

The Texas Company

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The Constitution of The Oxo Alcohols

The additive combination of carbon monoxide and hydrogen with cracked olefins, which contain, according to previous studies made in Ludwigshafen, Oppau and Leuna, mostly a terminal double bond, leads after hydrogenation of the reaction product to alcohols; these alcohols have a melting point which is considerably lower than the melting point of the corresponding n-fatty alcohols. Also the fatty acids prepared by alkali fusion of the oxo alcohols have a very low melting point. The soaps prepared from these fatty acids differ from the soaps derived from the n-fatty acids: their solubility is much greater. These properties of the oxo products led to the assumption that the oxo products are not only mixtures consisting of straight chain and α -methyl branched compounds, but that more extensively branched compounds are present as well.

The tridecyl alcohol prepared from n-dodecylene with terminal double bond, by means of the oxo reaction, was examined by the ozonization method; it was found that the product is a mixture of isomeric alcohols, consisting only of 40% n-alcohol, whereas the other 60% are made up by α -alkyl branched alcohols (dialkyl ethanols).

It was further established that, in the component consisting of the branched compounds, the concentration decreases with in-

creasing size of the alkyl radical. The α -alkyl branched alcohols could, with the exception of the α -methyl branched ones, only have been formed from the olefins. This leads to the assumption that during the reaction a migration of the double bond takes place.

The double bond shift in the olefins with terminal double bond could be determined also directly. It was found that, in the absence of water-gas and in the presence of cobalt carbonyl, a shift of the double bond occurs at already relatively low temperatures (Ref. No. 13 662, J 73 149 IVd/120 und. Ref. No. 13 972, J 74 240 IVd/120).

At 150°, in the presence of Fischer synthesis catalyst and under 100 atm. carbon monoxide pressure, olefin isomers of a dodecylene in almost equal amounts were formed in a one hour experimental period. The position of the double bond was determined by the ozonization method.

~~The fact that during the course of the oxo-reaction not all the alcohol isomers are formed in equal amounts may be explained as follows: during the shift of the double bond, also a saturation of the double bond occurs because carbon monoxide and hydrogen combine with the product. Thus, the shift of the double bond and the oxo reaction may be regarded as two competing simultaneous reactions. The oxo reaction seems to have a faster rate.~~

The presence of nickel carbonyl does not cause a double bond shift. This is to be noted in connection with the fact that this nickel carbonyl is also ineffective for the oxo synthesis.

Summary

In the oxo synthesis, with a straight chain olefin contain-

ing a terminal double bond, 40% straight chain alcohols and 60% branched alcohols are formed. This is caused by a migration of the double bond, which in turn is due to the presence of cobalt-carbonyl. The branched alcohols are mostly α -methyl branched alcohols, besides α -alkyl branched alcohols. The amount of isomeric α -alkyl branched alcohols decreases with increasing size of the alkyl radical.

Signed:

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