

ACROLEIN
and
CERTAIN OF ITS DERIVATIVES

Thesis
by
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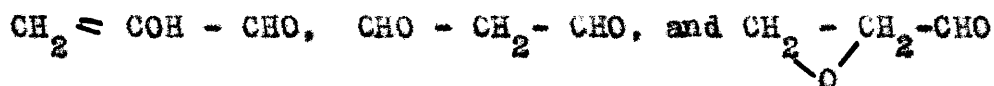
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INTRODUCTION

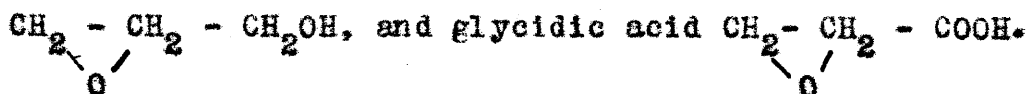
In connection with a theory as to the mechanism of alcoholic fermentation, certain of the unknown trioses were desired in order that their properties might be studied. Those compounds which were of particular interest were:



Of these the last was selected as offering greatest possibilities.

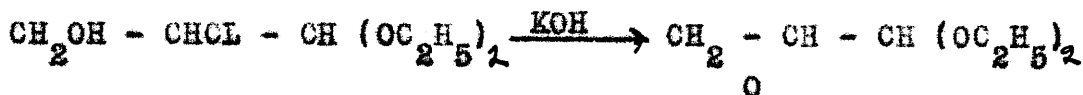
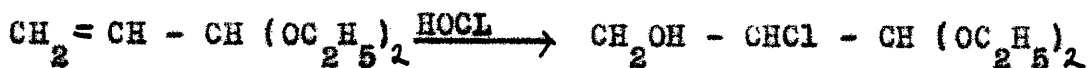
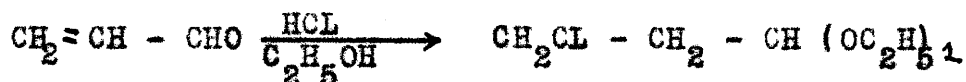
By a rather long syntheses Wohl (1) had prepared the acetal of the desired compound, but mentioned no attempt to hydrolyze the acetal. The object of this study was therefore two-fold, first to repeat the work of Wohl, and second to devise, if possible, a more direct method of preparing this unknown substance.

For convenience in the discussion it is purposed to name this compound glycidic aldehyde, by analogy to glycid



DISCUSSION

Schematically Wohl's synthesis of the glycidic aldehyde acetal may be represented as follows:



In repeating this work advantage was taken of the more recent publications of Moreau (2) on acrolein, and Witzemann (3) on the preparation of glyceric aldehyde. Moreau claimed a 70% yield of acrolein from glycerol by employing a mixed catalyst of potassium sulfate and bisulfate, using an iron container equipped with a stirrer. As this work was on a much smaller scale it was necessary to employ glass vessels and the yields were much smaller. The process is nicely adapted to small scale work, however, as the catalyst is easily secured and standard apparatus may be employed. The method is less troublesome than that of Witzemann, (4) using anhydrous magnesium sulfate as catalyst and on the laboratory scale gives about the same yield. The best results were secured by employing a good stirrer and allowing the temperature to rise rapid-

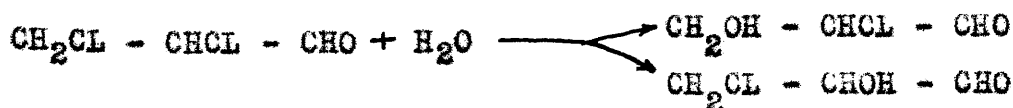
ly to 200°. At this temperature considerable charring occurs, but the yield is much higher than when lower temperatures or slower heating are employed.

The procedure of Moreau for stabilizing the acrolein was tried and found to work well. The crude acrolein, treated with sodium bicarbonate^{rbonate}, was kept for several months without appreciable polymerization in the ice box. The crude acrolein was purified by drying with calcium chloride and distilled from a water bath. The purified acrolein was stabilized by the addition of a small amount of pyrogallol and could then be kept at least a week in the ice box.

Following Witzemann's procedure the acrolein was converted to the ~~trichloro~~³ propionic aldehyde diethyl acetal. This proceeds smoothly and the yield is very good. The conversion of this product to acrolein acetal was next attempted. Due to the moisture in the air it was impossible to prepare the 60 mesh potassium hydroxide in a dry condition and as Witzemann had previously observed, the yields were very poor. In an attempt to remedy this difficulty both sodium ethylate and soda lime were tried. The former produced almost no unsaturation, and the latter too little to be practicable. As this step was one of the earliest in the synthesis, and as the yields were so low it became obvious that the method was hardly profitable. Instead of continuing along this line we therefore examined other possible methods.

The first possibility which occurred was based on the work of Taylor, MacMullen and Gammal (5) on hypochlorous acid and hypochlorites. They found that on shaking a carbon tetrachloride solution of alcohol with an aqueous solution of hypochlorous acid that a practically quantitative yield of ethyl hypochlorite was secured with almost no oxidation. This led to hope that in a similar manner a carbon tetrachloride solution of acrolein might add hypochlorous acid at the double bond much more rapidly than it was oxidized. Several trials indicated, however, that though the hypochlorous acid rapidly disappeared, that almost no additional product was obtained. Although oxidation is thus much too rapid, yet it is true that in one case a small yield of additional product did result.

The other method which appeared to offer possibilities was the partial hydrolysis of the dichlor or dibrom addition product. Thus no matter which of the halogens were removed,



the product should be capable of being converted to the desired glycid by the removal of HCL. The literature on the subject is quite meager. Moreau found that heat was evolved on treating acrolein dichloride with water, but did not further investigate the change. The dichloride was therefore prepared and treated with water under different conditions. In every case however the product was identified as chlor

acrolein $\text{CH}_2=\text{CCL} - \text{CHO}$. This has previously been prepared only by heating the dichloride for some time with sodium acetate solution. Our results would indicate that the removal of HCL is relatively easy. Even in strong HCL the dichloride decomposed in this same fashion.

Recourse was then had to acrolein dibromide, but a trace of moisture in the preparation was sufficient to cause the decomposition into Brom acrolein.



This would not appear to confirm the result of Lobry de Buyn (6) who thought glyceric aldehyde to be formed on hydrolysis of the dibromide. Wohl (7) however, found only complex condensation products on hydrolysis with barium hydroxide solution.

Although none of the above methods leads to useful results, two alternative methods still appear available. The first is the addition of hypochlorous acid under anhydrous conditions, and the second the preparation of $\text{CH}_2\text{Cl} - \text{CHCl} - \text{CH}(\text{OC}_2\text{H}_5)_2$ and its hydrolysis in alkaline solution to either,



This work was carried out at the suggestion and under the direction of Dr. A. L. Raymond.

Acknowledgement is also made to Professor H. J. Lucas for suggestions, especially as to the experimental.

EXPERIMENTAL

The Preparation of Acrolein.

1. 400 gm. of K_2SO_4 and 80 gm. of $KHSO_4$ were intimately mixed and placed in a 3 liter balloon flask. To this was then added 120 gm. of glycerol and the mass well mixed. This flask is equipped with a stopper containing a thermometer, dropping funnel for the introduction of additional glycerol, and a vapor tube. The vapor tube leads into a short condenser and into a 1 liter balloon flask, equipped with a thermometer, containing about 100 gm. Na Cl and heated by a water bath to 70° . Thence the vapors are led into a long well cooled condenser and into an ice cooled receiver. The reaction flask was heated by ~~acid~~ of several burners to about 200° . After a reasonable length of time however, only very small traces of acrolein were found in the receiver and not a sufficient quantity to encourage the repetition of this procedure.

2. In this attempt, instead of using K_2SO_4 and $KHSO_4$, the corresponding quantities of Na_2SO_4 and $NaHSO_4$ were employed. This method apparently did not fare any better than the previous and was obviously discarded.

3. The quantities of the dehydrating catalysts were reversed, that is 400 gm. of $KHSO_4$ and 80 gm. of K_2SO_4 were

taken, with 120 gm. of glycerol as before. This mixture was heated slowly with several burners. At about 130°, the mixture suddenly burst open and began to evolve large quantities of dark brown foam. The flames were immediately reduced and the temperature allowed to drop to 90°. Full heat was then again applied, with increasing foaming. At this point some liquid passed over into the first receiver, and of this a few drops collected in the final receiver. The mass could not be gotten to 200° with the burners available, and only a small amount of the liquid was obtained. It was evident however that the reaction was progressing favorably.

4. In this attempt the flask was heated with the aid of several Meker burners. While the yield of acrolein was appreciable for a short time, yet the mass soon charred and the yield decreased rapidly.

5. The mixture was now heated slowly to prevent charring until the temperature of foaming was reached, this assisting in producing a reasonable circulation which is necessary. Above this temperature all heat was applied and the additional glycerol slowly admitted. This method gave a fairly good yield of acrolein, but as the previous trial after proceeding nicely for about two hours begins to char badly, and has to be discontinued because the charring on the flask prevents circulation and induces more charring.

The crude acrolein accumulated during these experiments was combined and treated with NaHCO_3 . After fractionation a yield of 190 gm. of acrolein (51° - 53°) was obtained. This was soon used up and a new quantity was desired. The apparatus was changed in that the reaction flask was increased to 5 liters and equipped with a motor driven glass stirrer.

6. The charge in the flask consisted of 133 gm K_2SO_4 and 666 gm of KHSO_4 and 200 gm glycerol. The mixture was slowly heated and, as soon as liquid enough, the stirrer was started. The mixture has the favorable quality of becoming quite fluid at a low temperature and is fairly easily agitated in this manner. As the temperature reached 150° violent foaming took place and the vapors began to pass out very rapidly. Glycerol was now added at a corresponding rate as the vapors condensed and the temperature raised to 190° - 200° . However it was soon found that the higher the temperature the better the yield of acrolein with time, but the mixture also had a tendency to develop gas bubbles at the hot glass surface and to char. These char spots immediately increase in size and prevent the stirring action to a serious degree. After a time the entire mass became sticky and tarry, in which the stirrer broke off the paddle. After 500 gm of glycerol had been added, the heating was continued until no more vapors came off at 250° . The crude acrolein was treated with NaHCO_3 and separated from the excess water.

| | | |
|----------|---------------------------|--------|
| Results: | Glycerol added, 200 + 500 | 700 gm |
| | Acrolein theoretical | 425 " |
| | Acrolein crude | 192 " |
| | Yield | 45% |

7. Another run with the same apparatus, using 160 gm K_2SO_4 , 800 gm $KHSO_4$ and 240 gm glycerol showed the following facts. By careful watching and control of the heat, charring can be reduced to a negligible degree. The mixture, however slowly browns, indicating some decomposition. This has a deterrent effect on the acrolein yield. It therefore is very apparent that the higher temperatures give a much better yield, the optimum being at 200° . However at this temperature the charring becomes serious even when stirred vigorously with a good stirrer. The stirrer used consisted of the familiar tee glass form, as large as would permit insertion into the flask. If a stirrer could be secured which would cover the entire heating surface and thus break up the char spots, the problem would be solved. Since this implies special apparatus, the best yields in standard apparatus will be obtained by the aid of high speed, effective stirrers in small flasks and small quantities of catalyst. This is due to the fact that the openings in small flasks are correspondingly larger than those of larger flasks. In cleaning the reaction flask, the soluble matter is first removed with the aid of warm water, then very concentrated sodium

hydroxide solution is boiled in the flask. The caustic aids effectively in the removal of the tarry matter.

Results:

| | | |
|----------------------|------------|---------|
| Glycerol used | 240 + 1000 | 1240 gm |
| Acrolein theoretical | | 752 " |
| Acrolein crude | | 220 " |
| Yield | | 29% |

Properties of Acrolein.

Crude has a light yellow color. The purified is colorless. Pure acrolein boils at 52.5°C at 760 m.m., has a decidedly pungent odor, and a very aggressive action on the mucous membranes and eyes, producing tears and great discomfort. The reactions involving its use and preparation are therefore best carried out in a hood or well ventilated position.

Preparation of B chloro Propionic Aldehyde Acetal

1. 380 gm of absolute ethyl alcohol were saturated at 0° with dry HCL gas, prepared by dropping conc HCL into conc. H_2SO_4 and passing the resulting gas through conc H_2SO_4 in a wash bottle. The flask containing the saturated alcohol is surrounded by an ice bath and equipped with a stopper, containing a dropping funnel and a slot in the side for the removal of the trapped air. Through the dropping funnel 190 gm of acrolein were slowly added with constant agitation. After the addition of all of the

acrolein the mixture was agitated for about an hour and then allowed to stand. The alcohol and acetal form distinct layers and were separated with the aid of a separatory funnel. The acetal was then treated with NaHCO_3 until neutral to moist litmus. The mixture of Na Cl and acetal was filtered in a Buchner funnel under strong suction and washed with a little absolute alcohol. The filtrate was further washed several times with cold water, and dried over night with K_2CO_3 . The acetal was distilled at 8 m. m. and came over at $54^\circ - 56^\circ$.

Results:

| | |
|---------------|--------|
| Acrolein | 190 gm |
| Alcohol | 380 " |
| Acetal theory | 220 " |
| Acetal yield | 560 " |
| Yield | 26% |

Preparation of Acrolein Diethyl Acetal

1. 50 gm of the chlor acetal were placed in a 250 c.c. R.B. flask and 100 cc of 60 mesh dry KOH slowly added. The mixture was well agitated during this addition. After all of the KOH was added the mixture was heated in a paraffine bath to 200° . Some liquid came over at $76^\circ - 80^\circ$, the boil point of the alcohol, while the remainder at 150° , apparently some of the unchanged acetal. Considerable difficulty was met in this procedure due to the powdering of the KOH

to 60 mesh. KOH is very hygroscopic and irritating to handle while powdering. The screening was more difficult. The screen would take a charge of the powder, and immediately clog up, due to the KOH becoming moist. Apparently from the results the KOH employed was not dry enough, resulting in the failure.

2. A modification of the procedure was made by the use of sodium ethylate. 24.5 gm of Na were dropped into 150 gm of absolute alcohol and refluxed until all was dissolved. The mixture was then cooled in an ice bath and the acetal slowly added. After allowing to stand for an hour the mixture was fractionated as before in a paraffine bath. The alcohol came over at 70° - 80°, but no intermediate fraction until 150°, which shows the unchanged acetal. Evidently the ethylate while easy to prepare and anhydrous does not lend itself to this reaction.

3. Another modification employed was the use of soda lime Ca(OH)_2 (NaOH). 100 gm of 60 mesh soda lime was added to the acetal. This addition showed no evidence of heat. On heating in the paraffine bath to 200°, no noticeable quantities of product were obtained and no reaction was observed. On dismantling the apparatus it was found that the unchanged acetal was held in the powder. This indicated that too great an excess of soda lime had been used, about 6 fold.

4. Accordingly a 100% excess was used. 70 gm of the acetal were treated in this way. The mixture of acetal and soda lime formed a homogenous cream colored moist ball in the flask. The mass was heated slowly in a paraffine bath, to allow the heat to penetrate into the entire mass evenly. At 120° the mass suddenly darkened and gave out vapors at 125° at a very rapid rate. Apparently the reaction was proceeding in the right direction, heating was continued until the mass was charred.

5. 49 gm of the acetal were treated with 12.5 gm of 60 mesh CaO. This mixture behaved just as the soda lime trial and gave the same results.

The yields from the soda lime ~~and~~ CaO treatment were combined and fractionated. The liquid boiled at 84°, with a vigorous decomposition, turning the entire liquid brown. This may have been due to the presence of some of the undecomposed chlor acetal. HCL was noted in the last fraction coming over just before the end of the distillation.

Hypochlorous Acid and Acrolein

1. 25 gm of CaCO_3 were placed in a liter graduate filled with water. The graduate was provided with a motor driven stirrer and a tube for introducing the Cl_2 into the solution. The chlorination was continued until all of the CaCO_3 had dissolved. A quantity of CaCO_3 was now added, until the solution remained turbid after standing some time. The solution

was then filtered to remove the excess carbonate. 500 cc of CCl_4 and 22 cc of acrolein were thoroughly mixed and shaken with the HOCL solution. This action produced an appreciable warming. After being well agitated for some time the CCl_4 layer was removed, and the aqueous layer extracted with 200 cc of Ether. The aqueous layer after the extraction by CCl_4 and ether did not smell of HOCL and was rejected. Both extractions were dried with anhyd. Na_2SO_4 over night and evaporated to about 50 cc and combined. This residue was then vacuum distilled. On distillation the CCl_4 came over in copious quantities, however only about 1cc of liquid came over near 118° , the boil. point of the aldehyd at 30 m.m. This was a light brown heavy liquid, with an odor resembling cloves. The yield is negligible. Acrolein was not noticed in the distillate.

2. On the belief that perhaps a large excess of Cl_2 had been employed, the run was repeated, the CaCO_3 solution being chlorinated until about .5 n in HOCL as determined by iodine titration. 25 gm of acrolein were mixed with 500 cc of CCl_4 . As the acrolein was added to the CCl_4 a small whitish precipitate was noted. The CCl_4 solution was then mixed with the HOCL solution, (the carbonate having been removed by filtration.) The mixture was well agitated for some time, ice added to keep the temperature from rising too much. It was allowed to stand over night

and then separated. The water solution was tested for HOCL and showed a positive result. The CCl_4 layer was evaporated to 50 cc and the vacuum distilled, but no distillate was obtained in the desired region. Either the acrolein had polymerized before contact or had been oxidized to the acid by the HOCL.

3. The phenomena of the whitish precipitate in the mixing of acrolein and CCl_4 was investigated and found to be due to the use of moist acrolein and moist CCl_4 . When both agents were dry the action was not observed, and a colorless solution resulted. Another run on 25cc of acrolein and 500 cc CCl_4 was made using a .5 n solution of HOCL. Heat was again noted. The mixture was well shaken and allowed a 30 minute contact and then separated. The water layer had lost its yellow color, but still showed some HOCL. The CCl_4 layer was dried with anhyd K_2CO_3 and was left over night. The solution had a light yellow color and was quite clear. The CCl_4 was now evaporated to 40cc. and the vacuum distilled at 30 m.m.. A dark brown residue resulted. The odor of acrolein was noted in both the water layer and in the CCl_4 distillate.

Preparation of Dichlor Acrolein

1. 100 gm of purified acrolein was dissolved in 225 gm of CCl_4 and placed in a flask cooled by means of an ice bath.

Cl_2 dried by passing through conc. H_2SO_4 is slowly led into the acrolein until 127 gm are absorbed. During the addition a large quantity of heat was given out. The chlorination proceeded very smoothly and at a fairly rapid rate. The mixture of Dichlor ~~and~~ acrolein was then evaporated and distilled at 14 m. m., $47-50^\circ$.

Results:

| | |
|----------------|--------|
| Acrolein | 100 gm |
| Dichlor theory | 226 " |
| Dichlor yield | 195 " |
| Yield | 86.5% |

Properties.

The Dichlor is a slightly yellow heavy liquid, fairly mobile. It has a slight not unpleasant odor. When in contact with water it evolves much heat and gives off a slight odor, with very irritating vapors. This was especially noticeable when cleaning apparatus which had contained the Dichlor.

Hydrolysis of Dichlor Acrolein

1. 20 gm of the Dichlor was placed in a flask to which was then added 20 cc of water. A great deal of heat was soon noticed, more so during the first part of the dilution than later. After cooling ~~down~~ the mixture was extracted by ether. The ether extract was then evaporated and the residue vacuum distilled at 30 m.m. A liquid distilling

at 57° results, only in small quantities. This product did not reduce silver, and gives off HCL fumes. It has a profoundly irritating odor and soon becomes very viscous on contact with air. It evidently does not have any of the properties of the original nor of Oxy chlor propion aldehyde, $\text{CH}_2\text{Cl} - \text{CHOH} - \text{CHO}$. On investigation of the literature it was found that the boiling point of chlor acrolein, $\text{CH}_2 = \text{CCl} - \text{CHO}$, corresponds to the boiling point of the product.

2. 20 gm of Dichlor and 10 cc of water were next tried. this was then treated with CaCO_3 until no more reaction was noted. The *sludge* was filtered off and the filtrate extracted with ether. After the evaporation of the ether, the solution was distilled under 30 m.m. and yielded a product at 57°.

3. In the next experiment 20 gm of the Dichlor and 100 cc of 12 n HCL were mixed in a 200 cc balloon flask. Much heat was evolved on mixing. The resulting liquid was of a light yellow color and was extracted with about 200 cc of ether. The ether was evaporated and the residue distilled under vacuum with no result.

4. Employing the same treatment, 20 gm of Dichlor and 50 cc of 6n H_2SO_4 were mixed, the mixture evolving very little heat, but on refluxing the color of the solution first darkened, became a dark brown. The mixture was ex-

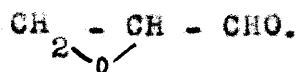
tracted as before with 200 cc ether, the ether evaporated, and the residue distilled at 30 m.m. A sticky tarry residue refusing to distill resulted. The H_2SO_4 had evidently caused the condensation of the aldehyde.

Preparation of Dibrom Acrolein

1. 107 gm of purified acrolein was dissolved in 500 cc of CCl_4 . The acrolein solution was placed in a 1 liter balloon flask surrounded by ice and the Br_2 ^(97 gm in 250 cc CCl_4) ~~had been~~ added slowly. The reaction proceeds along very nicely with evolution of heat. When all of the Br_2 had been added the mixture retained a slight color of the Br_2 indicating a slow reaction at the end. The CCl_4 was now distilled off. Copious fumes of a choking nature began to evolve and issue from the apparatus. The color of the solution changed from a light orange to a light green and then to a light red. On distilling the product a small amount came over below 70° at 25 m.m. The main product came over steadily at 75° - 85° at 25 m.m. It was a very heavy oily liquid, and carries with it the already described fumes, and is of a slight dark yellow color. On investigation of the literature that the constants of the Brom acrolein $CH_2=CHBr - CHO$ agree very well with those of the product. Evidently the slight amount of moisture in the CCl_4 and Br_2 was sufficient to catalyze the reaction to the unsaturation of the compound.

SUMMARY

1. Acrolein and several of its derivatives have been prepared in an endeavor to synthesize glycidic aldehyde



2. It has been found that in contact with water, hypochlorous acid does not add appreciably to the double bond in acrolein.

3. It has been found that the hydrolysis of acrolein dichloride does not readily occur, but that unsaturation to form chlor and brom acrolein predominates.

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