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Abstract

Full Text

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The Action of Carbon Dioxide on Aluminum Trialkyls

Synthesis of Carboxylic Acids

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On the question of the action of carbon dioxide on organoaluminum compounds, contradictory information is available in the literature. Thus, Gilman and Marple report ([1]) that in the reaction of tri-*p*-tolylaluminum with carbon dioxide, *p*-toluic acid is obtained. Ziegler ([2]), in his last review article, states that aluminum trialkyls do not give carboxylic acids with carbon dioxide and that the reaction of triethylaluminum with carbonic acid proceeds only according to the scheme:

$$3(C_2H_5)_3Al + CO_2 \rightarrow (C_2H_5)_3COAl(C_2H_5)_2 + (C_2H_5)_2AlOAl(C_2H_5)_2$$

$$\xrightarrow[H_2O]{} \quad (C_2H_5)_3C\text{—}OH$$

According to Grignard and Jenkins ([3]), fatty organoaluminum compounds of the type R_2AlJ and $RAlJ_2$ do not react at all with carbon dioxide.

In the present work we found that aluminum trialkyls react with carbon dioxide under pressure and at elevated temperature with formation, chiefly, of carboxylic acids; moreover, under the conditions we investigated, about two equivalents of the organoaluminum compound enter into this reaction. This indicates, at least, that compounds of the type $R_2AlOCOCH_3$ also interact with carbon dioxide with formation of carboxylic acids. In the reaction of aluminum trialkyls with carbonic acid, along with carboxylic acids, we always also obtained some amount of neutral substances, which in the present work were not investigated in detail.

In the interaction of tripropylaluminum and carbon dioxide at a temperature of 220–240°, butyric acid was obtained in a yield of about 60% of the theoretical:

$$(n\text{-}C_3H_7)_3Al + CO_2 \rightarrow (n\text{-}C_3H_7COO)_mAlR_{3-m} \rightarrow CH_3CH_2CH_2COOH.$$

In a similar manner, from triethylaluminum and triisobutylaluminum, propionic and isovaleric acids, respectively, were obtained. This method of synthesis of carboxylic acids from aluminum trialkyls and carbon dioxide may be of known interest for obtaining normal fatty acids of both the even and the odd series, if one starts from triethyl- and tripropylaluminum and ethylene according to the scheme:

$$(C_2H_5)_3Al + nC_2H_4 \rightarrow [H(CH_2CH_2)_{n+1}]_3Al \xrightarrow{CO_2} CH_3CH_2(CH_2CH_2)_nCOOH$$

$$(C_3H_7)_3Al + nC_2H_4 \rightarrow [CH_3(CH_2CH_2)_{n+1}]_3Al \xrightarrow{CO_2} CH_3(CH_2CH_2)_{n+1}COOH.$$

When carbon dioxide was allowed to act on a mixture of aluminum trialkyls prepared directly from triethylaluminum and ethylene (see (2)), we obtained, in about 50% yield, a mixture of normal fatty acids of the odd-numbered series, from which propionic, valeric, enanthic, pelargonic, and undecanoic acids were isolated. In an analogous experiment, starting only from tripropylaluminum, we obtained a mixture of normal fatty acids from which butyric, caproic, and caprylic acids were isolated.

Experimental Part

Reaction of tripropylaluminum with carbon dioxide. Synthesis of butyric acid. 29 g of tripropylaluminum in 200 ml of heptane and 40 ml of ether were charged into a rocking 0.5-liter autoclave cooled to −70°, and saturated with carbon dioxide from a cylinder. The autoclave was heated for 5 h at 220–240°, the pressure rising to 300 atm. After cooling, the reaction mass was discharged, the solvent was distilled off, and the residue was decomposed with 10% sulfuric acid. The sulfuric-acid solution was extracted with ether. The ether extract was treated with 10% alkali solution. The alkaline solution was acidified, and the butyric acid was extracted with ether. 29.6 g of butyric acid was obtained, b.p. 114–115°/130 mm, n_D^{20} 1.3990. From the acid, the anilide was prepared in the usual way, m.p. 93–94° (from benzene), which gave no depression of the melting point in a mixed sample with a known specimen of butyric acid anilide. Also obtained were 4.5 g of neutral substances.

Reaction of triethylaluminum with carbon dioxide. Synthesis of propionic acid. 30 g of triethylaluminum in 200 ml of heptane and 40 ml of ether were treated with carbon dioxide at 230–240°, as described in the preceding experiment. 24.1 g of propionic acid was obtained, b.p. 140–141°, n_D^{20} 1.3860. From the acid, the anilide was obtained, m.p. 104° (from benzene), which gave no depression of the melting point in a mixed sample with a known specimen of propionic acid anilide.

Reaction of triisobutylaluminum with carbon dioxide. Synthesis of isovaleric acid. 24.3 g of triisobutylaluminum in 200 ml of ether were charged into an autoclave cooled to −70° and saturated with carbon dioxide from a cylinder. The autoclave was heated at 230-250° for 3.5 h. The maximum pressure was 140 atm. After the usual work-up, 22 g of isovaleric acid was obtained, b.p. 95-96°/34 mm, n_D^{20} 1.4030. From the acid, the anilide was obtained, m.p. 109° (from benzene). Literature data (4): isovaleric acid anilide melts at 109-110°.

Action of carbon dioxide on a mixture of aluminum trialkyls prepared from triethylaluminum and ethylene. 58.7 g of triethylaluminum in 100 ml of heptane were charged into a 0.5-liter autoclave and saturated with ethylene to a pressure of 40 atm. The mixture was heated to 120-130°; the ethylene pressure fell almost to zero. After cooling, the reaction mass was diluted with 200 ml of heptane and 60 ml of ether and transferred to a 1-liter autoclave cooled to −70°. After saturation with carbon dioxide from a cylinder, it was heated at 200-220° for 3 h. After the usual work-up, 85 g of a mixture of carboxylic acids and 25 g of neutral substances were obtained. Fractionation in vacuo gave 10.1 g of propionic acid, b.p. 61-62°/30 mm, n_D^{20} 1.3860; 26.3 g of valeric acid, b.p. 105-107°/32 mm, d_D^{20} 1.4085; 18.3 g of enanthic acid, b.p. 133-135°/32 mm, n_D^{20} 1.4220; 10.2 g of pelargonic acid, b.p. 157-159°/30 mm, n_D^{20} 1.4321; 7 g of undecanoic acid, b.p. 176-178°/30 mm (anilide m.p. 70-71°), and 12 g of a residue of higher acids. From all the acids

Anilides were prepared from all the acids; their melting points corresponded to the literature data.

Action of carbon dioxide on a mixture of aluminum trialkyls prepared from tripropylaluminum and ethylene. Into a 0.5-l autoclave were charged 70 g of tripropylaluminum in 150 ml of heptane, and the mixture was saturated with ethylene to a pressure of 40 atm. It was heated to 130-140°; the ethylene pressure fell almost to zero. The reaction mixture was diluted with heptane to a total volume of 500 ml and transferred to a 1-liter autoclave cooled to −70°. After saturation with carbon dioxide from a cylinder, the autoclave was heated for 4 hr at 220-250°; the pressure rose to 320 atm. After the usual work-up, 38 g of a mixture of carboxylic acids was obtained; from this mixture, by vacuum fractionation, there were isolated 8.1 g of butyric acid, b.p. 82-83°/30 mm, n_D^{20} 1.3992; 12.2 g of caproic acid, b.p. 119-120°/30 mm, n_D^{20} 1.4160; 6.8 g of caprylic acid, b.p. 146-148°/30 mm, n_D^{20} 1.4258, and 9 g of a residue of higher acids. Anilides were prepared from all the acids; their melting points corresponded to the literature data.

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