[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

THE CATALYTIC SYNTHESIS OF THE ACETALS AND THEIR HALOGENATION

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The Preparation of the Acetals

The substitution of acetylene for acetaldehyde in the preparation of quinaldine by Nieuwland and Vogt[1] led to the investigation of the possibility of a similar substitution of acetylene for acetaldehyde in the synthesis of the acetals.

The process described in this paper consists in the condensation of acetylene with the alcohols into the corresponding acetals, which may be effected in the presence of a mercury salt and an acid other than the halogen acids.

It is a well-known fact that acetaldehyde is produced when acetylene is passed into a dilute acid solution in the presence of a mercury salt. There is substantial proof to the effect that acetylene first forms complex intermediate compounds with water and the mercury salt with the simultaneous formation of an acid; and that the acetaldehyde is formed by the subsequent reaction between this intermediate mercury-acetylene compound and the acid produced in the first reaction. Disregarding whatever intermediate compounds are formed with the catalyst, the reaction in its simplest form may be expressed by the equation: $H{-}C{\equiv}C{-}H + 2H_2O \longrightarrow CH_3{-}CH(OH)_2 \longrightarrow CH_3{-}CHO + H_2O$. If we consider the alcohols as analogs of water, the formation of the acetals from the acetylene may be represented in a similar manner: $H{-}C{=}C{-}H + 2ROH \longrightarrow CH_3{-}CH(OR)_2$.

The acetals have been prepared by the reaction of acetaldehyde on the alcohols. Since, however, dry acetylene gas reacts with anhydrous alcohols in the presence of concd. sulfuric acid and a mercury salt to form the acetals, the absence of water as such in the reaction leads us to assume that in this synthesis acetaldehyde is not formed as an intermediate compound and that acetylene functions as anhydrous acetaldehyde.

The Preparation of Dimethyl Acetal.—A mixture of 500 cc. of methyl alcohol, 50 cc. of concd. sulfuric acid and 5 g. of mercuric sulfate was put into a 1 liter flask fitted with a 2-hole stopper, one hole being closed by inserting a glass rod, the other carrying a glass tube. The flask was then tared and connected with a gasometer containing acetylene over water under a pressure of about 1.5 meters of water. The acetylene was washed through concd. sulfuric acid. By removing the glass rod from the stopper the system was swept free from air. The absorption of acetylene was slow at the start, but soon increased to a very rapid rate, which was also greatly increased by shaking the flask and was accompanied by the evolution of heat. When, at intervals the absorption slackened noticeably, the glass rod was removed from the stopper to

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[1] Nieuwland and Vogt, THIS JOURNAL, **43**, 2071 (1921).

allow the escape of foreign gases which gradually accumulated in the flask. The amount of acetylene absorbed was determined by weighing the flask and its contents. When approximately $^2/_3$ of the theoretical amount of acetylene calculated according to the equation, $C_2H_2 + 2\ CH_3OH \longrightarrow CH_3CH(OCH_3)_2$, had been absorbed, the catalyst, which up to this point remained white, began to turn gray. The absorption was continued until the theoretical amount had been absorbed. The liquid remained colorless throughout the reaction. There was no evidence of the formation of aldehyde resins. As the reaction approached completion the odor of crotonaldehyde became evident. In the later runs the reaction was stopped when $^2/_3$ to $^3/_4$ of the alcohol had been used up. To isolate the acetal, the reaction mixture was diluted with approximately an equal amount of water and neutralized with potassium carbonate. The catalyst was removed by filtration. The filtrate was saturated with potassium carbonate, extracted with ether, the extract washed with a neutral solution of calcium chloride, and dried over anhydrous potassium carbonate. The ether was removed by fractionation. The boiling points of methyl alcohol and dimethyl acetal are almost identical. The alcohol must, therefore, be removed as completely as possible by means of calcium chloride; yield, 25–30%.

The catalyst, recovered by filtration, washed free from carbonate, dried and pulverized, was used in 4 successive runs without any apparent diminution in activity. When the reaction was allowed to proceed beyond the point at which a darkening of the catalyst became evident, the recovered catalyst was less effective.

The amount of catalyst was varied in the different runs. The rate of absorption increased with the use of increasing amounts of the catalyst. The use of 5 g. of the catalyst with 500 cc. of alcohol and 50 cc. of acid was found to be sufficient in the case of methyl alcohol. The absorption was not too fast to allow proper washing of the gas through the wash bottle. With suitable shaking, 50 g. of acetylene was absorbed in a period of 3 to 4 hours.

The Preparation of Diethyl Acetal.—Diethyl acetal was prepared in a manner similar to that just described for dimethyl acetal, with the substitution of ethyl alcohol for methyl alcohol. The use of alcohol and concd. sulfuric acid in the ratio of 10 to 1 was found most satisfactory. Both 95% and absolute alcohol dehydrated with calcium carbide were used with success. With 500 cc. of alcohol, 50 cc. of acid and 5 g. of the catalyst, the absorption of acetylene took place at a much slower rate than in the preparation of methyl acetal under similar conditions. The use of an increased amount of catalyst increased the rate of absorption; but even when the amount of catalyst was increased to 50 g. the rate of absorption was lower than with 5 g. in the case of methyl alcohol. With 10 g. of the catalyst and proper shaking, the mixture absorbed 50 g. of acetylene in a period of 6–8 hours. The catalyst showed no signs of darkening until about $^1/_2$ of the theoretical amount of acetylene calculated according to the equation, $C_2H_2 + 2\ C_2H_5OH \longrightarrow CH_3{-}CH(OC_2H_5)_2$, had been absorbed. The odor of crotonaldehyde also developed at this time. When the reaction was continued until the calculated amount had been absorbed, the catalyst turned gray, the odor of crotonaldehyde became stronger and stronger, the liquid turned brown, and toward the end the entire mass turned a dark color as a result of the formation of a black resin. The reaction should, therefore, be discontinued when about $^1/_2$ of the alcohol has been converted into the acetal; yield, 30–35%.

The acetal may be separated like the methyl acetal, but the following procedure gave better yields. The reaction mixture was submitted directly to a vacuum distillation, which was continued until all of the alcohol, water and acetal had passed over. The catalyst that remained behind in the residue was washed free from acid, dried and pulverized for use in a later run. The distillate, a neutral liquid, was saturated with potassium carbonate and extracted with ether. The ether extract was washed with a neutral solution of calcium chloride and dried over anhydrous potassium carbonate. The ether and other remaining impurities were removed by repeated fractionation. In the product obtained from both methods of separation the presence of traces of crotonaldehyde was evident from its odor. Since diethyl acetal and crotonaldehyde have approximately the same boiling point, the separation of these 2 substances cannot be effected by means of fractionation. The odor of crotonaldehyde can be removed to some extent by washing the mixture with a solution of potassium carbonate. This washing process, however, entails the loss of an appreciable amount of the acetal.

Reactions of Acetylene with the Higher Alcohols.—In a manner similar to the one described for the preparation of methyl and ethyl acetals the condensation of acetylene with the higher alcohols was attempted. The reaction mixture darkened as the absorption of acetylene continued. When acetylene was absorbed up to the theoretical amount a black viscous mass was obtained. The separation of the products yielded most of the original alcohol and a small amount of the acetal. Propyl, *iso*propyl, butyl, *iso*butyl, allyl and amyl alcohols all gave a very small yield of the corresponding acetal. The allyl acetal, (b. p., 162°) had an ethereal odor entirely different from the penetrating odor of allyl alcohol. The effect of acetylene on ordinary fusel oil was unusual. The mixture soon thickened into a jelly-like mass and gradually hardened into a solid body resembling hard rubber.

The Halogenation of the Acetals

The Chlorination of Dimethyl Acetal.—When dimethyl acetal prepared according to the process described above was chlorinated at a temperature not above 60°, the products were formaldehyde, monochlorodiethyl ether, small amounts of symmetrical dichlorodimethyl ether, hydrogen chloride, trioxymethylene, and a liquid heavier than water which boiled over a range of 127–138°.

The chlorination was carried out in a flask provided with a reflux condenser. At first the reaction was very vigorous, so that cooling was required. When the reaction was nearly completed the application of heat was required. Starting with 150 g. of the acetal, 130 g. of chlorine had been absorbed in 2$^3/_4$ hours. At this point white crystals of trioxymethylene appeared. Further chlorination caused little gain in the weight of the contents of the flask. The mixture was filtered and the filtrate, upon distillation, evolved formaldehyde and hydrogen chloride, very freely. Between 60° and 100° a small fraction consisting of water and monochlorodimethyl ether was obtained; this compound, upon hydrolysis, evolved methyl alcohol, formaldehyde and hydrogen chloride. The temperature then rose rapidly to 127°, the bulk of the liquid distilled with a gradual rise in temperature up to 138°, and a small amount of a charred residue was left in the flask. This fraction was a clear, colorless liquid with a sharp odor. Upon treatment with sulfuric acid it yielded an almost quantitative amount of monochloro-acetaldehyde and a small amount of dichloro-acetaldehyde.

When the reaction mixture was washed with water before distillation the temperature rose almost immediately to 127°, and the entire volume had distilled when the temperature reached 138°.

This primary product of the reaction is α,β-dichloro-ethylmethyl ether. Its reaction with the sulfuric acid is analogous to the reaction of sulfuric acid on dichlorodiethyl ether as described by Natterer,[2] and gives mono-

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[2] Natterer, *Monatsh.*, 5, 496 (1862).

chloro-acetaldehyde, methyl hydrogen sulfate, and hydrogen chloride thus,

$$CH_2Cl—CHCl—OCH_3 + H_2SO_4 \longrightarrow CH_2ClCHO + CH_3HSO_4 + HCl \tag{1}$$

The formation of α-β-dichloro-ethylmethyl ether from the chlorination of dimethyl acetal takes place thus,

$$CH_3—CH(OCH_3)_2 + Cl_2 \longrightarrow CH_2Cl—CH(OCH_3)_2 + HCl \tag{2}$$

$$CH_3Cl—CH(OCH_3)_2 + HCl \longrightarrow CH_2Cl—CHCl(OCH_3) + CH_3OH \tag{3}$$

The methyl alcohol from (3) accounts for the presence of formaldehyde, monochlorodimethyl ether, trioxymethylene, and symmetrical dichlorodimethyl ether, thus,

$$CH_3OH + Cl_2 \longrightarrow ClCH_2OH + HCl \tag{4}$$

$$ClCH_2OH \longrightarrow CH_2O + HCl \tag{5}$$

$$ClCH_2OH + CH_3OH \longrightarrow ClCH_2OCH_3 + H_2O \tag{6}$$

$$ClCH_2OCH_3 + Cl_2 \longrightarrow ClCH_2OCH_2Cl + HCl \tag{7}$$

$$3ClCH_2OCH_2Cl + 3H_2O \longrightarrow 2(CH_2O)_3 + 6HCl \tag{8}$$

The Bromination of Dimethyl Acetal.—When dimethyl acetal was treated with liquid bromine, considerable heat was evolved, the bromine was decolorized and there was no evolution of hydrogen bromide until after a little over 1 molecular equivalent had been added. The reaction mixture separated into 2 layers, the top layer being about $^1/_3$ of the volume of the lower. The mixture was then heated over a boiling water-bath and more bromine was added until a little over 3 molecular equivalents had been introduced, when the reaction ceased and the bromine was no longer decolorized, even after long-continued boiling on the water-bath. The reaction with the last 2 molecular equivalents appeared to be entirely with the lower liquid layer.

The upper layer was a mixture of formaldehyde, water, hydrobromic acid, methyl alcohol, and monobromomethyl ether. The lower layer was α-monobromo-β-tribromo-ethylmethyl ether, (or the bromohydrin methylate of bromal) and small amounts of the α-monobromo-β-dibromo-ethylmethyl ether and symmetrical dibromodimethyl ether.

The reactions involved in the formation of these products are analogous to the action of chlorine upon the acetal. With the use of chlorine the halogenation stops with the formation of α,β-dichloro-ethylmethyl ether, while with bromine the corresponding α,β-dibromo-ethylmethyl ether is easily brominated to the α-monobromo-β-tribromo-ethylmethyl ether. The first converts the acetal into the dibromo ether and methyl alcohol. The dibromo ether is then further brominated to the tetrabromo-ether, while the methyl alcohol is converted into formaldehyde and monobromodimethyl ether. A small amount of the monobromodiethyl ether is brominated to the symmetrical dibromodimethyl ether.

Complete Bromination.—To 90 g. of methyl acetal in a tared flask fitted with a reflux condenser, was added 85 g. of bromine. The bromine was completely decolorized but no hydrogen bromide was given off. Another 85 g. of bromine was then added, which also was decolorized; there was no evolution of hydrogen bromide until nearly all of this portion of bromine had been added, and at the very end of this addition the reaction mixture separated into 2 layers. With the addition of another 85 g. of bromine, large quantities of hydrogen bromide were evolved and a distinct odor of formaldehyde developed. The addition of a fourth 85 g. of bromine gave a similar result. The reaction slowed and the flask had to be warmed to obtain complete decolorization of the bromine. The addition of a fifth and sixth 85g. portion of bromine was accompanied in each case by the evolution of hydrogen bromide and formaldehyde. After the addition of the sixth portion the bromine was not completely decolorized even upon heating the mixture for an hour on an actively boiling water-bath.

The 2 layers were separated and each was fractionally distilled. The upper layer boiled at 90° and gave off formaldehyde, and the temperature rose gradually to 100°. The small residue remaining in the distilling flask at this time was probably a part of the lower layer which had been dissolved in the upper layer. The distillate from the upper layer was a mixture of monobromomethyl ether and water. Upon hydrolysis it gave formaldehyde, methyl alcohol and hydrobromic acid.

The lower layer upon distillation gave first a small amount of the contents of the upper layer which had been dissolved in it. The temperature then rose rapidly to 148–150° where a small quantity of symmetrical dibromomethyl ether distilled. The bulk of the liquid started to boil a little above 180°, with a violent decomposition, which continued even when the distillation was carried out in a vacuum. The compound was the bromohydrin methylate of bromal. Upon treatment with sulfuric acid it gave hydrogen bromide, methyl sulfuric acid and bromal hydrate, which distilled with the steam and crystallized from the distillate in large white crystals. The crystals were completely decomposed by caustic potash to give potassium formate and almost pure bromoform, boiling sharply at 151°.

Incomplete Bromination.—To 90 g. of dimethyl acetal in a flask, fitted with a reflux condenser, was added 170 g. of bromine. There was a rapid and complete combination with the evolution of heat. At the end of the addition the mixture separated into 2 layers and a little hydrogen bromide was evolved. The upper layer was the same as that from the complete bromination. The lower layers from a number of these experiments were combined and fractionated. A small amount of the dissolved material of the upper layer distilled first; the temperature then rose rapidly and the bulk of the liquid distilled with a slight decomposition at 152–157°. This fraction was α,β-dibromoethylmethyl ether. When it was treated with sulfuric acid monobromo-acetaldehyde, boiling with decomposition at 80–105°, was obtained.

The Chlorination of Diethyl Acetal.—In the preparation of chloral from ethyl alcohol, Fritsch[3] demonstrated that diethyl acetal is an intermediate product in the formation of chloral. If such be the case, then by preparing the acetal from alcohol and acetylene, 1 molecule of acetylene will take the place of both 1 molecule of alcohol and 1 molecule of chlorine, as indicated by the equations, $3C_2H_5OH + Cl_2 \longrightarrow CH_3—CH(OC_2H_5)_2 + 2HCl + H_2O$; $2C_2H_5OH + C_2H_2 \longrightarrow CH_3—CH(OC_2H_5)_2$.

In a study of the halogenation of the acetals it was found that the chlorination of diethyl acetal gave a good yield of chloral. It was further found possible to combine the synthesis of the acetal from acetylene and alcohol with its chlorination into one process, thus eliminating entirely the isolation of the acetal.

Acetylene was first passed into ethyl alcohol in the presence of concd. sulfuric acid and mercuric sulfate. After partial neutralization the reaction mixture was chlorinated and a good yield of chloral was obtained.

Experimental.—Pure diethyl acetal prepared according to the method described above was chlorinated to completion; heat was evolved, and the process proceeded best at 60–70°. The product was treated with concd. sulfuric acid. Hydrogen chloride was evolved in great quantities and the liquid separated into 2 layers. The chloral was isolated from the upper layer by fractionation and then converted into chloral hydrate.

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[3] Fritzsch, *Ann.*, **279**, 288 (1894).

By a similar procedure the product of the action of acetylene on ethyl alcohol, without the separation of the acetal, was converted into chloral. The best yield, about 70%, was obtained by chlorination at a temperature of 60° to 80°.

Summary

1. Dimethyl acetal and diethyl acetal were prepared by passing acetylene into the corresponding alcohol in the presence of concd. sulfuric acid and mercuric sulfate.
2. In the presence of the higher alcohols the acetylene is converted largely into the condensation products of acetaldehyde, other than the corresponding acetals.
3. The rate of absorption of acetylene by the alcohol, acid and catalyst mixture decreases with an increasing molecular weight of the alcohol. It is also more rapid in the case of the normal alcohols than in the case of the secondary alcohols.
4. The rate of absorption of acetylene by the mixture of alcohol, acid and catalyst is proportional to the amount of the catalyst used.
5. The products of the partial and complete bromination of dimethyl acetal and the chlorination of dimethyl and diethyl acetal have been determined.
6. A successful method for the preparation of chloral from acetylene has been developed.

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REDUCTION PRODUCTS OF BENZALPINACOLINE

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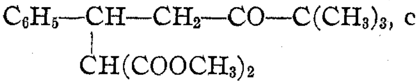
In the course of an investigation of dimethyl β-phenyl-γ-trimethylacetyl ethyl malonate,  $C_6H_5\text{—}\underset{\displaystyle CH(COOCH_3)_2}{\underset{|}{CH}}\text{—}CH_2\text{—}CO\text{—}C(CH_3)_3$, carried on by one of us[1] certain new compounds were obtained which were thought to be reduction products of benzalpinacoline. This surmise was shown to be well founded, for the same substances were later prepared by subjecting benzalpinacoline to the action of aluminum amalgam. At the time, however, no attempt was made to identify them further, or to determine their structures.

As a typical α,β unsaturated ketone, and consequently one possessing the conjugated system, —CH=CH—C=O, benzalpinacoline would be expected[2] to yield with reducing agents, a saturated ketone, A, a saturated

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[1] E. P. Kohler and G. A. Hill; results not yet published.

[2] Thiele, *Ann.*, **306**, 87 (1899).