The Growth Reaction of an α, ω-Dialuminoalkane Compound

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It is well known that ethylene undergoes a stepwise addition to trialkylaluminum to form a long-chain alkylaluminum[1]:

$$\text{R-al} + n\text{C}_2\text{H}_4 \rightarrow \text{R-}(\text{C}_2\text{H}_4)_n\text{-al} \quad (\text{al} = 1/3\text{Al})$$

If this growth reaction can be applied to an organoaluminum compound with two aluminum atoms attached to both ends of a polymethylene chain, it is expected to synthesize long-chain bifunctional compounds by adding ethylene to the above-mentioned organoaluminum compound; and converting the resulting aluminum compound into other product (diolefin, diol).

With the object of synthesizing an α, ω-dialuminoalkane compound, various attempts have been made by several workers to add dialkylaluminum hydride to α, ω-dienes. Ziegler[2] reported that the reaction of 1, 5-hexadiene with diisobutylaluminum hydride afforded a cyclopentylmethylaluminum compound, instead of the expected 1, 6-dialuminohexane derivative. Zakharkin[3] reported that the reaction of butadiene with diethylaluminum hydride yielded mainly polymeric (di- and trimeric) hydrocarbons, accompanied by a small amount of a 1, 4-dialuminobutane derivative. The present authors[4] previously investigated the reaction between diisobutylaluminum hydride and α, ω-dienes with carbon numbers from five to eleven (molar ratio 1 : 1) and found that the facile ring-closure reaction is specific only to 1, 5-hexadiene and that other α, ω-dienes gave the α, ω-dialuminoalkane compounds. Especially, the 1, 7-dialuminoheptane derivative is stable at the temperature of the growth reaction of alkylaluminum.

These facts suggest that the growth reaction of the 1, 5-dialuminopentane derivative by means of the addition of ethylene can be carried out without forming cyclic compounds. We confirmed, as expected, that the growth reaction of this compound proceeds without ring closure.

Results and Discussion

The 1, 5-dialuminopentane derivative*[1] was prepared by the addition of diisobutylaluminum hydride to 1, 4-pentadiene. The growth reaction of this compound was carried out at an ethylene pressure of 130 kg./cm^2 at 100°C for five hours. To avoid the influence of the metal surface of the autoclave which catalyses the displacement reaction of alkylaluminum by ethylene, a glass tube with a small hole was used as the reaction vessel. On hydrolysis, the reaction product

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[1] K. Ziegler, H. G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Söll and W. R. Kroll, *Ann.*, **629**, 121 (1960).

[2] K. Ziegler, " Organometallic Chemistry," Ed. by H. Zeiss, Reinhold Publishing Corp., New York, N. Y. (1960), p. 234.

[3] L. I. Zakharkin, L. A. Savina and L. M. Antipin, *Bull. Acad. Sci. U. S. S. R.*, **6**, 931 (1962).

[4] G. Hata and A. Miyake, *J. Org. Chem.*, **28**, 3237 (1963).

*[1] The initial product from the reaction of 1,4-pentadiene with diisobutylaluminum hydride should be 1,5-bis(diisobutylalumino)pentane (I),

$$(i\text{-Bu})_2\text{Al-}(\text{CH}_2)_5\text{-Al}(i\text{-Bu})_2$$

(I)

which, however, might be converted through alkyl exchange reaction to a mixture of $(i\text{-Bu})_3\text{Al}$, $(i\text{-Bu})_2\text{Al-}(\text{CH}_2)_5\text{-Al}(i\text{-Bu})_2$, $(i\text{-Bu})_2\text{Al}\left\langle\begin{matrix}(\text{CH}_2)_5\text{-Al}(i\text{-Bu})_2\\(\text{CH}_2)_5\text{-Al}(i\text{-Bu})_2\end{matrix}\right.$, etc. This sort of alkyl exchange reaction occurs readily at room temperature (K. Ziegler, W. R. Kroll, W. Larbig and O. W. Steudel, *Ann.*, **629**, 53 (1960)). For the sake of simplicity, the product is hereafter called 1, 5-dialuminopentane derivative and written as al-$(\text{CH}_2)_5$-al.

afforded a mixture of *n*-pentane, *n*-heptane, *n*-nonane, *n*-undecane, *n*-tridecane and higher hydrocarbons with odd carbon numbers. In addition to the *n*-paraffins, small amounts of 1-pentene (10% of C_5 hydrocarbons) and 1-heptene (4% of C_7 hydrocarbons) were formed. However, no appreciable amount of α,ω-diene was found. The formation of these *n*-paraffins indicates the occurrence of the following growth reaction (Eq. 1):

$$\text{al-}(CH_2)_5\text{-al} \xrightarrow{nC_2H_4} \text{al-}(CH_2)_5\text{-}(C_2H_4)_n\text{-al} \qquad (1)$$

$$\downarrow H_2O$$

$$CH_3\text{-}(C_2H_4)_{n+1}\text{-}CH_2CH_3$$

$$\text{al-}(CH_2)_5\text{-al} \xrightarrow{C_2H_4} \text{al-}(CH_2)_3\text{-}CH{=}CH_2 + \text{al-}CH_2CH_3$$

$$\downarrow H_2O \qquad (2)$$

$$CH_3CH_2CH_2CH{=}CH_2$$

1-Pentene was formed by the displacement of the 1, 5-dialuminopentane derivative by one mole of ethylene (Eq. 2). The formation of 1-heptene is due to the displacement of the 1, 7-dialuminoheptane derivative by one mole of ethylene and/or to the addition of ethylene to the 4-pentenylaluminum derivative.

The distribution of the hydrocarbons produced by hydrolysis was determined by gas chromatographic analysis. In this procedure, hydrocarbons higher than *n*-heneicosane were neglected, since they were present in very small amounts. The results are shown in Table I and Fig. 1. The average number of added ethylene per aluminum-carbon bond of the 1, 5-dialuminopentane derivative was 1.1.

TABLE I. DISTRIBUTION OF HYDROCARBONS OBTAINED BY HYDROLYSIS OF THE PRODUCT FROM al-$(CH_2)_5$-al+1.1C_2H_4

Hydrocarbon	Composition, mol. %	
	Obs.	Calcd.
C_5[a]	15.5	12.6
C_7[b]	22.5	26.1
C_9	25.8	27.2
C_{11}	19.9	18.8
C_{13}	10.2	9.7
C_{15}	4.2	4.0
C_{17}	1.5	1.4
C_{19}	0.4	0.4

a) *n*-pentane 90%, 1-pentene 10%
b) *n*-heptane 96%, 1-heptene 4%

In order to compare the distribution of the grown chains from the 1, 5-dialuminopentane derivative with that of those from trialkylaluminum, the results of the growth reaction of the *n*-pentylaluminum derivative under the same reaction conditions are shown in Table II and Fig. 2.

TABLE II. DISTRIBUTION OF HYDROCARBONS OBTAINED BY HYDROLYSIS OF THE PRODUCT FROM al-$(CH_2)_4$-CH_3+1.5C_2H_4

Hydrocarbon	Composition, mol. %	
	Obs.	Calcd.
C_5[a]	23.3	23.4
C_7	34.2	34.0
C_9	24.6	24.7
C_{11}	12.1	11.9
C_{13}	4.2	4.3
C_{15}	0.3	0.3
C_{17}	0.1	0.1

a) *n*-pentane 95%, 1-pentene 5%

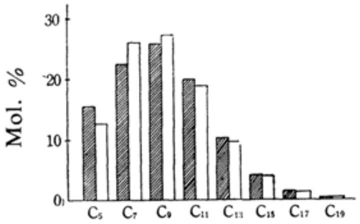

Fig. 1. Distribution of hydrocarbons by hydrolysis of the product from al-$(CH_2)_5$-al+1.1 C_2H_4.

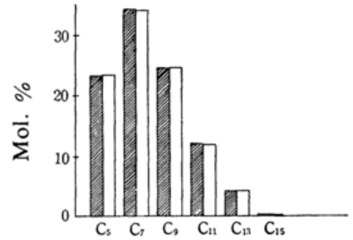

Fig. 2. Distribution of hydrocarbons by hydrolysis of the product from al-$(CH_2)_4$-CH_3+1.5 C_2H_4.

▨ Observed value
☐ Calculated value

Ziegler[1] reported that the distribution of the different chains resulting from the addition of ethylene to trialkylaluminum was found to be very close to that calculated on the assumption that all aluminum-carbon bonds present in the reaction mixture have the same probability of being added to ethylene during the entire period of the reaction (Poisson distribution). If the addition of ethylene to the 1, 5-dialuminopentane derivative proceeds in the same manner as is assumed above, the theoretical distribution of the grown chains can be given by the following equations:

$$X_r = \sum_{p=0}^{r} X_p X_{(r-p)}$$

$$X_p = \frac{n^p e^{-n}}{p\,!} \qquad X_q = \frac{n^q e^{-n}}{q\,!}$$

In these equations, X_r is mole fraction of the chain $-(\mathrm{C_2H_4})_p-(\mathrm{CH_2})_5-(\mathrm{C_2H_4})_q-$ in which $p+q$ is equal to r and n is defined, according to the equation $\mathrm{al}-(\mathrm{CH_2})_5-\mathrm{al} \xrightarrow{2n\mathrm{C_2H_4}} \mathrm{al}-(\mathrm{C_2H_4})_n-(\mathrm{CH_2})_5-(\mathrm{C_2H_4})_n-\mathrm{al}$, as the average number of moles of ethylene taken up per aluminum-carbon bond. The theoretical values in the case of $n=1.1$ are given in Table I and Fig. 1. As may be seen from Fig. 1, the agreement between the observed and the theoretical distributions is relatively good. The slight discrepancies in $\mathrm{C_5}$ and $\mathrm{C_7}$ hydrocarbons indicate that conditions are somewhat unfavorable for the formation of $\mathrm{C_7}$ chain from a $\mathrm{C_5}$ chain.

By the displacement of the growth product of the 1,5-dialuminopentane derivative by ethylene in the presence of a nickel catalyst, α, ω-dienes with odd carbon atoms (1,4-pentadiene, 1,6-heptadiene, 1,8-nonadiene and 1,10-undecadiene) were obtained (Eq. 3):

$$\mathrm{al{-}(CH_2)_5{-}(C_2H_4)_r{-}al} \xrightarrow[\mathrm{C_2H_4}]{\mathrm{Ni(acac)_2}} \mathrm{2alCH_2CH_3} + \mathrm{H_2C{=}CH{-}CH_2{-}(C_2H_4)_r{-}CH{=}CH_2} \tag{3}$$

The two aluminum-carbon bonds of the 1,5-dialuminopentane derivative are not displaced completely by ethylene, unlike those of the 1,7-dialuminoheptane derivative and the 1,9-dialuminononane derivative. The composition of those hydrocarbons with the same carbon number is shown in Table III.

Further investigation is necessary of these different reactivities of the 1,5-dialuminopentane derivative in growth reaction and in displacement reaction.

TABLE III. DISPLACEMENT REACTION OF THE GROWTH PRODUCT BY ETHYLENE (HYDROLYZED PRODUCTS)

Carbon number	Products (composition %)[a]		
	α,ω-Diene	α-Olefin	n-Paraffin
$\mathrm{C_5}$	1,4-Pentadiene (70)	1-Pentene (22)	n-Pentane (8)
$\mathrm{C_7}$	1,6-Heptadiene (93)	1-Heptene (7)	—
$\mathrm{C_9}$	1,8-Nonadiene (94)	1-Nonene (6)	—

a) Ratio of peak area of gas chromatogram.

Experimental

The Growth Reaction of the 1,5-Dialuminopentane Derivative. — The 1,5-dialuminopentane derivative was prepared from 1,4-pentadiene (0.03 mol.) and diisobutylaluminum hydride (0.063 mol.) by a method previously reported.[4)] The 1,4-dialuminopentane derivative in 10 ml. of n-hexane was introduced into a glass tube with a small hole. This glass tube was then set in an autoclave. The pressure of ethylene and the reaction temperature were kept at 130 kg./cm^2 and 100°C respectively for 5 hr. while the mixture was being shaken. The reaction product was decomposed by the successive addition of ethanol, water and 6 N hydrochloric acid. The organic layer was washed with water and dried over sodium sulfate. The hydrocarbons[*2] thus produced were analyzed by gas chromatography, using either a squalane column (2.5 m.) or a silicone DC 550 column (2.5 m.). n-Pentane, n-heptane, n-nonane and n-undecane were identified by a comparison of their gas chromatographic retention times and infrared spectra with those of authentic samples. n-Tridecane, 1-pentene and 1-heptene were identified by gas chromatographic comparison.

***α, ω*-Dienes from the Growth Product.** — To the growth product obtained under the same reaction conditions as have been described above, 8 mg. of nickel acetylacetonate and 80 mg. of phenylacetylene in 5 ml. of n-hexane were added. The pressure of ethylene and the temperature were kept at 55 kg./cm^2 and 70°C respectively for 2 hr. The reaction product was then hydrolyzed and the organic layer separated by gas chromatography, using a squalane column. 1,4-Pentadiene 1,6-heptadiene, 1,8-nonadiene and 1,10-undecadiene were identified by comparing their gas chromatographic retention times and infrared spectra with those of authentic samples prepared by the method previously reported.[4)] 1-Pentene, n-pentane, 1-heptene and 1-nonene were identified by gas chromatographic comparison.

The Growth Reaction of the *n*-Pentylaluminum Derivative.—n-Pentylaluminum derivative was prepared from the reaction of 0.07 mol. of 1-pentene with 0.09 mol. of diisobutylaluminum hydride at 70°C for 16 hr. The growth reaction of this compound was carried out under the same reaction conditions as have been described above.

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[*2] The hydrocarbons derived from the growth reaction of isobutyl group are completely distinguished from those with odd carbon atoms by gas chromatography.