

A NEW ALLENE HEXAMER

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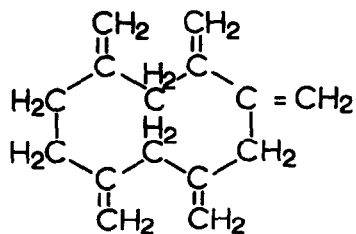
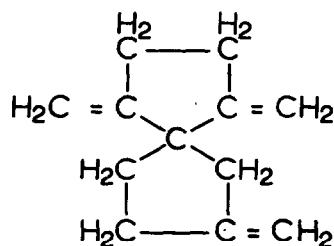
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There has been considerable interest focused recently on the reaction between allene and transition metal complexes (1-8). In most publications Rh-complexes played the main rôle. Various types of reactions have been observed, such as formation of complexes of rhodium (I) with allene (1-5) or oligomers of allene (5-7), catalytic cyclo-oligomerization (6-8) and linear polymerization (1,9).

Most of these studies were concerned with Rh(I) complexes.

In the course of our investigations on the polymerization of allene by Rh-based catalyst systems (9), we have isolated a series of allene-oligomers as by-product.

From these oligomers two could be identified as the earlier published tetramer (I) (7,8) and pentamer (II) (6)



The polymerization, from which the oligomers were isolated was carried out in a glass autoclave. To a catalyst solution, consisting of 1 eq. Rh(CO)<sub>2</sub>Cl<sub>2</sub> rhodium dicarbonylchloride dimer- and 2 eq. Pφ<sub>3</sub>-triphenylphosphine- in ethanol, an excess of allene was added under its own pressure and the reaction was carried out for 6 hours at 40°C, during which time the pressure generally fell from 5 to 2 atmosphere.

After the solution had been separated from the solid polymer 1,2 polyallene, the solvent was evaporated under diminished pressure and the residu was fractionally distilled. A gas chromatogram of the undistilled residu showed three major components and some lower boiling material. These last peaks may be attributed to lower oligomers (di- and trimers) which however, were not identified by us.

We isolated by distillation three compounds viz:

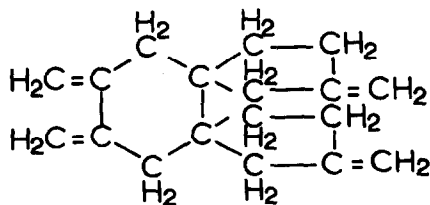
I	$n_D^{20} = 1,5102$	bp=77-78°C/10 mm Hg	(Otsuka: $n_D^{25} = 1,5055$	bp= 59-60 1 mm Hg
II	$n_D^{20} = 1,5289$	bp=75-77°C 0,5mm Hg	(Otsuka: $n_D^{25} = 1,5314$	bp= 73°C/ 2 mm Hg
III	bp = 118-120/		$n_D^{20} = 1,5358$	

Compounds I and II could be identified as resp. the tetramer (I) (7-8) and the pentamer (II) (6). The IR, NMR and MS data were in good agreement with the data from the literature as well as their boiling points and refractive indices. The compound III had a molecular weight of 240, as determined by Mass-spectrometry.

This proved it to be a hitherto unknown hexamer.

To elucidate the further structural details we have used various spectroscopic techniques such as IR, NMR (60 mC) and Mass-spectroscopy.

From the data there-of we propose the following structure (III).



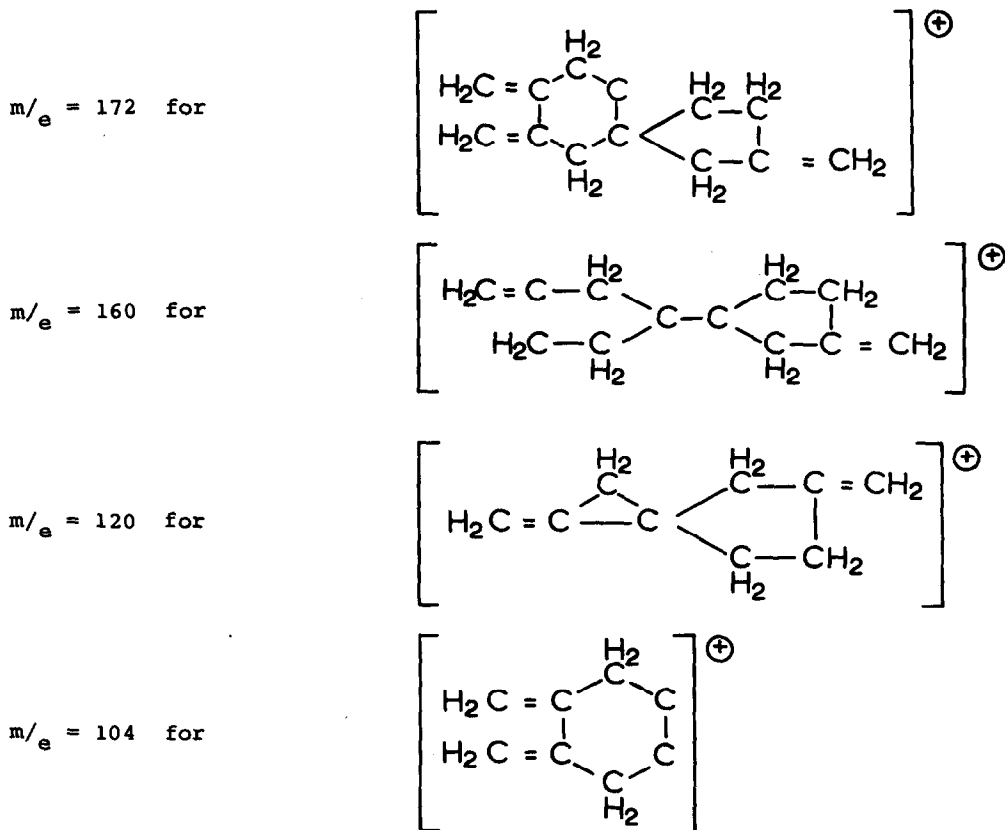
IR 1640-1590 $\text{cm}^{-1}$	conjugated double band
3070-1430 $\text{cm}^{-1}$	alifatic methylene-groups
890 $\text{cm}^{-1}$	exocyclic methylene group (double band)

NMR	Chemical shift	relative intensity	assignment
	5.10 (m)	1 } 1 }	exocyclic conjugated = CH <sub>2</sub>
	4.80 (m)		
	2.4 (m)	2	C=C-CH <sub>2</sub> -C
	1.8 (t)	2	-CH <sub>2</sub> -CH <sub>2</sub> -C-

As in the work of Lindsey (8) and Otsuka (5-7) the spectrum was rather complex, which is probably due to the complicated sterical structure of the hexamer.

### Mass-spectrometry

As mentioned earlier a parent peak was found at  $m/e = 240$ . Other strong peaks were found at:



As the objective of our research was not the synthesis of allene-oligomers, but the polymerization of allene we have not tried to improve the yield of the above mentioned oligomers, which was rather low (less than 3%). We have indications to believe that the polymer/oligomer ratio is i.a. dependent from the triphenylphosphine content of the catalyst-molecule. We have, however, not further investigated this line (see also ref.7.). What again is demonstrated here is the potentiality of low-valent transition-metal complexes as catalysts for the synthesis of complicated organic compounds in one step.

Acknowledgement:

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