

ALDEHYDES AS STARTING MATERIAL FOR THE SYNTHESIS OF ORGANIC COMPOUNDS

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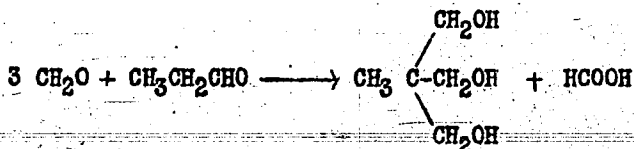
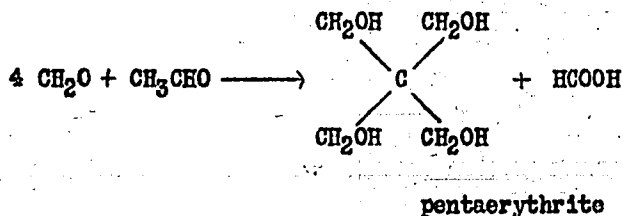
(Meeting on methods of organic chemistry, March 21, 1941)

(The paper discusses the use of aldehydes as starting materials for various organic syntheses. The presentation is of a general nature and does not discuss details of processes. The following items are abstracted from the paper since they appear to be of interest and partly present new processes and products.)

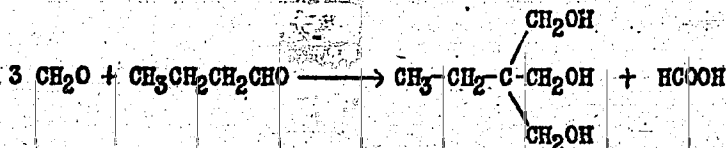
A condensation reaction which has become important is the condensation of formaldehyde with acetaldehyde to pentaerythrite. Similar condensations, e. g. 3 moles formaldehyde with propionaldehyde to trimethylolethane, or formaldehyde with butyraldehyde to trimethylolpropane, give compounds which are important because they can be used as substitutes for glycerine.

Another interesting reaction of formaldehyde with a compound with a reactive methylene group is represented by its condensation with nitromethane to nitrotrimethylolmethane which can be reduced to aminotrimethylolmethane. These reactions are given in the following table:

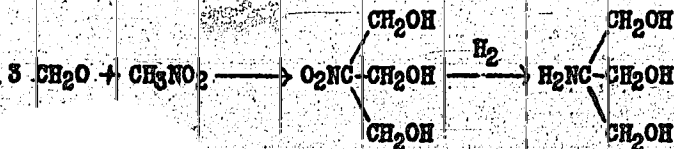
Table 1



trimethylolethane



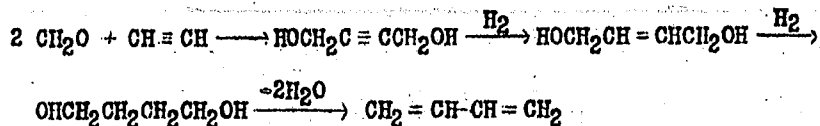
trimethylolpropane



nitrotrimethylolmethane      aminotrimethylolmethane

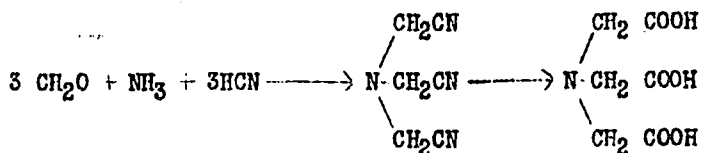
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Another type of formaldehyde condensation is the reaction of 2 mols formaldehyde with acetylene to butynediol, a condensation which takes place in the presence of certain catalysts, especially copper catalysts and which has been found by Dr. Reppe. The product can be further hydrogenated yielding, at first, butenediol and then butanediol. 1,4-Butanediol splits off 2 mols. of water and thereby is converted into butadiene.

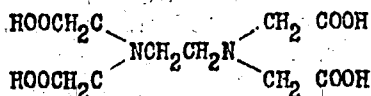
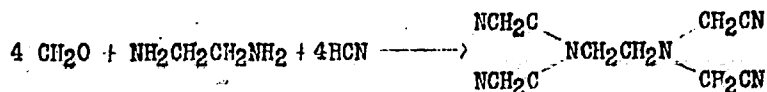


Condensation of 3 mols. of formaldehyde with 1 mol. ammonia and 3 mols. HCN leads to the trinitrile of nitrilotriacetic acid which can be hydrolyzed to nitrilotriacetic acid. The same reaction using 4 mols. formaldehyde, 4 mols. HCN and 1 mol. ethylenediamine yields ethylenediaminetetraacetic acid. These two compounds are interesting because they can form soluble calcium compounds and are, therefore, important in the manufacture of detergents. The compounds which make it possible to use soap in hard water are sold under the name of "Trilon A" and "B". Table 4, shows the reactions by which these compounds are formed and also their structures:

Table 4

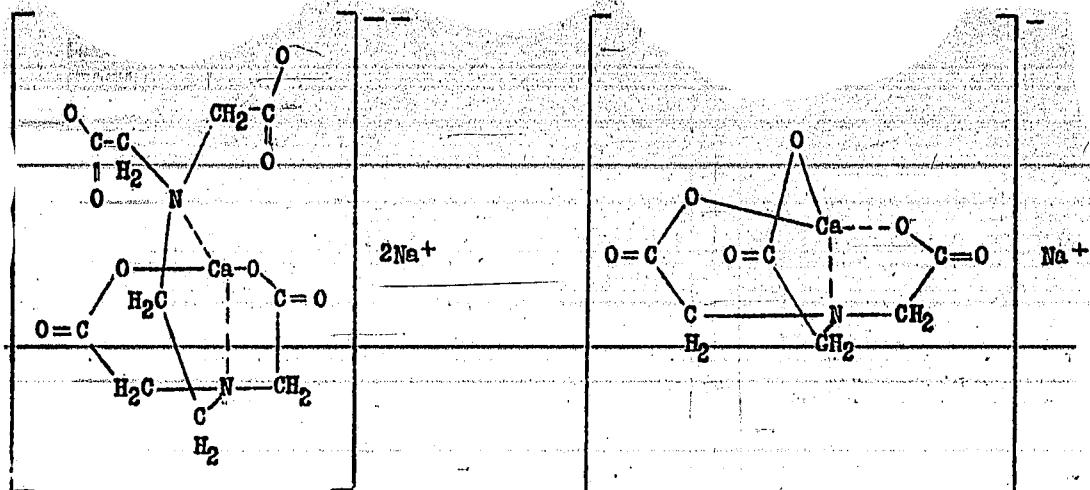


nitrilotriacetic acid, Trilon A

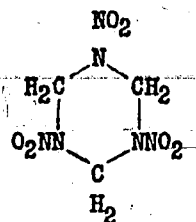


Ethylenediaminetetraacetic acid, Trilon B

(Over)



The reaction of formaldehyde with ammonia leads to hexamethylenetetramine which by nitration gives the explosive hexogene,



Of the reactions of acetaldehyde aldolization is of importance. The aldol is reduced to 1,3-butyleneglycol from which butadiene is obtained by splitting off 2 mols. of water.

Butyraldehyde can be prepared from the aldol by dehydration and hydrogenation. The butyraldehyde can be further oxidized to butyric acid. The butyraldehyde can also be reduced to butyl alcohol. Butyraldehyde also can be used to form an aldol from which ethylpropylacroleine is obtained which can be reduced to ethylhexaldehyde and further to ethylhexanol from which octylic acid (caprylic acid) can be made by oxidation.

Condensation of acetaldehyde with ammonia and HCN yields the nitrile of  $\alpha$ -aminopropionic acid from which, by hydrolysis,  $\alpha$ -aminopropionic acid is obtained; this acid is important because its sodium salt is used in the Alkaid process for the purification of technical gases by removal of  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . Isohexaldehyde and isohexaldehyde are available from the corresponding isoalcohols which are obtained as by-products in the isobutanol synthesis from CO and hydrogen. These alcohols can, on the one hand, be converted into the aldehydes, on the other hand they can be converted to the corresponding isoacids by fusion with alkali; the acids are important in the chemistry of solvents, plasticizers and dryers. Higher alcohols can be obtained by reacting olefins with CO under pressure in the presence of certain catalysts; in this case the carbon monoxide adds to the olefins and yields straight-chain and branched aldehydes which can be reduced to the corresponding primary alcohols.

The high-pressure hydrogenation of sugars is also of importance. In this reaction fission of the molecules into 2 parts with 3 carbon atoms each takes

place simultaneously with the reduction of the aldehyde groups. A mixture of glycerine and 1,2-dihydroxypropane is obtained by hydrogenation at high pressure of a sugar solution in the presence of hydrogenation catalysts. This product is used as a glycerine substitute and is sold under the name of "Glycerogen".

An interesting group of compounds is obtained by reacting formaldehyde with polyvinylalcohol. In this way polyformals are obtained which are sold under the trade name "Motital" and are used for the manufacture of foil, non-shattering glass and for injection molding.

Treatment of regenerated cellulose (synthetic textile fibers, rayon) with formaldehyde is used to improve its wet strength. The treatment is carried out by reacting the synthetic fiber with formaldehyde in the presence of acidic catalysts at higher temperatures. The reaction must be controlled very carefully in order to avoid damage to the fiber by acid. The process is further studied in order to circumvent loss in elasticity as a result of the treatment.

Treatment of synthetic fibers and of cotton with a urea-formaldehyde plastic which is formed in the fiber is practiced in order to increase the resistance of the finished fabric to creasing. The chemistry of this reaction and how the plastic improves the properties of the fiber has not been elucidated as yet.