An Attempted Preparation of Optically Active Organometallic Compounds as Polymerization Catalysts[*]

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A number of investigations on isotactic polymerization have been carried out in recent years. As regards the mechanism of isotactic polymerization by heterogeneous catalysts, it seems to be of great interest to see if the use of optically active organoaluminum compound in combination with a titanium halide might influence the steric structure of the resulting polymer.

Polymerization of Styrene with an Optically Active Triamylaluminum.—From the viewpoint mentioned above, we attempted to prepare trialkylaluminum containing three optically active 2-methylbutyl groups, starting from (−)-2-methylbutanol of 96% optical purity, $[\alpha]_D^{13^\circ}=-5.70^\circ$.

(−)-2-Methylbutanol was purified by repeated fractional distillation of fusel oil through a Stedman column of about 70 theoretical plates. Calculation of the optical purity is based on the value −5.90° for the pure substance[1]. Treatment of the alcohol with thionyl chloride and pyridine gave (+)-2-methylbutyl chloride of 95% purity, $[\alpha]_D^{14^\circ}=+1.62^\circ$ (+1.70° for the pure substance[2]).

A widely used preparative method of organoaluminum compounds is that using the reaction between metallic aluminum and an alkyl halide. The method, however, was by no means feasible in the case of higher alkyl halides, such as amyl chloride, because of the occurrence of vigorous decomposition reaction[3], and hence an alternative method was adopted in the present work as shown in the following equations:

$$HgCl_2+2AmMgCl \rightarrow Hg(Am)_2+2MgCl_2 \quad (1)$$

$$2Al+3Hg(Am)_2 \rightarrow 2Al(Am)_3+3Hg \quad (2)$$

$$(Am=-CH_2-CH(CH_3)-CH_2-CH_3)$$

(+)-Bis-(2-methylbutyl)mercury was obtained in 80% yield by the reaction of Eq. 1. An ethereal solution of 2-methylbutylmagnesium chloride (from 11.0 g. of the active chloride) and mercuric chloride (12 g.) was refluxed for one hour, and then after the removal of ether by distillation the residual mass was heated in an oil bath at 120°C for one hour. The reaction mass was combined with the ether distillate, decomposed by saturated aqueous ammonium chloride, and distilled to yield the product, b. p. 135∼7°C (30 mmHg), $d_4^{27.5}=1.657$, $[\alpha]_D^{27.5^\circ}=+7.65^\circ$.

Found: Hg, 56.6%. Calcd. for $C_{10}H_{22}Hg$: Hg, 58.5%.

As the reaction between metallic aluminum and (+)-bis-(2-methylbutyl)mercury was found to be very vigorous, leading occasionally to decomposition of the product, the exothermic reaction was suppressed by the portion-wise addition of granular aluminum into (+)-bis-2-methylbutyl)mercury, which was kept at 100∼110°C in an oil bath. The yield of tris-(2-methylbutyl) aluminum was 56% based on (+)-bis-(2-methylbutyl)mercury used, b. p. 85∼105°C (0.5 mmHg).

Found: Al, 11.50%. Calcd. for $C_{15}H_{33}Al$: Al, 11.24%.

The optical purity of tris-(2-methylbutyl)-aluminum thus obtained was estimated by the following procedures, i.e., oxidation with oxygen, subsequent hydrolysis to 2-methylbutanol, and checking its optical rotatory power:

$$2Al(Am)_3+3O_2 \rightarrow 2Al(OAm)_3 \quad (3)$$

$$Al(OAm)_3+aq.\,HCl \rightarrow AlCl_3aq.+AmOH \quad (4)$$

The recovered 2-methylbutanol was found to have an optical purity of 27%, $[\alpha]_D^{30^\circ}=-1.58^\circ$, which indicates that an extensive racemization had taken place in some stages of the synthetic process (Eqs. 1 and 2) or of recovering process (Eqs. 3 and 4). In our experiment, therefore, the optical purity of tris-(2-methylbutyl)aluminum should be estimated at 27% at the lowest.

Polymerization of styrene was carried out at 70°C in *n*-heptane using this aluminum compound (0.3 g.) in combination with titanium trichloride (3 g.) for 2 to 7.5 hr. The isotactic fractions of the polymers showed no difference

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[1] W. Markwald and A. Mackenzie, *Ber.*, **34**, 485 (1907).

[2] A. Mackenzie and G. W. Clough, *J. Chem. Soc.*, **103**, 698 (1913).

[3] A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 108 (1940).

[4] The content of mercury was determined by decomposition of the sample with sulfuric acid in a Kjeldahl flask and by titration of mercuric ions with ammonium rhodanate, M. Hiral and R. Hayatsu, *J. Pharm. Soc. Japan* (*Yakugakuzashi*), **70**, 76 (1950).

in the physical properties, such as melting points, X-ray diffraction pattern and optical rotation in toluene solution, in comparison with isotactic polystyrenes that were prepared with racemic tris-(2-methylbutyl) aluminum and titanium trichloride.

Polymerization of Styrene with Optically Active Amylsodium. — In the course of our study on the polymerization of styrene with Alfin catalysts, it was found that amylsodium alone could produce isotactic polystyrene in a suitable solvent, though in a small yield, together with a large amount of atactic polymer. Based on this observation, the amylsodium prepared from optically active amyl chloride was tested in the same way. Amylsodium was prepared from (+)-2-methylbutyl chloride and sodium dispersion in the usual manner[5] and was used as a catalyst in *n*-heptane solvent. However, the isotactic polystyrene here obtained showed again no unusual character and was quite identical with that obtained by an inactive catalyst, isoamylsodium.

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[5] J. J. R. Williams, J. Van Den Berghe, K. R. Dunham and W. J. Dulmage, *J. Am. Chem. Soc.*, **79**, 1716 (1957).