

Table 8.2: Assignment of the fragments from the isomer appearing at a retention time of 15.32 minutes.

m/z	Rel. Int.	Assignment	m/z	Rel. Int.	Assignment
27	31.0	$[\text{CH}_2=\text{CH}]^+$	68	14.9	$[\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2]^+$
29	35.0	$[\text{CH}_3-\text{CH}_2]^+$	69	100	$[\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}]^+$
39	24.3	$[\text{CH}_2=\text{C}=\text{CH}]^+$	70	23	$[\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2]^+$
41	70.3	$[\text{CH}_3-\text{CH}=\text{CH}]^+$	71	2.7	$[\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2]^+$
42	8.1	$[\text{CH}_3-\text{CH}=\text{CH}_2]^+$	97	6.8	$[\text{CH}_3-(\text{CH}_2)_4-\text{CH}=\text{CH}]^+$
43	24.3	$[\text{CH}_3-\text{CH}_2-\text{CH}_2]^+$	98	6.5	$[\text{CH}_3-(\text{CH}_2)_4-\text{CH}=\text{CH}_2]^+$
51	2.7	$[\text{CH}_2=\text{CH}-\text{CH}=\text{CH}]^+ - 2\text{H}$	110	2.7	$[\text{CH}_3-(\text{CH}_2)_5-\text{CH}=\text{CH}]^+ - \text{H}$
53	10.8	$[\text{CH}_2=\text{CH}-\text{CH}=\text{CH}]^+$	111	24.3	$[\text{CH}_3-(\text{CH}_2)_5-\text{CH}=\text{CH}]^+$
55	98.6	$[\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}]^+$	112	4.1	$[\text{CH}_3-(\text{CH}_2)_5-\text{CH}=\text{CH}_2]^+$
56	35.1	$[\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2]^+$	126	2.7	$[\text{CH}_3-(\text{CH}_2)_6-\text{CH}=\text{CH}_2]^+$
57	21.6	$[\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2]^+$	168	17.6	$[\text{CH}_3-(\text{CH}_2)_9-\text{CH}=\text{CH}_2]^+$
65	4.0	$[\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}]^+ - 2\text{H}$	169	2.3	$[\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}]^+$
67	17.6	$[\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}]^+$			

Two features are clearly apparent from the dimer spectrum in Figure 8.5:

- The spectrum contains about 20 isomers (12 carbon atoms for each isomer)
- No one isomer is dominant

The mass spectrum of each of the peaks of the dimeric fraction in Figure 8.5 was recorded and an attempt was made to match the spectral pattern with data contained in the GC-MS reference library. From this analysis it was possible to convincingly identify some isomers. However in many instances speculation still exists as to the isomer corresponding to a specific peak. Clearly spiking by injection of known isomers into the GC-MS would have provided unambiguous confirmation of a spectral-structure

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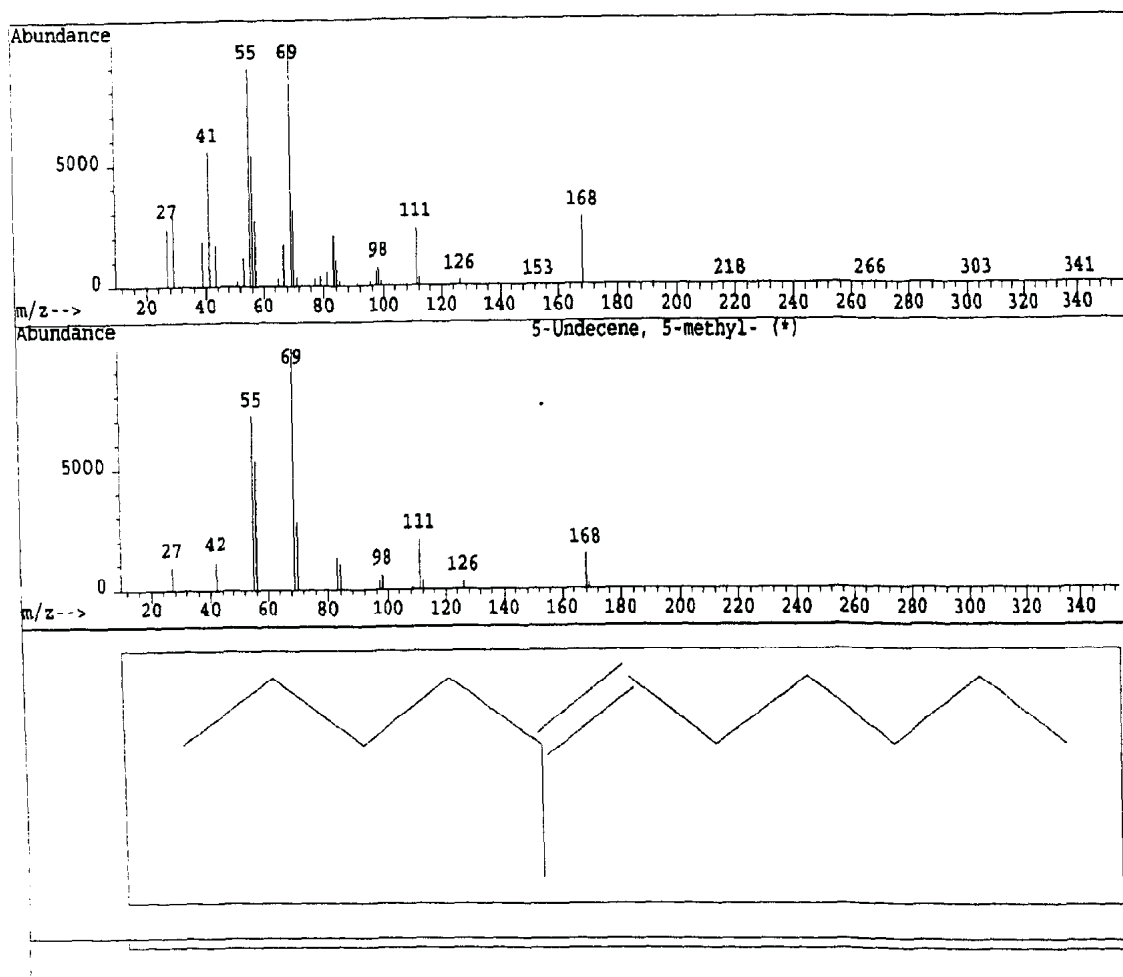
correlation. However very few pure isomers were available to achieve this objective. The results obtained by spiking with the C_{12} isomers that were available are shown below:

- i) 2-,3-,4-,5- and 6-methyl undecane: These species were not present in the spectrum (retention time < 15 min)
- ii) dodecane: Identified with retention time 15.64 minutes (1 % of product)
- iii) 1-dodecene: Identified with retention time 15.53 - 15.57 minutes (20 % of product)

When taking possible reaction pathways into account for the formation of linear dimer alkenes, the formation of 4-, 5- and 1-dodecene seems the most likely, while the formation of 2-,3- and 6-dodecene would be less likely (unless isomerisation takes place after oligomerisation).

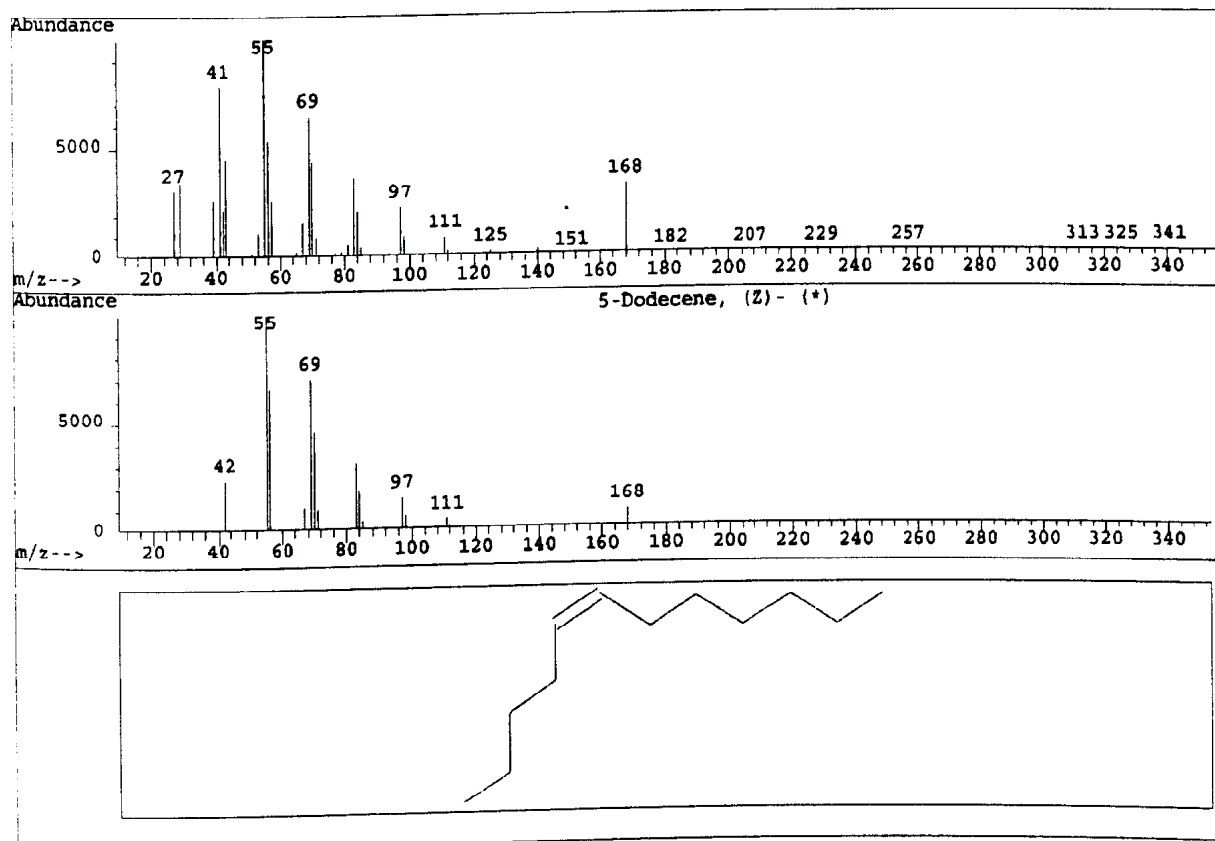
No other isomers of C_{12} , than those indicated above, were available for spiking. Hence many of the isomers in Figure 8.5 were thus identified by comparison of the fragmentation pattern of the observed isomer with that predicted from the GC-MS library. Examples of two such fits are shown in Figures 8.7 and 8.8. The fragmentation pattern of the isomer occurring at 15.131 minutes is compared to the fragmentation pattern of 5-methyl-5-undecene (E) (Figure 8.7) and the fragmentation pattern of the isomer occurring at 15.503 minutes is compared to the fragmentation pattern of 5-dodecene (Z) (Figure 8.8).

Figure 8.7: Fragmentation pattern of isomer at 15.131 minutes compared to the fragmentation pattern of 5-methyl-5-undecene (E)



The accuracy of the above fit (Figure 8.7) was shown to be 97% while the match in Figure 8.8 was indicated to have a 94% accuracy. In both Figures 8.7 and 8.8 the fragmentation pattern of the isomer does differ slightly from the isomer to which it has been compared to. It has however been found that even for isomers that have been positively identified by spiking, the fragmentation pattern from the library is not completely identical to the fragmentation pattern of the specific dimer isomer under investigation.

Figure 8.8: Fragmentation pattern of isomer at 15.503 minutes compared to the fragmentation pattern of 5-dodecene (Z)



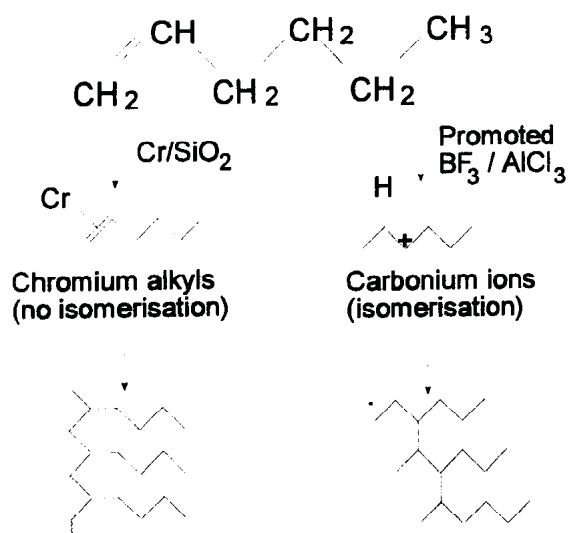
In a similar fashion attempts were made to match GC-MS peaks with other predicted isomers; in particular those expected from a classical oligomerisation reaction. Further, the isomers shown in Table 8.1 were all expected to be present in the oligomer product spectrum. Except for 2-butyl-1-octene and 2-butyl-3-methyl-1-heptene, all the other isomers (both cis and trans) were identified. The assignment of isomer peaks is shown in Table 8.3. From the number of dimer peaks in the GC-MS spectrum which have not been assigned, two would thus possibly represent 2-butyl-1-octene and 2-butyl-3-methyl-1-heptene. As can be seen in Table 8.3 there are still a number of peaks which have not as yet been assigned.

Table 8.3: Assignment of the various isomer peaks shown in Figure 8.5

Retention time (minutes)	Assigned structure
12.18	?
12.41	?
13.17	?
13.88	?
14.09	?
14.17	?
14.22	?
14.29	?
14.41	?
14.46	?
14.52	7-methyl-5-undecene (Z)
14.57	5-methyl-3-undecene (cis/trans)
14.68	5-methyl-4-undecene
14.72	5-methyl-4-undecene
14.84	7-methyl-4-undecene
14.92	7-methyl-4-undecene
15.05	5-methyl-5-undecene (E)
15.13	7-methyl-3-undecene (E)
15.28	5-methyl-5-undecene (Z)
15.32	7-methyl-5-undecene (E)
15.53	4,5,6-dodecene (cis/trans)
15.57	1-dodecene (cis/trans)
15.64	n-dodecane

A diagram representing a comparison of the product obtained by the HVI-PAO reaction catalysed by Cr/SiO_2 (i.e. Arlman-Cossee mechanism) with the product obtained from the conventional $\text{BF}_3/\text{AlCl}_3$ catalysed PAO reaction is shown in Figure 8.9 (Wu, 1989 a).

Figure 8.9: HVI-PAO compared to conventional PAO reaction (Wu, 1989 a)



From the identity of the structures that were present in the oligomeric product the Arlman-Cossee mechanism seems to be the most likely mechanism to take place during the oligomerisation reaction. The presence of such a large number of dimer isomers is however not explained by this mechanism, unless some form of isomerisation did indeed occur. From the nature of the products formed (only 5- and 7-methyl branching) it seems as if the monomers were indeed α -olefinic in character. Minimal isomerisation thus appears to have occurred prior to the oligomerisation reaction. Some degree of double bond isomerisation thus probably took place **after** oligomerisation, which would explain the various positions of the double bond in the product isomers. The assumption that no isomerisation takes place after oligomerisation has thus been proven to be invalid from the GC-MS data. It is believed that hydrogenation of the above product would have given a product with a larger number of isomers than that reported by Wu (1989 a). Interestingly Cr^{3+} rich catalysts

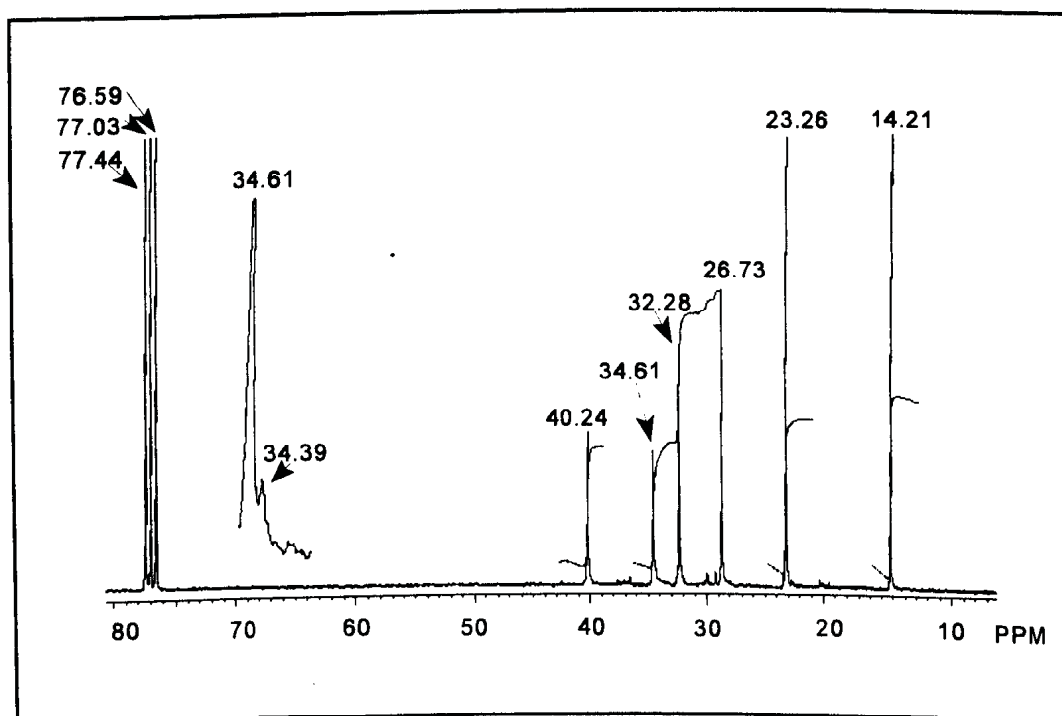
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have been reported to catalyse 1-butene isomerisation with a 10^3 higher activity than the polymerisation of 1-butene (Wu, 1989 a). If the catalyst employed in this study contained a quantity of Cr^{3+} due to some or other reason, this might result in the isomerisation that is believed to have taken place after oligomerisation of the 1-hexene monomers.

8.4.2. NMR spectroscopy

In recent years the use of NMR spectroscopy to derive detailed information on the tacticity of oligomers and polymers has been reported (Asakura *et al.*, 1991; Coughlin & Bercaw, 1992; van der Linden *et al.*, 1995; Babu *et al.*, 1994). In particular, and of pertinence to this study, the experimental as well as theoretical ^{13}C NMR spectra of a range of polymers formed from α -olefins have been reported. The ^{13}C NMR spectra of a series of polymers derived from specifically 1-hexene under a range of experimental conditions have been reported and analysed by Babu *et al.*, (1994) and van der Linden *et al.*, (1995) (Figure 8.10).

Figure 8.10: ^{13}C NMR of isotactic polyhexene (van der Linden *et al.*, 1995)



The spectra in the studies of Babu *et al.*, (1994) and van der Linden *et al.*, (1995) clearly reveal that there is a predominantly isotactic polymer formed but end group analysis did reveal the presence of 1,2 disubstituted and 1,1,2 trisubstituted vinylene and vinylidene end groups. A reaction scheme was shown which rationalized the

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presence of these end groups. Theoretical calculations based on CSPEC and SPECINFO were used to predict the position of the resonances shown in the scheme (Babu *et al.*, 1994).

A theoretical analysis of the expected spectrum for 1-hexene polymers based on the heterogeneous catalysts $\text{TiCl}_3\text{-MgCl}_2\text{-SiO}_2\text{-AlEt}_2$ and $\text{Ti}(\text{OBu})_4\text{-MgCl}_2\text{-AlEt}_2\text{Cl}$ have also been reported by Asakura *et al.*, (1991) and the data are in good agreement with the study of Babu *et al.*, (1994). Van der Linden *et al.*, (1995) have managed to synthesize oligomers of 1-hexene, but no comment has been made on the ^{13}C NMR spectra of these products.

Interestingly, and to our knowledge, no mention has been made of the use of ^1H or ^{13}C spectra to assess features of the 1-hexene oligomers (prior to hydrogenation). Details of our study on the use of NMR spectroscopy in this analysis are given below.

The ^1H and ^{13}C NMR spectra of a sample oligomer which is a predominantly dimer mixture (see Section 8.4), were recorded and are shown in Figures 8.11 and 8.12 respectively.

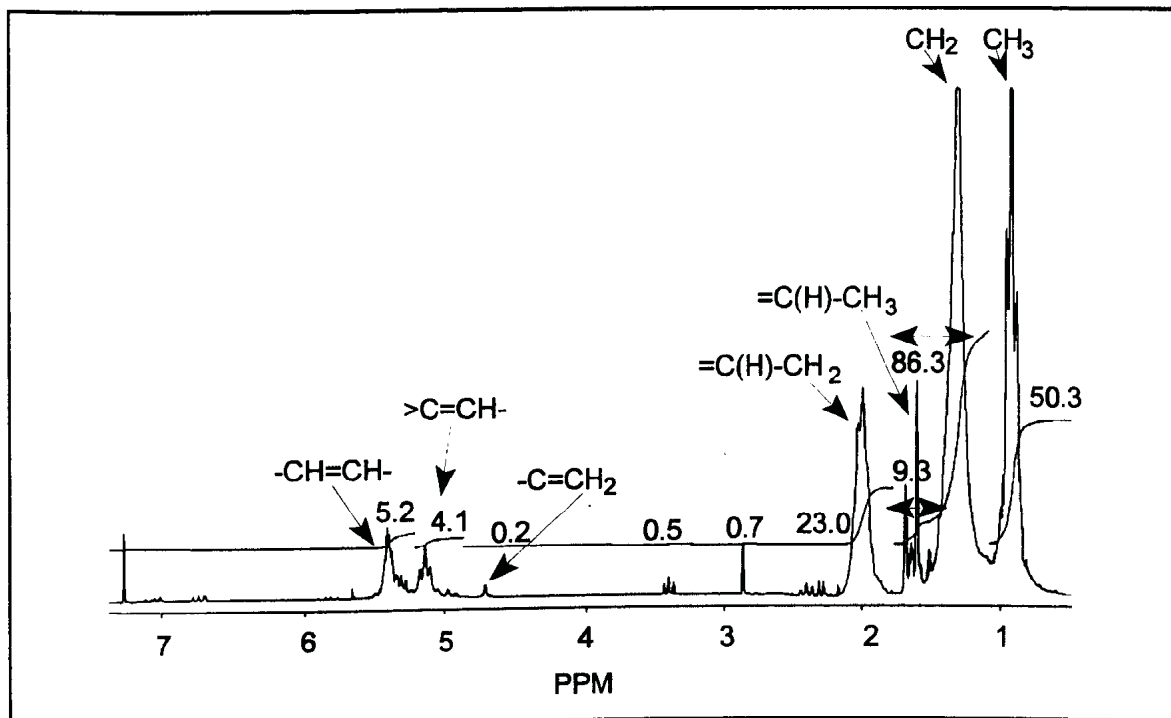
8.4.2.1. ^1H spectrum (Figure 8.11)

The ^1H spectrum reveals that the product consists of a number of different isomers, consistent with the GC analysis. Notwithstanding this an analysis of the gross features of the dimer is possible. The spectrum can be broken down into two regions - absorptions between 4.5 and 6.0 ppm and absorptions between 0 and 2.5 ppm. The assignment of these regions is straightforward and is given in Table 8.4 (Doskočilová *et al.*, 1994; Pretsch *et al.*, 1989).

Table 8.4: Chemical shifts in the ^1H regions of 4.5 - 6.0 ppm and 0 - 2.5 ppm and assignments of the various peaks

Group	Chemical shift (ppm) Literature	Chemical shift (ppm) Experimental ^a
cis/trans -CH=CH-	5.50 - 5.40	5.45 (5.2)
>C=CH-	5.20	5.15 (4.1)
>C=CH ₂	4.75	4.70 (0.2)
H ₂ C=CH(CH ₂)-	5.70, 4.97, 5.03	5.70, 4.95, 5.05
CH ₃ CH=CH ₂	1.71	1.70 (9.3)
CH ₃ CH ₂ CH=CH ₂	2.00	2.00 (23.0)
CH ₃ CH ₂ CH=CH ₂	1.00	0.9 (50.3)
CH ₃ CH ₂ CH ₂ -----	1.33	1.35 (86.3)

^aIntensities shown in brackets

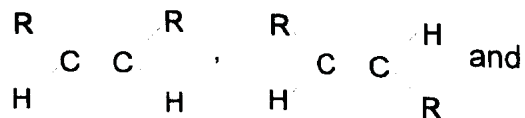
Figure 8.11: ^1H NMR spectrum of fraction 2

An analysis of the spectrum between 4.5 and 6.0 ppm gives information on the olefinic character of the dimer. This region is dominated by two (multiplet) peaks at 5.2 and 5.4 ppm.

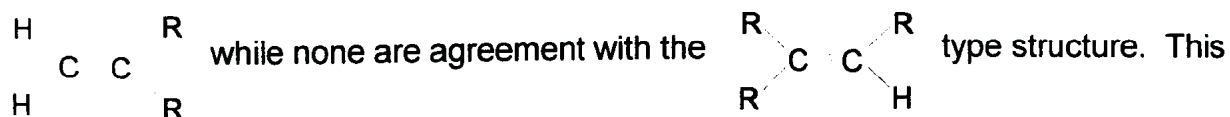
As shown in Table 8.4, these correspond to $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array} - \begin{array}{c} \text{R} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$ and $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array} - \begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R} \end{array}$ (5.2 intensity), and $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R} \end{array} - \begin{array}{c} \text{R} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$ (4.1 intensity) respectively. There is also an absorption

at 4.7 ppm (0.2 intensity) corresponding to $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array} - \begin{array}{c} \text{R} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R} \end{array}$, but this olefin concentration is low.

When comparing the above structures to the six possible structures formed according to the Ziegler-Natta catalysed classical route, it can be seen that four of the suggested complexes in Table 8.1 are in agreement with



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would suggest that isomerisation of the double bond probably takes place after the oligomerisation reaction.

i). *Nature of the R groups*

A consideration of the 1.0 to 2.5 ppm region reveals that the spectrum is dominated by CH_2 and CH_3 groups and it is predicted that the R groups in the isomers suggested above will hence be predominantly CH_2 and CH_3 groups (some CH is possible). It is assumed that no (or very little) aromatic or oxygenated hydrocarbon groups are present in the dimer fraction - no evidence eg. IR or NMR for the presence of such compounds has been observed.

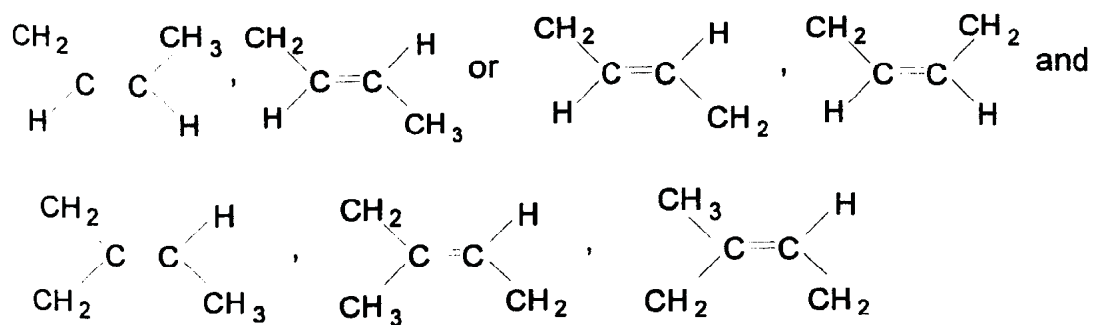
ii). *Olefinic substituents*

It is assumed that the dimer has the formula $\text{C}_{12}\text{H}_{24}$ and that no alkane or di-olefin product is present in this product. The total intensity of the protons in the NMR spectrum is 169 units and this means that each proton corresponds to an intensity of 7.08 units.

If only unsubstituted olefins are present, there should be 2 protons per double bond. The sum of all the resonances in the olefinic region (between 5.00 and 6.00 ppm) is 10.5. The intensity of the protons attached α , relative to the olefin, is thus ~ 10.5 units which corresponds to ~ 1.5 protons per double bond when divided by 7.08 which is the intensity per proton. Since the value obtained is much lower than a value of 2, this would indicate substitution at the double bond. The broad peak at ~ 2.00 ppm corresponds to the CH_2 unit in $\text{C}=\text{C}(\text{H})\text{CH}_2$ and suggests that there are almost 2 CH_2 units per double bond. Further the region at ~ 1.7 ppm corresponds to a series of

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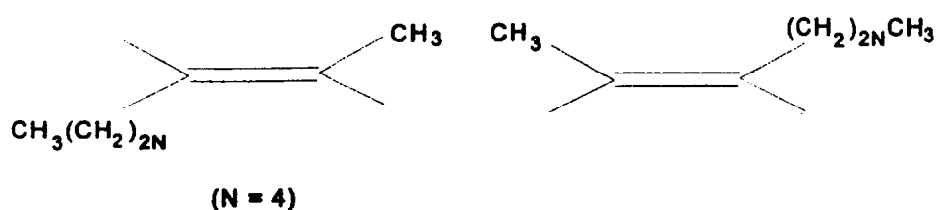
strong sharp absorptions (at least 3) of intensity 9.3 and thus could correspond to a CH_3 group attached directly to the olefin (i.e. about 0.4 CH_3 groups per double bond). Hence it can be deduced that nearly all the substitution at the double bond is *via* CH_2 and CH_3 groups - as predicted from the olefinic proton intensities. This thus suggests $\text{R} = \text{CH}_2$ or CH_3 . The number of isomers thus possible includes:



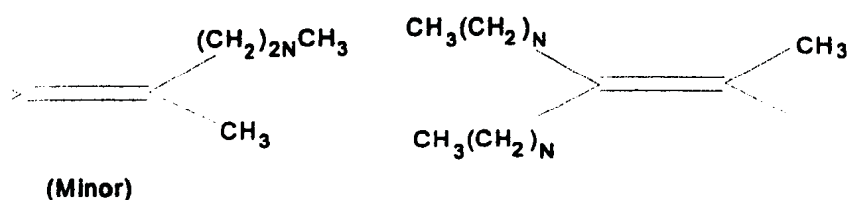
iii). CH_2 and CH_3 ratio

Terminal CH_3 groups ($\delta \approx 1$ ppm) correspond to ± 7 protons (i.e. at least 2 methyl groups per dimer). Interestingly at least 3 peaks are observed in the spectrum suggesting that CH_3 groups are in different environments. The presence of CH_2 groups in a chain is given by the absorption at ~ 1.4 ppm and is equivalent to ± 12 protons (i.e. 6 CH_2 units) *viz* a $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ structural type is predicted.

From the data obtained this far the structure of the dimer isomers can be deduced with some degree of certainty. The following range of structures can thus be proposed for the dimer:



and the

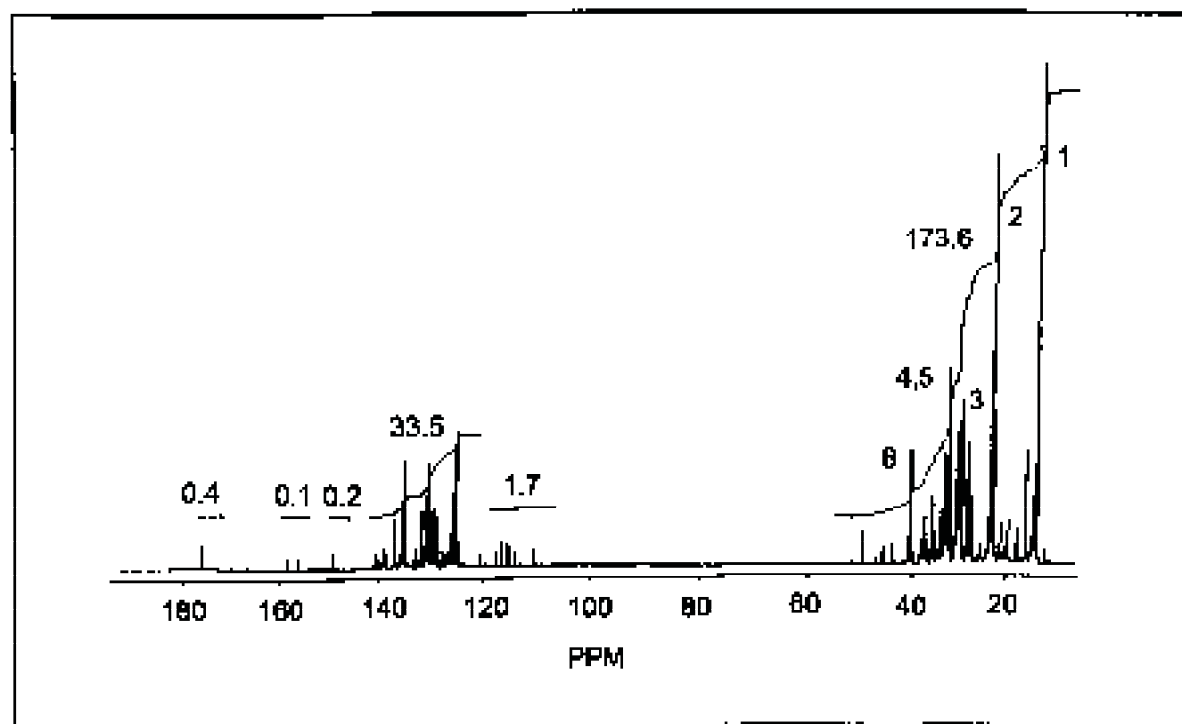


various isomers based on the last mentioned structure.

8.4.2.2. ^{13}C NMR spectrum (Figure 8.12)

The ^{13}C NMR spectrum shows a complex set of multiple absorptions, but again two distinct regions can be detected. The peaks between 120 and 140 ppm correspond to olefinic carbon atoms while those between 10 and 40 ppm correspond to aliphatic carbon atoms.

Figure 8.12: ^{13}C NMR spectrum of a predominant 1-hexene dimer fraction (i.e fraction 2)



Certain data which relate to the analysis of the dimer are given below and together with the analysis of oligomers reported in this work make assignment of the dimer possible.

Table 8.5: Assignment of a dimer structure

CH_2	$-\text{CH}_2$	$-\text{CH}_2$	$-\text{CH}_2$	
14.1	22.8	32.1	29.5	Next to alkane
13.6	22.4	32.2	34.5	Next to alkene

The above would suggest some differences regarding the analysis of a hydrogenated oligomer given by Wu (1989 a) (Figure 8.13):

- 1). CR_2H occurs at - 30.1 ppm, not at - 33 ppm (peak 5)
- 2). Peak 6 is CH_2 but is very high and difficult to assign

A spectrum of a hydrogenated dimer prepared by Wu (1989 a) is shown in Figure 8.13. This spectrum was analysed by Wu (1989 a) and a possible structure for an oligomer, shown in Figure 8.14, was proposed.

Figure 8.13: ^{13}C NMR of HVI-PAO obtained from 1-hexene (Wu, 1989 a)

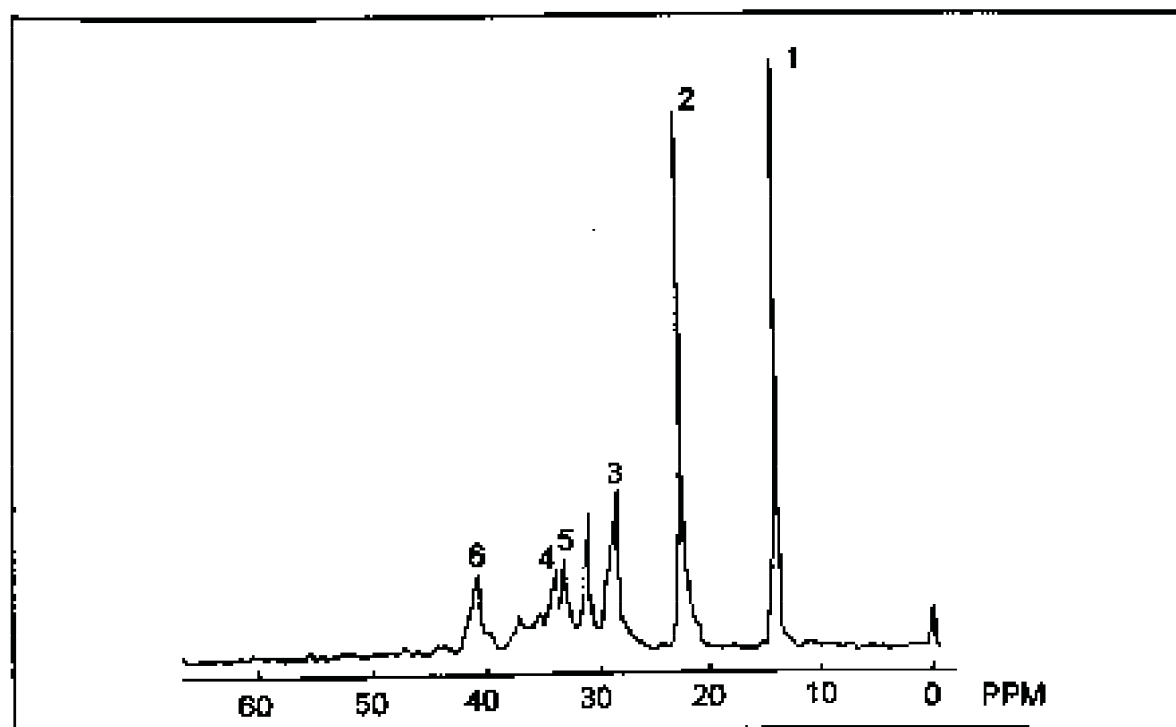
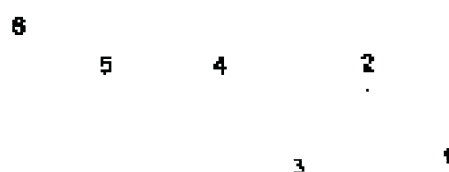


Figure 8.14: Possible structure for a 1-hexene oligomer (Wu, 1989 a)



A dimer would entail chain termination via double bond formation to provide a structure

of the type  (i.e. 5-methyl-5-undecene) suggesting that

changes to the spectrum will be visible at carbon atoms 4 through 8. Indeed a comparison of the spectra shown in Figures 8.11 and 8.12 is given in Table 8.6 and indicates that whereas most of the peaks are found in both spectra, differences in intensities at carbon atoms 4 and 5 are particularly striking.

Whereas the intensity data from the ^1H spectrum can be used to quantify the proton spectrum, care must be used when attempting the same process for the ^{13}C spectrum. If there are any carbon atoms which are not attached to protons, then their intensities will be much less than for carbon atoms attached to protons.

Table 8.6: Chemical shifts in the ^{13}C NMR of fraction 2 and assignments of the various carbon atoms

Assignment	Carbon atom number	Observed chemical shift (ppm)	Chemical shifts observed by Wu (1989 a) (ppm)
terminal CH_3	1	± 13	± 14
$\text{CH}_3\text{CH}_2\text{CH}_2-$	2	± 23	± 23
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2(\text{CH}_3)-$	3	± 29	± 29
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)$ and	4	± 35	± 34.5
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}=\text{C}$	5	± 35	± 33.5
$-\text{CH}_2-$	6	± 41	± 41

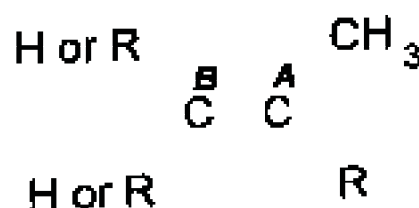
i). *Methyl and methylene CH₂ ¹³C spectrum*

The absorptions at ~ 13 ppm consist of one dominant peak, plus two or three other peaks. The position is consistent with a terminal CH₃ next to a CH₂ or (CH₂)_n group. The dominant CH₂ peak at 22 ppm is flanked by two or more smaller peaks and again this spectrum is consistent with the ¹H spectrum. The ratio of CH₂/CH₃ is ~ 1:1. A series of peaks are found at approximately 30 ppm (for δ carbons) and 32 ppm (for γ carbons) consistent with CH₂ groups in a chain and the peak ratio is also about 1:1. Again consistency with the ¹H spectra is noted to give an overall structure of the type CH₃CH₂CH₂CH₂-. There are many other smaller absorptions in the CH₂/CH₃ ¹³C region of this spectrum including some significant peaks at ~ 40 ppm. These were assigned as peak 6 in Figures 8.11 and 8.12.

ii). *Olefinic ¹³C spectrum*

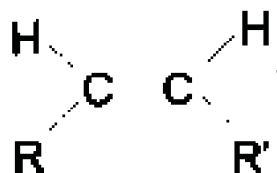
This portion of the spectrum has three clusters of resonances with intensity ratio of ~ 1 : 2 : 1 (126, 130, 136 ppm). The resonance at 136 ppm is suggestive of an olefin carbon atom (**A** in Figure 8.15) bonded to a CH₃ group and a cis/trans longer alkyl chain (Couperus *et al.*, 1976). This would constitute 25% of the olefin carbon atoms; a figure predicted from the ¹H spectrum. The resonance at ~ 126 ppm could correlate with the second olefinic carbon atom (**B** in Figure 8.15). The central resonance at 130 ppm correlates with a more symmetrical longer chain isomer (Figure 8.16).

Figure 8.15: Indication of the position of the olefinic carbon atoms **A** and **B**



with R an alkyl group longer than one carbon atom

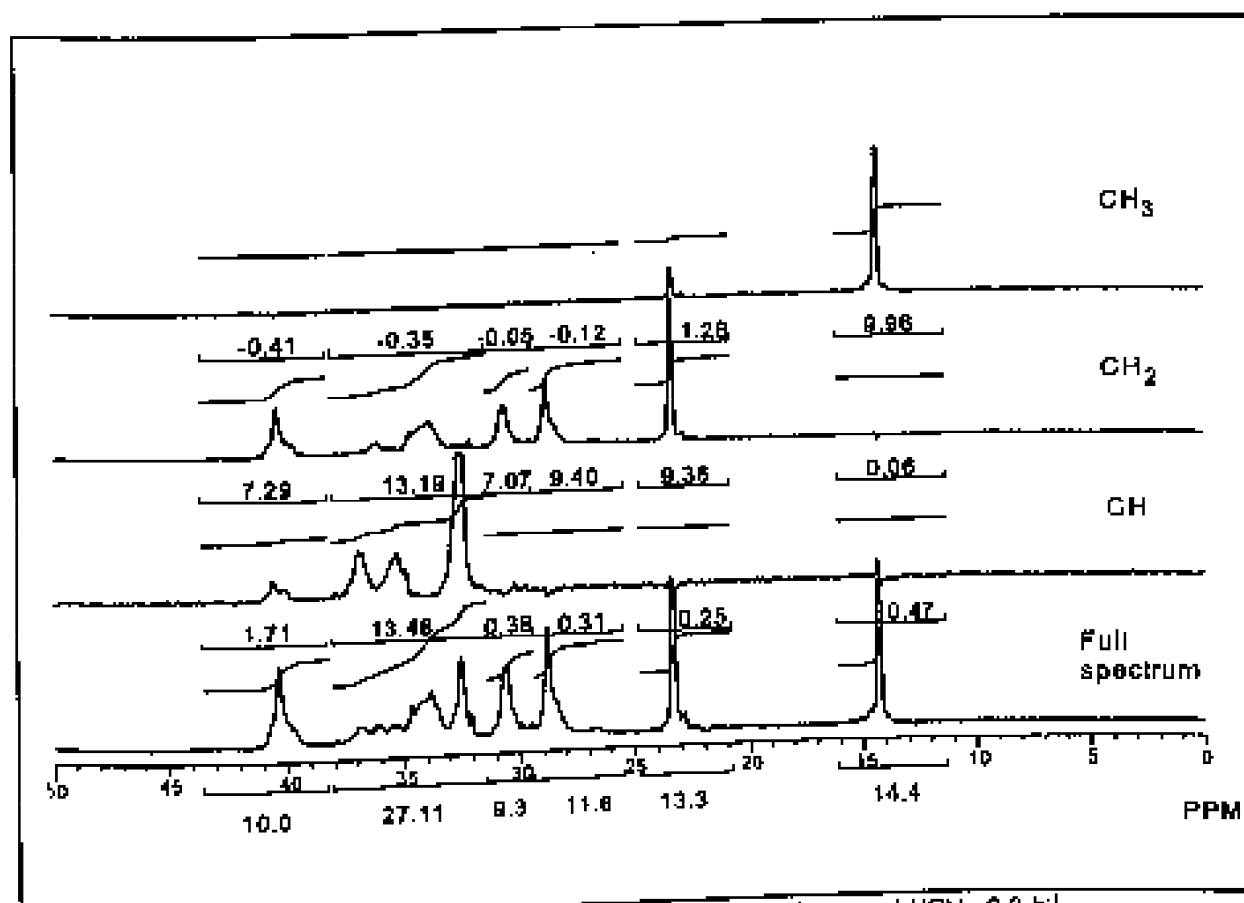
Figure 8.16: Illustration of a symmetrical longer chain isomer



8.4.2.3. DEPT spectra

DEPT spectra were recorded on a range of samples. An example of a DEPT spectrum is shown in Figure 8.17.

Figure 8.17: DEPT spectrum of a clear product obtained at 88°C^a



^aReaction conditions: Pressure: 8 bar; Temperature: 88°C; 1-hexane LHSV: 0.8 h⁻¹

The DEPT spectrum permits assignment of the isomers in the 10 - 40 ppm region to CH, CH₂ or CH₃ groups. In general the data confirm all earlier analyses. Further information obtained includes:

- a) Confirmation of two types of CH₃ groups. A terminal CH₃ at ~ 14 ppm and another peak at ~ 24 ppm. This second CH₃ group, of much lower intensity, may be due to a CH₃ attached to a CH₂=CH(CH₃) type moiety
- b) The peak at ~ 40 ppm is due to a CH₂ group
- c) Of most significance is the observation of a substantial concentration of aliphatic CH groups in the complex. In particular a major peak is observed at ~ 32 ppm
- d) It was also found that a variation in the reaction conditions (eg. increase or decrease in pressure, LHSV or temperature) resulted in the formation of products with very similar DEPT spectra

The complexity of the spectrum is consistent with multiple isomer production in the reaction. In the case of a *rac*-ethylenebis(1- η^5 -indenyl)dichlorozirconium-methylaluminoxane catalysed polymerisation reaction of 1-hexene, Babu *et al.*, (1994) found that various poly-hexene isomers can be formed due to migration of the zirconium moiety:

- i) along the carbon backbone and
- ii) along the 1-hexene chain.

The ¹³C spectra of these various isomers have been reported and provide a reference source for the interpretation of the data obtained in this study. The products of the two possible reactions listed above, made applicable to the Cr/SiO₂ catalysed dimerisation of 1-hexene, can be seen in Figures 8.18 and 8.19 respectively.

Figure 8.18: Migration of Cr along the backbone to form various vinylenes isomers

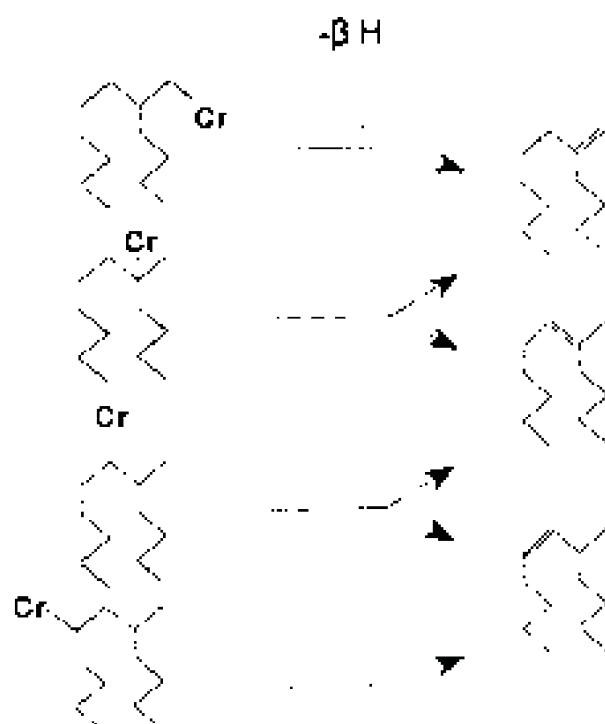
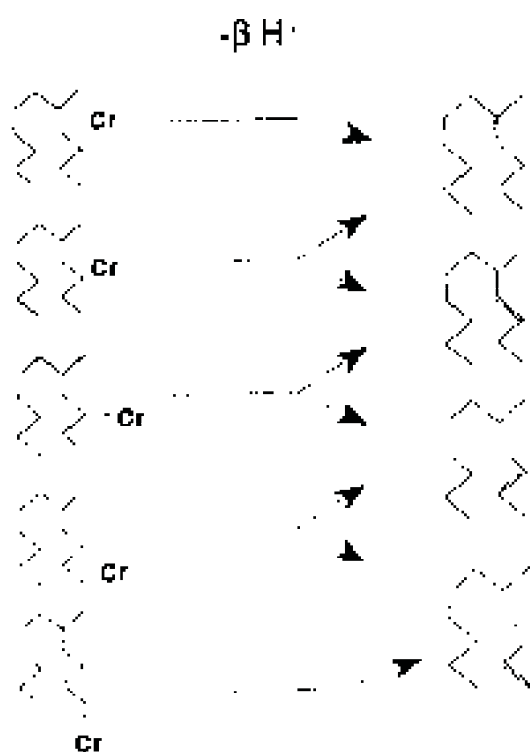


Figure 8.19: Migration of Cr along the 1-hexene chain to form various isomers



The ^{13}C NMR spectrum in this investigation was more complex than those reported by

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Babu *et al.*, (1994) and van der Linden *et al.*, (1995) once again implying isomerisation occurring under the reaction conditions of this investigation or possible isomerisation after the oligomerisation reaction has taken place.

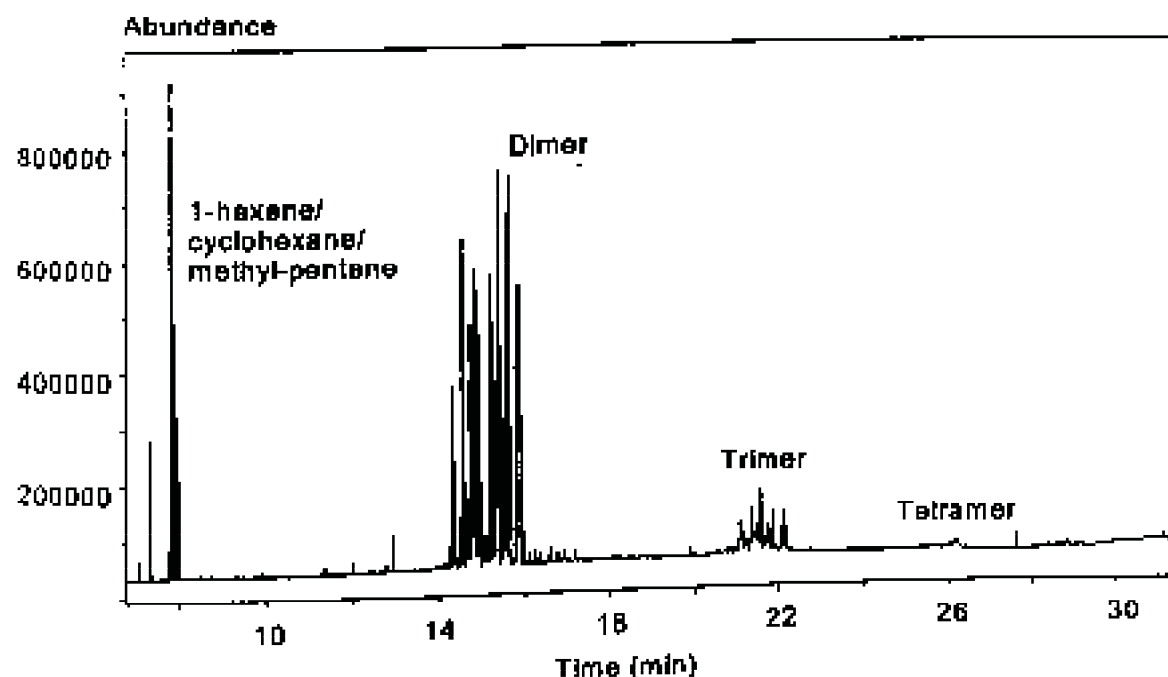
8.4.3. Effect of reaction temperature on the NMR spectra of the products

It was indicated in Chapter 6 that the oligomerisation temperature has an effect on the colour of the product, with a low temperature (88°C) producing a clear product and a high temperature (124°C) producing a yellow product. GC-MS and NMR spectral analyses of the clear and yellow oligomers were undertaken to assess whether the reason for the yellow colouration could be associated with the composition of the oligomer. To this end, ^1H , ^{13}C and DEPT spectra were recorded. The spectra were very similar to the spectra described in the previous section.

8.4.3.1. GC-MS spectra

In Figure 8.20 the GC-MS spectrum of a yellow sample can be seen. A comparison of the GC-MS spectrum of the yellow sample (Figure 8.20) with that of a clear sample (Figure 8.4) reveals variations in the intensity ratios of the various peaks. Especially of interest is the presence of a large number of isomers between 16 and 18 minutes in the yellow fraction which were of much lower intensity in the clear product. The distribution of the dimer isomeric peaks also differs from that in Figure 8.4 implying a variation of the degree of isomerisation taking place (probably due to the higher reaction temperature).

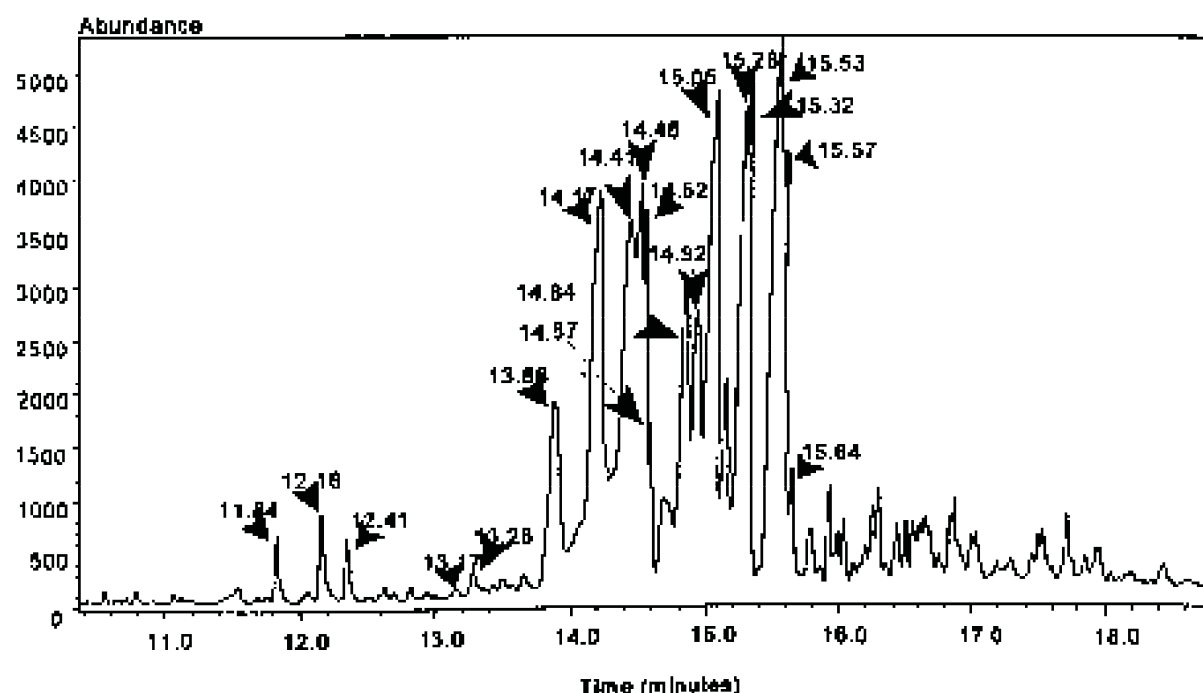
Figure 8.20: GC-MS spectrum of a distilled yellow sample (reaction temp: 124°C)*



*Sample: 0.4 μ l, column: 50 m PONA; split: 1:100; Temperature: 50°C to 300°C at a rate of 4°C.min⁻¹

In Figure 8.21 the dimer fraction of the GC-MS spectrum of the yellow high temperature product can be seen.

Figure 8.21: Magnified fraction of the dimer bundle of the yellow product



A comparison of the above spectrum with a similar GC-MS fraction (Figure 8.5) of a clear product reveals the following differences between the yellow and the clear products:

- i). An additional peak at 11.84 minutes in the yellow product. Identification of this peak proved to be difficult
- ii). Almost complete absence of a peak at 13.17 minutes, while this peak was quite prominent in the clear product
- iii). Much higher Intensity ratio of the peaks occurring at 13.88, 14.17, 14.41, 14.46 and 14.52 minutes relative to the other dimer isomeric peaks. This would indicate a higher olefinic content since these peaks occur in the olefinic region. Unfortunately only the peak at 14.52 could be identified: 7-methyl-5-undecene (Z)
- iv). Between 15.8 and 18.00 minutes a number of unidentified peaks are present in the yellow product while these are less prominent in the clear product.

Oligomerisation mechanism

The differences between the GC-MS spectra of the clear and yellow product mostly occur in the olefinic region, which suggests that the oligomeric products differ in terms of the quantity of double bonds, with the yellow product representing a higher concentration of double bonds. This observation is supported by the fact that a much higher bromine number was obtained for the yellow product (Chapter 6).

8.4.3.2. ¹H spectra

i). Clear product (88°C)

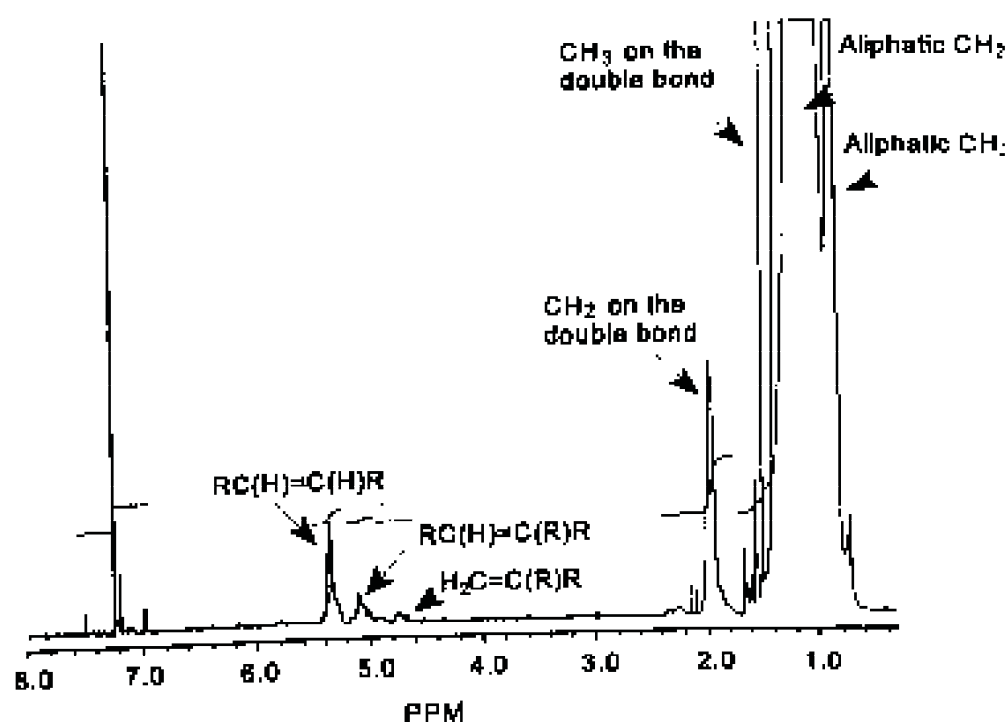
The spectrum is shown in Figure 8.22. Comparison with Figure 8.11 reveals many similarities between this product and the dimer/trimer mixture^a shown in Figure 8.11.

Differences include:

- 1). A higher CH=CH to >C=CH ratio (at ~ 5.3 ppm and ~ 5.1 ppm respectively) implying more linear chains. Further the intensity of the α -olefin CH₂ resonance at ~ 4.7 ppm is also higher
- 2). The CH₂ and CH₃ linear peaks are substantially increased in intensity

^aFraction 2 oligomer product obtained by oligomerisation at 99°C followed by distillation into separate fractions

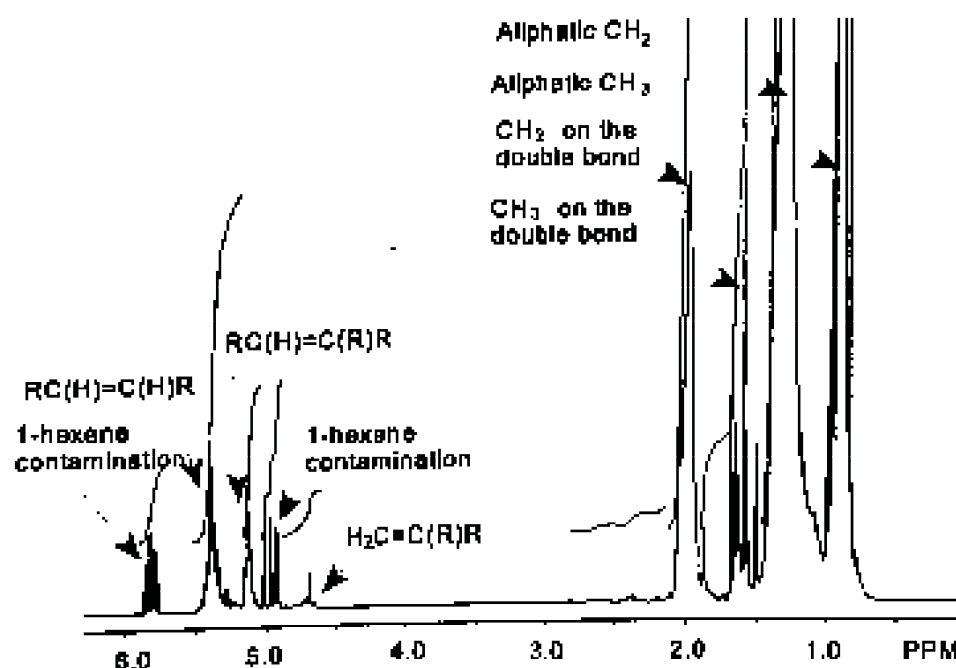
Figure 8.22: ^1H NMR spectrum of the low temperature product (88°C)



ii). *Yellow product (124°C)*

The yellow product was distilled and the ^1H NMR spectrum recorded (Figure 8.23). The GC-MS spectrum revealed that the product consisted predominantly of dimer material (Figure 8.20) and some 1-hexene.

Figure 8.23: ^1H NMR spectrum of the yellow distilled sample



A comparison of the ^1H spectrum of the low temperature product (Figure 8.22) with that of the high temperature product (Figure 8.23) reveals the following differences in the yellow high temperature product:

- A drop in intensity ratio of especially the aliphatic CH_2 peak
- An increase in the linear chain alkene CH_2 to CH_3 ratio
- A decrease in the RC(H)=C(H)R to RC(H)=C(R)R ratio, suggesting a greater degree of branching at the olefinic carbon atoms

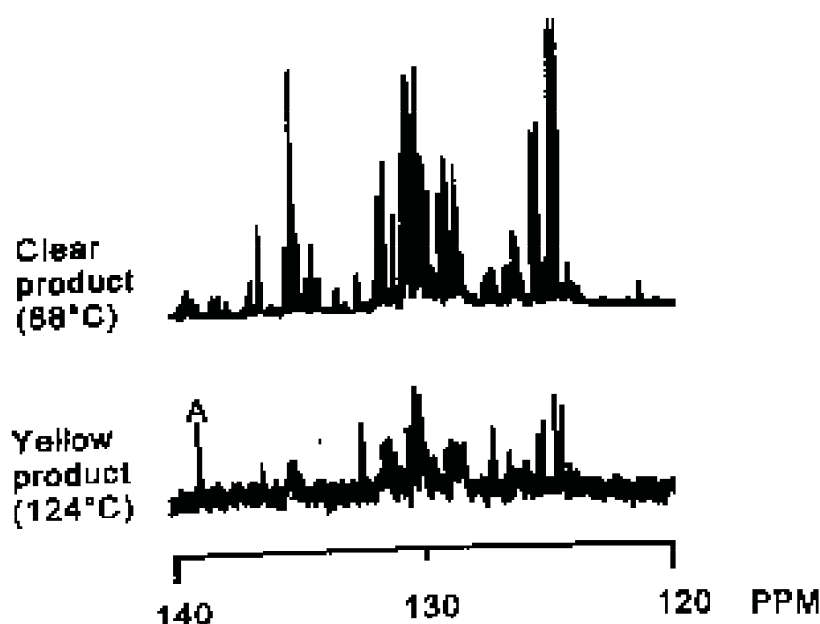
The colouration of the product with an increase in the reaction temperature thus seems to be related to changes occurring in the double bond characteristics of the oligomeric product.

Oligomerisation mechanism

8.4.3.3. ^{13}C NMR spectra

In Figure 8.24 the ^{13}C NMR spectrum of the clear product obtained at 88°C is compared to the ^{13}C NMR spectrum of the yellow product obtained at 124°C in the region between 120 and 140 ppm.

Figure 8.24: ^{13}C NMR spectrum of the clear low temperature (88°C) product compared to that of the yellow high temperature (124°C) product



*1-hexene contaminant

A comparison of the ^{13}C NMR spectra of the two products revealed a variation in the intensity ratios of the three major clusters of resonances (126, 130 and 136 ppm). The following differences were observed:

- i). The clear material indicates a higher intensity ratio of peaks at ~ 136 ppm. As mentioned in Section 8.4.2.2, this peak corresponds to an olefinic carbon atom bonded to a CH_3 group and a *cis/trans* longer alkyl chain

Oligomerisation mechanism

- ii). The intensity ratio of the peak bundle at 130 ppm relative to the peak bundle at 124 ppm is higher in the yellow product. The peak at 130 ppm corresponds to a more or less symmetrical longer chain isomer (see Section 8.4.2.2.)
- iii). The intensity ratio of the peak at 126 ppm seems to be lower in the high temperature product. In Section 8.4.2.2. this peak was identified as corresponding to an olefinic carbon atom bonded to alkyl chains or hydrogen atoms
- iv). The intensity ratio of the resonances at 126, 130 and 136 ppm was found to be ~ 1:2:1 in the clear product while this ratio was ~ 1:4:0.5 in the yellow product

8.5. CONCLUSION

From the detailed GC-MS and NMR analyses that were performed on oligomer fractions obtained by shortpath distillation of a clear product it was found that isomerisation of the double bond was responsible for the presence of large quantities of isomers in the oligomerisation product. The Ziegler-Natta head-to-tail mechanism was identified as the mechanism predominating during the Cr/SiO₂ catalysed oligomerisation of 1-hexene.

From the nature of the branching in the products that were identified, isomerisation of the double bond before the oligomerisation reaction seems unlikely. In agreement with the findings of Babu *et al.*, (1994) for zirconium migration along a carbon oligomer backbone, two schemes (Figures 8.18 and 8.19) were proposed for the Cr/SiO₂ catalysed oligomerisation of 1-hexene. These schemes agree with the nature of the products identified by GC-MS techniques.

An in-depth investigation was also done on the effect of temperature on the NMR and GC-MS spectra of oligomer products. The GC-MS; ¹H-NMR and ¹³C-NMR data supported the results obtained with IR, Bromine number and TCNE determinations (Chapter 6) which indicated that the yellow product contains a larger quantity of certain

olefinic compounds. Unfortunately no identification of the specific isomers responsible for the colouration was possible.