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A study of poly(vinyl chloride) microstructure

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A STUDY OF POLY(VINYL CHLORIDE) MICROSTRUCTURE

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APPROVAL SHEET

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ABSTRACT

High-field ^{13}C and ^{1}H NMR spectroscopies have been used to investigate some unusual features of the molecular microstructure of poly(vinyl chloride) (PVC). The results obtained have illuminated several significant aspects of the mechanism for vinyl chloride (VC) polymerization, and they also relate to the very important question of the reasons for the thermal instability of the polymer.

Several model monochloroalkenes were synthesized in order to determine ^{13}C shift increments for the replacement of H by Cl at positions that are α, β, or γ to an isolated internal double bond in a linear carbon chain. These increments then were used to predict the ^{13}C shifts of the internal allylic chloride structure in PVC. The predictions were not satisfactory, a result which showed that, as expected, the increments were not additive.

It was shown that during conventional VC polymerization, the chloroallylic chain end ($-CH_2CH{=}CHCH_2Cl$) does not copolymerize with the monomer and is not destroyed by a mechanism involving allylic rearrangement, macroradical addition, and chlorine-atom β-scission to produce a $-CHClCH_2CH{=}CHCH_2CHCl-$ structure. Nevertheless, that mechanism was found to operate during the preparation of a special type of PVC [made at 0 °C with $(t\text{-Bu})_2Mg$ initiation] which contained the rearranged chain end, $-CH_2CHClCH{=}CH_2$, at an abnormally high concentration.

During the preparation of PVC under subsaturation VC pressures, small amounts of a 1,3-di(2-chloroethyl) branch structure were found to be formed by a "double backbiting" mechanism involving two intramolecular H abstractions in succession. The presence of this structural defect, which is believed to be very unstable to heat, was established by the 125.77-MHz ^{13}C NMR spectra of reductively dechlorinated PVC specimens. At 55-80 °C, the two backbites leading to the defect differ substantially in relative rate, in that the backbiting:addition rate ratio is larger for the second backbite by a factor of 15-16 (mean value), irrespective of temperature. Remarkably, no evidence was obtained for the presence of the 2-ethyl-*n*-hexyl branch structure that would have resulted from double backbiting by an alternative route. The absence of this structure and the presence of the 1,3-di(2-chloroethyl) branch array were confirmed by spectral comparisons with the ^{13}C shifts of two reference models, 9,11-diethylnonadecane and 9-(2-ethyl-*n*-hexyl)heptadecane, that were prepared by unambiguous tactical methods.

Polymerizations of VC were performed in the presence of two potential transfer agents, *trans*-1-chloro-2-hexene and *trans*-1,5-dichloro-2-pentene. Preliminary examination of the resulting polymers by high-field NMR provided evidence for the destruction of the $-CH_2CH{=}CHCH_2Cl$ chain end, during polymerization, by a mechanism involving H abstraction to form the $-CH_2CH{=}CHC^{\bullet}HCl$ radical, followed by the addition of that species to VC in order to give the thermally unstable structure, $-CH_2CH{=}CHCHClCH_2-$.

A STUDY OF POLY(VINYL CHLORIDE) MICROSTRUCTURE

CHAPTER 1

INTRODUCTION

1.1 General

Polymers are everywhere. People began to use natural polymers at the same time that they themselves appeared in the world. Such polymers as cellulose, starch, natural rubber, etc., were used for ages long before they were recognized as polymers.

It is impossible to imagine modern life without polymers. Herman F. Mark wrote in 1985: "We would have no Bible, no Greek epics and tragedies, and no Roman history without parchment and papyrus. There would be no paintings of Leonardo, Raphael, and Rembrandt without canvas and polymerizing oils. And there would be no music of Corelli, Beethoven, and Tchaikovsky without string instruments, all of which consist entirely of natural organic polymers such as wood, resins, and lacquers".[1] Many modern technologies are based on the use of polymeric composite materials which are lighter and very often much more durable than natural products and/or metals.

The importance of the invention of polymers and polymerization has been emphasized many times and in many places. Lord Todd (former president of the Royal Society of London) answered the question, "What do you think has been chemistry's biggest contribution to science, to society?", as follows: "I am inclined to think that the development of polymerization is, perhaps, the biggest thing chemistry has done, where it has had the biggest effect on

everyday life. The world would be a totally different place without artificial fibers, plastics, elastomers, etc. Even in the field of electronics, what would you do without insulation? And there you come back to polymers again".[2]

1.2 Poly(vinyl chloride) (PVC)

With a consumption of about twenty million tonnes worldwide (Table 1.1),[3] poly(vinyl chloride) (PVC) continues to be the second most important commodity plastic (polyethylene ranks first).

Table 1.1

Worldwide PVC consumption according to regions (in 1000 t)

	1992	1995
Western Europe	5,200	5,320
Eastern Europe	1,260	850
North America	4,600	5,050
Japan	1,870	1,830
Southeast Asia	3,900	5,500
Rest of the world	1,670	1,850
Total	18,500	20,400

Until the year 2000, an average increase in worldwide consumption of 4% per year is expected, with Western Europe accounting for about 2%, but the growing Asian market for 6%. The growth rates for the various applications differ, as the data for Western Europe illustrate (Table 1.2).[3]

Table 1.2

Western Europe PVC consumption according to major applications (share in %)

Application	1992	1995
PVC-unplasticized (total)	66	68
Pipe/fittings	28	29
Profiles/sheet	16	19
Film	10	9
Bottles/hollow articles	8	7
Miscellaneous	4	4
PVC-plasticized (total)	34	32
Film	8	7
Tubing/profiles	4	4
Coatings	4	5
Flooring	5	5
Cable	8	8
Miscellaneous	5	3

Developments in PVC production which are expected to enable a direct conversion of ethane to vinyl chloride could secure a cost advantage for PVC.[4] The main focus of the process development was and is on the reduction of production costs by energy conservation and on the reduction of chemical emissions to air and water. Today's modern polymerization units operate with such low emissions that they fall below current strict limits imposed by the law.[5]

The preparation of vinyl chloride was reported in 1835 from the reaction of ethylene dichloride with alcoholic potassium hydroxide.[6] The first "metamorphosis" (polymerization) of vinyl bromide was observed in 1860, and the polymerization of a number of vinyl halides, including vinyl chloride, by exposing them to sunlight was reported in 1872.[7] In 1914 Hoechst reported the use of organic peroxides to accelerate the reaction and announced the first use of free-radical initiators.[8] Commercial production of PVC was started in Germany in 1932, using emulsion technology.[9] The first PVC plant to be built in the USA (in 1936) was the Carbide and Carbon Chemical Companies (now Union Carbide) plant at South Charleston, West Virginia.[10] In the USA and later in the UK, PVC production was based primarily on suspension polymerization, rather than on the emulsion polymerization that was favored in Germany.

However, PVC was still far away from full acceptance, because its processing and heat stability problems had to be solved. The first breakthrough came in 1932 when B. F. Goodrich patented the use of plasticizers with PVC.[11] After examining a wide range of chemicals, the Goodrich group identified bis(2-ethylhexyl) phthalate as the best plasticizer.[11] The use of PVC stabilizers also was developed in the 1930s. In Germany, alkalis had been used to improve the stability for some time, and in 1934, the use of lead stabilizers was patented.[12] In the same year two researchers from Union Carbide patented the use of "one or more alkali metal, cadmium,

lead, or manganese salts of weak carboxylic acids" as stabilizers.[13] The use of dialkyltin soaps as stabilizers was discovered soon thereafter.

PVC owes its popularity to its versatility. The polymer itself is chemically inert (to a large degree) and nonflammable, burning only in the presence of a source of ignition. It is compatible with many additives, including plasticizers, heat stabilizers, lubricants, fillers, and other polymers. All of these features have made PVC one of the world's major bulk polymeric materials.

1.3 Microstructure of polymers

A complete knowledge and understanding of the physical and chemical properties of polymeric materials is difficult, if not impossible, without the understanding and characterization of polymer microstructure. In most cases microstructures are formed during polymerization and are determined by processes such as the stereochemistry of monomer addition, initiation, propagation, termination, and chain transfer. The modification of polymers, by reactions such as "polymer-analogous" transformations or graft polymerization, can certainly cause other changes in polymer microstructure leading to branches, grafts, crosslinks, and new functional groups.

It is known that even in low concentrations, microstructures can provide significant effects on certain properties of polymeric materials, such as morphology and thermal stability. Powerful modern analytical methods allow one to determine and characterize polymer microstructures at very low concentrations and to reveal the presence of very complex moieties. For instance, this dissertation has confirmed the existence, in PVC, of 1,3-di(2-

chloroethyl) branch structures which were impossible to detect several years ago.[14]

Knowledge of the nature, concentrations, and formation mechanisms of the microstructures in polymers is very important for an understanding of the mechanism-structure-property sequence which is crucial in the design of new materials, the improvement of polymer properties, and the control of polymer processing.

CHAPTER 2

BACKGROUND

2.1 Degradation and stabilization of PVC

2.1.1 General

PVC is a unique polymer. Although it is produced in millions of tonnes (metric) per year, it is perhaps the most thermally and photochemically unstable commercial resin. The loss of HCl from PVC was discovered in the early 1930s in Germany:[1]

Scheme 2.1: Dehydrochlorination of PVC

$$\text{-(CH}_2\text{-CHCl)}_n\text{-} \xrightarrow{180\text{-}200\ ^\circ\text{C}} x\text{HCl}\uparrow + \text{-(CH=CH)}_x\text{-(CH}_2\text{-CHCl)}_{n-x}\text{-}$$

When x reaches a value of 7, PVC acquires color: pale yellow in the beginning (x = 7-8), then brown and eventually black. Larger values of x lead to more intense colors. Actually, coloration first occurs at *ca.* 0.1% of dehydrochlorination. The presence of conjugated polyenes in the polymer leads to oxidation and crosslinking, and as a result, the polymer loses its useful properties. An interesting phenomenon has been discovered: polyene sequences grow up to an x value of *ca.* 20-30 and then stop. The mechanism that is responsible for this result is not yet clear.[2]

Originally, the question about stability of this polymer was raised immediately after PVC was first prepared. What was (and still is) responsible for the remarkable instability of this material? To investigate the stability of the repeating unit in PVC, a model compound was studied:

$$CH_3\text{-}CHCl\text{-}CH_2\text{-}CHCl\text{-}CH_2\text{-}CHCl\text{-}CH_3$$

It was found that this compound begins to degrade only at temperatures above 250 °C, which are significantly higher than those where PVC degrades thermally.[3] On the basis of this experimental fact, the answer emerged: there are some structural defects in PVC, and they are responsible for the thermal degradation. Tertiary and allylic chloride were suggested to be the two major structures that are responsible for this degradation. However, their relative importance was not clear. Finally, the answer to this question was shown to be linked to the concentration of free HCl in the system. This conclusion emerged from a study of the degradation of several different model compounds containing either allylic or tertiary chloride structures.[4,5] The authors found that the degradation rate of a model compound incorporating tertiary chloride (5-chloro-5-methylnonane) was not sensitive to the rate of argon flow, which controlled the concentration of free HCl in the system. On the other hand, two stereoisomers with an allylic chloride group in their structures (*cis*- and *trans*-4-chloro-5-decene) showed a decreasing rate of dehydrochlorination when the argon flow rate was raised. Increasing the argon flow rate decreased the concentration of the free HCl. Eventually, both allylic chloride stereoisomers were found to be less reactive than 5-chloro-5-methylnonane at the highest flow rate and more reactive than that substance at the lowest flow rate. These results led to the conclusion that the dehydrochlorination of internal allylic chloride structures is more

susceptible to HCl catalysis than that of tertiary chlorides. This difference in susceptibility is so large that the relative reactivity of these two types of chloride can be changed merely by changing the concentration of HCl in the system.[5] The same difference in reactivity was observed later by other researchers.[6,7]

However, in the degradation of PVC it is difficult, if not impossible, to determine the concentration of HCl. This concentration is determined by a number of factors, such as temperature, viscosity, morphology, and the ability of the stabilizer system to scavenge HCl.

Another interesting result is the low dehydrochlorination reactivity expected[8] and found[9] for the chloroallylic chain-end models *cis*- and *trans*-1-chloro-2-hexene. Their reactivity was similar to that of a conventional *sec*-alkyl chloride.[9] Therefore, R-CH=CH-CH_2Cl structures are not unstable defects in PVC.

The existence of a unique structure has been proposed by Minsker *et al.*[10,11] It is a ketoallyl arrangement: -CO-$(CH=CH)_n$-CHCl-. The authors[10,11] argue that this is the only structural defect that contributes significantly to the thermal instability of PVC. It was proposed to result from a very selective and quantitative oxidation of allylic methylene moieties upon exposure of the polymer to air under ambient conditions. In studies of the stability of model compounds,[4,12] it was found that *trans*-R-CO-CH=CH-CHCl-R' (where R is *n*-Bu, R' is *n*-Pr) actually is much more stable that ordinary vinyl chloride units; whereas *cis*-R-CO-CH=CH-CHCl-R' undergoes dehydrochlorination very rapidly at room temperature to form furanoid structures that are very unstable as well.[12] In the case of PVC itself, the transformation of cis ketoallylic structures into furanoid ones would be followed by a facile dehydrochlorination to produce polyenes.[12] Minsker reported the amount of ketoallylic groups to be at the level of

0.05/(1000 C).[13] However, the existence of those structures at that level has not been confirmed by high-field (125-MHz) ^{13}C NMR spectroscopy, which would have been capable of detecting them.[9] Instead, the NMR results showed the presence, in samples obtained from Minsker, of nonoxidized internal allylic structures at the level of 0.1/(1000 C).[9]

It has been shown that the ordinary monomer units do play an initiatory role in thermal degradation[2,14] and that tacticity does influence polyene sequence growth.[15] The total concentration of both allylic and tertiary chlorides decreases with decreasing temperature of polymerization.[16] However, it has been found[17] that the thermal stability of PVC made at very low temperature is very poor and does seem best explained by a polyene length enhancement that is caused by increased syndiotacticity. Another relevant finding is that the thermal dehydrochlorination of PVC continues at about the same rate after the kinetic effects of labile structures introduced during polymerization are no longer detectable.[2,18] This constant rate of dehydrochlorination seems to require initiation by ordinary monomer units, whose conversion to allylic chlorides can occur as a result of HCl catalysis.[18]

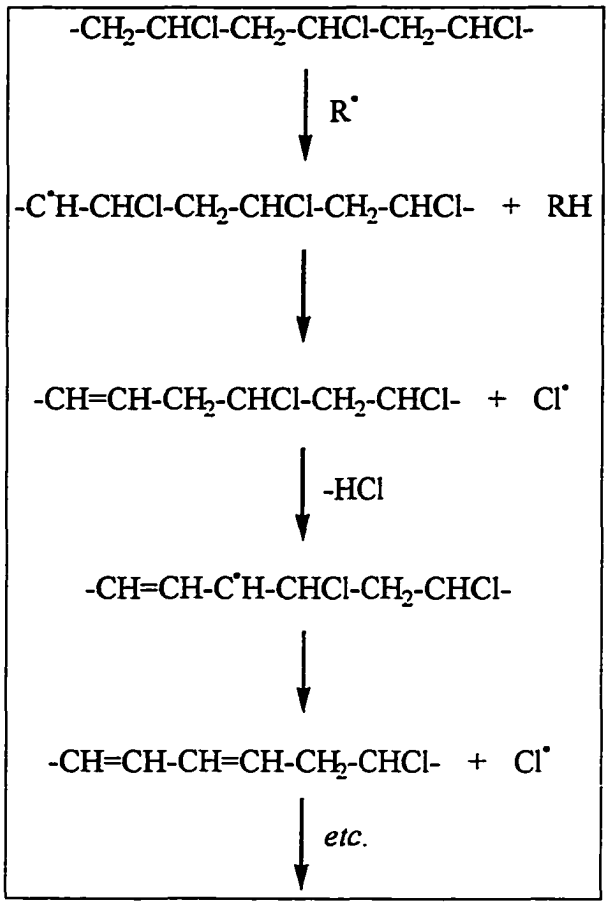
A survey of PVC microstructure will be undertaken below in Section 2.2.

2.1.2 Degradation of PVC

2.1.2.1 Free-radical mechanism

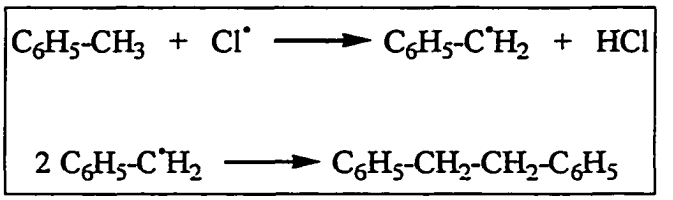
Several different mechanisms have been proposed for the growth of conjugated polyene sequences during the thermal degradation of PVC. Some of these mechanisms involve free radicals[19] according to the general scheme:

Scheme 2.2: Free-radical mechanism of PVC degradation



It has been found that the addition of free-radical sources accelerates polyene propagation, but this type of mechanism cannot explain the following observation: $Cl^{\bullet}$ is a very reactive and unselective radical and thus should be able to abstract hydrogen from other parts of the polymer, rather than exclusively from allylic CH_2 groups.[15] Also, if free $Cl^{\bullet}$ radicals were formed, they should be scavenged by radical traps. However, when toluene was present in systems containing decomposing model compounds, 1,2-diphenylethane was not formed:[5,9]

Scheme 2.3: Formation of 1,2-diphenylethane

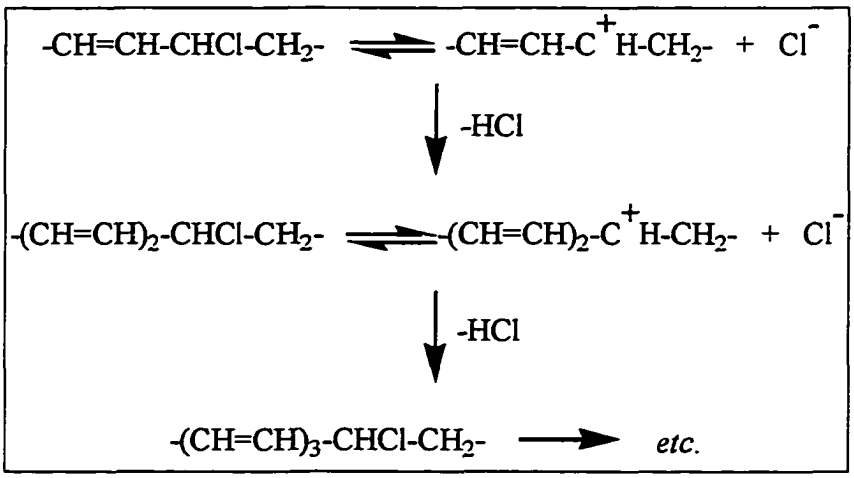


It now is known that $Cl^{\bullet}$ is so reactive that it abstracts hydrogen from aliphatic compounds in "cage" reactions (even in very fluid media) and that this abstraction is so fast that it competes efficiently with diffusion of $Cl^{\bullet}$ from the cage.[20] According to the radical scheme for dehydrochlorination, the rate of formation of polyene structures should be similar to the rate of dehydrochlorination.[9] However, experimental data published by Hjertberg and co-workers[21,22] show that the dehydrochlorination rate actually is about twenty times faster than the rate of polyene sequence formation during the nonoxidative degradation of the pure polymer at 190 °C.

2.1.2.2 Ion-pair mechanism

A much more likely mechanism for the dehydrochlorination[9] is depicted below. Actually there are two "submechanisms": "pure" ionic,[23] in which Cl^- is totally separated from the macrocation, and quasiionic, when a transition state with highly separated charges is involved. In the quasiionic mechanism, the breaking bond $C^{\delta+}$---$Cl^{\delta-}$ is much longer than the breaking bond $C^{\delta-}$--$H^{\delta+}$.[15,23]

Scheme 2.4: Ion-pair mechanism of PVC degradation



It is well-known that HCl is a very good catalyst for PVC dehydrochlorination. Recently its importance was reconfirmed[24] when it was found that the presaturation of PVC powder with HCl significantly increases the rate of subsequent thermal dehydrochlorination. It was also shown that the dehydrochlorination rate decreased with decreasing specimen thickness when nonpretreated films of PVC were used,[24] apparently owing to the faster diffusion rate of HCl from the thinner samples. Actually, HCl can take part in all of the steps that are involved in the formation of PVC polyenes: initiation, propagation, and termination. Some researchers found an acceleration of initiation in the presence of HCl,[22,25] and the ability of HCl to elongate polyenes owing to its catalysis of propagation was suggested by the same authors.

It is interesting that HCl may inhibit benzene formation from PVC by inhibiting intramolecular cyclization involving a triene whose central double bond is cis.[26] Inhibition could occur owing to HCl-catalyzed isomerization of the cis double bond into the trans configuration.

The rate of dehydrochlorination is much higher in polar solvents,[27] a result that strongly supports the operation of the ionic mechanism.

2.1.2.3 Other mechanisms

Another mechanism of dehydrochlorination (the so-called "polaron" one) was suggested in recent years.[28-31] It involves the formation of an allylic cation radical as a chain-carrying intermediate. However, this mechanism is not well-developed yet and has recently received some criticism.[9]

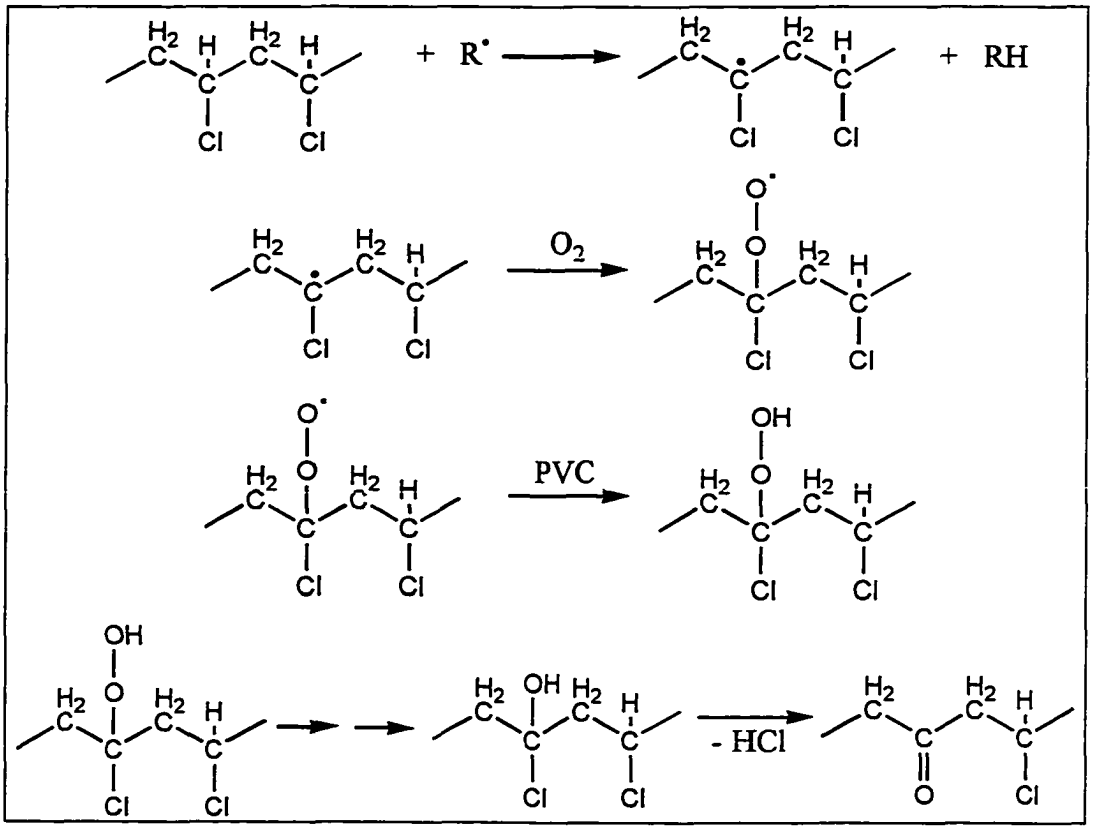
Some theoretical calculations have led to the conclusion that the formation of PVC polyenes involves the loss of several HCl molecules in a single step.[32] For example, 22 molecules of HCl were proposed to leave simultaneously, when the first one has left in an ionic process.[32] All of the excess energy needed to effect the first dehydrochlorination (*i.e.*, $\Delta H_{activation} - \Delta H_{reaction}$) was assumed to remain in the original polymer molecule and to cause ejection of the other HCls from that molecule in a process requiring no additional energy input.[32] However, any excess of vibrational or rotational energy would be most unlikely to remain localized near the first-formed double bond in a system of this type.[9] It should be transferred very rapidly, instead, (within 10^{-11}-10^{-12} s) to the condensed-phase matrix.[9,33] Moreover, this "one-step unzipping mechanism"[32] does not account for the considerable effects of catalysts, stabilizers, and temperature on the length of the polyene sequences.[9]

2.1.2.4 Effect of oxygen on PVC dehydrochlorination

It has been found that the rate of PVC dehydrochlorination increases in the presence of

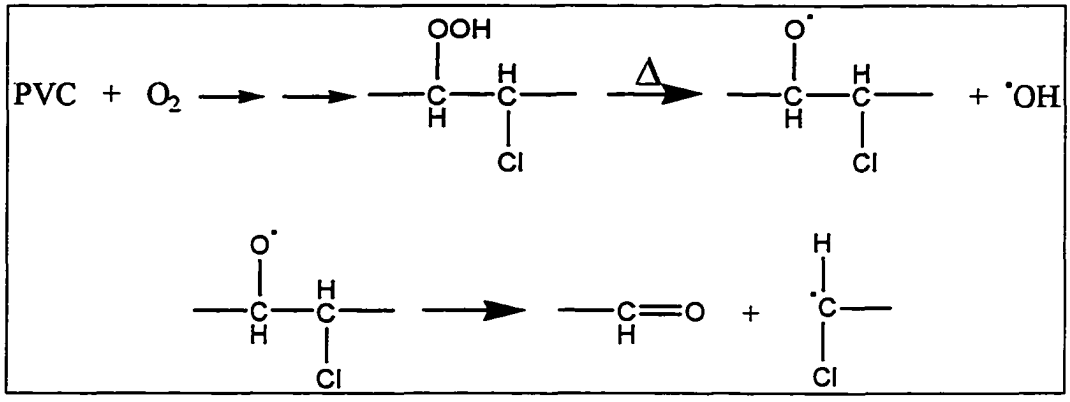
molecular oxygen and that oxygen increases chain scission during the thermodegradation of PVC.[34] At least two mechanisms for these effects have been proposed; one leads to HCl loss,[35] but the other one does not.[36]

Scheme 2.5: Oxidative degradation of PVC with HCl loss



The free radical at -C•Cl- does not β-cleave to break the PVC backbone, because the activation energy of that process is too high. An alkoxy radical attached to the backbone can β-cleave, but actually another mechanism also takes place (as shown): the peroxy radical abstracts hydrogen from another molecule of PVC to form a hydroperoxide that is converted into a geminal chlorohydrin whose dehydrochlorination produces a backbone keto group.

Scheme 2.6: Oxidative degradation of PVC without HCl loss

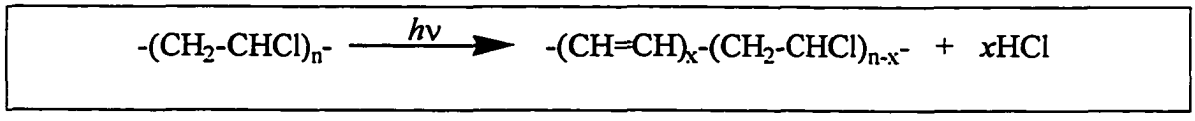


The β-scission of alkoxy radicals attached to polymer backbones is responsible for most of the chain cleavage occurring during the oxidation of PVC and other addition polymers.

2.1.2.5 Photodegradation of PVC

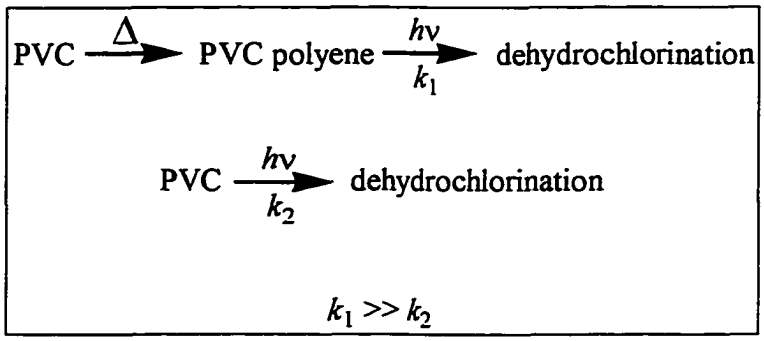
When it is exposed to direct sunlight, PVC undergoes degradation to form the same type of polyene sequences as in the case of thermal degradation:

Scheme 2.7: Photodegradation of PVC



Both thermo- and photodegradation are very facile processes. Some "initiators" of photodegradation must occur in virgin PVC. The presence of either C-Cl or isolated double bonds cannot account for the photoinitiation. Owen[37] deduced the following kinetic scheme:

Scheme 2.8: Kinetic scheme of PVC photodegradation



This scheme indicates that the photodegradation of PVC containing unsaturated sequences is the major process.

In 1982 Decker studied the degradation of PVC by UV radiation.[38] He reported that the value of the quantum yield ϕ_{HCl} (the number of HCl molecules produced per photon absorbed) was only 0.011 under an atmosphere of nitrogen. He also found independence of ϕ_{HCl} on the irradiation time (for extended periods) and on the initial amount of unsaturation in the polymer. An observed decrease of ϕ_{HCl} at very long irradiation times was attributed to the formation of a highly absorbing surface layer consisting of totally degraded PVC.

The initiating chromophores for photodegradation needed to be identified. By using laser Raman spectroscopy and other techniques, Maddams[39] and other workers had detected peroxy, carbonyl, and polyene groups in virgin PVC. In order to find the relative importance of these groups, the number of 300-nm photons absorbed by equal amounts of the chromophores was determined. The results showed the superiority of the polyene structures in photon absorbance; that is, a value of 10^4 *vs.* 10 for carbonyl groups and only 1 for peroxides. Therefore, the polyenes in virgin PVC are recognized to be the principal structure that is

responsible for photoinitiation.

Recently, Denizligil and Schnabel[40] studied the photooxidation of PVC in the absence and presence of phthalate plasticizers. They showed the formation of a number of carbonyl structures in the PVC backbone, including -CHCl-C(=O)-CHCl-. On the other hand, the cleavage of C-Cl bonds and crosslinking were retarded by the phthalates.

2.1.3 Stabilization of PVC

Since PVC is the second most widely produced polymer in the world and one of the least stable commercial resins, the topic of its stability is of great importance. This subject has been covered recently in several books and reviews.[2,9-11,19,41-44]

2.1.3.1 PVC thermal stabilizers

There are several groups of PVC heat stabilizers:

1) Organotin compounds

Some specific examples of these stabilizers are the following:

1. $Bu_2Sn[OCO(CH_2)_{10}CH_3]_2$ **2.** $Bu_2Sn[SCH_2COOC_8H_{17}]_2$

3. $Bu_2Sn[S(CH_2)_{11}CH_3]_2$ **4.** $-[Sn(Bu)_2\text{-}S\text{-}CH_2\text{-}COO]_x-$

5. $-[Sn(Bu)_2\text{-}OCO\text{-}CH{=}CH\text{-}COO]_x-$ **6.** $Bu_2Sn(OCO\text{-}CH{=}CH\text{-}COOR)_2$

where Bu is *n*-butyl, and R is alkyl.

Stabilizer **1** is one of the oldest used by industry. The effectiveness for long-term stability can be expressed by this sequence:[42]

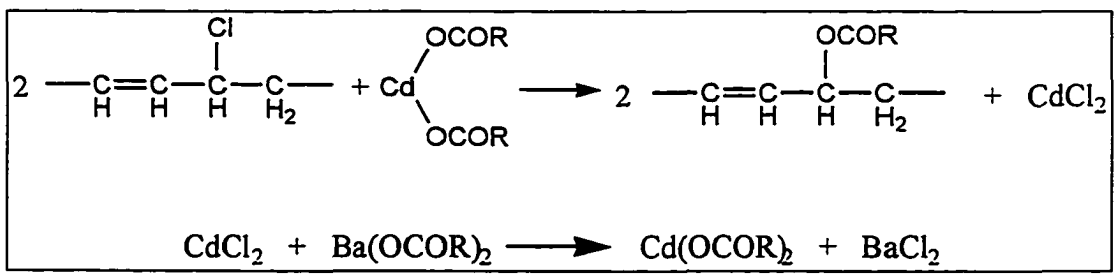
2 and **4** > **3** > **5** and **6** > **1**

The superiority of **2**, **3**, and **4** is due to nucleophilicity. Sulfur-containing nucleophiles are more reactive than those containing oxygen, while **2** and **4** probably are better than **3** because of their greater solubility in PVC. Stabilizers **5** and **6** act as Diels-Alder dienophiles to stop the growth of polyenes. Recently, Oct_2Sn(*iso*-octylthioglycollate)$_2$ was shown to be an effective thermal stabilizer.[45]

2) Metal soaps

The synergistic system consisting of $Ba(OCOR)_2$ and $Cd(OCOR)_2$ was used for years until cadmium compounds were classified as toxic substances. This system works according to this scheme:

Scheme 2.9: Stabilization of PVC by Ba/Cd soaps



In these reactions cadmium soap (for example, the stearate) replaces labile (both allylic and tertiary) chlorines in PVC to form more thermally stable structures. The disadvantage of this reaction is the production of the strong Lewis acid, $CdCl_2$, which causes dehydrochlorination.[46] However, the barium soap then plays an excellent role by converting the $CdCl_2$ into the stabilizer $Cd(OCOR)_2$ and concurrently forming the weak Lewis acid, $BaCl_2$, which is not a

dehydrochlorination promoter. According to this mechanism, it can be expected that in the case of barium-cadmium carboxylate mixtures, the stabilization effect would increase continually as the barium-to-cadmium ratio is increased.[19,47,48] Its failure to do so has been taken as evidence against the Frye-Horst stabilization theory (just described), which is discussed in more detail below. However, a recent model-compound study, carried out by Grossman[49] and incorporating both kinetic and product evidence, showed that the most effective Frye-Horst reagent is actually a 1:1 complex obtained from equal parts of the carboxylates of cadmium and barium. It also was shown that since this complex is much more reactive toward labile chlorine than the barium carboxylate itself, increasing the barium:cadmium ratio above 1:1 does not affect the rate of dehydrochlorination.

Because of the cadmium toxicity, other mixed-metal systems (such as calcium/zinc[50] or barium/zinc soaps[51,52]) were developed and already are widely used in industry. According to a recent report,[51] European PVC-producing plants use 70% lead, 11% barium/zinc, 9% calcium/zinc, 7% tin, and 3% other heat stabilizers. In the European marketplace, cadmium-free self-lubricating products now dominate in demanding areas such as calendering and extrusion.[53]

3) Lead compounds

Several different lead compounds are widely used as PVC stabilizers. Their costs are low, and they have very good electrical properties. The most useful of them probably are:

$3PbO \bullet PbSO_4 \bullet H_2O$ $2PbSO_4 \bullet Pb(OOC)_2C_6H_4$ $2PbO \bullet PbHPO_3 \bullet 1/2H_2O$

However, the structures of lead stabilizers have been revised recently.[54] Infrared and NMR

spectra of basic lead carboxylates that are used as heat stabilizers indicate that these salts are not complexes or double salts of lead oxide, as suggested in most textbooks, but rather are unique compounds of interesting structure. According to this report,[54] lead stabilizers probably function by reacting with hydrogen chloride and thus by interfering with acid catalysis of the elimination reaction.

4) Other stabilizers

Other stabilizers are "chelators" such as mixed alkyl-aryl phosphites or epoxides. These materials can scavenge HCl or replace labile chlorine in the PVC. Several other types of nonmetallic substances have been used as secondary components of PVC stabilizer packages.

2.1.3.2 Mechanisms of thermal stabilization

There are two main mechanisms for thermostabilization. They are the destruction of thermally labile structures (*i.e.*, allylic and tertiary chloride) and the scavenging of HCl, which is an effective catalyst for dehydrochlorination.

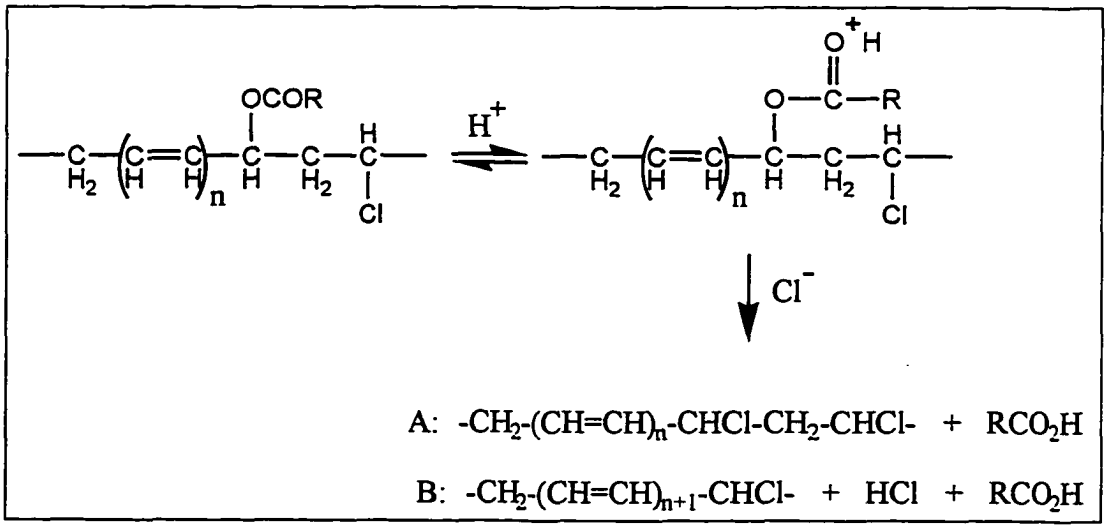
A very general formula for many organic metal-salt stabilizers is MY_2, where M is a cation such as R_2Sn^{2+} [R is methyl, butyl (most frequently), or octyl], Ba^{2+}, Ca^{2+}, Cd^{2+}, Pb^{2+}, or Zn^{2+}, and Y is an anion such as thiolate (mercaptide) or carboxylate.[2,10,19,42,44] Two researchers, Frye and Horst, first proposed the replacement of labile chlorine atoms in PVC by the more stable Y groups[55-57] and suggested that this replacement can improve the thermal stability of the polymer. Frye and Horst also considered the possibility that the Y groups could be removed pyrolytically or catalytically in β-elimination reactions that regenerate allylic chloride. In fact,

they obtained experimental evidence for such elimination from PVC during the latter stages of thermal stabilization by dibutyltin β-mercaptopropanoate[57] and the 2-ethylhexanoate salts of barium,[56] cadmium,[56] and zinc.[55,56]

A "reversible blocking mechanism" involving the replacement of allylic chlorine at polyene ends and the subsequent removal of the replacing groups has been proposed by Iván *et al.*.[58-60] They showed that the reversible blocking of polyene growth occurs in both the presence and the absence of molecular oxygen. Also, they proposed, specifically, the conversion of growing polyenyl chlorides into allylic carboxylates via the blocking process.[59] Other authors[9] agreed with this conclusion and showed that the data of Iván *et al.* confirmed it.

A likely mechanism for the HCl-catalyzed unblocking of polyenyl chloride elongation is shown in the following scheme:[61]

Scheme 2.10: Probable mechanism of HCl-catalyzed unblocking of stabilized PVC



Iván *et al.*[59] found a reactivity order of $CdSt_2 < PbSt_2 < BaSt_2$ (where St is stearate) for the initial rates of dehydrochlorination after unblocking occurred. They[59] also showed that the initial rates of dehydrochlorination after unblocking increased with increasing initial concentration of stabilizer, a result that could be ascribed[9] to the formation of additional potentially labile structures during the induction periods. The authors of a recent review[9] demonstrated that these and other observations were consistent with the formation and subsequent destruction of allylic carboxylates that were produced in Frye-Horst displacement reactions.

An interesting explanation for the thermal stabilization of PVC was proposed by Naqvi.[62-65] He found a stabilization effect resulting from the incorporation of hydrocarbons or ethylene monomer units in amounts which did not cause phase separation. These results are in agreement with the known stabilizing effects of non-polar solvents[2,19,41,66] and are strong evidence in favor of the ionic or quasiionic mechanism of thermal dehydrochlorination.

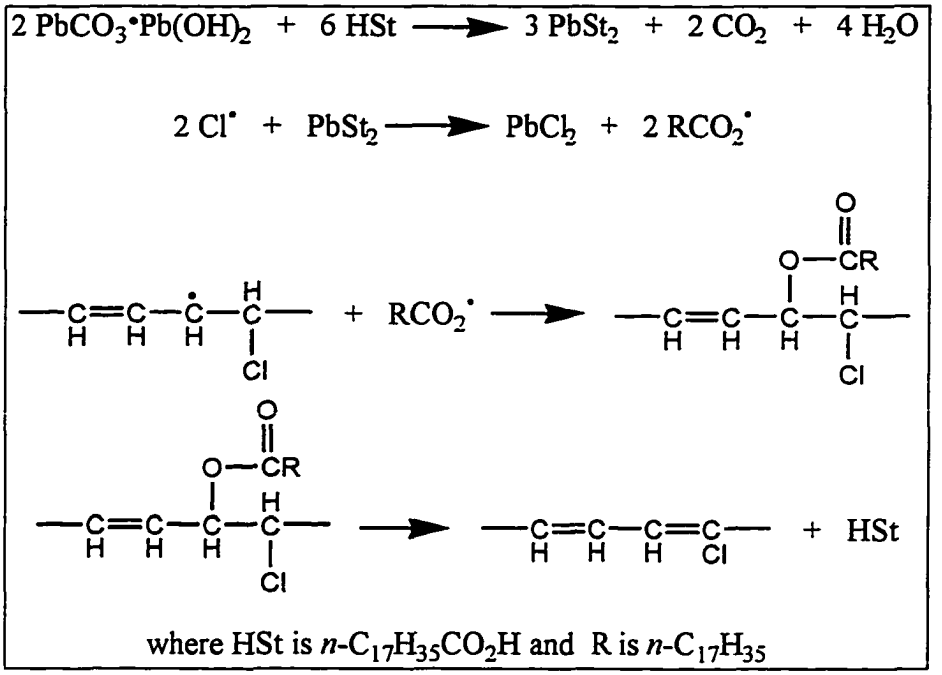
An argument against the Frye-Horst theory has been that several organic metal salts do not lower the rate of thermal dehydrochlorination (*i.e.*, they do not cause true chemical stabilization)[47] when they are used either as PVC additives or as chemical pretreatment agents. This phenomenon was pointed out in a publication[67] where possible causes of such behavior were described. They are, for example, low concentration of stabilizer, mild reaction conditions, and dehydrochlorination catalysis by metal chlorides formed *in situ*.

Naqvi *et al.*[68] made another attempt to increase the thermal stability of PVC by introducing nonpolar (alkyl) moieties into the polymer matrix. They used laurates, palmitates, and stearates of zinc and calcium and observed some stabilization. However, the effect of alkyl

chain length on polymer/stabilizer compatibility obviously could be important.

An alternative stabilization theory has been proposed by Michell.[69] It relates to "basic lead" stabilizers when they are used together with long-chain fatty acids. The suggested scheme is as follows:

Scheme 2.11: Michell's stabilization theory



It represents a "true stabilization" mechanism.[69] In the first step of this mechanism, lead stearate is formed. Then radicals taking part in the degradation are converted into nonradical products, and ester-containing structures are thermolyzed to regenerate stearic acid and produce a group which has a relatively stable vinylic carbon-chlorine bond. However, Starnes and Girois[9] have criticized this mechanism on several grounds: (1) A free-radical mechanism for polyene growth now is highly dubious. (2) The proposed reaction of chlorine radical with lead stearate probably

cannot occur, and even if it could, other reactions of $Cl^{\bullet}$ are more likely. This radical is extraordinarily reactive and unselective in the condensed phase,[70] where the rates of its reactions come close to being diffusion-controlled.[71] So, in the presence of a great excess of PVC, very few chlorine radicals would attack $PbSt_2$. (3) Stearyloxy radical ($RCO_2^{\bullet}$) should be very unstable because a similar species, acetoxy radical, decarboxylates thermally at rates which are so rapid that noncage competing reactions of this radical are not observed.[72] Consequently, if the radical mechanism were occurring, it is very probable that stearyloxy radicals would be converted very quickly into alkyl (stearyl) radicals that should be reactive enough to continue the degradation kinetic chain. (4) The ester pyrolysis reaction actually should yield other products. The pyrolysis of similar compounds has been reported in a number of papers[12,73,74] which suggest that the carbonyl group would facilitate dehydrochlorination to produce -CH=CH-C(O_2CR)=CH- or an even less stable chloroallylic structure, -CH=CH-CH(O_2CR)-CH=CH-CHCl-.

2.1.3.3 Stabilization by nonmetallic organic compounds

Because there are more and more environmental constraints on the usage of heavy metal compounds, scientists have been trying to discover non-metal-containing stabilizers for PVC. They have achieved some success,[2,44] but since the activity of such stabilizers is rather low, it is premature to consider them for use as primary stabilizers.

As was noted above, Naqvi[65,68] has used some nonpolar compounds to improve the stability of PVC, in keeping with the matrix-polarity reduction proposal. He has obtained significant improvements in PVC heat stability by blending the polymer with low-molecular-

weight polyethylene or *cis*-polybutadiene. The addition of HCl to alkene linkages might contribute to these stabilizing effects, but owing to differences in carbocation stability, addition to the polyene sequences of degraded PVC would seem to be more favorable than addition to the isolated double bonds of *cis*-polybutadiene. However, the latter addition should produce a relatively stable alkyl chloride structure, rather than a shorter but still labile allylic chloride one.[75]

Two of the major vitamins, A_1 (*trans*-β-carotene)[76] and E (α-tocopherol)[77], have been used as PVC stabilizers. Significant thermal stabilization caused by β-carotene was observed in solutions of PVC.[76] The authors made the interesting observation that highly degraded PVC also can stabilize the virgin resin. In the same article,[76] the authors describe the use of calcium stearate as a scavenger of HCl and their finding that dehydrochlorination was faster when the HCl was removed. This phenomenon was ascribed to the prevention of HCl readdition by the basic additive. Actually, the possibility of the readdition of HCl to PVC polyene sequences was described earlier,[78] and obviously it is one of the factors that may contribute to the termination of polyene growth.

It has been reported[77] that α-tocopherol (vitamin E) is a universal polyfunctional low-toxicity stabilizer with a complex action. When it is used as a chemical additive to PVC, α-tocopherol exhibits the properties of a high-efficiency stabilizer-antioxidant. It provides synergistic effects if it is used with metal-, epoxy-, sulfur- or phosphorus-containing stabilizers, and it is an excellent mechanical and chemical stabilizer-lubricant. It also provides some plastification for PVC. The use of PVC-α-tocopherol formulations simplifies processing, reduces the cost of the final products, and improves their operational characteristics. For

example,[77] PVC-α-tocopherol systems can be used in the electrical, chemical, lighting, and other industries (in cables, films, artificial leather, etc.) in order to (a) reduce the consumption of lead- and other metal-containing stabilizers by factors of 1.5 to 4, b) eliminate lubricants (waxes, paraffins, potassium stearate, and others) and synthetic stabilizer-antioxidants (hindered phenols, aminophenols, etc.) from standard formulations, and c) decrease the consumption of ester plasticizers. There is only one disadvantage: α-tocopherol is a very dark-colored material. Thus it can only be used in dark-colored products such as cables, for instance.

Some *N*-arylmaleimides were found to be effective heat stabilizers for both rigid[79] and plasticized[80] PVC. They were proposed to work as radical traps, but as was noted above, the radical theory of PVC degradation is highly unlikely to be correct. Maleimides also could act as Diels-Alder dienophiles to stop the polyene growth in the same manner as stabilizers **5** and **6**. Later it was shown[81] that pretreatment with several maleimides significantly improved the intrinsic stability of the polymer. The same authors[81] pointed out that the maleimides evidently deactivated labile sites in PVC.

Recently, 3-mercapto-1,2,3-triazine-5-ones were found to be effective heat stabilizers and antioxidants for plasticized PVC.[82]

Finally, a few exotic methods for the stabilization of PVC should be mentioned. Some researchers used rubber seed oil[83-85] or Jatropha seed oil[86] for the nonoxidative and oxidative stabilization of PVC but met with little success. Others[87] investigated the influence of different sands on the resistance of PVC to ultraviolet light. Three different kinds of sand were used as fillers: mine, river, and beach. The major conclusion of this research was as follows: "Mine or river sands protect against PVC degradation. The best results were obtained with a PVC-mine

sand composite and the worst with beach sand. The optimum sand concentration in the composite was 56 vol %".[87]

2.1.3.4 Stabilization by chemical modification

Pourahmady *et al.*[88,89] have found that the partial reductive dechlorination of PVC significantly enhances both the static and dynamic thermal stability. When used as reducing agents, both lithium aluminum hydride and tri-*n*-butyltin hydride provide less stabilization than lithium triethylborohydride. When the latter reagent was employed, dramatic changes occurred even at low reduction levels. For example, the rate of static dehydrochlorination at 190 °C was decreased by a factor of 30 when only 10-15 % of the total amount of chlorine had been replaced. It was noted that reduction by BH_3 also improves the stability of PVC.

Other chemical modifications to improve the stability of PVC have been studied. Several years ago, stabilization by pretreatment with trimethylaluminum or an ethanol:water (1:1) mixture was examined,[90] and somewhat earlier, enhanced stability was found for PVC that had been made in the presence of an organotin ester.[91,92]

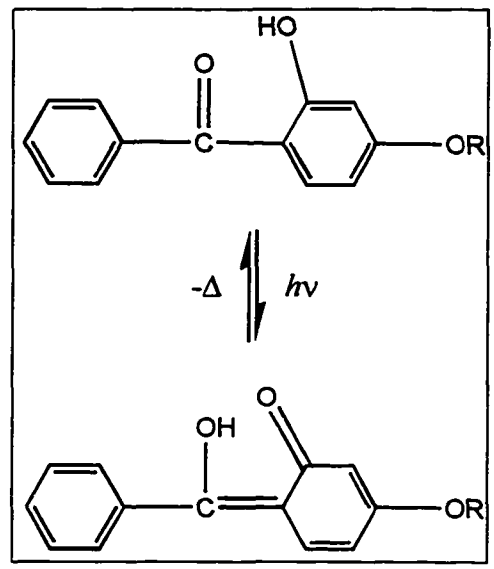
2.1.3.5 Photostabilization

There are several different types of UV stabilizers for PVC that are used in industry. They can be subsumed under one of four major groups, as follows.

1. UV absorbers[93]

The main objective here is to convert photon energy into heat. The reverse reaction

Scheme 2.12: Photostabilization of PVC by a UV absorber

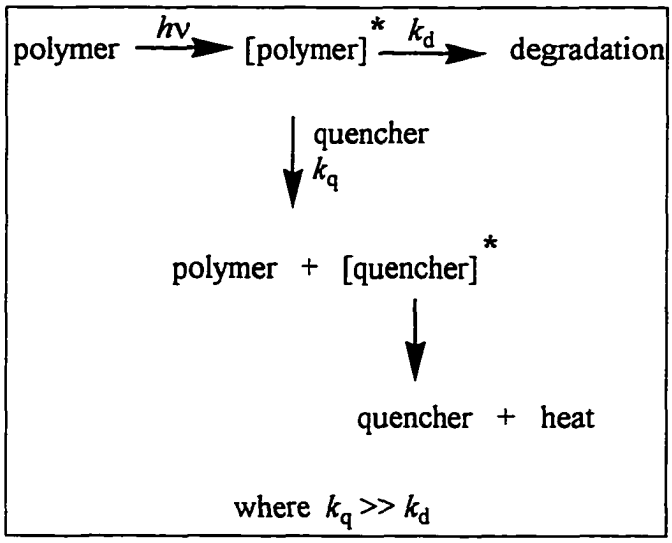


(see Scheme 2.12) is exothermic. Very useful UV absorbers are carbon black, titanium dioxide, and other pigments that can dissipate the absorbed radiant energy in innocuous ways. The most effective photostabilizer is the carbon black, but its color precludes its use in many applications.

2. Excited-state quenchers[94]

These quenchers are heavy-metal chelates, *e.g.*, nickel compounds and others, with a large variety of ligands. The quenchers deactivate the excited states of chromophores according to this general scheme:

Scheme 2.13: Photostabilization of PVC by excited-state quenchers



3. Radical scavengers[95]

A number of sterically hindered phenols are very useful as radical scavengers that prevent photodegradation. These phenols [or the hindered amine light stabilizers (HALS)] trap the chain-carrying radical intermediates that are involved in photooxidation. A general formula for hindered phenols is 2,6-di-*tert*-alkyl-4-R-phenol, where R usually is alkyl or substituted alkyl.

4. Peroxide decomposers[96]

Some sulfides and triaryl phosphites are active as peroxide decomposers which remove potential photooxidation initiators. These stabilizers are especially active when they are used with hindered phenols, a combination that may give strong synergistic effects.

Scheme 2.14: Photostabilization of PVC by peroxide decomposers

$$ROOH + P(OAr)_3 \rightarrow ROH + O{=}P(OAr)_3$$

$$ROOH + RSR' \rightarrow ROH + RS(O)R'$$

An interesting method to improve the photostability of PVC was reported by Decker.[97] The method involves covering the article to be protected with a photocurable acrylic coating that contains one or more additives that are photostabilizers. When such an article is exposed to a source of UV light, the coating produces a clear, crosslinked layer that prevents photodegradation for a long period of time.

In another recent photodegradation study,[98] the authors showed that plasticizer contributes to discoloration, not only by its influence on the PVC, but also by its own change in color.

A recent project[99] compared plasticized PVC samples aged under natural or artificial conditions and samples recovered after use for long periods of time (15-30 years) at -20 - +27 °C. The authors found that the predominant process in dark, low-temperature aging was loss of plasticizer by desorption. However, the major process in photoaging was degradation of both polymer and plasticizer, proceeding generally on the irradiated side of the sample and depending upon the wavelength distribution of the light.

The problem of PVC degradation obviously has not been solved entirely and thus is still quite attractive as a topic for study. Other recent articles pertaining to this problem appear in the list of references.[100-104]

Finally, it has to be pointed out here that, in contrast, some researchers are investigating the possibility of dehydrochlorinating PVC completely in order to produce a conductive polymer[105] comprised of conjugated double bonds. Dehydrochlorination caused by chemical[106,107] or physical[108,109] treatments has been studied for the purpose of preparing polyacetylene-like film specimens exhibiting easy processability. Upon irradiation with ion beams, PVC films become dark, and their resistivity decreases dramatically.[110]

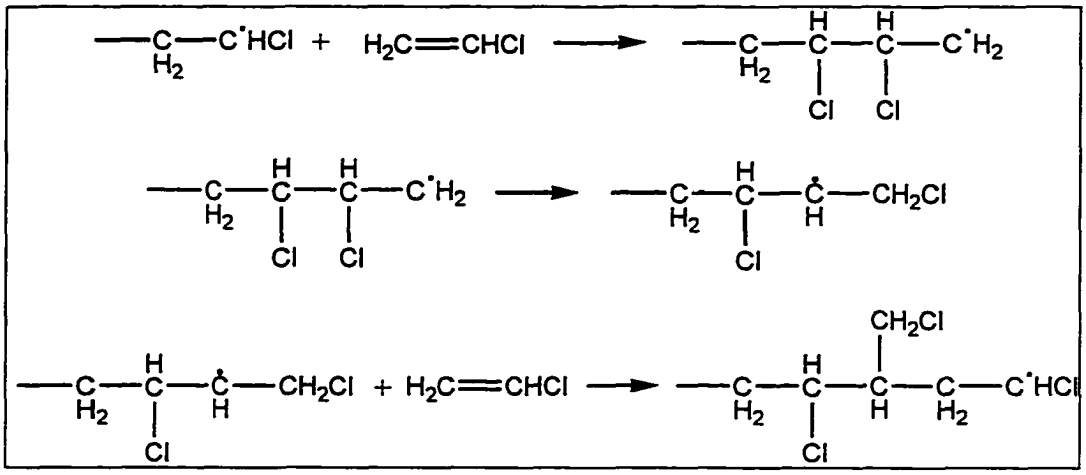
2.2 Possible microstructures formed during polymerization

The microstructure of PVC has been studied extensively in recent years.[111-118] A number of different structural defects are formed during the polymerization of vinyl chloride. The formation of most of them is much more facile in the latter stages of the polymerization when the monomer concentration is low. The structural defects can be divided into two major groups: those that are thermally stable and those that are not.

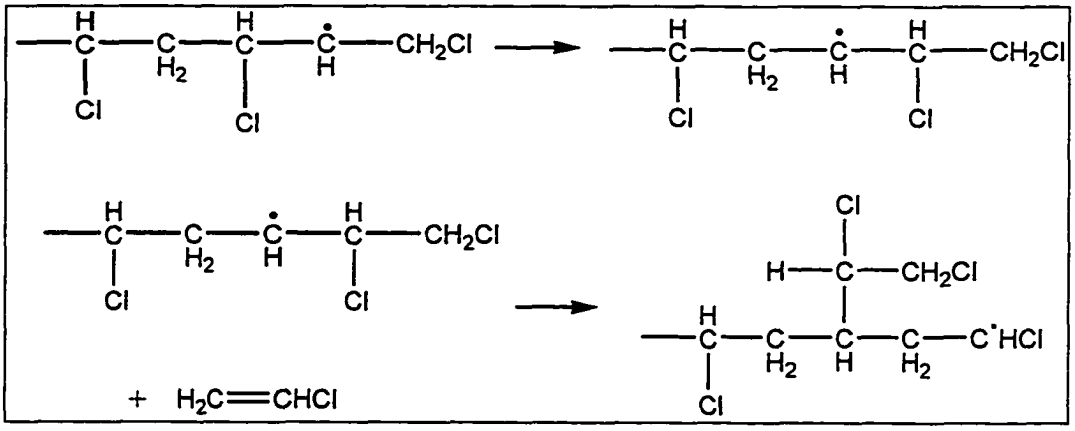
Several thermally stable structures can result from the head-to-head addition of the monomer to the growing macroradical, for example, as in Scheme 2.15.

The last reaction shown in this scheme gives a stable chloromethyl branch. Conventional PVC has 2-3 of such structures per 1000 backbone carbons.[113] However, a radical intermediate leading to this branch can undergo another shift of chlorine that yields a stable dichloroethyl branch structure according to Scheme 2.16.

Scheme 2.15: Formation of chloromethyl branch caused by head-to-head addition in VC polymerization

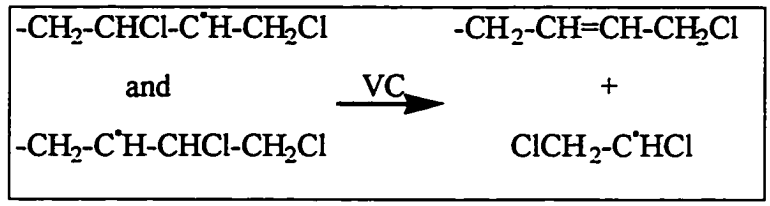


Scheme 2.16: Formation of dichloroethyl branch caused by head-to-head addition in VC polymerization



There are about 0.3 dichloroethyl branches per 1000 backbone carbons.[113] Also, the macroradicals formed by chlorine shifts can transfer Cl• to monomer to yield an unsaturated chain end which is fairly stable:

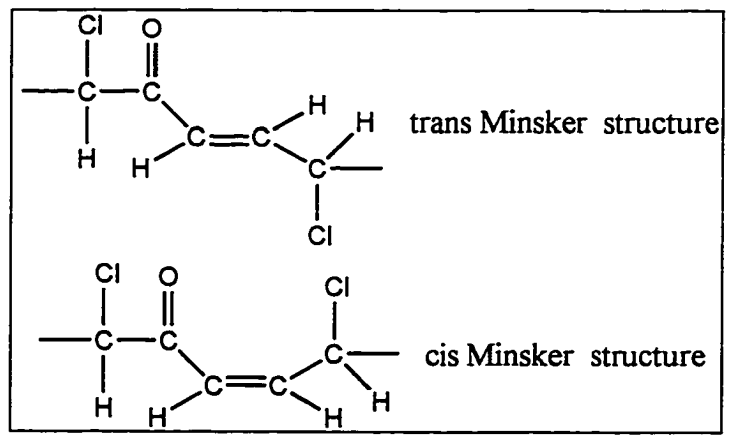
Scheme 2.17: Formation of unsaturated chain end caused by head-to-head addition in VC polymerization



The concentration of this chain end varies, of course, with the molecular weight.[113]

Another structural defect was proposed by Minsker,[11] as was mentioned briefly above in Section 2.1.1. He wrote that this structure is formed by air oxidation and that its cis isomer is the only defect that is responsible for the thermal degradation of PVC.[10,119,120]

Scheme 2.18: Minsker structures



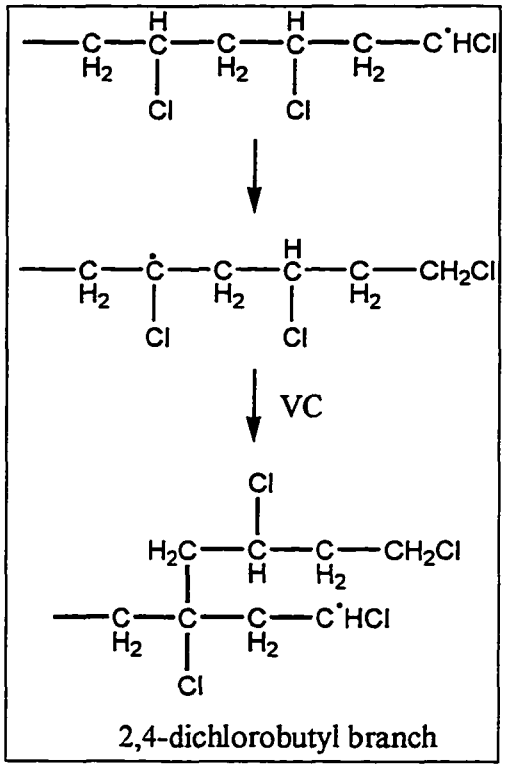
Minsker published a number of indirect pieces of evidence for the existence of the cis structure, including the chain scission of PVC by acid or base.[10] He demonstrated the possibility of this reaction by using a model compound, and Panek *et al.*[12] confirmed, with other models, the fast

conversion of the cis structure into a furan group that should greatly facilitate the dehydrochlorination of PVC. However, as mentioned already, attempts to find the Minsker structure by 500-MHz ^{1}H and 125-MHz ^{13}C NMR have failed, and no direct evidence for such a structure exists thus far.

Several thermally unstable structures might result from "backbiting" reactions. This type of mechanism was applied to polyethylene, and the existence of backbiting structures in that polymer was established.[121,122]

The growing macroradical can form a six-membered cyclic transition state that leads to an intramolecular chain transfer (backbite) which produces a butyl (or in the case of PVC, a 2,4-dichlorobutyl) branch after monomer addition:

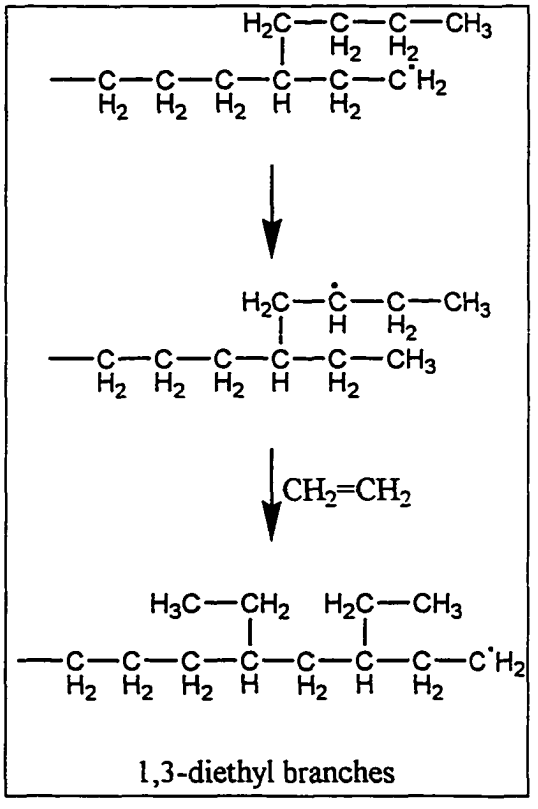
Scheme 2.19: Formation of 2,4-dichlorobutyl branch caused by backbiting mechanism



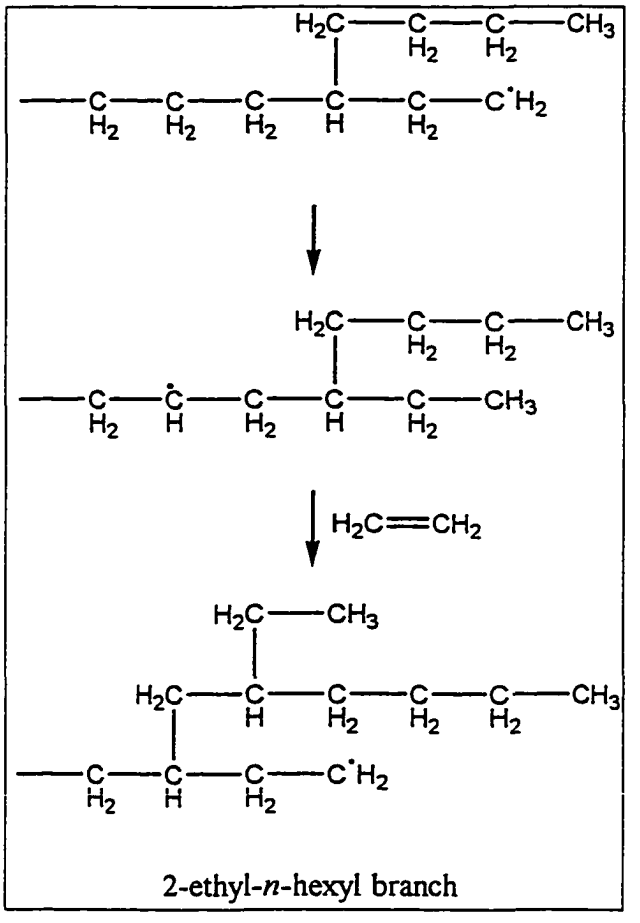
Actually, the formation of 2,4-dichlorobutyl branches via backbiting has been known for years.[123] This mechanism obviously creates tertiary chloride at the branch point, a very labile structure that causes dehydrochlorination.

For polyethylene, a "double backbiting" mechanism has been described in the literature.[121,122] However, there has been no proof for the operation of an analogous mechanism in the case of PVC. According to this mechanism, 1,3-diethyl and/or 2-ethyl-*n*-hexyl branches are formed in polyethylene:

Scheme 2.20: Formation of 1,3-diethyl branches caused by double backbiting mechanism



Scheme 2.21: Formation of 2-ethyl-*n*-hexyl branch caused by double backbiting mechanism



In the case of PVC, similar mechanisms would produce structures that should be unstable thermally, because each of them would incorporate two tertiary chloride moieties.[123]

2.3 Objectives

The major objectives of the research described in this dissertation were twofold: (1) to identify various PVC microstructures that were expected to have low thermal stabilities and (2) to determine their mechanisms of formation.

The specific research topics were:

- the possible formation of the "common" isolated double bond via the reaction of

macroradicals with alkene chain ends during the polymerization (see Sections 4.2 and 4.4).

- the existence of previously proposed[123] 1,3-di(2-chloroethyl) and 2-(2-chloroethyl)-2,4,6-trichloro-*n*-hexyl short-branch structures formed by "double backbiting" routes (see Section 4.3).

During the course of these studies, a number of vinyl chloride polymerizations were carried out, both in the presence and in the absence of model compounds for allylic long-chain ends. Molecular weights and molecular weight distributions were determined, and several other models were synthesized for use as NMR reference substances. Reductive dechlorination and subsequent analysis by ^{13}C NMR was the principal approach to the polymer microstructure determinations.

The characterization of the microstructures provided considerable insight into the mechanism of vinyl chloride free-radical polymerization and the formation of some of the thermally labile groups in PVC.

CHAPTER 3

EXPERIMENTAL

3.1 Model compounds for possible microstructures

3.1.1 Materials

(1) *trans*-2-Hepten-1-ol, $HO\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_3\text{-}CH_3$, #6084, 96%, bp 178 °C, Lancaster Synthesis, Inc.

(2) Triphenylphosphine, $(C_6H_5)_3P$, #T8,440-9, 99%, mp 79-81 °C, Aldrich Chemical Company, Inc.

(3) Carbon tetrachloride, CCl_4, #31,996-1, 99.9%, bp 76-77 °C, Aldrich Chemical Company, Inc.

(4) Diethyl ether, anhydrous, $H_5C_2\text{-}O\text{-}C_2H_5$, #0852, 99.9%, bp 35 °C, Mallinckrodt Group, Inc.

(5) Magnesium sulfate, anhydrous, $MgSO_4$, #M65-500, Fisher Scientific Company

(6) Trimethylaluminum, $(CH_3)_3Al$, #25,722-2, 97%, Aldrich Chemical Company, Inc.

(7) Methylene chloride, CH_2Cl_2, #D37-4, 99.5%, Fisher Scientific Company

(8) Titanium(IV) chloride, $TiCl_4$, 1 M solution in dichloromethane, #24,986-6, Aldrich Chemical Company, Inc.

(9) Hydrochloric acid, HCl, #A508-212, 35.6%, Fisher Scientific Company

(10) Sodium chloride, NaCl, #S271-10, 99.0%, Fisher Scientific Company

(11) 5-Hexyn-3-ol, CH_3-CH_2-CHOH-CH_2-C≡CH, #3602.90, 97%, Wiley Organics

(12) Thionyl chloride, $SOCl_2$, #23,046-4, 99+%, bp 79 °C, Aldrich Chemical Company, Inc.

(13) Dimethylformamide (DMF), $HCON(CH_3)_2$, #D119-4, 99.8%, Fisher Scientific Company

(14) Propylene, CH_2=CH-CH_3, #29,566-3, 99+%, Aldrich Chemical Company, Inc.

(15) Zinc chloride, $ZnCl_2$, 1.0 M solution in diethyl ether, #27,683-9, Aldrich Chemical Company, Inc.

(16) 3-Chloro-1-butene, CH_2=CH-CHCl-CH_3, #25,205-0, 98%, Aldrich Chemical Company, Inc.

(17) Ammonium hydroxide, NH_4OH, #A512-500, 20.2%, Fisher Scientific Company

(18) 2-Ethyl-1-hexanol, $HOCH_2$-$CH(C_2H_5)$-$(CH_2)_3$-CH_3, #E2,916-8, 99+%, bp 183-186 °C, Aldrich Chemical Company, Inc.

(19) Bromine, Br_2, #32,813-8, 99%, bp 60 °C, Aldrich Chemical Company, Inc.

(20) Magnesium turnings, Mg, #20,090-5, 98%, Aldrich Chemical Company, Inc.

(21) Iodine, I_2, #37,655-8, 99%, Aldrich Chemical Company, Inc.

(22) 9-Heptadecanone, CH_3-$(CH_2)_7$-CO-$(CH_2)_7$-CH_3, #H0536, 91%, T. C. I. America, Inc.

(23) Ammonium chloride, NH_4Cl, #A661-500, 99.5%, Fisher Scientific Company

(24) Cyclohexane, C_6H_{12}, #C556-4, 99.0%, Fisher Scientific Company

(25) Palladium on activated carbon (Pd = 5%), Pd, #20,568-0, Aldrich Chemical Company, Inc.

(26) Hydrogen, H_2, Industrial Grade, 99.95%, Air Products and Chemicals, Inc.

(27) Lithium borohydride, $LiBH_4$, 2 M solution in tetrahydrofuran, #21293-1000, Acros Organics USA

(28) 3-Undecanol, CH_3-CH_2-CHOH-$(CH_2)_7$-CH_3, #9487.00, 99%, Wiley Organics

(29) Bis(cyclopentadienyl)zirconium chloride, $C_{10}H_{10}Cl_2Zr$, #18792-0050, 98+%, Acros Organics USA

(30) 1-Decene, CH_2=CH-$(CH_2)_7$-CH_3, #11191-0010, *ca.* 95%, bp 181 °C, Acros Organics USA

(31) Ethylmagnesium chloride, C_2H_5MgCl, 2.0 M solution in diethyl ether, #30,033-0, Aldrich Chemical Company, Inc.

(32) Sodium, Na, lump, in kerosene, #28,205-7, 99%, Aldrich Chemical Company, Inc.

(33) Hexanes, C_6H_{14}, #N3S-4, bp 60-90 °C, Fisher Scientific Company

(34) Bis(1,5-cyclooctadiene)nickel(0), $(1,5\text{-}C_8H_{12})_2Ni$, #28-0010, 98+%, mp 60 °C, Strem Chemicals, Inc.

(35) Propionaldehyde, C_2H_5CHO, #22.051.32, 99+%, bp 46-50 °C, Janssen Chimica

(36) 1,3-Butadiene, H_2C=CH-CH=CH_2, #29,503-5, 99+%, Aldrich Chemical Company, Inc.

(37) Ethyl alcohol, C_2H_5OH, anhydrous, denatured, #27,764-9, 90%, bp 78 °C, Aldrich Chemical Company, Inc.

(38) Tetrahydrofuran, C_4H_8O, #2858-05, 99.92%, bp 66 °C, Mallinckrodt Chemicals

(39) Chloroform-*d*, $CDCl_3$, #38,096-2, 99 atom % D, Aldrich Chemical Company, Inc.

(40) Tetrahydrofuran-d_8, C_4D_8O, #36,543-2, 99 atom % D, Aldrich Chemical Company, Inc.

(41) Acetone-d_6, CD_3COCD_3, #17490-0500, 99+ atom % D, Acros Organics USA

(42) Tetramethylsilane, $(CH_3)_4Si$, #13847-0250, 99.9+%, NMR grade, Acros Organics USA

3.1.2 NMR and GC/MS measurements

Proton-decoupled ^{13}C NMR spectra were obtained at 125.77 MHz with a Bruker AMX500 spectrometer or at 75.57 MHz with a GE QE-300 instrument that also served to record the 300.52-MHz ^1H NMR spectra of low-molecular-weight compounds. A 60° pulse angle and a pulse repetition time of 10 s were used for the 125.77-MHz ^{13}C NMR spectra, which were acquired at 100 or 110 °C from 15-20% solutions (w/v) of the samples in 1,2,4-trichlorobenzene/*p*-dioxane-d_8 (*ca.* 4:1 v/v) containing hexamethyldisiloxane as an internal reference (δ 2.00 ppm *vs.* Me_4Si). The ^{13}C NMR spectra recorded at ambient temperature and all of the ^1H spectra were obtained from solutions in chloroform-*d*, THF-d_8, or acetone-d_6/CS_2 and are referenced to internal Me_4Si (δ 0.00

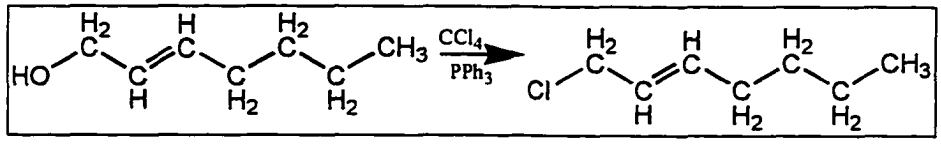
ppm).

The (gas chromatography)-(mass spectroscopy) (GC/MS) measurements were performed with a Hewlett-Packard HP 5890A/5988A or HP 5890/5971A apparatus equipped with a fused-silica HP-1 capillary GC column [crosslinked methylsilicone gum, 12 m x 0.2 mm (i.d.), 0.33 mm film thickness]. The mass spectrometer was operated in the total ion concentration (TIC) mode. Helium was used as the carrier gas, and the heating rate was 10-20 °C/min.

IR spectra were obtained on a Perkin-Elmer 1320 infrared spectrophotometer in the range of 600 - 4000 cm^{-1}.

3.1.3 Synthesis of *trans*-1-chloro-2-heptene

Scheme 3.1: Synthesis of *trans*-1-chloro-2-heptene



trans-1-Chloro-2-heptene was synthesized by a method similar to a literature procedure.[1] *trans*-2-Hepten-1-ol (5.00 g, 43.8 mmol) was added to a stirred solution of triphenylphosphine (16.14 g, 61.52 mmol) in carbon tetrachloride (29.6 mL, 307 mmol) under nitrogen. The mixture was stirred under nitrogen for 3 days; then the suspension was filtered, and *trans*-1-chloro-2-heptene was removed from the filtrate by extraction

with ether (3 x 100 mL). The ethereal solution was dried over anhydrous $MgSO_4$ and concentrated with a rotary evaporator under aspirator vacuum. The yield of crude *trans*-1-chloro-2-heptene was 3.65 g (62.8%), and the purity was 78% (by GC/MS); mass spectrum (Fig. 3.1), *m/e* (relative intensity, %): 27(28), 29(13), 39(46), 40(7), 41(67), 42(19), 43(20), 51(12), 53(42), 51(71), 55(100), 56(78), 57(9), 65(13), 67(50), 68(14), 69(27), 70(26), 75(12), 77(9), 81(59), 83(21), 89(11), 90(20), 91(9), 96(16), 97(38, M^+-Cl), 104(10), 132(23, M^+), 134(7, M^+); ^{13}C NMR (75.57 MHz, THF-d_8, 50 °C) (Fig. 3.2), δ: 45.28(C-1), 135.93(C-2), 127.01(C-3), 32.25(C-4), 31.72(C-5), 22.70(C-6), and 14.20(C-7) ppm; ^1H NMR (300.52 MHz, THF-d_8, 50 °C) (Fig. 3.3), δ: 0.79-0.96 (3H, -CH_3), 1.17-1.49 (4H, -CH_2-), 1.93-2.12 (2H, -CH_2-), 3.86-4.02 (2H, -CH_2Cl), 5.46-5.65 (1H, -CH=CH-), and 5.65-5.86 (1H, -CH=CH-) ppm; IR (neat) (Fig. 3.4), strong peak at 960 cm^{-1} (*trans*-CH=CH).

3.1.4 Synthesis of *trans*-5-chloro-2-heptene

(i) Synthesis of *trans*-5-hepten-3-ol

trans-5-Hepten-3-ol was prepared by a method similar to that in the literature.[2] Three solutions were prepared first:

Solution 1: Trimethylaluminum (3.83 mL, 40.0 mmol) was dissolved in 75 mL of methylene chloride in a 250-mL 3-neck round-bottom flame-dried flask under nitrogen.

Solution 2: Titanium(IV) chloride (18 mL of a 1 M solution in CH_2Cl_2, 18 mmol) was

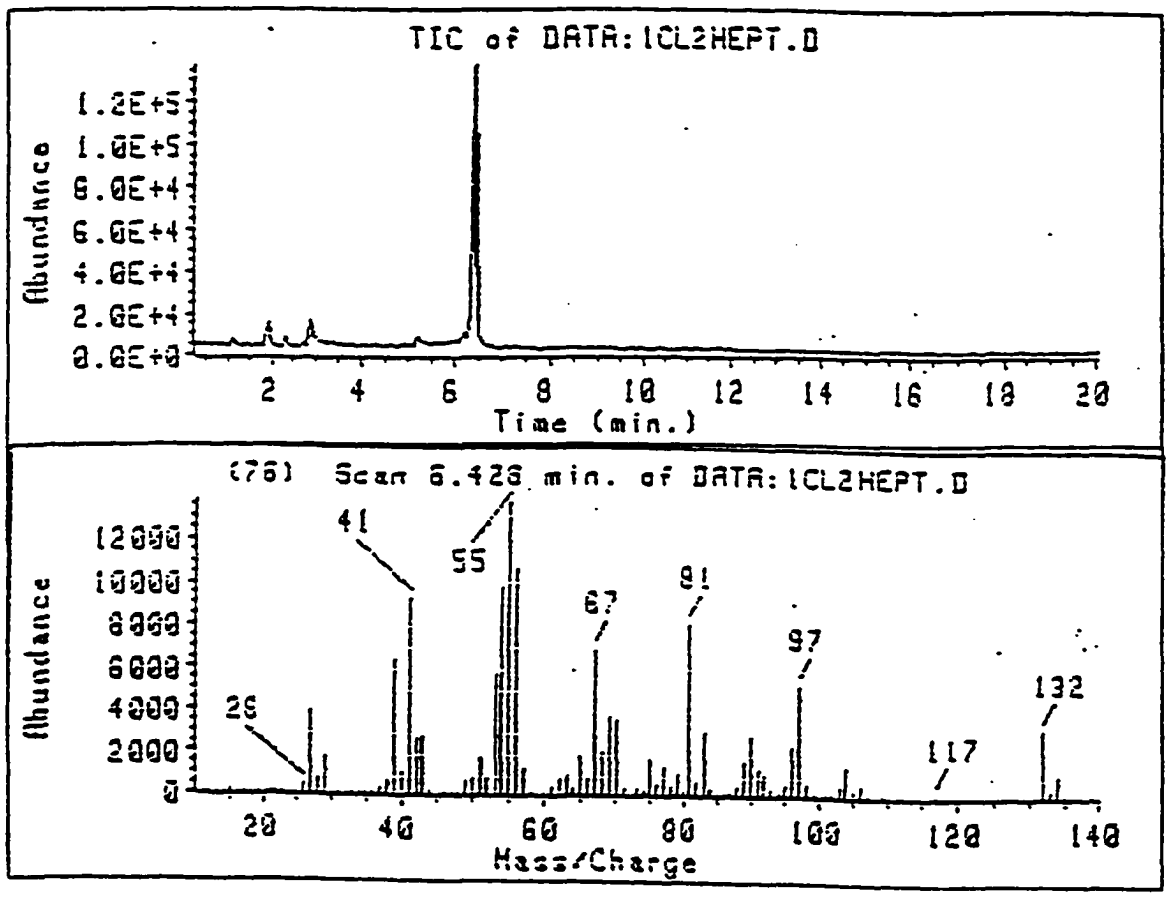


Fig. 3.1: Mass spectrum and gas chromatogram of

trans-1-chloro-2-heptene

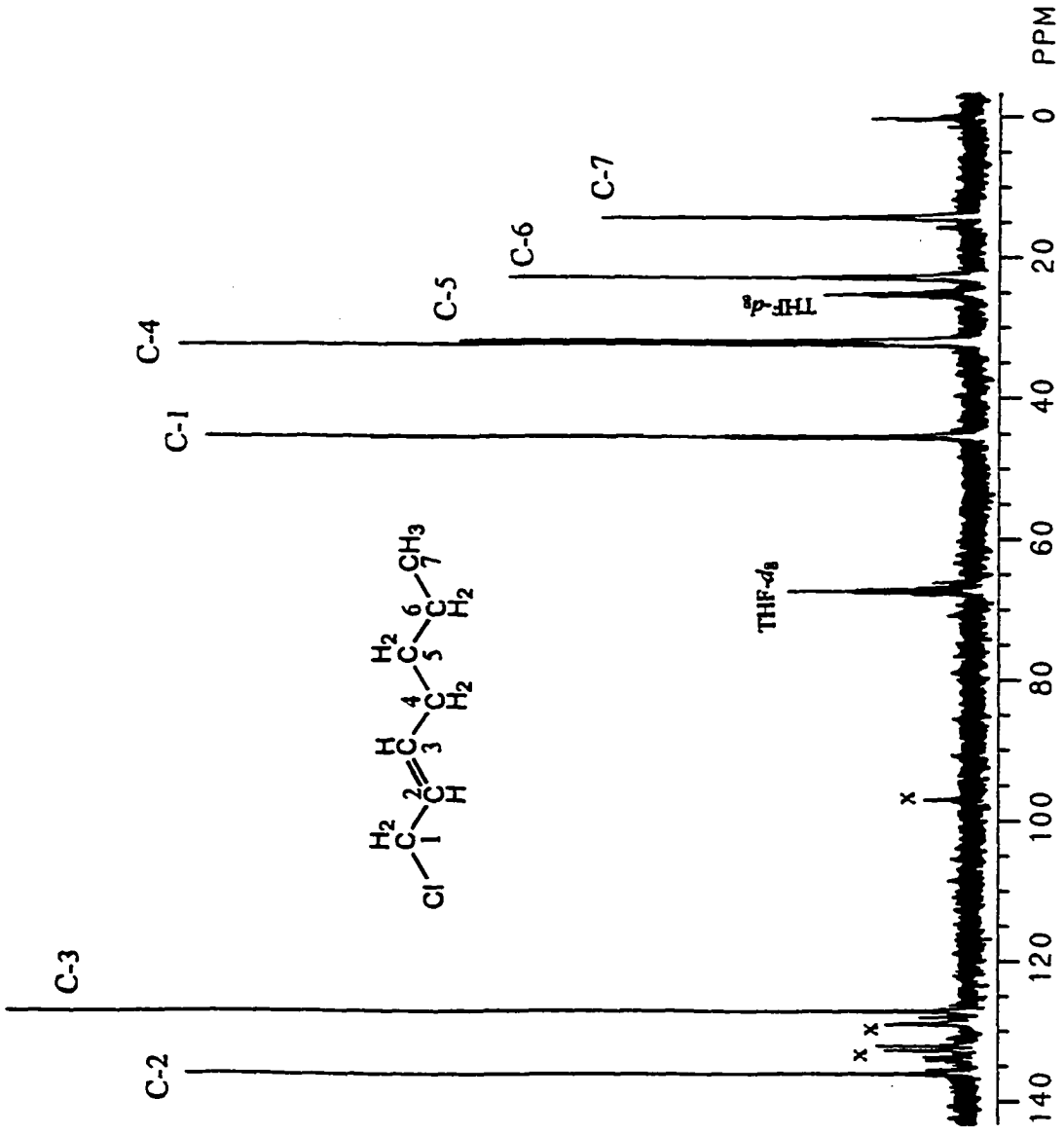


Fig. 3.2: ^{13}C NMR spectrum (75.57 MHz) of *trans*-1-chloro-2-heptene (x: impurity)

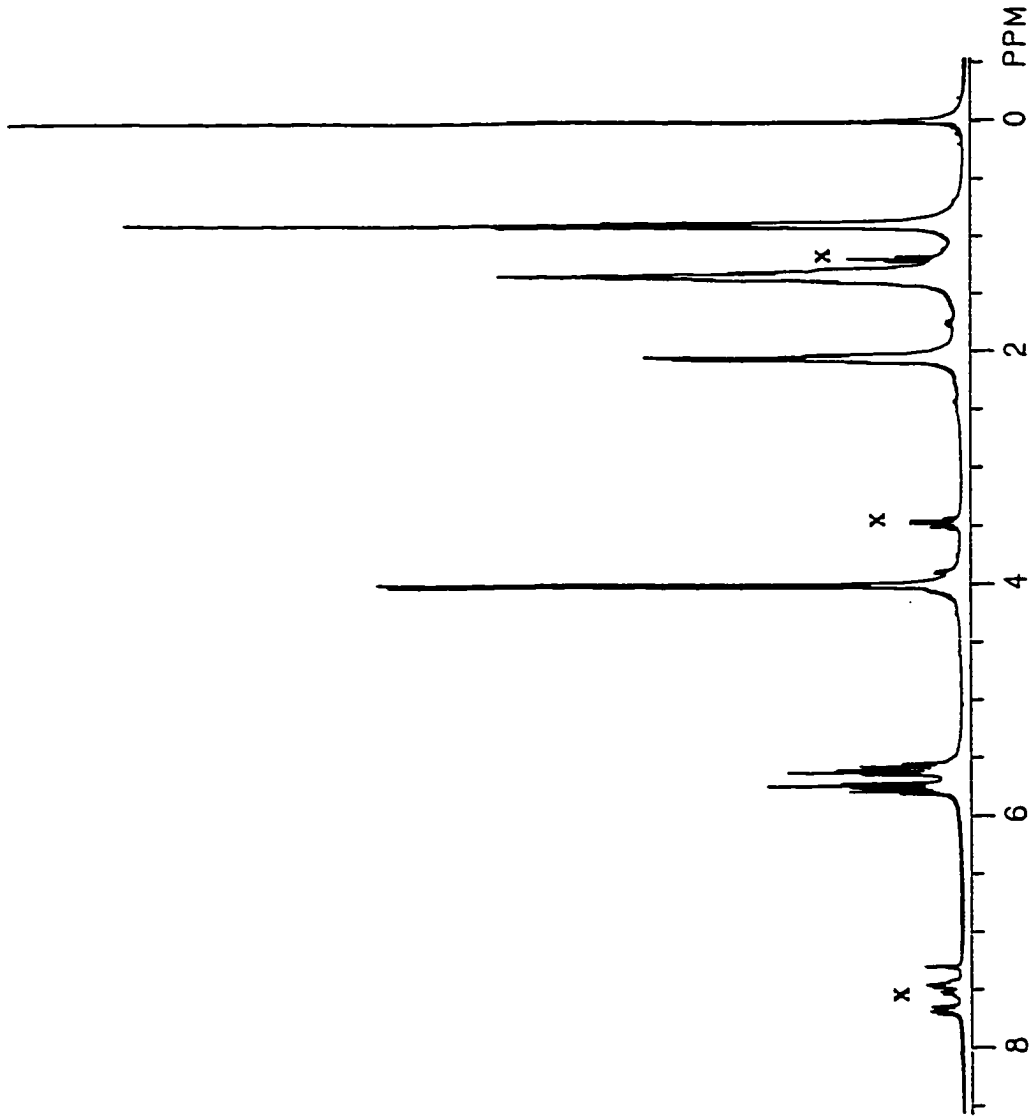


Fig. 3.3: ^{1}H NMR spectrum (300.52 MHz) of *trans*-1-chloro-2-heptene (x: impurity)

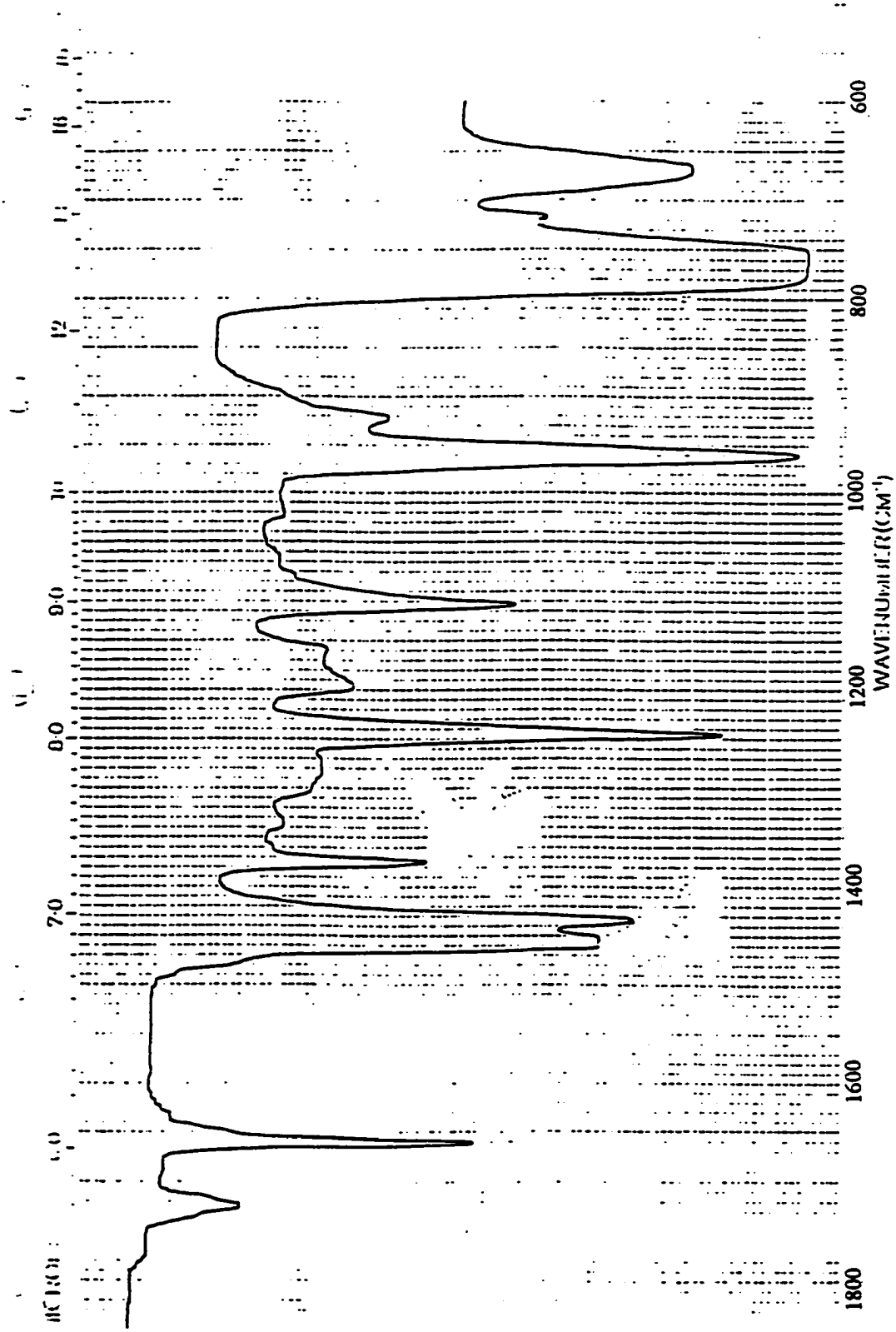
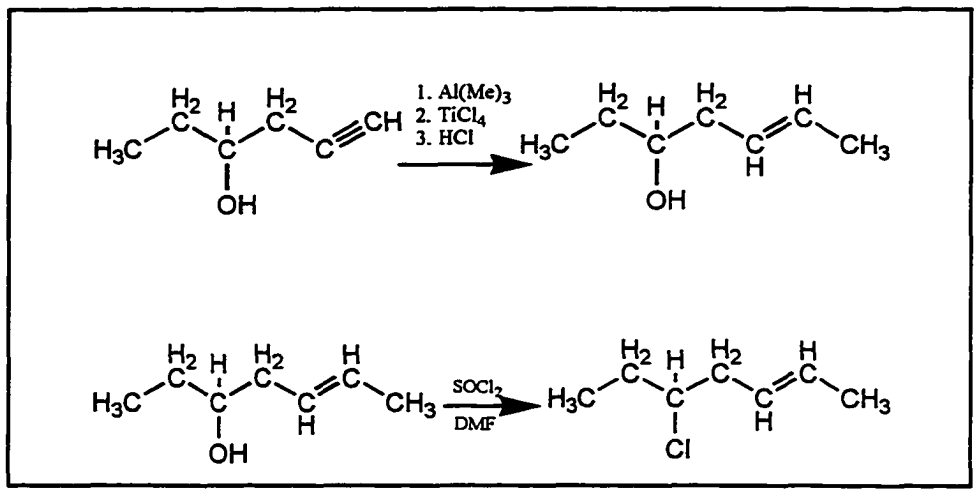


Fig. 3.4: IR spectrum of *trans*-1-chloro-2-heptene

Scheme 3.2: Synthesis of *trans*-5-chloro-2-heptene



dissolved in 32 mL of methylene chloride in a 100-mL 3-neck round-bottom flame-dried flask under nitrogen.

Solution 3: A 35.6% aqueous solution of HCl (30 mL) was added to 70 mL of deionized (DI) water. This solution then was saturated with NaCl.

Solution 1 was cooled to 0 °C with an ice bath under nitrogen, and 5-hexyn-3-ol (1.96 mL, 18.0 mmol) was added slowly by syringe through a rubber septum. The liberated methane was vented through the gas outlet. Solutions 1 and 2 then were cooled to -45 °C with a mixture of chlorobenzene and liquid nitrogen, and solution 2 was transferred within 1 min into solution 1 by using a double-tipped needle. The reaction mixture was stirred for 30 min and quenched by the addition via syringe of precooled (0 °C) methyl alcohol (10 mL). Solution 3 was then added. The mixture was allowed to warm to room temperature, stirred for 30 min, and extracted with ether (3 x 100 mL). The ethereal solution was dried over anhydrous $MgSO_4$ and concentrated on a rotary

evaporator under aspirator vacuum to obtain 1.16 g (56 %) of residual *trans*-5-hepten-3-ol in a purity of 79% by GC/MS; mass spectrum (Fig. 3.5), *m/e* (relative intensity, %): 27(12), 29(18), 31(25), 39(17), 41(39), 43(12), 55(18), 56(100), 57(22), 59(80), 67(11), 85(18), 96(7, M^+-H_2O), 114(4, M^+); ^{13}C NMR (75.57 MHz, $CDCl_3$, ambient temperature) (Fig. 3.6), δ: 10.01(C-1), 29.36(C-2), 72.52(C-3), 40.23(C-4), 127.64 and 127.79(C-5 and -6), and 18.06(C-7) ppm; ^1H NMR (300.52 MHz, $CDCl_3$, ambient temperature) (Fig. 3.7), δ: 0.48-1.12 (3H, $-CH_3$), 1.12-1.60 (3H, $-CH_3$), 1.60-1.92 (2H, $-CH_2-$), 1.92-2.45 (2H, $-CH_2-$), 2.68-2.93 (1H, -CH(OH)-), and 5.20-5.69 (2H, -CH=CH-) ppm.

(ii) Synthesis of *trans*-5-chloro-2-heptene

The procedure is based on a published method[3] for converting secondary alcohols into the corresponding chlorides.

Under a nitrogen atmosphere, thionyl chloride (2.30 g, 19.3 mmol) was added dropwise with stirring to 15 mL of DMF while the temperature was kept at 0-5 °C with an ice bath. *trans*-5-Hepten-3-ol (2.00 g, 17.5 mmol) was then introduced slowly, and the resulting mixture was heated at 85-90 °C for 30 min. After cooling to room temperature and addition of 100 mL of deionized (DI) water, the mixture was extracted with ether (3 x 150 mL), and the combined extracts were washed with DI water (3 x 100 mL). The ethereal solution was dried with anhydrous $MgSO_4$ and concentrated on a rotary evaporator under aspirator vacuum to obtain 2.28 g (98%) of residual *trans*-5-chloro-2-heptene in a purity of 95% by GC/MS; mass spectrum (Fig. 3.8), *m/e* (relative intensity,

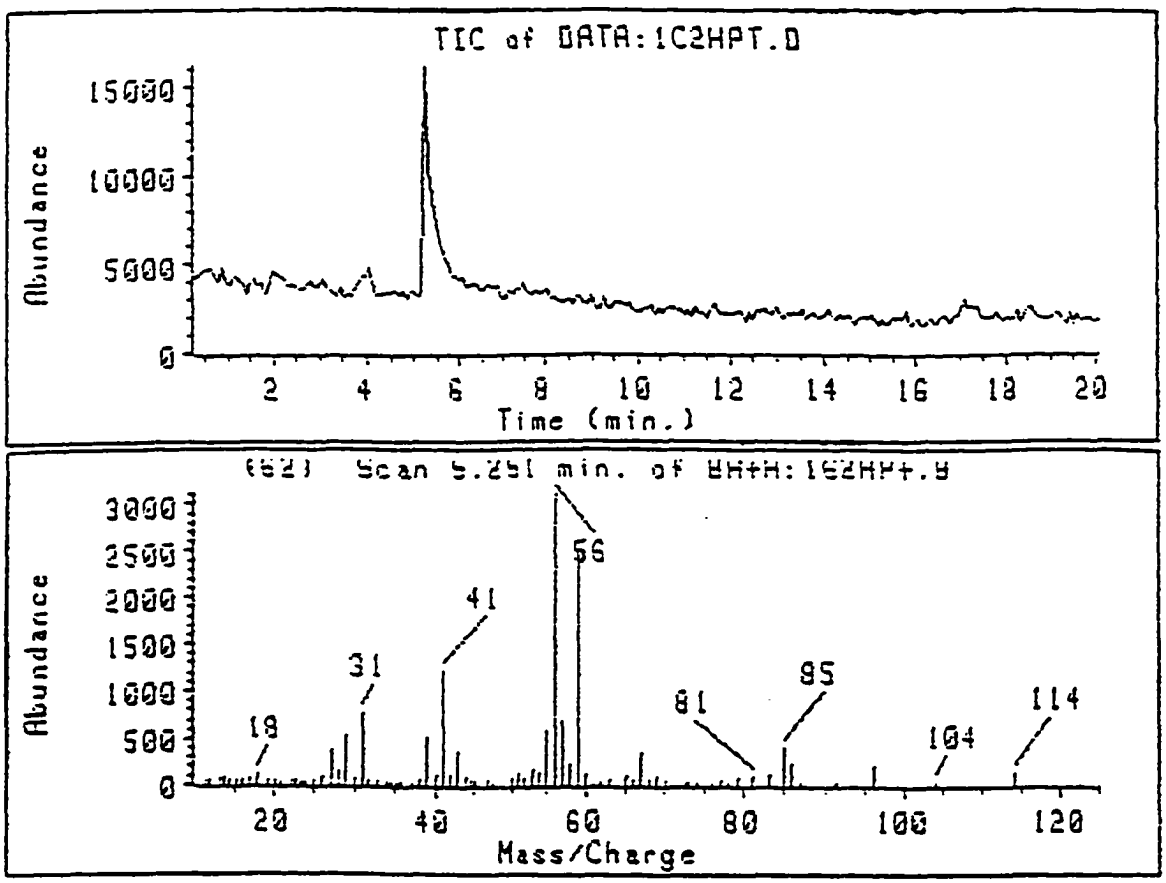


Fig. 3.5: Mass spectrum and gas chromatogram of

trans-5-hepten-3-ol

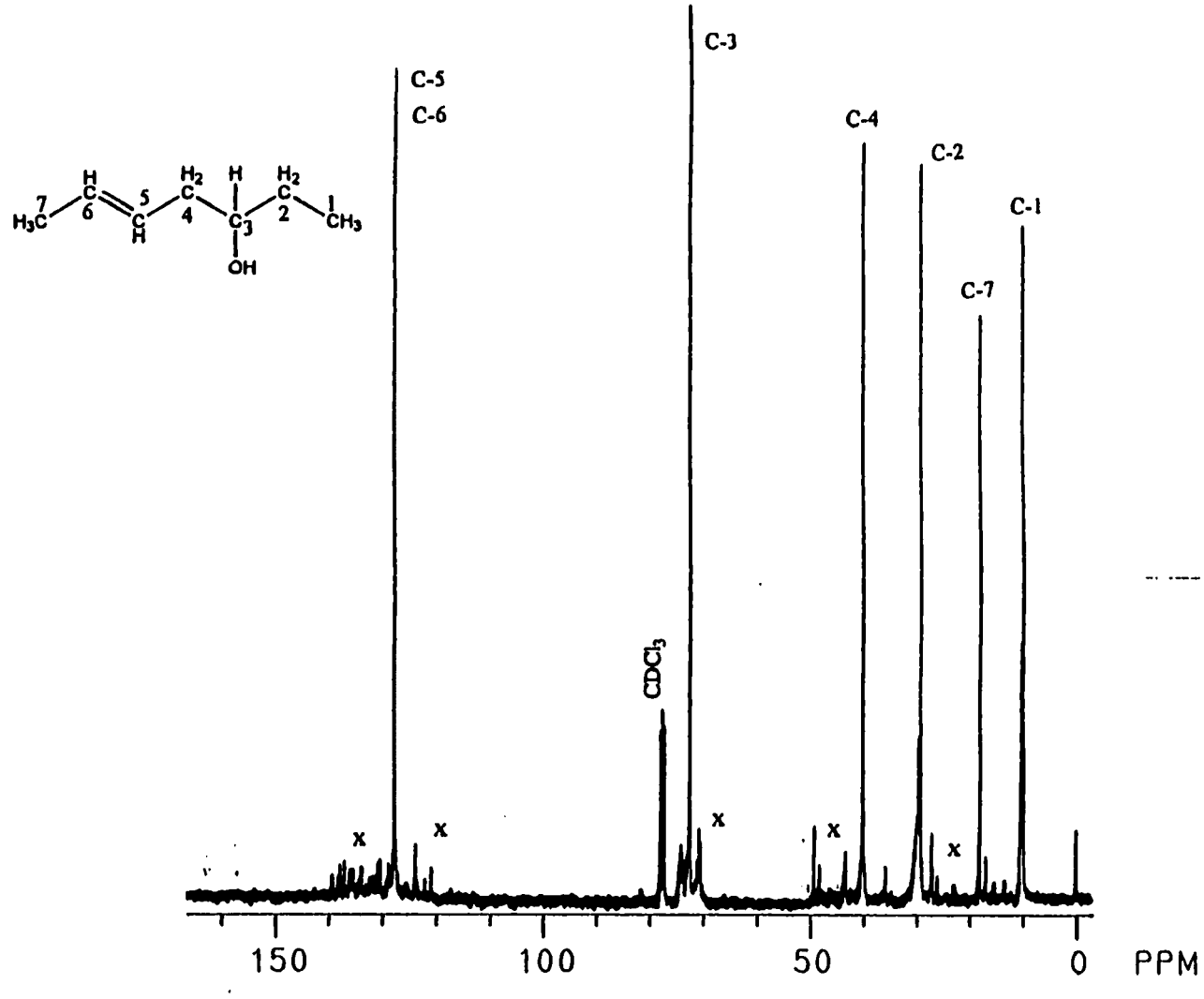


Fig. 3.6 ^{13}C NMR spectrum (75.57 MHz) of *trans*-5-hepten-3-ol (x: impurity)

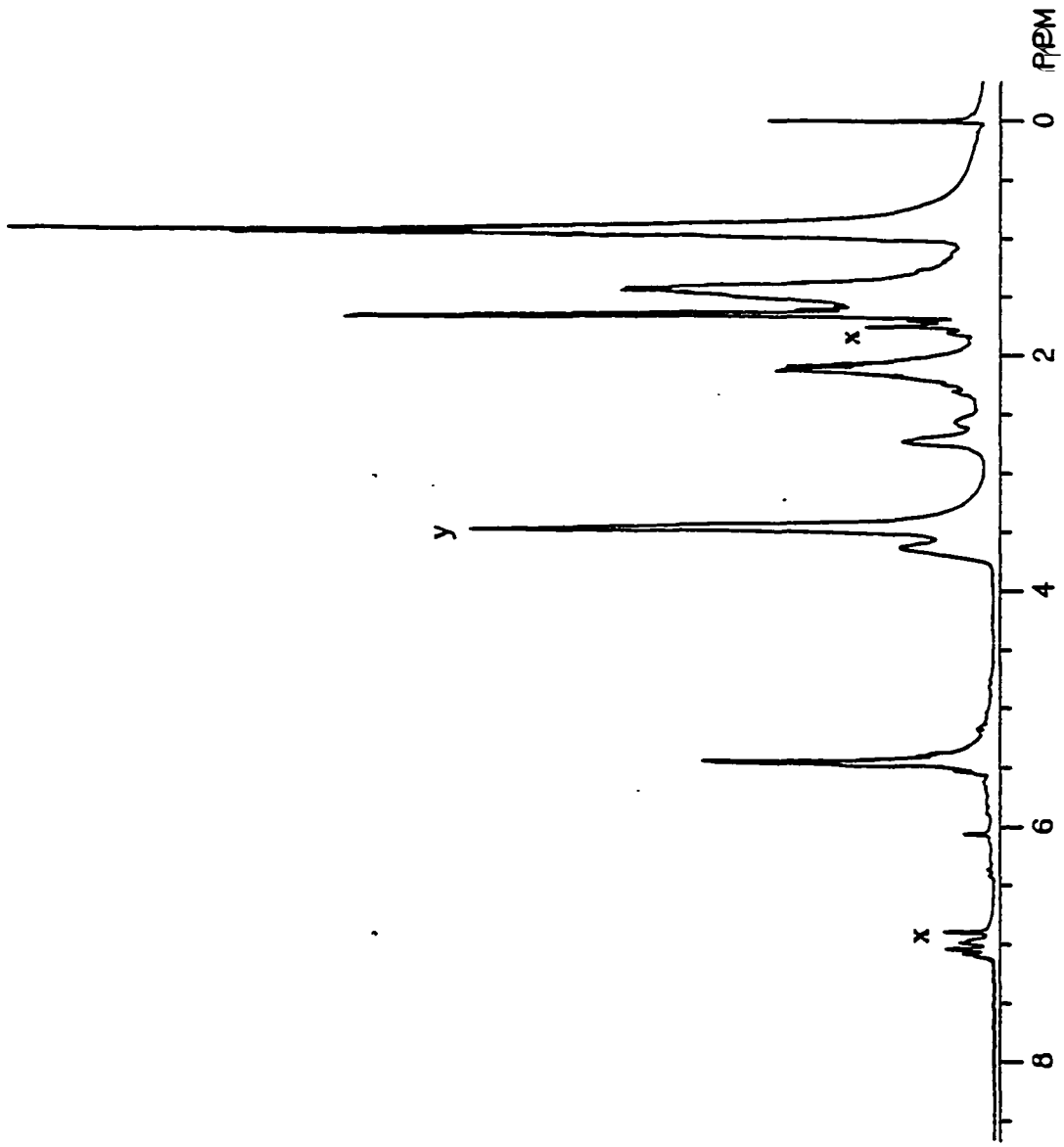


Fig. 3.7: ^1H NMR spectrum (300.52 MHz) of *trans*-5-heptien-3-ol (x: impurity, y: H_2O?)

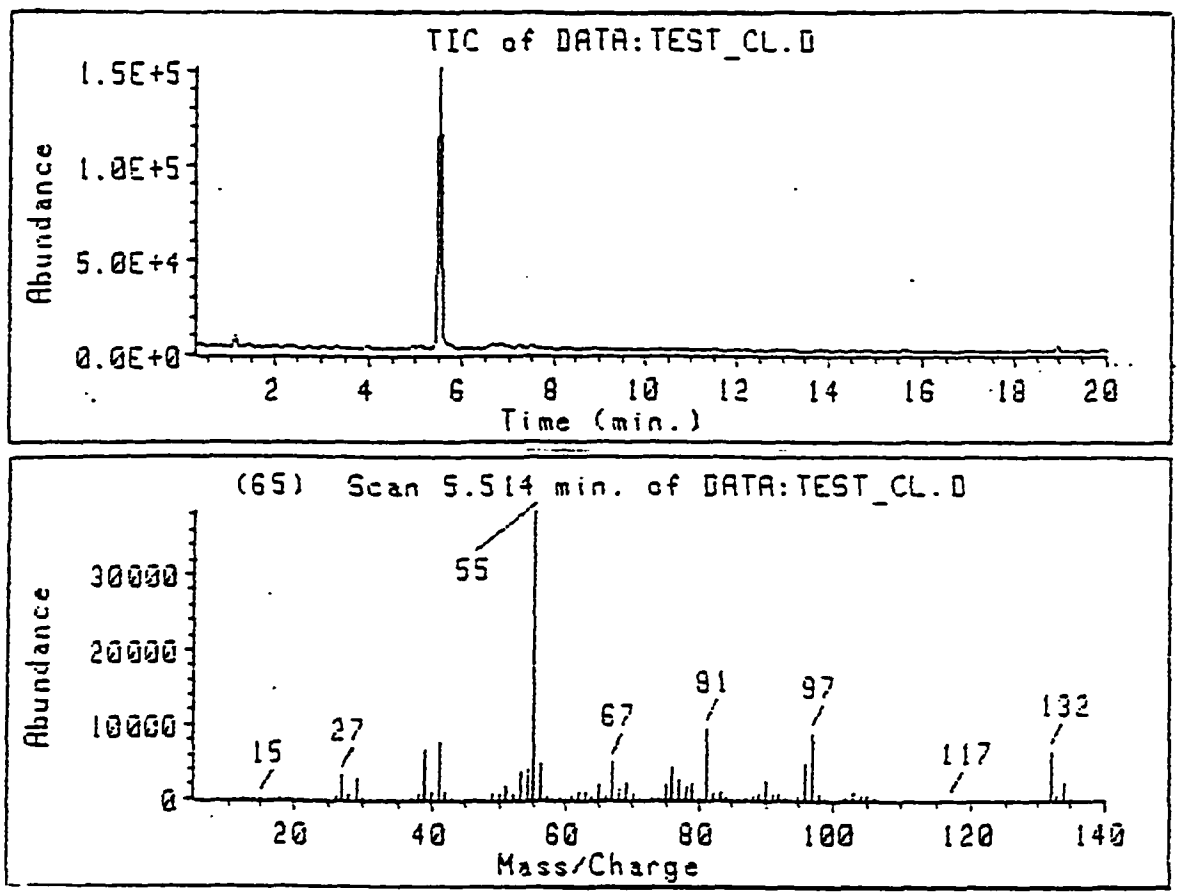


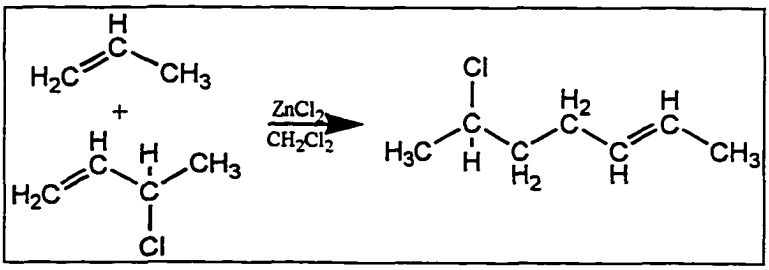
Fig. 3.8: Mass spectrum and gas chromatogram of

trans-5-chloro-2-heptene

%): 39(17), 41(20), 53(10), 54(10), 55(100), 56(13), 67(13), 76(11), 81(25), 96(13),97(23, M^+-Cl), 132(17, M^+), 134(6, M^+); ^{13}C NMR (75.57 MHz, THF-d_8, 50 °C) (Fig. 3.9), δ: 17.85(C-1), 127.19 and 128.23 (C-2 and C-3), 41.54(C-4), 64.71(C-5), 30.96(C-6), and 10.86(C-7) ppm; ^1H NMR (300.52 MHz, THF-d_8, 50 °C) (Fig. 3.10), δ: 0.30-1.15 (3H, $-CH_3$), 1.15-1.70 (3H, $-CH_3$), 1.70-1.90 (2H, $-CH_2-$), 2.30-2.40 (2H, $-CH_2-$), 3.65-3.80 (1H, -CHCl-), and 5.20-5.60 (2H, -CH=CH-) ppm. The IR spectrum of the product (neat) (Fig. 3.11) displays a strong band at 960 cm^{-1} which corresponds to a trans alkene. There is no band at 700-830 cm^{-1} corresponding to a cis alkene.

3.1.5 Synthesis of *trans*-6-chloro-2-heptene

Scheme 3.3: Synthesis of *trans*-6-chloro-2-heptene



trans-6-Chloro-2-heptene was prepared by a method similar to a literature procedure.[4]

Propylene (14.25 g, 339.3 mmol) was added to a solution of $ZnCl_2$ (44.3 mL of a 1 M solution in ether) and CH_2Cl_2 (45 mL) at -84 °C; then 3-chloro-1-butene (10.00 g, 110.5 mmol) was introduced with stirring. The reaction mixture was warmed to ~0 °C and

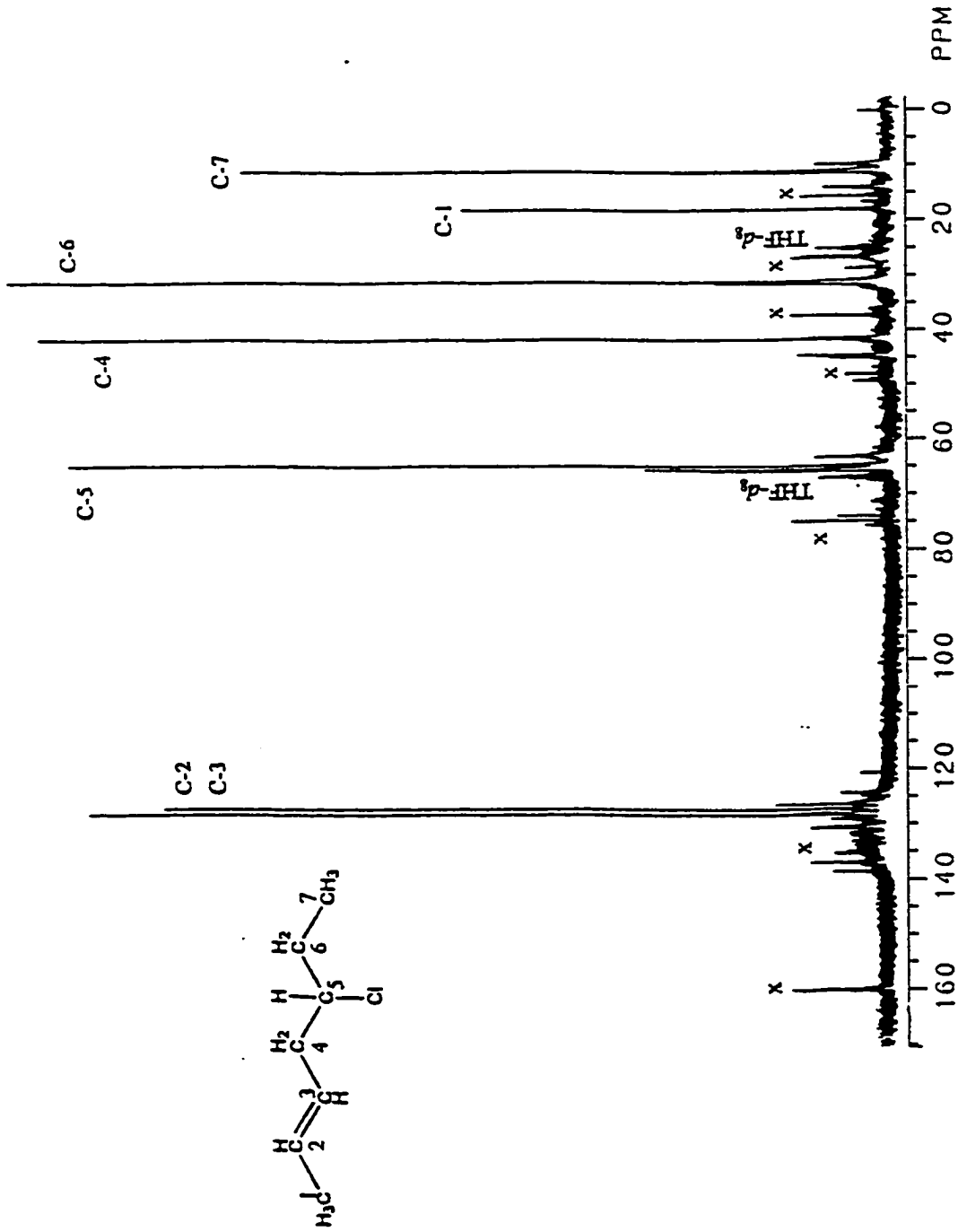


Fig. 3.9: ^{13}C NMR spectrum (75.57 MHz) of *trans*-5-chloro-2-heptene (x: impurity)

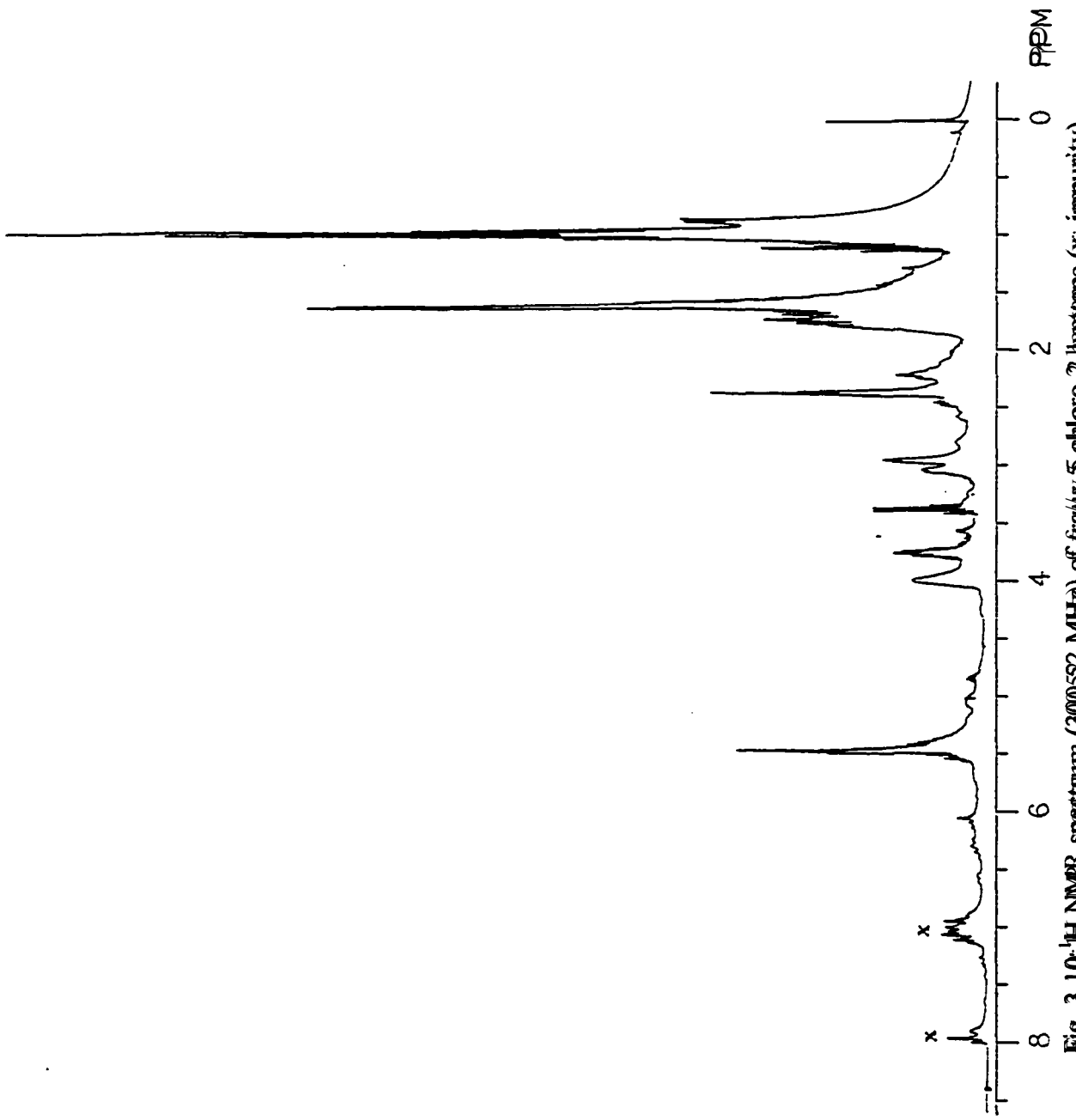


Fig. 3.10: ^{1}H NMR spectrum (300.532 MHz) of *trans*-5-chloro-2-heptene (x: impurity)

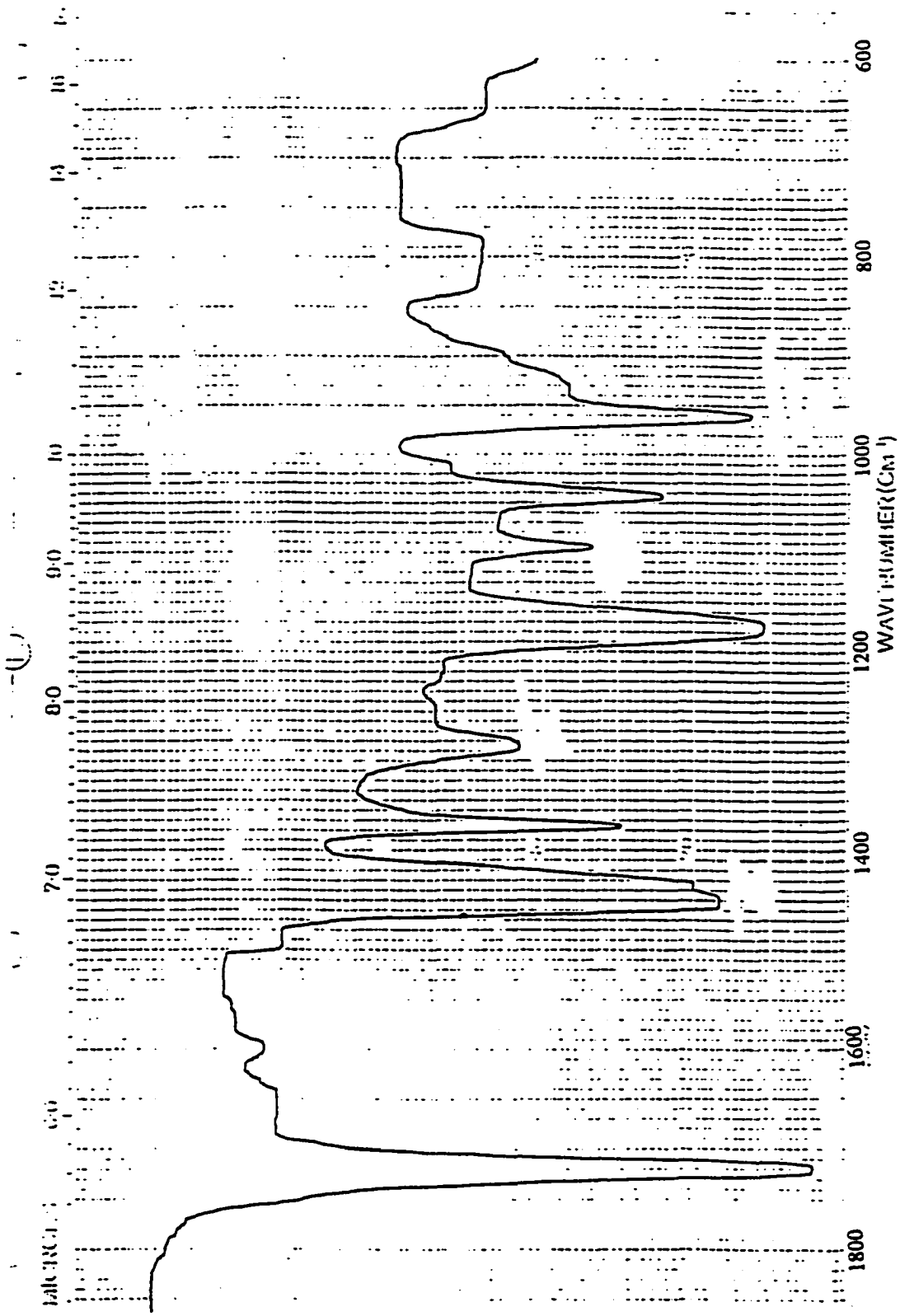


Fig. 3.11: IR spectrum of *trans*-5-chloro-2-heptene

allowed to stand for 5 days (the temperature did not exceed 10 °C). After removal of the catalyst by washing with 100 mL of NH_4OH solution (30%), the mixture was extracted with ether (3 x 100 mL). The ether solution was dried with anhydrous $MgSO_4$, concentrated on a rotary evaporator under aspirator vacuum, and subjected to short-path distillation to obtain 1.52 g (10 % yield) of *trans*-6-chloro-2-heptene: bp 39-41 °C (5 torr), purity 94.8% by GC/MS; mass spectrum (Fig. 3.12), *m/e* (relative intensity, %): 39(19), 41(31), 53(12), 54(14), 55(69), 56(11), 67(12), 69(29), 81(100), 96(16, M^+-HCl), 97(9, M^+-Cl), 132(22, M^+), 134 (7, M^+); ^{13}C NMR (75.57 MHz, THF-d_8, 50 °C) (Fig. 3.13), δ: 17.84(C-1), 126.10(C-2), 130.42(C-3), 30.16(C-4), 40.84(C-5), 57.98(C-6), and 25.45(C-7) ppm; ^1H NMR (300.52 MHz, THF-d_8, 50 °C) (Fig. 3.14), δ: 1.32-1.53 (3H, -CH_3), 1.53-1.68 (3H, -CH_3), 1.68-1.88 (2H, -CH_2-), 1.98-2.30 (2H, -CH_2-), 3.82-4.16 (1H, -CHCl-), and 5.18-5.70 (2H, -CH=CH-) ppm; IR spectrum (neat sample) (Fig. 3.15), reveals strong peak at 960 cm^{-1} for trans alkene, no peak at 700-830 cm^{-1} for cis alkene.

3.1.6 Synthesis of 9-(2-ethyl-*n*-hexyl)heptadecane

(i) Synthesis of 1-bromo-2-ethylhexane

This compound was prepared by a method similar to a literature procedure.[5]

To a solution of 2-ethyl-1-hexanol (15.6 mL, 13.0 g, 99.8 mmol) and triphenylphosphine (28.1 g, 107 mmol) in DMF (100 mL) that had been dried over molecular sieves, bromine was added dropwise until 2 drops caused the solution to acquire a permanent orange coloration. The resulting exothermic reaction raised the

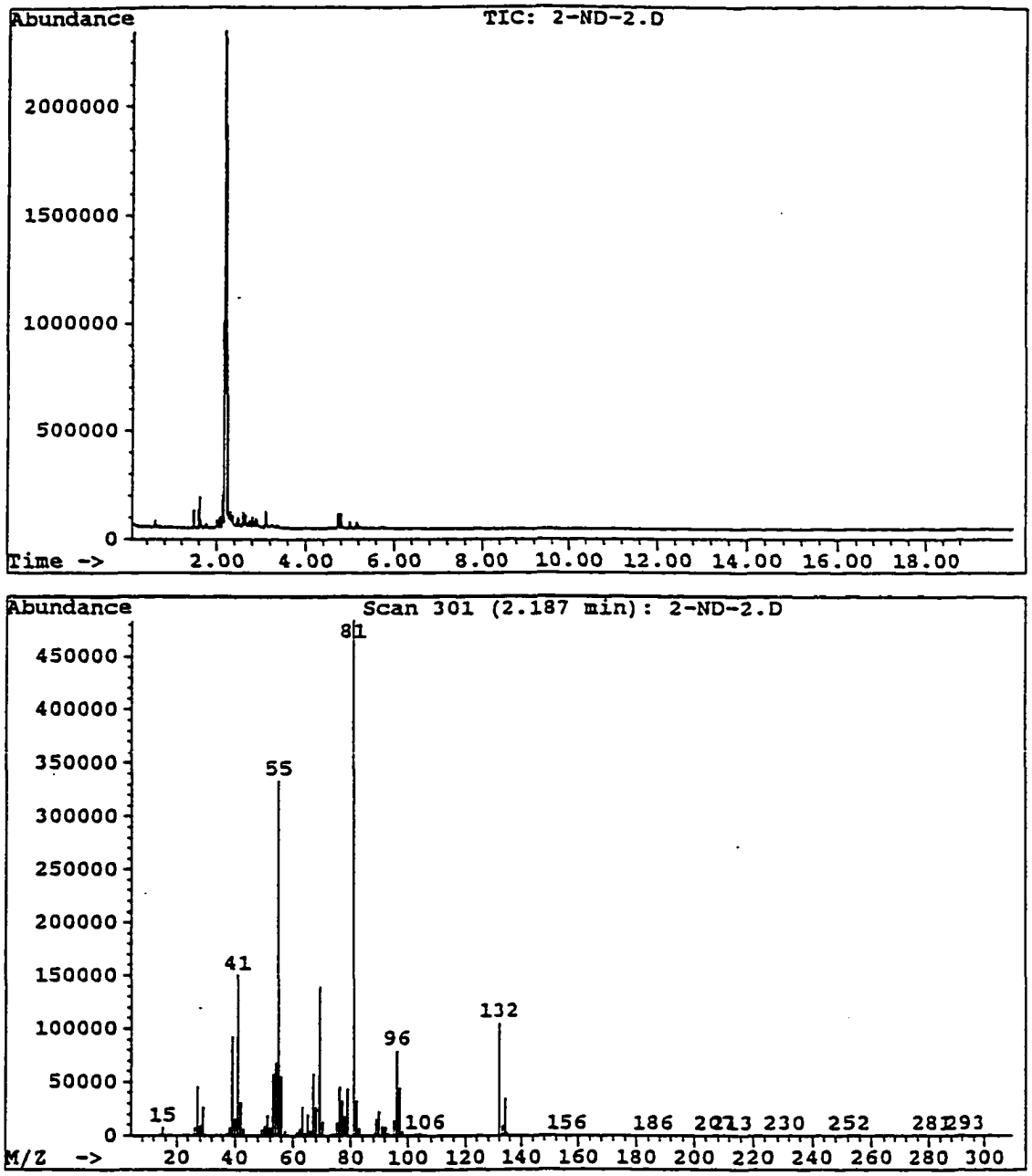


Fig. 3.12: Mass spectrum and gas chromatogram of

trans-6-chloro-2-heptene

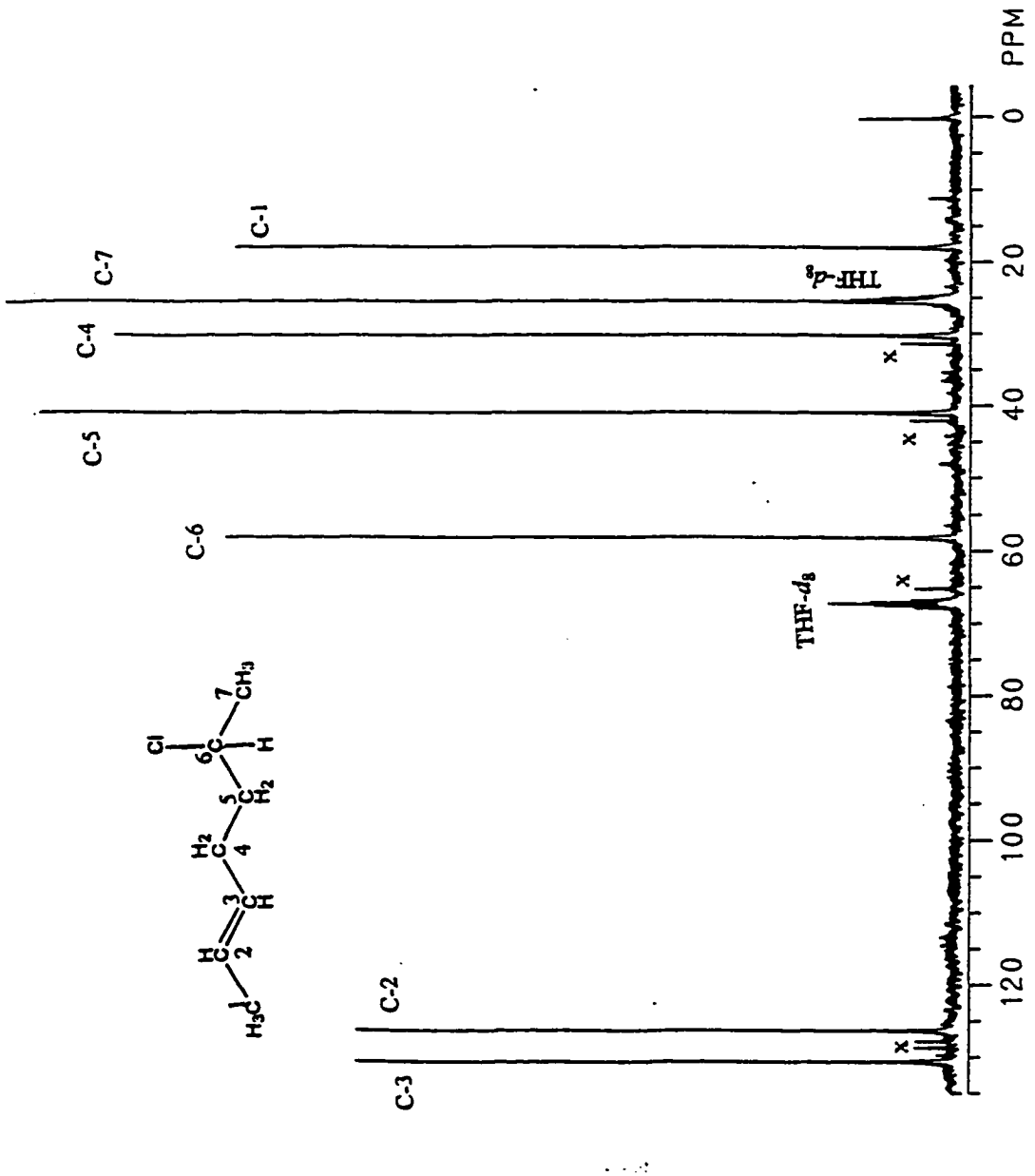


Fig. 3.13: ^{13}C NMR spectrum (75.57 MHz) of *trans*-6-chloro-2-heptene (x: impurity)

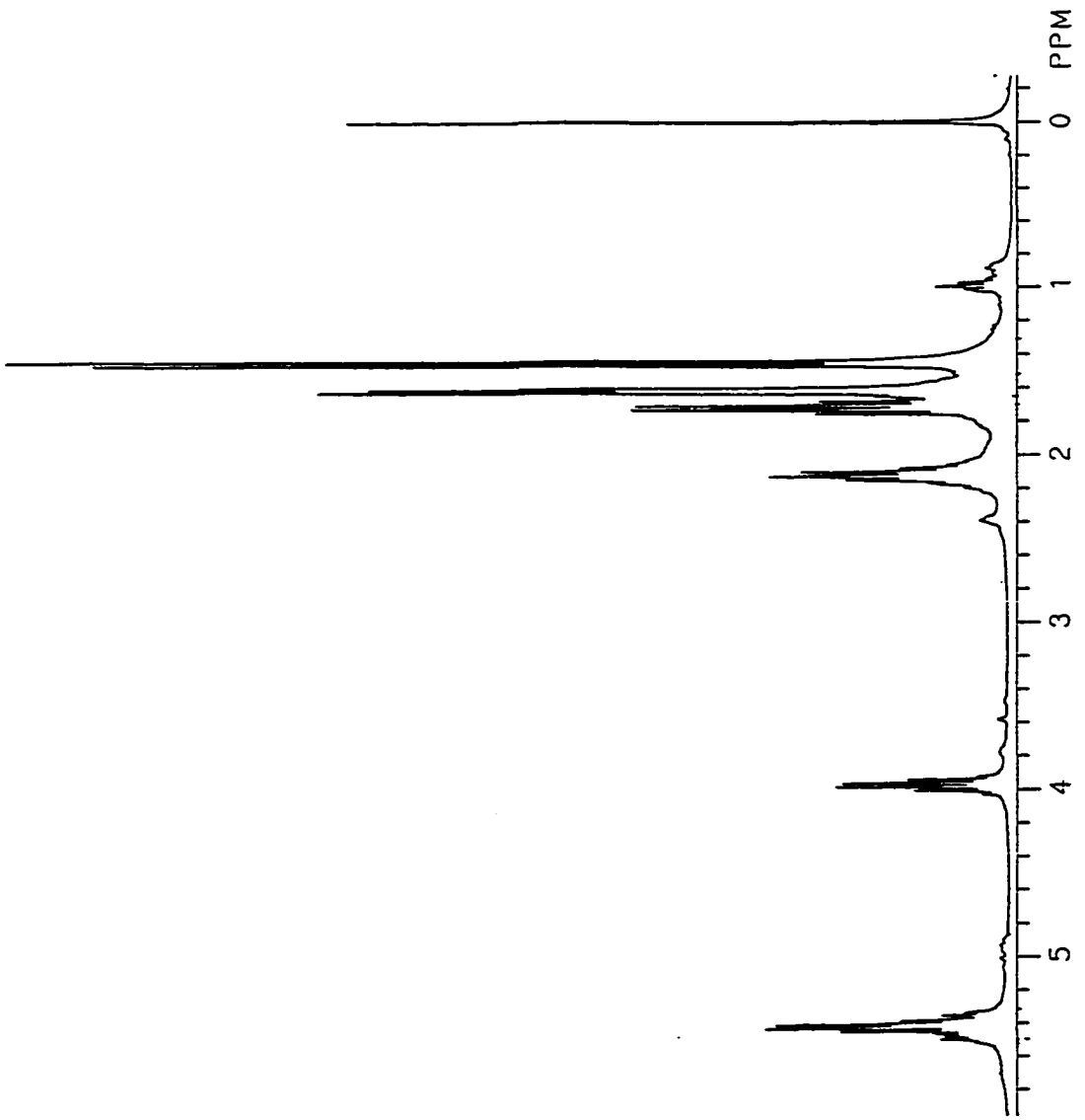


Fig. 3.14: ^{1}H NMR spectrum (300.52 MHz) of *trans*-6-chloro-2-heptene

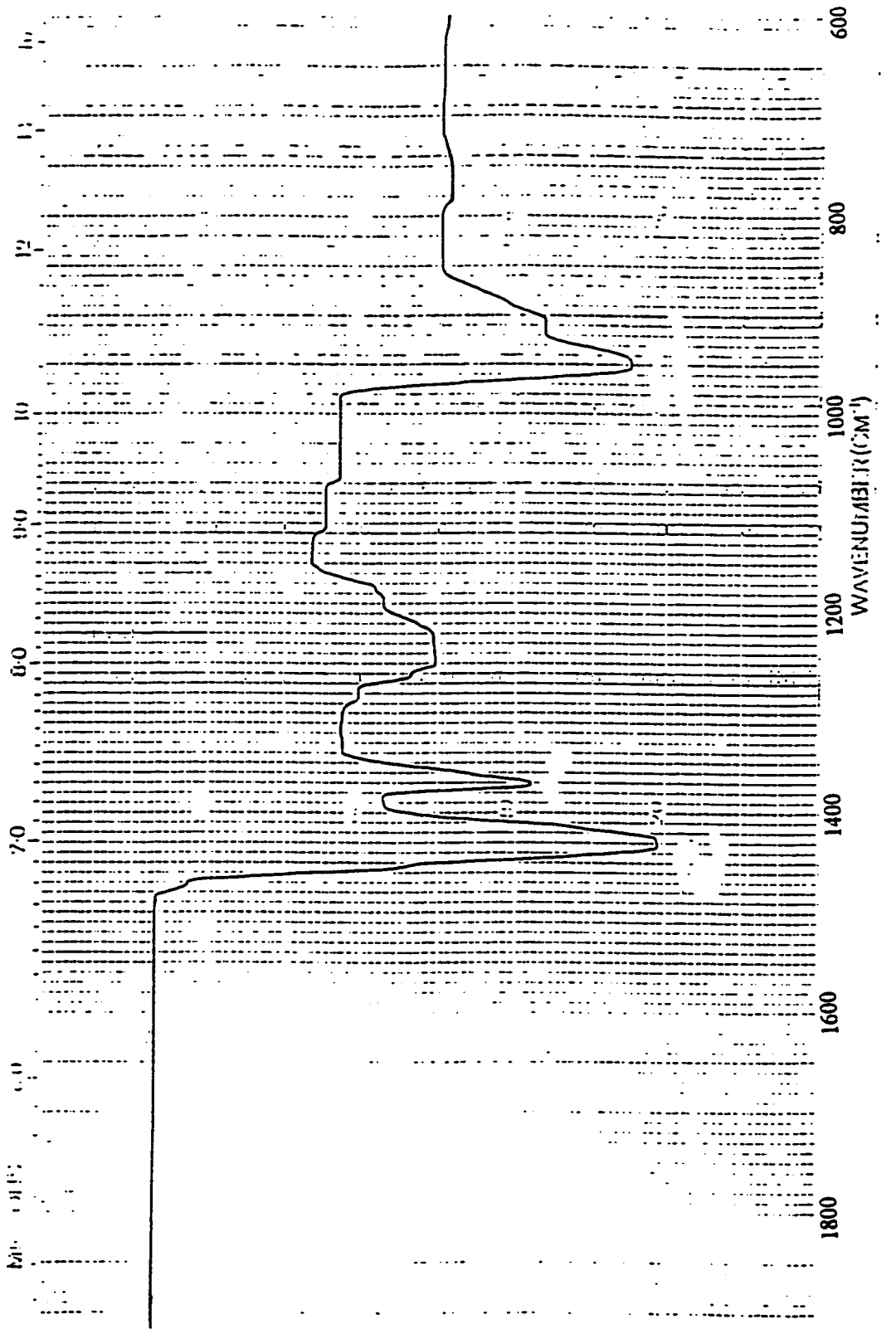
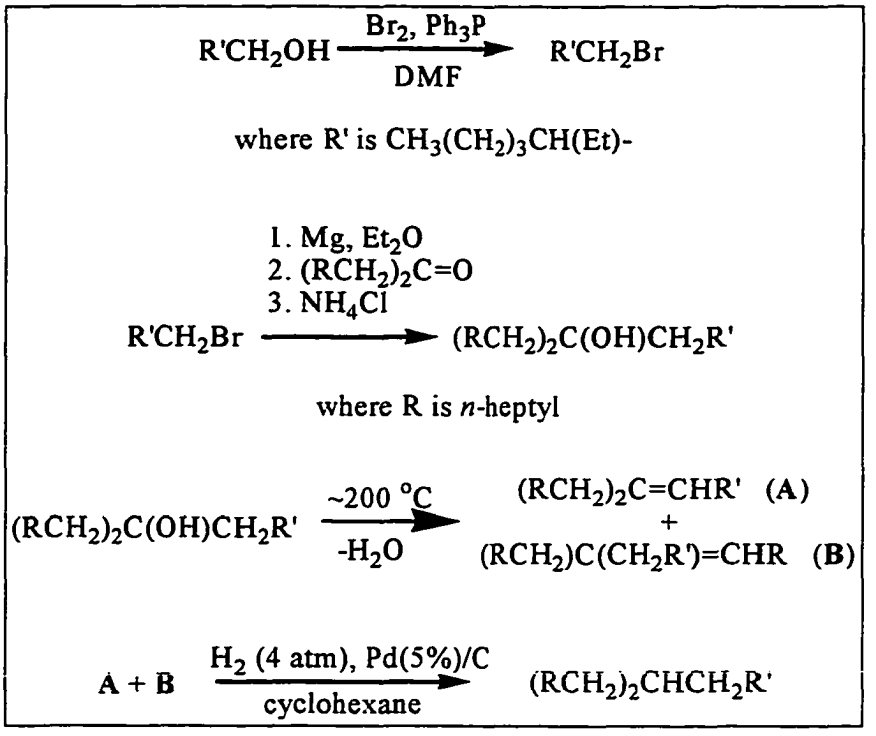


Fig. 3.15: IR spectrum of *trans*-6-chloro-2-heptene

Scheme 3.4: Synthesis of 9-(2-ethyl-*n*-hexyl)heptadecane



temperature of the mixture to 55 °C. After the mixture had cooled to room temperature, it was extracted with 3 x 200 mL of ether, and the combined extracts were washed with 3 x 200 mL of a solution prepared from equal volumes of deionized water and concentrated aqueous HCl. The organic portion then was washed with 3 x 300 mL of DI water, dried over anhydrous $MgSO_4$, and concentrated on a rotary evaporator at 35 °C under aspirator vacuum. Fractional distillation of the residue was performed with an H. S. Martin spinning band micro still equipped with a Teflon band and having a maximum separation efficiency of 150 theoretical plates. The yield of 1-bromo-2-ethylhexane thus obtained was 17.6 g (91%) (bp 31-35 °C at 0.10 torr), and its purity was 99% according to GC/MS analysis

(Fig. 3.16), *m/e* (relative intensity, %): 27(14), 29(15), 39(16), 41(38), 43(20), 55(52), 56(15), 57(100), 70(10), 71(62), 83(18), 113(13, M^+-Br), 135(5, M^+-Bu), 137(5, M^+-Bu), 163(7, M^+-Et), 165(7, M^+-Et), 192(1.0, M^+), 194(0.9, M^+); ^{13}C NMR (75.57 MHz, $CDCl_3$, *ca.* 25 °C) (Fig. 3.17), δ: 38.67(C-1), 41.50(C-2), 32.16(C-3), 29.06(C-4), 22.96(C-5), 13.99(C-6), 10.90(C-2'), and 25.46(C-1') ppm; ^1H NMR (300.52 MHz, $CDCl_3$, *ca.* 25 °C) (Fig. 3.18), δ: 0.64-1.10 (6H, 2 CH_3), 1.10-1.87 (8H, 4 CH_2; 1H, CH), and 3.24-3.69 (2H, CH_2Br) ppm.

(ii) Synthesis of 9-(2-ethyl-*n*-hexyl)-8-heptadecene and 5-ethyl-7-*n*-octyl-6-pentadecene

In a flame-dried flask, a solution of 1-bromo-2-ethylhexane (12.64 g, 65.4 mmol) in anhydrous ether (100 mL) was added slowly to a mixture of anhydrous ether (300 mL), magnesium turnings (1.59 g, 65.4 mg-atom), and two small iodine crystals. Several turnings were broken with a glass rod to generate fresh metal surfaces. The mixture was heated under reflux until the iodine color disappeared and then was allowed to stand at room temperature overnight. Following the slow introduction of a solution of 9-heptadecanone (4.00 g, 15.7 mmol) in dry ether (50 mL), the reaction was allowed to continue at room temperature for 3 h and subsequently was terminated by adding a saturated aqueous solution of ammonium chloride (50 mL). The ether layer was separated, and the aqueous moiety was extracted with 3 x 150 mL of ether. All of the ethereal fractions then were combined, dried over anhydrous $MgSO_4$, and freed of ether by rotary evaporation under aspirator vacuum. Low-boiling materials were distilled from the residue

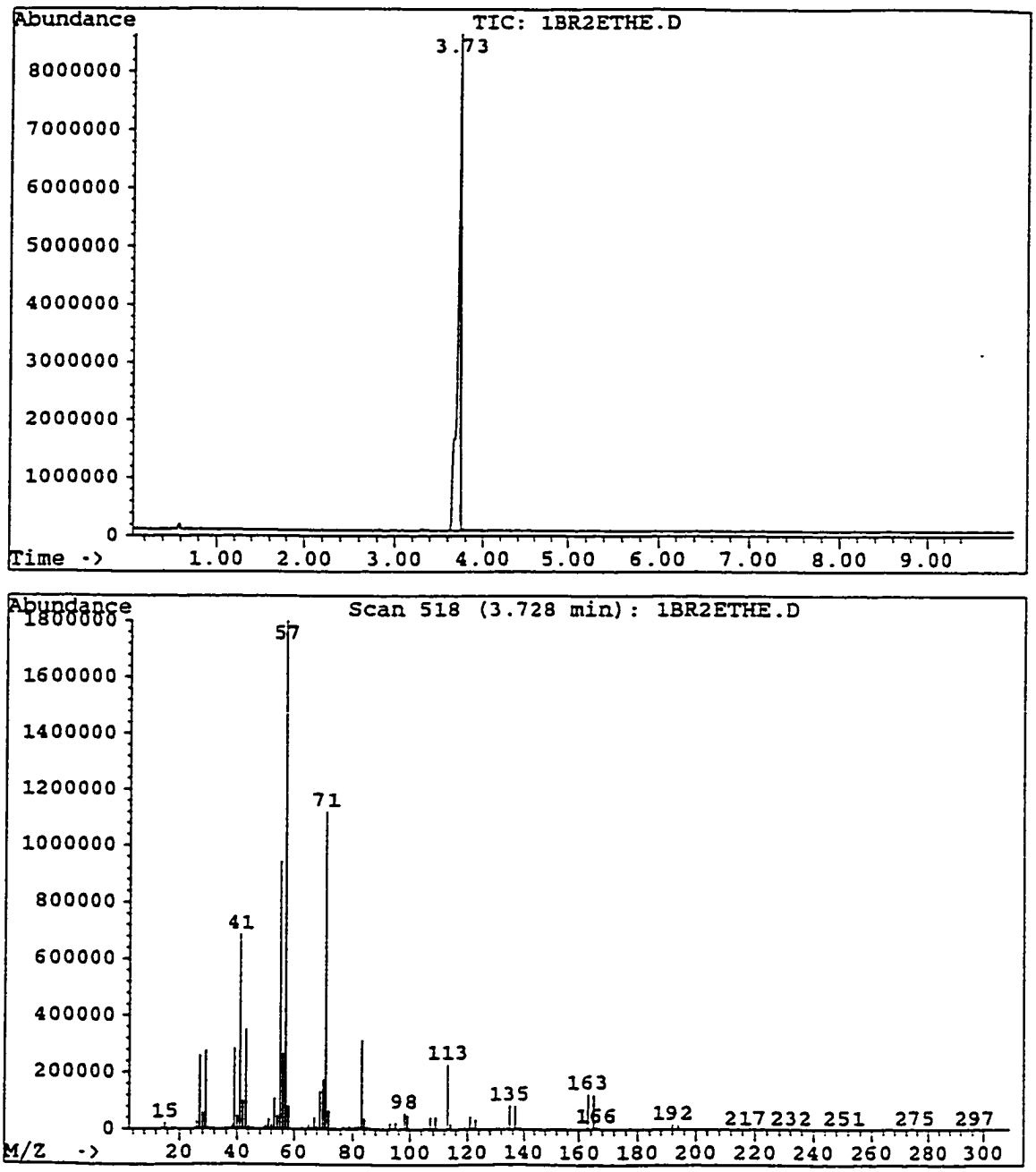


Fig. 3.16: Mass spectrum and gas chromatogram of

1-bromo-2-ethylhexane

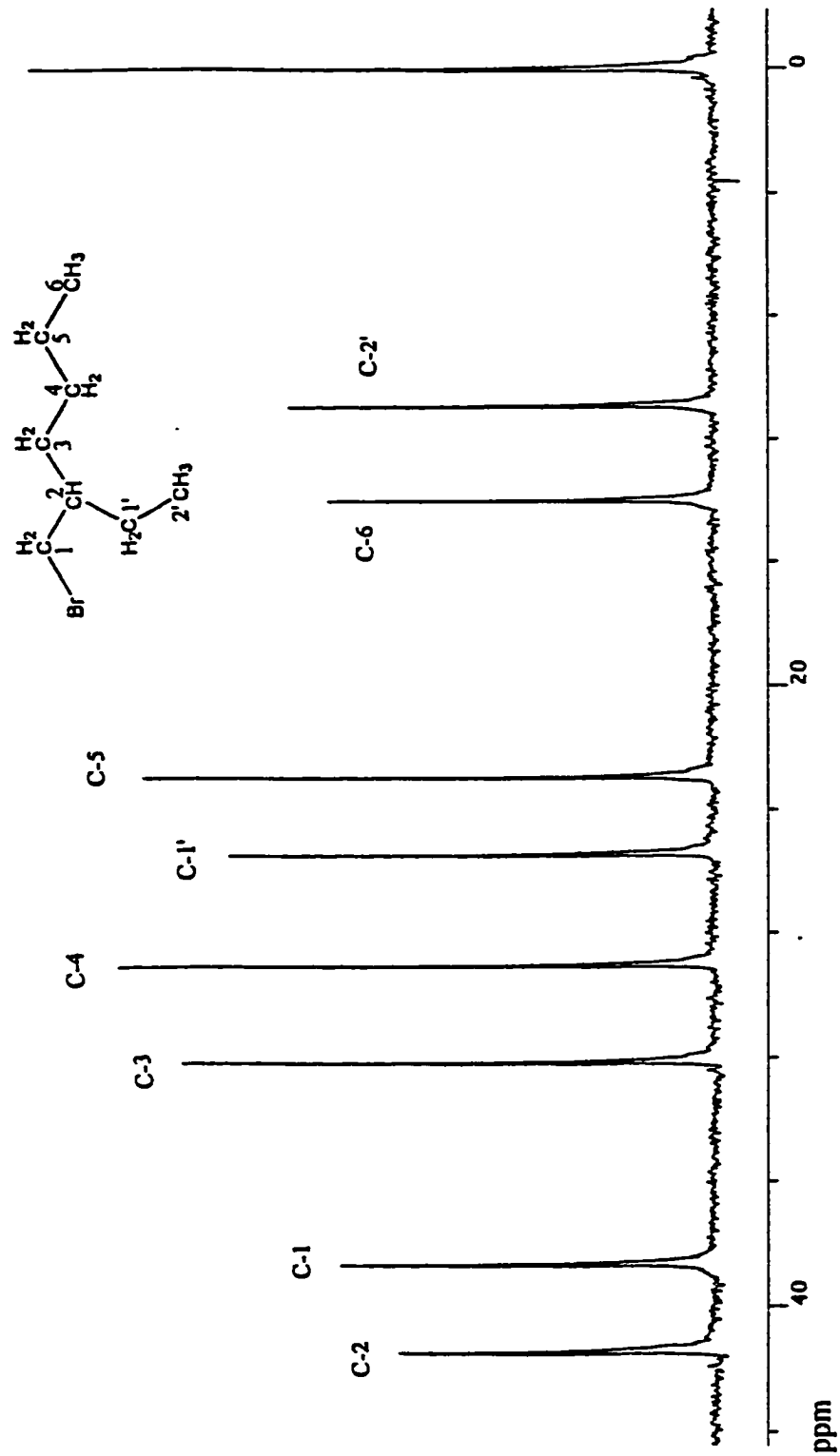


Fig. 3.17: ^{13}C NMR spectrum (75.57 MHz) of 1-bromo-2-ethylhexane

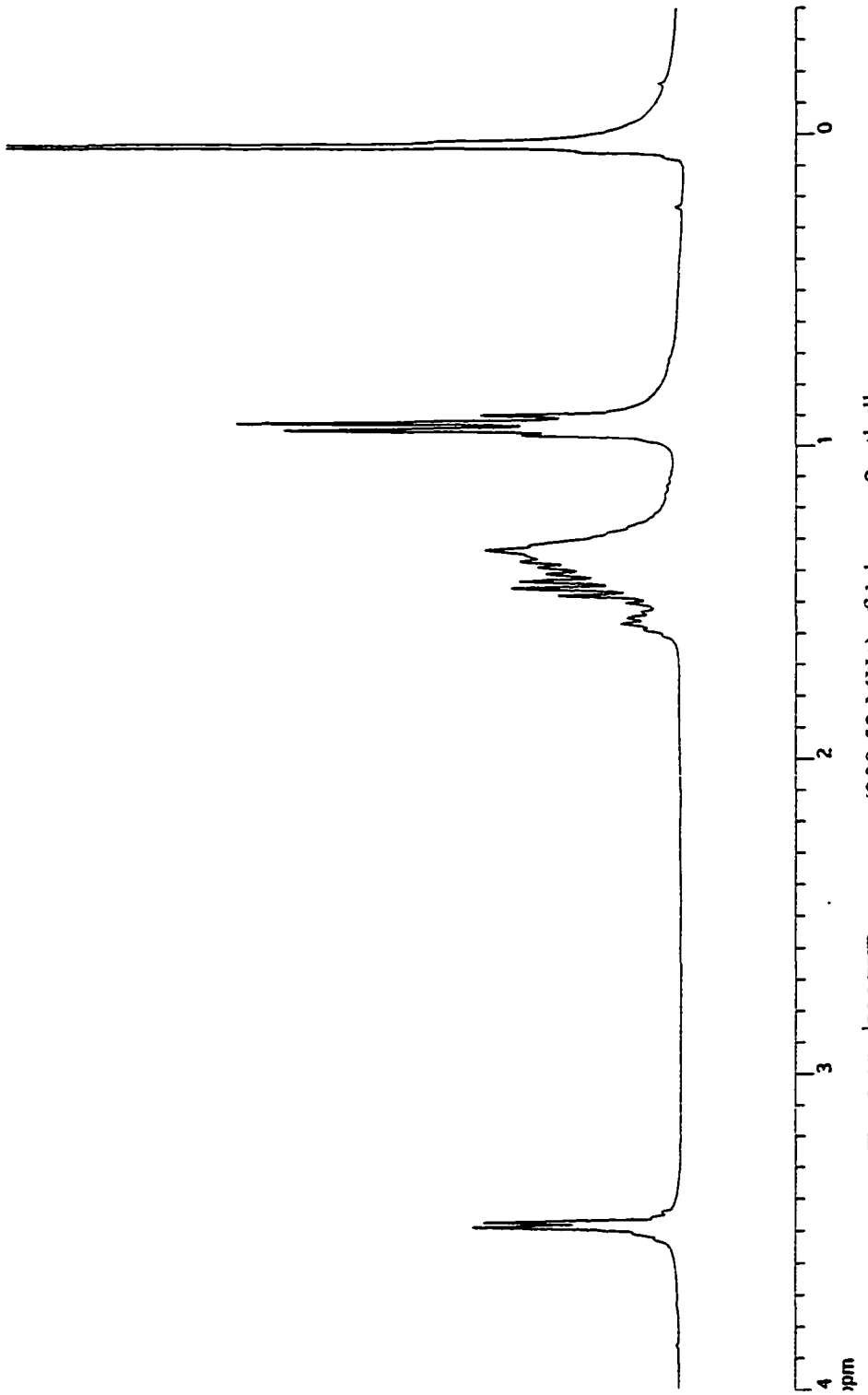


Fig. 3.18: ^{1}H NMR spectrum (300.522 MHz) of 1-bromo-2-ethylhexane

(0.10 torr, bp 45 - 136 °C with a final pot temperature of 198 °C), an operation that caused the quantitative dehydration of the 9-(2-ethyl-*n*-hexyl)heptadecan-9-ol intermediate. The final mixture included the following compounds: unconverted 9-heptadecanone (25.2%), 9-heptadecanol (9.6%), and two unsaturated compounds related to dehydrated 9-(2-ethyl-*n*-hexyl)heptadecan-9-ol: product 1 (20.0%) and product 2 (37.1%), with GC retention times of 10.47 and 10.60 min, respectively (the yields were not determined); mass spectra (Fig. 3.19), *m/e* (relative intensity): product 1 (5-ethyl-7-*n*-octyl-6-pentadecene?), 29(11), 41(21), 43(22), 55(30), 57(24), 67(17), 69(40), 71(14), 81(27), 83(46), 85(15), 95(26), 96(12), 97(63), 109(14), 111(51), 125(32), 139(13), 237(100, M^+-C_8H_{17}), 238(20), 253(4, M^+-C_7H_{13}), 293(63, M^+-Bu), 294(15), 321(69, M^+-Et), 322(17), 350(21, M^+); product 2 [9-(2-ethyl-*n*-hexyl)-8-heptadecene?], 27(10), 29(26), 41(52), 43(66), 55(60), 56(22), 57(94), 67(36), 68(24), 69(63), 70(20), 71(28), 79(17), 81(42), 82(17), 83(74), 84(14), 85(31), 95(35), 96(28), 97(81), 98(65), 99(23), 109(17), 110(13), 111(59), 112(26), 113(18), 125(25), 126(34), 127(11), 138(35), 139(100), 140(22), 154(63), 155(37), 223(10), 237(35, M^+-C_8H_{17}), 238(14), 252(33, M^+-C_7H_{14}), 253(49, M^+-C_7H_{13}), 293(12, M^+-Bu), 321(14, M^+-Et), 350(39, M^+).

(iii) Synthesis of 9-(2-ethyl-*n*-hexyl)heptadecane

This substance was synthesized by adapting a literature procedure.[6]

A 3.47-g portion of the mixture containing 9-(2-ethyl-*n*-hexyl)-8-heptadecene and 5-ethyl-7-*n*-octyl-6-pentadecene was dissolved in cyclohexane (80 mL) and subjected to

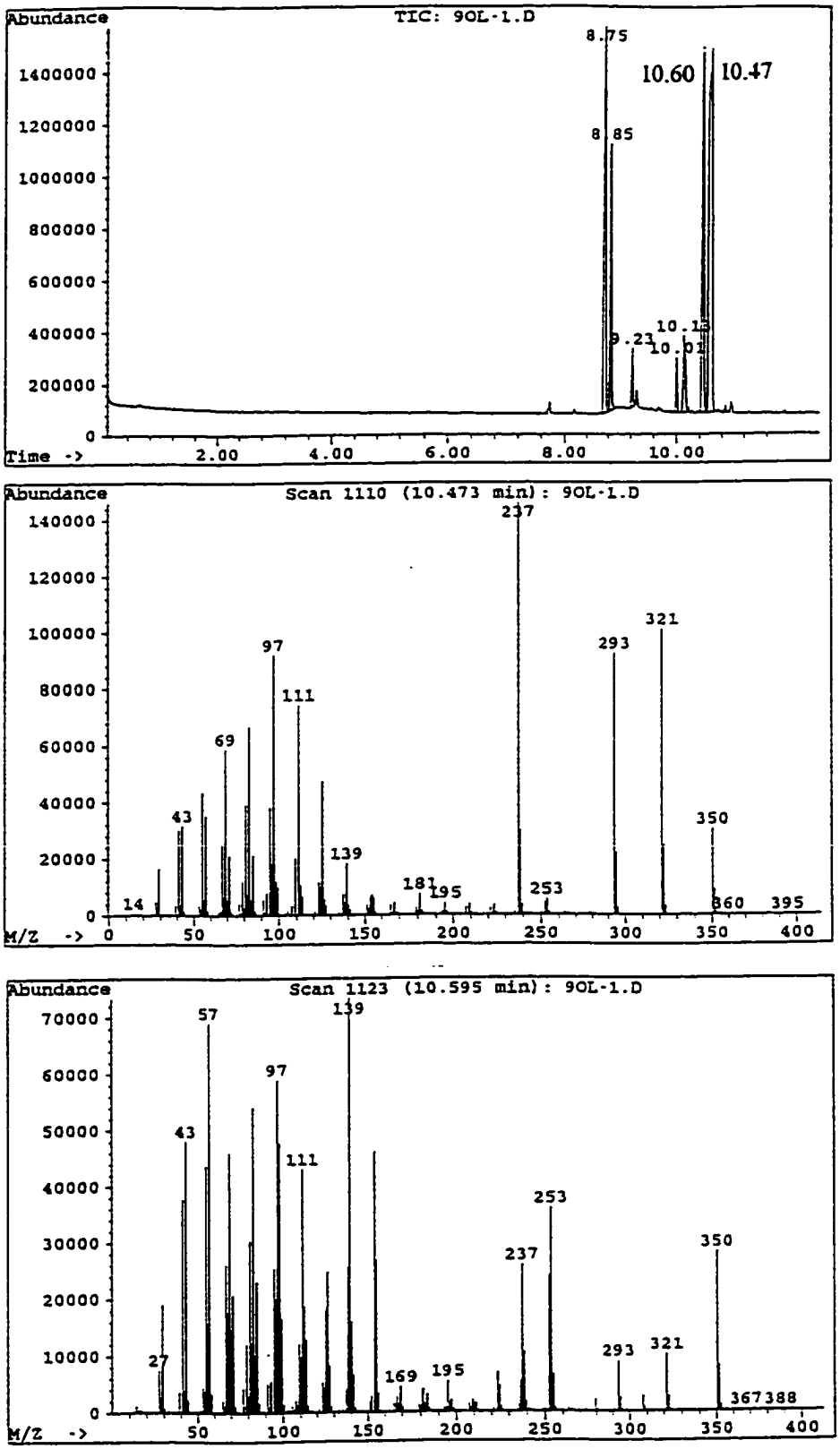


Fig. 3.19: Mass spectra and gas chromatogram of products resulting from the dehydration of 9-(2-ethyl-*n*-hexyl)heptadecan-9-ol

catalytic hydrogenation at room temperature in the presence of 1.0 g of a Pd(5%)/C catalyst. The reaction was carried out for 6 h with constant shaking under a hydrogen pressure of 4 atm. Filtration and subsequent rotary evaporation of the filtrate gave a residue that was shown by GC/MS analysis to consist of 9-(2-ethyl-*n*-hexyl)heptadecane, 9-heptadecanone, 9-heptadecanol, and minor impurities in a ratio of *ca.* 70:15:10:5, respectively. The starting ketone and the alcohol were identified by comparing their GC retention times and mass spectra with those of authentic specimens, and the distinctive resonances of these compounds were assigned easily in the ^{13}C NMR spectrum of the mixture. Mass spectrum of 9-(2-ethyl-*n*-hexyl)heptadecane (Fig. 3.20), *m/e* (relative intensity, %): 57(16), 85(12), 99(12), 113(17), 127(15), 141(14), 155(13), 169(11), 238(53), 239(100, M^+-C_8H_{17}), 240(18), 295(11), 323(20, M^+-Et), 352(1, M^+); ^1H NMR (300.52 MHz, $CDCl_3$, ambient temperature) (Fig. 3.21), δ: 0.70-1.00 (12H, 4 CH_3), 1.00-1.79 (38H, 19 CH_2), and 2.29-2.48 (2H, 2 CH) ppm; ^{13}C NMR [125.77 MHz, 1,4-dioxane-d_8:1,2,4-trichlorobenzene = 1:4 (v/v), 100 °C] (Fig. 3.22), δ:

9-(2-ethyl-*n*-hexyl)heptadecane: 14.11(C-1), 22.96(C-2), 32.28(C-3), 29.68(C-4*), 30.01(C-5*), 30.55(C-6), 27.07 and/or 27.12(C-7*), 34.81 and 34.88(C-8), 35.79(C-9), 39.53(C-1'), 37.22(C-2'), 33.97(C-3'), 29.76(C-4'), 23.48(C-5'), 14.16(C-6'), 26.98(C-1"), and 10.98(C-2") ppm.

9-heptadecanone: 24.34(C-7), 42.85(C-8), and 208.20 (C-9, off scale) ppm.

9-heptadecanol: 26.12(C-7), 38.27(C-8), and 71.78(C-9) ppm.

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* Tentative assignment

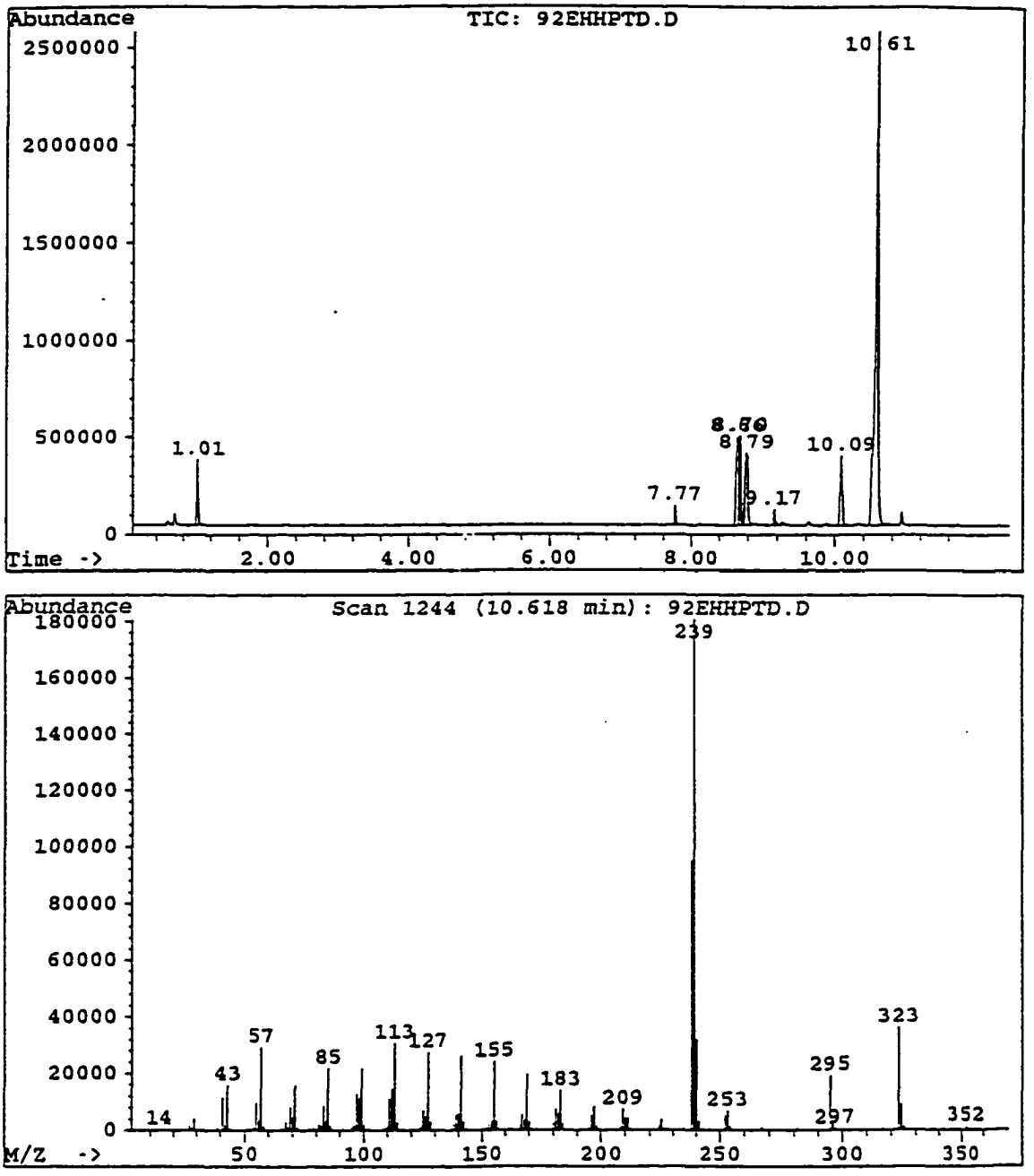


Fig. 3.20: Mass spectrum and gas chromatogram of

9-(2-ethyl-*n*-hexyl)heptadecane

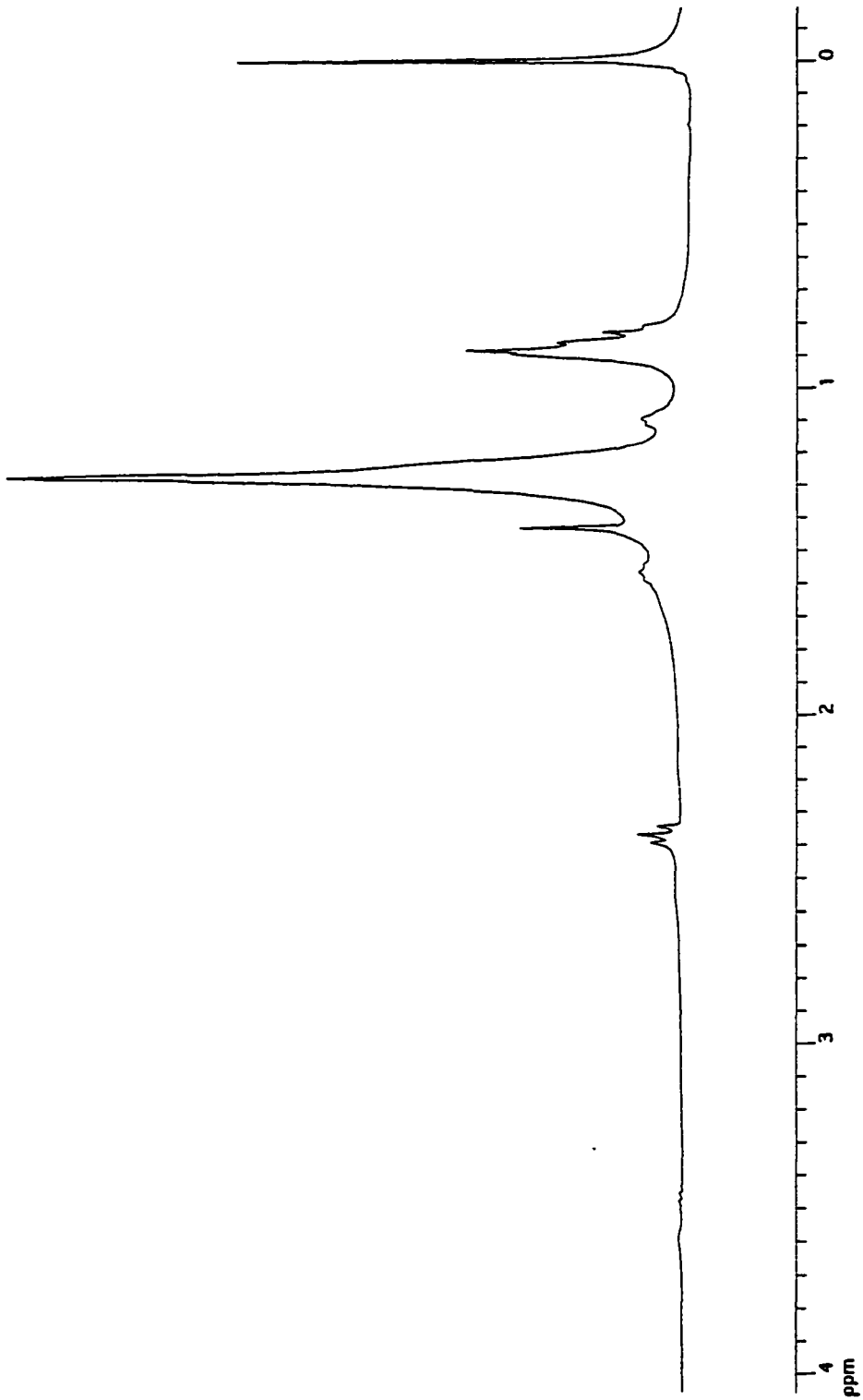


Fig. 3.21: ^{1}H NMR spectrum (300.532 MHz) of 9-(2-ethyl-*n*-hexyl)heptadecane

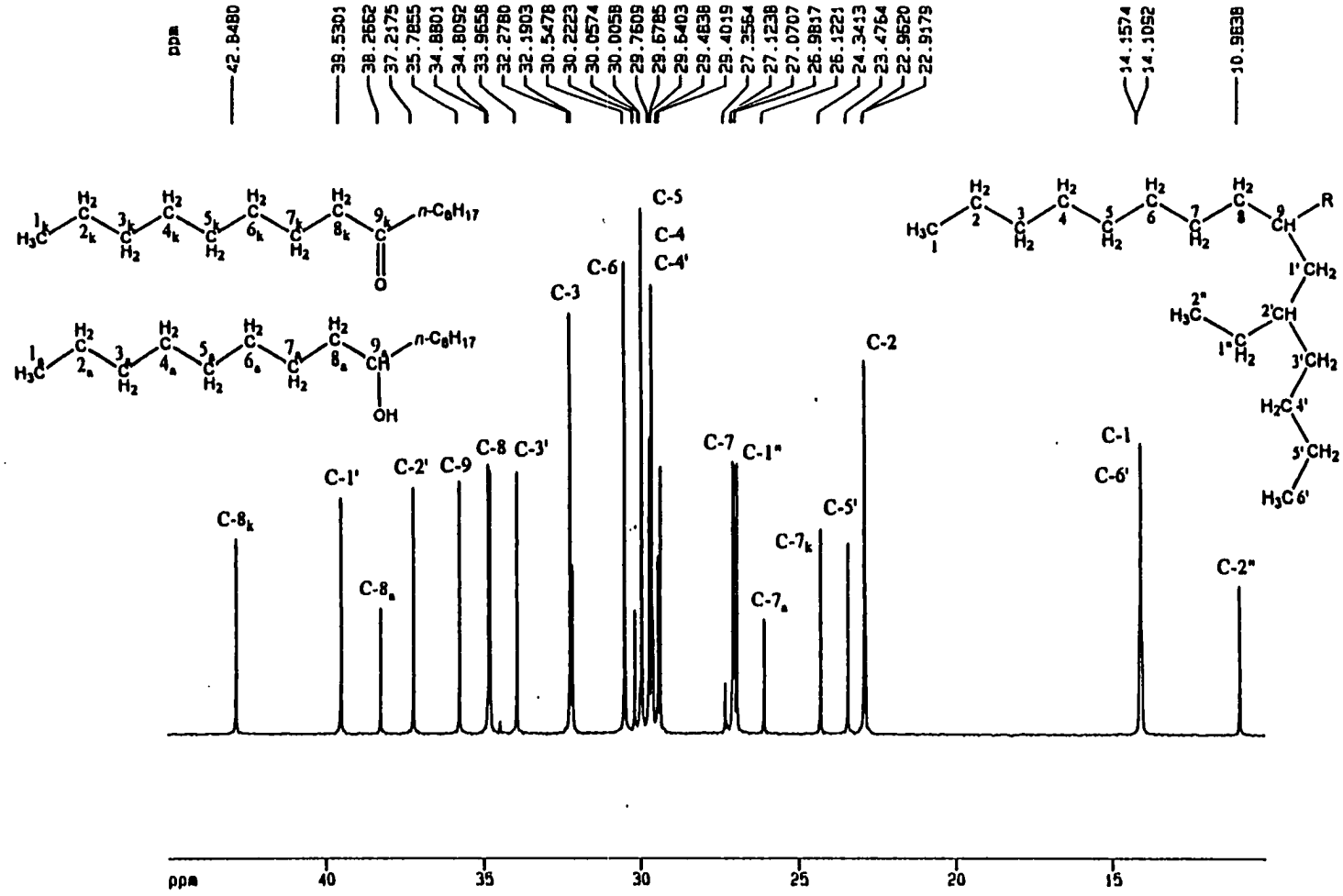


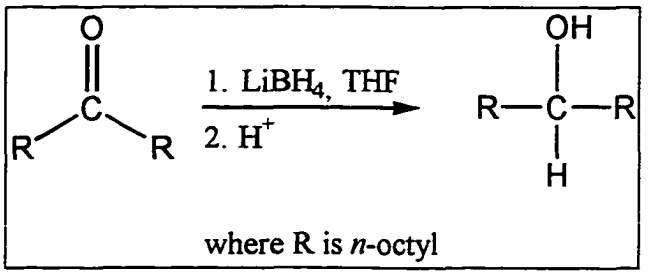
Fig. 3.22: ^{13}C NMR spectrum (125.77 MHz) of 9-(2-ethyl-*n*-hexyl)heptadecane

9-heptadecanone (from TCI, 91%) (Fig. 3.23): 14.03(C-1), 22.88(C-2), 32.16 (C3), 9.45(C-4), 29.73(C-5), 29.76(C-6), 24.38(C-7), 42.87(C-8), and 208.40(C-9, off scale) ppm.

(iv) Synthesis of 9-heptadecanol

9-Heptadecanol was synthesized by adapting a literature method.[7]

Scheme 3.5: Synthesis of 9-heptadecanol



A 2 M solution of lithium borohydride in THF (10 mL, 20 mmol) was added during 1 h to a solution of 9-heptadecanone (3.00 g, 11.8 mmol) in freshly distilled anhydrous THF (20 mL) while the temperature was kept near 0 °C by external cooling. After 3 h of reaction at 0-5 °C, methanol (5 mL) was introduced during 20 min while cooling was continued, and the mixture was kept at room temperature for an additional 3 h. Dilution with ether (50 mL), followed by washing with DI water (3 x 200 mL), drying over anhydrous $MgSO_4$, and concentration in a rotary evaporator under aspirator vacuum left a residue comprised of 3.4% of 8-heptadecene, 9% of heptadecane, and 87.6% of 9-heptadecanol (by GC/MS). The yield was not determined. Mass spectrum (Fig. 3.24), *m/e*

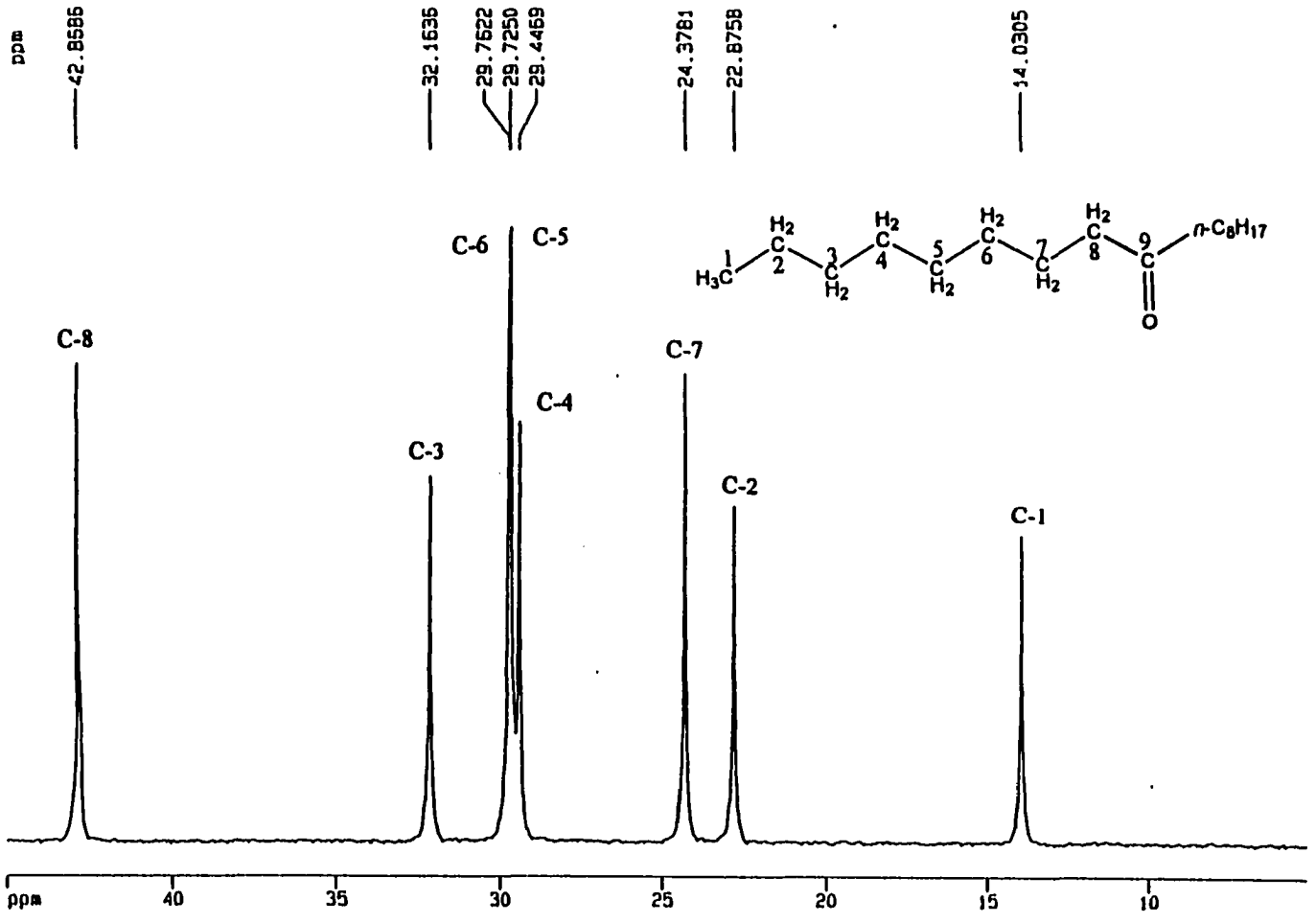


Fig. 3.23: ^{13}C NMR spectrum (125.77 MHz) of 9-heptadecanone (TCI, 91%)

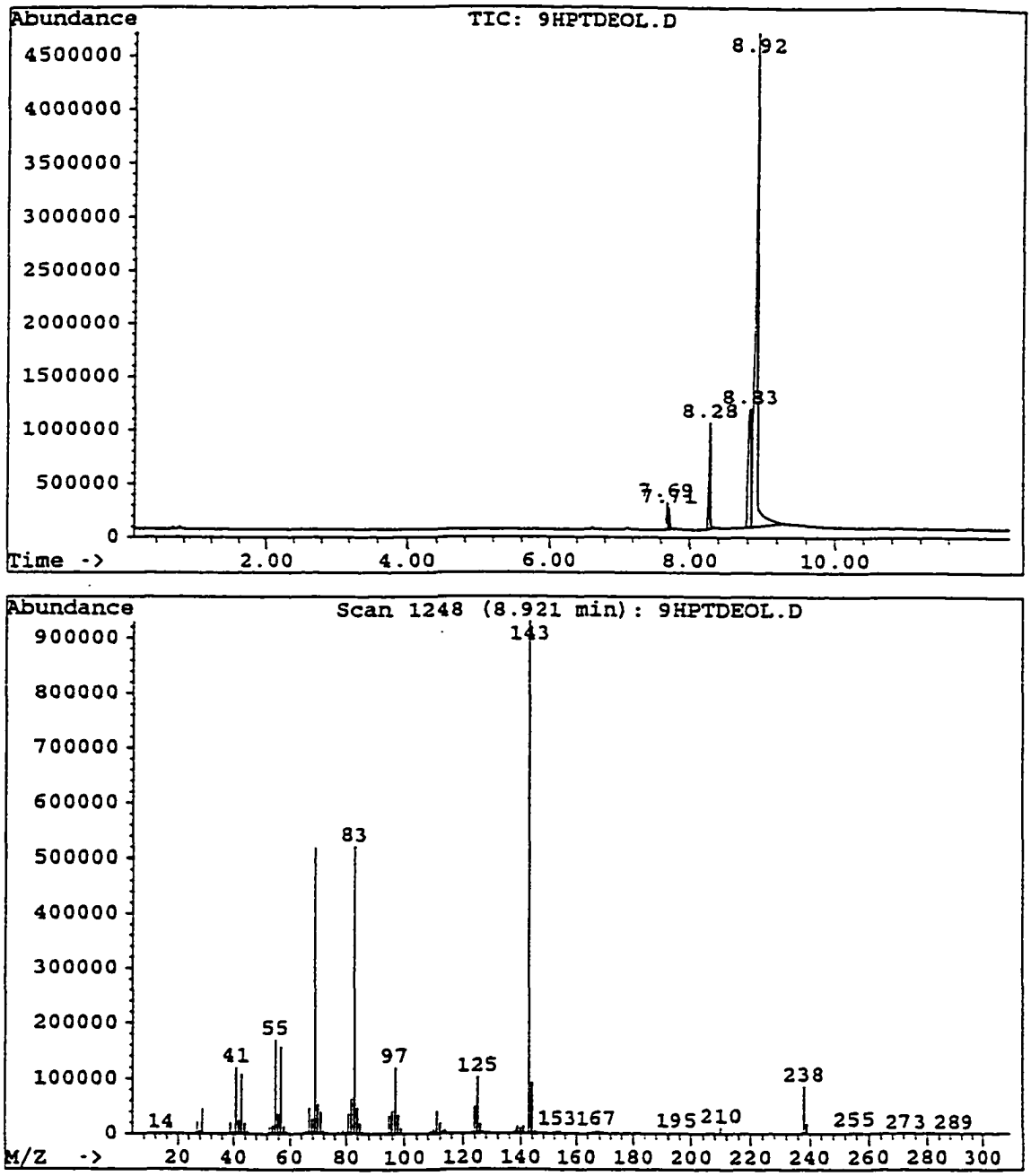


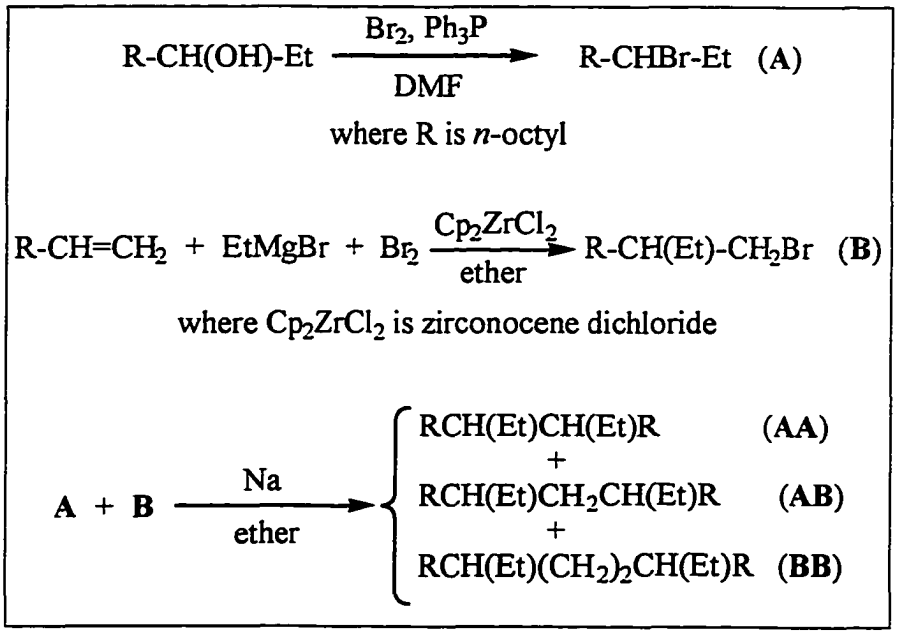
Fig. 3.24: Mass spectrum and gas chromatogram of

9-heptadecanol

(relative intensity, %): 41(13), 43(12), 55(18), 57(17), 69(56), 83(56), 97(13), 125(11), 143(100, M^+-C_8H_{17}), 144(10), 238(9, M^+-H_2O), 256(0.1, M^+); ^{13}C NMR [125.77 MHz, 1,4-dioxane-d_8:1,2,4-trichlorobenzene = 1:4 (v/v), 100 °C] (Fig.3.25), δ: 14.05(C-1), 22.92(C-2), 32.24(C-3), 29.60(C-4), 29.98 and 30.20(C-5 and -6), 26.09(C-7), 38.26(C-8), and 71.91(C-9) ppm; ^1H NMR (300.52 MHz, $CDCl_3$, ambient temperature) (Fig. 3.26), δ: 0.66-0.99 (6 H, 2 CH_3), 0.99-1.65 (28 H, 14 CH_2), and 3.44-3.75 (1 H, CH) ppm.

3.1.7 Synthesis of 9,11-diethylnonadecane

Scheme 3.6: Synthesis of 9,11-diethylnonadecane



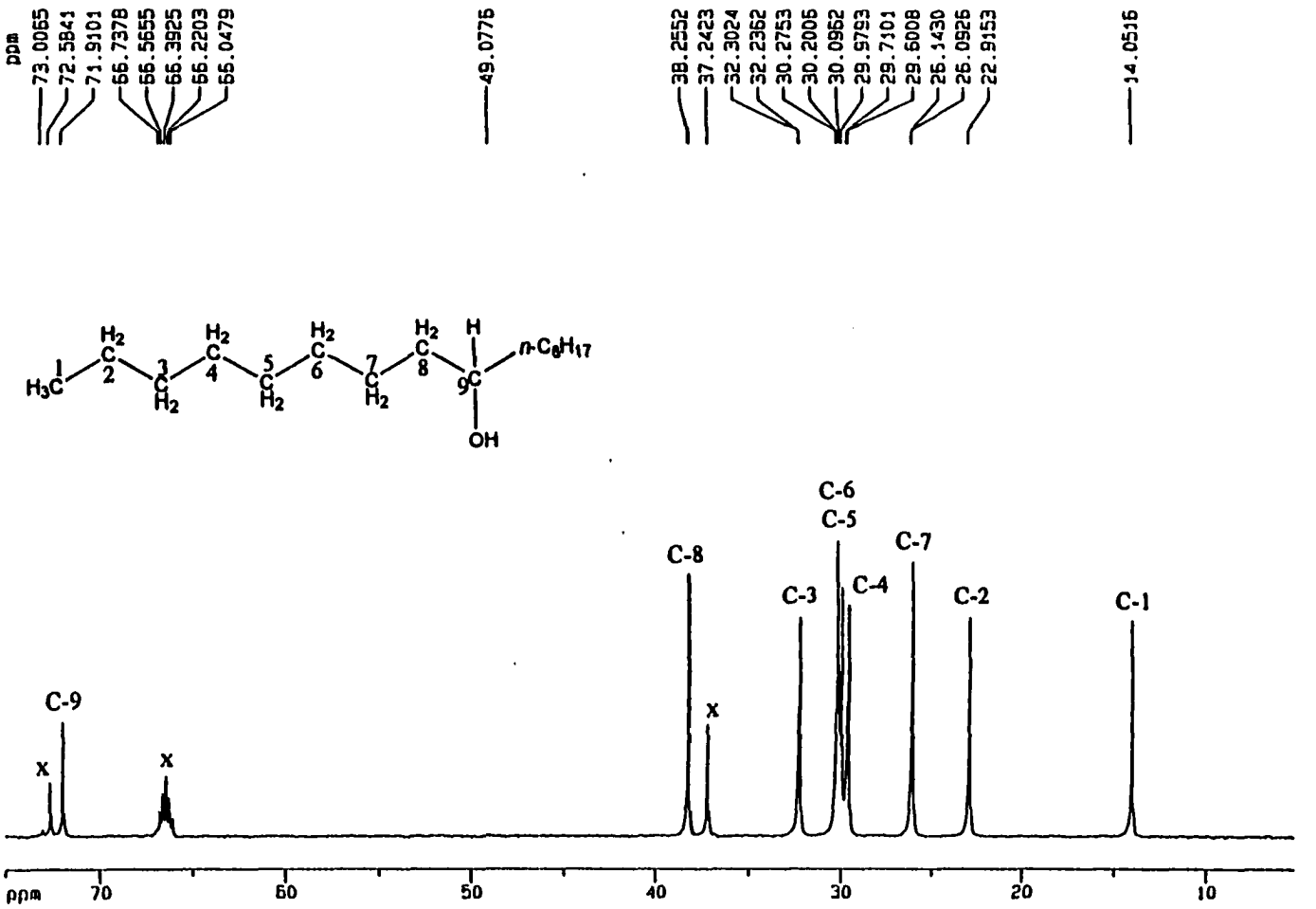


Fig. 3.25: ^{13}C NMR spectrum (125.77 MHz) of 9-heptadecanol (x: impurity)

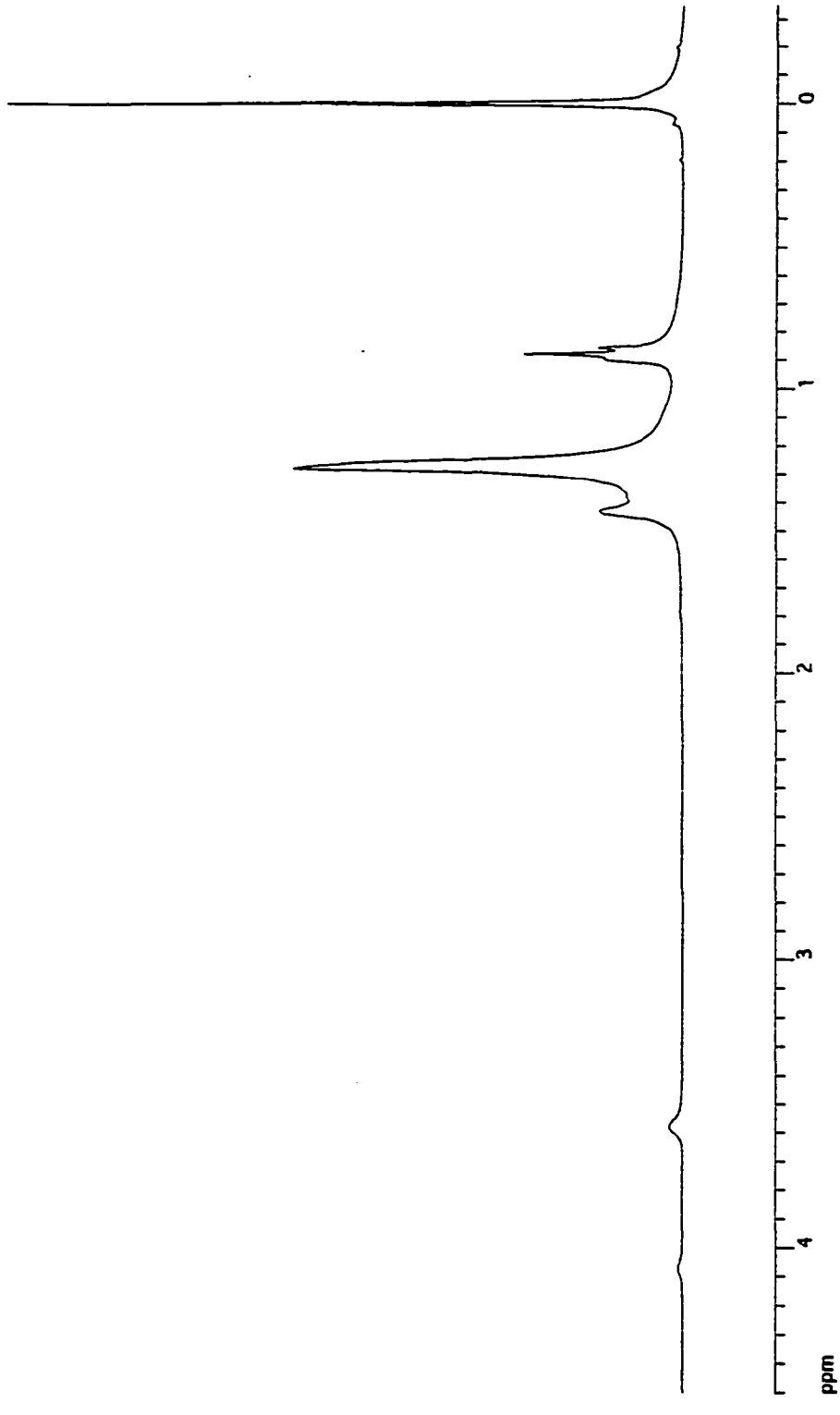


Fig. 3.26: ^{1}H NMR spectrum (300.52 MHz) of 9-heptadecanol

(i) Synthesis of 3-bromoundecane

3-Bromoundecane was prepared by the reaction of 3-undecanol with Br_2 in the presence of Ph_3P, using an adaptation of a literature procedure.[5]

Bromine (3.00 mL, 9.36 g, 58.6 mmol) was added dropwise to a solution of triphenylphosphine (16.73 g, 63.8 mmol) and 3-undecanol (12.00 mL, 9.95 g, 57.7 mmol) in DMF (100 mL). When the mixture had cooled to room temperature, it was extracted with 3 x 200 mL of ether, and the combined extracts were washed with 3 x 200 mL of a solution prepared from equal volumes of DI water and concentrated aqueous HCl. The ether solution then was washed with 3 x 150 mL of DI water, dried over anhydrous $MgSO_4$, concentrated in a rotary evaporator under aspirator vacuum, and fractionally distilled in the spinning band micro still to obtain 3-bromoundecane (bp 74-76 °C at 0.15 torr) in a purity of 94% (yield was not determined), according to GC/MS analysis (Fig. 3.27), *m/e* (relative intensity, %): 27(15), 29(21), 39(18), 41(57), 42(14), 43(42), 55(52), 57(100), 69(25), 70(12), 71(83), 83(10), 85(89), 99(37), 113(17), 155(58, M^+-Br); ^{13}C NMR (75.57 MHz, $CDCl_3$, ambient temperature) (Fig. 3.28), δ: 12.08(C-1), 31.94(C-2), 60.34(C-3), 38.90(C-4), 27.71(C-5), 29.18, 29.34, and 29.55 (C-6, -7, and -8; exact assignments uncertain), 32.24(C-9), 22.73(C-10), and 14.12(C-11) ppm; ^1H NMR (300.52 MHz, $CDCl_3$, ambient temperature) (Fig. 3.29), δ: 0.72-0.97 (3H, CH_3), 0.96-1.13 (3H, CH_3), 1.12-1.66 (12H, CH_2), 1.66-2.10 (4H, CH_2), and 3.83-4.12 (1H, CHBr) ppm.

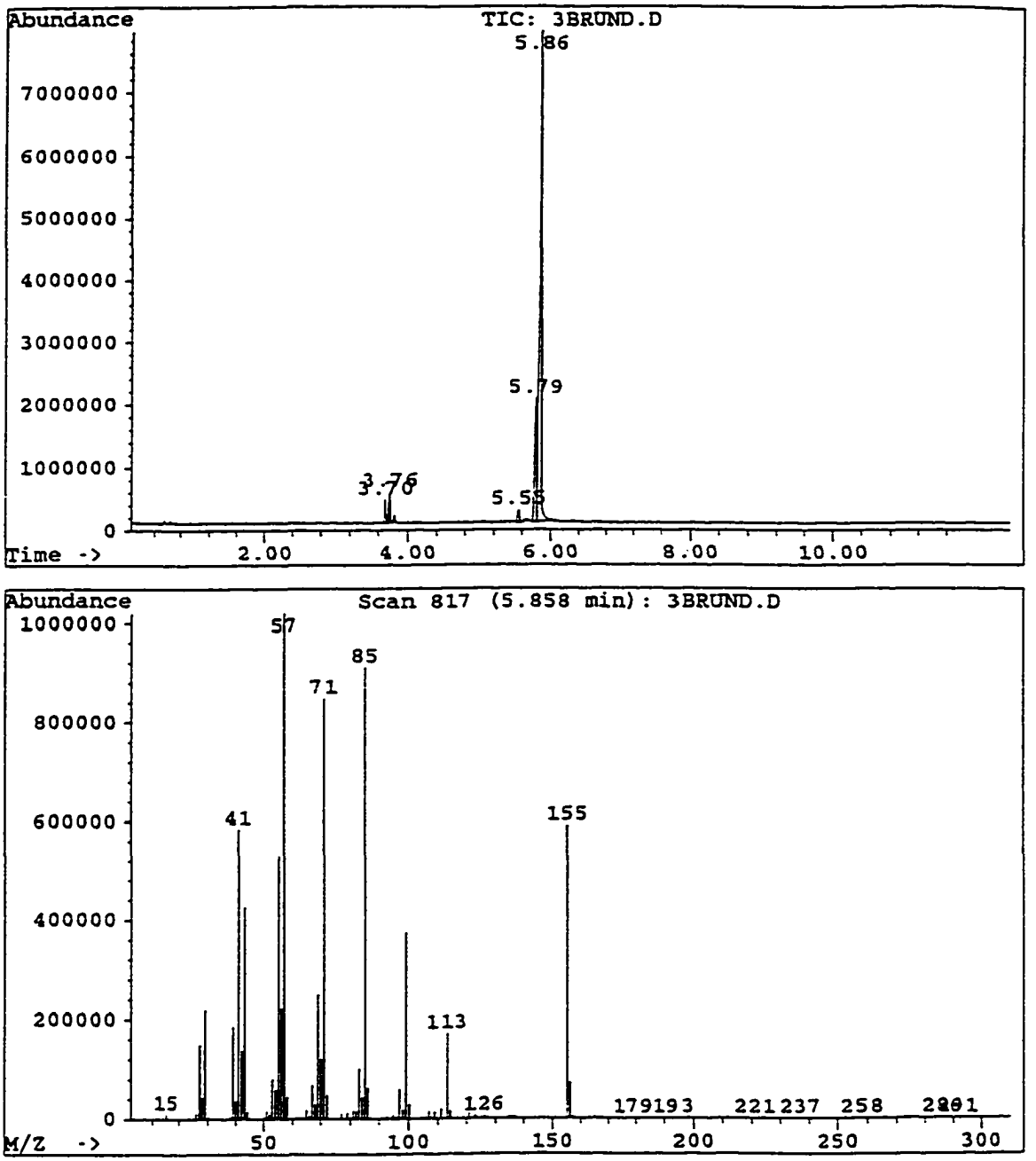


Fig. 3.27: Mass spectrum and gas chromatogram of

3-bromoundecane

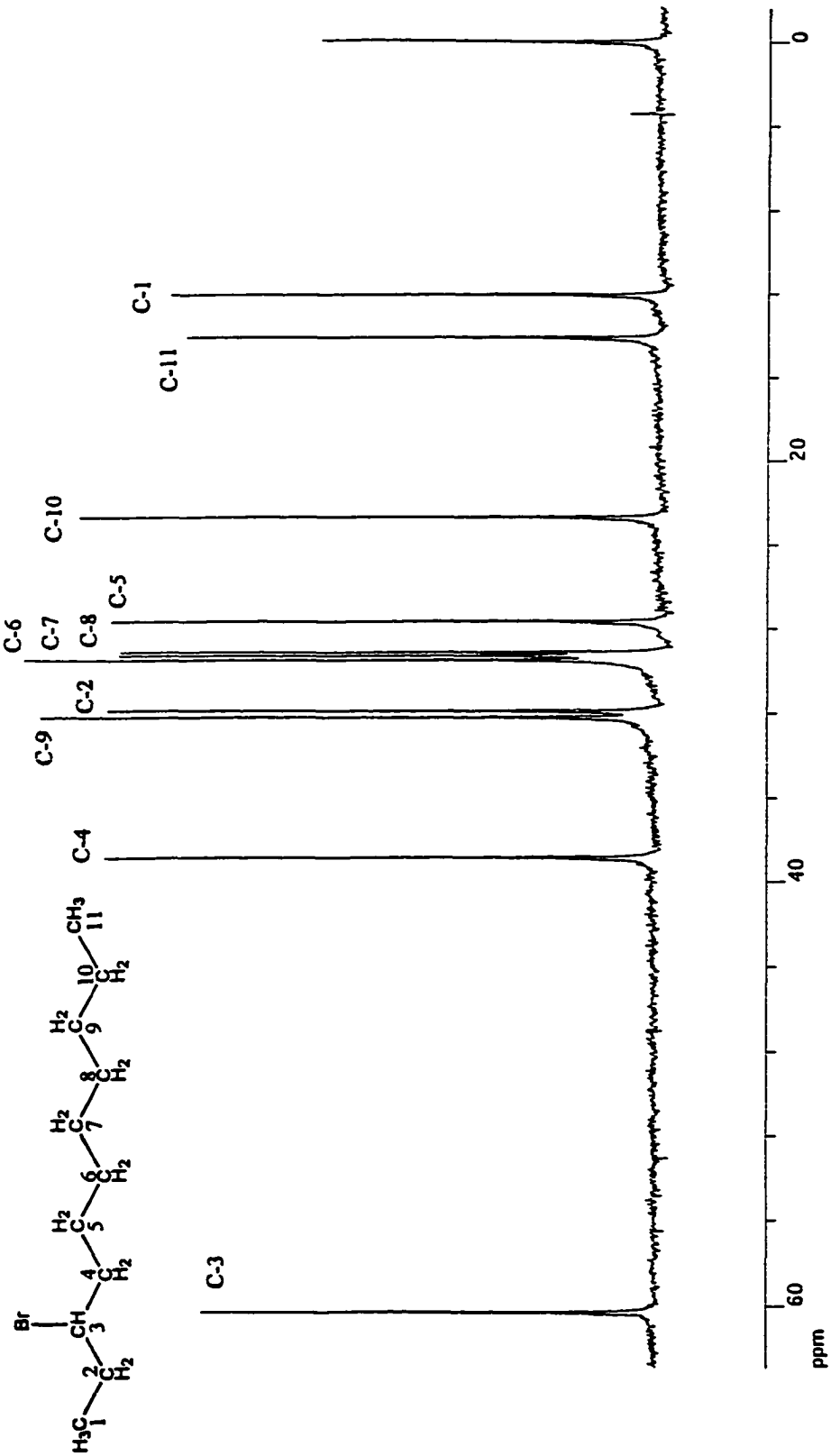


Fig. 3.28: ^{13}C NMR spectrum (75.57 MHz) of 3-bromoundecane

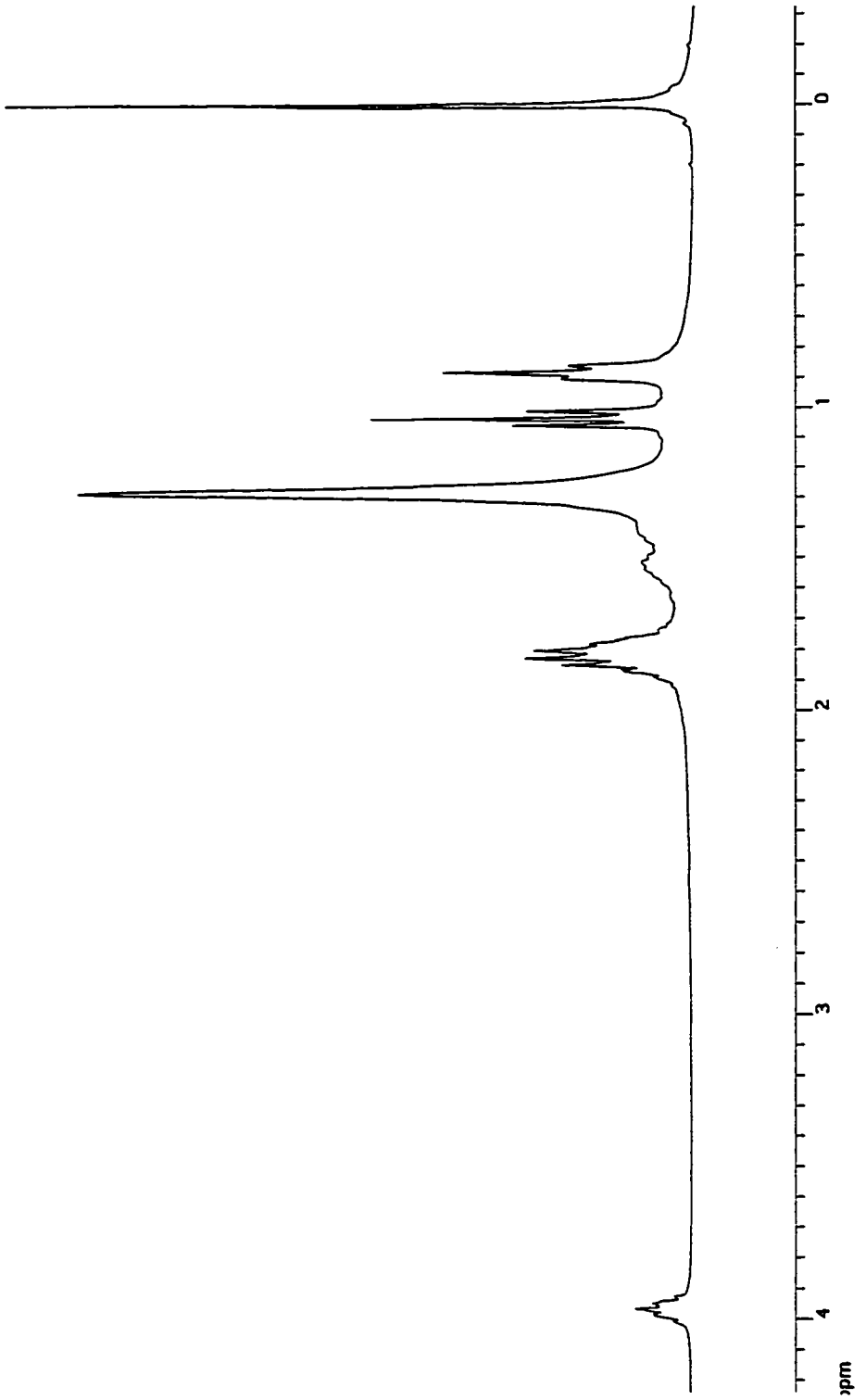


Fig. 3.29: ^{1}H NMR spectrum (300.532 MHz) of 3-bromoundecane

(ii) Synthesis of 1-bromo-2-ethyldecane

This compound was prepared by adapting a literature procedure.[8]

Bis(cyclopentadienyl)zirconium dichloride (0.49 g, 1.7 mmol) and 1-decene (6.31 mL, 4.67 g, 33 mmol) were introduced into a flame-dried flask in a glove bag under argon. Ethylmagnesium chloride (2.0 M solution in ether, 50.0 mL, 100 mmol) was added under nitrogen, and the mixture was allowed to remain at room temperature for 12 h. After cooling to -78 °C, bromine (6.90 mL, 21.5 g, 134 mmol) was introduced during 30 s, and the mixture was kept for 1 h at room temperature. It then was extracted with 3 x 150 mL of ether. The combined extracts were concentrated in a rotary evaporator under aspirator vacuum and fractionally distilled in the spinning band micro still to obtain a 1-bromo-2-ethyldecane sample (bp 89-93 °C at 0.20 torr) that was shown to be *ca.* 90-95% pure by ^{1}H NMR and GC/MS analysis (the yield was not determined): (Fig. 3.30), *m/e* (relative intensity, %): 27(13), 29(20), 39(16), 41(52), 42(10), 43(34), 55(79), 56(20), 57(87), 69(33), 70(20), 71(100), 83(44), 85(93), 97(16), 99(45), 113(31), 127(11), 135(14, M^{+}-C_8H_{17}), 137(13, M^{+}-C_8H_{17}), 163(55, M^{+}-C_6H_{13}), 165(55, M^{+}-C_6H_{13}), 169(26, M^{+}-Br), 248(0.7, M^{+}), 250(0.6, M^{+}); ^{13}C NMR (75.57 MHz, $CDCl_3$, room temperature) (Fig. 3.31), δ: 38.85(C-1), 41.13(C-2), 31.99(C-3), 26.70(C-4), 29.89(C-5), 29.64(C-6), 29.39(C-7), 32.28(C-8), 22.75(C-9), 14.15(C-10), 10.90(C-2'), and 25.23(C-1') ppm; ^{1}H NMR (300.52 MHz, $CDCl_3$, room temperature) (Fig. 3.32), δ: 0.55-1.01 (6H, CH_3), 0.99-1.68 (16H, CH_2), 2.37-2.80 (1H, CH), and 3.14-3.60 (2H, CH_2Br) ppm.

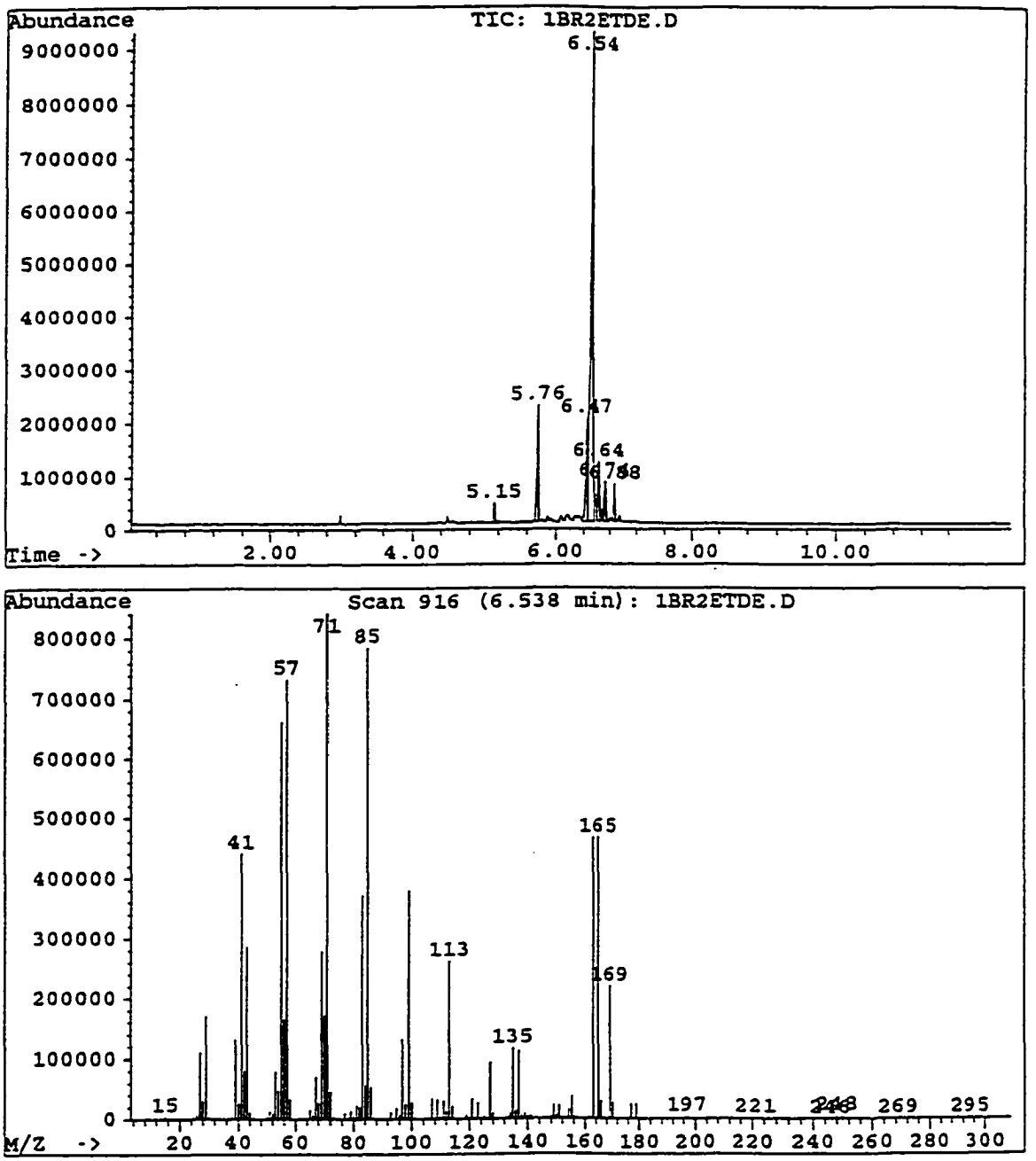


Fig. 3.30: Mass spectrum and gas chromatogram of

1-bromo-2-ethyldecane

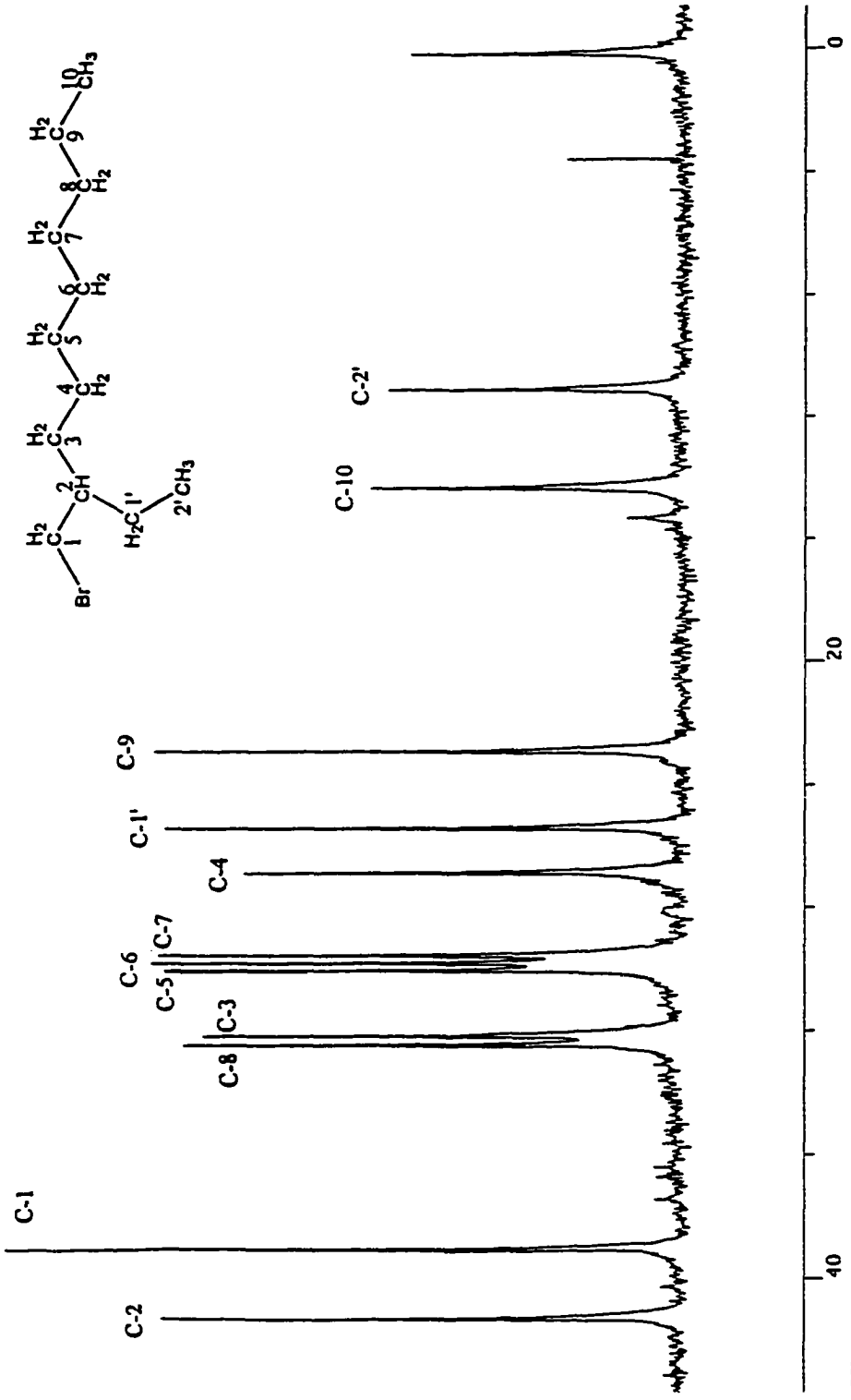


Fig. 3.31: ^{13}C NMR spectrum (75.57 MHz) of 1-bromo-2-ethyldecane

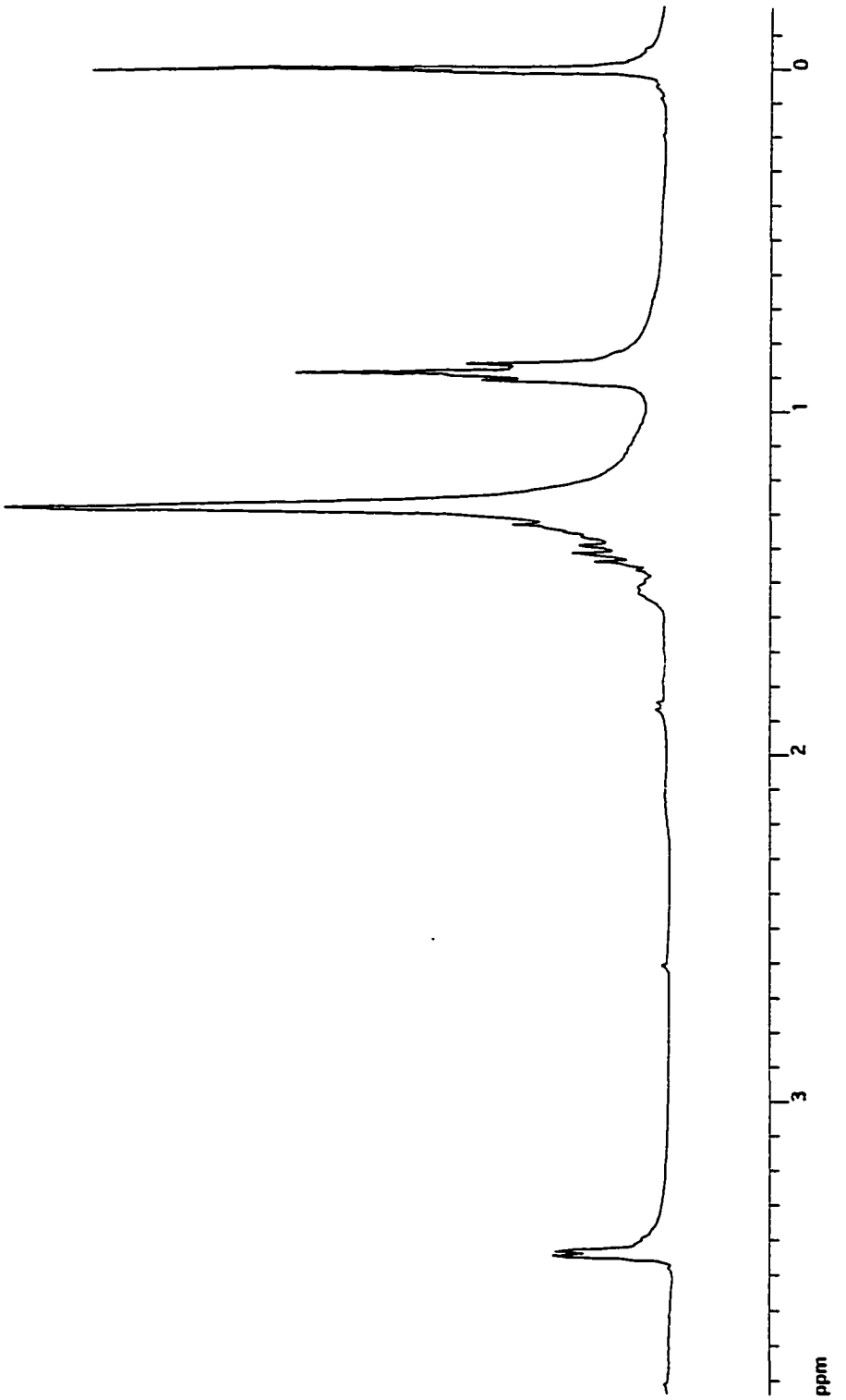


Fig. 3.32: ^{1}H NMR spectrum (300.52 MHz) of 1-bromo-2-ethyldecane

(iii) Synthesis of 9,11-diethylnonadecane

9,11-Diethylnonadecane was prepared by a Wurtz reaction, via an adaptation of a method in the literature.[9]

Sodium (*ca.* 1.0 g, 43 mg-atom) was added to a solution of 3-bromoundecane (1.52 g, 6.46 mmol) and 1-bromo-2-ethyldecane (1.61 g, 6.46 mmol) in dry ether (50 mL), and the mixture was kept at room temperature for *ca.* 3 days. Unchanged sodium was destroyed by the careful addition of a slight excess of isopropanol, and the mixture was diluted with additional ether (100 mL). It then was washed with DI water (3 x 200 mL), dried over anhydrous $MgSO_4$, concentrated in a rotary evaporator under aspirator vacuum, and subjected to short-path distillation in order to remove all materials with boiling points below 50 °C at 5 torr. Analysis by GC/MS and ^{1}H NMR indicated that the residue was a 32:41:27 mixture of 9,10-diethyloctadecane (homocoupling product from 3-bromoundecane), 9,11-diethylnonadecane (heterocoupling product, the desired compound), and 9,12-diethyleicosane (homocoupling product from 1-bromo-2-ethyldecane), respectively, containing minor amounts of impurities. Yields were not determined. The identities of 9,10-diethyloctadecane and 9,12-diethyleicosane were confirmed by comparing their GC retention times (9.4 min for 9,10-diethyloctadecane and 10.3 min for 9,12-diethyleicosane), mass spectra, and diagnostic ^{13}C NMR shifts with those of the authentic specimens whose preparations are described in subsequent sections. 9,11-Diethylnonadecane (GC retention time, 9.8 min) also was identified conclusively from its distinctive ^{13}C NMR resonances and its mass spectrum, *m/e* (relative intensity, %):

9,10-diethyloctadecane (Fig. 3.33.1): 29(13), 41(35), 43(54), 55(35), 56(24), 57(100), 69(26), 70(22), 71(67), 83(16), 84(15), 85(57), 97(21), 98(11), 99(20), 111(18), 113(10), 125(12), 154(100, M^+- $C_{11}H_{24}$), 155(21, M^+- $C_{11}H_{23}$), 197(8, M^+- C_8H_{17}), 281(15, M^+- Et), 310(0.5, M^+).

9,11-diethylnonadecane (Fig. 3.33.2): 29(22), 41(56), 42(12), 43(80), 55(47), 56(25), 57(100), 69(34), 70(22), 71(82), 83(20), 85(72), 97(16), 99(30), 113(22), 127(14), 141(13), 154(28, M^+- $C_{12}H_{26}$), 155(16, M^+- $C_{12}H_{25}$), 169(10), 210(11), 211(42, M^+- C_8H_{17}), 295(85, M^+- Et), 324(0.4, M^+).

9,12-diethyleicosane (Fig. 3.33.3): 29(22), 41(56), 42(16), 43(87), 55(53), 56(17), 57(100), 69(35), 70(27), 71(78), 83(21), 84(10), 85(74), 97(20), 99(31), 111(11), 113(21), 127(15), 141(12), 154(38, M^+- $C_{13}H_{28}$), 155(18, M^+- $C_{13}H_{27}$), 169(10), 224(10), 225(35, M^+- C_8H_{17}), 309(85, M^+- Et), 338(0.8, M^+).

^{13}C NMR [125.77 MHz, 1,4-dioxane-d_8:1,2,4-trichlorobenzene = 1:4 (v/v), 100 °C] (Fig. 3.34), δ:

9,10-diethyloctadecane: 14.11(C-1), 22.96(C-2), 32.31(C-3), 29.70(C-4), 30.03(C-5), 30.55(C-6), 28.67(C-7), 31.39 and 31.41(C-8), 42.71 and 42.73(C-9), 24.25(C-1'), and 12.80(C-2') ppm.

9,11-diethylnonadecane: 14.11(C-1), 22.96(C-2), 32.31(C-3), 29.70(C-4), 30.03 (C-5), 30.55 and 30.57(C-6), 27.19 and 27.23* (C-7), 34.43 and 34.46(C-8), 37.38 and 37.42(C-9), 39.15(C-10), 27.05 and 27.13(C-1'), and 10.98 and 11.01(C-2') ppm.

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* Tentative assignment

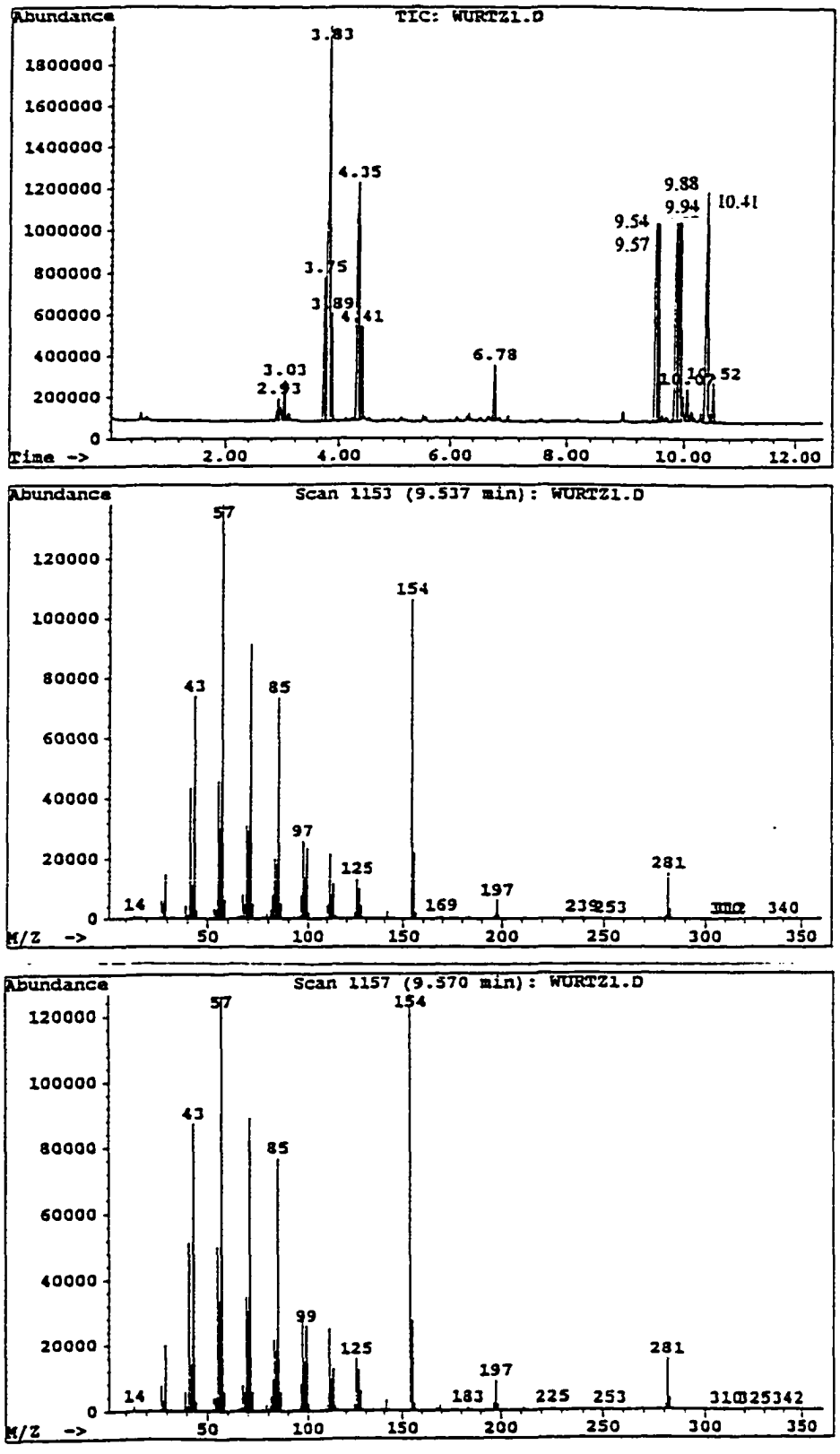


Fig. 3.33.1: Mass spectra and gas chromatogram of 9,10-diethyloctadecane

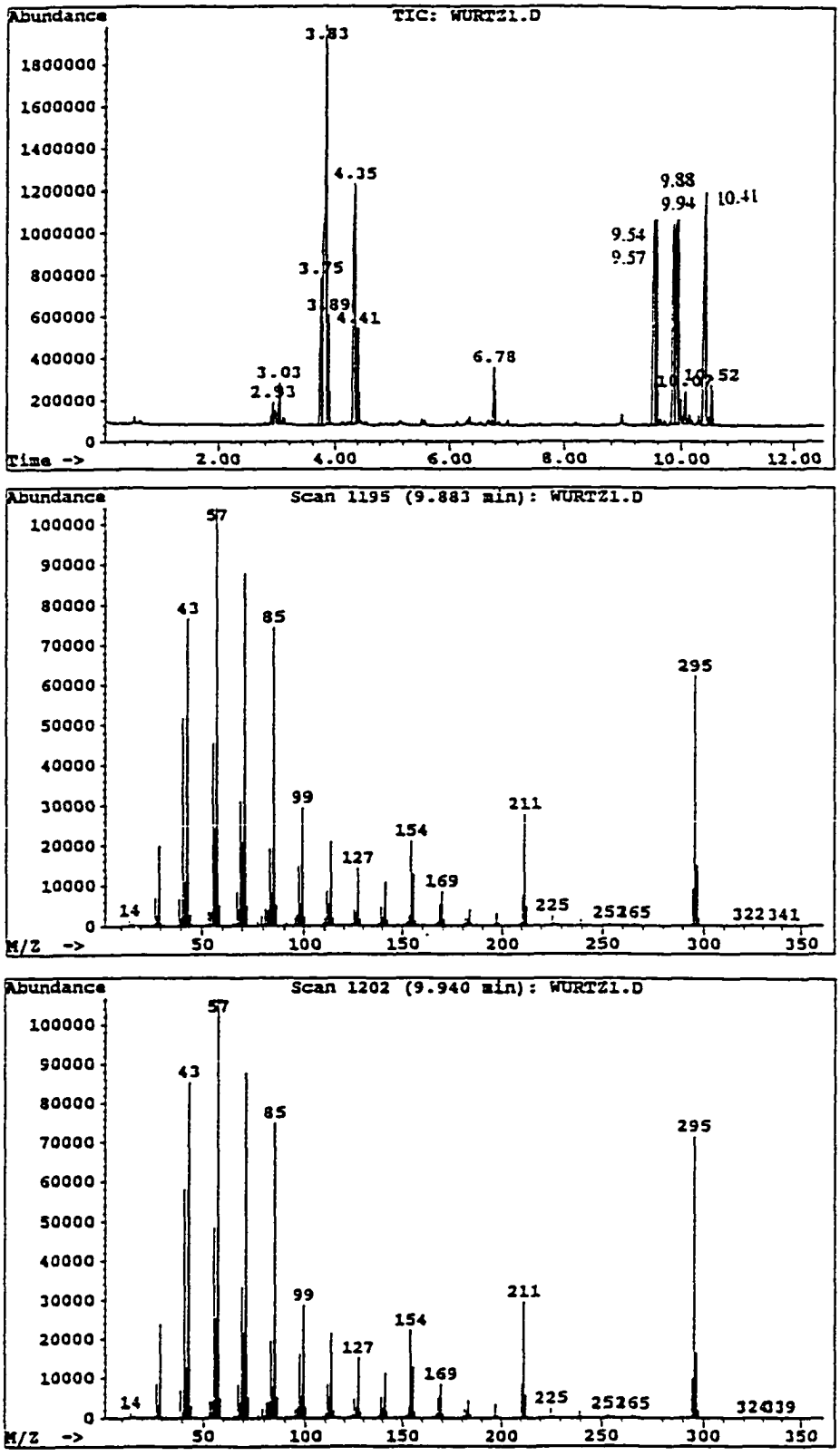


Fig. 3.33.2: Mass spectra and gas chromatogram of 9,11-diethylnonadecane

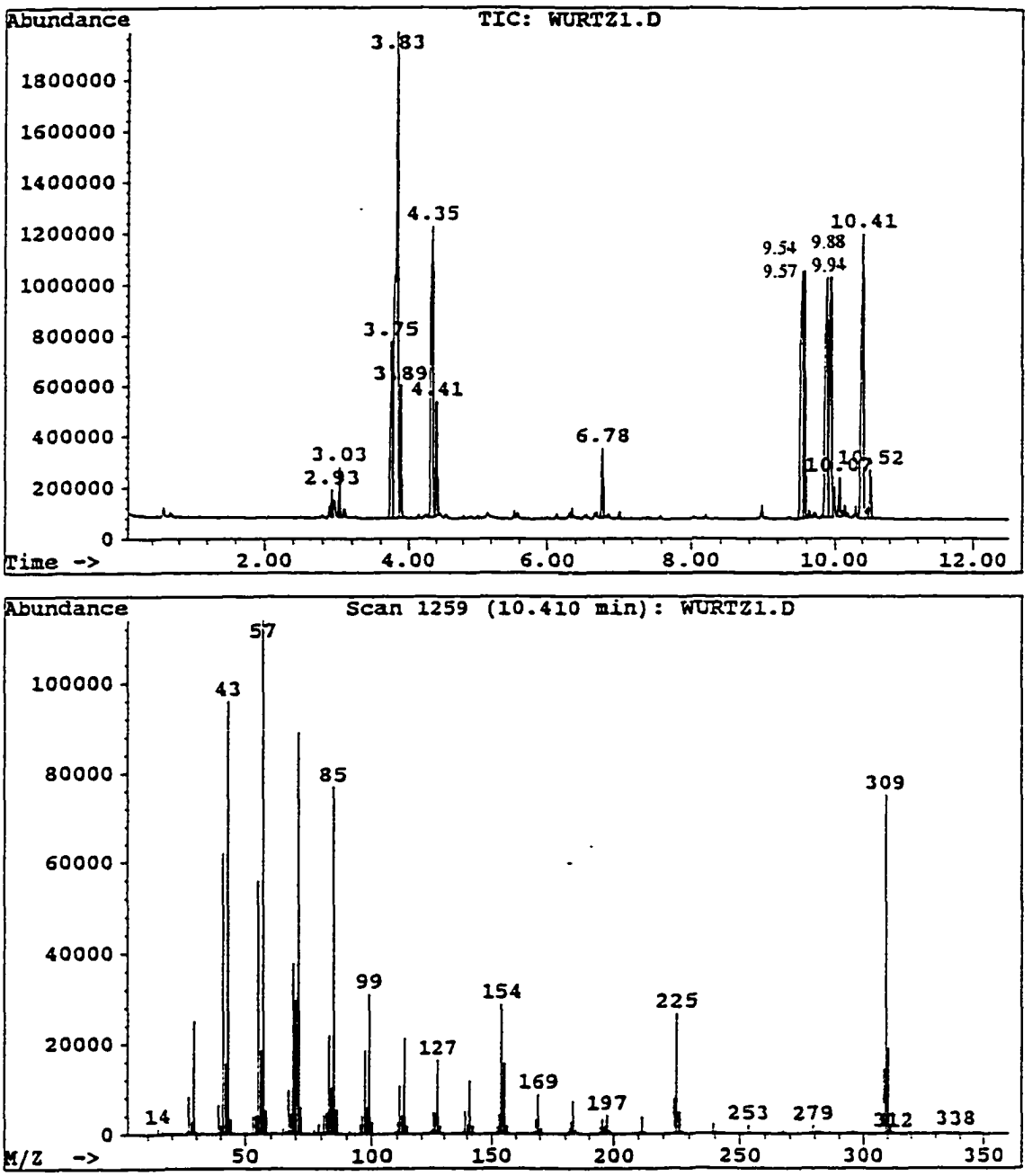


Fig. 3.33.3: Mass spectrum and gas chromatogram

of 9,12-diethyleicosane

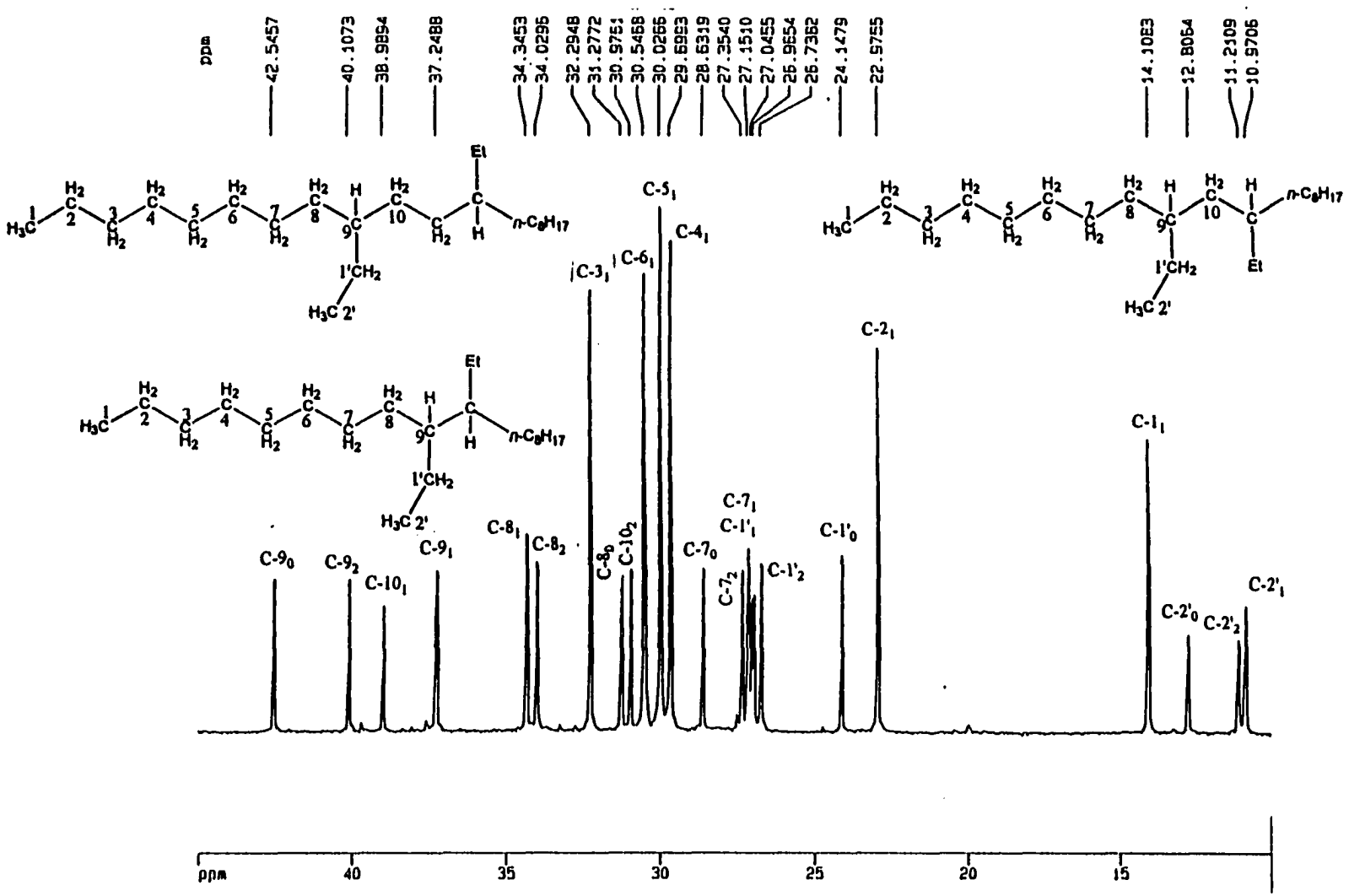


Fig. 3.34: ^{13}C NMR spectrum (125.77 MHz) of the products of the Wurtz cross-coupling reaction

(subscript: 0 - 9,10-diethyloctadecane, 1 - 9,11-diethylnonadecane, 2 - 9,12-diethyleicosane)

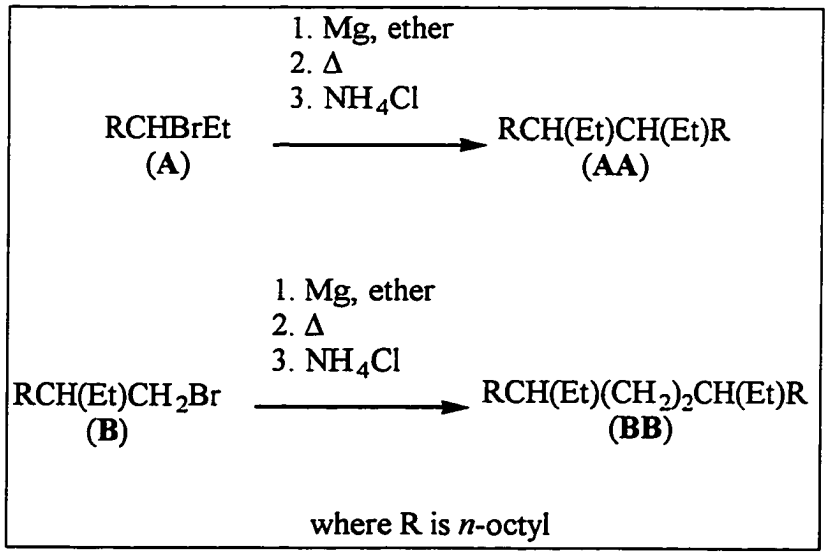
9,12-diethyleicosane: 14.11(C-1), 22.96(C-2), 32.31(C-3), 29.70(C-4), 30.03(C-5), 30.55(C-6), 27.40(C-7), 34.11(C-8), 40.21(C-9), 31.12(C-10), 26.82(C-1'), and 11.22(C-2') ppm.

^{1}H NMR (300 MHz, $CDCl_3$, ambient temperature) (Fig.3.35) δ: 0.71-1.03 (12H, CH_3), 1.01-1.62 (34H, CH_2), and 2.07-2.22 (2H, CH) ppm.

(iv) Synthesis of 9,10-diethyloctadecane

Magnesium turnings (0.16 g, 6.6 mg-atom), 3-bromoundecane (1.50 g, 6.39 mmol), and anhydrous ether (50 mL) were heated under reflux overnight. A saturated

Scheme 3.7: Synthesis of 9,10-diethyloctadecane and 9,12-diethyleicosane



aqueous solution of ammonium chloride (50 mL) and additional ether (100 mL) were added in succession; then the ether layer was separated, washed with 3 x 200 mL of DI

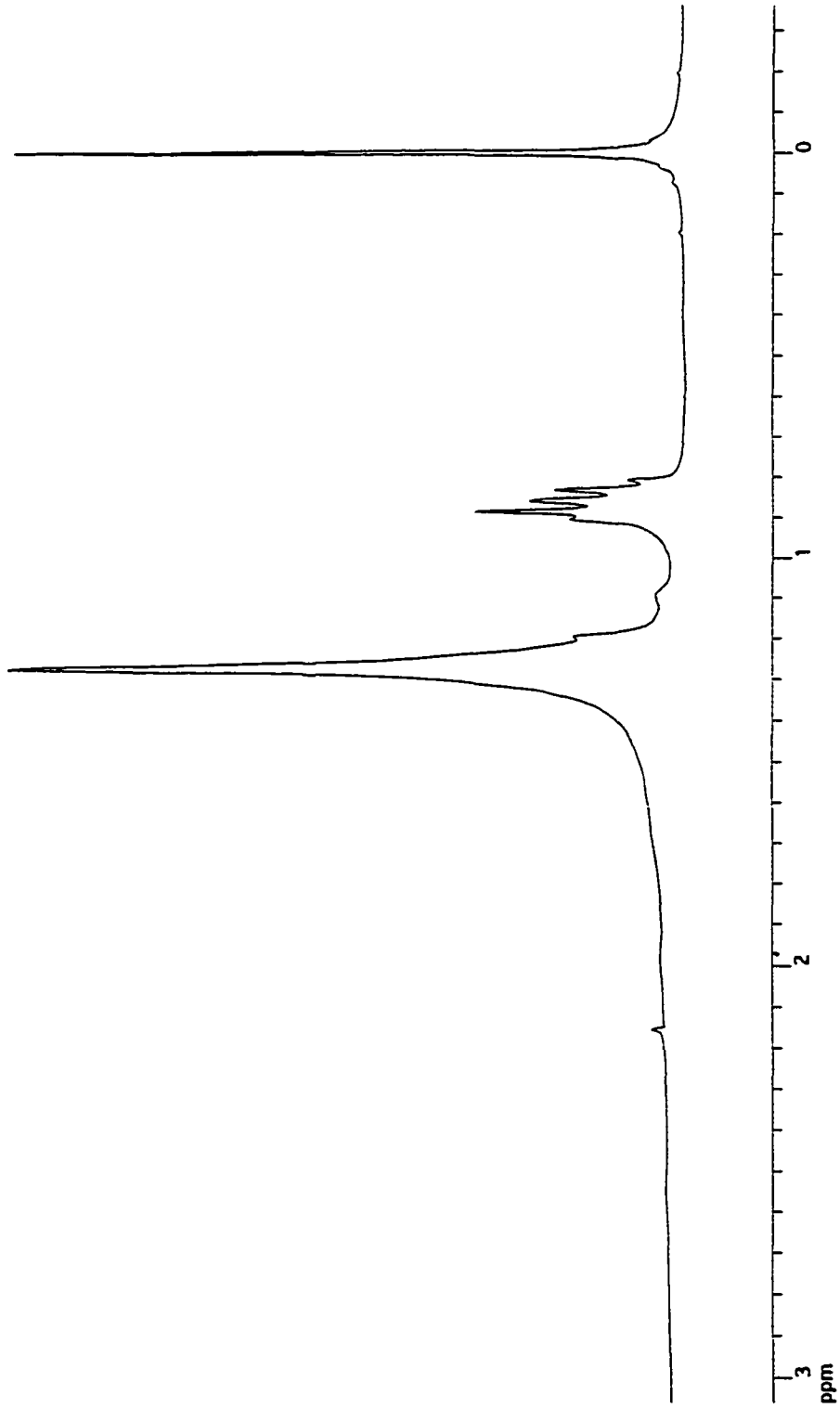


Fig. 3.35: ^{1}H NMR spectrum (300.22 MHz) of the products of the Wurtz cross-coupling reaction

water, dried over anhydrous $MgSO_4$, concentrated in a rotary evaporator under aspirator vacuum, and subjected to short-path distillation at 5 torr in order to remove compounds boiling below 50 °C. Analysis by GC/MS showed that the residue was 9,10-diethyloctadecane in a purity of 98% (the yield was not determined). Mass spectrum (Fig. 3.36), *m/e* (relative intensity, %): 41(19), 43(27), 55(19), 56(13), 57(37), 69(11), 70(10), 71(26), 85(26), 97(13), 99(11), 111(14), 125(10), 154(100, M^+- $C_{11}H_{24}$), 155(21, M^+-$C_{11}H_{23}$), 197(9, M^+- C_8H_{17}), 281(18, M^+- Et), 310(0.4, M^+); ^{13}C NMR [125.77 MHz, 1,4-dioxane-d_8:1,2,4-trichlorobenzene = 1:4 (v/v), 100 °C] (Fig. 3.37) δ: 14.05(C-1), 22.91(C-2), 32.24(C-3), 29.64(C-4), 29.96(C-5), 30.49(C-6), 28.62(C-7), 31.38 and 31.41(C-8), 42.71 and 42.73(C-9), 24.26(C-1'), and 12.79(C-2') ppm; ^1H NMR (300 MHz, $CDCl_3$, ambient temperature) (Fig. 3.38) δ: 0.72-1.03 (12H, CH_3) and 1.01-1.62 (32H, CH_2) ppm.

(v) Synthesis of 9,12-diethyleicosane

A coupling reaction of 1-bromo-2-ethyldecane (1.50 g, 6.02 mmol) was carried out with magnesium turnings (0.15 g, 6.02 mg-atom) in dry ether (50 mL) according to the procedure used to synthesize 9,10-diethyloctadecane, as described above. An analogous workup and distillation afforded residual 9,12-diethyleicosane in a purity of 97%, according to GC/MS and ^1H NMR analysis (the yield was not determined). Mass spectrum (Fig. 3.39), *m/e* (relative intensity, %): 29(11), 41(26), 43(59), 55(25), 57(100), 69(13), 70(12), 71(62), 85(39), 99(14), 154(11, M^+- $C_{13}H_{28}$), 155(5, M^+-$C_{13}H_{27}$), 225(5, M^+- C_8H_{17}), 309(12, M^+- Et), 338(0.1, M^+); ^{13}C NMR [125.77 MHz, 1,4-dioxane-d_8:

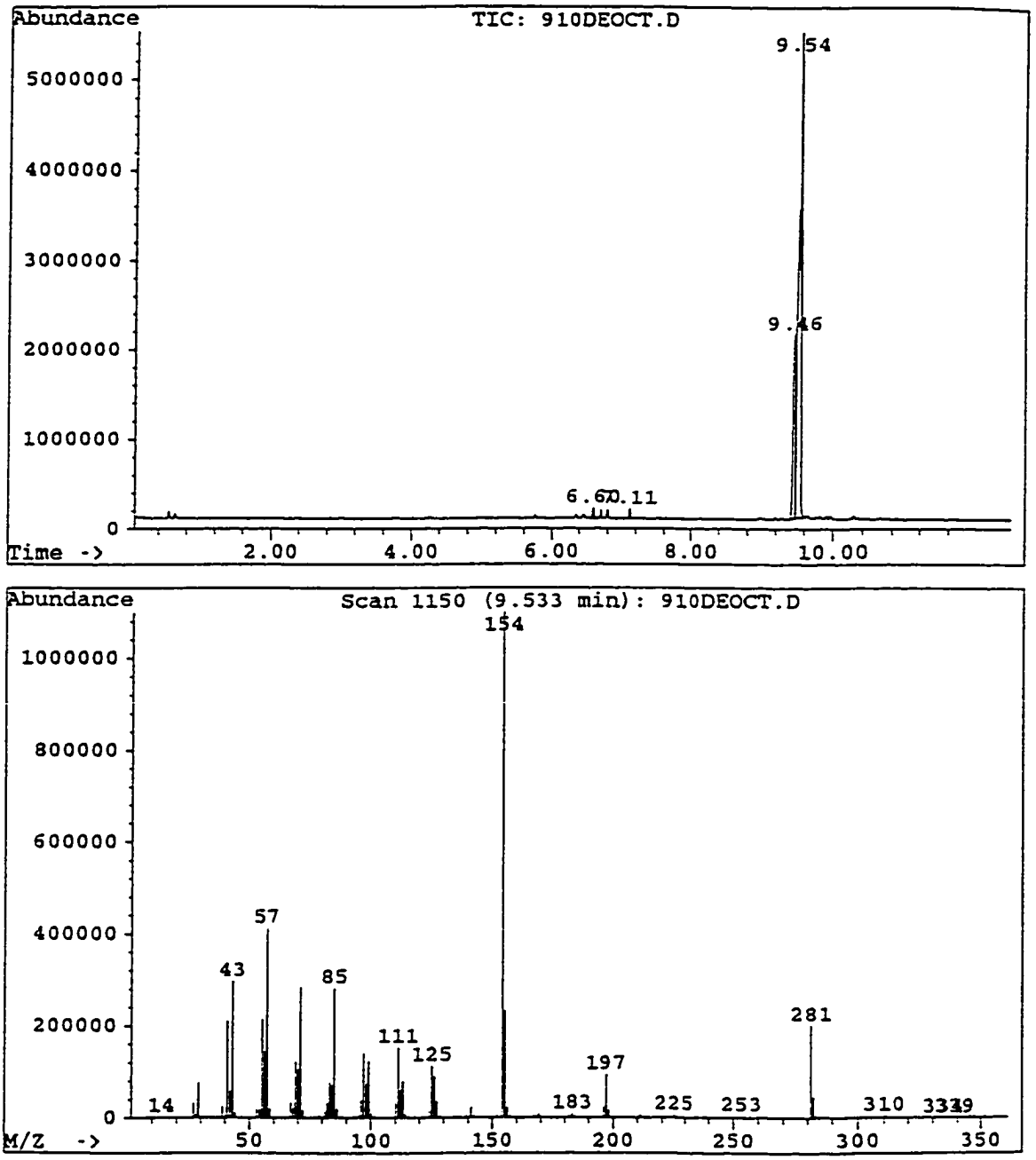


Fig. 3.36: Mass spectrum and gas chromatogram of 9,10-diethyloctadecane prepared by homocoupling

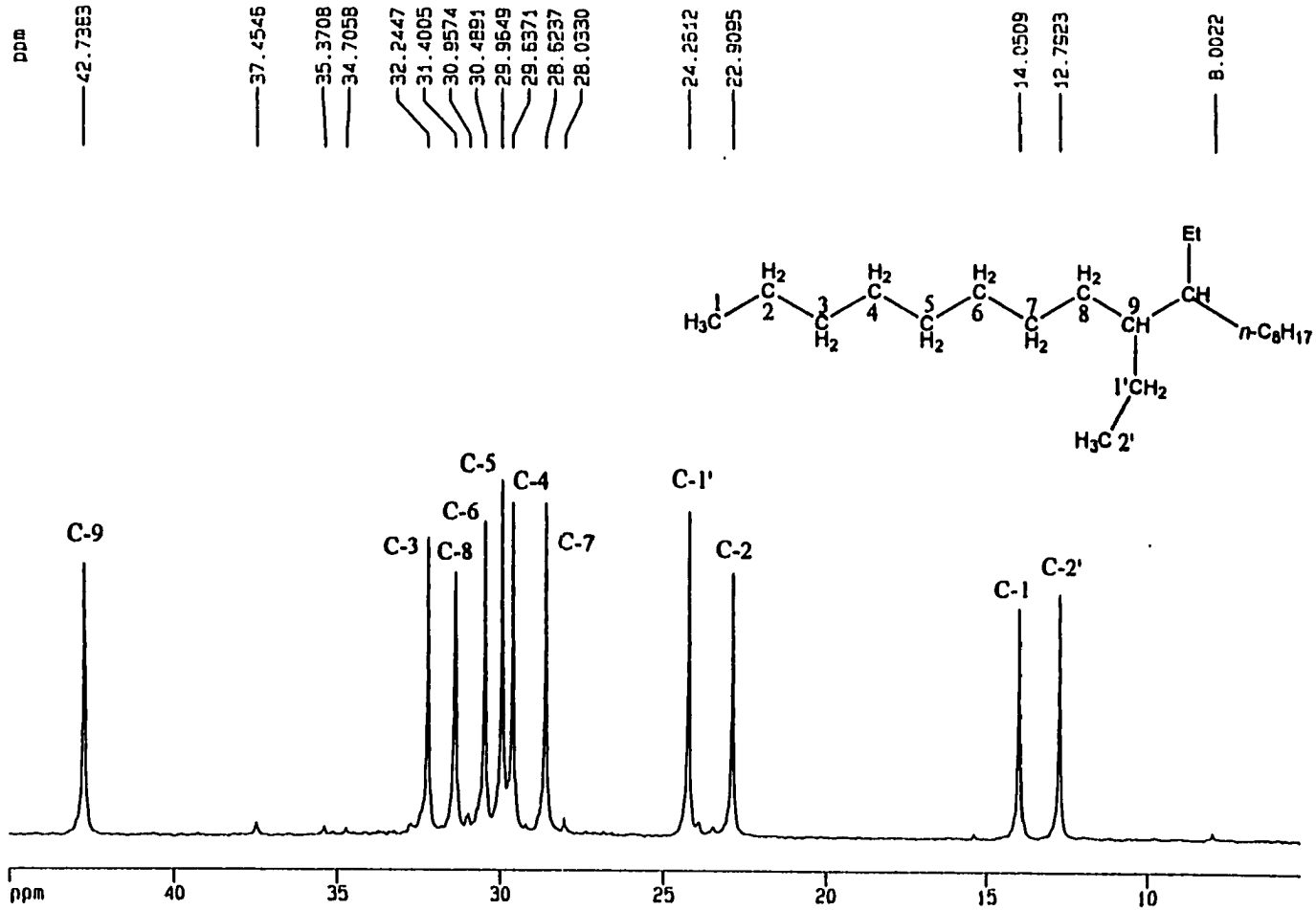


Fig. 3.37: ^{13}C NMR spectrum (125.77 MHz) of 9,10-diethyloctadecane prepared by homocoupling

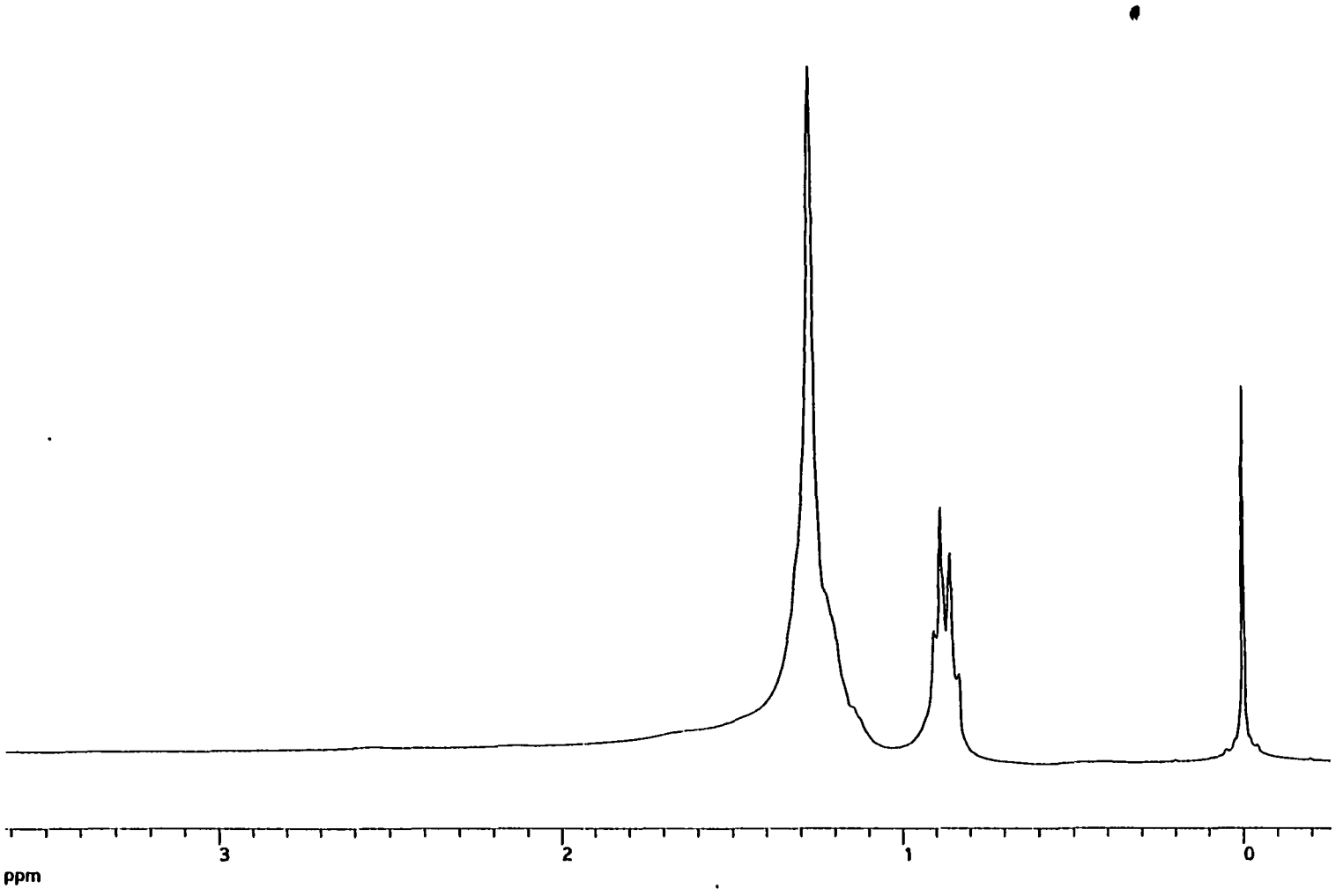


Fig. 3.38: ^{1}H NMR spectrum (300.22 MHz) of 9, 10-diethyloctadecane prepared by homocoupling

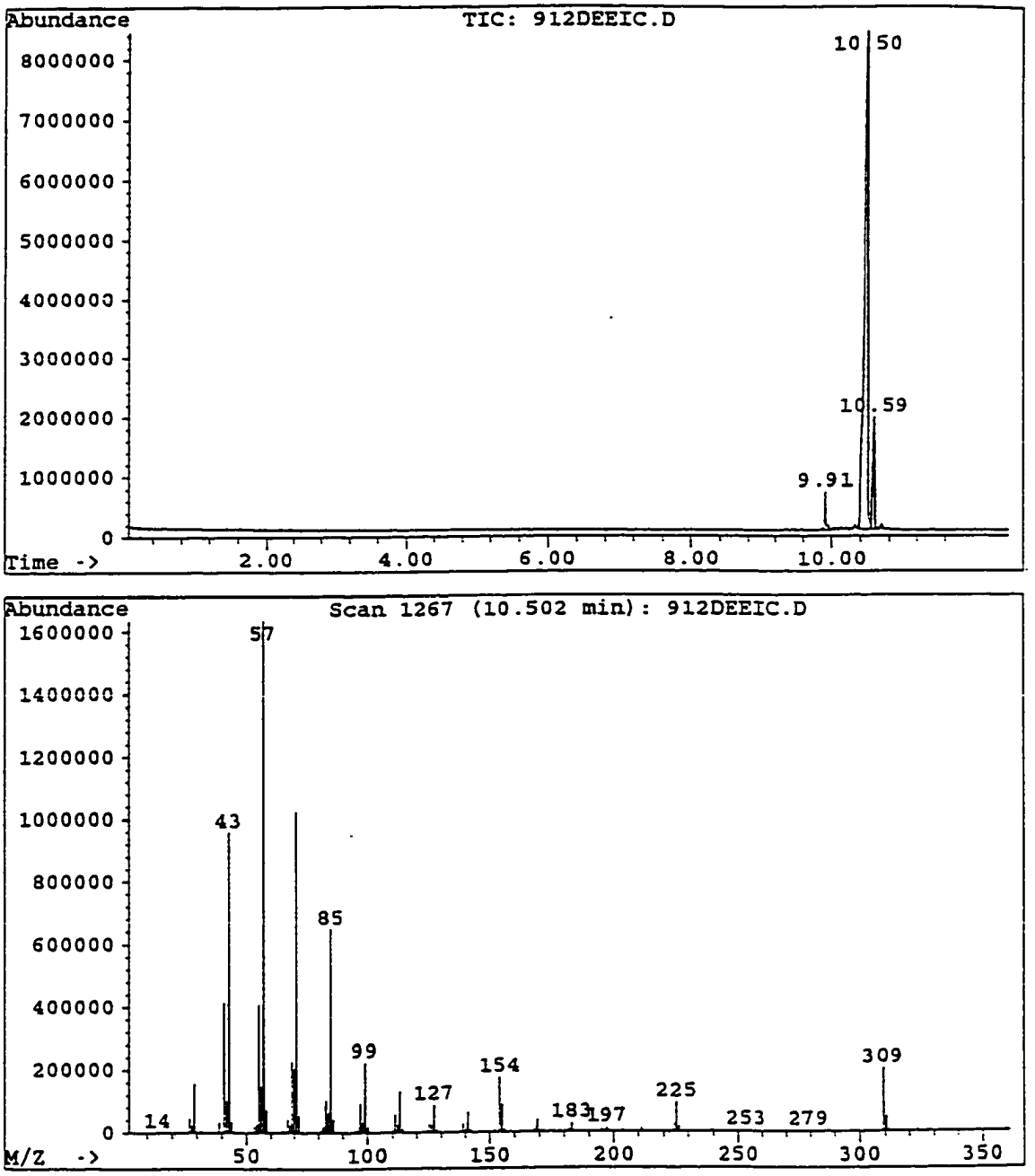


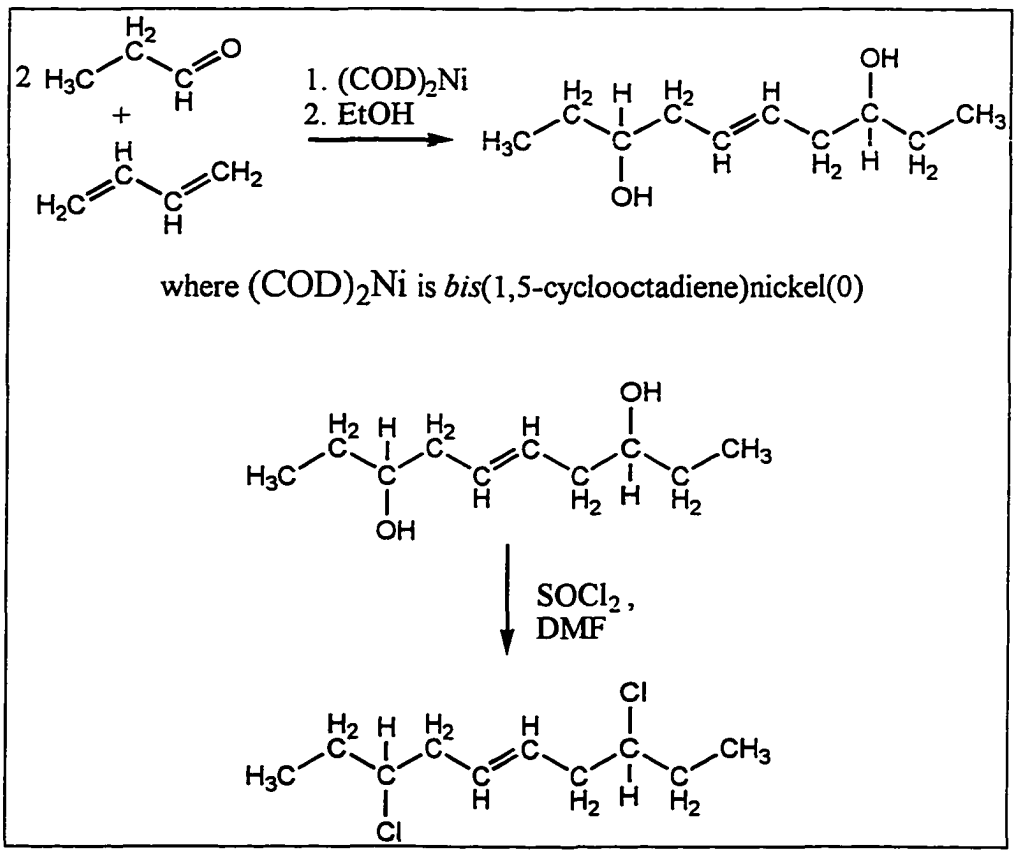
Fig. 3.39: Mass spectrum and gas chromatogram of 9,12-diethyleicosane prepared by homocoupling

1,2,4-trichlorobenzene = 1:4 (v/v), 100 °C] (Fig. 3.40) δ: 14.05(C-1), 22.92(C-2), 32.25(C-3), 29.64(C-4), 29.99(C-5), 30.51(C-6), 27.38(C-7), 34.11(C-8), 40.19(C-9), 31.14(C-10), 26.82(C-1'), and 11.22(C-2') ppm; ^{1}H NMR (300 MHz, $CDCl_3$, room temperature) (Fig. 3.41) δ: 0.59-1.05 (12H, CH_3), and 1.02-1.91 (36H, CH_2) ppm.

3.1.8 Synthesis of *trans*-3,8-dichloro-5-decene

(i) Synthesis of 5-decen-3,8-diol

Scheme 3.8: Synthesis of *trans*-3,8-dichloro-5-decene



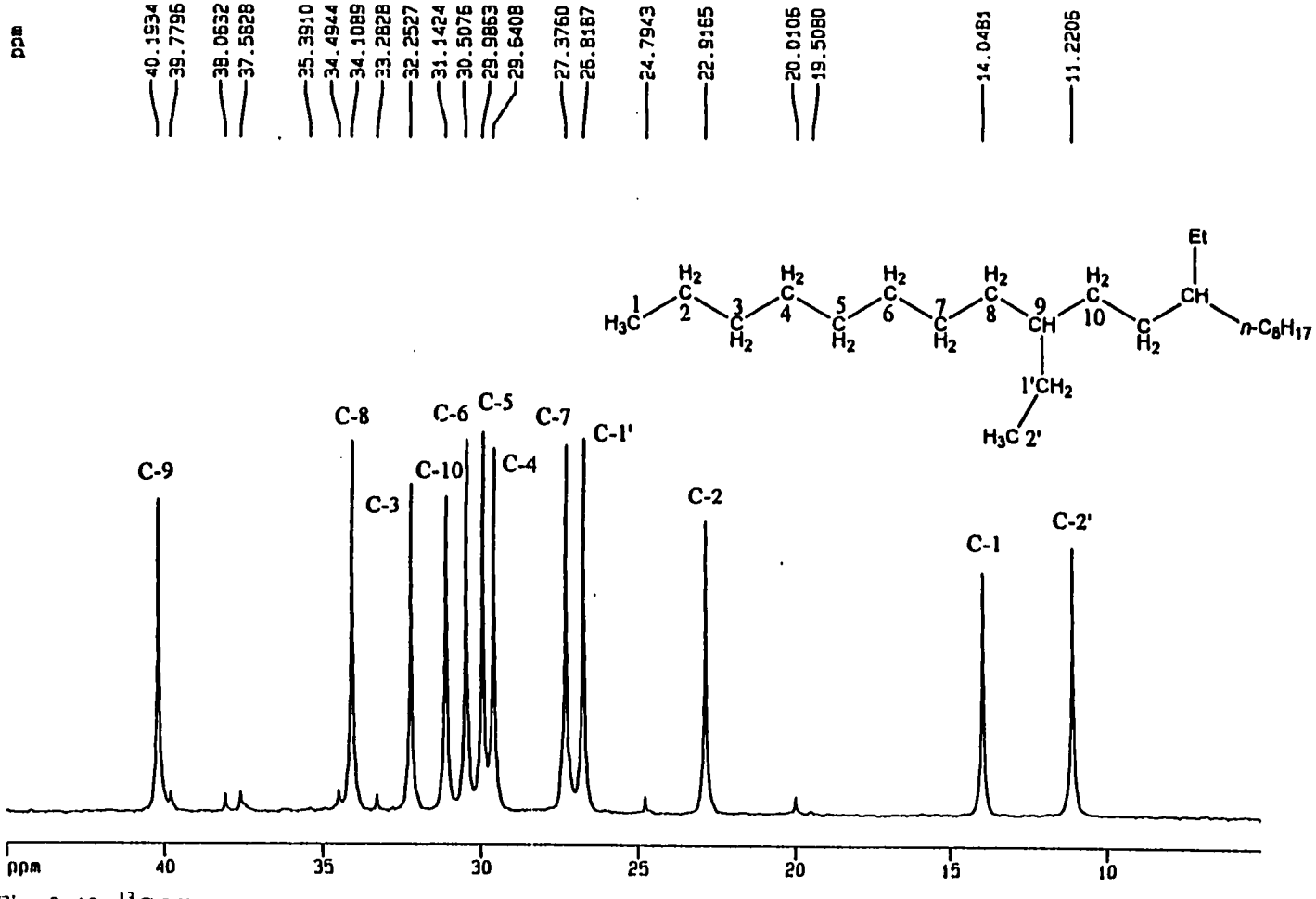


Fig. 3.40: ^{13}C NMR spectrum (125.77 MHz) of 9,12-diethyleicosane prepared by homocoupling

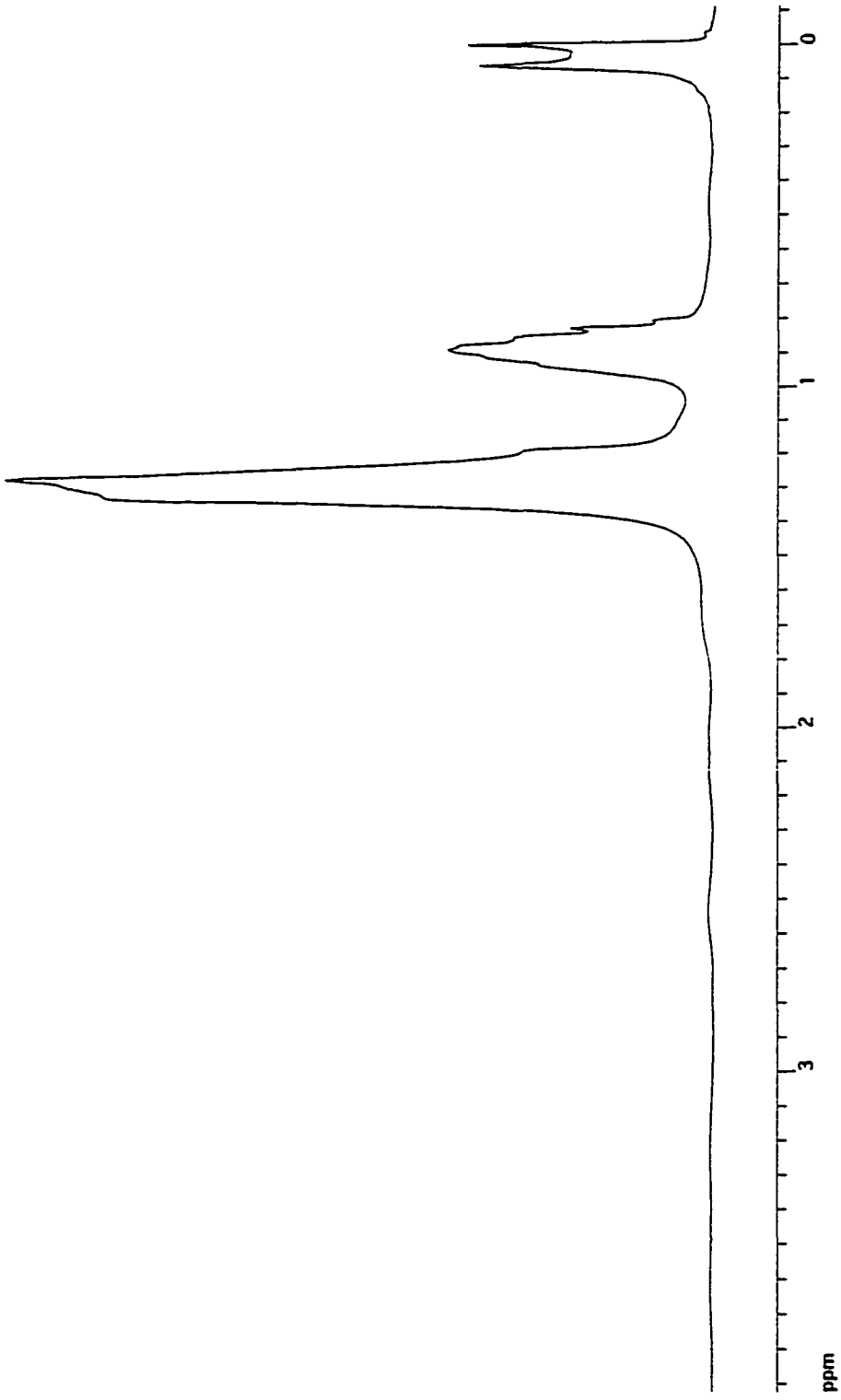


Fig. 3.41: ^{1}H NMR spectrum (300.52 MHz) of 9,12-diethyleicosane prepared by homocoupling

5-Decen-3,8-diol was prepared by a method similar to a literature procedure[10] that had been used for the synthesis of 4-octen-2,7-diol.

A suspension of *bis*(1,5-cyclooctadiene)nickel(0) (9.79 g, 35.6 mmol) in 100 mL of ether was mixed under nitrogen at -45 °C with a solution of propionaldehyde (6.90 g, 119 mmol) in 20 mL of ether. Butadiene (3.20 g, 59.3 mmol) dissolved in 15 mL of ether was added, and the mixture was stirred at 27 °C for 24 h under argon (argon was bubbled first; then static argon pressure was applied by using a balloon). After removal of ether under vacuum, 200 mL of ethanol was introduced, and stirring was continued for an additional 24 h. Ethanol then was evaporated under reduced pressure (50 °C, 5 torr), and the green residue was extracted with ether (3 x 150 mL). The ethereal solution was dried with anhydrous $MgSO_4$, concentrated in a rotary evaporator under aspirator vacuum, and then distilled with a short-path apparatus to obtain 1.62 g (yield, 16.0%) of an oily material that was shown to be 5-decen-3,8-diol: bp 134-145 °C (5 torr). The purity was 86% by GC/MS analysis. Mass spectrum (Fig. 3.42), *m/e* (relative intensity, %): 18(13), 41(30), 55(26), 67(74), 82(71), 93(50), 109(22, M^+- 2OH - C_2H_5), 123(31, M^+- 2OH - CH_3), 138(100, M^+- 2OH), and 172(0.8, M^+); ^{13}C NMR (75.57 MHz, $CDCl_3$, room temperature) (Fig. 3.43) δ: 10.07(C-1), 29.52(C-2), 72.43(C-3), 40.17(C-4), and 129.51(C-5) ppm.

(ii) Synthesis of *trans*-3,8-dichloro-5-decene

The procedure used was based on a published method[3] for converting secondary alcohols into the corresponding chlorides without rearrangement.

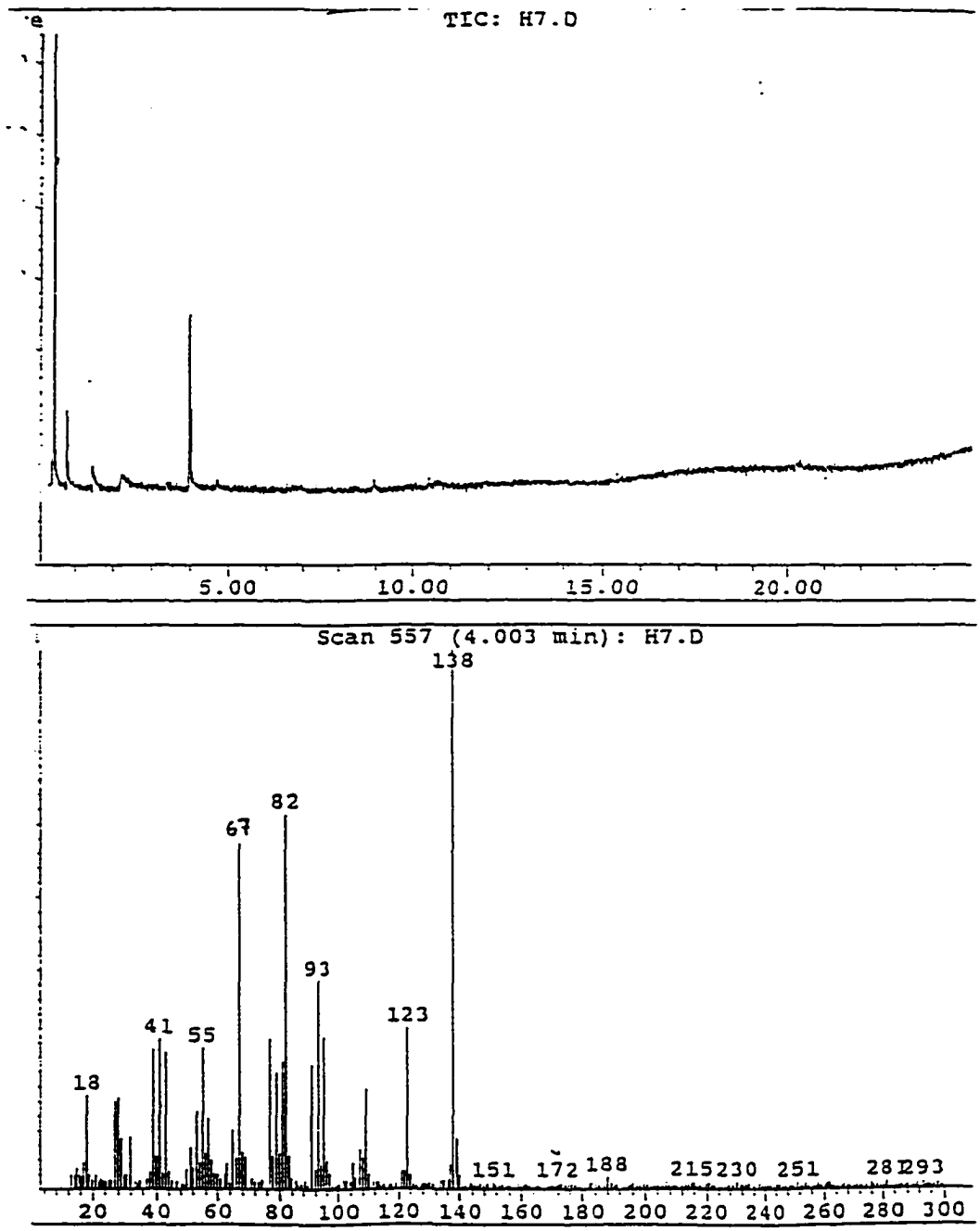


Fig. 3.42: Mass spectrum and gas chromatogram of 5-decen-3,8-diol

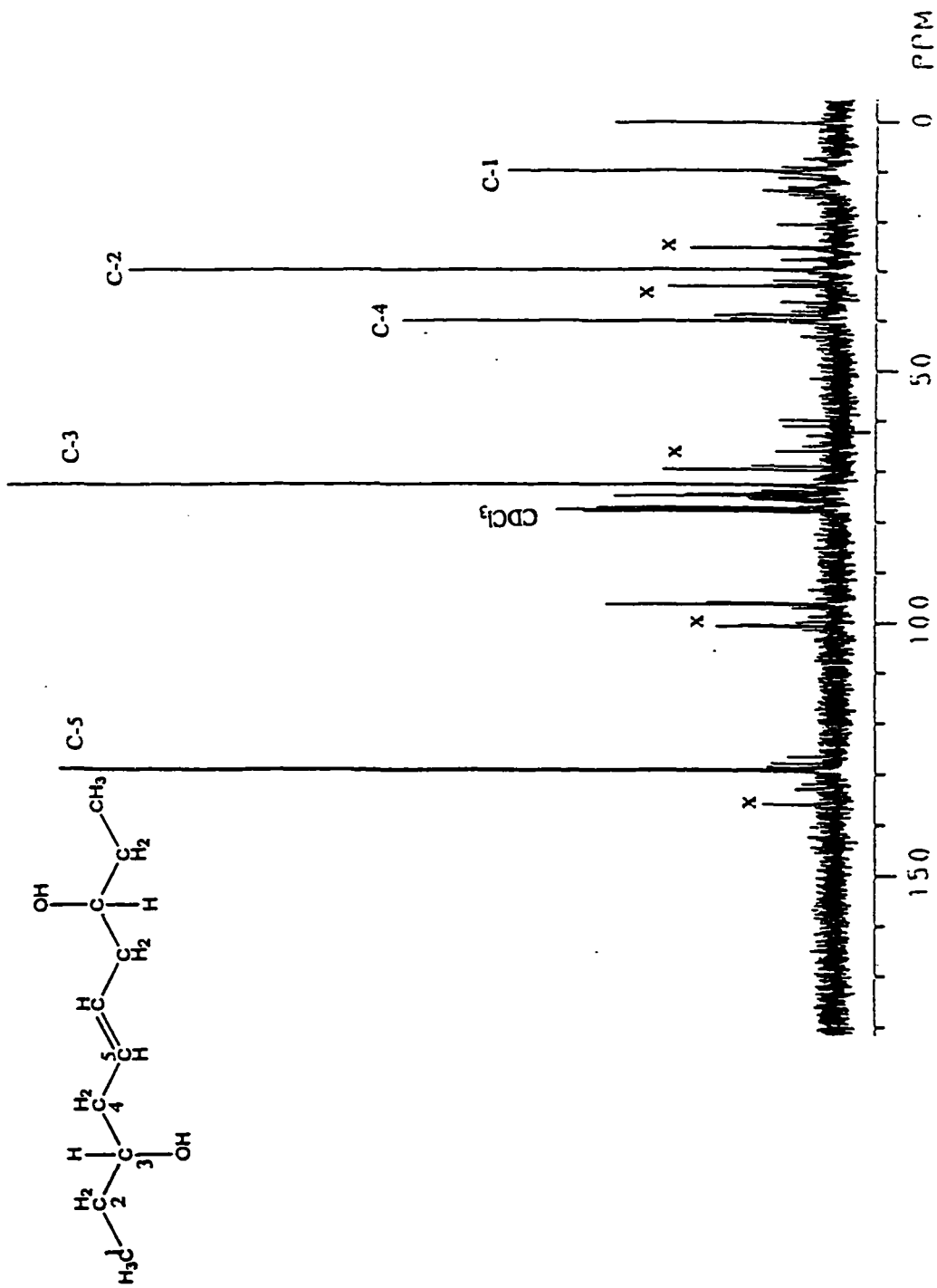


Fig. 3.43: ^{13}C NMR spectrum (75,57 MHz) of 5-decen-3,8-diol (x: impurity)

Thionyl chloride (2.46 g, 20.7 mmol) was added dropwise with stirring to 7.5 mL of DMF under a nitrogen atmosphere while the temperature was kept at 0-5 °C by an ice bath. 5-Decen-3,8-diol (1.6 g, 9.3 mmol) then was introduced slowly, and the resulting mixture was heated at *ca.* 85-90 °C for 30 min. After cooling to room temperature and addition of DI water (100 mL), the mixture was extracted with ether (3 x 150 mL), and the combined extracts were washed with DI water (3 x 200 mL). The ether solution was dried with anhydrous $MgSO_4$, concentrated in a rotary evaporator under aspirator vacuum, and then distilled with a short-path apparatus to obtain three fractions. The second fraction (0.3 g) was the purest sample (80% by GC/MS) of 3,8-dichloro-5-decene: bp 100-110 °C (5 torr), mass spectrum (Fig. 3.44), *m/e* (relative intensity, %): 27(7), 29(6), 41(43), 55(33), 67(35), 95(100), 116(12), 137(30, M^+- Cl - HCl), 172(8, M^+- HCl), 174(3, M^+- HCl), 208(2.1, M^+), and 210(1.6, M^+); ^{13}C NMR (75.57 MHz, THF-d_8, 50 °C) (Fig. 3.45) δ: 10.98(C-1), 31.50(C-2), 65.06(C-3), 41.90(C-4), and 129.99(C-5) ppm; ^1H NMR (300.52 MHz, THF-d_8, 50 °C) (Fig.3.46) δ: 0.81-1.15 (6H, $2CH_3$), 1.74-1.92 (4H, $2CH_2$), 2.35-2.62 (4H, $2CH_2$), 3.75-3.95 (2H, 2CHCl), and 5.48-5.74 (2H, -CH=CH-) ppm; IR (neat) (Fig. 3.47): strong absorption for trans double bond at 961 cm^{-1}.

3.2 Bulk polymerization of vinyl chloride with chain transfer agents

3.2.1 Materials

(1) Vinyl chloride, CH_2=CHCl, #38,762-2, 99.5+%, bp -13.4 °C, Aldrich Chemical

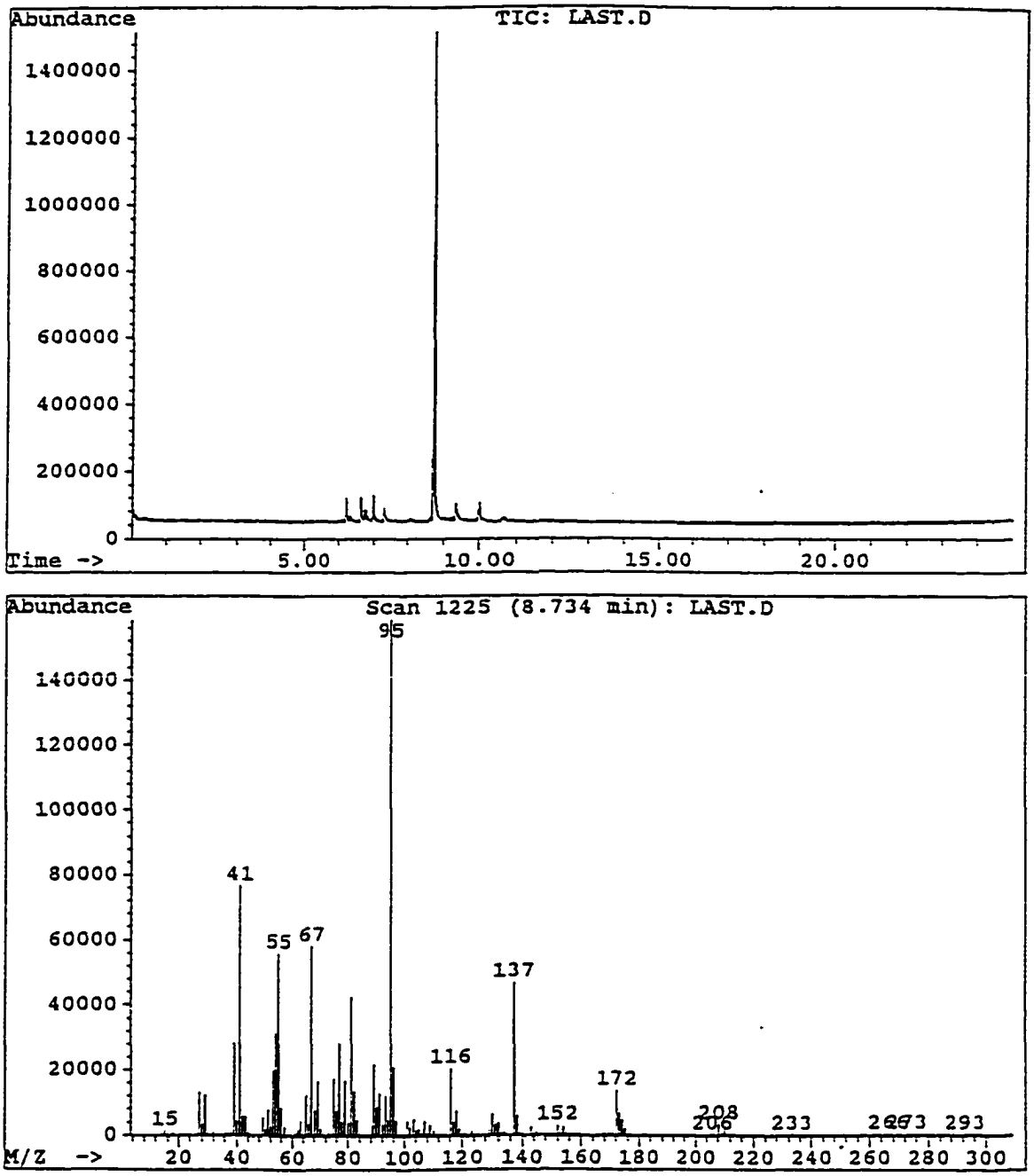


Fig. 3.44: Mass spectrum and gas chromatogram of *trans*-3,8-dichloro-5-decene

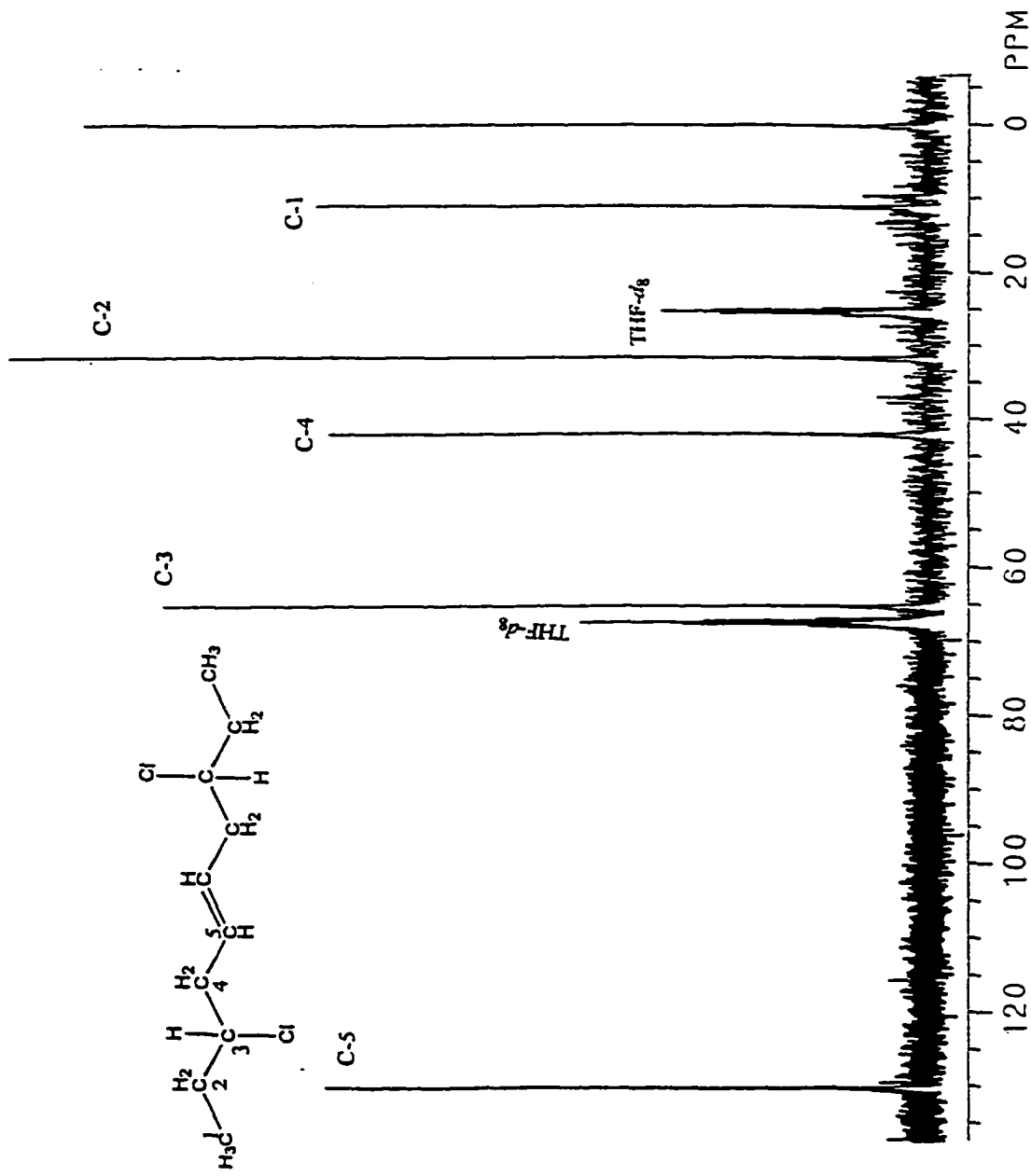


Fig. 3.45: ^{13}C NMR spectrum (75.57 MHz) of *trans*-3,8-dichloro-5-decene

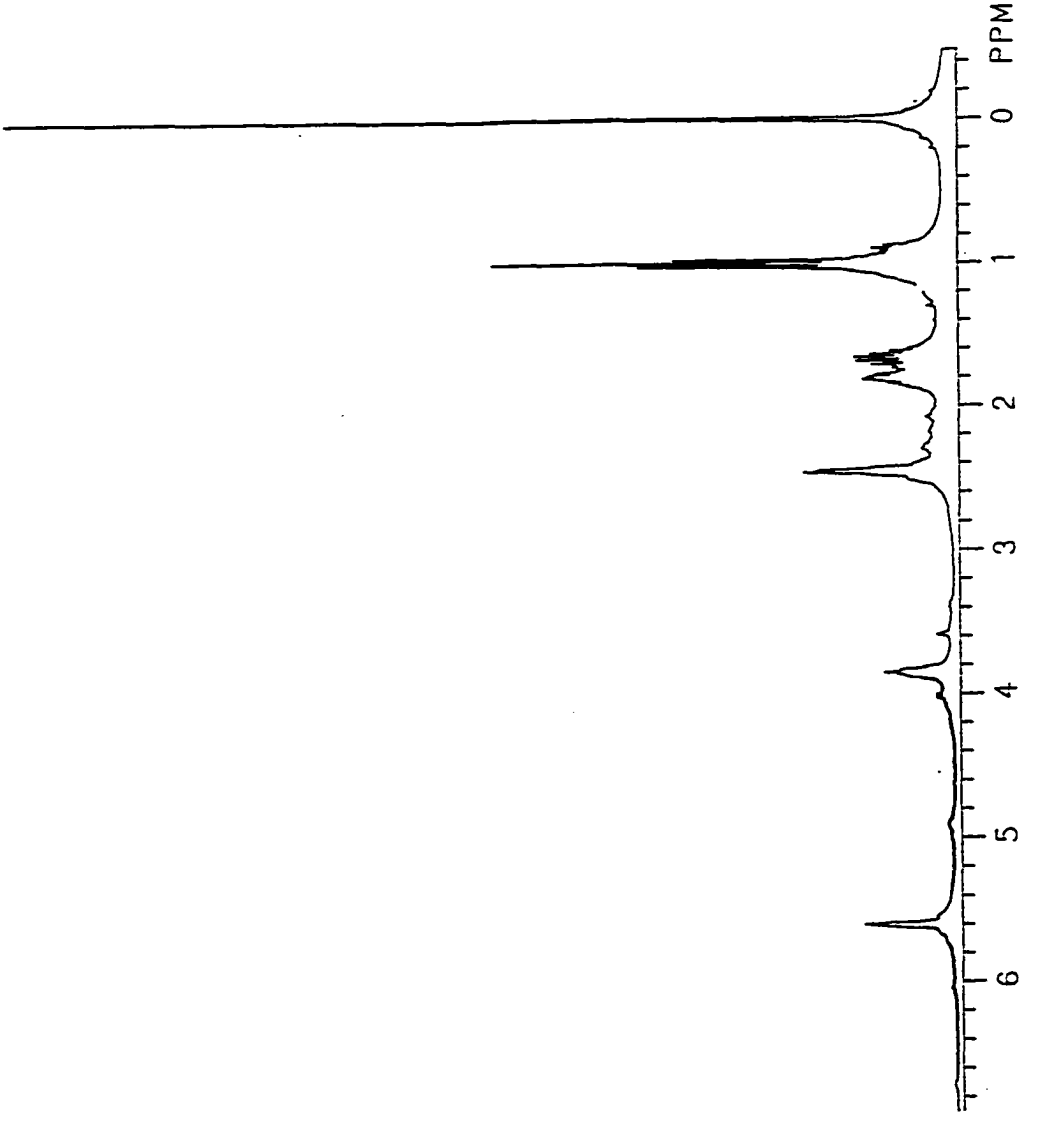


Fig. 3.46: ^{1}H NMR spectrum (300.52 MHz) of *trans*-3,8-dichloro-5-decene

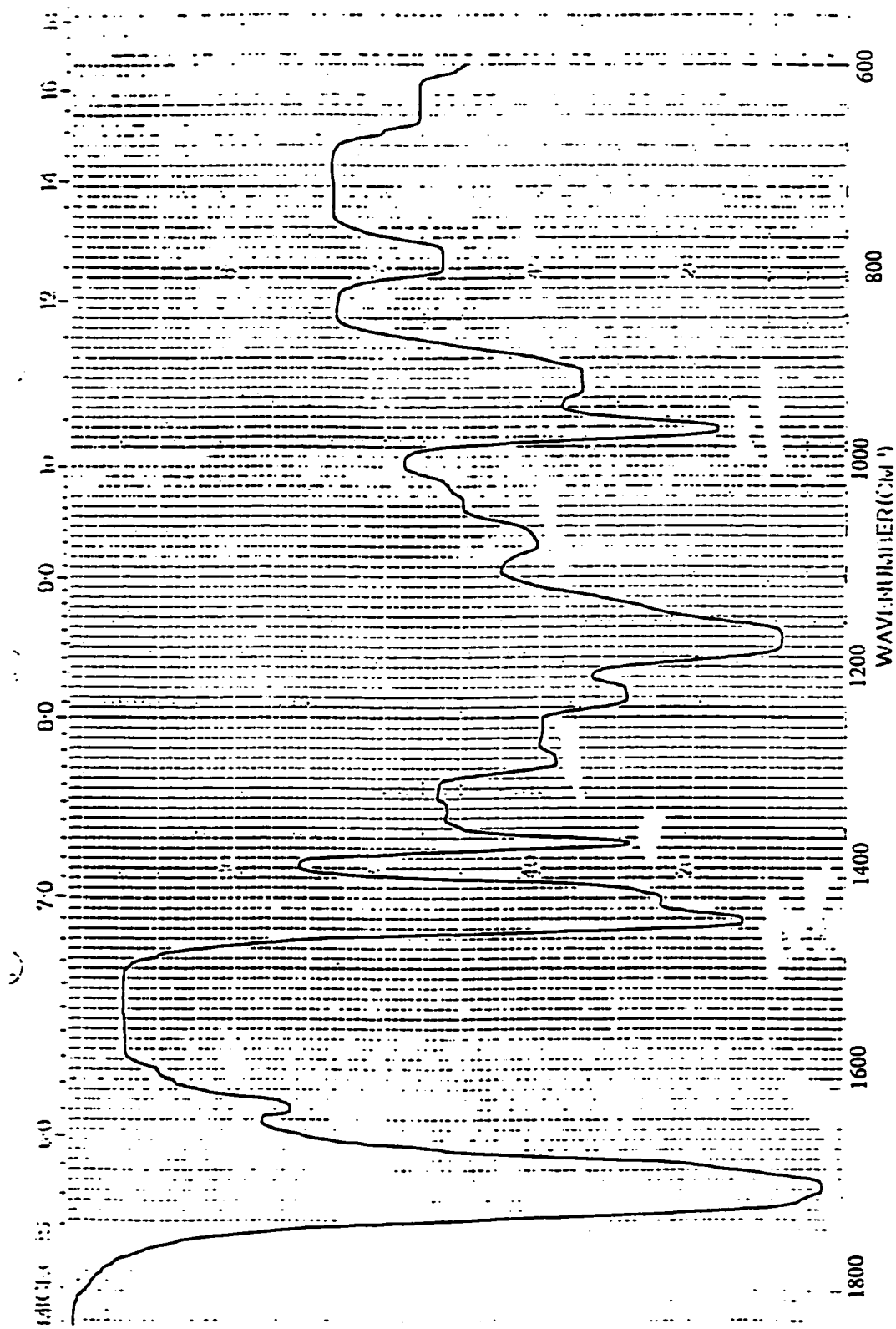


Fig. 3.47: IR spectrum of *trans*-3,8-dichloro-5-decene

Company, Inc.

(2) Dimethyl 2,2'-azobisisobutyrate, $(CH_3)_2C(COOCH_3)$-N=N-$C(COOCH_3)(CH_3)_2$, #KCQ 7587, 99.5%, mp 22-28 °C, Wako Chemicals USA, Inc.

(3) *trans*-1-chloro-2-hexene, 98.3%[1] (Figs. 3.48-3.50)

(4) *trans*-1,5-dichloro-2-pentene, 89.5%[1] (Figs. 3.51-3.53)

3.2.2 Polymerization of vinyl chloride

Polymerizations were carried out in sealed Pyrex tubes (12.5 mm o. d., 7.5 mm i. d., 19.5 cm in length) contained in a stainless steel bomb. A vacuum manifold was used to transfer vinyl chloride from a lecture cylinder to the tubes.

3.2.2.1 With no additives (PVC-0)

Dimethyl 2,2'-azobisisobutyrate (0.74 g, 3.2 mmol) was placed into a reaction tube that then was connected to the manifold and chilled with liquid nitrogen. A lecture bottle of vinyl chloride was connected to the manifold, and high vacuum was applied during 15 min to remove air. Transfer of vinyl chloride was carried out under static vacuum. When the valve of the lecture bottle was opened, the monomer condensed in the reaction tube until 3.72 g (59.5 mmol) of it had been introduced. Freeze-thaw degassing was carried out three times in order to remove any oxygen from the reaction mixture; then the tube was sealed with a torch and placed (while cold) in the bomb, together with *ca.* 10 mL of

[1] Synthesized by Dr. H. T. Chung and S. Frantz

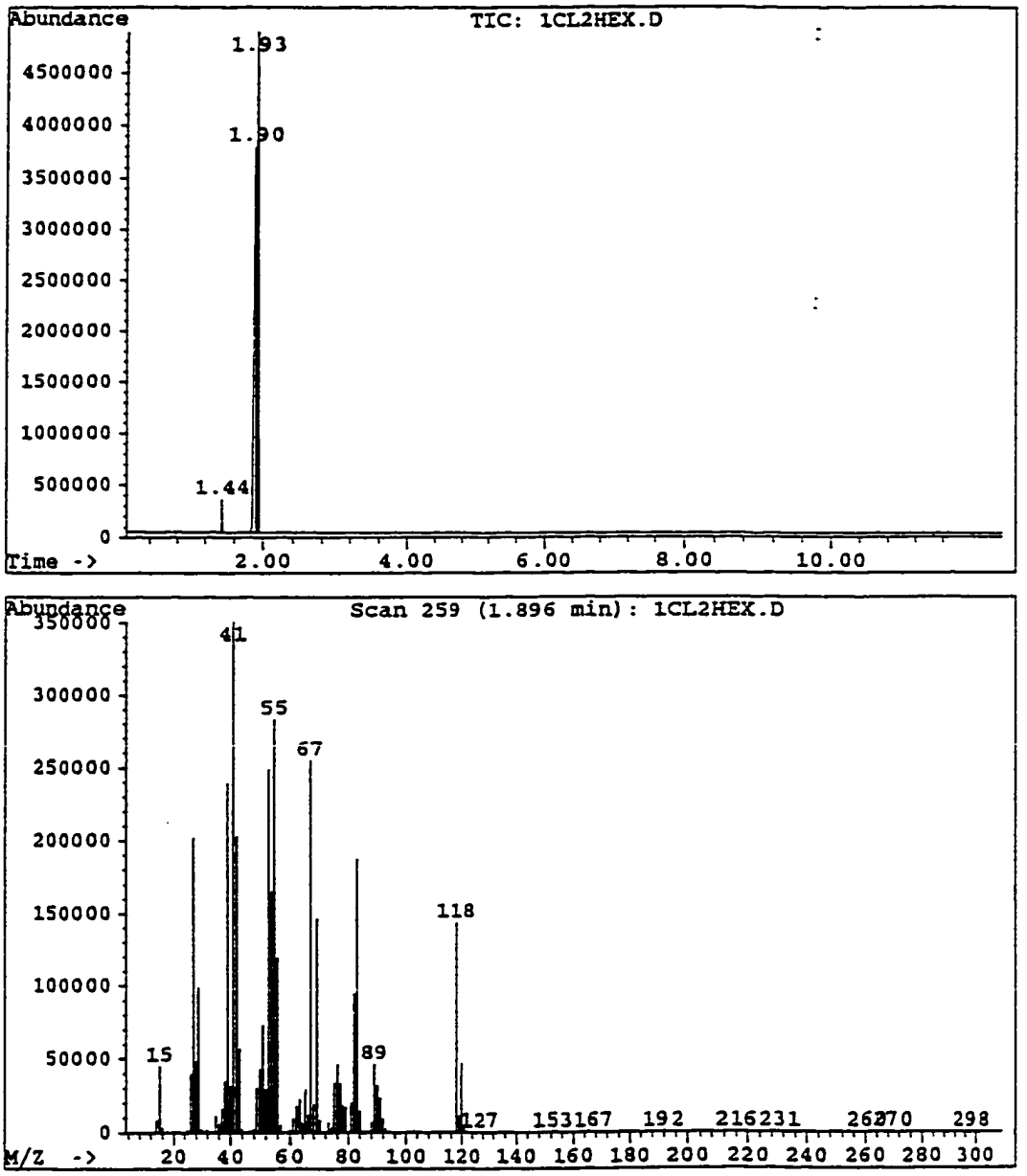


Fig. 3.48: Mass spectrum and gas chromatogram of

trans-1-chloro-2-hexene

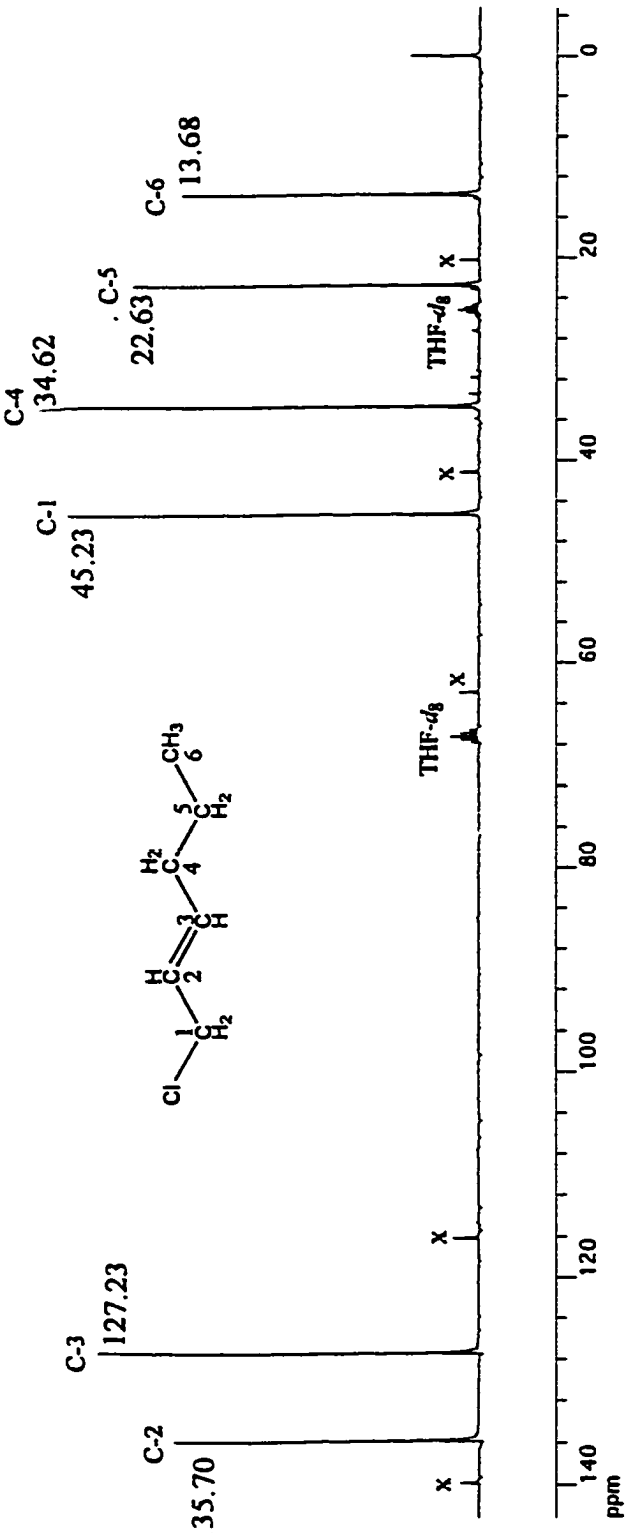


Fig. 3.49: ^{13}C NMR spectrum (75.57 MHz) of *trans*-1-chloro-2-hexene (THF-d_8, 50 °C, x: impurity)

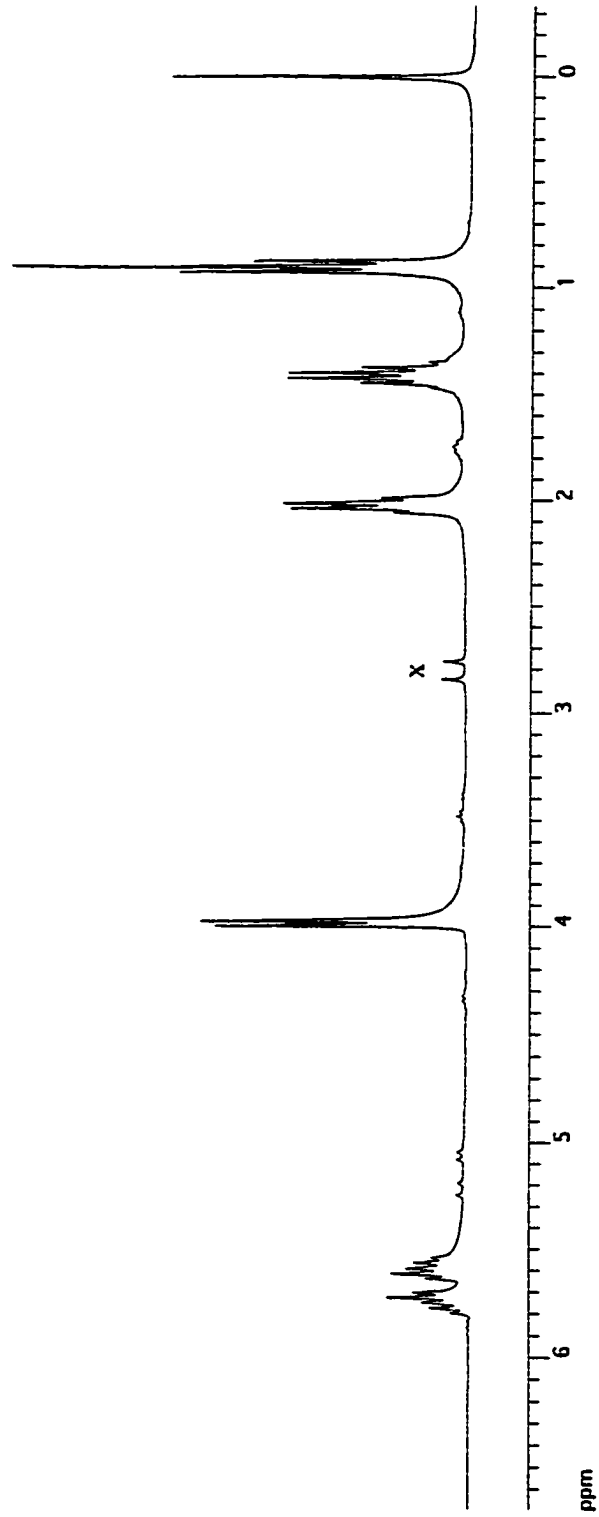


Fig. 3.50: ^{1}H NMR spectrum (300.52 MHz) of *trans*-1-chloro-2-hexene (THF-d_8, 50 °C, x: impurity)

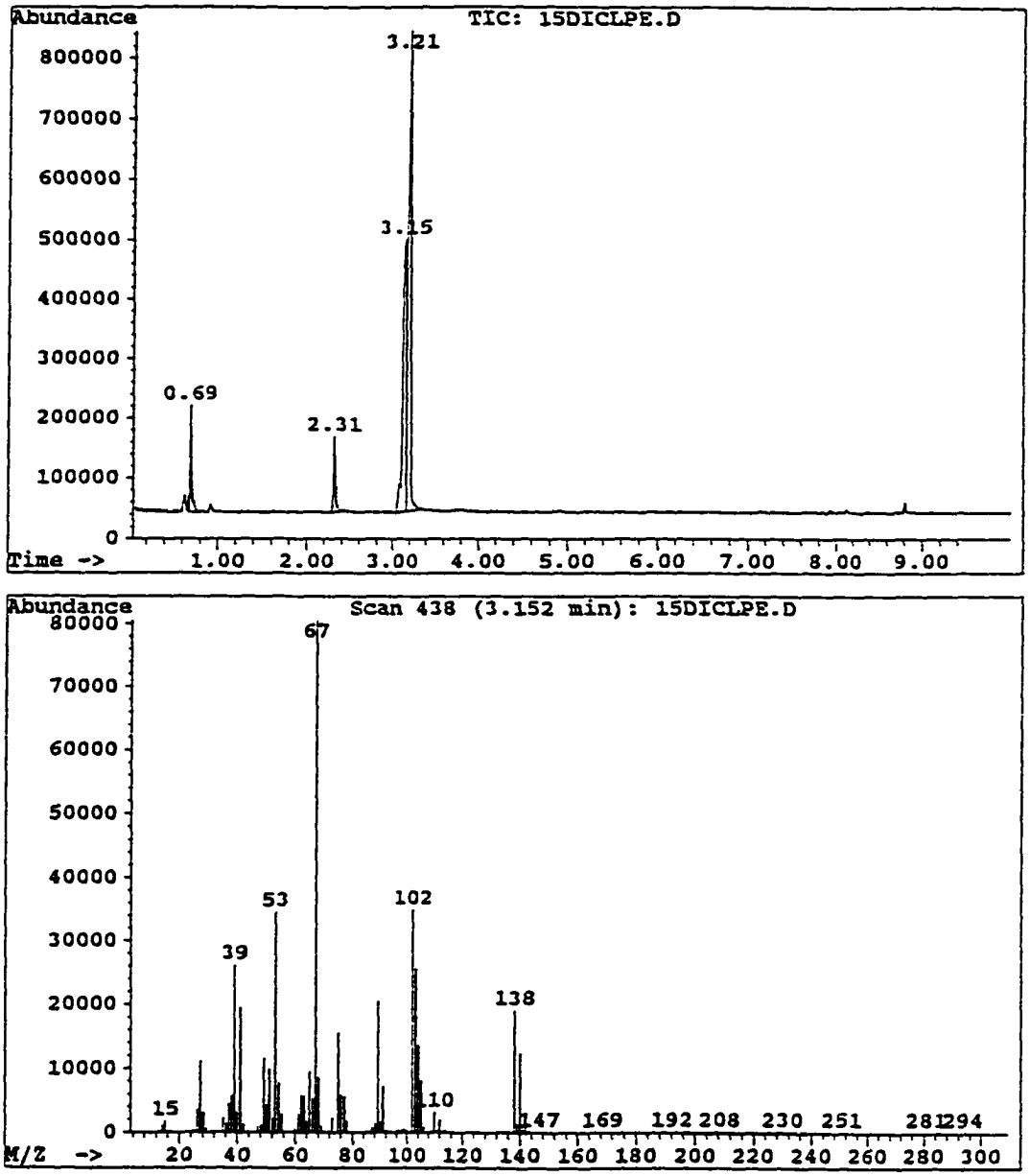


Fig. 3.51: Mass spectrum and gas chromatogram of

trans-1,5-dichloro-2-pentene

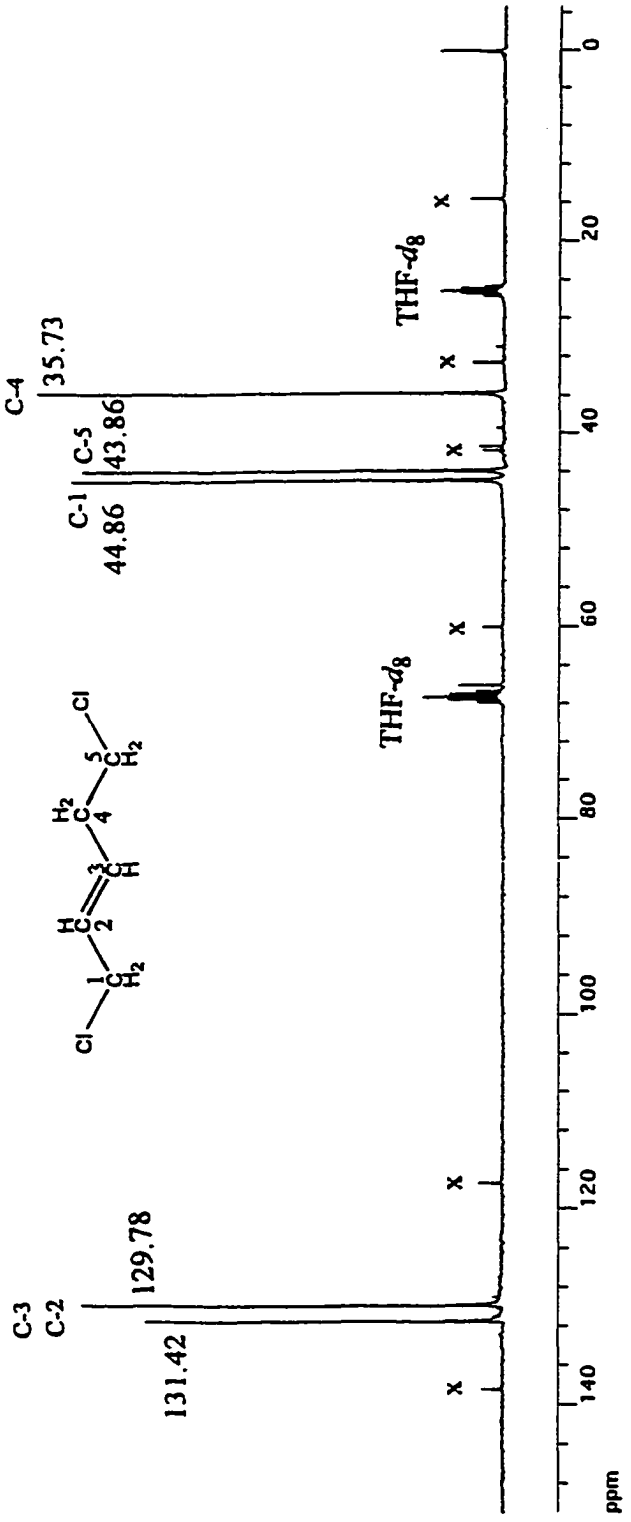


Fig. 3.52: ^{13}C NMR spectrum (75.57 MHz) of *trans*-1,5-dichloro-2-pentene (THF-d_8, 50 °C, *x*: impurity)

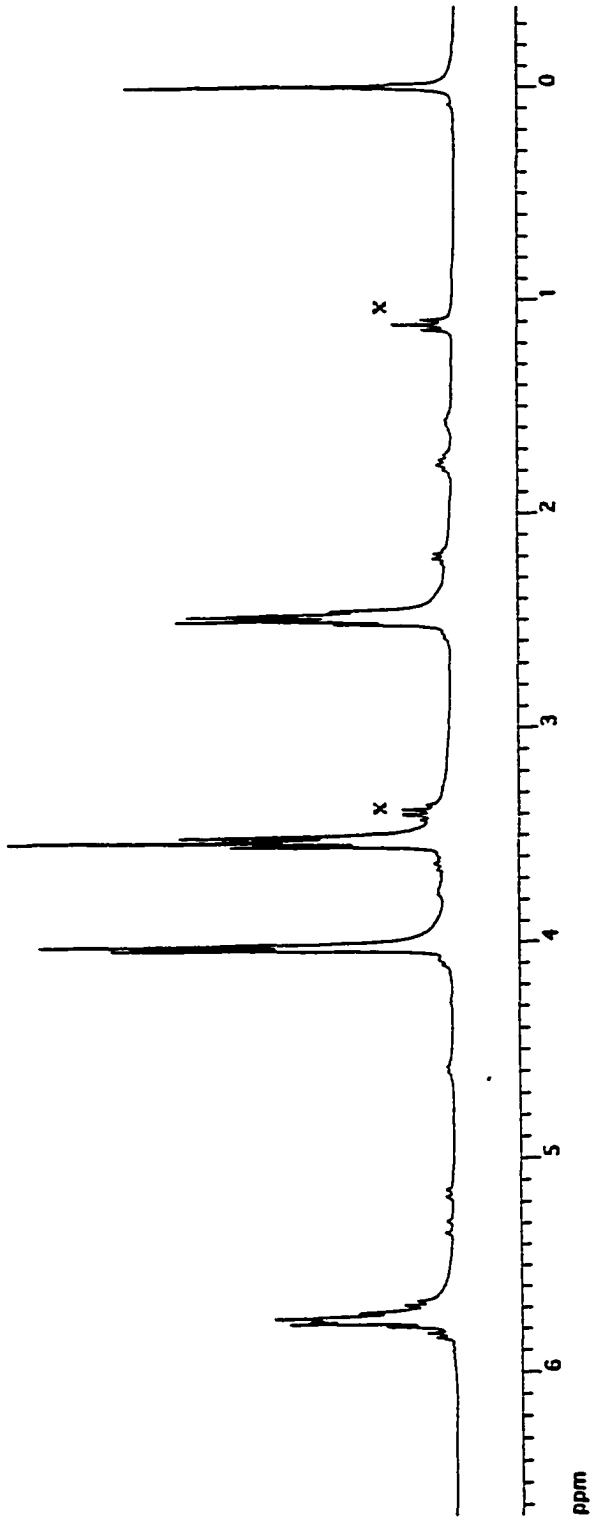


Fig. 3.53: ^{1}H NMR spectrum (300.52 MHz) of *trans*-1,5-dichloro-2-pentene (THF-d_8, 50 °C, x: impurity)

pentane, which was used to create a counter pressure at the reaction temperature. When the bomb was closed, additional pressure (*ca.* 4 atm) was applied with nitrogen gas. The bomb then was thermostatted in an oil bath for 45 h at 80±1 °C. At the end of this time, the product was removed from the reaction tube, dissolved in THF (*ca.* 30 mL), and precipitated into a large excess of methanol (*ca.* 1 L). Drying at room temperature gave 3.22 g of purified PVC (yield, 86.5%). (See the cumulative data in Table 3.3).

3.2.2.2 With *trans*-1-chloro-2-hexene (PVC-1)

The procedure was the same, in general, as that described above. The *trans*-1-chloro-2-hexene was introduced into the reaction tube along with the initiator, and the amounts of these materials used in various polymerizations are given in Table 3.1. (See cumulative data in Table 3.3.)

3.2.2.3 With *trans*-1,5-dichloro-2-pentene (PVC-2)

The procedure was the same, in general, as that already described. The amounts of materials used for a number of polymerizations are listed in Table 3.2. Representative NMR spectra for two of the synthesized PVCs appear in Figs. 3.54 - 3.57.

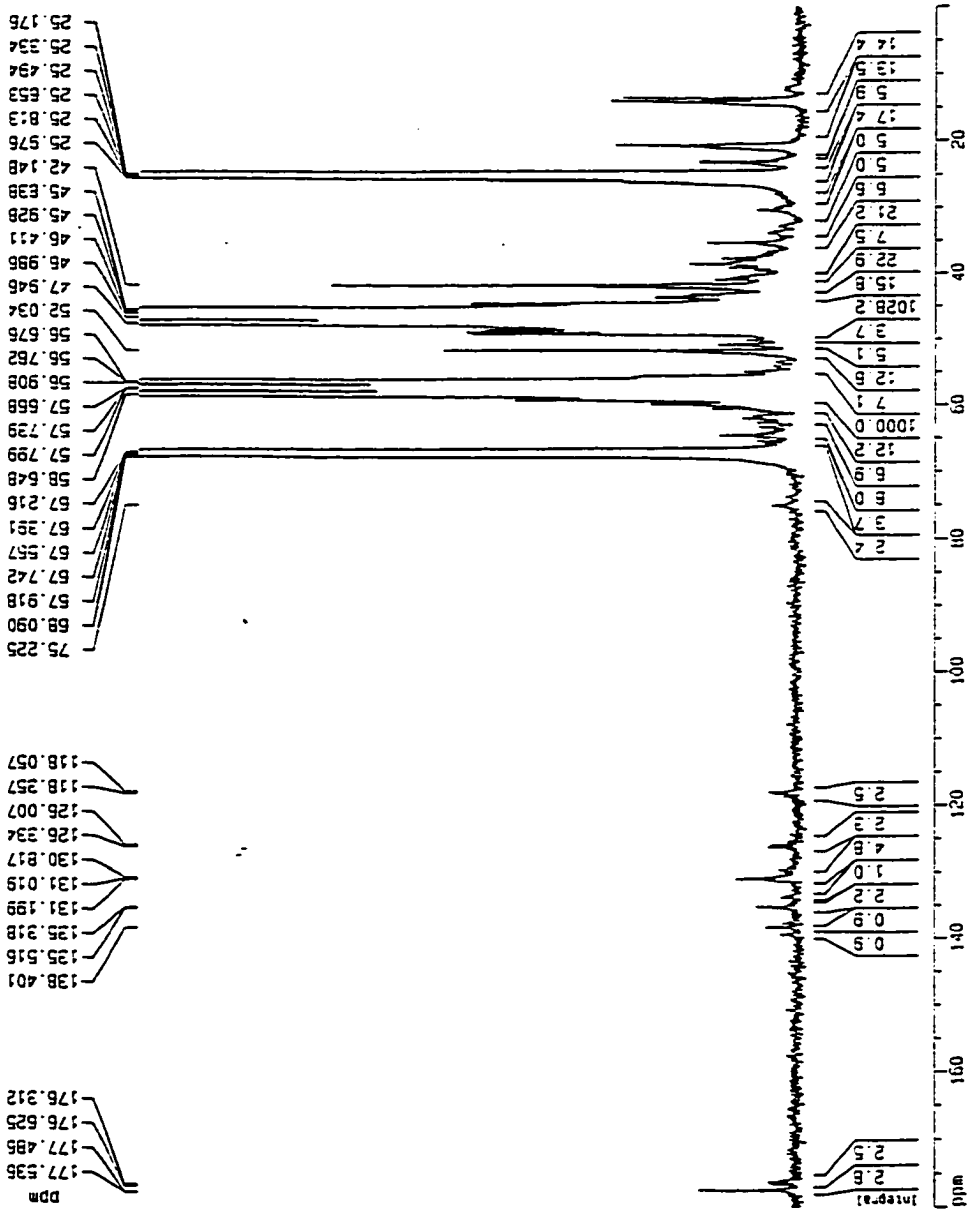


Fig. 3.54: ^{13}C NMR spectrum (125.77 MHz) of PVC-1 (#5) (THF-d_8, 23 °C)

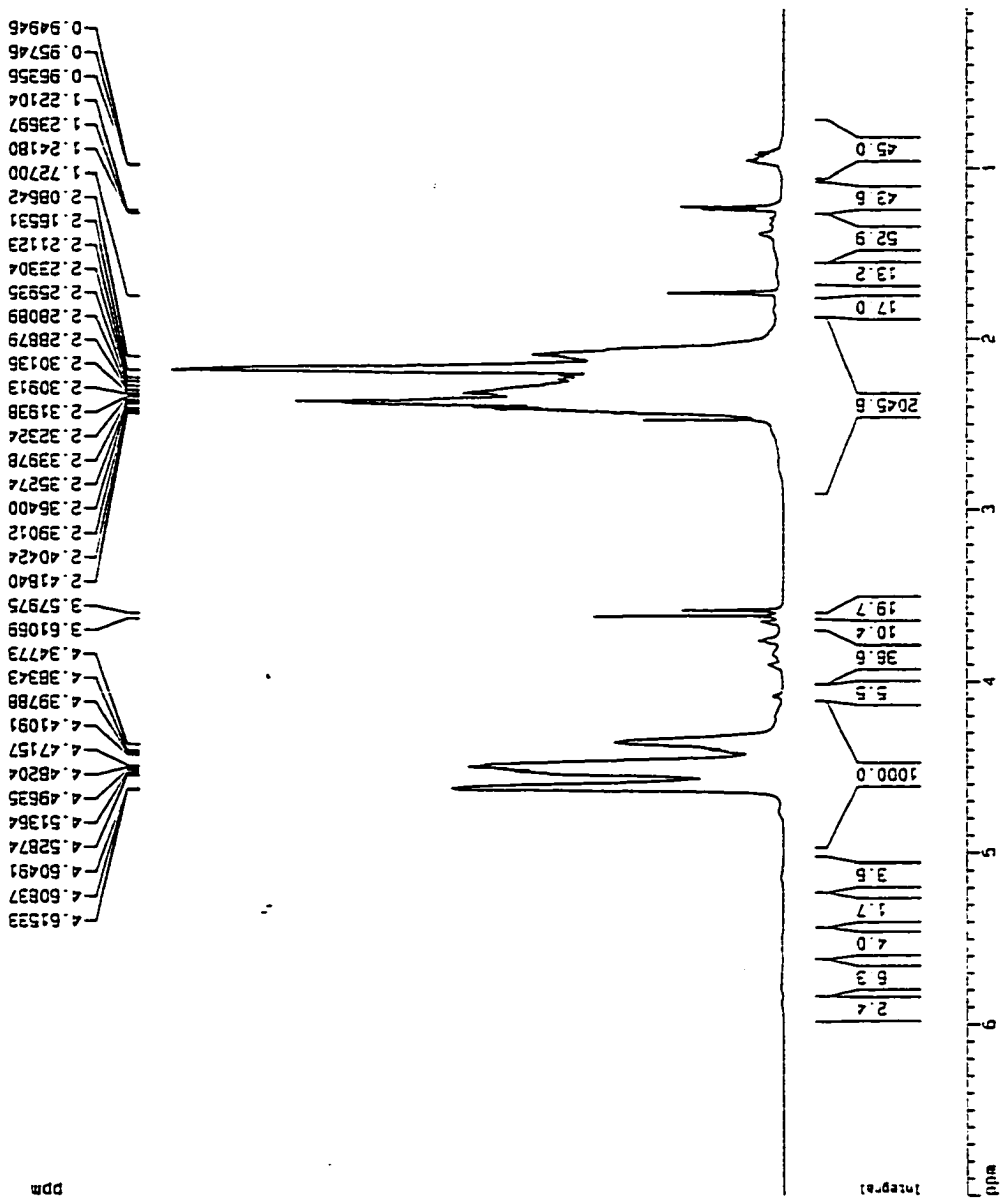


Fig. 3.55: ^{1}H NMR spectrum (500.14 MHz) of PVC-1 (#5) (THF-d_8, 23 °C)

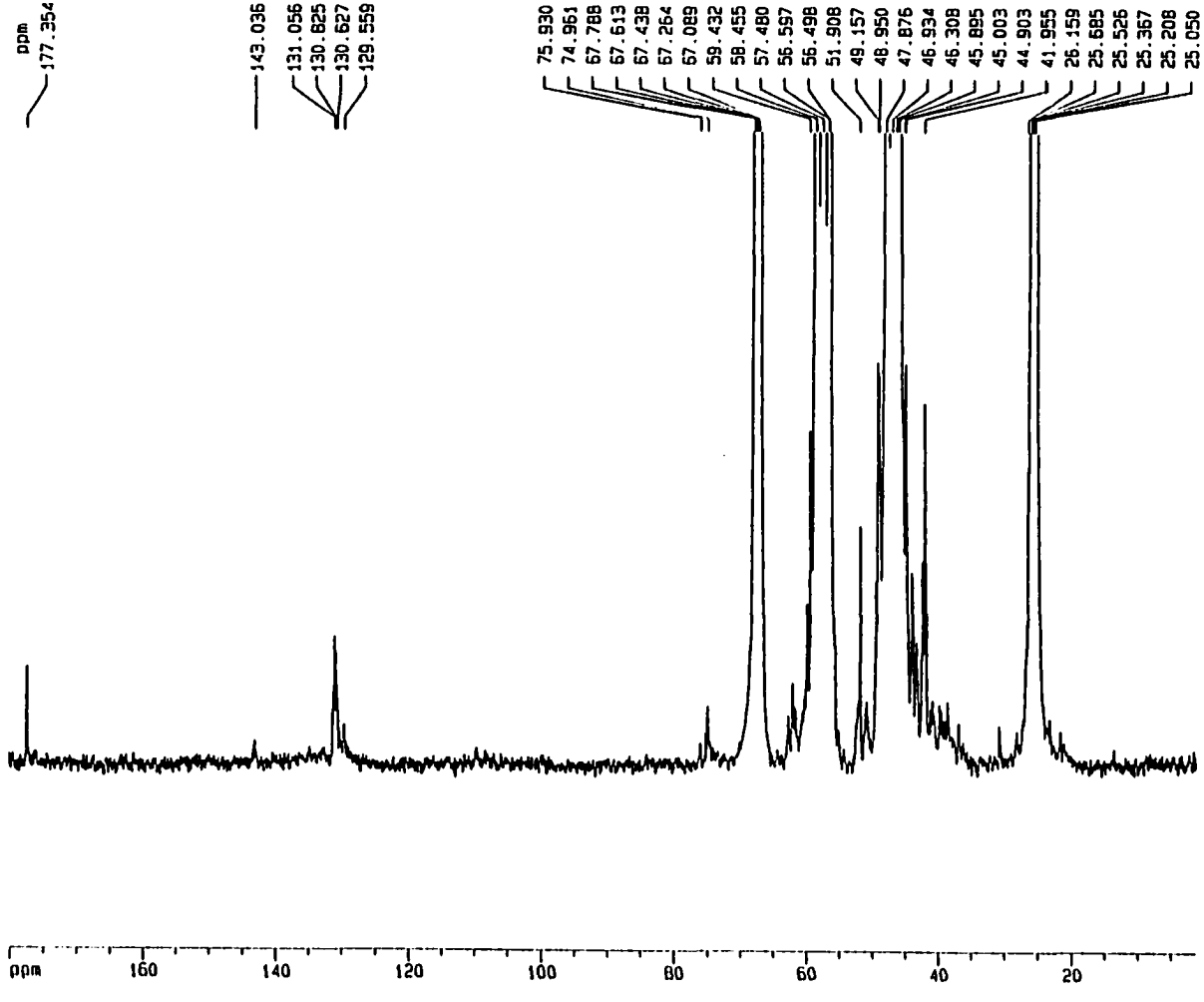


Fig. 3.56: ^{13}C NMR spectrum (125.77 MHz) of PVC-2 (#6) (THF-d_8, 50 °C)

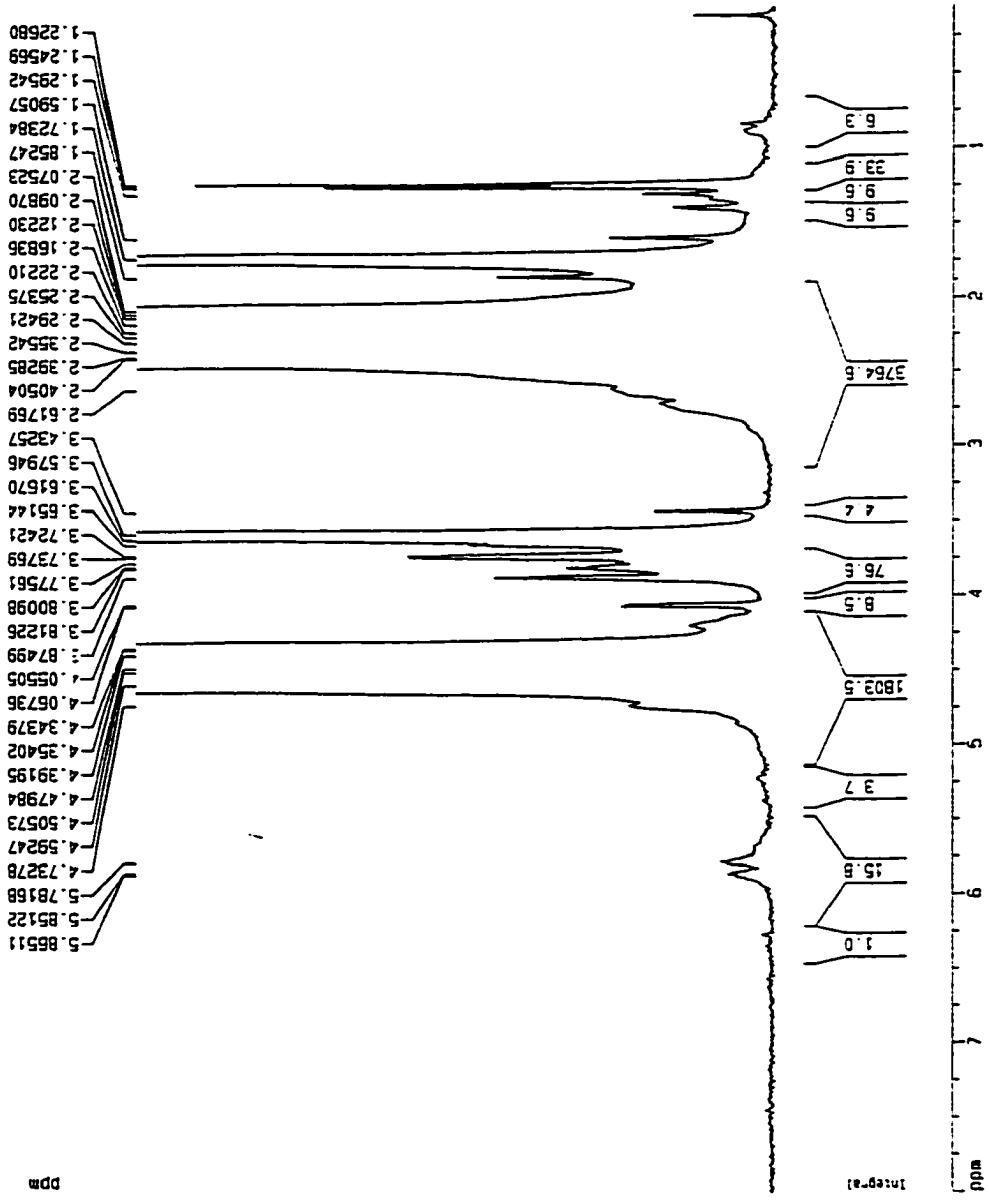


Fig. 3.57: ^{1}H NMR spectrum (500.14 MHz) of PVC-2 (#6) (THF-d_8, 50 °C)

Table 3.1

Amounts of materials for various polymerizations

No.	Initiator, mg(mmol)	1-Chloro-2-hexene, mg(mmol)	Vinyl chloride, g(mmol)
2	25.2(0.110)	107.3(0.9055)	2.0899(33.44)
3	44.8(0.195)	109.6(0.9249)	3.0583(48.93)
4	68.0(0.296)	102.3(0.8633)	3.0923(49.68)
5	86.0(0.379)	365.6(3.085)	1.6098(25.76)

3.2.3 Molecular weight measurements by viscosity

An Ubbelohde viscometer (CANNON #OC B237; viscometer constant, 0.003214 centistokes/s) was used for molecular weight determinations of the synthesized PVCs. Experimental data taken at 30±0.1 °C are shown in Table 3.3;

Table 3.2

Amounts of materials for various polymerizations

No.	Initiator, mg(mmol)	1,5-Dichloro-2-pentene, mg(mmol)	Vinyl chloride, g(mmol)
6	75.8(0.330)	420.1(3.022)	3.5247(56.40)
7	17.0(0.0739)	52.6(0.444)	0.9984(15.79)
8	41.5(0.180)	75.0(0.633)	2.6677(42.68)

Table 3.3

Polymerizations of vinyl chloride (VC) alone and with transfer agents (TA)

No.	Init./VC mmol/mol (mg/g)	TA/VC mmol/mol (mg/g)	Viscometry			Yld, %
			Efflux time, s (at least 20 runs)	$\eta_{inh.}$	Molecular weight	
1, no TA	54.1 (198.9)	-	703.75±0.16 variance: 0.1797 st. deviation: 0.4239	0.7181	M_n=29,977 DP=480 M_w=60,149 M_w/M_n=2.01	86
2, with 1-chloro-2-hexene	3.227 (12.06)	27.08 (51.34)	654.03±0.13 variance: 0.1043 st. deviation: 0.3230	0.3530	M_n=12,440 DP=199 M_w=24,328 M_w/M_n=1.95	78
3, with 1-chloro-2-hexene	3.981 (14.65)	18.90 (35.84)	663.51±0.62 variance: 3.9891 st. deviation: 1.9973	0.4248	M_n=15,646 DP=250 M_w=30,719 M_w/M_n=1.96	79
4, with 1-chloro-2-hexene	5.976 (21.99)	17.45 (33.08)	658.17±0.18 variance: 0.2082 st. deviation: 0.4562	0.3847	M_n=13,838 DP=221 M_w=27,058 M_w/M_n=1.96	83
5, with 1-chloro-2-hexene	14.52 (53.42)	119.8 (227.1)	-	-	-	73
6, with 1,5-	5.844 (21.51)	53.59 (119.2)	637.74±0.12 variance: 0.2022	0.2276	M_n=7,224 DP=116	74

dichloro-2-pentene			st. deviation: 0.4497		M_w=13,821 M_w/M_n=1.91	
7, with 1,5-dichloro-2-pentene	4.627 (17.03)	27.80 (52.68)	643.45±0.18 variance: 0.2319 st. deviation: 0.4816	0.2731	M_n=9,053 DP=145 M_w=17,452 M_w/M_n=1.93	72
8, with 1,5-dichloro-2-pentene	4.227 (15.56)	14.83 (28.11)	643.84±0.16 variance: 0.1837 st. deviation: 0.4286	0.2712	M_n=8,975 DP=144 M_w=17,297 M_w/M_n=1.93	78
			643.29±0.26 variance: 0.5683 st. deviation: 0.7538	0.2710	M_n=8,967 DP=143 M_w=17,283 M_w/M_n=1.93	

confidence intervals were calculated for 95% probability; the efflux time of cyclohexanone was 609.27±0.26 (variance, 0.4581; standard deviation, 0.6768). Molecular weights were calculated using inherent viscosity (η_{inh}) values:[11]

$$\eta_{inh} = \ln(\eta_{rel})/[C], \text{ where } \eta_{rel} = t/t_o$$

Here, t and t_o are efflux time of solution and solvent, respectively, at 30±0.1 °C; and [C] is the amount of PVC in grams (*ca.* 0.2) per 100 mL of solution.

Number-average and weight-average molecular weights were calculated according to equations found in the literature:[12]

$$\log M_n = 4.6549 + 1.2385 \log \eta_{inh}$$

$$\log M_w = 4.9633 + 1.2799 \log \eta_{inh}$$

CHAPTER 4

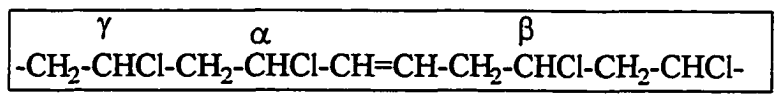
RESULTS AND DISCUSSION

The goal of this study was to elucidate several aspects of the microstructure of PVC. As was mentioned in the Background chapter, the microstructure of PVC is of particular interest because of its effects on PVC stability.

4.1 Attempts to predict the ^{13}C chemical shifts of isolated internal allylic structures in PVC

The number of isolated internal double bonds in virgin PVC is typically ≤ 0.6 per thousand carbons,[1] a concentration large enough to have a considerable effect on thermal stability. Most of these groups are formed due to hydrogen abstraction from PVC by growing macroradicals. Recently this pathway was named the "auxiliary" transfer mechanism and was combined theoretically and experimentally with another scheme for transfer to monomer during the free-radical polymerization of vinyl chloride.[1]

So far the specific chemical shifts of the unique carbons in the following structure



are not known with certainty. In order to try to predict them, three model compounds were synthesized for reference purposes: *trans*-1-chloro-2-heptene (an α-chloro model),

trans-5-chloro-2-heptene (a β-chloro model), and *trans*-6-chloro-2-heptene (a γ-chloro model). The ^{13}C shifts of these substances were used to determine shift increments for the replacement of H by Cl, and these increments then were used to predict the unique shifts of the internal chloroallylic structure. However, the predictions did not agree satisfactorily with the shifts of the relevant resonances in the spectrum of the polymer. As is well known to be the case with a number of other polar substituents, the shift increments obtained from monochlorides evidently are not additive.

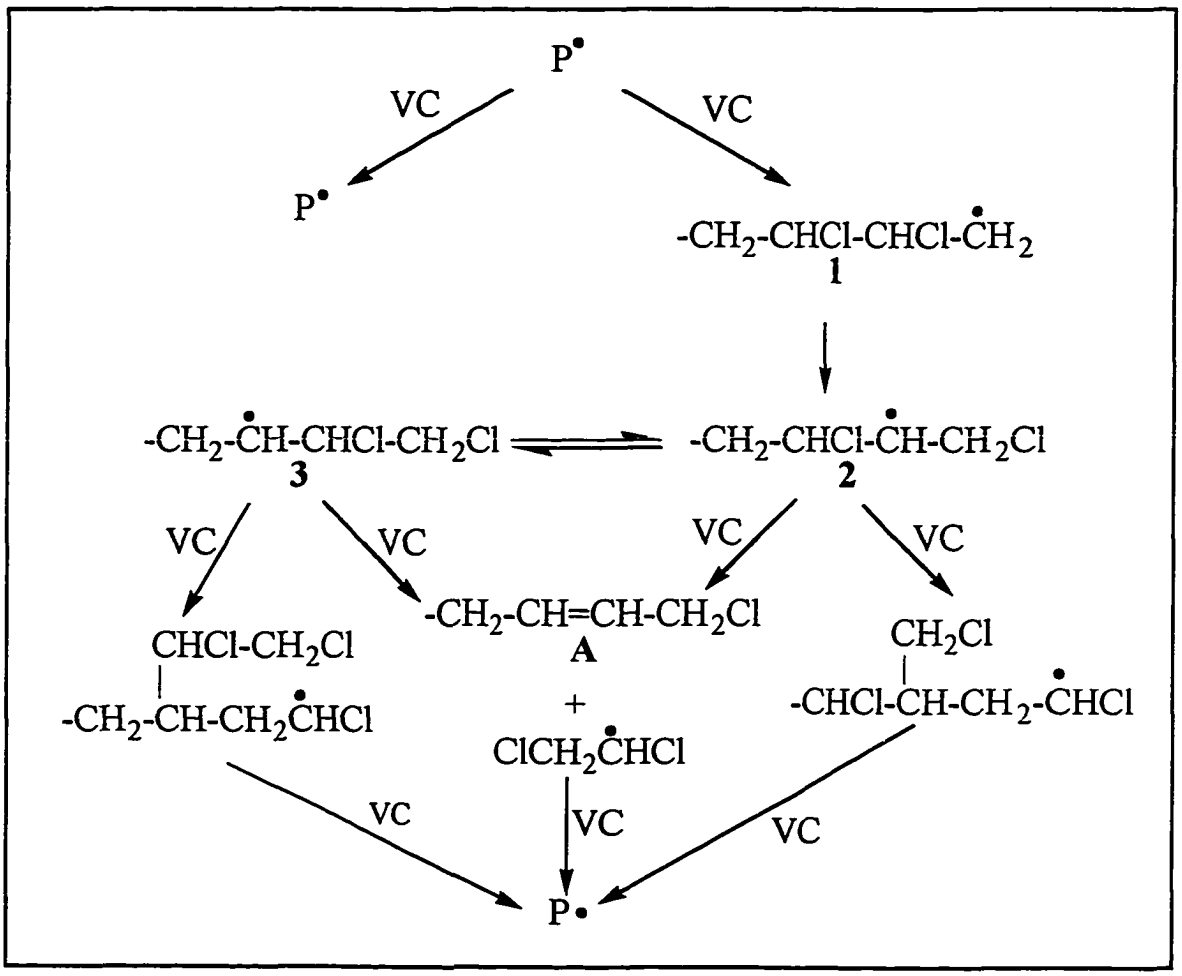
4.2 The addition of macroradicals to alkene chain ends during the polymerization of vinyl chloride

In several recent publications the outcome of head-to-head addition in vinyl chloride polymerization was discussed.[1-4] It also was shown that chain transfer to monomer occurs in two distinct ways. One of them, the "auxiliary" pathway,[1,2] begins with hydrogen abstraction from PVC. The importance of this pathway increases significantly when the concentration of the monomer declines.[1-3] Another route is a consequence of head-to-head VC addition. This pathway first produces radical **1** and then leads to the direct transfer of a chlorine atom to the monomer from rearranged radicals **2** and **3** in Scheme 4.1.

At a given polymerization temperature, the allylic chain end (**A**) concentration decreases with decreasing concentration of VC in a dramatic manner that allows the total alkene concentration to remain at the level of 1 per macromolecule[1,2] but seems to require the radical-induced conversion of **A** into an internal double bond.[1] This transformation

seems likely to play a significant role in molecular-weight development, and the elucidation of its detailed chemistry is essential for the complete understanding of the monomer-transfer processes.

Scheme 4.1: Sequential reactions resulting from head-to-head addition during the free-radical polymerization of VC, where P$^{\bullet}$ is the ordinary head-to-tail macroradical



It has been known for some time that the concentration of **A** can decrease significantly when the VC concentration is reduced.[5] Dramatic evidence for such a decrease appears in Fig. 4.1, which compares the partial ^{1}H NMR spectra of two samples

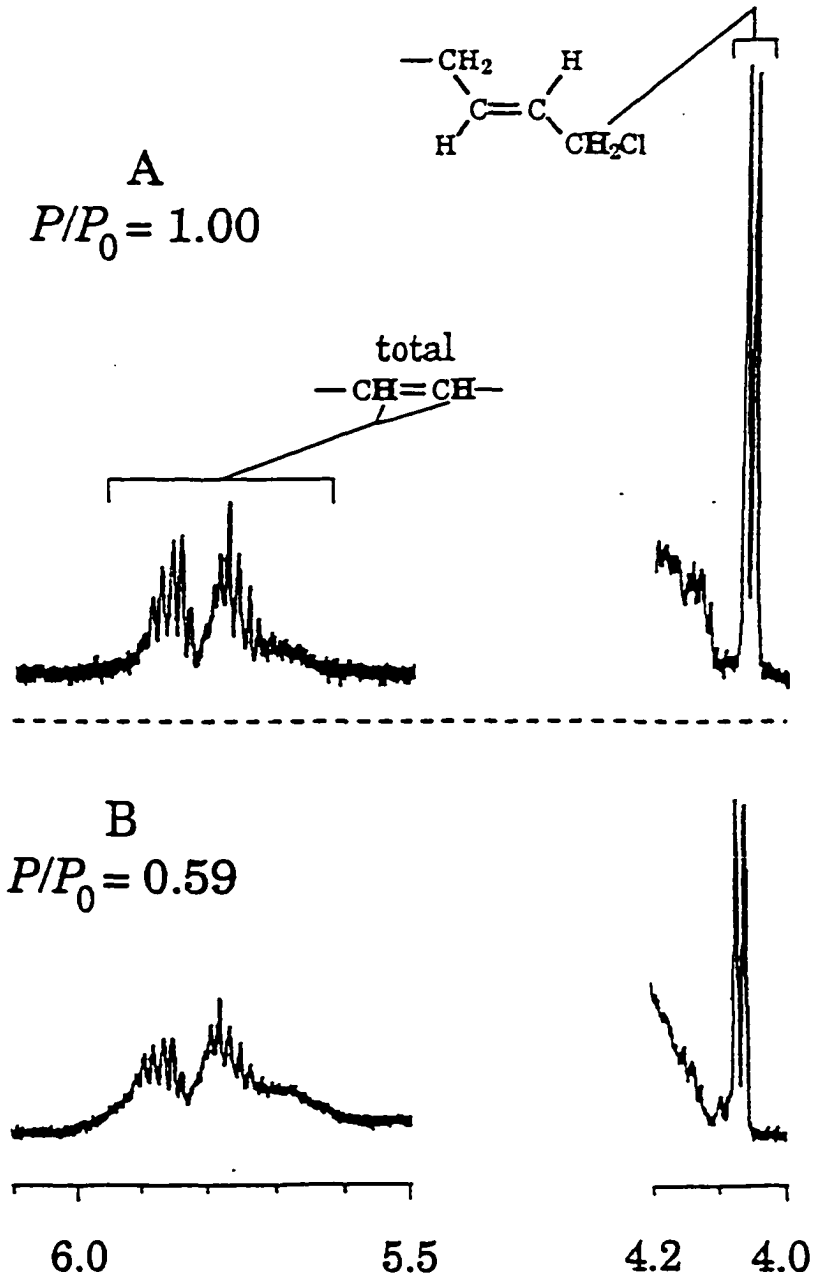
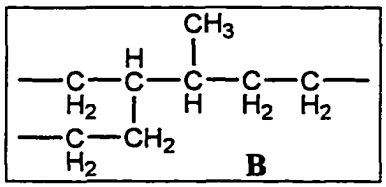


Fig. 4.1: Partial ^{1}H NMR spectra (500.14 MHz, THF-d_8, 50 °C) of PVC made at 80 °C with P/P_0 = 1.00 (A) or 0.59 (B). The spectra were recorded with identical plotting parameters and thus are directly comparable.

of PVC made at 80 °C under constant VC pressures,[1] where **P** is the actual pressure of monomer and P_0 is its pressure at saturation.[6] It is clearly seen that the 4.06-ppm doublet of the CH_2Cl protons of *trans*-**A** undergoes a major reduction upon going from saturation conditions to a P/P_o value of 0.59. At the same time a significant increase in the intensity of the complex olefinic proton absorption[1] at 5.5-6.0 ppm is observed.

The concentrations of **A** at saturation and subsaturation conditions were found to be 1.8×10^{-3} and $1.0_5 \times 10^{-3}$ mol/(VC unit), respectively,[7] and the latter polymer was shown to incorporate $0.7_5 \times 10^{-3}$ mol/(VC unit) of internal double bonds derived from **A**.[1] The formation of such double bonds must have been a free-radical process, because it was favored by the decrease in the concentration of the principal radical scavenger in the system (vinyl chloride). This conclusion has been confirmed by the NMR spectra of other subsaturation PVC specimens.[1]

Theoretically, copolymerization of **A** with VC can be considered, but different researchers have reported that it does not occur.[7,8] Such copolymerization would not convert **A** into an internal alkene but would lead to structure **B** in dechlorinated PVC.



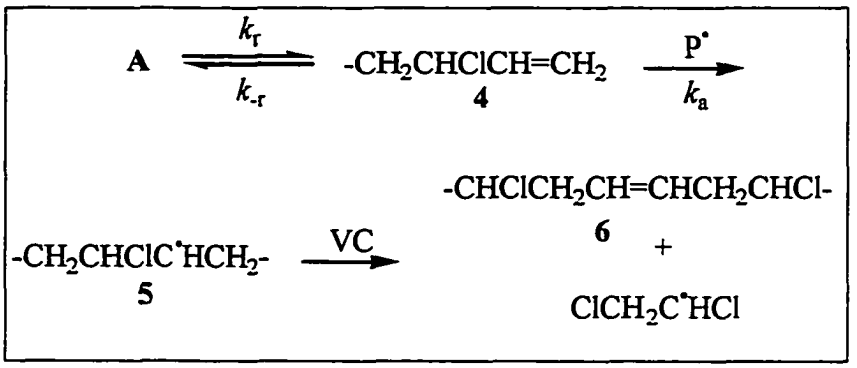
B

Shift calculations made with the Grant-Paul parameters[9] and the NMR spectra of model compounds reveal that the unique resonances of **B** are absent from the ^{13}C NMR spectra of Bu_3SnH-reduced PVC samples made under subsaturation conditions.[7]

However, there is another mechanism for **A** destruction that incorporates macroradical addition and requires close scrutiny. This mechanism is shown in Scheme

4.2.

Scheme 4.2: Possible mechanism for the formation of additional internal double-bond structures



This mechanism involves interaction of the growing macroradical, P•, with a rearranged isomer of **A** (**4**) in order to form a new radical (**5**) that then is converted into the internal alkene structure **6** by a β-scission reaction[1-3] with VC. In conventional industrial PVC, structure **4** usually cannot be detected,[3] and because of its relatively low thermodynamic stability, both the rate constant k_r and the equilibrium constant $K_r = k_r/k_{-r}$ are predicted to be small. However, published reactivity-ratio data for the VC/propene system[10] suggest that the reactivity of **4** toward P• addition should resemble that of VC. Thus the situation when $k_a >> k_r$ and $k_a >> K_r$ seems quite possible, and considerable amounts of **6** could be formed even when the steady-state concentration of **4** is too low to be detected.

Very strong evidence for the conversion of **4** into **6**, during polymerization, has now been obtained from the microstructure of a PVC specimen synthesized by a very special procedure. This unusual PVC was made at 0 °C with initiation by (t-Bu)$_2$Mg,[11,12] and its 2D ^{1}H NMR spectrum is displayed in Fig. 4.2.

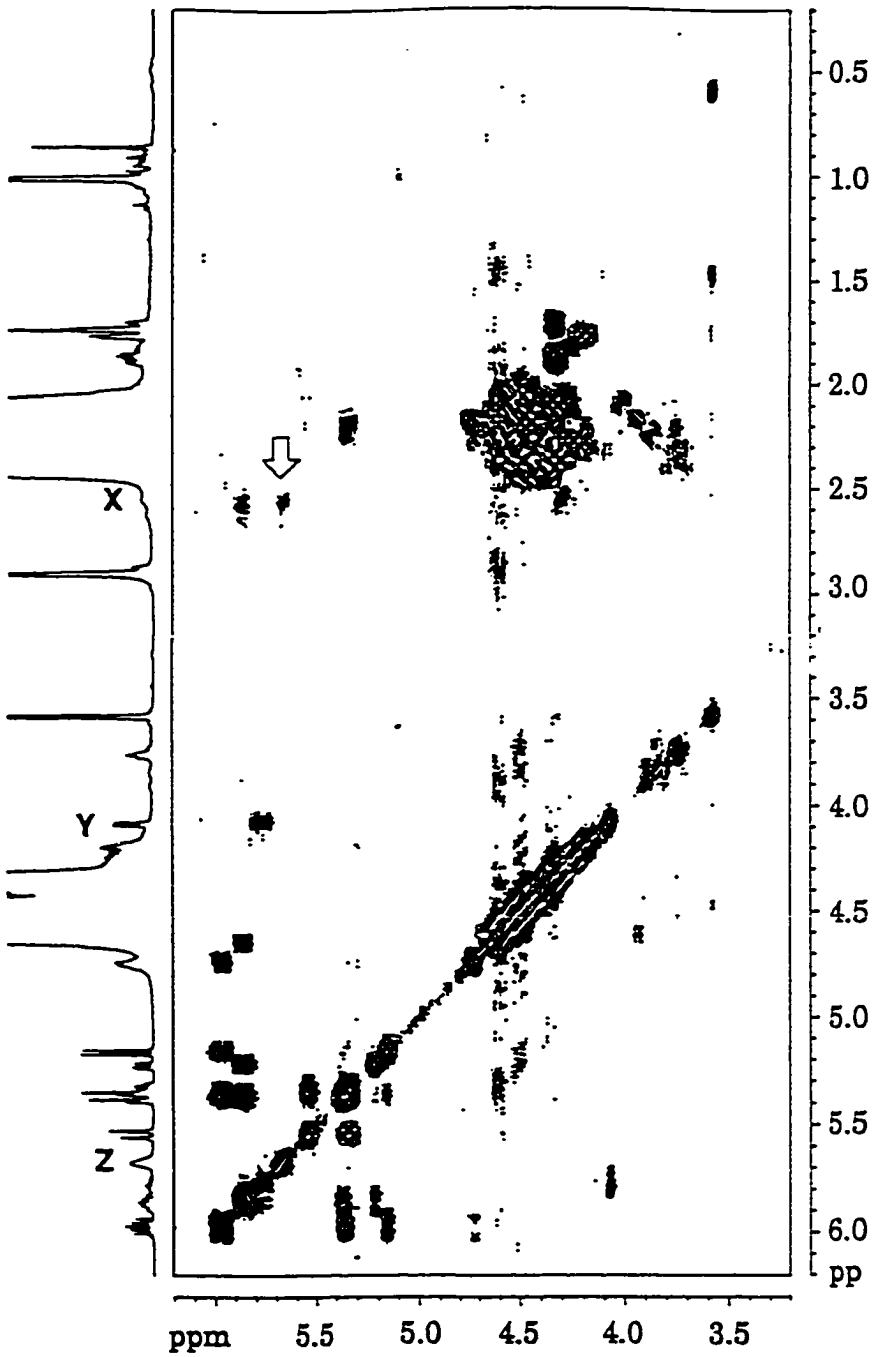


Fig. 4.2: Phase-sensitive DQF-COSY 2D ^{1}H NMR partial spectrum (500.14 MHz, THF-d_8, 23 °C) of $(t\text{-Bu})_2$Mg-initiated PVC

The low intensity of doublet **Y** (the same resonance as in Fig. 4.1) shows that the concentration of **A** is very low. At the same time the concentration of the rearranged end group **4** is seen to be unusually high, as is revealed by the alkene peaks at 5.1-5.6 ppm,[12,13] which also establish the presence of some *t*-BuCH=CH- terminal groups.[12] However, the broad singlet denoted as **Z** and centered at 5.67 ppm is of greater interest. It can be seen from the spectrum that the alkene protons producing this resonance are coupled only to the allylic protons denoted as **X**, which appear at *ca.* 2.5_4 ppm. From their chemical-shift positions it is clear that the latter protons are not attached to chlorinated carbons. On the other hand, the spectrum reveals that they also are coupled to protons in the principal CHCl region. All of these observations point to the presence of structure **6** in this particular PVC specimen.

Figure 4.3 depicts the corresponding portion of the 2D ^{1}H-^{13}C NMR correlation spectrum of an acetone extract of the polymer made with $(t\text{-Bu})_2Mg$. This spectrum reveals that the olefinic protons (**Z**) of **6** are attached to carbons having chemical shifts of *ca.* 130 ppm (shown by the arrow). Those carbons also are shown by the spectrum to resonate slightly upfield from the alkene carbons of **A**.

In order to confirm the spectral assignments for **6** and to prove its existence in at least this specific PVC, the model compound *trans*-3,8-dichloro-5-decene was synthesized (see the Experimental part of this thesis). The alkene carbons of this substance resonate at 129.96 and 129.99 ppm (racemic and meso isomers), while its allylic and olefinic protons appear at 2.47 (multiplet center) and 5.60 ppm (broad singlet), respectively. All of these chemical shift values are in very good agreement with those found for polymer structure **6**,

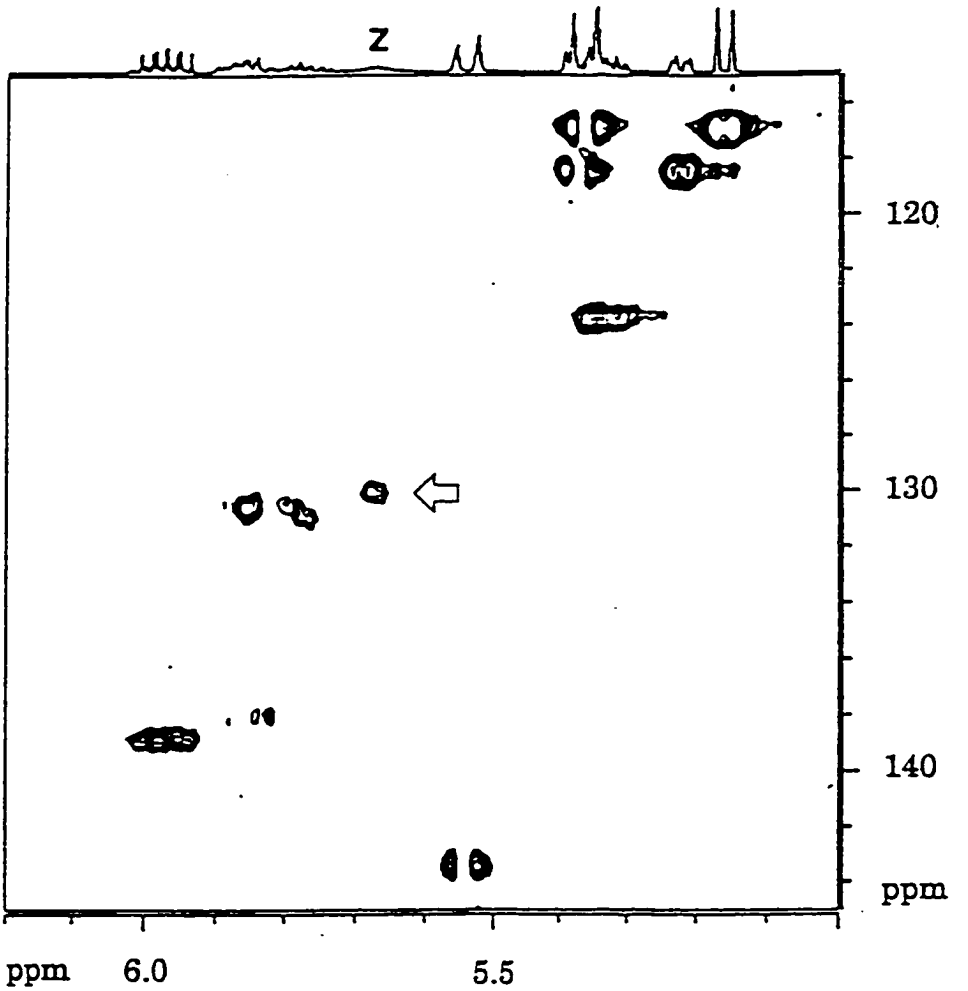


Fig. 4.3: HMQC 2D ^{1}H-^{13}C NMR partial spectrum (500.14 MHz and 125.77 MHz, THF-d_8, 50 °C) of an acetone-soluble fraction of (t-Bu)$_2$Mg-initiated PVC

with some minor perturbations being due to structure and temperature differences.

Fig. 4.4, parts A and B, shows ^{13}C NMR partial spectra for the same PVCs that are noted in Fig. 4.1. From Fig. 4.3 it follows that the peaks at 130.4-131.1 ppm in Fig. 4.4-A must come from the alkene carbons of the end group **A** (trans isomer, evidently). The four small peaks at 129.4-130.1 ppm can be attributed to the analogous carbons of the *cis*-**A** structure. Those four resonances are not revealed in Fig. 4.3, probably because of their very low intensities.

Fig. 4.4-C displays a part of the ^{13}C NMR spectrum of the (t-Bu)$_2$Mg-initiated polymer. Detailed comparisons of intensities and chemical shifts in the spectra of Figs. 4.4-A and -C show that the five resonances with dots in Fig. 4.4-C are the only ones that could have arisen from the olefinic carbons of **6**. Figure 4.4-B shows a partial ^{13}C NMR spectrum of a PVC that was synthesized under subsaturation conditions. Comparison of Figs. 4.4-A and -B clearly shows the disappearance of the **A** structure when subsaturation occurs. This comparison also shows that the subsaturation PVC contains several additional alkene peaks which arise, apparently, from isolated internal double bonds. Actually this result was predictable, because the total concentrations of internal double bonds (as calculated from Fig. 4.1) were 0.6×10^{-3} and 2.3×10^{-3} mol/(VC unit) for the saturation and subsaturation samples, respectively.[1] Moreover, Fig. 4.4-B clearly shows that there are no **6** structures formed under subsaturation conditions, because the dotted peaks at 129.91 and 130.08 ppm do not increase in intensity upon going from saturation to subsaturation. Those resonances have the same chemical shifts as two of the dotted peaks in Fig. 4.4-C (perhaps accidently), and they are the only resonances which appear in

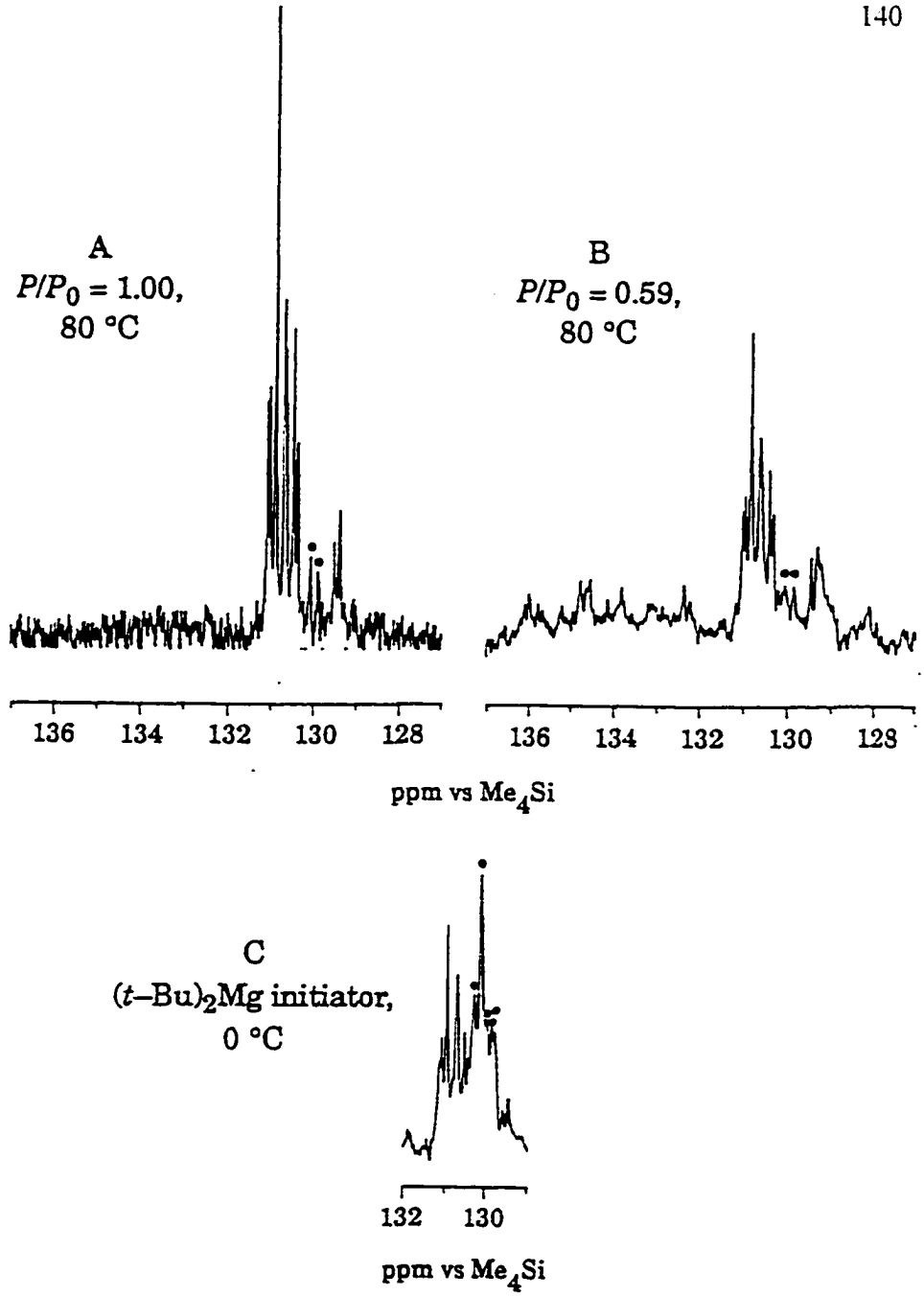


Fig. 4.4: Proton-decoupled ^{13}C NMR partial spectra (125.77 MHz, THF-d_8, 50 °C) of PVC samples made at: A, 80 °C with P/P_0 = 1.00; B, 80 °C with P/P_0 = 0.59; C, 0 °C with (t-Bu)$_2$Mg initiation. The spectra were recorded with identical plotting parameters and thus are directly comparable.

all of the spectra in Fig. 4.4. Thus, the final conclusion is that, in ordinary commercial PVC, the mechanism depicted in Scheme 4.2 is *not* responsible for the disappearance of **A** structures during the latter stages of polymerization.

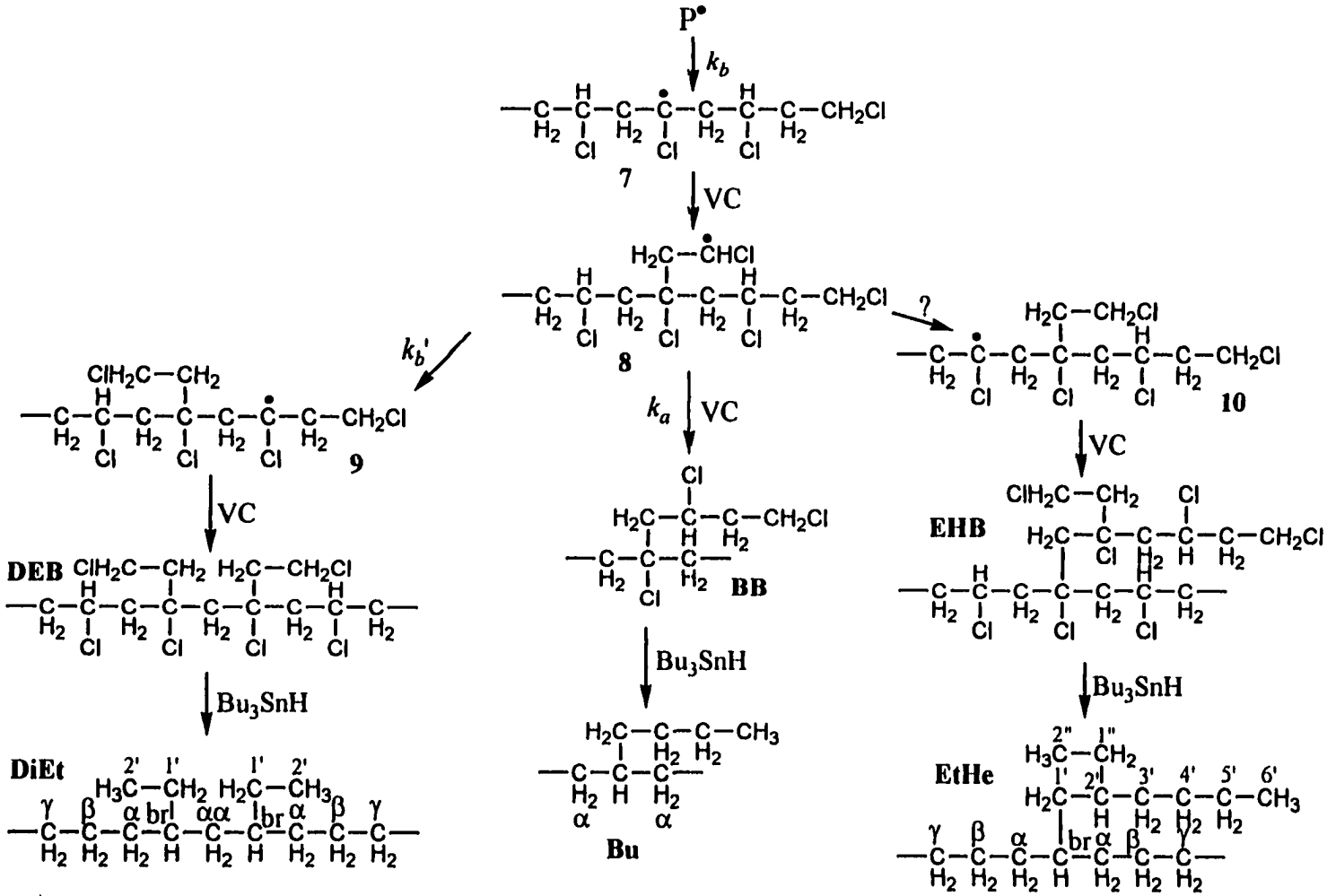
Several other pathways for **A** destruction can be considered. They include addition followed by termination, addition followed by transfer of Cl to VC, and numerous possibilities involving the intermediate allylic radicals that would result from hydrogen abstraction. Since this work has failed to reveal any new structures into which **A** is transformed upon going to subsaturation conditions, a mechanism whereby **A** produces larger amounts of "old" isolated internal double bonds seems more likely. An attractive scheme that meets these requirements[2] involves the conversion of **A** into the allylic radical $-CH_2CH{=}CHC^{\bullet}HCl$, whose addition to VC creates the same internal alkene structure that results from transfer to monomer by the so-called auxiliary route.[1,2] The practical possibility of this pathway will be discussed in Section 4.4.

4.3 Double backbiting mechanism

The presence of short-chain branches in many important addition polymers that are produced on a large scale has been known for years. Such structures have been well-investigated and described for polyethylene and several ethylene copolymers.[14-17] The concentrations and distributions of these branches strongly affect the morphologies and physical properties of the host materials. Therefore, knowledge of such microstructural particularities helps one to understand the behavior of a material and very often to predict its properties.

For PVC, the study of short-chain branching is of great interest for another very practical reason. Some of the branch-point carbons are attached to a chloro substituent and thus yield tertiary-chloride structures, which are believed by most PVC scientists to contribute greatly to PVC instability. However, as described in the Background chapter, some short-branch structures do not contain tertiary chloride. For instance, chloromethyl or dichloroethyl structures resulting from head-to-head addition during polymerization (see Scheme 4.1) are attached to a CH carbon and are quite stable for that reason.

Roedel[18] was the first to suggest a formation mechanism for the *n*-butyl branches in low-density polyethylene. This mechanism involves intramolecular hydrogen abstraction ("backbiting") by the propagating macroradical, via a cyclic six-membered transition state.[14,15,17] Similar processes can be proposed for VC polymerization[19-21] (see Scheme 4.3). For PVC, the first backbiting step has been known for some time.[21,22] Continual head-to-tail addition of monomer to the macroradical formed by that intramolecular transfer (7) then gives, in a typical concentration of 1 per 1000 carbons,[22] a dichlorobutyl branch structure (**BB**) containing tertiary chloride. When one molecule of VC is added to **7**, macroradical **8** results and subsequently experiences similar backbiting transformations. In the same manner as P$^{\bullet}$, radical **8** can form six-membered transition states, but now in two different ways, in order to generate radical **9** and/or radical **10**, whose subsequent addition to monomer should yield a 1,3-diethyl branch pair (**DEB**) or a 2-ethyl-*n*-hexyl branch structure (**EHB**). This double backbiting mechanism was first proposed for ethylene polymerization[23] and then confirmed to occur in that system on the basis of ^{13}C NMR studies by a number of researchers.[14,15,24-31] The possibility of double backbiting for

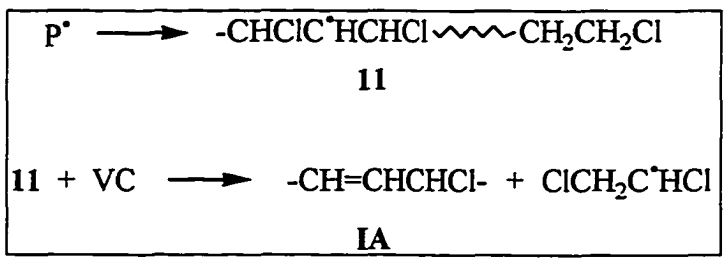


Scheme 4.3: Creation and reduction of branch structures formed by backbiting during the polymerization of VC,

where P• is the head-to-tail macroradical, and *k*s are rate constants

PVC has been noted previously,[32] as well as the likely thermal lability of the **DEB** and **EHB** structures,[32] resulting from their incorporation of two tertiary chloride moieties. In that study, the researchers[32] used a 50.31-MHz ^{13}C NMR instrument which was not able to detect these structures at low concentrations. We now have solved this analytical problem by using 125.77-MHz ^{13}C NMR. Proof for the existence of double backbiting structures in PVC has not appeared in the literature heretofore.

The same authors[32] described another process that starts with backbiting but produces the thermally unstable structure, internal allylic chloride. This process involves the abstraction of methylene hydrogen to form a rearranged radical, **11**, that can transfer adjacent chlorine to VC by β-scission and thus yield an **IA** array.



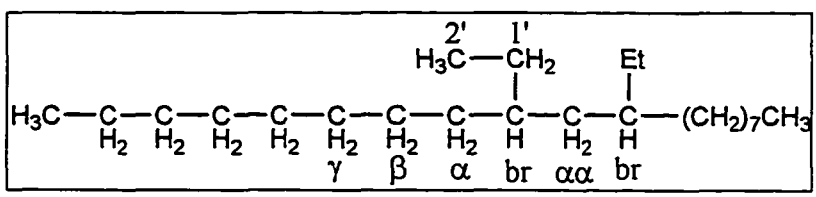
The intermolecular counterpart of the reaction that gives **11** is very likely to be involved in the polymerization, as is the donation of Cl• to VC from the resulting radicals. This overall process now is known to be important for chain transfer to the monomer.[1,2]

The experimental approach used in the work of this thesis involved the comparison of the ^{13}C chemical shifts of the model compounds 9-(2-ethyl-*n*-hexyl)heptadecane and 9,11-diethylnonadecane with those of PVC that had been reduced with tri-*n*-butyltin hydride.

4.3.1 Models for the 1,3-diethyl and 2-ethyl-*n*-hexyl branch structures

Prior to this investigation, ^{13}C chemical shifts had been reported for two **DiEt** models (5,7-diethyldocosane and 5,7-diethyldodecane)[27,28,33] and an **EtHe** model [12-(2-ethyl-*n*-hexyl)tricosane[27,28]]. Unfortunately, the conditions under which those shifts were measured (temperature and solvent) differed significantly from those under which all of our previous spectra of reduced PVC and PVC models had been obtained. Thus we found it necessary to prepare our own model compounds.

Our model for the **DiEt** structure was 9,11-diethylnonadecane:

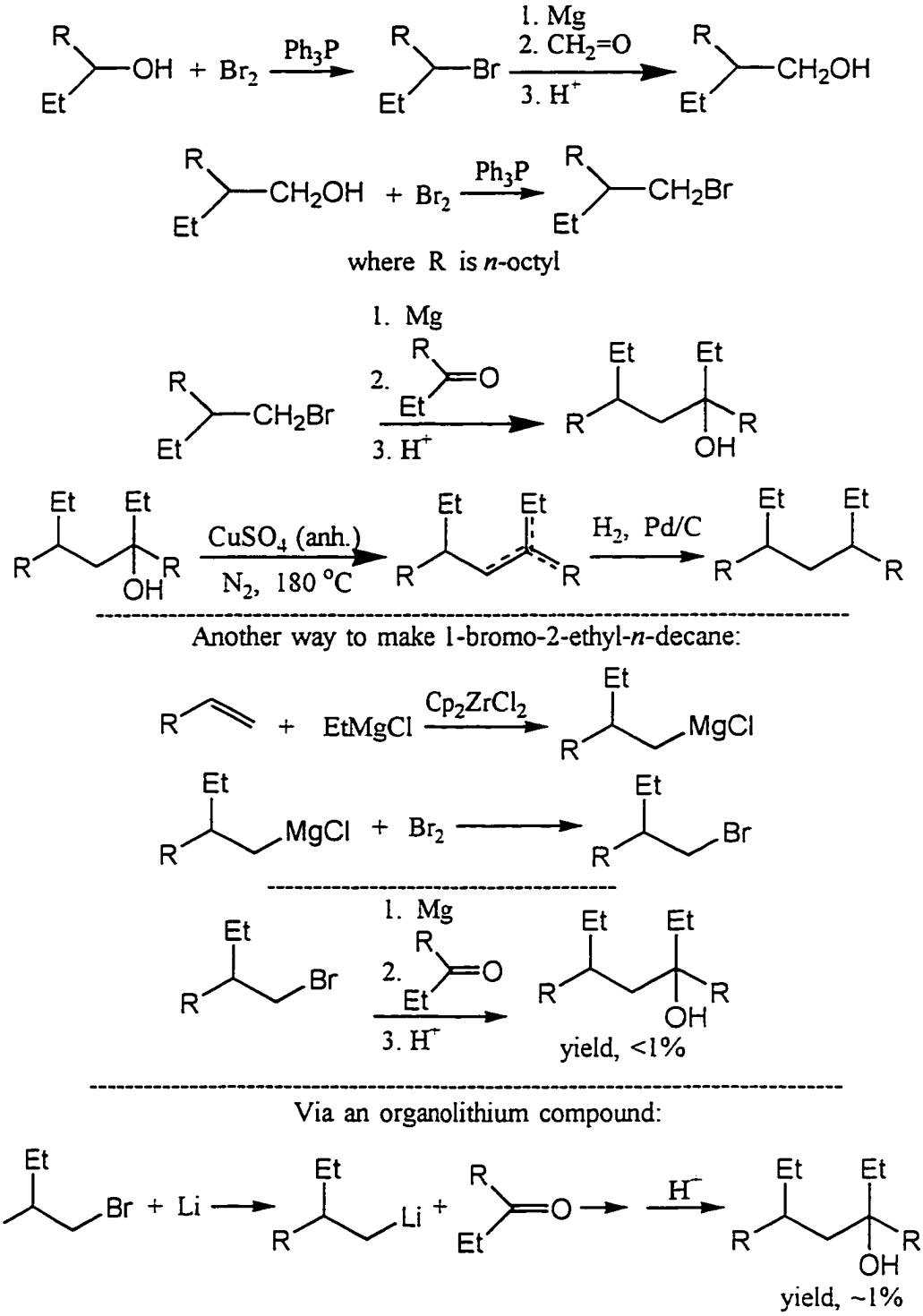


Such long alkyl chains were chosen because the chemical shift of a given backbone carbon in a model will be essentially identical with a polymer shift if a linear chain of at least six carbons is attached to the carbon of interest. In this particular case, we were interested in the exact shifts of branch-point carbons and their α and β neighbors, as well. As was described in the Experimental chapter, 9,11-diethylnonadecane was made by a Wurtz reaction of 3-bromoundecane and 1-bromo-2-ethyldecane. The 3-bromoundecane was obtained from the corresponding alcohol by adapting a well-known procedure. The other precursor, 1-bromo-2-ethyldecane, was acquired by adapting an elegant two-step sequence that involves the Cp_2ZrCl_2-promoted addition of a Grignard reagent to an alkene, followed by reaction of the adduct with an electrophile (Br_2 in our case). The Wurtz reaction gave 9,11-diethylnonadecane, the cross-coupling product, together with two dimers, 9,10-diethyloctadecane and 9,12-diethyleicosane, resulting from the

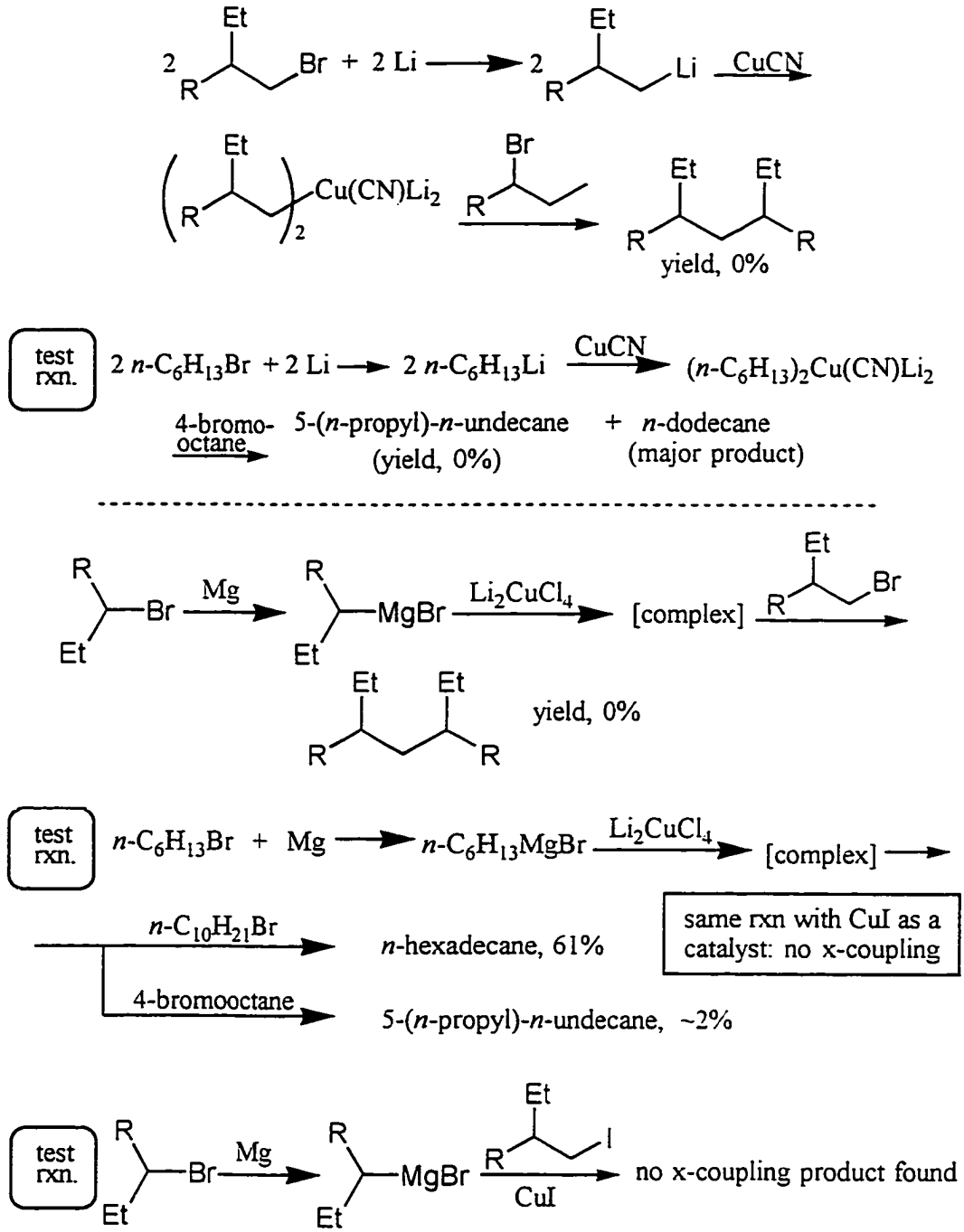
homocoupling of 3-bromoundecane and 1-bromo-2-ethyldecane, respectively. The isolation of 9,11-diethylnonadecane was not attempted and, in fact, was not required, because the diagnostic chemical shifts of that compound were determined easily from the ^{13}C NMR spectrum of the mixture of the three coupling products. Resonance assignments of these products were confirmed by comparisons with the spectra of authentic samples of 9,10-diethyloctadecane and 9,12-diethyleicosane that were made by the magnesium-promoted homocoupling of the corresponding bromides.

Prior to our successful synthesis of 9,11-diethylnonadecane by a Wurtz reaction, some unsuccessful attempts to prepare this model compound were made. The first route depicted in Scheme 4.4 failed at the second step, in that we were not able to make the primary alcohol by a Grignard reaction of 3-undecylmagnesium bromide with formaldehyde. When 1-bromo-2-ethyl-*n*-decane was eventually synthesized successfully, another problem arose. The yield in the Grignard reaction of 2-ethyl-*n*-decylmagnesium bromide with 3-undecanone (to obtain 9,11-diethylnonadecan-9-ol) was found to be less than 1%. Replacement of the Grignard reagent by an organolithium compound was not helpful, probably because of the high steric hindrance of the reactants. Therefore, this pathway was abandoned.

Other unsuccessful approaches employed cross-coupling reactions between 3-bromoundecane and 1-bromo-2-ethyl-*n*-decane in the presence of very effective cross-coupling catalysts[34] such as CuCN and Li_2CuCl_4, as is shown in Scheme 4.5. For simpler, less branched compounds, these catalysts work well, but in our reactions the yields were never more than a few percent. Replacement of a bromo compound with an iodide or the



Scheme 4.4: Unsuccessful attempts to synthesize 9,11-diethylnonadecane via organometallic compounds



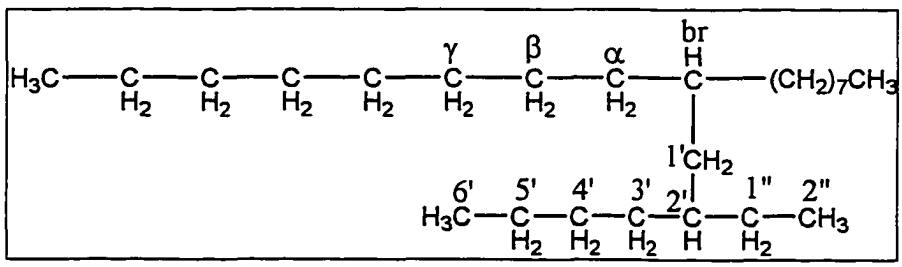
Scheme 4.5: Unsuccessful approaches to the synthesis of 9,11-diethylnonadecane via cross-coupling reactions

use of organolithium reagents were ineffective, and so this pathway was abandoned as well.

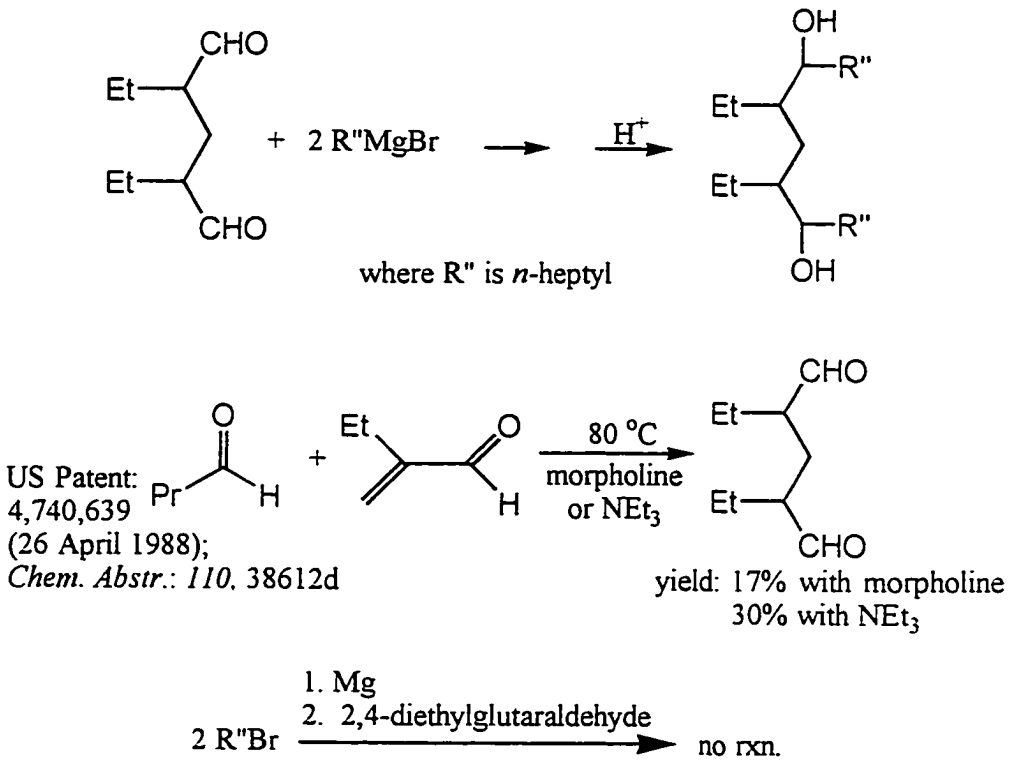
Our next attempt to obtain the model compound included a Grignard reaction between 2,4-diethylglutaraldehyde and *n*-octylmagnesium bromide (see Scheme 4.6). This reaction was to be followed by the dehydration of 9,11-diethylnonadecan-8,12-diol and catalytic hydrogenation. However, we failed to obtain 2,4-diethylglutaraldehyde in sufficient purity, and the Grignard reaction simply did not occur.

The last unsuccessful approaches were to involve the Wolff-Kishner reduction of the corresponding ketone to obtain 9,11-diethylnonadecane directly (see Scheme 4.7). Unfortunately, all of our attempts to prepare 9,11-diethylnonadecan-10-one met with failure.

Our model compound for structure **EtHe** was 9-(2-ethyl-*n*-hexyl)heptadecane:

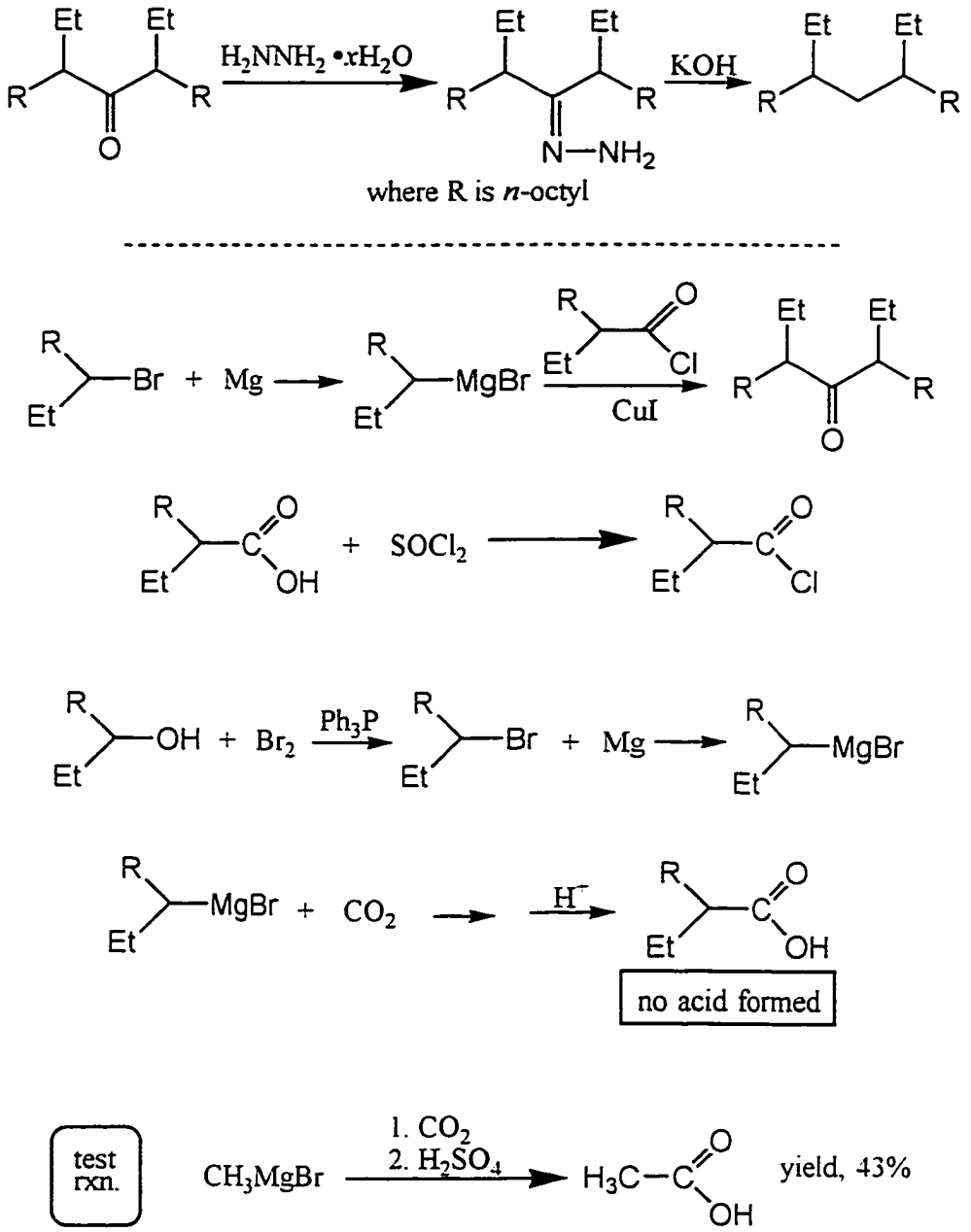


The last three steps in our synthesis of this material were similar to those used by Freche *et al.*[35] in order to obtain a series of 12-(*n*-alkyl)tricosanes. 1-Bromo-2-ethyl-*n*-hexane, prepared from the corresponding alcohol, was converted into a Grignard reagent that was allowed to react with 9-heptadecanone in the conventional way. The product tertiary alcohol was not isolated because of its dehydration during its attempted purification. It eventually was converted quantitatively into an alkene mixture by heating under vacuum.

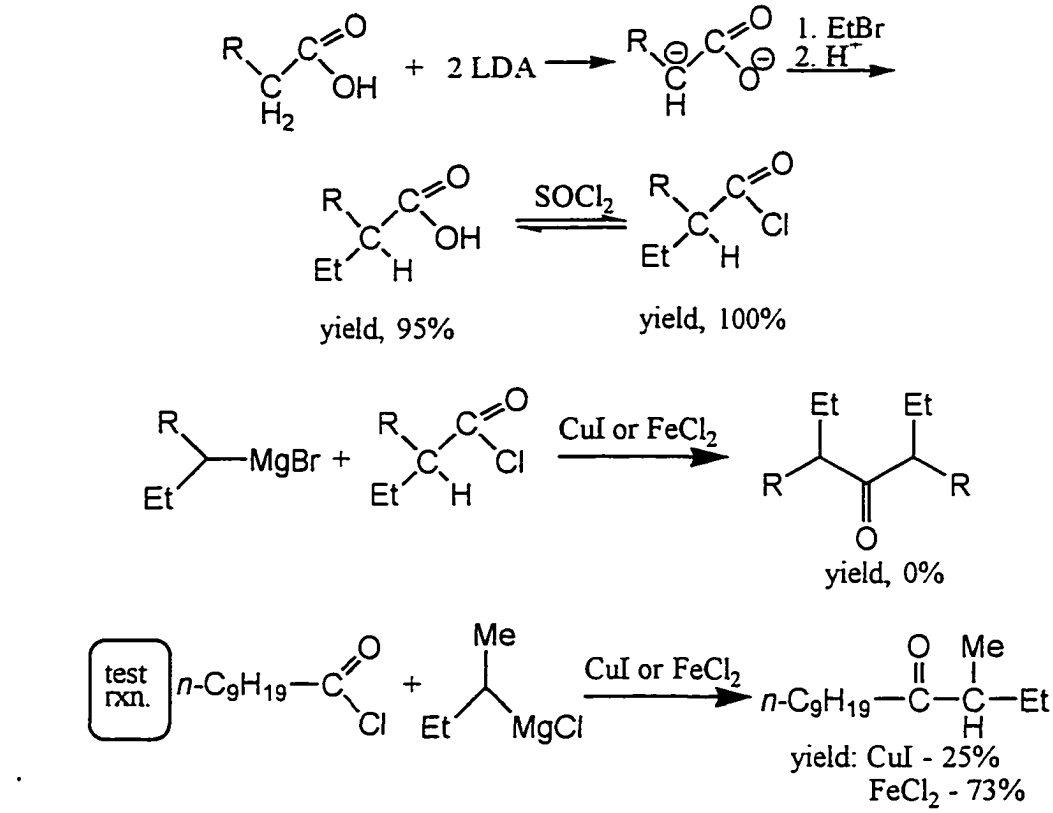


Scheme 4.6: Unsuccessful approach to 9,11-diethylnonadecane

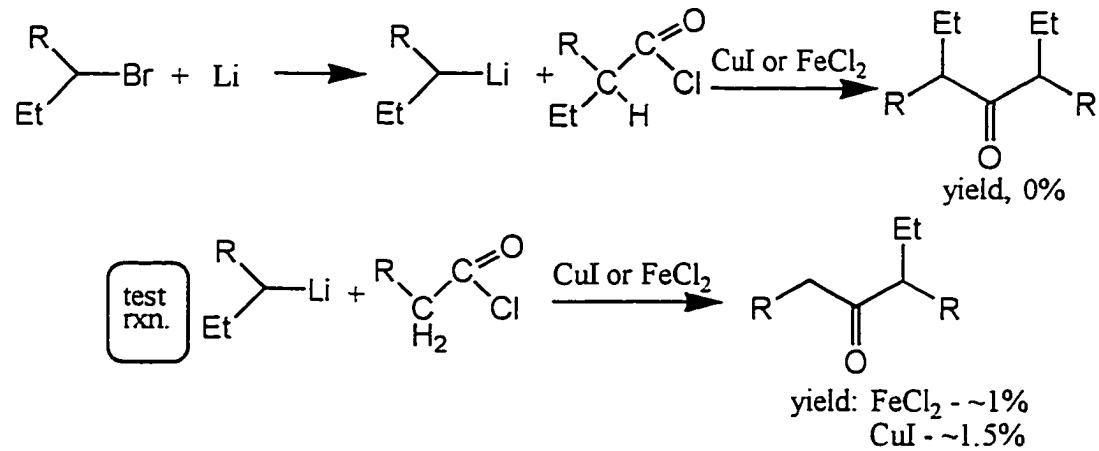
via 2,4-diethylglutaraldehyde



Scheme 4.7: Unsuccessful approaches to 9,11-diethylnonadecane via Wolff-Kishner reduction



Via an organolithium compound:



Scheme 4.7: Unsuccessful approaches to 9,11-diethylnonadecane via Wolff-Kishner reduction (continued)

The alkenes were identified as 9-(2-ethyl-*n*-hexyl)-8-heptadecene and 5-ethyl-7-*n*-octyl-6-pentadecene on the basis of their mass spectra, and both of them were reduced to 9-(2-ethyl-*n*-hexyl)heptadecane by catalytic hydrogenation. Analysis by GC/MS showed that the final mixture contained minor amounts of 9-heptadecanone and 9-heptadecanol as impurities. Their presence was confirmed by ^{13}C NMR. Fortunately, the diagnostic resonances of 9-(2-ethyl-*n*-hexyl)heptadecane, 9-heptadecanone, and 9-heptadecanol were not coincident and thus were easily assigned. A reference sample of 9-heptadecanol was synthesized by reduction of the corresponding ketone with lithium borohydride.

Table 4.1 contains predicted shift values and the diagnostic ^{13}C NMR shifts of the model compounds 9,11-diethylnonadecane and 9-(2-ethyl-*n*-hexyl)heptadecane, together with the corresponding shifts found for PVC.

In order to calculate the predicted values, temperature-corrected Grant-Paul parameters[36] were used to modify the chemical shifts of poly(ethylene-*co*-1-alkene)s[37] containing ethyl or *n*-hexyl branches. The specific temperature corrections[36] and starting shifts[37] were chosen because they had been obtained under conditions of solvent and temperature that were rather close to the conditions used in the work of this dissertation.

The experimental shifts of both model compounds are in good general agreement with both the predicted values and with the shifts of similar models measured under other conditions.[27,28,33,38] Owing to the mutual close proximity of the DiEt-1' and DiEt-β resonances, as well as the EtHe-1" and EtHe-β peaks, the assignments for all of those signals are tentative and might need to be transposed. The doubling found for most of the **DiEt** resonances appears to result from the presence of both the meso and the racemic

Table 4.1

^{13}C NMR chemical shifts of some possible structures resulting from "backbiting" and subsequent reductive dechlorination

carbon	δ,[a] ppm *vs.* Me_4Si		
	predicted[b]	model	polymer
DiEt-1'	27.22	27.05,[c] 27.13[c]	26.99, 27.06
DiEt-2'	11.25	10.98, 11.01	10.96, 11.00
DiEt-br	37.17	37.38, 37.42	37.30, 37.34
DiEt-αα	38.54	39.15	39.05
DiEt-α	34.52	34.43, 34.46	hidden
DiEt-β	27.36	27.19,[c] 27.23[c]	27.13, 27.16
EtHe-1'	39.05	39.53	not found
EtHe-2'	37.17	37.22	not found
EtHe-3'	34.09	33.97	not found
EtHe-4'	29.87	29.76[c]	not found
EtHe-5'	23.53	23.48	not found
EtHe-6'	14.35	14.16	not found
EtHe-1"	27.22	26.98[c]	not found
EtHe-2"	11.25	10.98	not found
EtHe-br	35.74	35.79	not found
EtHe-α	35.03	34.81, 34.88	not found

EtHe-β	27.48	27.07,[c] 27.12[c]	not found
EtHe-γ	30.68	30.55	not found

[a]Determined at 100 °C and 125.77 MHz from 15-20% (w/v) solutions in 1,2,4-trichlorobenzene/*p*-dioxane-d_8 (*ca.* 4:1 v/v). [b]See text for discussion. [c]Tentative assignment.

stereoisomers. However, the doubling of the EtHe-α and EtHe-β resonances must be ascribed to the presence of the single chiral center. An analogous phenomenon is the magnetic nonequivalence of the isopropyl methyl carbons of $(CH_3)_2CH\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_2\text{-}CH_3$.[39]

4.3.2 Identification of doubly branched structures in reduced PVC

The diagnostic resonances of the model compounds were searched for in the ^{13}C NMR spectra of dechlorinated samples of PVC that had been made previously[1] at constant VC pressures which ranged from 59% to 100% of the pressure at saturation. After dechlorination, the polymers made at the lowest VC pressures displayed several **DiEt** resonances in their spectra. The chemical shifts of the **DiEt** carbons in such a reduced PVC specimen are given in Table 4.1, and the resonances are assigned in Fig. 4.5, which displays partial spectra for both the model compound (Part A) and the polymer (Part B).

Some of the **DiEt** peaks in Fig. 4.5-B can be identified easily, *e.g.*, DiEt-br and DiEt-2'. The DiEt-αα peak also is present, but its assignment is rather tentative, and the assignment shown might need to be interchanged with that for the Cl-β signal. In spite of

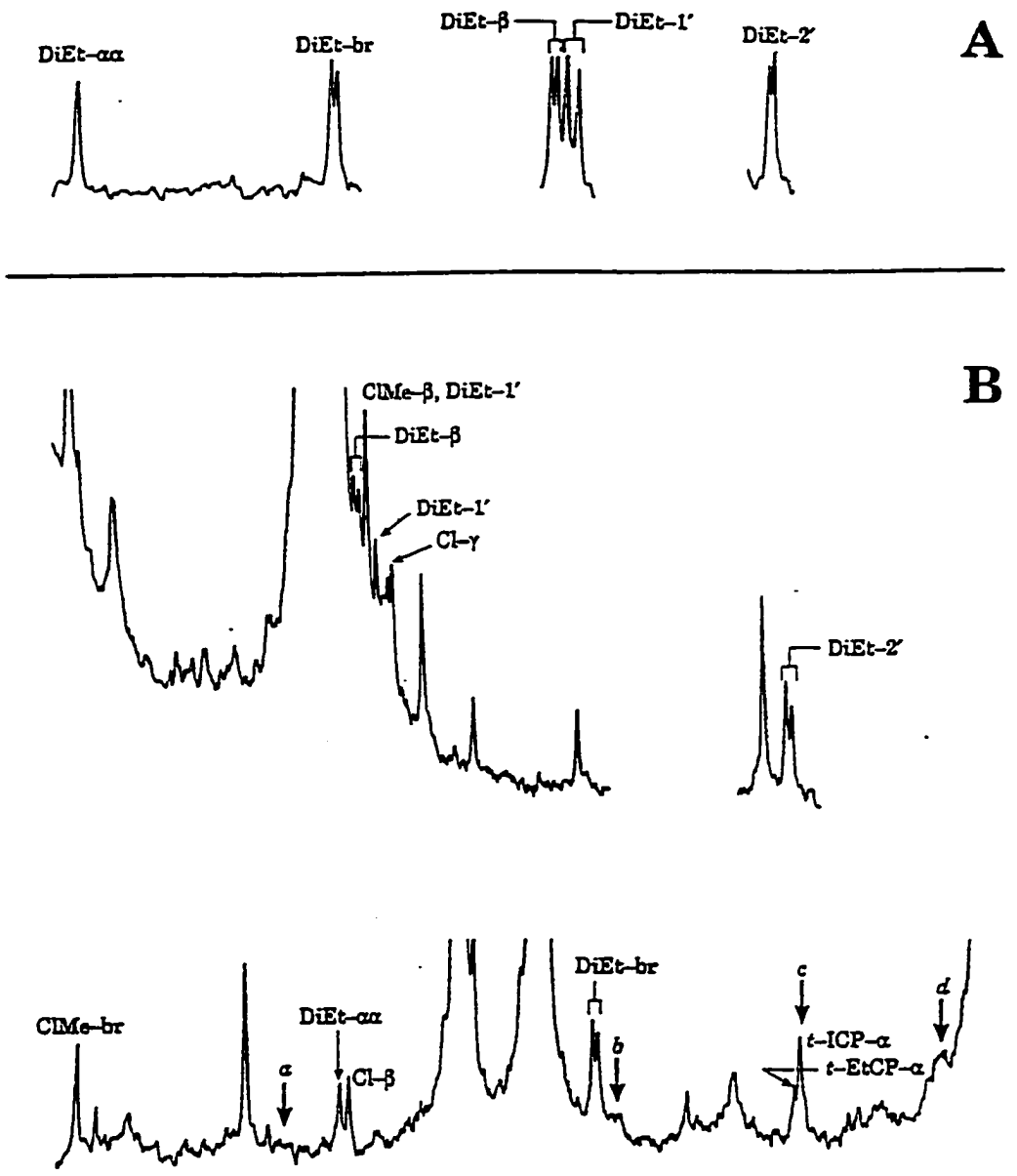
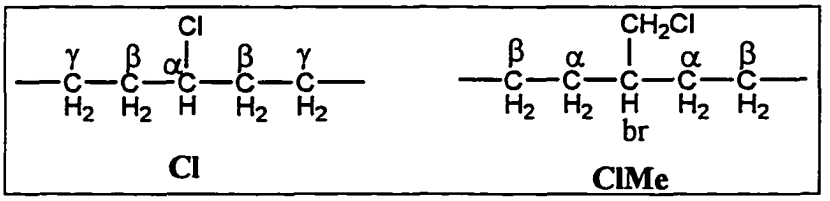


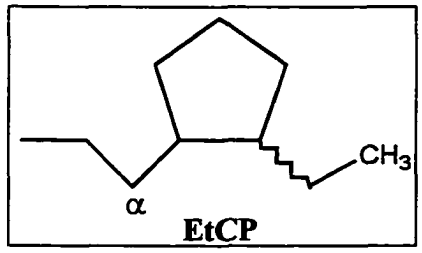
Fig. 4.5: Proton-decoupled ^{13}C NMR partial spectra [125.77 MHz, 100 °C, 1,2,4-trichlorobenzene/*p*-dioxane-d_8 (*ca.* 4:1 v/v)] of (**A**) model compound 9,11-diethylnonadecane and (**B**) a Bu_3SnH-reduced PVC specimen made at 55 °C with a VC pressure at 59% of the pressure at saturation. Because of insufficient agitation, the VC concentration in the polymer particles was less than the equilibrium value and, as a result, the M_n of the unreduced polymer (2.5×10^4) was abnormally low (see ref. 1). Arrows *a* - *d* denote the expected shift positions of some of the **EtHe** carbons listed in Table 4.1.

very high conversion in the reductive dechlorination, very small amounts of isolated residual chlorines still are found, as in these structures:



The assignments made for the DiEt-β and DiEt-1' signals are quite consistent with the spectrum of the model compound (Fig. 4.5-A), despite the obvious coincidence of the downfield branch of the DiEt-1 doublet with the ClMe-β peak. The presence of the **ClMe** structure[40] was established by the observation of all of its unique resonances, including the ClMe-br peak shown in Fig. 4.5-B. The only **DiEt** peaks that do not appear in the polymer spectrum are those for the DiEt-α carbons. However, their absence was expected, because they would be obscured by the much stronger Bu-α resonance[32] that is identified in Scheme 4.3.

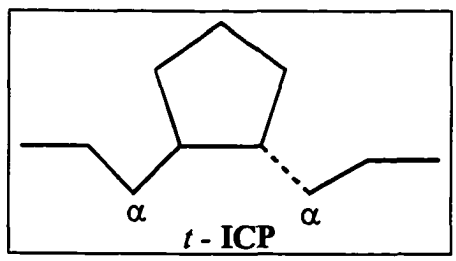
There is some uncertainty about the presence of a DiEt-γ signal. According to its calculated shift value (30.40 ppm), this resonance is likely to be obscured by the huge peak for conventional -CH_2- groups. However, a spectrum of a similar reduced PVC sample revealed two weak shoulders at 30.61 and 30.65 ppm. It is possible that one or both of those resonances came (at least in part) from DiEt-γ carbons. On the other hand, it must be noted that the cis isomer of the **EtCP** structure studied prevously[41] would also produce a resonance at *ca.* 30.6 ppm. Moreover, the ^{13}C NMR spectrum of the mixture of 9,10-diethyloctadecane, 9,11-diethylnonadecane, and 9,12-diethyleicosane contained two peaks at 30.55 and 30.57 ppm; whereas purified samples of 9,10-diethyloctadecane and



EtCP

9,12-diethyleicosane exhibited only singlets in this region. The doubling observed in the polymer spectrum could have resulted from the presence of two DiEi-γ resonances or from a difference in the shifts of signals associated with different compounds.

In contrast to our clear proof for the existence of the **DiEt** structure in PVC made under monomer-starved conditions, no good evidence was obtained for the presence of the **EtHe** moiety in our reduced PVC samples. There are no unambiguous peaks at positions where signals from the **EtHe** structure should appear in our ^{13}C NMR spectra. For example, the singlet denoted by arrow *b* at *ca.* 37.0 ppm and the doublet *d* at *ca.* 34.7 ppm might be recognized as the resonances of the EtHe-2' and EtHe-α carbons, respectively. However, these peaks are very weak or undetectable in other spectra of reduced PVC which reveal the presence of significant amounts of the **DiEt** moiety. Moreover, it is impossible to conclude that the resonance denoted by arrow *c* belongs to the EtHe-br carbon, because the signal of that carbon should overlap the *t*-ICP-α/*t*-EtCP-α composite peak.[42] The EtHe-br peak might appear as an upfield shoulder on the



t - ICP

t-ICP-α/*t*-EtCP-α composite signal, but other reduced-PVC spectra do not contain it.

Perhaps the strongest evidence for the absence of the **EtHe** structure from reduced PVC is the failure of the EtHe-1' resonance to appear at its expected position, which is denoted by arrow *a* (at *ca.* 39.5 ppm) in Fig. 4.5-B. The spectrometer used has a high enough field strength to resolve this resonance from both of its nearest neighbors, whose shapes and intensities give no evidence for its presence as a coincident peak. Furthermore, a change of solvent from 1,2,4-trichlorobenzene to tetrachloroethane-d_2 did not cause the emergence of any new resonances from the peaks that are closest to arrow *a*.[42]

The **DiEt**:**EtHe** ratio for low-density polyethylene (LDPE), as derived from statistical calculations,[43,44] is exactly 1:1. On the other hand, in striking contrast, our ^{13}C NMR spectra indicate that the **EtHe** concentration in our reduced PVC samples was always less than that of the **DiEt** structure by a factor of 3-4, at least.

4.3.3 Concentrations of the branch structures formed by backbiting

The formation rates of the **BB** and **DEB** structures, produced as in Scheme 4.3 under steady-state conditions, are given by equations 1 and 2 (molar concentrations are denoted by brackets).

$$d[\mathbf{BB}]/dt = k_b k_a[P^\bullet][VC]/(k_a[VC] + k'_b) \quad (1)$$

$$d[\mathbf{DEB}]/dt = k_b k'_b[P^\bullet]/(k_a[VC] + k'_b) \quad (2)$$

$$d[PVC]/dt = k_p[P^\bullet][VC] \quad (3)$$

Since most of the P$^\bullet$ radicals are conventional head-to-tail ones, the polymerization rate can be described by equation 3, where k_p is the conventional rate constant for propagation,

and [PVC] is the concentration of polymerized VC units. The concentrations of **BB** and **DEB** per monomer unit (ρ_{BB} and ρ_{DEB}) then are given by equations 4 and 5, which when added or divided yield equations 6 and 7, respectively. Equation 8 is obtained by dividing equation 7 by equation 6.

$$\rho_{BB} = \frac{d[\mathbf{BB}]/dt}{d[\mathrm{PVC}]/dt} = \frac{k_b k_a}{k_p(k_a[\mathrm{VC}] + k'_b)} \tag{4}$$

$$\rho_{DEB} = \frac{d[\mathbf{DEB}]/dt}{d[\mathrm{PVC}]/dt} = \frac{k_b k'_b}{k_p[\mathrm{VC}](k_a[\mathrm{VC}] + k'_b)} \tag{5}$$

$$\rho_{BB} + \rho_{DEB} = k_b/k_p[\mathrm{VC}] \tag{6}$$

$$\rho_{DEB}/\rho_{BB} = k'_b/k_a[\mathrm{VC}] \tag{7}$$

$$\rho_{DEB}/\rho_{BB}(\rho_{BB} + \rho_{DEB}) = k'_b k_p/k_b k_a \tag{8}$$

The values of k_a and k_p should be similar, owing to the structural resemblance of macroradicals P$^\bullet$ and **8** (see Scheme 4.3). The **DiEt** concentration per monomer unit is equal to ρ_{DEB} (when the very low concentrations of incompletely reduced[40] **DEB** structures are ignored), and ρ_{BB} represents the sum of the concentrations of the fully reduced **Bu** unit and another partially unreduced structure, -CH_2-CH(CH_2-CH_2-CH_2-CH_2Cl)-CH_2-.[21,40] Thus the values of ρ_{DEB} and ρ_{BB} for the original, unreduced polymer could be obtained from the complete spectrum shown in part as Fig. 4.5-B. They were found to be $0.3_3 \times 10^{-3}$ and 4.8×10^{-3}, respectively, and they lead to a value of 13 for $k'_b k_p/k_b k_a$ ($\approx k'_b/k_b$), according to equation 8. An analogous approach gave an approximate

k'_b/k_b value of 17 for another polymerization performed at 55 °C with a constant VC pressure at 59% of saturation. In this case the respective values of ρ_{DEB} and ρ_{BB} were found to be $0.3_0 \times 10^{-3}$ and 4.1×10^{-3}. This change is attributed to agglomeration during polymerization that resulted from inefficient agitation and led to a PVC M_n value of 2.9×10^4. The mean k'_b/k_b value of 15±2 for 55 °C confirms an expectation based upon relative rates of backbiting during LDPE synthesis,[23,43] *i.e.*, that the second backbite would occur significantly faster than the first one.

The backbiting reactions of P$^\bullet$ and **8** are very similar with regard to reactants, transition states, and products. Hence, according to the analogy with LDPE,[43] the inequality of k_b and k'_b can reasonably be ascribed to differences in conformer populations. In the case of ethylene polymerization, the conformational statistics predicted a very small effect of temperature on the rate ratio for backbiting.[43] Recently, for ethylene the maximum conformational contribution to the difference between the activation energies of the first and second backbites has been estimated to be only 1.8 kcal/mol.[42] Moreover, due to structural similarities, the activation energies associated with k_a and k_p should be nearly equivalent. Therefore, the expression $k'_b k_p/k_b k_a$ should be nearly insensitive to temperature changes. This conclusion has been verified by the data obtained for a PVC sample prepared at 80 °C under a constant monomer pressure that was 59% of the pressure at saturation.[1] In this case, the $k'_b k_p/k_b k_a$ value was 16, as deduced from the ρ_{DEB} and ρ_{BB} values, which were $0.3_3 \times 10^{-3}$ and 4.4×10^{-3}, respectively. We conclude that within the error limits of our measurements, the values of $k'_b k_p/k_b k_a$ obtained at 55 and 80 °C are identical.

In a recent publication,[21] good straight lines were obtained from plots of ρ_{BB} *vs.* $[VC]^{-1}$ that were based on Hjertberg and Sörvik's data for polymers made at various temperatures.[6] From equation 6 it is obvious that such linearity can occur only when ρ_{DEB} is small. Rearrangement of equation 8 yields equation 9, which was used to calculate

$$\rho_{DEB} = \frac{(\rho_{BB})^2}{(k_b k_a / k'_b k_p) - \rho_{BB}} \tag{9}$$

values of ρ_{DEB} from the Hjertberg and Sörvik[6] ρ_{BB} data and $k'_b k_p / k_b k_a$ values of 15 or 16. The results revealed that ρ_{DEB} was never greater than 0.1×10^{-3}. This finding shows that the inclusion of ρ_{DEB} in the ρ_{BB} *vs.* $[VC]^{-1}$ plots[21] would have had only minor effects on their slopes. However, ρ_{DEB} inclusion should slightly improve the regression fits of some of those plots by increasing the higher branch concentrations.

A straight line also was obtained for some polymers made at 40 °C in solution when their ρ_{BB} values were plotted *vs.* $[VC]^{-1}$.[21] For this series of samples, the values of ρ_{BB} fall within the range, $(0.9 - 5.6) \times 10^{-3}$,[21] and the **DEB** concentrations found from equation 9 (with $k'_b k_p / k_b k_a$ set equal to 15) are in the range, $(0.01 - 0.5) \times 10^{-3}$. A double-regression plot of equation 6 made with these data has an R^2 value of 0.97 and gives a k_b/k_p ratio of 3.0×10^{-3} M. This ratio corresponds well with the k_b/k_p value of 2.5×10^{-3} M found previously[21] for heterogeneous polymerizations at 40 °C. The k_b/k_p ratio actually should be larger in heterogeneous media than in solution if propagation is controlled by diffusion at high conversions under heterogeneous conditions.[21] Thus, the present work confirms the argument that was made earlier[21] against the occurrence of diffusion-controlled propagation in heterogeneous polymerization.

Inversion of equation 5 gives equation 10, which can be used for the calculation of ρ_{DEB} as a function of VC concentration if the k_p/k_b and k_a/k'_b values are available for the temperature of interest. These ratios can be obtained from equations 6 and 7 when the required data have been collected for one or more PVC samples.

$$(\rho_{DEB})^{-1} = \frac{k_p[VC]}{k_b}\left(\frac{k_a[VC]}{k'_b} + 1\right) \tag{10}$$

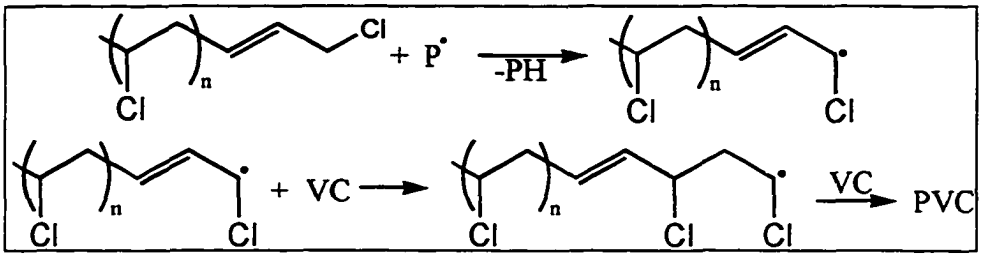
In accordance with equation 5, ρ_{DEB} depends in part on $[VC]^{-2}$, rather than exclusively on $[VC]^{-1}$. For this reason, ρ_{DEB} increases more rapidly with conversion than do the concentrations of the other thermally labile defect structures.[1,21] Thus, the **DEB** structure may significantly reduce the thermal stability of polymer fractions that are made when the monomer concentration in the polymerizing system has reached low levels. On the other hand, the **DEB** concentrations in commercial polymers should be relatively low.

4.4 Chain transfer by H$^{\bullet}$ abstraction from PVC chain ends

It was shown previously[1] that the number of $-CH_2CH{=}CHCH_2Cl$ chain ends in PVC decreases significantly when the polymerization of vinyl chloride is carried out under subsaturation VC pressures. Simultaneously, the concentration of internal allylic groups increases substantially, but the total number of double bonds per polymer molecule remains essentially the same. One approach toward an understanding of these phenomena was discussed above in Section 4.2. Another approach will now be briefly described.

According to information published earlier,[1] the mechanism shown in Scheme 4.8 can account for all of the facts. In order to prove or disprove this mechanism, two model

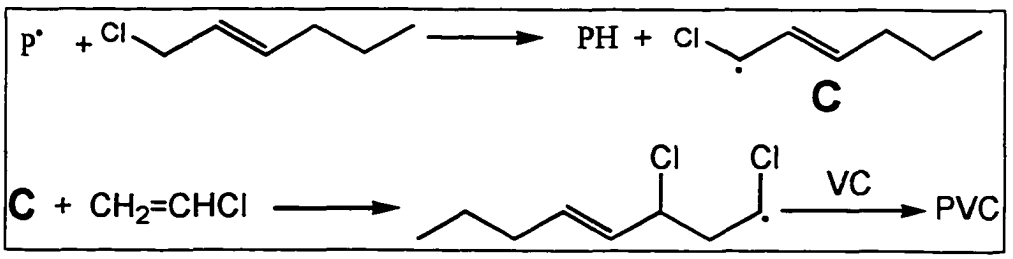
Scheme 4.8: Chain transfer by H• abstraction from allylic ends



compounds were synthesized* and used as transfer agents in some polymerizations of vinyl chloride that were initiated by dimethyl 2,2'-azobisisobutyrate at 80±1 °C. These models were *trans*-1-chloro-2-hexene and *trans*-1,5-dichloro-2-pentene. High-field NMR was used to characterize the resulting polymers.

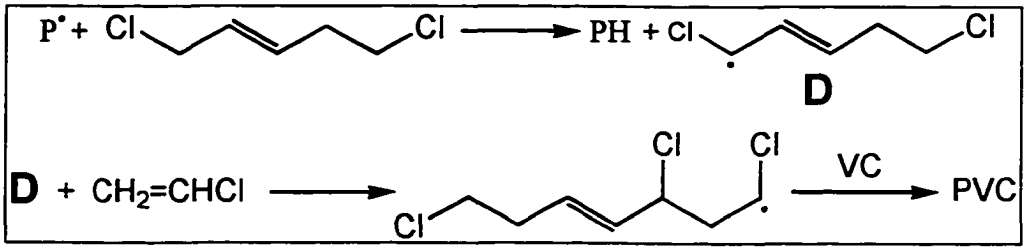
The purpose of these experiments was to detect, if possible, specific peaks in the NMR spectra that corresponded to atoms in end groups derived from the model compounds. The anticipated routes to those end groups are shown in Schemes 4.9 and 4.10.

Scheme 4.9: Chain transfer to *trans*-1-chloro-2-hexene during VC polymerization



* By Dr. H. T. Chung and S. Frantz

Scheme 4.10: Chain transfer to *trans*-1,5-dichloro-2-pentene during VC polymerization



Our preliminary ^{1}H and ^{13}C NMR work strongly suggests that both of the model compounds were incorporated into the polymers in the ways that these schemes depict. The mechanism of Scheme 4.8 also is supported by several pieces of indirect evidence that will be described in a forthcoming publication on this subject.[45]

CHAPTER 5

CONCLUSIONS

1. Several model monochloroalkenes were synthesized in order to determine ^{13}C shift increments for the replacement of H by Cl at positions that are α, β, or γ to an isolated internal double bond in a linear carbon chain. These increments then were used to predict the ^{13}C shifts of the internal allylic chloride structure in PVC. The predictions were not satisfactory, a result which showed that, as expected, the increments were not additive.
2. During conventional VC polymerization, the chloroallylic chain end (-CH_2-CH=$CHCH_2Cl$) does not copolymerize with the monomer and is not destroyed by a mechanism involving allylic rearrangement, macroradical addition, and chlorine-atom β-scission to produce a -$CHClCH_2CH$=$CHCH_2CHCl$- structure. Nevertheless, that mechanism was found to operate during the preparation of a special type of PVC [made at 0 °C with (t-Bu)$_2$Mg initiation] which contained the rearranged chain end, -CH_2-$CHClCH$=CH_2, at an abnormally high concentration.
3. During the preparation of PVC under subsaturation VC pressures, small amounts of a 1,3-di(2-chloroethyl) branch structure were found to be formed by a "double backbiting" mechanism involving two intramolecular H abstractions in succession. The presence of this structural defect was established by the 125.77-MHz ^{13}C NMR spectra of reductively dechlorinated PVC specimens. At 55-80 °C, the two backbites leading to the defect differ substantially in relative rate, in that the backbiting:addition rate ratio is larger for the second backbite by a factor of 15-16 (mean value), irrespective of temperature. No evidence was obtained for the presence of the 2-ethyl-

n-hexyl branch structure that would have resulted from double backbiting by an alternative route. The absence of this structure and the presence of the 1,3-di(2-chloroethyl) branch array were confirmed by spectral comparisons with the ^{13}C shifts of two reference models, 9,11-diethylnonadecane and 9-(2-ethyl-*n*-hexyl)heptadecane, that were prepared by unambiguous tactical methods.

4. Polymerizations of VC were performed in the presence of two potential transfer agents, *trans*-1-chloro-2-hexene and *trans*-1,5-dichloro-2-pentene. Preliminary examination of the resulting polymers by high-field NMR provided evidence for the destruction of the $-CH_2CH=CHCH_2Cl$ chain end, during polymerization, by a mechanism involving H abstraction to form the $-CH_2CH=CHC^{\bullet}HCl$ radical, followed by the addition of that species to VC in order to give the thermally unstable structure, $-CH_2CH=CHCHClCH_2-$.

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CHAPTER 4. RESULTS AND DISCUSSION

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VITA

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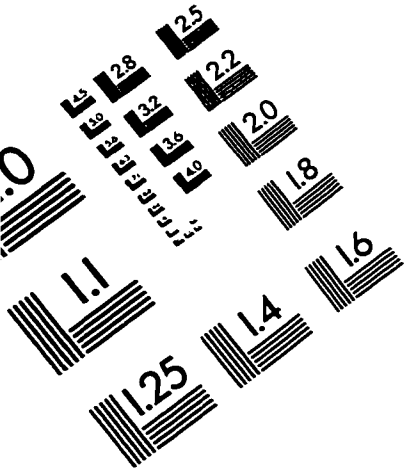
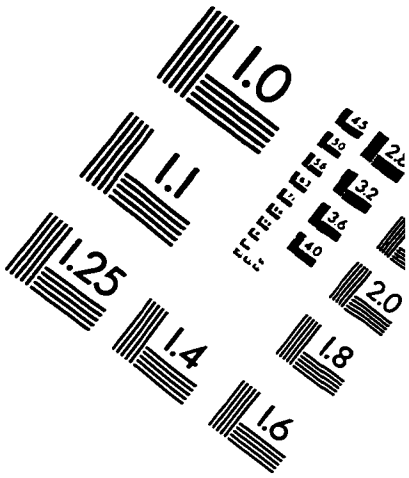
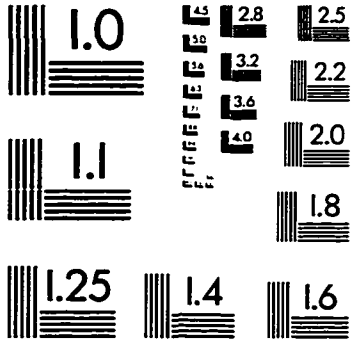
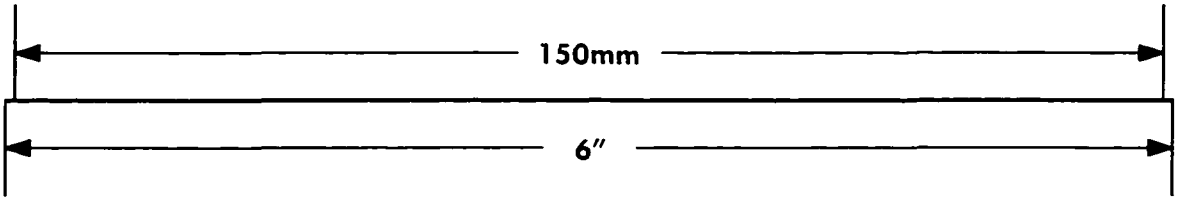
The author entered the Department of Applied Science, College of William and Mary, in August 1992 to do doctoral research under the guidance of Dr. William H. Starnes, Jr., in the field of polymer science.

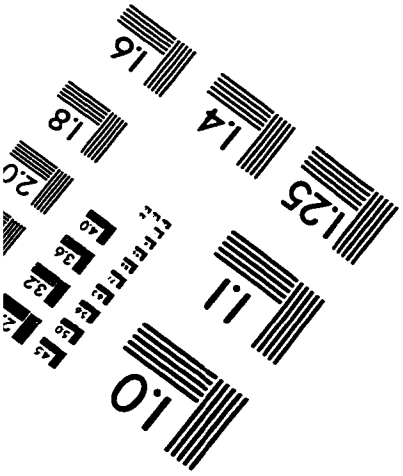
IMAGE EVALUATION TEST TARGET (QA-3)

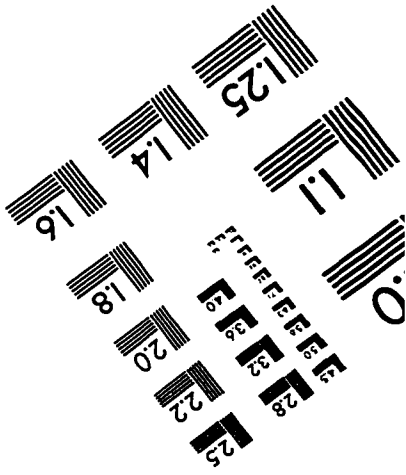












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