

done with solutions of strong acids with $I = 0.1$ (KNO_3 or NaClO_4) with $\text{pH} = -\log [\text{H}^+]$. The limited concentration range for $[\text{L}]_t$ and $[\text{RHg}]_t$ ($0.5:2 \cdot 10^{-3} \text{M}$) is due to the low solubility of the substances and of complications for the dimerization equilibrium of the cations.

Support by *Ciba-Geigy S.A.*, Basle, is gratefully acknowledged. I thank Mr. *P. Corbat* for experimental assistance.

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150. Stereoselective Ring Closure of Methyl-5-hexenyl-aluminium Systems¹⁾

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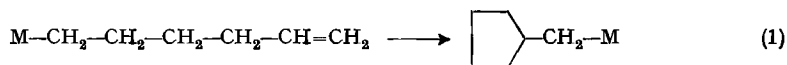
Summary. A remarkable intramolecular stereoselectivity was observed in the ring closure reactions of 1-, 2-, 3-, and 4-methyl-5-hexenyl-aluminium systems. The possible relationship between this stereoselectivity and the relative thermodynamic stabilities of the conformers involved in the cyclization reactions, is discussed.

The persisting controversy on the mechanism of the *Ziegler-Natta* α -olefin polymerization, after two decades of extensive debating²⁾, is far from being settled, and

¹⁾ The kind of stereoselectivity discussed in the present paper can be considered, in our opinion, as a case of intramolecular asymmetric induction, even if it concerns racemic mixtures. However, in acceptance of the opinion of the Editorial Committee, we avoid for historical reasons the use of the term 'asymmetric induction', which is conventionally used only in the case of optically active materials.

²⁾ For a full discussion of the matter see [1].

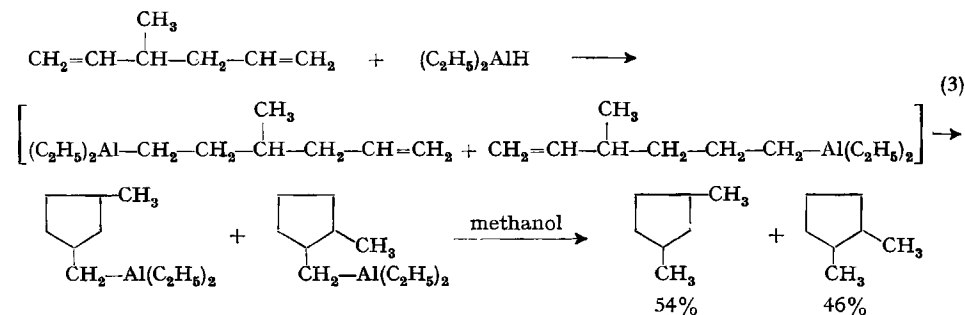
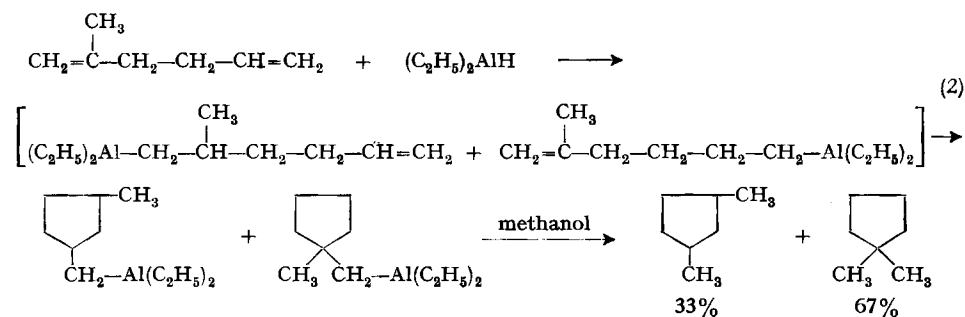
the basic question concerning the origin of the stereoregulating forces still remains unanswered. Some information on the steric course of the monomer insertion step in the polymerization process, could be obtained from a simplified model in which a single addition of an alkyl-metal to a double bond takes place. Such a model can be conveniently provided by a 5-hexenyl-metal system, capable of intramolecular addition to the double bond according to equation (1):



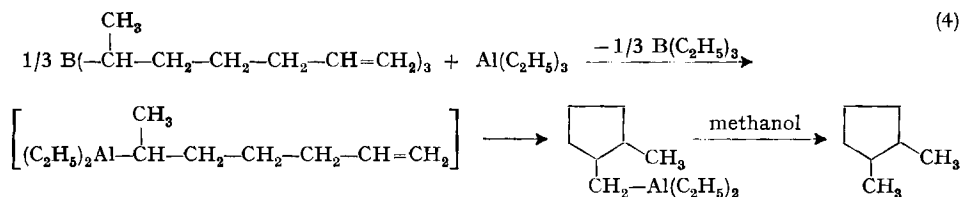
The cyclization reaction (1) was found as the result of the addition of diisobutyl-aluminium hydride to 1,5-hexadiene [2], and the intermediacy of 5-hexenyl-aluminium as the primary addition product was later demonstrated through the isolation of the unsaturated species as ether adduct, and its cyclization in a separate step [3]. A wide range of metals, other than aluminium, have been shown to promote cyclizations of type (1), though more vigorous conditions are required in most cases [4] [5].

For the purpose of investigating the stereochemical aspects of this reaction, we studied the ring-closure of 5-hexenyl-aluminium systems, containing a methyl substituent in different positions, examining the composition of the products obtained after hydrolysis of the reacted species. Aluminium was chosen as the metal, both for its special role played in the *Ziegler-Natta* catalysis and for the exceptionally mild conditions of the addition reaction [6].

2- resp. 3-Methyl-1,5-hexadiene were added to diethyl-aluminium hydride: 2- and 5-methyl-hexenyl-, resp. 3- and 4-methyl-hexenyl-aluminium systems were assumed to be formed in the two cases, according to equations (2) and (3), as unstable intermediates, that cyclized immediately to the corresponding cyclopentane derivatives.



1-Methyl-5-hexenyl-aluminium was also formed by a redistribution reaction between tris-(1-methyl-5-hexenyl)-boron and triethyl-aluminium (equation (4)); ring closure of the unsaturated organo-aluminium system occurred again, and the corresponding cyclopentane derivative was produced³⁾.



The products obtained in the three reactions were separately treated with methanol, and the liquid hydrocarbon portion of each mixture was analyzed by VPC. and MS. against standard samples. In any case dimethylcyclopentanes accounted for more than 96% of the products, being present in trace amounts open chain mono-olefins and paraffins.

Except for the formation of the 1,1-disubstituted cyclopentane, ring closure produced two diastereoisomers, having *cis* or *trans* configuration respectively. The prevalence of one diastereomer in each case, was taken as a direct measure of the influence exerted by the preexisting asymmetric centre, on the newly formed one upon ring closure. In Table 1 is reported the composition of *cis/trans*-dimethylcyclopentanes obtained as ultimate products of the ring closure reactions, as a function of the position of the methyl substituent in the reacting chain.

A remarkable stereoselectivity is evident in all the cases examined. The alternating prevalence of *cis* or *trans* isomer in both 1,2- and 1,3-dimethylcyclopentane, depending on the position of the methyl group in the open-chain precursor, indicates that no simple steric hindrance is the stereocontrolling factor, and that the relative thermodynamic stability of each pair of diastereomeric products is not reflected in a determinant way in energy difference between the respective transition states.

Table 1. *Diastereomeric compositions (%) of the products obtained from the reactions (2), (3), and (4), as a function of the position of the methyl substituent*

Substitution in the 5-hexenyl chain	1,2-Dimethylcyclopentane		1,3-Dimethylcyclopentane	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
1-methyl ^{a)}	72.3	27.7		
2-methyl			4.1	95.9
3-methyl			91.1	8.9
4-methyl	2.3	97.7		

a) The *cis/trans* product composition of the cyclization preceding the formation of the alkenyl-aluminium intermediate [compare note²⁾], did not differ significantly from the value reported here (see Experimental Part), and did not alter therefore the result of the reaction (4).

³⁾ About 50% of the alkenyl groups underwent ring closure during the preparation of the boron derivative (see Experimental Part), possibly in the step involving the *Grignard* reagent (compare [4]). The presence in the redistribution mixture, of previously cyclized product as a possible source of error in the following considerations, will be taken into account.

The degree of stereocontrolling influence, as appears from the results shown in Table 1, differs only slightly when the methyl substituent is in 2-, 3-, or 4-position, corresponding to energy differences between the pairs of diastereomeric transition states of 1.8, 1.4, and 2.2 kcal/mol respectively⁴). In the case of the 1-substituted hexenyl-aluminium, considerably lower stereoselectivity was observed, and a value of about 0.6 kcal/mol can be calculated for the energy difference between the two diastereomeric transition states.

The way how the stereoregulation might occur, can be intuitively understood considering that in order to cyclize, the alkenyl chain has to assume a coil-like form; such a coil can be right-handed or left-handed, and the choice between the two forms controls the chirality of the asymmetric centre being formed upon ring closure. According to this view, the stereoselectivity observed in the cases examined, means that a methyl-branching at a given position of the alkenyl chain induces the prevalence of one direction of spiralization, in dependence on the chirality of the branched carbon atom.

A more rigorous explanation for the origin of the energy differences constituting the driving force for the stereoregulation, can be attempted on the basis of conformational analysis [7].

In the Figure are represented, according to the *Newmann* projection, two enantiomeric conformers of a 5-hexenyl-aluminium system in a favorable position for ring closure (compare [8]); the hydrogen atoms are designated with their prochirality symbols.

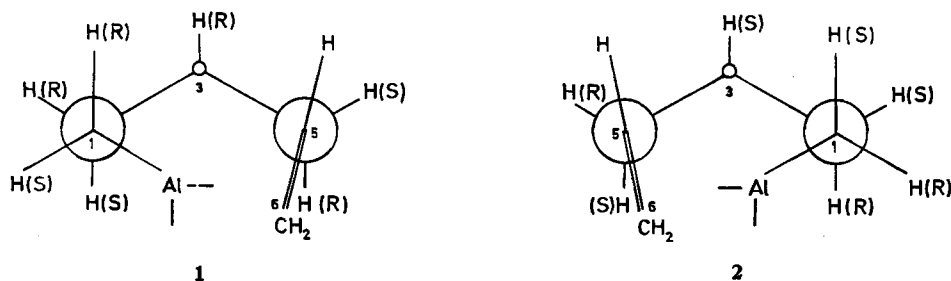


Figure. Enantiomeric conformers of a 5-hexenyl-aluminium system

The three bonds C(1)–C(2)–C(3)–C(4) assume three consecutive *gauche* conformations: respectively *g(l)g(r)g(l)* in **1** (left-handed coil), and *g(r)g(l)g(r)* in **2** (right-handed coil). No other low energy conformer can approach so closely the five-membered ring being formed. In absence of substituents the two conformers are energetically equivalent, but when a substituent, say a methyl group, occupies the position 1, 2, 3, or 4, they become diastereomers and possess different energies. More precisely, if a methyl group replaces H(S) at 1-position, the conformation **1** will be stabilized; if H(R) is replaced instead, at the same position, the conformation **2** will have lower energy. That is, in both cases the substituent will prefer *trans* rather than *gauche* conformation,

⁴) In the calculation of the energy differences, according to the *Arrhenius* equation, a possible influence of the frequency factor was disregarded, in view of the similarity between the geometrical features involved for diastereomeric transition states.

among the rotamers around the bond C(1)-C(2). This choice, dictated by the energy difference between a *trans* and a *gauche* conformation, leads to the prevalence of *cis*-1,2-disubstituted cyclopentane upon ring-closure. For analogous reasons (*R*)-2-methyl-, (*S*)-3-methyl-, and (*S*)-4-methyl-hexenyl-systems will prefer the conformation **1**, and their antipodes the conformation **2**, giving rise, upon ring closure, to the prevalence of *trans*-1,3-, *cis*-1,3-, and *trans*-1,2-disubstituted cyclopentanes respectively: the agreement with the experimental results is qualitatively complete.

Assuming for the energy difference between *trans* and *gauche* conformations the same value given for hydrocarbon systems, 0.8 kcal/mol [7], the energy difference between the conformers **1** and **2**, brought about by the presence of a methyl substituent, will amount to 0.8 kcal/mol in the case of 1-substitution, and 1.6 kcal/mol in the case of 2- or 3-substitution. The corresponding value for the substitution in 4-position is uncertain for the lack of exact data on the energy levels of the rotamers about sp^3 - sp^2 C-C bonds (C(4)-C(5)) in analogous systems⁵⁾; qualitatively, being a CH_2 -H eclipsed conformation preferred over a CH_2 - CH_3 eclipsed one for similar hydrocarbon systems [9], a methyl substituent in 4-position of the conformers **1** and **2** can only simultaneously occupy, with respect to both bonds involved, either an energetically favored or an unfavored conformation [*trans*-C(3)-C(4)/ CH_2 -H eclipsed or *gauche*-C(3)-C(4)/ CH_2 - CH_3 eclipsed]; that is, the energy difference between the two conformers will be higher than 1.2 kcal/mol.

The comparison between the energy differences thus evaluated for the four pairs of diastereomeric conformers considered, and the values calculated on the basis of the experimental data for the corresponding pairs of diastereomeric transition states of the cyclization reactions (2), (3) and (4), shows a fairly good, though imperfect approximation. Therefore it is suggestive to assume that the relative thermodynamic stability of the diastereomeric conformers, necessary intermediates for the ring closure, is the decisive stereoregulating factor, while additional factors may play only a minor role in determining the degree of stereoselectivity.

As a conclusion it is worth emphasizing the evidence that the stereoselectivity observed, is not the result of a direct interaction between the asymmetric centre present and that being formed, but is obtained through the intermediacy of a preferred asymmetric conformation. Although the limitations inherent to the particular system investigated, do not allow any generalization or extension to intermolecular reactions, the model discussed provides an interesting example of stereoselective process in which a direct relationship can be established between stereoselectivity and thermodynamic equilibria between asymmetric intermediate conformers.

Experimental Part⁶⁾

Organometallic materials were handled in a dry nitrogen atmosphere. VPC. analyses were performed with a *Perkin-Elmer* 990 gas-chromatograph, equipped with FID detector, and connected to a *Hitachi Perkin-Elmer* RMU-6L mass spectrometer, for direct VPC.-MS. analyses. All the products reported were identified by comparison of their retention times and mass spectra with those of authentic samples, either commercially available or prepared by known methods.

⁵⁾ A value > 0.4 kcal/mol is given for ΔH between CH_2 -H eclipsed and CH_2 - CH_3 eclipsed conformations in 3-methyl-1-butene [9].

⁶⁾ The experimental work was made by Mr. D. Tatone.

Compositions percent of the product mixtures were determined by VPC. Separation of the dimethylcyclopentanes was performed on a 100 m × 0.25 mm column coated with squalane; the order of elution was: 1,1-, *cis*-1,3-, *trans*-1,3-, *trans*-1,2-, and *cis*-1,2-dimethylcyclopentane.

Tris-(1-methyl-5-hexenyl)-boron. Boron trifluoride etherate (0.037 mol) was added dropwise to a solution of *Grignard* reagent (0.12 mol) prepared from 6-chloro-1-heptene [10] in ether (100 ml). The reaction mixture was refluxed for 1 h, and then filtered through a sintered glass septum. The solvent was removed under vacuum. An attempt of distillation at reduced pressure showed a tendency of the product to decompose upon heating (b.p. > 100°/0.1 Torr); therefore the crude product was used in the subsequent reactions.

A sample of the product, oxidized with alkaline hydrogen peroxide in tetrahydrofuran [11], gave 6-hepten-2-ol (44%) and 2-methyl-hydroxymethylcyclopentane (33% *cis*, 14% *trans*).

Ring closure reactions. A) 2-Methyl-1,5-hexadiene (*Fluka*; 20 mmol) was added to a solution of diethyl-aluminium hydride (*K & K Lab.*; 20 mmol) in toluene (10 ml). After standing 24 h at room temp., the mixture was heated at 50–60° (6 h). The solvent was removed at reduced pressure (room temp.), then methanol was cautiously added to the residue cooled in an ice bath, and the mixture distilled. Addition of water to the distillate caused separation of an organic layer (2.4 ml) consisting of 1,1-dimethylcyclopentane (64.8%), 1,2-dimethylcyclopentane (31.9%, *cis/trans* = 4.1/95.9), 2-methylhexane (2.6%) and traces of mono-olefins.

B) The reaction between 3-methyl-1,5-hexadiene (*K & K Lab.*) and diethyl-aluminium hydride was performed by analogous procedure. The organic product collected after treatment with methanol contained almost exclusively 1,2-dimethylcyclopentane (45.6%, *cis/trans* = 2.3/97.7) and 1,3-dimethylcyclopentane (53.1%, *cis/trans* = 91.1/8.9).

C) *Tris*-(1-methyl-5-hexenyl)-boron (5 mmol) was added at room temp. to a solution of triethylaluminium (*Fluka*; 15 mmol) in toluene (10 ml). After standing overnight, the mixture was treated with methanol and worked up as described in A). The product obtained (1.6 ml) consisted of practically pure 1,2-dimethylcyclopentane (*cis/trans* = 72.3/27.7).

I wish to thank Prof. *P. Pino* for the discussion of the results.

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