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Abstract

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PREPARATION OF CERTAIN PRIMARY ALCOHOLS THROUGH ORGANOALUMINUM COMPOUNDS

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In connection with the appearance in the literature (^{1}) of an indication of the possibility of obtaining alcohols through organic compounds of aluminum, we investigated a set of reactions permitting the conversion of α-olefins into primary alcohols according to the schemes:

$$1)\quad \mathrm{R{-}CH{=}CH_2 + al + H \rightarrow R{-}CH_2{-}CH_2{-}al}\quad (\mathrm{I})$$

$$2)\quad (\mathrm{I}) + \mathrm{O_2} \rightarrow \mathrm{R{-}CH_2CH_2{-}O{-}al}\quad (\mathrm{II})$$

$$3)\quad (\mathrm{II}) + \mathrm{H_2O} \rightarrow \mathrm{RCH_2CH_2OH + al(OH)},\quad \text{where al} = 1/3\,\mathrm{Al}$$

Reaction 1 was carried out by us with 2-methylpentene-1 and 2-ethylhexene-1 as examples, which were prepared by dimerization of propylene and n-butylene. The aluminum trialkyls obtained from these olefins, as well as triethylaluminum synthesized by another method, were oxidized with air to alcoholates, which were hydrolyzed to the corresponding alcohols. In a specially designed experiment on the oxidation of tridecylaluminum at low temperature, it was shown that the reaction proceeds through the stage of formation of a peroxide compound, which, apparently as a result of intramolecular rearrangement or interaction with an aluminum alkyl, is converted into an aluminum alcoholate:

$$\mathrm{R_3Al + O_2 \rightarrow R{-}OO{-}AlR_2}$$

$$\mathrm{R{-}OO{-}AlR_2 \rightarrow (RO)_2AlR}\quad \text{and so on}$$

$$\text{or}\quad \mathrm{R{-}OO{-}AlR_2 + R_3Al \rightarrow 2ROAlR_2}\quad \text{and so on}$$

The results of the study showed that alcohols can be obtained through aluminum alkyls comparatively simply and in sufficiently high yields (60-65%).

As by-products at the stage of preparing aluminum trialkyls, hydrogenation products of the olefins are always formed. Thus, from 2-methylpentene-1, 2-methylpentane is formed; from 2-ethylhexene-1, 2-ethylhexane. Hydrogenation apparently occurs owing to the presence in the active aluminum of finely dispersed iron, which plays the role of a specific catalyst of the type of the skeletal metals of Group 8 of the periodic system of the elements. The iron content in some aluminum samples was 12–15%.

In the dimerization of butene-1 it was found that the required reaction temperature is considerably higher (by 100°) than in the dimerization of propylene. Preliminary results of analysis of the off-gas after carrying out the dimerization showed that butene-2 practically does not enter into the reaction. Along with 2-ethylhexene-1, there is always formation of hexene-1 (from butylene and triethylaluminum) and 2-methylpentene-1 (from propylene contained in the technical butylene fraction). Despite the presence of these by-products, the yield of the butene-1 dimer is very high (up to 90% of theoretical).

Experimental Part

Starting materials. 2-Methylpentene-1 was obtained by dimerization of propylene in the presence of triethylaluminum according to K. Ziegler (^{2}). Yield of product with b.p. 62—62.5°/760 mm: 90% of theoretical; $n_D^{20} = 1.3920$; $d_4^{20} = 0.6793$; literature data (^{3}): b.p. 61.5—62°/760 mm; $n_D^{20} = 1.3921$; $d_4^{20} = 0.6817$. 2-Ethylhexene-1 was obtained by dimerization of butene-1. Triethylaluminum was synthesized by an exchange reaction between didecylmercury and metallic aluminum (^{4}). Triethylaluminum was prepared from ethyl iodide and a magnesium–aluminum alloy by a modified procedure described in an American patent (^{5}). Active aluminum was used in the form of a suspension in benzine (95—100°), with an average particle size of 1—5 μ*.

Preparation of 2-ethylhexene-1. Into an autoclave of 1 l capacity, equipped with a stirrer, manometer, and electric heating, are charged 360 g of a technical butylene fraction containing ~40% butene-1 and 200—250 g of ligroin (b.p. 150—220°), in which 5—10 g of triethylaluminum has been dissolved. The contents of the autoclave are heated with stirring to 280—295°. On reaching this temperature, the pressure begins to fall; this continues for 6 h. After the pressure drop has ceased, the autoclave is cooled and the discharged reaction products are subjected to distillation. As a result of the distillation, 109 g of 2-ethylhexene-1 are obtained (90% of theoretical), with b.p. 118—119°/760 mm, $n_D^{18} = 1.4150$; $d_4^{18} = 0.7270$; MR calc. 38.68; MR found 38.65. Literature data (^{6}): b.p. 120°/760 mm, $d_4^{20} = 0.7270$; $n_D^{20} = 1.4157$.

Synthesis of triethylaluminum. In a four-necked flask equipped with a stirrer, reflux condenser, dropping funnel, and gas-inlet tube, 65 g of an alloy ground to powder and containing stoichiometric amounts of magnesium and aluminum are placed. The reaction is carried out in a weak stream of dry nitrogen freed from oxygen. The contents of the flask are heated on an oil bath to 70—80°, and at this temperature 2—5 ml of ethyl iodide are introduced to initiate the reaction. The reaction usually begins at once. After all the ethyl iodide has entered the reaction, as is evident from the disappearance of drops flowing from the condenser into the flask, a further 300 g of ethyl iodide are gradually added in 10—15 ml portions. Each subsequent portion of ethyl iodide is added after the preceding portion has entered into reaction.

When all the ethyl iodide has been added, the reaction mixture is heated for another hour. The flask is cooled in a stream of nitrogen, mineral oil is added (for example, grade VM-4), and the triethylaluminum is distilled off from the reaction flask under reduced pressure, after replacing the stirrer with a Wurtz attachment with a mercury seal. The yield of triethylaluminum is 80% of theoretical, calculated on ethyl iodide.

Preparation of higher aluminum trialkyls. Into an autoclave are charged 2 moles of 2-methylpentene-1 or 2-ethylhexene-1 and a twofold excess of a suspension of aluminum in benzine, activated with 2—5% triethylaluminum. The reaction mixture is heated to 120—130°, and at this temperature dry hydrogen, freed from oxygen, is introduced into the autoclave to a pressure of 50—70 atm. As the pressure falls, the next portion of hydrogen is forced in, until the pressure ceases to fall. The reaction mass is stirred for another hour, then the autoclave is cooled, and the reaction products are discharged in an inert atmosphere.

Oxidation of higher aluminum trialkyls and hydrolysis of the alcoholates. The reaction mass from the preceding experiment is decanted from the sediment and transferred to a conical flask equipped— stirrer, a reflux condenser, a thermometer, and an air-inlet tube reaching almost to the bottom of the flask.

With rapid stirring, a stream of air is passed through at such a rate that the temperature does not rise above 65-70°. Air is passed continuously until the temperature falls to 30°, after which oxygen is passed for one hour; in this process the temperature at first rises to 50-60°, then falls. After the final drop in temperature, the supply of oxygen is stopped, the air-inlet tube is replaced by a dropping funnel, and through it dilute (10-20%) hydrochloric acid is added, at first dropwise and then in larger portions. After hydrolysis is complete, the upper oily layer is separated, dried over anhydrous potassium carbonate, and distilled.

From 2-methylpentene-1, 2-methylpentanol-1 is obtained (yield 60% of theory, calculated on 2-methylpentene-1, and 54% of theory, calculated on propylene), with b.p. 145-147°/744 mm, $n_D^{21} = 1.4171$; $d_4^{21} = 0.8224$; literature data (7,8): b.p. 148°/762 mm; $n_D^{20} = 1.4182$; $d_4^{20} = 0.8263$; *MR* found 31.24, *MR* calc. 31.43.

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* We take this opportunity to express our gratitude to A. F. Zhigach for providing us with samples of active aluminum.

Correspondingly, from 2-ethylhexene-1, 2-ethylhexanol-1 is obtained (yield, calculated on butene-1, 58%; calculated on ethylhexene, 65% of theory), with b.p. 183-184°/760 mm, $n_D^{18} = 1.4310$, $d_4^{18} = 0.8344$; literature data (9): b.p. 184.2-185°/760 mm; $n_D^{20} = 1.4313$; $d_4^{20} = 0.8324$.

Oxidation of triethylaluminum and hydrolysis of aluminum ethylate. The reaction is carried out while cooling the reaction mass to −15°. Air is first blown through at such a rate that the temperature does not rise above −5°; then the rate of air passage is increased somewhat, and oxidation is continued for one hour at room temperature. Oxidation is completed by heating the reaction mass to 40-50° (2 hours).

The reaction products are hydrolyzed as indicated above. By distillation on a column, 20.3 g of ethyl alcohol was isolated in the form of an azeotrope with water (b.p. 78°/756 mm). The yield of ethyl alcohol was 80% of theory.

Oxidation of tridecylaluminum. A 10% solution of tridecylaluminum in isopentane is oxidized by passing oxygen through it at a temperature of −70° for 5 hours. The reaction mixture was poured, with vigorous stirring, into a 10% aqueous solution of caustic soda at −10°. The aqueous (alkaline) layer was treated to saturation with carbon dioxide, after which the aqueous layer was extracted with ether. The ethereal solution gave a distinct reaction for the presence of hydroperoxides (iodometric determination).

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Note: Figure translations are in progress. See original paper for figures.