

## Ring-opening Polymerization of Norbornene Catalysed by Ethyl Aluminium Dichloride; Olefin Metathesis in the Absence of a Transition Metal

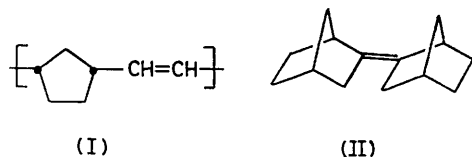
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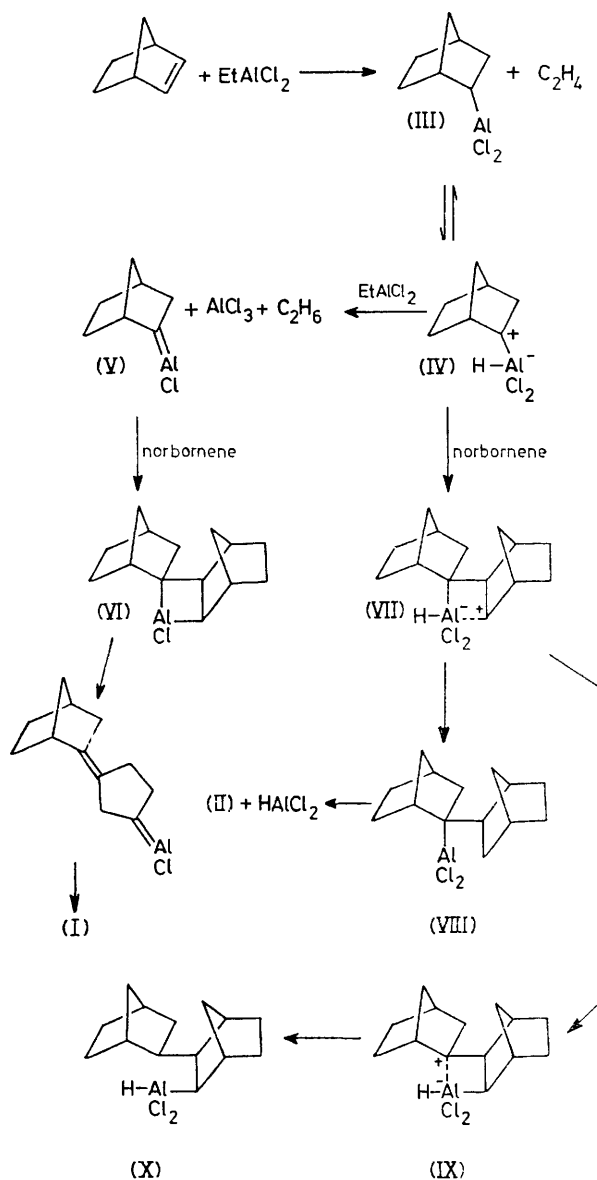
**Summary** Ethyl aluminium dichloride under certain conditions catalyses the ring-opening polymerization of norbornene as well as the formation of oligomers; the possible wider significance of this observation for Ziegler-Natta polymerization is briefly discussed.

THE ring-opening polymerization of cycloalkenes is a special case of the olefin metathesis reaction which is catalysed by a great variety of transition-metal compounds, either alone or in the presence of other compounds, especially those of aluminium.<sup>1</sup> Here we report that under the right conditions  $\text{EtAlCl}_2$  alone is capable of inducing ring-opening polymerization of norbornene.

The reaction was conducted at room temperature in a dry box. To a solution of 5 g of norbornene in 4 cm<sup>3</sup> of chlorobenzene was added 0.5 cm<sup>3</sup> of a 25% solution of  $\text{EtAlCl}_2$  in toluene (Aldrich; used either as received or distilled *in vacuo*). The mixture turned pale yellow, and heat was evolved. A little gas containing ethane and ethylene was given off. After 1 min a second portion of 0.5 cm<sup>3</sup> of  $\text{EtAlCl}_2$ -toluene was added. More heat was liberated and the mixture began to gel. After 5 min the reaction was stopped by the addition of ethanol. A white precipitate was formed which, after a second precipitation, gave a <sup>13</sup>C n.m.r. spectrum identical with that<sup>2</sup> of the ring-opened polymer (I) (yield, 0.5 g; 50% *cis*, 50% *trans* double bonds). These samples of (I) were rather insoluble gels only swelling in  $\text{CHCl}_3$ , so some cross-linking may have occurred.<sup>2</sup> The more-soluble products (yield, ca. 3.0 g) were found to contain (by g.l.c.-mass spectroscopy) tetra-substituted dimeric olefins of type (II) (four isomers) together with higher oligomers, as previously observed in the  $\text{WCl}_6$ -initiated reaction.<sup>3</sup> The formation of (I) and (II) was not suppressed by the presence of pyridine ( $\text{Al/py} = 4$ ), and (II) was still obtained, in the presence of  $\text{EtAlCl}_2$  with an excess of  $\text{Bu}^n\text{Li}$ , so that, as in the  $\text{WCl}_6$ -initiated reaction, the formation of (II) does not appear to involve a conventional cationic mechanism.<sup>4</sup> In the



absence of the second dose of  $\text{EtAlCl}_2$  only trace amounts of (I) were formed but substantial quantities of oligomers of type (II) were still obtained.  $\text{EtAlCl}_2$  is a rather indifferent catalyst for ring-opening polymerization since it failed to convert cyclopentene into any polypentenamer. In this respect it resembles several transition metal complexes<sup>5</sup> which are quite active for ring-opening polymerization of norbornene but are practically inert for metathesis of less-strained cycloalkenes and alkenes.



In order to account for these results we postulate the following. (i) That the second dose of  $\text{EtAlCl}_2$  generates an active aluminium-carbene species (V); Scheme. The hydride shift, (III)  $\rightarrow$  (IV), should be favoured by the formation of the tertiary carbonium ion<sup>5</sup> and may precede elimination of  $\text{HCl}$  by reaction with  $\text{EtAlCl}_2$ , but it is not clear why so little of (V) is formed during the first addition of  $\text{EtAlCl}_2$ . (ii) That carbene (V) forms metalocycle (VI) and sets in motion the usual type of chain reaction<sup>1,2</sup> for

ring-opening polymerization; the Scheme is oversimplified in two respects: first, it ignores the known propensity for aluminium halide compounds to dimerize; and second, formation of (VI) from (V) may be step-wise rather than the formally disallowed concerted ( $\pi^2s + \pi^2s$ ) addition as written, but we propose that this Scheme provide a basis for the understanding of ring-opening polymerization catalysed by  $\text{EtAlCl}_2$ . (iii) That the oligomers of type (II) *etc.* are formed by the mechanism also shown in the Scheme, in which we postulate carbenoid-type intermediates (VII) and (IX). We suppose that (VII) may either form (VIII) by transfer of  $\text{H}^-$  to the positive centre, followed by *cis*  $\beta$ -H elimination to give (II), or may switch to the more stable species (IX) containing a tertiary carbonium ion centre, which in turn can form (X), analogous to (III), and so lead on to the formation of higher oligomers.

A mechanism of the type shown in the Scheme offers a more satisfactory route to (II) in the  $\text{WCl}_6$ -catalysed

reaction, since the originally proposed scheme<sup>3</sup> involved an unlikely *trans*  $\beta$ -H elimination to yield a dimeric olefin, which must then undergo double bond shift to give (II). It will also be evident that the Scheme provides a novel mechanism for Ziegler-Natta polymerization.<sup>6</sup> The present work suggests that ring-opening and Ziegler-Natta polymerizations proceed independently through distinct intermediates. There is as yet no evidence in systems where ring-opening polymerization and Ziegler-Natta polymerization proceed simultaneously, *e.g.*, the polymerization of norbornene catalysed by  $\text{TiCl}_4$ - $\text{Et}_3\text{Al}$ ,<sup>7</sup> to indicate whether the polymer consists of two distinct types of chain or whether both types of unit can be incorporated in the same chain.

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<sup>1</sup> See review by J. J. Rooney and A. Stewart, 'Catalysis,' (Specialist Periodical Reports), Vol. 1, ed. C. Kemball, The Chemical Society, London, 1977, p. 277.

<sup>2</sup> K. J. Ivin, D. T. Lavery, and J. J. Rooney, *Makromol. Chem.*, 1977, **178**, 1545.

<sup>3</sup> D. T. Lavery, M. A. McKervey, J. J. Rooney, and A. Stewart, *J.C.S. Chem. Comm.*, 1976, 193.

<sup>4</sup> J. P. Kennedy and H. S. Madowski, *J. Macromol. Sci. (Chem)*, 1967, **A1**, 345.

<sup>5</sup> G. A. Olah, *Chem. in Britain*, 1972, **8**, 281.

<sup>6</sup> K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green, and R. Mahtab, following communication.

<sup>7</sup> T. Saegusa, T. Tsujino, and J. Furukawa, *Makromol. Chem.*, 1964, **78**, 231; 1965, **85**, 71.