

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF KETO-ALCOHOLS

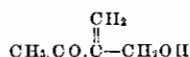
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It is known that by reacting ketones with formaldehyde, keto-alcohols may be obtained but all the processes disclosed in the biography do not allow the obtention of higher yields and pure products.

In fact by condensation in the presence of basic substances, other products other than keto-alcohols are formed, i. e. from acetone are obtained diacetone-alcohol, phorone and homologues, formoses and further products of condensation or resinification. In order to lower the formation of resins, somebody has suggested to operate in the presence of a great excess of ketone, but in such conditions the formation of products of polymerization of ketones and other secondary reactions may not completely be avoided.

By the present invention it is instead possible to obtain keto-alcohols with an high yield. E. g. starting from acetone, keto-butanol 3.1 (known also under the name of acetoethyl alcohol or methoxy ethylketone) $\text{CH}_3\text{CO.CH}_2\text{CH}_2\text{OH}$ may be obtained with a practically quantitative yield. The same process, when effected by the use of greater proportion of formaldehyde as will thereafter be disclosed, allows the obtention of methylen-ketobutanol (2 methylen-3.1.ketobutanol)



instead than ketobutanol 3.1.

The process is effected by employing a diluted aqueous solution of ketone and formaldehyde in the presence of a given concentration of hydrogen ions and within given intervals of temperature.

The pH of the solution must be kept during the condensation below 10 and preferably between 8 and 9. For lower concentrations of hydrogen ions secondary reactions are developed; while for higher concentrations the reaction becomes very slow.

The temperature must be kept below 50°C and when it is desired to obtain only keto-butanol by condensation of acetone with formaldehyde it is convenient that the same be kept between 25°C and 32°C, while it may preferably be kept between 35°C and 40°C when it is desired to obtain methylenketobutanol.

Under this conditions it is possible to operate with equimolecular concentrations of acetone and formaldehyde, but a slight excess of acetone is not harmful as it may be completely recovered. Even when operating with equimolecular concentrations secondary reactions are practically eliminated. In the presence of an excess of formaldehyde till a proportion of 2 molecules to 1 mole-

cule of acetone and for slightly higher temperatures, the reaction proceeds with formation of methylenketobutanol, but also under these conditions the formation of resins and other secondary reactions is eliminated.

The concentration of the aqueous solution of acetone may vary within broad limits and e. g. it may range between 30% to 70% when operating with a solution of formaldehyde at 30%+40%.

It could also be possible to operate with more diluted solutions but practically, in order to shorten the time of reaction, it is convenient to operate with concentration of acetone at about 50%.

Of no importance is the nature of the condensation medium (soda, potash, magnesia, lime, borax, a.s.o.), provided that substances which do not readily react with aldehyde and acetone be used and the pH value results between the above mentioned limits.

The speed of reaction depends exclusively on the concentration of the oxidriles ions and on the temperature; when operating with a pH between 8.5+9 and at 30°C, the reaction is completed in about 4 hours.

By slightly increasing the temperature, the reaction is more rapid but small quantities of methylenketobutanol are formed. Methylenketobutanol is prevalent also when, besides than operating at a higher temperature, an excess of formaldehyde is used.

When condensation is completed the solution is neutralised and the separation by distillation of ketoalcohols from water may be carried out. After elimination of water, the vacuum distillation may be effected and e. g. ketobutanol and methylenketobutanol completely distill without leaving any residue.

Without further treatment and purification the neutral or acid solution of ketobutanol and methylenketobutanol may be hydrogenated into butylenglycol 1.3 and 2. methylbutylenglycol 1.3 respectively.

The mentioned process may be of importance in the manufacture of synthetic rubber for the fact that butylenglycol 1.3 gives, by dehydration, as known, butadiene and methylbutylenglycol gives, even by dehydration, isoprene.

The same processes may also be of interest in the manufacture of explosives for the fact that glycols obtained by reduction of ketoalcohols may give by nitration nitric esters which possesses very interesting properties as explosives.

Other higher ketoalcohols supply the corresponding glycols.

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