REACTION OF ALUMINUM TRIALKYLS WITH

CARBON DIOXIDE

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It is known that aluminum trialkyls when reacted with CO_2 are converted either to tertiary alcohols or to carboxylic acids, depending on the conditions [1, 2]. The following scheme was proposed for the formation of the acids, according to which 2 moles of acid are formed from 1 mole of the aluminum trialkyl [3].

 $R_{3}AI \xrightarrow{CO_{2}} R_{2}AIOCOR \xrightarrow{CO_{2}} RAI(OCOR)_{2} \xrightarrow{HO_{3}} 2RCO_{2}H + RH$

The simultaneous formation of acids, tertiary alcohols, and hydrocarbons was observed when the reactions of organoaluminum compounds, containing cyclic and aliphatic di- and triene radicals, with CO_2 were studied. Thus, the reaction of tris-[2-(3-cyclohexenyl)-1-ethyl]aluminum (I) [4] with CO_2 at 140°C in xylene solution gave 3-(3-cyclohexenyl)propionic acid (II), tris-[2-(3-cyclohexenyl)-1-ethyl]carbinol (III), and ethyl-3-cyclohexene (IV). If the carbonation is run in an autoclave at 250°C and 200 atm, then only acid (II) and tertiary alcohol alcohol (III) are formed. The reaction of tris-[1-(2-methyl-3-cyclohexenyl)-2- propyl]aluminum (V) [5] with CO_2 in xylene at 140°C proceeds in a similar manner, and here the products are 3-(1-methyl-2-cyclohexen-6-yl)-2-methylpropionic acid (VI), 3-methyl-4-propylcyclohexene (VIII) and tertiary alcohol (VII). Carbonation under drastic conditions gives acid (VI) and alcohol (VII).

A study was made of the reaction of unsaturated aliphatic aluminum trialkyls with CO_2 at 140°C. The carbonation of compounds of similar type was not studied previously, although the application of this reaction to polyunsaturated hydrocarbons is a convenient method for the preparation of unsaturated acids. The reaction between tris-(3-methyl-4,6-heptadienyl)aluminum (IX) [6] and CO_2 leads to 4-methyl-5,7-octadienoic acid (X), 3-methyl-4,6-heptadiene (XI), and tris-(3-methyl-4,6-heptadienyl)carb ol (XII). 4-Methyl-5,9,11-dodecatrienoic acid (XIV) was obtained from tris-(3-methyl-4,8,10-undecatrienyl)aluminum (XIII) under these conditions.



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As a result, the reaction of aluminum trialkyls with CO_2 at 140°C and atmospheric pressure leads to a mixture that consists of acid, tertiary alcohol, and hydrocarbon. Under CO_2 pressure the yield of the acid is increased almost double, while the hydrocarbon is not formed.

In a search for a satisfactory explanation of these data we studied the carbonation of one of the possible intermediate products of the reaction, namely an alumoxane of type $R_2AIOAIR_2$. At 140°C alumoxane (XV) is converted to a mixture of acid (II) and hydrocarbon (IV), whereas only acid (II) is formed under drastic conditions. In both cases the formation of the tertiary alcohol was not observed. These experimental data make it possible to refine the scheme for the carbonation of aluminum trialkyls. The reaction begins with the formation of the dialkylacyloxyaluminum (XVI), which when reacted with the trialkylaluminum is converted to the ketone and alumoxane (XVII). The ketone reacts with the trialkylaluminum and is converted to the dialkylaluminum alcoholate of the tertiary alcohol (XVIII). The carbonation of alumoxane (XVII) and alcoholate (VIII) leads after hydrolysis to a mixture of acid, tertiary alcohol, and hydrocarbon.



Complete carbonation of compounds (XVII) and (XVIII) occurs under more drastic conditions, and after hydrolysis only a mixture of acid and tertiary alcohol is formed.

$$(\text{XVII}) \xrightarrow{4\text{CO}_2} \begin{pmatrix} O \\ \parallel \\ R\text{CO} \end{pmatrix}_2 \text{AlOAl} \begin{pmatrix} O \\ \parallel \\ O\text{CR} \end{pmatrix}_2 \xrightarrow{\text{H}_2\text{O}} 4R\text{CO}_2\text{H}$$
$$(\text{XVIII}) \xrightarrow{2\text{CO}_2} \text{R}_2\text{COAl} \begin{pmatrix} O\text{CR} \\ \parallel \\ O \end{pmatrix}_2 \xrightarrow{\text{H}_2\text{O}} R_3\text{COH} + 2R\text{CO}_2\text{H}$$

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer, while the NMR spectra were recorded on a BS-487 B instrument (80 MHz), using CCl_4 as the solvent and HMDS as the internal standard.

The organoaluminum compounds were obtained by the general transalkylation procedure [4, 6].

Carboxylation of Tris-[2-(3-cyclohexenyl)-1-ethyl]aluminum (I). A CO₂ stream was passed through a solution of compound (I) in 100 ml of xylene for 4 h at 140°C. The reaction mixture was treated with 10% HCl solution. The organic layer was separated and treated with 20% KOH solution. The alkaline solution was extracted three times with ether and acidified with HCl solution. The liberated acid was extracted with ether. We obtained 8.0 g (31% yield) of 3-(3-cyclohexenyl)propionic acid (II), bp 130°C (4 mm), mp 32-33°C. Infrared spectrum (ν , cm⁻¹): 740, 1280, 1380, 1720, 3020. NMR spectrum (δ , ppm): 2.29 (2H), 5.54 (2H), 11.72 (H); m/e 154.

Ethylcyclohexene (IV) [8.1 g (43.5%)] was isolated by chromatographing the xylene solution on Al_2O_3 , bp 135-136°C (760 mm); n_D^{20} 1.4555; cf. [7].

Tris-[2-(3-cyclohexenyl)-1-3thyl]carbinol (III) [5 g (20%)] was removed from the aluminum oxide by elution with chloroform; mp 41-42 °C. Infrared spectrum (ν , cm⁻¹): 740, 1050, 1150, 3030, 3350. NMR spectrum (δ , ppm); 3.35 (H), 5.50 (6H).

Carboxylation of (I) under Drastic Conditions. A solution of 20 g of compound (I) in 100 ml of heptane was loaded into an autoclave and 75 g of solid CO_2 was added under cooling. The reaction mixture was kept at 250 °C and 200 atm for 5 h. Further treatment was the same as described above. We obtained 15.6 g (60%) of acid (II) and 4.5 g (18%) of alcohol (III).

Carboxylation of Tris-[1-(2-methyl-3-cyclohexenyl)-2-propyl]-aluminum (V). Under similar conditions, from 60 g of compound (V) we obtained 19 g (26% yield) of 3-(1-methyl-2-cyclohexen-6-yl)-2-methyl-propionic acid, bp 165-170°C (0.5 mm); n_D^{20} 1.5025. Infrared spectrum (ν , cm⁻¹): 740, 1480, 1710, 3040. NMR spectrum (δ , ppm): 0.94 (3H, J 7 Hz); 1.04 (3H, J 7 Hz); 5.04 (2H); 11.20 (H). We isolated by chromatographing on Al₂O₃: 1) 25.5 g (45% yield) of 3-methyl-4-propylcyclohexene (VIII), bp 180-181°C (760 mm); n_D^{20} 1.4529. Infrared spectrum (ν , cm⁻¹): 690, 1380, 1460, 3020. NMR spectrum (δ , ppm): 0.90 (3H, triplet, J 7 Hz); 0.95 (3H, J 7 Hz); 5.30 (2H); 2) 7 g (12% yield) of tetriary alcohol (VII), bp 205-210°C (0.5 mm); n_D^{20} 1.5070. Infrared spectrum (ν , cm⁻¹): 740, 1150, 1480, 1460, 3450.

The carboxylation of 30 g of compound (V) with 80 g of CO_2 gave acid (VI) [yield 19.5 g (54%)] and tertiary alcohol (VII) [yield 6 g (21%)].

Carboxylation of Tris-(3-methyl-4,6-heptadienyl)aluminum (IX). From 45 g of compound (IX) we obtained 25 g (42% yield) of 4-methyl-5,7-octadienoic acid (X), bp 129-130 °C (0.5 mm); n_D^{20} 1.4780. Infrared spectrum (ν , cm⁻¹): 910, 1100, 1710, 3040. Ultraviolet spectrum: λ_{max} 227 nm, log ε 4.83. NMR spectrum (δ , ppm): 1.05 (3H, doublet, J 6 Hz); 4.78-6.40 (5H, multiplet); 10.73 (H, singlet); m/e 154. We isolated by chromatographing on Al₂O₃: 1) 15 g (36% yield) of 3-methyl-4,6-heptadiene (XI), bp 95°C (760 mm): n_D^{20} 1.4471. Infrared spectrum (ν , cm⁻¹): 900, 1010, 1380, 1460, 1650. Ultraviolet spectrum: λ_{max} 227 nm, log ε 4.2; m/e 110; 2) 2.5 g (5.5% yield) of tris-(3-methyl-4,6-heptadienyl)carbinol (XII), bp 200-202°C (0.4 mm; n_D^{20} 1.4885. Infrared spectrum (ν , cm⁻¹): 910, 1000, 1070, 1150, 3040, 3350. Ultraviolet spectrum: λ_{max} 227 nm, log ε 5.05; m/e 356.

The carboxylation of 20 g of compound (IX) gave acid (X) [yield 18 g (67%)] and tertiary alcohol (XII) [yield 3 g (15%)].

 $\begin{array}{l} & \begin{array}{c} \mbox{Carboxylation of Tris-(3-methyl-4,8,10-undecatrienyl)aluminum (XIII).} & \mbox{From 70 g of compound} \\ \mbox{(XIII)} \hline we obtained 19 g (22\% yield) of 4-methyl-5,9,11-dodecatrienoic acid (XIV), bp 145-148°C (0.5 mm);} \\ \mbox{n}_{D}^{20} 1.4875. & \mbox{Infrared spectrum (ν, cm^{-1}$): 910, 1000, 1460, 1710. Ultraviolet spectrum: $\lambda_{max} 232 nm, log ϵ 4.80. & \mbox{NMR spectrum (δ, ppm): 1.05 (3H); 268 (H); 4.80-5.40 (7H); 11.60 (H).} \end{array}$

Alumoxane (XV). As described in [7], we obtained (XV) in $\sim 100\%$ yield from 40 g of compound (I) and 0.1 g of water.

CONCLUSIONS

Some polyunsaturated carboxylic acids were synthesized and the scheme for the carboxylation of aluminum trialkyls was refined.

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