest since the trimethylene glycol diacetate could serve as an intermediate stage in a synthesis of glycerin.

Baker (57) independently repeated the reaction between ethylene and para-formaldehyde at room temperature in a 100% acetic acid-100% sulfuric acid mixture. The diacetate of trimethylene glycol diacetate was isolated and characterized. Some evidence for the existence of the corresponding formal was found.

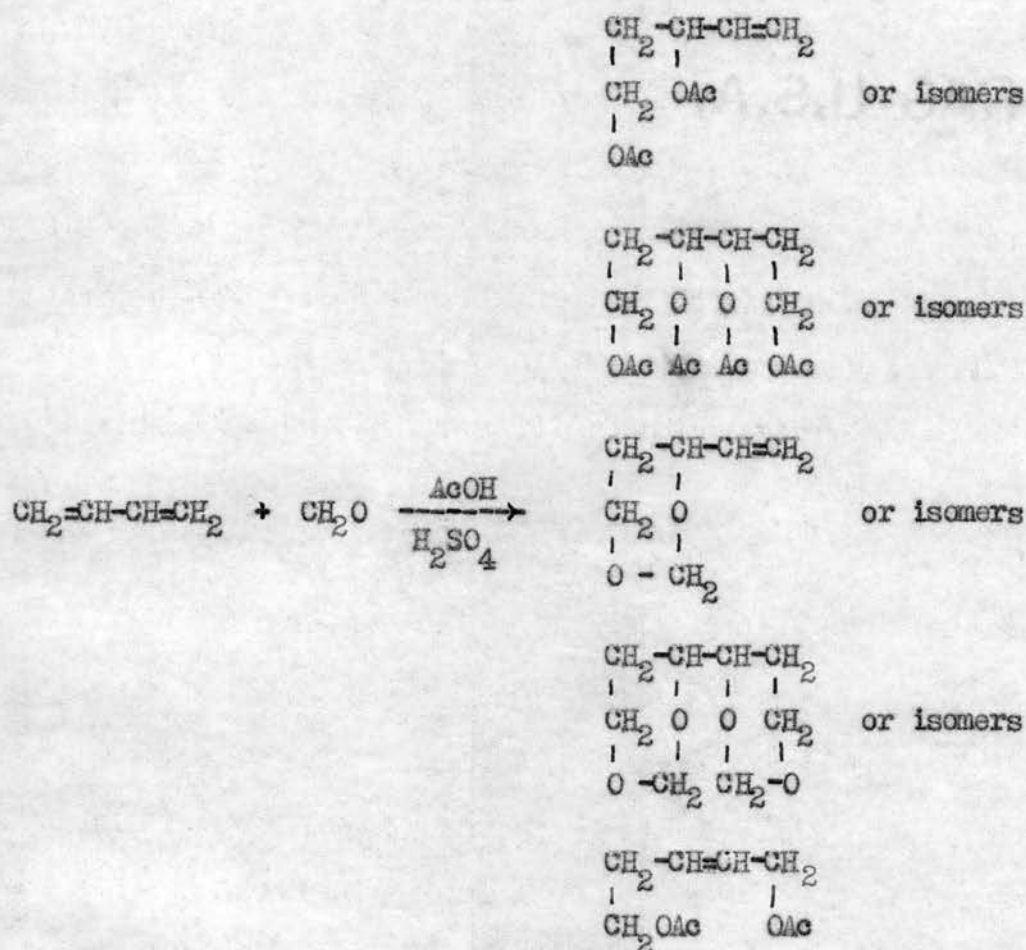
The structural conditions in the olefin which favor the acid-catalyzed addition of formaldehyde into a double bond have been set forth by Baker (57). In order for an olefin to give satisfactory yields of the 1,3-glycol derivatives, it must be of the type $\text{CHR}'=\text{CH}_2$ or $\text{CHR}'=\text{CHR}''$ where R' =alkyl or aryl and R'' =alkyl

or hydrogen. If the activation resulting from the presence of R' and R'' becomes too great, self-polymerization and side reactions may reduce the yield of the desired product.

The Prins reaction is rapidly growing in importance in the field of industrial chemicals and will undoubtedly become one of the standard synthetic methods available for the production of 1,3-glycols and glycol derivatives.

EXPERIMENTAL

The solvent most widely used in effecting the Prins reaction is glacial acetic acid, while concentrated sulfuric acid is the most common catalyst. The initial reaction between butadiene and formaldehyde was therefore performed in a solution of sulfuric acid in glacial acetic acid. The expected reaction was:



The reaction was carried out according to the directions given by Emerson (60).

The following mixture was prepared:

600 g. glacial acetic acid

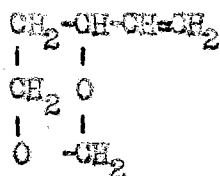
40 g. concentrated sulfuric acid

30 g. paraformaldehyde

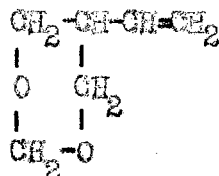
The sulfuric acid was slowly added to the cooled acetic acid. The paraformaldehyde

was added and the slurry placed in a 2-liter, 3-necked flask equipped with an electric stirrer fitted with a mercury seal. While the stirred mixture was held at 0-10° with an ice-water bath, butadiene gas (Phillips pure grade) was slowly and steadily bubbled into the slurry for five hours. The mixture darkened appreciably. The stirring and cooling was continued for an additional five hours and the solution added to water. This diluted solution did not give an immediate test for aldehydes with 2,4-dinitrophenylhydrazine in 2N hydrochloric acid (65), which indicated that all of the paraformaldehyde had been used in the reaction. The diluted reaction mixture was extracted with ether and the extract distilled to remove the solvent. The remaining dark liquid gave a positive hydroxamic test for esters (66). After a sample had been refluxed with aqueous potassium hydroxide, the solution gave a test for alcohols with ceric ammonium nitrate reagent (65). The original extract was distilled at atmospheric pressure from a distilling flask without apparent decomposition up to 150°. The distillate decolorized bromine in carbon tetrachloride and aqueous potassium permanganate solution but did not give a test for alcohols or esters. This liquid was redistilled and found to yield a 142-145° fraction. Addition of a small amount of this liquid to the 2,4-dinitrophenylhydrazine reagent gave no immediate precipitate but cloudiness gradually appeared and still later a light-yellow precipitate formed. This solid melted at 162°. The literature value for the melting point of the 2,4-dinitrophenylhydrazone of formaldehyde is 166°.

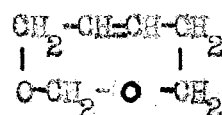
The 142-145° cut was again redistilled and the 143-144° fraction collected separately. The bromine number of this colorless liquid was experimentally determined (67) to be 143, which is equivalent to a molecular weight of 112 if the compound contains but one double bond. The molecular weight as determined by the freezing point depression of benzene was 111. This molecular weight corresponds to that of a compound resulting from the addition of two molecules of formaldehyde to one molecule of butadiene. Three possible structures, all of formals, are:



I



II



III

Compound III is unlikely because it is an eight-membered ring but it would be the product of 1,4 addition to butadiene. Compounds I and II as vinyl-type compounds would be expected to polymerize readily but attempted polymerization of the new liquid using benzoyl peroxide, stannic chloride and sodium as catalysts failed. The formal reacted with sodium at ordinary temperatures. This reaction was unexpected since neither ordinary olefins nor ordinary ethers so react. However, it was found by trial that sodium reacts with allyl ether under the same conditions. Compound I, 4-vinyl-1,3-dioxane, has an allylic structure similar to that of allyl ether. The known facts that simple allyl compounds do not polymerize readily and can be distilled under ordinary pressure favor belief that the unknown is 4-vinyl-1,3-dioxane. Moreover, this compound would be expected if the orientation of addition at one double bond of the diolefin is the same as such orientation at the double bond of an unsymmetrical mono-olefin.

The liquid formal was redistilled through a Todd semi-micro column packed with a Monel metal spiral at atmospheric pressure. The greatest amount of liquid boiled between 144.0-144.5°. The formal is colorless and has a sharp odor. The following physical constants were determined:

$$\text{B.P. } ^{742} = 144^{\circ}\text{C.}$$

$$\text{R.I. } ^{20} = 1.4439$$

$$\text{D}_4^{20} = 1.00$$

The molar refraction (68) for 4-vinyl-1,3-dioxane is 30.3. The liquid formal has a molar refraction of 30.3 as determined from the above physical constants. The compound has a theoretical carbon content =63.13% and hydrogen content =8.83%.

The actual values are carbon =63.30 and 63.39 and hydrogen =8.94 and 8.93.

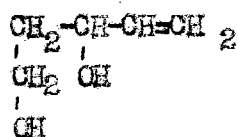
It was decided to discontinue dilution of the reaction mixture in isolating products since the formal might be hydrolyzed in dilute acid. In order to obtain more material the following mixture was made.

600 ml. glacial acetic acid

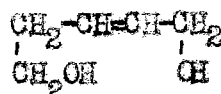
150 ml. concentrated sulfuric acid

100 g. paraformaldehyde

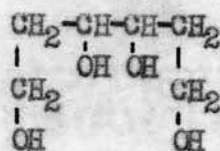
The mixture was prepared as before but was held at 20° while butadiene was slowly bubbled in until about 115 g. had been absorbed; this occurred readily. The reaction mixture darkened gradually and after five hours had a dark-brown color. After fifteen hours at room temperature, no paraformaldehyde was noted. In order to neutralize the reaction mixture without promoting hydrolysis of the esters, it was slowly added to a slurry of sodium carbonate in water. The light-yellow neutralized mixture was filtered and exhaustively extracted with ether. The ether was removed by distillation and the dark concentrate refluxed for three hours with 20% sodium hydroxide solution to saponify the acetates. This solution was ether-extracted. A preliminary rough vacuum distillation at 30 mm. Hg pressure yielded 50 ml. of a yellow, viscous liquid boiling between 150-170°. Some decomposition was noted and about 20% of the initial liquid remained as a semi-solid, dark-colored residue. The distillate gave a test for alcohols and decolorized bromine in carbon tetrachloride. About 20 ml. of the distillate was refractioned at 2-3 mm. pressure through the Todd semi-micro column. This gave two principal boiling ranges; 93-102° and 128-133°. These fractions were found to be alcohols contaminated with esters and formals. The 93-102° cut absorbed bromine in carbon tetrachloride; a bromine number determination gave a value of 140-146 which corresponds to a molecular weight of 110-114. This cut could be a hitherto unknown pentenediol of structure



or

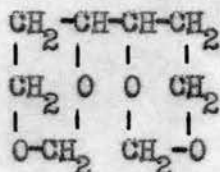


which would have a molecular weight of 102. Saturated impurities would have the effect of increasing the apparent molecular weight. The 128-133° cut was saturated and extremely viscous. This could be:



The higher-boiling liquid was less soluble in ether than the lower cut, as would be expected if the postulated structures are correct. Further fractionation to remove impurities did not promise to be successful since the high viscosity of the liquids prevented efficient separation. Hence the remaining crude glycols were esterified by reaction with acetic anhydride in pyridine. The acetates were distilled through the Todd semi-micro column at 30 mm. pressure. The greatest portion of the distillate boiled between 159-172° but gave saponification equivalents which were too high for any possible product. The distillate gave a test for formals and it was assumed that the impurities were the cause of the high values.

The absence of the previously reported liquid formal was probably due to failure to form any considerable amount of it and loss of this in subsequent treatment of the reaction mixture. The presence of a formal in the high-boiling fraction was evidence for the production of another formal, possible of the structure:



The formals have since been found to be the most simple of the products to separate since they can be distilled at atmospheric pressure without decomposition. In an effort to improve the yield, the amount of paraformaldehyde and sulfuric acid in a reaction mixture was increased:

600 ml. glacial acetic acid

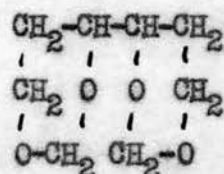
150 ml. concentrated sulfuric acid

200 g. paraformaldehyde

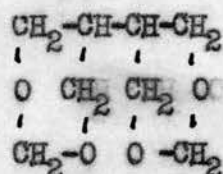
The slurry was prepared as before and held at 20-25° with stirring while about 170 g. of butadiene was slowly bubbled in. After fifteen hours at room temperature, an excess of paraformaldehyde was still present. The darkened mixture was neutralized by addition of soda ash and exhaustively extracted with ether. The stripped extract was then found to give a test for only esters and formals but a sodium fusion and sodium nitroprusside test (65) showed sulfur present. Experience has shown that distillation of the extract at this point leads to production of sulfuric acid and subsequent ruinous oxidation. Alkyl sulfates are known to decompose upon heating to liberate sulfuric acid and it may be that such sulfates were formed in this reaction by the addition of sulfuric acid into the double bonds of butadiene. A reaction of this type has been observed with other dienes (69). The extract was therefore refluxed with 20% sodium hydroxide solution to hydrolyze these sulfates and incidentally other esters. This solution was extracted with ether and the ether removed by distillation. The concentrate gave a test for formals and alcohols but not for esters. Distillation at atmospheric pressure yielded a fraction of 40 g. which boiled at 190-210°. This cut gave a test only for formals and solidified at 0°.

The 190-210° fraction was redistilled over sodium to remove impurities. This is a convenient method of purification since ethers and formals are not ordinarily attacked by sodium, even at elevated temperatures. About 30-35 g. of a liquid distilling at 205-210° was obtained. The liquid solidified at room temperature but showed a pronounced tendency to supercool and seeding was necessary. The colorless solid was recrystallized from petroleum ether and then melted at 51.0-51.5°. A determination of the molecular weight by depression of the freezing point of water yielded a value of 165 while a similar determination

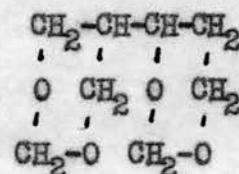
in benzene gave values of 170-175. The compound is fully saturated and therefore must be a bi-1,3-dioxane of molecular weight 174. Such a compound would have a carbon content =55.17% and hydrogen =8.05%. The actual values were C = 58.17, 58.17 and H = 8.19, 8.21. Since this indicated that heavy ends left by the ligroin used in recrystallization were contaminating the compound, it was again recrystallized from ligroin known to be clean and resubmitted to analysis: C = 58.34, 58.39 and H = 8.28, 8.35. These persistent high values for carbon are unaccountable except on the basis of hydrocarbon residues as impurities; yet the compound melted sharply. This still requires clarification. The following possibilities exist:



I



II



III

Structure I, 4,4'-bi-1,3-dioxane, is most probable since the Prins reaction would presumably give this compound. The compound is soluble in water and is only slightly hydrolyzed by dilute acids. A sample of the formal was partially hydrolyzed by refluxing with dilute sulfuric acid for several hours. Sulfate was removed by exact neutralization with barium hydroxide followed by filtration, and some water by evaporation. The concentrate gave a test for alcohols and also for glycols having hydroxyl groups on adjacent carbon atoms with the periodic acid reagent (65). Only structure I upon hydrolysis would yield such a glycol. Possible impurities such as formaldehyde and the formal were found not to affect the test. Reaction of the formal with 2,4-dinitrophenylhydrazine in 2N hydrochloric acid should lead to quantitative hydrolysis and formation of the 2,4-dinitrophenylhydrazone of formaldehyde. Thus the amount of the 2,4-dinitrophenylhydrazone formed from a known amount of formal would serve as a chemical method

of determining the molecular weight of the formal. However, the compound proved to be extremely resistant to hydrolysis in the cold and the amount of precipitate formed in four trials lasting up to three days at room temperature was always much too low. Heating of the solution would lead to decomposition of the 2,4-dinitrophenylhydrazine and inaccurate results.

In order to avoid formation of acetates in the reaction and to simplify the neutralization procedure, anhydrous ether was tested as a solvent in place of glacial acetic acid. The following reaction mixture was prepared:

600 ml. anhydrous ethyl ether

150 ml. concentrated sulfuric acid

250 g. paraformaldehyde

The concentrated sulfuric acid was slowly added to the ether with cooling as appreciable heat of solution was evolved. The paraformaldehyde was added and the slurry held at 25° and stirred while butadiene was bubbled in. The flow of gas was halted after about 110 g. had been absorbed. The mixture was allowed to stand overnight at room temperature, neutralized by careful addition to a cool concentrated sodium hydroxide solution, and finally extracted with ether. A sodium fusion with the extract gave a solution which contained sulfur, so the extract was refluxed with a dilute sodium hydroxide solution for several hours. The alkaline solution was steam-distilled and the distillate extracted with ether. Distillation yielded 30 ml. of a colorless liquid boiling at 143-145°, evidently 4-vinyl-1,3-dioxane. The non-steam-volatile residue was also extracted with ether and 40 g. of an impure liquid of boiling range 205-215° separated while 25 g. of higher-boiling residue remained. This distillate when redistilled over sodium gave 30 g. of liquid boiling at 205-207°, solidifying at ice-water temperature and otherwise recognized to be the bi-1,3-dioxane. Thus the reaction takes the same course in ethyl ether as in glacial acetic acid and the recovery of products is simplified, especially since the liquid formal is steam-volatile

while the solid formal is not.

Since previous runs were primarily exploratory, no attempt has been made up to this point to measure the yield of formals accurately. The amount of butadiene absorbed in the succeeding runs was measured by weighing the reaction flask and contents before and after absorption of butadiene. The error was at most ± 1 gram.

The following mixture was prepared as before:

- 400 ml. anhydrous ethyl ether
- 200 ml. concentrated sulfuric acid
- 150 g. paraformaldehyde (5.0 moles)

Butadiene was slowly bubbled into the slurry held at 25-30° with stirring until 102 g. (1.89 moles) had been absorbed. The mixture darkened appreciably and was allowed to stand overnight at room temperature. A total of 66 g. of the bi-1,3-dioxane and none of the vinyl-1,3-dioxane was obtained by the usual procedure. This corresponds to a 30% yield based on formaldehyde.

In order to determine the reproducibility of the yield, a similar mixture was prepared:

- 400 ml. anhydrous ethyl ether
- 200 ml. concentrated sulfuric acid
- 200 g. paraformaldehyde (6.65 moles)

120 g. butadiene (2.22 moles) was added as before. By the usual treatment, 7 g. of the liquid formal and 89 g. of the solid formal were recovered. This made the total conversion of formaldehyde into formals 34% of the theoretical value.

Up to this point the bi-1,3-dioxane has appeared as the chief product regardless of conditions. In order to suppress formation of the diformal and to increase yield of the monoformal, the following mixture, in which formaldehyde was added to excess butadiene, was prepared:

- 600 ml. anhydrous ethyl ether
- 150 ml. concentrated sulfuric acid
- 134 g. butadiene (2.48 moles)

The concentrated sulfuric acid was slowly added to the cooled ether. The solution was held at 0-5° and the butadiene bubbled in. The colorless solution was held at 10-20° while 150 g. of paraformaldehyde (5.0 moles) was added slowly. The solution darkened and was stirred for four hours at 10-20°. After standing overnight at room temperature, 25 g. of paraformaldehyde remained. The usual treatment yielded 10 ml. of 4-vinyl-1,3-dioxane (3% yield based on formaldehyde) and no diformal. The presence of unreacted paraformaldehyde complicated recovery of the monoformal.

Production of the liquid formal was again attempted as follows:

I	II
200 ml. anhydrous ethyl ether	200 ml. anhydrous ethyl ether
100 ml. concentrated sulfuric acid	100 ml. conc. sulfuric acid
56 g. butadiene (1.04 moles)	60 g. paraformaldehyde (2.0 moles)

Mixture I was prepared by carefully adding the sulfuric acid to the cooled ether. The solution was held at 0-5° and butadiene bubbled in. Mixture II was made again initially mixing the acid with cooled ether. The paraformaldehyde was added and the slurry cooled to 0-5°. Mixture II was slowly poured into Mixture I with cooling and stirring. An appreciable heat of reaction was noted and the mixture darkened greatly. The mixture was stirred and held at room temperature for five hours. At this point, no paraformaldehyde remained. Neutralization with a solution of sodium hydroxide gave a dark-colored mass which resembled tar. This was separated and found to be soluble in water and in absolute alcohol but insoluble in ethyl ether, petroleum ether, and carbon tetrachloride. In strongly alkaline solutions, it had a reddish-brown color and resembled the side-products obtained in other runs. After refluxing with dilute alkali, neither the solution nor the remaining tarry material gave a test for alcohols. Acid hydrolysis yielded an altered tar and a solution both of which gave tests for alcohols and had a definite odor of formaldehyde. A sodium fusion with the original material yielded a solution which

gave a positive test for sulfur. Hence the tar was probably the product of the addition of sulfuric acid into the double bonds of butadiene and 4-vinyl-1,3-dioxane. The expected products from such an addition are sulfuric and sulfonic esters. Since basic hydrolysis should convert organic sulfates to alcohols, the products in this case are probably sulfonic acids. No reference to the reaction between butadiene and sulfuric acid could be found in the literature but formation of sulfonic acids would be unusual.

Since it seemed that the butadiene reacted undesirably with the sulfuric acid, the procedure was revised as follows:

I

200 ml. anhydrous ethyl ether
25 ml. conc. sulfuric acid
50 g. butadiene (0.93 mole)

II

200 ml. anhydrous ethyl ether
75 ml. conc. sulfuric acid
60 g. paraformaldehyde (2.0 moles)

The mixtures were prepared as before; it will be noted that both contain less sulfuric acid. No appreciable heat of reaction was noted upon blending them. The reaction mixture was held at 0-5° and stirred for eight hours. The dark solution was treated as usual and 10 g. of 4-vinyl-1,3-dioxane (9% yield) and 20 g. of the 4,4'-bi-1,3-dioxane (23% yield based on formaldehyde) were obtained. The overall yield was 32%. The appearance of so much solid formal was unexpected since the reaction mixture contained only 2 moles formaldehyde/mole butadiene while 4 moles formaldehyde/mole butadiene is required to produce the diformal. It is possible that some of the butadiene was used in side-reactions so that there was effectively an excess of formaldehyde; or the addition of formaldehyde into the second double bond may have proceeded more rapidly than the initial addition. The steam-distillation residus contained a layer of tarry material which was separated. This substance was not appreciably soluble in ether. Addition of acetone caused sodium sulfate to precipitate, whereupon the mixture was filtered and the acetone removed from the filtrate by distillation. The stripped filtrate was soluble in water.

When burned, the material charred initially and left an ash. The substance appeared to be the sodium salt of the alkylsulfuric or -sulfonic acids produced.

Since the molar ratio 2 formaldehyde/1 butadiene still gave chiefly the bixoxane, the effect of an excess of butadiene was again investigated.

I

200 ml. anhydrous ethyl ether

25 ml. conc. sulfuric acid

90 g. butadiene (1.65 moles)

II

200 ml. anhydrous ethyl ether

25 ml. conc. sulfuric acid

60 g. paraformaldehyde (2.0 moles)

The mixture was prepared and combined as before but held at 0-5° with continuous stirring for eight hours. The mixture was allowed to stand overnight at room temperature. At this point, a slight odor of butadiene was noted and a small amount of undissolved paraformaldehyde remained. By working up as before, the mixture gave 22 g. of the monoformal (20% yield based on formaldehyde, but an excessive amount of butadiene was consumed) and none of the diformal. The layer of non-steam-volatile products in the neutralized mixture was separated and acidified. The water entrained in this material was removed azeotropically with carbon tetrachloride. The dark-colored solution was filtered to remove salts and the carbon tetrachloride was boiled off. This residual concentrate of side-products was stored for use in later work.

The effect of temperature on a run with excess butadiene was studied:

I

200 ml. anhydrous ethyl ether

25 ml. conc. sulfuric acid

88 g. butadiene (1.63 moles)

II

200 ml. anhydrous ethyl ether

75 ml. conc. sulfuric acid

60 g. paraformaldehyde (2.0 moles)

The mixtures were prepared and combined as before but held at 20-30° with stirring for three hours. The dark-colored solution contained no undissolved paraformaldehyde and gave only a trace test for aldehydes with 2,4-dinitrophenylhydrazine. The mixture treated as usual yielded 31 g. of the monoformal (30% yield

based on formaldehyde). Evidently increasing the temperature shortened the time necessary for completion of the reaction and increased the yield.

Since it is known that the addition of formaldehyde into a double bond is accompanied by side-reactions which are all in equilibrium with each other, the effect of the addition of side-products obtained in a previous run was studied.

I

200 ml. anhydrous ethyl ether
25 ml. conc. sulfuric acid
About 25 g. of side-products
54 g. butadiene (1.0 mole)

II

200 ml. anhydrous ethyl ether
75 ml. conc. sulfuric acid
60 g. paraformaldehyde (2.0 moles)

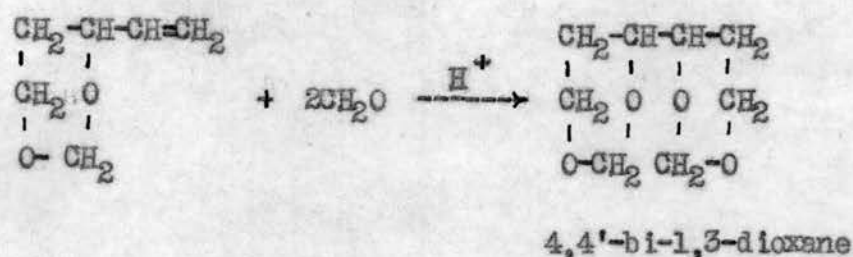
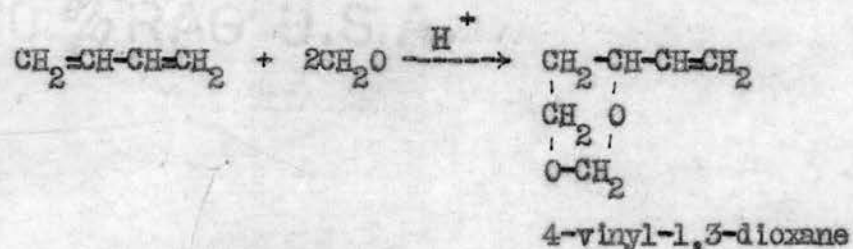
The mixture was prepared and combined as before and held at 20-30° with stirring for four hours. This run gave 23 g. of 4-vinyl-1,3-dioxane (20% yield) and 28 g. of 4,4'-bi-1,3-dioxane (31% yield based on formaldehyde). The overall conversion of formaldehyde into formals is 51%. This was the best yield obtained and the run confirms the idea that the reaction comprises a series of reactions which are all in equilibrium with each other.

An important piece of evidence in the characterization of the solid formal and in the formulation of the reaction scheme is the conversion of the 4-vinyl-1,3-dioxane into 4,4'-bi-1,3-dioxane by reaction with paraformaldehyde under the usual conditions. The following reaction mixture was therefore prepared:

300 ml. anhydrous ethyl ether
100 ml. concentrated sulfuric acid
40 g. 4-vinyl-1,3-dioxane (0.36 mole)
30 g. paraformaldehyde (1.0 mole)

The sulfuric acid was slowly added to the cooled ether. The paraformaldehyde and liquid formal were then added and the mixture held at 20-30° and stirred. After 4.5 hours, the stirring was halted and the mixture allowed to stand overnight at room temperature. At this point, the mixture had darkened and some undissolved

paraformaldehyde remained. The mixture was neutralized and steam-distilled. The distillate contained only a trace of unreacted 4-vinyl-1,3-dioxane. The steam-distillation residue upon ether extraction yielded a fraction boiling between 205-220°. This liquid was redistilled over sodium and a colorless liquid distilling at 205-210° was obtained. The liquid solidified at ice-water temperature and melted at 50° after recrystallization from petroleum ether. This is evidently the solid formal previously obtained. The overall reaction was therefore:



The yield of diformal was about 25% based on the monoformal. The side-products were tarry materials resembling those obtained from the butadiene runs. This furnishes a possible explanation for the fact that not more than 34% of the original formaldehyde has ever been accounted for as isolated dioxanes. The 4-vinyl-1,3-dioxane may react with sulfuric acid to yield addition products or the unsaturated formal may be polymerized; the former is more probable.

A 32% formalin solution containing sulfuric acid to make a 10% solution yielded no products upon addition of butadiene under the usual conditions. The butadiene was not very soluble in the acidified formalin solution and the failure to react may have been due to the presence of the water.

The use of methylal as a source of formaldehyde in the Prins reaction has been claimed (15). The reaction between butadiene and methylal with sulfuric acid catalyst was found to give products other than formals but no attempt was made to

identify these compounds. Mr. Hawkins is continuing work on the reaction in this laboratory.

Sulfuric acid is not an ideal catalyst since it enters into side-reactions. Phosphoric acid (85%) was tested for catalytic activity but no reaction was noted. This failure may have been due to the water added along with the acid; perhaps anhydrous phosphoric acid would work. Anhydrous aluminum chloride has been used as catalyst in the Prins reaction and was therefore tested by the following run:

300 ml. anhydrous ethyl ether

75 g. C.P. anhydrous aluminum chloride

60 g. paraformaldehyde (2.0 moles)

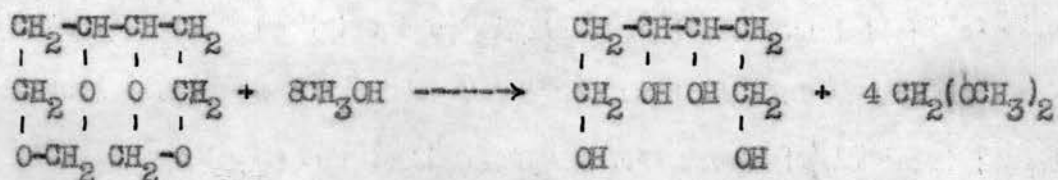
The anhydrous aluminum chloride was carefully added to the cooled ether. An appreciable heat of mixing was evolved. The mixture was cooled to $0-5^{\circ}$ and the paraformaldehyde added. Butadiene was then bubbled in until 74 g. (1.37 moles) had been absorbed. The mixture was stirred and held at $20-30^{\circ}$ for four hours whereupon it was added to a cooled, dilute sodium hydroxide solution and steam-distilled. The distillate yielded 5 g. of 4-vinyl-1,3-dioxane (4% yield based on formaldehyde) but none of the solid formal. The side-product was a brown tarry material soluble in ether and insoluble in water. This was probably a polymer of butadiene or 4-vinyl-1,3-dioxane. p-Toluenesulfonic acid was found to be too insoluble in ether to serve as a catalyst.

The 4,4'-bi-1,3-dioxane should be convertible to the corresponding alcohol, 1,3,4,6-hexanetetrol, according to the following reaction:



Attempted hydrolysis by refluxing with 5% sulfuric acid was very slow and incomplete. A 50% sulfuric acid solution decomposed the formal at reflux temperatures. Formals have been converted to diols by treatment with an alcohol such as methanol

in the presence of an acid catalyst (15,70). The following reaction should then be possible:



This was tried by means of the following reaction mixture:

75 ml. C.P. methanol

25 ml. concentrated sulfuric acid

16 g. 4,4'-bi-1,3-dioxane

The solution was refluxed for three hours but distillation did not yield any methylal. From this it was assumed that the reaction failed. The hydrolysis of diformals such as the diformal of pentaerythritol is extremely difficult (71) and it is not surprising that the alcoholysis did not work under the conditions used.

DISCUSSION

The acid-catalyzed addition of formaldehyde into butadiene has been found to proceed in the same manner as the addition of formaldehyde into mono-olefins and therefore to yield derivatives of 1,3-glycols. Since anhydrous ethyl ether, a non-reactive solvent, was employed in place of the usual glacial acetic acid, the products isolated were the monoformal (4-vinyl-1,3-dioxane), and the diformal (4,4'-bi-1,3-dioxane), although it was demonstrated that in the presence of glacial acetic acid, acetate esters were also produced.

The two formals, which have been fully characterized, are new compounds. The unsaturated liquid monoformal has an allylic structure and therefore is not polymerized readily and cannot be used to produce an ordinary vinyl-type polymer. It can, however, probably be copolymerized with other vinyl compounds to give useful plastics. This cyclic ether could be hydrogenated to yield 4-ethyl-1,3-dioxane, a known compound which can be used as a solvent. The saturated solid diformal would have little use itself, unless possibly as a plasticizer, but acid hydrolysis must yield a new polyhydroxy alcohol, 1,3,4,6-hexanetetrol, suitable as an intermediate similar to pentaerythritol, sorbitol and glycerol for making alkyd resins, explosives, etc. A practical method for the hydrolysis has not been found but no intensive search has been made and similar hydrolyses are claimed in recent patents.

The yield based on the conversion of formaldehyde into formals was only 30 to 34% but addition of side-products increased the conversion to 51%. Higher reaction temperatures and pressures should permit the use of less sulfuric acid or other acid as catalyst, thereby decreasing the magnitude of the side-reactions and increasing the yield of desired products. Such conditions should also allow the use of formalin solutions as a source of formaldehyde, which could be made to yield 1,3-glycols directly. This could possibly give 2-pentenediol-1,5, the

product of the 1,4-addition of methylene glycol into butadiene.

The side-products arise chiefly from the addition of sulfuric acid into the double bonds of butadiene and 4-vinyl-1,3-dioxane. Little is known of such additions but the products are probably alkyl sulfates and/or sulfonic acids. Upon attempted distillation these compounds decompose with liberation of sulfuric acid. Failure to remove or destroy them prior to distillation causes ruinous oxidation. Alkaline hydrolysis has been found to be effective but somewhat inconvenient for this purpose. A separate study of the reaction of butadiene with sulfuric acid is recommended.

The tendency of sulfuric acid to complicate reaction by adding into double bonds suggests the use of some other acid catalyst. Unfortunately no other has yet been found as active as sulfuric acid. Anhydrous aluminum chloride showed some activity but 85% phosphoric acid had none. Boron trifluoride may prove effective even though at least one instance of its inactivity is recorded in the literature. Hydrogen fluoride is another potential catalyst; indeed if hydrolysis of products is contemplated, there is no reason why hydrogen chloride should not be tried. It will probably give chloromethyl ethers instead of formals but these can be hydrolyzed.

An obvious extension of this work would be the use of other dienes in the Prins reaction. This would yield new compounds similar to those described herein.

SUMMARY

The Prins reaction, i.e. the acid-catalyzed addition of formaldehyde at a carbon-carbon double bond, has been extended to the diolefin butadiene. The reaction in anhydrous ethyl ether solvent yields two new compounds, 4-vinyl-1,3-dioxane and 4,4'-bi-1,3-dioxane. These have been isolated in total yields up to 34% (51% with recycling of by-products) and fully characterized. The reaction in glacial acetic acid or with methylal as source of formaldehyde proceeds readily but gives more numerous and complex products not yet identified. Sulfuric acid gives better yields than other acids under the conditions used, but generates too much sulfur-containing by-product to be thoroughly satisfactory.

BIBLIOGRAPHY FOR STYRENE-FORMALDEHYDE COPOLYMERIZATION

- (1) Davidson, D., Ind. Eng. Chem., Anal. Ed. 12, 40 (1940).
- (2) Shriner and Fuson, "The Systematic Identification of Organic Compounds,"
3rd. ed., New York, Wiley (1948).

BIBLIOGRAPHY FOR ETHYLENE OXIDE - FORMALDEHYDE COPOLYMERIZATION

- (1) Perry, S., and Hibbert, H., J. Am. Chem. Soc. 62, 2599 (1940).
- (2) Walker, "Formaldehyde", p. 79-80, New York, Reinhold (1944).
- (3) Trillat, A. and Cambier, R., Bull. soc. chim. (3), 11, 752 (1894); via Walker, op. cit., p. 140.
- (4) Verley, A., Bull. soc. chim. (3), 21, 275 (1899); via Walker, op. cit., p. 140.
- (5) Gresham, W. F. (to E.I. duPont de Nemours), U.S. 2,350,350 (1944); via C. A. 38, 5340 (1944).
- (6) Gresham, W. F. (to E.I. duPont de Nemours), U.S. 2,395,365 (1946); via C. A. 40, 3010 (1946).
- (7) Gresham, W. F. (to E.I. duPont de Nemours), U.S. 2,394,910 (1946); via C. A. 40, 3022 (1946).
- (8) Gresham, W. F. (to E.I. duPont de Nemours), U.S. 2,376,354 (1945); via C. A. 39, 3703 (1945).
- (9) Walker, op. cit., p. 257.
- (10) Clarke, H. T., J. Chem., Soc. 101, 1804 (1912); via Walker, op. cit., p. 140.
- (11) Shriner and Fuson, "The Systematic Identification of Organic Compounds", 3rd. ed., New York, Wiley (1948).

BIBLIOGRAPHY FOR ADDITION OF FORMALDEHYDE INTO BUTADIENE

- (1) Prins, H. J., Chem. Weekblad 16, 1072 (1919), via C. A. 13, 3155 (1919).
- (2) Prins, H. J., Proc. Acad. Sci. Amsterdam 22, 51 (1919), via C. A. 14, 1662 (1920).
- (3) Prins, H. J., Chem. Weekblad 16, 1510 (1919), via C.A. 14, 1119 (1920).
- (4) Fournéau, Benoit and Firmenich, Bull. soc. chim. (4), 47, 894 (1930), via C.A. 24, 5740 (1930).
- (5) Société des Usines Chimique Rhone-Poulenc, Fr. 717,712 (1930), via Walker, "Formaldehyde", p. 229, New York, Reinhold (1944).
- (6) Prins, H. J., Rec. trav. chim. 51, 469 (1932).
- (7) Matti, J., Bull. soc. chim. (4), 51, 974 (1932).
- (8) Fitzky, W. (to I. G. Farbenindustrie), U.S. 2,143,370 (1939).
- (9) I. G. Farbenindustrie, Ger. 672,370 (1939), via C.A. 33, 3928 (1939).
- (10) I. G. Farbenindustrie, Brit. 511,966 (1939), via C.A. 35, 140 (1941).
- (11) Standard Oil Development Co., Brit. 544,737 (1942), via C.A. 36, 7030 (1942).
- (12) Rosen, R. and Arundale, E. (to Standard Oil Development Co.), U.S. 2,368,494 (1945); also in C.A. 39, 4529 (1945).
- (13) Mikeska, Arundale and Mottern (to Standard Oil Development Co.), Can. 434,624 (1946), via C.A. 40, 5445 (1946).
- (14) Hamblet, C. H. and McAlevy, A. (to E.I. duPont de Nemours), U.S. 2,426,017 (1947); also in C.A. 42, 206 (1948).
- (15) Arundale, E. and Mikeska, L. A. (to Standard Oil Development Co.), U.S. 2,421,862 (1947).
- (16) Hamblet, C. H. and McAlevy, A. (to E.I. duPont de Nemours), Brit. 590,571 (1947), via C.A. 42, 589 (1948).
- (17) Workman, A. R. (to Cities Service Oil Co.), U.S. 2,412,762 (1946); also in C.A. 41, 1694 (1947).
- (18) Marsh, N. H. (to Standard Oil Development Co.), U.S. 2,389,205 (1945); also in C.A. 40, 1533 (1946).
- (19) Arundale, E. and Mikeska, L. A. (to Jasco, Inc.), U.S. 2,350,485 (1944).
- (20) Mottern, H. O., (to Jasco, Inc.), U.S. 2,335,691 (1943).
- (21) E. I. duPont de Nemours, Brit. 483,828 (1938), via C.A. 32, 7167 (1938).

- (22) I. G. Farbenindustrie, Brit. 507,571 (1939), via C.A. 34, 449 (1940).
- (23) I. G. Farbenindustrie, Fr. 847,255 (1939), via C.A. 35, 5129 (1941).
- (24) Loder, D. J. (to E. I. duPont de Nemours), U.S. 2,289,548, (1942).
- (25) Arundale, E. and Mikeska, L. A. (to Standard Oil Development Co.),
U.S. 2,296,375 (1942); also in C.A. 37, 1129 (1943)
- (26) Fitzky, W. (to General Aniline), U.S. 2,325,760 (1943).
- (27) Ritter, J. J. (to Standard Oil Development Co.), U.S. 2,362,307 (1944).
- (28) Mikeska, L.A. and Arundale, E. (to Standard Oil Development Co.),
U.S. 2,356,683 (1944), via C.A. 39, 91 (1945).
- (29) Standard Oil Development Co., Brit. 559,041 (1944), via C.A. 39, 4632 (1945).
- (30) Standard Oil Development Co., Brit. 578,438 (1946), via C.A. 41, 3492 (1947).
- (31) Engel, K. H. (to Allied Chemical & Dye Co.), U.S. 2,417,548 (1947); also
in C.A. 41, 3493 (1947).
- (32) Standard Oil Development Co., Brit. 545,191 (1942), via C.A. 36, 7030 (1942).
- (33) Ritter, J. J. (to Standard Oil Development Co.), U.S. 2,335,027 (1943).
- (34) Mikeska, L. A. and Arundale, E. (to Standard Oil Development Co.), U.S.
2,308,192 (1943).
- (35) Arundale, E. and Mikeska, L.A. (to Standard Oil Development Co.), U.S.
2,307,872 (1943).
- (36) I. G. Farbenindustrie, Ger. 673,681 (1939), via C.A. 33, 6339 (1939).
- (37) Fitzky, W. (to I. G. Farbenindustrie), U.S. 2,124,851 (1939), via C.A.
32, 7055 (1938).
- (38) I. G. Farbenindustrie, Brit. 465,467 (1937), via C.A. 31, 7067 (1937).
- (39) I. G. Farbenindustrie, Fr. 812,292 (1937), via C.A. 32, 952 (1938).
- (40) Gresham, W. F. (to E.I. duPont de Nemours), U.S. 2,405,948 (1946), via
C.A. 41, 151 (1947).
- (41) Bain, J. P. (to Nello Resin Process Co.), U.S. 2,340,294 (1944), via
C.A. 38, 3990 (1944).
- (42) Harvey, M. T. (to Harvel Research Corp.), U.S. 2,350,230 (1944), via
C.A. 39, 1572 (1945).
- (43) Short, N. (to Imperial Chemical Ind.), U.S. 2,408,889 (1946); also in
C.A. 41, 773 (1947).
- (44) Short, N. (to Imperial Chemical Ind.), Brit. 579,855 (1946), via C.A. 41,
2431 (1947).

- (45) Roberts, A. M. (to Imperial Chemical Ind.), U.S. 2,379,104 (1945); also in C.A. 39, 4621 (1945).
- (46) Roberts, A. M. (to Imperial Chemical Ind.), Brit. 550,853 (1943), via C.A. 38, 1751 (1944).
- (47) Mead, A. (to Imperial Chemical Ind.), Brit. 550,854 (1943), via C.A. 38, 1751 (1944).
- (48) Crawford, J. W. C. and McLeish, N. (to Imperial Chemical Ind.), U.S. 2,233,835 (1941); also in C.A. 35, 3651 (1941).
- (49) Imperial Chemical Ind., Brit. 528,761 (1940), via C.A. 35, 7975 (1941).
- (50) McLeish, N. and Crawford, J. W. C. (to Imperial Chemical Ind.), Brit. 514,619 (1939), via Walker, "Formaldehyde", p. 231, New York, Reinhold (1944).
- (51) Imperial Chemical Ind., Fr. 845,230 (1939), via C.A. 35, 1070 (1941).
- (52) Kung, F. E. (to Goodrich Co.), U.S. 2,356,459 (1944), via C.A. 39, 88 (1944).
- (53) Steadman, T. R. (to Goodrich Co.), U.S. 2,424,589 (1947); also in C.A. 41, 7412 (1947).
- (54) Steadman, T. R. and Breyfogle, P. L. (to Goodrich Co.), U.S. 2,424,590 (1947), via C. A. 41, 7413 (1947).
- (55) Baker, J., J. Chem. Soc. 1944, 296.
- (56) Price, C.C., "Reaction at Carbon-Carbon Double Bonds", p. 45, New York, Interscience (1946).
- (57) Baker, J. W., J. Chem. Soc. 1948, 89.
- (58) Price, C. C. and Dickman, M. L., Ind. Eng. Chem. 40, 257 (1948).
- (59) Olsen, S. and Radberg, H., Z. Naturforsch. 1, 448 (1946).
- (60) Olsen, S., Z. Naturforsch. 1, 671 (1946).
- (61) Emerson, W. S., J. Org. Chem. 10, 464 (1945).
- (62) Nenitzescu and Przenetsky, Ber. 74B, 676 (1941), via C.A. 35, 6254 (1941).
- (63) Shortridge, R. W., J. Am. Chem. Soc. 70, 873 (1948).
- (64) Fitzky, W., Publication Board Report 58,826, Office of Technical Services, U. S. Dept. of Commerce (1946).
- (65) Olsen, S., Z. Naturforsch. 1, 676 (1946).
- (65') Shriner and Fuson, "The Systematic Identification of Organic Compounds", 3rd. ed., New York, Wiley (1948).
- (66) Davidson, D., J. Chem. Ed. 17, 81 (1940).

- (67) Francis, A. W., Ind. Eng. Chem. 18, 821 (1926).
- (68) Gilman, "Organic Chemistry", Vol. II, p. 1751, New York, Wiley (1943).
- (69) Cortese, F., Ber. 62B, 504 (1929).
- (70) Milneska, L. A. (to Standard Oil Development Co.), U.S. 2,307,894 (1943),
via C.A. 37, 3452 (1943).
- (71) Walker, "Formaldehyde", p. 141, New York, Reinhold (1944).

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