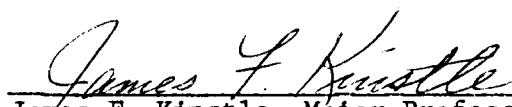
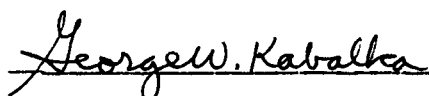


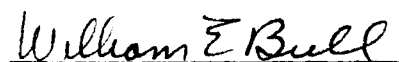
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I am submitting herewith a thesis written by George L. Quinlan entitled "The Preparation and Use of Boron Trifluoride Poly(p-Methoxystyrene) Etherate: A New Supported Phase Homogeneous Catalyst." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

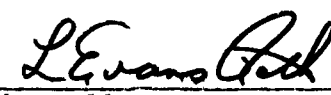
  
James F. Kinstle, Major Professor

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THE PREPARATION AND USE OF BORON TRIFLUORIDE  
POLY(p-METHOXYSTYRENE) ETHERATE: A NEW  
SUPPORTED PHASE HOMOGENEOUS  
CATALYST

A Thesis  
Presented for the  
Master of Science  
Degree  
The University of Tennessee

George L. Quinlan

March 1980

1116281

## DEDICATION

I wish to dedicate this thesis to my father, Reverend Ronald Frazer Quinlan, who truly gave life to the definition of the word "man." He was an inspiration, a motivation, a Christian in a world of sinners, and a very beloved father.

This one is for you, Daddy.

## ACKNOWLEDGEMENTS

I wish to thank Dr. James F. Kinstle for his friendship, guidance, and especially for his unending patience during the course of this research.

There are many other people who deserve thanks for their aid: Mr. Darrell Lay and Mr. Edward Wilson for their limitless resources and friendship; Mr. Paul Williams for his thin layer chromatography work; Mrs. Carrie Chambers and Mr. J. Erwin for their mass spectral and  $^1\text{H}$  NMR spectral data, and Mr. L. H. Norman for his expertise in glass blowing.

I also wish to express my thanks to all my friends who made my research experience endurable. Finally, I wish to express my gratitude to my wife. Her aid with typing as well as her endless love and patience are beyond description or repayment.

## ABSTRACT

The preparation and use of a new heterogeneous catalyst with homogeneous properties was undertaken. The catalyst made and studied was the boron trifluoride complex of poly(p-methoxystyrene).

The polymer for the catalyst was obtained by thermal and free radical polymerization of p-methoxystyrene. The polymer was dissolved and boron trifluoride gas was bubbled through the solution. The resulting complexed polymer was then precipitated and dried.

In order to use the catalyst effectively, the amount of  $\text{BF}_3$  attached to the polymer backbone had to be determined. This was attempted by the following methods: (a) NMR, which proved ineffective due to the model compounds freezing in the NMR tubes before an integration curve could be established. (b) U.V., which also failed since the anisole center had adsorptivity orders of magnitude greater than the  $\text{BF}_3$  in the same regions. (c) Titration with a pH meter, which proved the best way available and gave sufficient results ( $\pm 10\%$  error).

The utility of the polymeric catalyst was evaluated for rearrangement reactions, specifically that of 1-octene to 2-octene, and of limonene epoxide to dihydrocarvone. The catalyst was also used for preparation of the symmetrical ether from dicyclopropyl carbinol. Yields were achieved using this new catalyst, which were higher than those previously seen for the same reactions.

Along with testing productivity, experiments were done to examine polymer complex solubility and selectivity changes when using a cross-linked polymer backbone as a support.

Enhanced properties were noticed in ease of catalyst separation, handling, and in catalytic site protection. The major problem was determined to be polymer backbone rearrangement which led to the impossibility of rejuvenation and difficulties in solubility.

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## CHAPTER I

## INTRODUCTION

As most chemists know, there are basically two types of catalyst systems; the homogeneous system and the heterogeneous system. The one principally used by most industrial chemists is the heterogeneous type. Homogeneous (chelated transition metal) catalysis itself is fairly new to the industrial world, accounting for only 5% of catalysis in 1960, but increasing to 15% in 1970. As research continues, the homogeneous systems' uses increase more and more. With the introduction of the supported phase homogeneous catalyst, homogeneous catalysis in industry looks even more promising.<sup>1</sup>

The reasons for using homogeneous catalysts are simple. Firstly, a homogeneous catalyst often offers more selectivity and higher activity than does a heterogeneous catalyst. The entire metal atom in a homogeneous catalyst is "free" for the reaction, whereas only the metal atoms at or near the surface of a heterogeneous catalyst are available for reaction. This accounts for the higher activity of the homogeneous system. The increased selectivity results from the extra orbitals and electronic configurations open in the homogeneous catalyst. A heterogeneous catalyst atom usually has other metal atoms around it, leaving only a few orbitals open for reaction. The homogeneous catalyst atom is totally free with no other metal atoms attached to it, and so, provides more variation in electronic sites and orbitals for combination and reaction with other atoms.<sup>2</sup>

Another reason for using a homogeneous catalyst is the greater temperature control at the catalytic site. In a heterogeneous system,

heating of a solid and a liquid with different thermal coefficients allows temperature differences in the system. However, in the homogeneous case, one is, in theory, heating a continuous system with only one thermal coefficient.<sup>1</sup>

Even though a homogeneous catalyst has these desired properties, it has major defects, such as difficulties in separation from reaction media. In a chemical reaction, a heterogeneous catalyst can be removed by simple filtration, but removal of a homogeneous catalyst is often a multistep procedure.<sup>3</sup>

Not only is it difficult to separate the homogeneous catalyst, but it is even harder to separate the catalyst without destroying its catalytic properties. Thus, another major drawback of the homogeneous catalyst system is cost. No matter how much increased activity the homogeneous system gives, it is usually too expensive to use when a 50% loss occurs in separation. So it is that present day industry relies more on the heterogeneous catalyst.<sup>4</sup>

Still another drawback to the homogeneous catalyst system is the allowable concentrations. In a homogeneous system, one has free movement of the catalyst molecules, allowing the metal atoms to react inter- and intramolecularly. This forming of metal atom aggregates at a high concentration "poisons" the catalyst as the aggregates have little or no catalytic activity. In a heterogeneous system, the metal atoms are fixed relative to one another and cannot form aggregates.

Finally, a homogeneous catalyst is restricted to low temperatures since at high temperatures most homogeneous catalysts are not stable. In industry, most reactions are run at high temperatures and pressures. So by limiting oneself to low temperatures, one loses a number of

useful reactions. A heterogeneous catalyst, however, tends to be more stable at high temperatures and the temperature range of the catalyst is greatly increased as is its usefulness.<sup>1,2</sup>

From 1962-1965, Merrifield proposed and developed the synthesis of enzyme materials on a supported phase.<sup>5</sup> "Supported phase" synthesis has developed much since that time. As this method of chemical synthesis came into more prominence, a parallel activity started in attaching nonpeptide substances to a resin, substances such as catalysts. Since its conception, much research has been done on this type of system, mainly because the new type of catalysis shows the combined properties of homogeneous and heterogeneous catalysts.

Comparing a supported phase catalyst to each individual type previously mentioned, one can see many benefits or combinations of properties. Perhaps the easiest to see is the separation of the catalyst support from the solution and products; i.e., simple filtration vs. a many step process often found in homogeneous systems. Not only can one separate the catalyst from the reaction media, but one can often separate products that are otherwise hard to separate by leaving them attached to the solid matrix when washing off the starting materials. One can then go back and remove the products in a subsequent step as Rubinstein did using a polymeric arylsulfonyl chloride as compared to the solution used catalyst, mesitylenesulfonyl chloride.<sup>6</sup>

Another benefit is cost, since the cost of making a polymer attached catalyst is usually less than the cost of losing significant amounts of the catalyst during isolation of the products.<sup>4</sup>

One more benefit, not as readily noticed, is selectivity which is usually maintained or even increased relative to a homogeneous

catalyst. The metal atom in a solid phase support is not surrounded by other metal atoms and does not have the strong metallic bonding seen in solid metals. Instead the metal is physically entrapped or impregnated on the support, is held by a coordination bond or by a carbon metal bond. For example, Rony (1969) used bis(triphenylphosphine) rhodium carbonyl chloride catalyst dispersed on silica gel for the hydroformylation of propylene,<sup>7</sup> Grubbs (1973) used the same catalyst attached to a chloromethylated styrene-divinylbenzene resin for a hydrogenation catalyst,<sup>8</sup> and Pittman (1973) has conducted reactions with a pentacarbonylmanganese anion on a chloromethylated resin.<sup>4</sup> Not only does the metal atom have selectivity, but the support provides added selectivity through solvent channels and polarities.<sup>8,9</sup> If the solvent channel is small, then only small molecules can reach the catalyst. If a good solvent for the resin is used, it swells the resin, and solvent channels open, allowing larger molecules to reach the catalyst. Also, a nonpolar solvent can carry a molecule through a solvent channel of a nonpolar resin faster than a polar solvent can, providing a wide range of selectivities.

Closely related to the selectivity and ease of purification of the solid phase catalyst is its activity. Many researchers report yields far exceeding those found in solution with very few, if any, side reactions occurring. But as with selectivity, there are many variables which control the activity of the catalyst, namely: the temperature of the reaction, the percentage of cross-linking in the polymer support, and the concentration of the catalytic group on the solid support. The temperature affects the activity not only through increasing kinetic energies to overcome activation energies, but

through polymer movement. At high temperatures in solutions, homogeneous catalysts form aggregates which destroy the catalyst's activity, something they cannot do when held apart from each other by a fixed support. When the metal atoms are separated from each other by attachment to a resin, properties of infinite dilution can be realized. However, at higher temperatures, the  $T_g$  (glass transition temperature) of the polymer is surpassed, and the fixed support gains new mobility allowing the catalysts to form these self-poisoning aggregates. This mobility can be overcome, allowing one to use higher temperatures, by increasing the percentage of cross-linking in the polymer. As the amount of cross-linking goes up, however, pore size decreases and solvent penetration becomes more difficult, thereby increasing the amount of time it takes for a molecule to reach the catalytic site and decreasing the reaction rate. Another alternative to very high cross-linking is a low concentration of catalytic sites. If the metal atoms are very far away from each other, more polymer chain movement can be allowed as compared to the case where the metal atoms are in close proximity to one another. To increase catalyst concentration in a reaction, one would simply add more of the supported complex. If infinite dilution could be realized, unwanted side reactions might be avoided.<sup>4</sup> All of these variables and others give each solid phase supported catalyst its own selectivity and reactivity, which are determined principally by catalyst concentration and variation of metal aggregation in the resin.

Many illustrations of these concepts are in the literature.

For example, Patchornik allowed chloromethylated polystyrene-2%

divinylbenzene and phenyl acetic acid to react and obtained the polymer bound ester. The obtained ester was converted into the enolate by trityllithium in tetrahydrofuran (THF). After disappearance of the base, excess of an acid chloride was added and after cleavage from the support with dry HBr a single ketone and unreacted acid were the products.<sup>10,11,12</sup> Patchornik also mentions restrictions upon infinite dilution; i.e., temperature, concentration, and cross-linking. Another example, perhaps the best, is Grubb's use of a 20% divinylbenzene styrene support with a highly reactive titanocene catalyst.<sup>13</sup> To do this a 20% cross-linked macroreticular copolymer was 13.6% chloromethylated using chloromethylethyl ether and tin(IV) chloride. This chloromethylated polymer was then reacted with sodium cyclopentadiene to give methylcyclopentadiene substituted styrene. Using methyllithium reagent followed by cyclopentadiene titanium trichloride, Grubb's got a titanocene dichloride substituted polymer, with which he obtained remarkable yields of hydrogenation. Crowley, however, states that infinite dilution is impossible and attributes the reported successes to purification advantages and/or poor laboratory expertise.<sup>14</sup> It is indeed hard to imagine 100% site separation, due to the chemistry of polymers and the high probability that two sites will be in close some type of dilution process performed by the solid phase even though Crowley says that at 0.5% resin substitution, one cannot get site separation.

Along with selectivity, separation, activity and (the ultimate) infinite dilution properties, one has many other properties that are

promising. These include solvent protection and solvent-resin interaction for site-availability control, and the wide range of catalysis available.

Many reagents used today are very sensitive to air, very volatile, lachrymators, or possess some other undesirable property. When bonded to or trapped within a solid support, one may overcome many of these traits by expanding the resin and placing the catalyst deep inside the solvent channels. By changing the solvent and contracting the channels, one keeps air and water out as well as keeping the catalyst in. If water cannot get in, it cannot react with or dilute the catalyst. If the catalyst cannot get out, it will not evaporate or smell. Examples of reagent protection are those of Necker's polystyrene bound  $\text{AlCl}_3$ <sup>15</sup> and of Trost's supported Pd on silica gel.<sup>9</sup>

As mentioned earlier, solvent-resin interactions are very important. Not only does it change selectivity and activity, but by varying the solvent, one can theoretically go from pure heterogeneous to homogeneous behavior, or one can pick any desired intermediate between these extremes.<sup>4</sup>

Overall, the range of reactions promoted by these solid-phase catalysts is very wide including hydrogenation, hydrosilylation, hydroformylation, acetoxylation, polymerization, and oligomerization. Along with these reactions, there are many other examples found in patents. A few are listed in a table from Chauvin.<sup>16</sup>

Looking at all of these promising properties, one would imagine that industry would immediately shift to solid-phase supported homogeneous catalyst. However, there are many areas in the

field that are not well defined. Some discussed by Crowley and Rapoport are: (a) the effect of polymer structure on the catalyst; i.e., does atactic work better than syndiotactic, etc., (b) adequate analytical methods of analysis, (c) the nature of the kinetics of the reactions and (d) the exact nature of the catalytic site.<sup>14</sup>

Much research has been done to overcome these and other problems. For example in 1969, Rony did experiments to determine diffusion rates of supported catalysts.<sup>7</sup> Lately, the methods of temperature programmed desorption and temperature programmed reaction have been used to study the kinetics and mechanisms of methanation of CO on different supported catalysts.<sup>17</sup>

Understanding the nature of the catalytic site and the effect of the polymer structure upon reaction pretty much depends on the other problem mentioned; i.e., adequate methods of analysis. The most common method that shows some success is infrared spectroscopy (IR). Since IR detects twisting, bending, rotational and vibrational motions, one can get a wide variety of signals that lead to a complex spectrum which is unique for different functional groups and types of bonding.<sup>18</sup> The problem with IR is the obscurity added to the spectrum by the polymer backbone. The multiple bonds and varying configurations seen in the polymer chain give such a background that it is hard to pick out specifics. Still, IR has been used to identify species and amounts of gases absorbed on supported catalyst.<sup>19</sup> It has also been used to demonstrate site competition between different gaseous species as well as to characterize adsorption sites, adsorbate structure, and the mode of bonding. IR has also been used to determine the structure of

adsorbed reaction intermediates and products.<sup>20,21</sup> Crowley suggested using the support in the reference beam to cancel out backbone absorptions in the supported catalyst spectra.<sup>14</sup> However, the answer seems to be in the use of computerized IR as it greatly increases sensitivity and the scope of techniques one may use as well as permitting one to do quantitative handling of data along with background reduction, peak addition and averaging, and spectrum subtraction.<sup>22</sup>

Nuclear magnetic resonance spectroscopy (NMR) has been used a lot and is fairly common but it also has a problem of obscurity due to lack of resolution over the very small range of hydrogen shifts provided by proton NMR. <sup>13</sup>C is promising but has not been used extensively in this area.<sup>13</sup>

Elemental analysis, atomic absorption and potentiometric titration have been used but they can only provide a measure of amounts of catalysts present. These methods do not provide information about catalyst distribution or site arrangement.

Electron microscopy (EM) has been used to obtain the size and shape of metal clusters on the support, as well as information on the dispersion (defined as the % of atoms in a cluster present in the surface) and the distribution of the metal catalyst. EM can work where chemisorption cannot; for example, EM can be used when the metal is copper, where chemisorption is not analytically useful because Cu will not adsorb H<sub>2</sub>. Another EM benefit is that it gives information on all metal atoms in a sample where X-ray analysis gives information only on large clusters. One must be careful with EM however, for in

cases where the dispersion is high, it gives qualitative instead of quantitative results.<sup>23,24,25</sup>

A majority of surface analyses of supported catalysts have included chemisorption, mentioned above, because it is one of the best ways to find the degree of metal surface area. Chemisorption is based on two assumptions; (a) there is no chemisorption on the support, and (b) for a given metal adsorbate pair, the reaction stoichiometry depends neither on the particle size nor on the nature of the carrier. Its major drawbacks are that the assumptions are not always correct and that one cannot predict average particle size by chemisorption alone, but needs other information such as cluster size, amount of sintering, and cluster shape.<sup>23,24</sup>

To obtain particle size, one usually uses X-ray diffraction (XRD). XRD has been used to determine the amount of metal in clusters on the support as well as to determine particle size and to confirm results by chemisorption. To do a particle size determination, one has to use a calibration curve prepared from X-ray spectra of well defined salts with known particle sizes. XRD is a useful method to measure metal dispersion and is good even when the dispersion is poor. Though used often, XRD has many problems: (a) It cannot be used without chemisorption which enables one to calculate the extent to which the XRD detected metal represents the total amount of metal. (b) XRD experiments have to meet 3 constraints to be reliable; (i) instrumental conditions must be assumed constant over the entire period of the experiment, (ii) the amount of metal and the area irradiated must be kept constant, (iii) the sample must be effectively infinitely thick to X-rays. (c) Discrepancies arise from X-ray

absorption. (d) Areas calculated from XRD are too high when aggregation occurs. (e) One must assume particle shape unless using another method of analysis such as EM. (f) XRD is ineffective when particle size is below 3nm.<sup>23,24,25,26</sup>

The electron probe microanalyzer provides a rapid nondestructive technique for determination of distribution. The resolution is very good, several microns, and more than enough to do general analysis.<sup>27</sup>

Another method of X-ray analysis is proton induced X-ray emission (PIXE). PIXE has the qualities of a finely focussed beam and good scanning ability and is used to determine local distributions of trace elements in a selected area. Aside from this, it can be used for implanting heavy atoms in a selected pattern. PIXE has two problems (a) dead time effects and (b) fluctuations in beam intensity.<sup>28</sup>

Electron spin resonance (ESR) has been used in studies of structure of these materials. This technique is sensitive enough to measure low concentrations and oxidation states. It has been used to study  $S_3^-$  radicals and their attraction to the catalyst support and has also been used to gain information of coordination of surface ions and the extent of interaction between them. Its major problem is that  $O_2$  inhibits the ESR signal.<sup>29,30,31</sup>

One of the more widely used techniques is Electron Spectroscopy for Chemical Analysis (ESCA). ESCA is one of the few techniques that can give direct evaluation of a species on a support surface. ESCA has been used to gain information on dispersion and on distribution. It also has the property that peak intensities are proportional, in the first approximation, to the surface atom

concentration and the photoionization cross-section. It has also been used to get information on the metal atom's valence and physical state, as well as to demonstrate metal atom changes with different supports and variations in methods of catalyst preparation. In order to use ESCA, one needs some well defined spectra for comparison purposes but it has been shown that the spectrum of the supported metal differs from the unsupported metal.<sup>32,33,34,35</sup>

The ion microprobe has been used selectively in supported catalyst analysis for ion distributions in double metal layers. It is the one method that is independent of electrical or optical activation. Problems with the microprobe concern: (a) charge formation on the support surface, (b) variation in sputtering rates, (c) allowances have to be made for diffusion of metal atoms (d) yield changes for the secondary ions at the interface of the two metals and (e)  $O_2$  layers. Charge formation can be overcome by using an aluminum grid. Sputtering rates may be equalized by allowing  $O_2$  to enter the system but then problem (d) increases.<sup>36</sup>

Inelastic tunneling spectroscopy (ITS) has been used to measure the vibrational spectrum of the submonolayer coverages of organic molecules absorbed on surfaces. The method has good sensitivity, spectral range and resolution but one cannot use the method on "off the shelf" catalysts. ITS methods have many constraints, so one has to prepare special catalysts.<sup>37</sup>

Titration of chemisorbed  $O_2$  with  $H_2$  has been used as a more accurate method of determining the fraction of exposed metal surface

in supported catalysts. The method shows good reproducibility after the first titration which homogenizes the surface. There is no pattern for the first titrations of different catalysts due to the irreproducibility of the fresh catalyst surface.<sup>38</sup>

Other methods are X-ray absorption, used to get information or coordination numbers, interatomic distances, and vibrational motions of atoms in clusters;<sup>39</sup> Raman spectroscopy, used as a structural probe and done by comparison of catalyst spectra of well established salts, has a spatial resolution of one micron;<sup>40,41</sup> Auger electron spectroscopy, used in determination of dispersions and distributions;<sup>34</sup> and Transmission Electron Microscopy (TEM) used in metal particle size distribution, degree of metal dispersion, and metal surface area. Problems common to all of the previously mentioned methods of analysis are effective specimen preparation methods and representative handling.<sup>42</sup>

Not only does one have the regular problems to solve, specifically nature of kinetics, adequate methods of analysis, and nature of catalytic site, but when combining the properties of homogeneous and heterogeneous catalysts one also combines the problems and difficulties. For example, when gaining access to higher temperature regions by solid support, one loses temperature control at the catalytic site; i.e., one is again heating two phases, much like that in a heterogeneous catalyst. With the polymer support in solution, one is still maintaining even heat distribution outside the polymer, but the heat transferral inside the polymer to the catalytic site is different from the heat transferral available to the purely homogeneous catalyst.<sup>43</sup>

As can be seen above, much research has been done on the understanding of established catalysts as well as on producing new catalysts. Most all of the new catalysts produced, however, are those using a transition metal as the catalytic species. It has been reported by Neckers et al.,<sup>15</sup> that  $\text{AlCl}_3$  on polystyrene had good catalytic properties which represents the first time anyone used a Lewis Acid on a solid support. But there are many other Lewis Acids and many other supports.

Borontrifluoride has many desirable properties for a catalyst. It is a strong electron acceptor, Lewis Acid, and is small so that it imparts little hindrance when bound to or complexed with another molecule. Some reactions that it may be used to catalyze are alkylation, polymerization, addition of oxygen or sulfur to organic substances, isomerization, nitration, sulfonation, condensation, cracking, dealkylation, disproportionation, and the addition of oxygen containing organic compounds to acetylenic and trienic compounds.<sup>44</sup>

With so many qualities, one would expect it to be widely used and it is. But it does present some problems. For example,  $\text{BF}_3$  is a gas and until the use of  $\text{BF}_3$ -diethyletherate, one had to have vacuum lines, pressure gauges and other costly gas use apparatus. With the discovery of  $\text{BF}_3$ -etherate, one could easily measure out with conventional volumetric apparatus the amount of  $\text{BF}_3$  needed. But  $\text{Et}_2\text{O} \cdot \text{BF}_3$  is very sensitive to air and should be kept refrigerated. In air,  $\text{BF}_3$  forms a white cloud as it reacts with water to give boric acid and hydrogen fluoride. And if allowed to get too hot, the  $\text{BF}_3$  tends to leach out of the ether. A solution to these problems would seem to be to incorporate the  $\text{BF}_3$  onto a solid phase support. One could,

in principle, get protection from water, better thermal stability and easier handling.

In choosing a polymer as a support resin, Chauvin says that there are certain things to look for, specifically a functional group to which the catalyst can be attached and a backbone with good mechanical properties. Specific properties mentioned were attrition resistance, porosity, thermal stability, lack of solubility, and an easily accessible site for the catalytic species.<sup>16</sup>

It seemed natural to choose a polymer with an ether group for  $\text{BF}_3$  attachment, since so much is known about  $\text{BF}_3$  and its complex formation with ethers. It also seemed reasonable to use a polymer much like polystyrene since it has been the common support for many previous catalysts and since it has shown good mechanical properties. The combination of these two thoughts has led us to investigate the formation and utility of the complex formed between  $\text{BF}_3$  and poly-(p-methoxystyrene).

## CHAPTER II

## EXPERIMENTAL PROCEDURES

## A. Materials

Acetone - (certified) - Fisher Scientific, used as received.

Acetonitrile - (certified) - Fisher Scientific, used as received.

Ammonium Sulfate - (certified granular) - Fisher Scientific, used as received.

Anisole - (reagent) - Aldrich Chemical Company, redistilled from Na(s) under  $N_2(g)$  before use.

Argon Gas - (prepurified) - Selox Corporation, passed through  $CaCl_2$  drying tube.

Azobisisobutyronitrile - (reagent) - Eastman, recrystallized from methanol.

Benzene - (certified) - Fisher Scientific, dried over  $4\text{\AA}^O$  molecular sieves.

Benzophenone - (reagent) - Eastman, used as received.

Boron Trifluoride - (gas) - Matheson, Coleman and Bell, lecture bottle, used as received.

Boron Trifluoride Diethyl Etherate - (practical) - Eastman, used as received.

Bromobenzene - (certified) - Fisher Scientific, used as received.

Calcium Chloride - (lab grade) - Fisher Scientific, used as received.

Carbon Dioxide - (solid) - Air Products, used as received

Chloroform, Deuterated - (99.8 atom %, NMR quality) - Aldrich Chemical Company, used as received.

Dicyclopropyl Ketone - (reagent) - Pfaltz and Bauer, used as received.

Dimethylsulfoxide - (99 + % reagent) - Aldrich Chemical Company, used as received.

Dioxane - (certified) - Fisher Scientific, redistilled over Na.

Drierite - (anhydrous) - Hammond Drierite Company, used as received.

Ethanol - (reagent) - Fisher Scientific, used as received.

Ethyl Acetate - (certified reagent) - Fisher Scientific, used as received.

Ether, Diethyl - (certified anhydrous) - Fisher Scientific, used as received.

Fluorolube - Fisher Scientific, used as received.

Fluran - Fisher Scientific, used as received.

Formaldehyde - (certified) - Fisher Scientific, used as received.

Glycerol - (white) - Fisher Scientific, used as received.

Hexane - (certified) - Fisher Scientific, used as received.

Hydrochloric Acid - (reagent) - J. T. Baker Chemical Company, used as received.

Hydrogen Peroxide - (certified) - Fisher Scientific, used as received.

Limonene - (technical) - Eastman, used as received.

Lithium Aluminum Hydride (LAH) - (reagent) - Alfa Products, used as received.

Magic Acid - (spectro grade) - Aldrich Chemical Company, used as received.

Methanol - (certified) - Fisher Scientific, used as received.

p-Methoxystyrene - (reagent) - Aldrich Chemical Company, used as received.

Methylene Chloride - (certified reagent) - Fisher Scientific, used as received.

Methyl Red - (reagent) - Aldrich Chemical Company, used as received.

Molecular Sieves - (reagent) - Fisher Scientific, used as received.

Nitrobenzene - (reagent) - Metheson, Coleman and Bell, dried over <sup>0</sup><sub>4A</sub> molecular sieves.

Nitrogen Gas - (prepurified) - Selox Corporation, used as received.

Nitrogen Liquid - (coolant) - Air Products, used as received.

Nitromethane - (certified reagent) - Fisher Scientific, used as received.

1-Octene - (reagent) - Fisher Scientific, used as received.

Paraffin Wax - (block) - Sargent Welch, cut into small chips - used as received.

Phosphorus Pentoxide - (certified) - Fisher Scientific, used as received.

Phthalic Anhydride - (certified) - Fisher Scientific, used as received.

Potassium Hydrogen Phthalate - (99.95, gold label) - Aldrich Chemical Company, used as received.

Potassium Iodide - (certified granular) - Fisher Scientific, used as received.

Sodium - (metal) - Fisher Scientific, used as received.

Sodium Bisulfate - (certified anhydrous) - Fisher Scientific, used as received.

Sodium Chloride - (certified) - Fisher Scientific, used as received.

Sodium Hydroxide - (certified) - Fisher Scientific, used as received.

Sodium Sulfate - (anhydrous) - Fisher Scientific, used as received.

Sulfuric Acid - (reagent) - Allied Chemical Company, used as received.

Tetrachloroethylene - (certified) - Fisher Scientific, used as received.

Tetrahydrofuran - (certified) - Fisher Scientific, redistilled from LAH.

Tetramethylsilane - (99.9 +%, NMR grade) - Aldrich Chemical Company, used as received.

Toluene - (certified) - Fisher Scientific, redistilled over Na.

Triethylamine - (certified) - Fisher Scientific, used as received.

Xylenes - (certified) - Fisher Scientific, used as received.

Zinc - (reagent-mossy) - Allied Chemical Company, used as received.

#### B. Synthesis of Anisole-Boron Trifluoride Complex

A 17.84 g ( $1.65 \times 10^{-1}$  mole) portion of purified anisole, bp  $146.5^{\circ}\text{C}$  uncorrected (lit  $155^{\circ}\text{C}$  at 760 mm),  $^{45}\text{H}$  and  $^{13}\text{C}$  NMR spectra<sup>46,47</sup> shown in Figures 1a and 2a, respectively, was added

to a predried 3-necked round bottomed flask equipped with a stirring bar, reflux condenser, and gas inlet tube. The entire set up was heated with a bunsen burner and flushed with argon. After approximately 5 minutes, the heating was discontinued and the glassware was allowed to cool. After cooling to room temperature, the reaction flask was placed into an ice bath and brought to  $0^{\circ}\text{C}$  while still being flushed with argon. Once all air was assumed to be displaced by argon, the bubble tube was connected to a lecture bottle of boron trifluoride ( $\text{BF}_3$ ) gas. All ground glass joints and stopcocks were greased with  $\text{BF}_3$  resistant grease, Fluorolube<sup>R</sup>, to prevent them from freezing and all other glass connections were secured with Fluran<sup>R</sup> tubing to prevent gas leakage.  $\text{BF}_3$  was then bubbled through the anisole very slowly with slight stirring at  $0^{\circ}\text{C}$  for varying amounts of time.

Three differences could be noticed immediately upon completion of the  $\text{BF}_3$  addition to anisole.

1. The solubility had changed; e.g., TMS was no longer as soluble when added to a sample prepared for an NMR spectrum.

2. The  $^1\text{H}$  NMR spectrum was different in the aromatic region; i.e., instead of showing the multiplet of the substituted benzene ring, it changed progressively to nearly a singlet, as shown in Figure 1b. The  $^{13}\text{C}$  NMR spectrum also was altered, as shown by comparing Figure 2a with Figure 2b.

3. A slight red discoloration of the anisole had taken place. Several attempts were made to determine the origin of this color. A washing train according to the method of Stone was used to purify the argon gas.<sup>48</sup> The train consisted of two scrubbers, one with a solution of 0.4 M chrome alum, 0.05 M  $\text{H}_2\text{SO}_4$  and mossy zinc, followed by

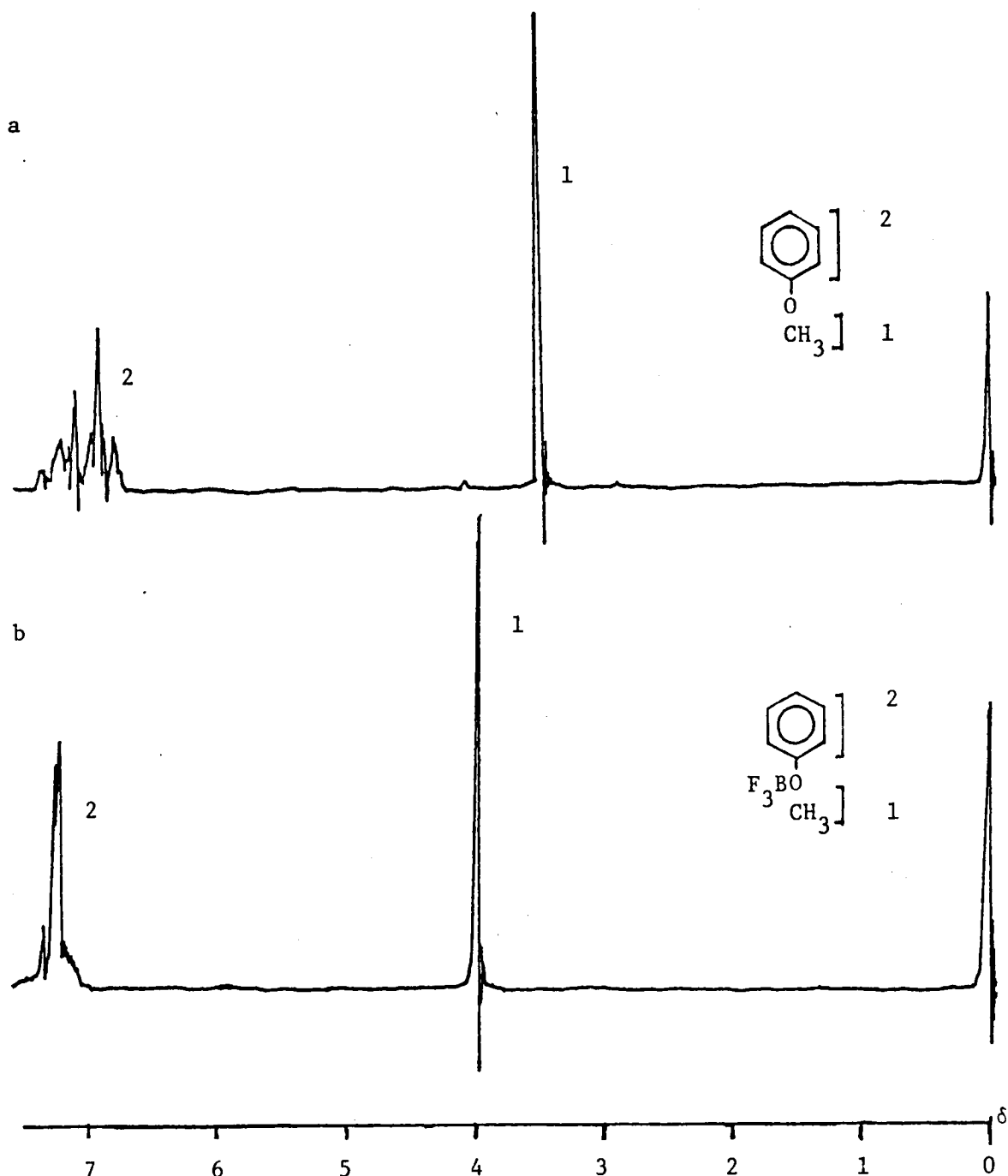


Figure 1.  $^1\text{H}$  NMR spectra of anisole and the saturated  $\text{BF}_3$  complex of anisole. Both (a) anisole and (b) the saturated complex were obtained neat at 60 MHz and  $25^\circ\text{C}$ . TMS was insoluble in the first attempts but would go into solution upon much agitation.

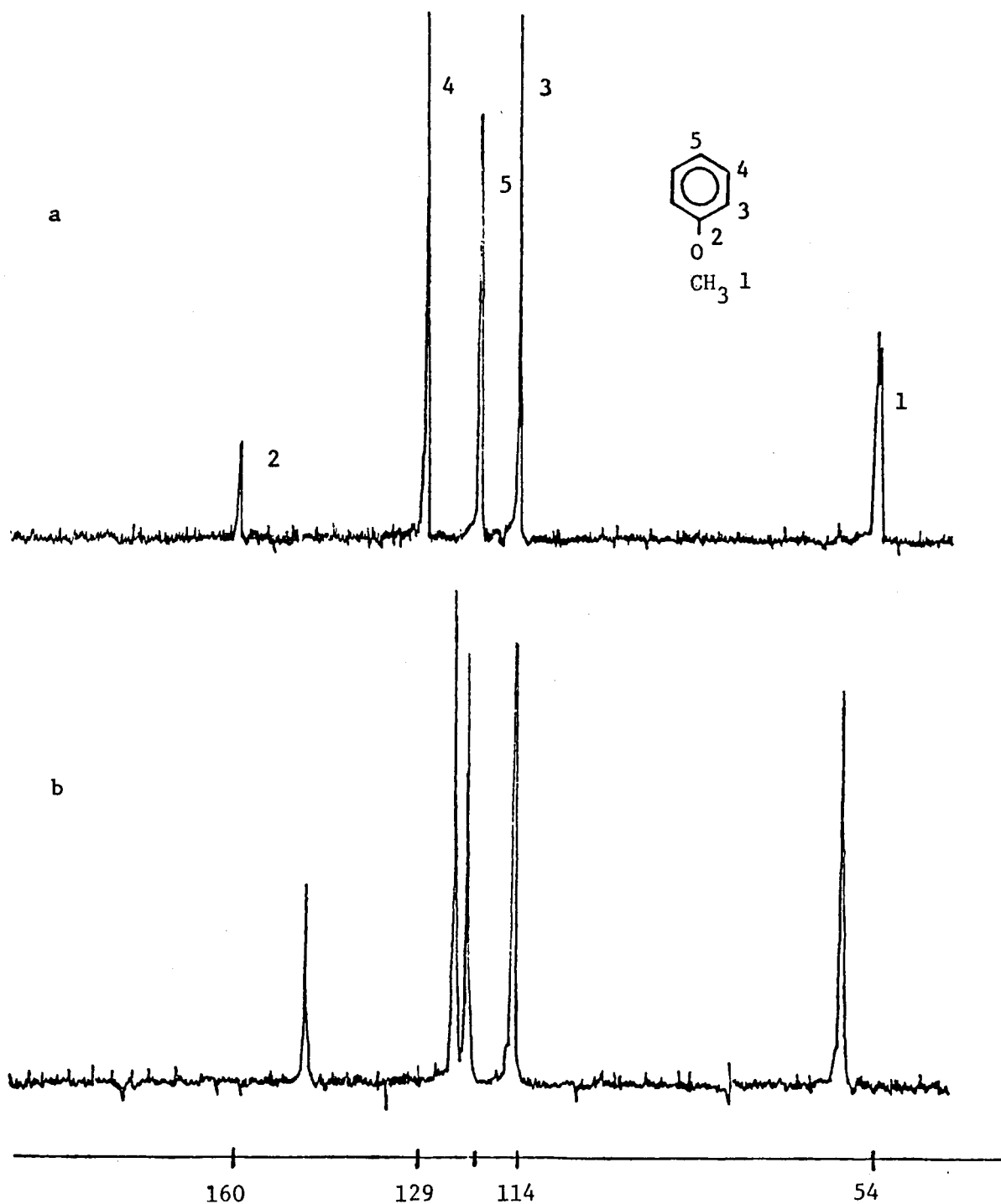


Figure 2.  $^{13}\text{C}$  NMR spectra of anisole and the saturated  $\text{BF}_3$  complex of anisole. Both (a) anisole and (b) the saturated complex were obtained neat, using  $\text{D}_2\text{O}$  as an external lock with a sweep of 4000 Hz. Spectra were run for relative comparisons only as the assignments for spectrum (b) are not known.

another of concentrated  $\text{H}_2\text{SO}_4$  for drying. The train did not help and apparently, the argon's purity was not the problem. A second trial froze the anisole in a  $\text{CO}_2(\text{s})$  and EtOH bath and then put a vacuum on the system to remove all the air and water. A third experiment followed the method of Palko in which  $\text{N}_2(1)$  was used in a series of traps to remove all HF from  $\text{BF}_3$  gas.<sup>49</sup> In no case could the formation of color be avoided; the solution with least color kept a greyish tint for 2 hr, then turned red. But since  $^{13}\text{C}$  NMR spectra compared very well between the grey (clearest) sample and the red sample, it was assumed that the concentration of the colored species was sufficiently low to not cause any problems. No additional attempts were made to determine the source or to remove the color.

### C. Determination of the Amount of $\text{BF}_3$ in the Anisole $\text{BF}_3$ Complex

#### 1. $\text{BF}_3$ Concentration Determination by $^1\text{H}$ NMR Techniques

As shown by Fratiello, Kubb, Liu, and Vidulich,<sup>50,51,52</sup> in the presence of excess base, and at low temperatures, it is possible to observe separate resonance signals for bulk and coordinated ligand molecules. From such data, chemical shifts may be determined for  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}$ . Also, the stoichiometry of the complex, steric hindrance in complex formation, and ligand preference of a boron trihalide, in a system containing more than one base, may be determined. To see if this procedure might have been used as a method of determining the amount of  $\text{BF}_3$  present in the complex two variations were tried, as described below.

a. Cooling and integration. The first attempt at  $\text{BF}_3$  determination involved separation of the bulk and coordinated ligand resonance peaks

and then integrating the signals to determine relative amounts. To do this, a mixture of 2.5486 g of anisole ( $2.356 \times 10^{-2}$  mole) and 3.5744 g of anisole- $\text{BF}_3$  complex ( $2.03 \times 10^{-2}$  mole) was prepared. At  $-65^\circ\text{C}$  the solution froze in the NMR tube and so the temperature needed to separate the NMR peaks of the bulk and coordinated ligand compounds was never reached. This prevented integration of the separated peaks for mole ratio determinations.

b. Chemical Shifts. The second experiment was the preparation of a calibration curve by plotting chemical shifts (defined as the difference in position of  $^1\text{H}$  NMR resonance peaks for the coordinated complex as compared to the noncomplexed ethers) versus the mole ratio of bulk to coordinated ligand. According to the literature<sup>53,54</sup>  $\text{BF}_3$  when complexed with a Lewis base, gives  $^1\text{H}$  NMR chemical shifts that are directly proportional to the mole ratio of  $\text{BF}_3$  to base. To explore the feasibility of this method, as a way to determine  $\text{BF}_3$  concentrations, calibration curves were prepared using  $\text{Et}_2\text{O} \cdot \text{BF}_3$  and anisole  $\cdot \text{BF}_3$  ( $\text{A} \cdot \text{BF}_3$ ) complexes.  $\text{Et}_2\text{O} \cdot \text{BF}_3$  gave a completely linear plot as was expected, however, the  $\text{A} \cdot \text{BF}_3$  showed a slight curve at very low acid to base molar ratios. Data for the  $\text{A} \cdot \text{BF}_3$  calibration curve, Figure 3, can be seen in Table I. This method was not fully tested as a  $\text{BF}_3$  concentration determination procedure for three reasons. (1) Early problems were encountered with impure  $\text{Et}_2\text{O} \cdot \text{BF}_3$  giving faulty data. (2) The  $^1\text{H}$  NMR calibration curve preparation depends on knowing the concentration of the  $\text{BF}_3$  complexes in advance, which means another method such as titration must be used in conjunction with an NMR calibration curve. (3) The poor solubility of the polymer prevented running a  $^1\text{H}$  NMR

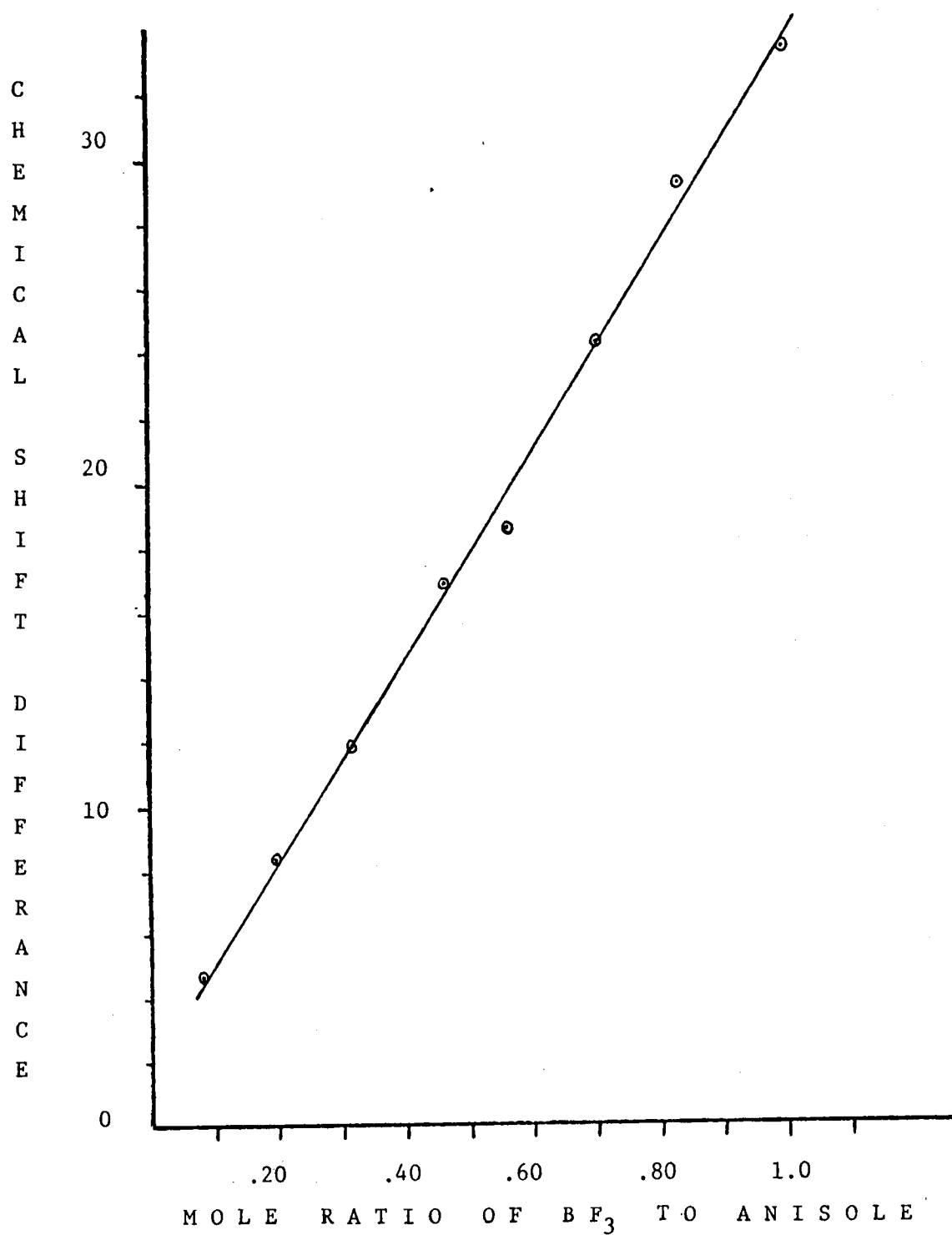


Figure 3. Calibration curve for determination of  $\text{BF}_3$  using  $^1\text{H}$  NMR chemical shift data. Samples used were  $\text{A} \cdot \text{BF}_3$  and were run at 60 MHz and  $25^\circ\text{C}$ .

TABLE I

A·BF<sub>3</sub> CONCENTRATIONS AND CHEMICAL SHIFT DATA FOR A <sup>1</sup>H NMR CALIBRATION CURVE

| Sample No. | BF <sub>3</sub> g | Anisole g | BF <sub>3</sub> (mole) x 10 <sup>-3</sup> | Anisole (mole) x 10 <sup>-2</sup> | Mole Ratio | Chemical Shift(Hz) |
|------------|-------------------|-----------|-------------------------------------------|-----------------------------------|------------|--------------------|
| 1          | .867              | 1.35      | 12.8                                      | 1.28                              | 1.00       | 33.3               |
| 2          | .855              | 1.64      | 12.6                                      | 1.51                              | .835       | 29.2               |
| 3          | .778              | 1.75      | 11.5                                      | 1.62                              | .708       | 24.3               |
| 4          | .643              | 1.83      | 9.48                                      | 1.69                              | .561       | 18.6               |
| 5          | .505              | 1.74      | 7.45                                      | 1.61                              | .463       | 16.9               |
| 6          | .425              | 1.76      | 6.27                                      | 1.63                              | .385       | 11.8               |
| 7          | .366              | 1.93      | 5.40                                      | 1.78                              | .303       | 8.4                |
| 8          | .254              | 2.04      | 3.74                                      | 1.89                              | .198       | 4.7                |
| 9          | .102              | 2.02      | 1.50                                      | 1.87                              | .080       | 0.00               |
| 10         | 0                 | 2.00      | 0                                         | 20.3                              | 0          | 0                  |

of a complexed polymer solution. (In order to run a  $^1\text{H}$  NMR, the solid complex was groundup and put into an NMR tube and anisole added as solvent. See Fig. 4.)

## 2. $\text{BF}_3$ Concentration Determination by U. V. Analysis

Pobiner<sup>55</sup> showed that a U.V. spectral calibration curve of boron trifluoride diethyletherate ( $\text{Et}_2\text{O}\cdot\text{BF}_3$ ) could be set up and using this, one could determine the concentration of  $\text{BF}_3$  in an unknown. The method suggested by the literature involved using  $\text{Et}_2\text{O}\cdot\text{BF}_3$  at various concentrations with dioxane as a solvent, since dioxane would itself form a complex with  $\text{BF}_3$ . Using this type of two solvent system to determine the  $\text{BF}_3$  content of another compound, anisole or later poly(p-methoxystyrene), would lead to complex U.V. spectra assuming that a dioxane and  $\text{BF}_3$  coordination compound ( $\text{D}\cdot\text{BF}_3$ ),  $\text{Et}_2\text{O}\cdot\text{BF}_3$ , anisole and  $\text{BF}_3$  complex ( $\text{A}\cdot\text{BF}_3$ ),  $\text{Et}_2\text{O}$ , and anisole itself all absorb U.V. light. In order to overcome this problem of complexity, a tetrahydrofuran boron trifluoride complex ( $\text{THF}\cdot\text{BF}_3$ ) was prepared. U.V. spectra at various concentrations using THF as solvent were then run to gain a calibration curve. The idea behind the experiment was to simplify the U.V. spectrum by using only one solvent. Since THF  $\text{BF}$  is stable enough to distill, once all  $\text{BF}_3$  is removed from the anisole or polymer by an excess of THF, the  $\text{THF}\cdot\text{BF}_3$  could then be separated from the anisole and a U.V. spectrum obtained.

a. THF. To do this, 25.00 g of THF, which gave a U.V. cut off at 220 nm, was complexed in the same manner as the anisole. The only difference in the complexation procedure was that  $\text{N}_2(1)$  was used to freeze the THF prior to evacuation of the

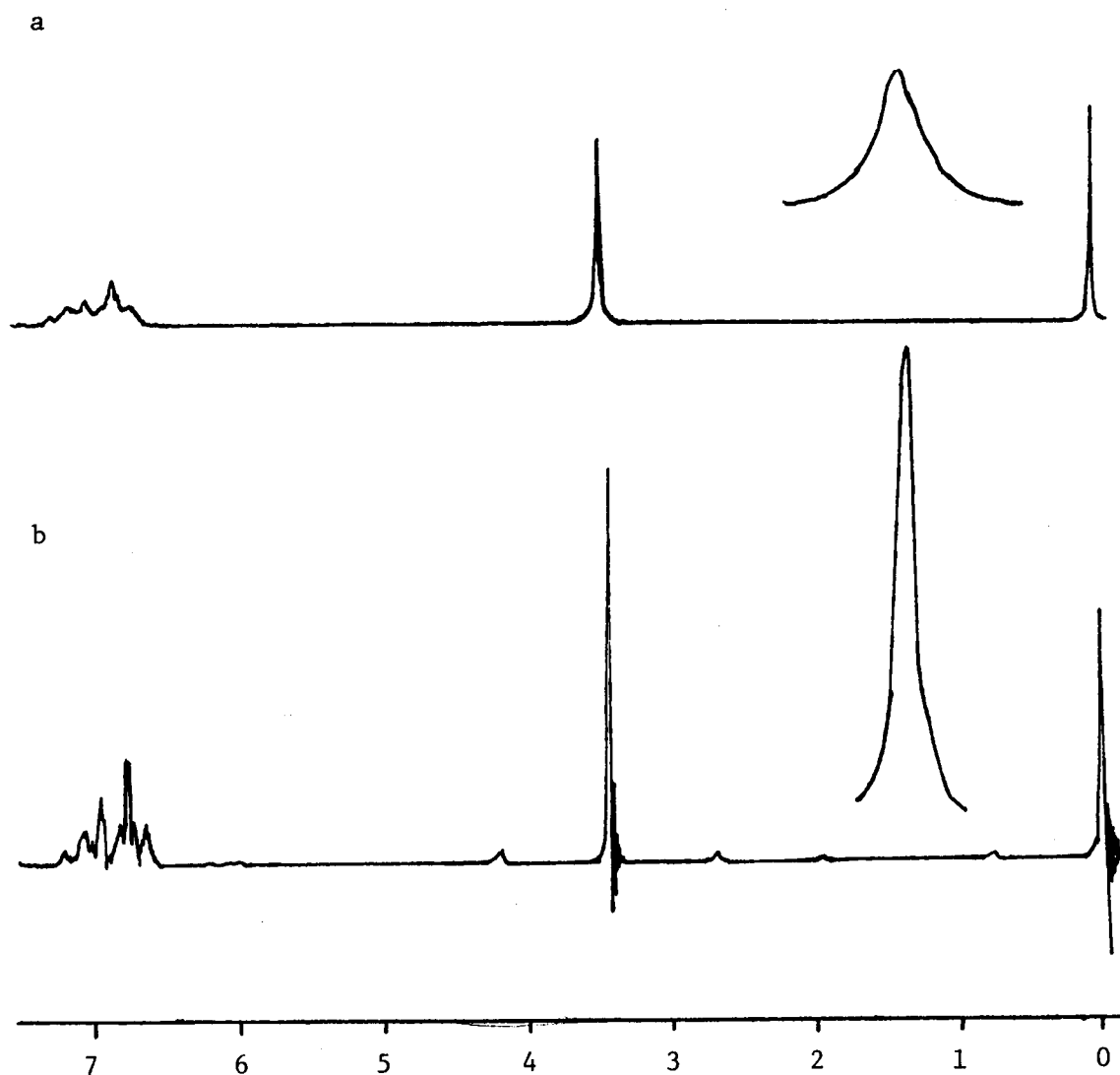


Figure 4.  $^1\text{H}$  NMR spectra of a mixture of anisole plus solid polymer complex, and pure anisole. The polymer complex in (a) was shown by titration to have  $\text{BF}_3$  molecules complexed to 55% of the methoxy units and (b) shows pure anisole. The inserts are the resonance peaks of the respective methyl protons taken at a 200 MHz offset and a spectrum width of 50 MHz for the maximizing of chemical shift calculation.

system to remove all the air and water. Three problems were met in trying to make the THF calibration curve. (a) The THF proved hard to purify and to keep pure at the levels needed for a U.V. spectrum (b) When the THF was extremely pure, the  $\text{BF}_3$  caused it to polymerize. (c) When THF was mixed with a different ligand- $\text{BF}_3$  complex, complete separation could not be achieved by distillation.

b. Dioxane. In the face of these problems, a calibration curve was prepared as given in the literature.<sup>55</sup> Purified dioxane was used as a solvent and  $\text{Et}_2\text{O} \cdot \text{BF}_3$  was diluted to various concentrations in the range from 1-10 g  $\text{BF}_3$   $\text{l}^{-1}$ . One ml of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  as measured by pipette was diluted to 100.0 ml with dioxane in a 100 ml volumetric flask. Then 1-20 ml of this solution was further diluted to 25.0 ml in volumetric glassware. U.V. spectra were then obtained for all the samples and the absorbance difference between each sample and a baseline, of dioxane versus dioxane, was measured. A calibration curve of absorbance versus concentration was then prepared and gave a straight line as expected. A second calibration was then prepared to check reproducibility of the method. The molar absorptivities,  $\epsilon$ , were calculated for each curve and compared. Curve 1 gave  $\epsilon$  of  $6.64 \times 10^{-2}$  and curve 2 gave  $\epsilon$  of  $6.54 \times 10^{-2}$  in units of  $\text{l/mol} \cdot \text{cm}$  at 275 nm (See Table II for data, Figure 5 for spectra, and Figure 6 for graphical display of Curve 2.) Once the calibration curves were made, they were used to calculate the amount of  $\text{BF}_3$  in anisole and later in the polymer complexes. However, the  $\text{BF}_3$  concentrations of the anisole and of the polymer complexes could not be determined accurately by the U.V. curves due to the absorptivity of the anisole and polymer

TABLE II

 $\text{Et}_2\text{O} \cdot \text{BF}_3$  CALIBRATION CURVE DATA FOR U.V. ANALYSIS

| Sample No. | conc. (g/l) | Absorbance (275 nm) |
|------------|-------------|---------------------|
| 1          | 0           | 0.0                 |
| 2          | 1.11        | .08                 |
| 3          | 2.33        | .15                 |
| 4          | 3.25        | .21                 |
| 5          | 4.68        | .325                |
| 6          | 5.52        | .365                |
| 7          | 6.65        | .44                 |
| 8          | 7.89        | .53                 |
| 9          | 8.99        | .595                |
| 10         | 10.34       | .68                 |
| 11         | 11.25       | .74                 |

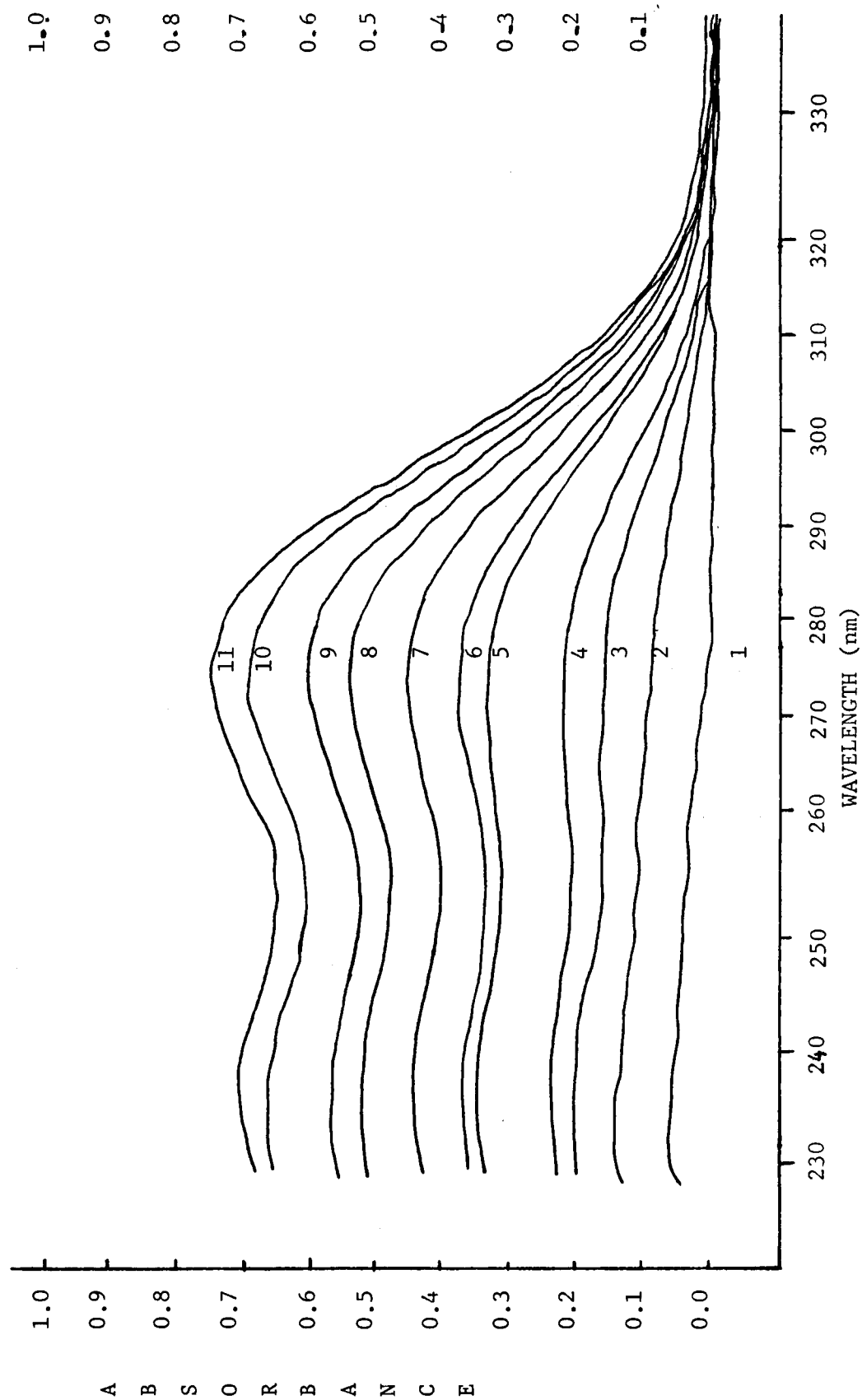


Figure 5. U.V. absorbance spectra of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  in dioxane at varying concentrations.

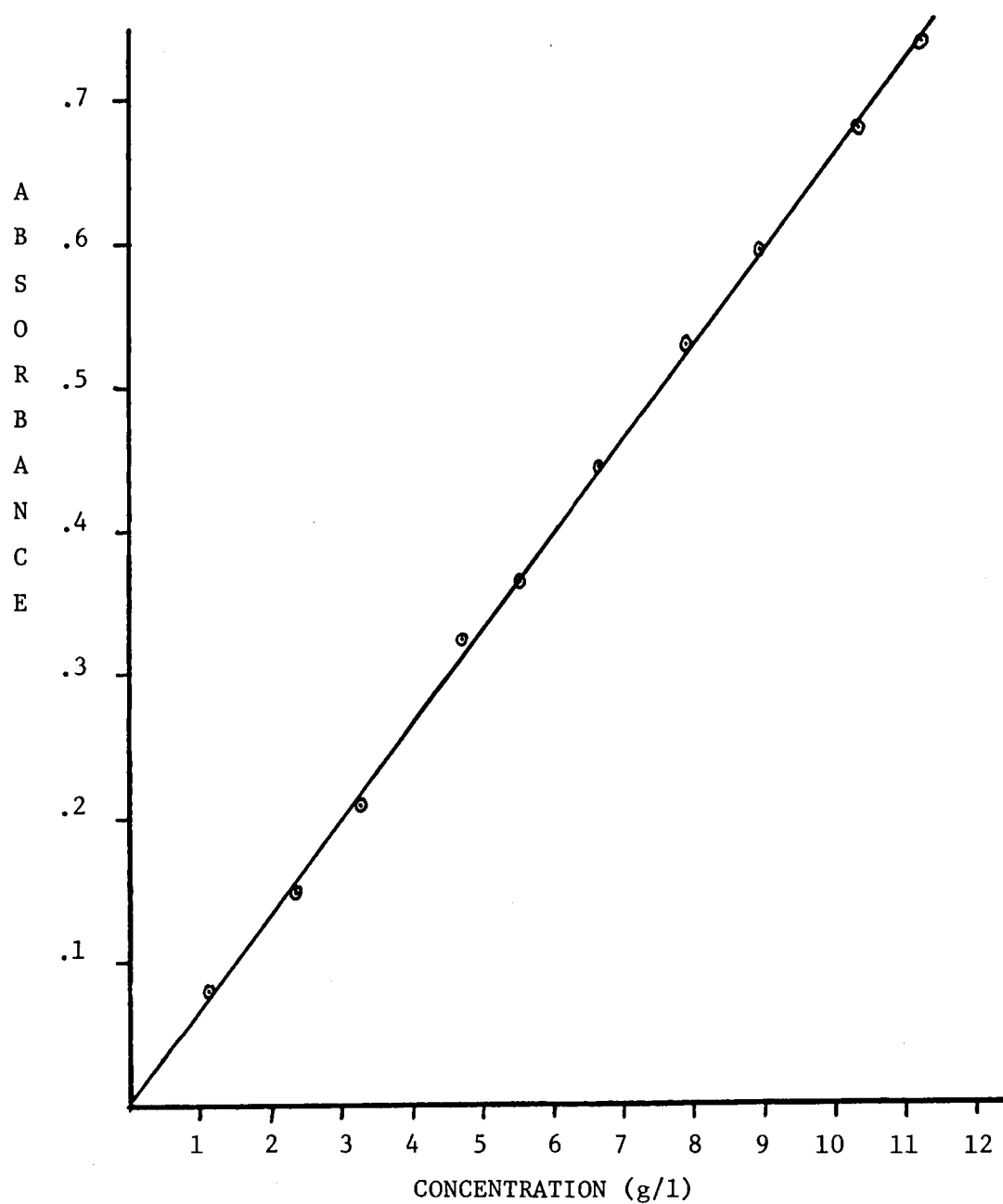


Figure 6. Calibration curve for  $\text{BF}_3$  concentration determinations using U.V. spectroscopy.

backbone in the 275 nm region. This and other problems leading to abandonment of this method are detailed in the Appendix, Section 1.

### 3. BF<sub>3</sub> Concentration Determined by Titration

The third method used to determine BF<sub>3</sub> concentration was titration as done by Emelin and Markova.<sup>56</sup> Since titration was the original method used to check the anisole-BF<sub>3</sub> molar ratio, and since Emelin and Markova dealt with BF<sub>3</sub> determinations in polymers, it looked like a good method of BF<sub>3</sub> determination. To do these titrations, the following solutions were needed (a) EtOH, (b) 20% CaCl<sub>2</sub> in H<sub>2</sub>O, and (c) 9 M glycerol in H<sub>2</sub>O all titrated with acid to a methyl red, red endpoint.

To obtain the EtOH solution, 95% EtOH (drum grade) was placed into a 3-necked round bottomed flask fitted with a distillation column, a magnetic stirrer and a heating mantle. The EtOH solution was distilled and then 2% HCl was added to reach a methyl red endpoint.

To prepare the CaCl<sub>2</sub> solution, 100 g of CaCl<sub>2</sub> was added to 400 ml of H<sub>2</sub>O, the total weight being 500 g which gave 20% by weight of CaCl<sub>2</sub>.

For the 9 M glycerol, 108.3 g of glycerol was diluted to 130 ml by water to give 9.04 M solution.

To do the titrations, a NaOH solution was needed and for this 1 g of NaOH was dissolved in 1000 ml of H<sub>2</sub>O. The NaOH was then standardized with potassium hydrogen phthalate (KHP). A 2.3011 g sample of KHP was diluted to 500 ml in a volumetric flask to give a  $2.446 \times 10^{-2}$  M solution. After five titrations, the average molarity for the NaOH was determined as  $2.65 \times 10^{-2}$  with a  $\pm 2\%$  deviation.

In doing the titrations, the procedure often used was to add 20 ml of EtOH and 10 ml of 20%  $\text{CaCl}_2$  to between 0.5 and 2.0 g of polymer complex. The solution was then fitted with a reflux column and heated for one hour at reflux temperature. After the heat was cut off, the EtOH was washed down the column with 10 ml of distilled water. This procedure converted the bound  $\text{BF}_3$  to "free" HF and  $\text{B(OH)}_3$  which could be titrated. The reaction mixture was placed into a 400-ml beaker fitted with a stirring bar, and titrated with the  $2.65 \times 10^{-2}$  M NaOH with constant stirring. The titration was monitored with a Beckman pH meter and a standard glass electrode. The base additions were made in 3 minute intervals and were made in amounts strong enough to move the pH meter about 0.2 pH units. Once the first equivalence point was reached (endpoint of  $\text{F}^{-1}$  titration) 10 ml of 9 M glycerol was added to the solution and the titration was continued through the second equivalence point (endpoint of boric acid titration).

The first series of titrations gave somewhat varying results but were within the 10-15% error range allowed (see Table III). This method was then selected for  $\text{BF}_3$  concentration determinations. The major drawback to this method was not the 10-15% error but the 4 hr needed for each titration.

The percentage of anisole groups that were complexed with Boron trifluoride were calculated as follows.

$$\frac{1 \text{ of base} \times \frac{\text{m base}}{1 \text{ base}} \times \frac{1 \text{ m HF}}{3 \text{ m base}} \times \frac{1 \text{ m BF}_3}{3 \text{ m HF}} \times \frac{108.14 \text{ g anisole}}{1 \text{ m anisole}}}{\text{g complex} - 1 \text{ of base} \times \frac{\text{m base}}{1 \text{ base}} \times \frac{1 \text{ m HF}}{1 \text{ m base}} \times \frac{1 \text{ m BF}_3}{3 \text{ m HF}} \times \frac{67.804 \text{ g BF}_3}{1 \text{ m BF}_3}} \times 100$$

TABLE III

## FIRST SERIES OF COMPLEX TITRATIONS

| Titration No.  | G Complex | Moles $F^{-1}$        | Moles $BF_3$           | First Endpoint | Percent Complexed |
|----------------|-----------|-----------------------|------------------------|----------------|-------------------|
| 1 <sup>a</sup> | 1.3323    | $2.04 \times 10^{-2}$ | $6.8 \times 10^{-3}$   | 67.6           | 84                |
| 2 <sup>a</sup> | 4.1930    | $4.5 \times 10^{-2}$  | $1.5 \times 10^{-2}$   | 150.           | 39                |
| 3 <sup>b</sup> | 2.9813    | $3.6 \times 10^{-2}$  | $1.2 \times 10^{-2}$   | 114.           | 60                |
| 4 <sup>b</sup> | 3.3832    | $3.32 \times 10^{-2}$ | $1.107 \times 10^{-2}$ | 106.           | 46                |
| 5 <sup>b</sup> | 1.9185    | $2.95 \times 10^{-2}$ | $9.851 \times 10^{-3}$ | 32.5           | 85                |
| 6 <sup>b</sup> | 1.7439    | $3.05 \times 10^{-2}$ | $9.53 \times 10^{-3}$  | 19.5           | 94                |

<sup>a</sup>Used .3017 M base in titrations.<sup>b</sup>Used .3126 M base in titrations.

Note: Samples 1 and 2 were suspect because the lecture bottle of  $BF_3$  was depleted of gas before the preparation of the complex was complete. Also 1 was run right after the complex was made and 2 was run a day later. Samples 3 and 4 were run after air had been permitted to enter into the complex mixture that was used in 1 and 2. Samples 5 and 6 were run sequentially as soon as a sample of anisole complex was prepared.

#### D. Stability of Anisole $\text{BF}_3$ Complex

Several series of experiments were conducted to evaluate the stability of the  $\text{A} \cdot \text{BF}_3$  complex and, for comparison, of the better known  $\text{Et}_2\text{O} \cdot \text{BF}_3$  complex. Several simple chemical reactions and conventional NMR techniques were used. The first test involved bubbling dried nitrogen gas ( $\text{N}_2$ ) through a sample of the complex. To do this, a 3-necked round-bottomed 100-ml flask with a magnetic stirrer, bubble tube, and a  $\text{CaCl}_2$  drying tube was used. Into the flask was placed approximately 20 ml of anisole complex which had had  $\text{BF}_3$  bubbled through it for 4 hours. A stream of  $\text{N}_2$  was then introduced at a very rapid rate (2 psi) for approximately 6 hours with stirring and at room temperature. At the end of the  $\text{N}_2$  flushing,  $\text{BF}_3$  was noticed to still be present in the anisole complex for the cloudiness appeared when air was added ( $\text{BF}_3$  forms a white cloud when mixing with  $\text{H}_2\text{O}$  vapor found in air) and by an NMR spectrum (see Figure 7c).

The second test involved placing a bottle of the complex on a shelf and checking it at intermittent intervals. The sample showed considerable  $\text{BF}_3$  still present even after a period of 3 months (see Figure 7d). But a bottle of the complex stored open to air (in a hood) showed no  $\text{BF}_3$  present, but instead 3 distinct layers, after only one day. The layers were thought to be anisole, water, and a white precipitate of boric acid respectively. NMR spectra were run to confirm the assumption. To be sure water was causing decomposition of the complex, a portion of the complex was stored open to air via a  $\text{CaCl}_2$  drying tube for 24 hr. After this time period,  $\text{BF}_3$  could still be noticed.

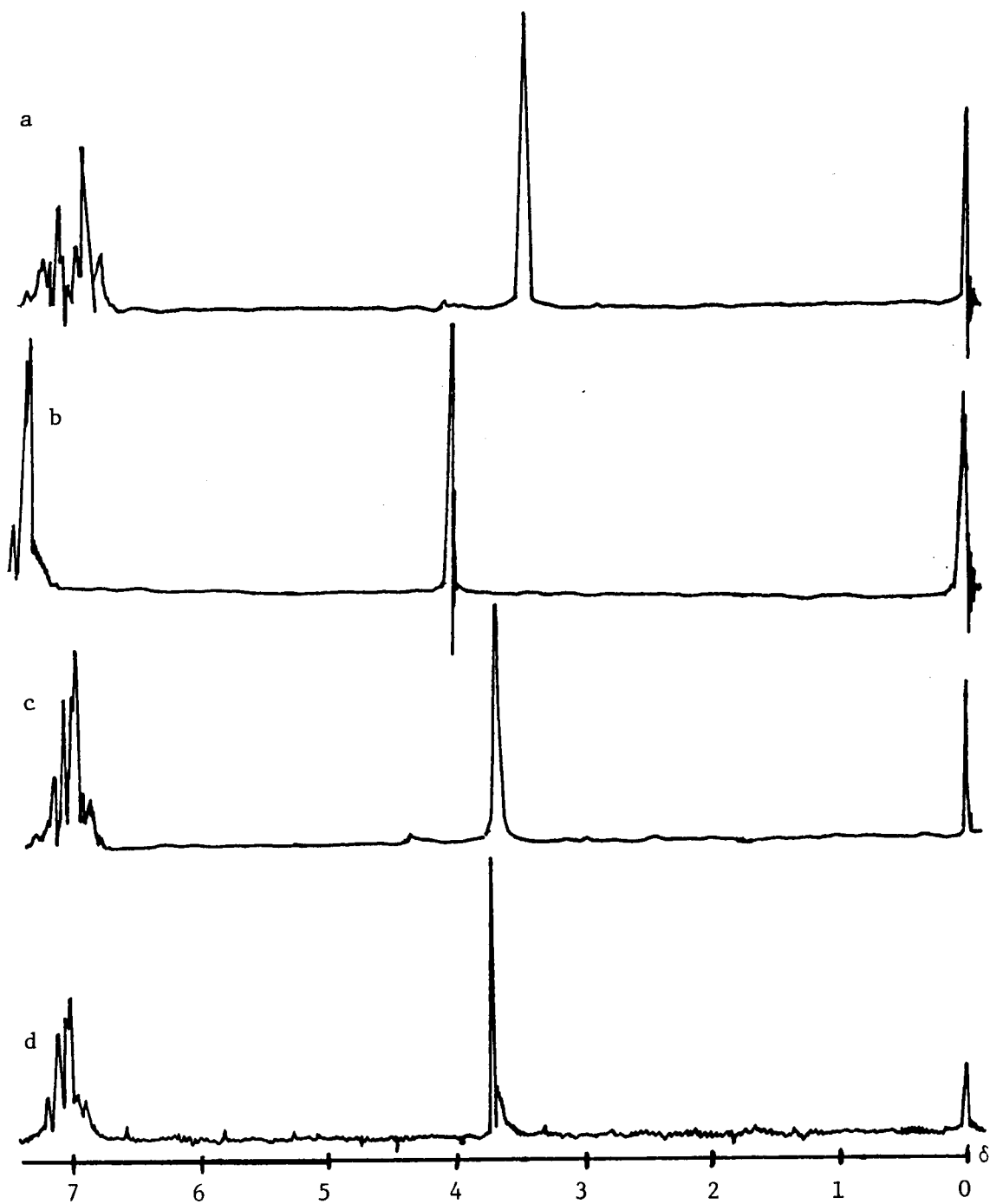


Figure 7.  $^1\text{H}$  NMR spectra for anisole- $\text{BF}_3$  stability tests. The spectra show (a) anisole, (b) 100% anisole  $\text{BF}_3$  complex, (c) anisole complex through which  $\text{N}_2$  gas was run for 6 hr and then left open to air via a drying tube for 3 days, and (d) anisole  $\text{BF}_3$  complex after sitting on the shelf for 3 months.

The third test involved determination of how much water the complex could withstand. To do this, various amounts of complex were mixed with various amounts of water with different results. Five ml of complex and 5 drops of water gave an NMR spectrum (see Figure 8) which showed a phenol type of peak meaning some type of rearrangement. As the mixture was allowed to set for a period of weeks, the phenol-looking rearrangement became more prominent (see Figure 8). When equivalent portions of water and complex were mixed, two layers and a white precipitate were noticed immediately (NMR spectra were similar to earlier ones). (See Appendix, Section E for proposed phenol reaction.)

To evaluate an analytical method that could provide information about the bonding stability, an NMR spectrum was run in the manner of Fratiello and co-workers using a 50:50 mixture of diethyl ether to diethyl etherate with  $\text{BF}_3$ .<sup>50</sup> The idea was that a weak bond would allow the boron trifluoride to exchange between methoxy groups very rapidly. The NMR signals for this type of bond would average out so that one could not separate peaks of the complex from those due to pure ether. If the  $\text{BF}_3$  was held by a strong sigma bond then resonance peaks for both molecules could be seen. For this experiment 1.99 ml of diethyl ether was mixed with 2.69 ml of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  giving a 1:1.2 mole ratio. NMR spectra were run at  $10^\circ\text{C}$  temperature intervals starting at  $0^\circ\text{C}$  and going successively lower (see Figure 9). At a temperature of  $-57^\circ\text{C}$  two sets of peaks could easily be distinguished. A mixture of anisole and anisole boron trifluoride complex was then tried. Results and conclusions drawn from these experiments are discussed in the next chapter.

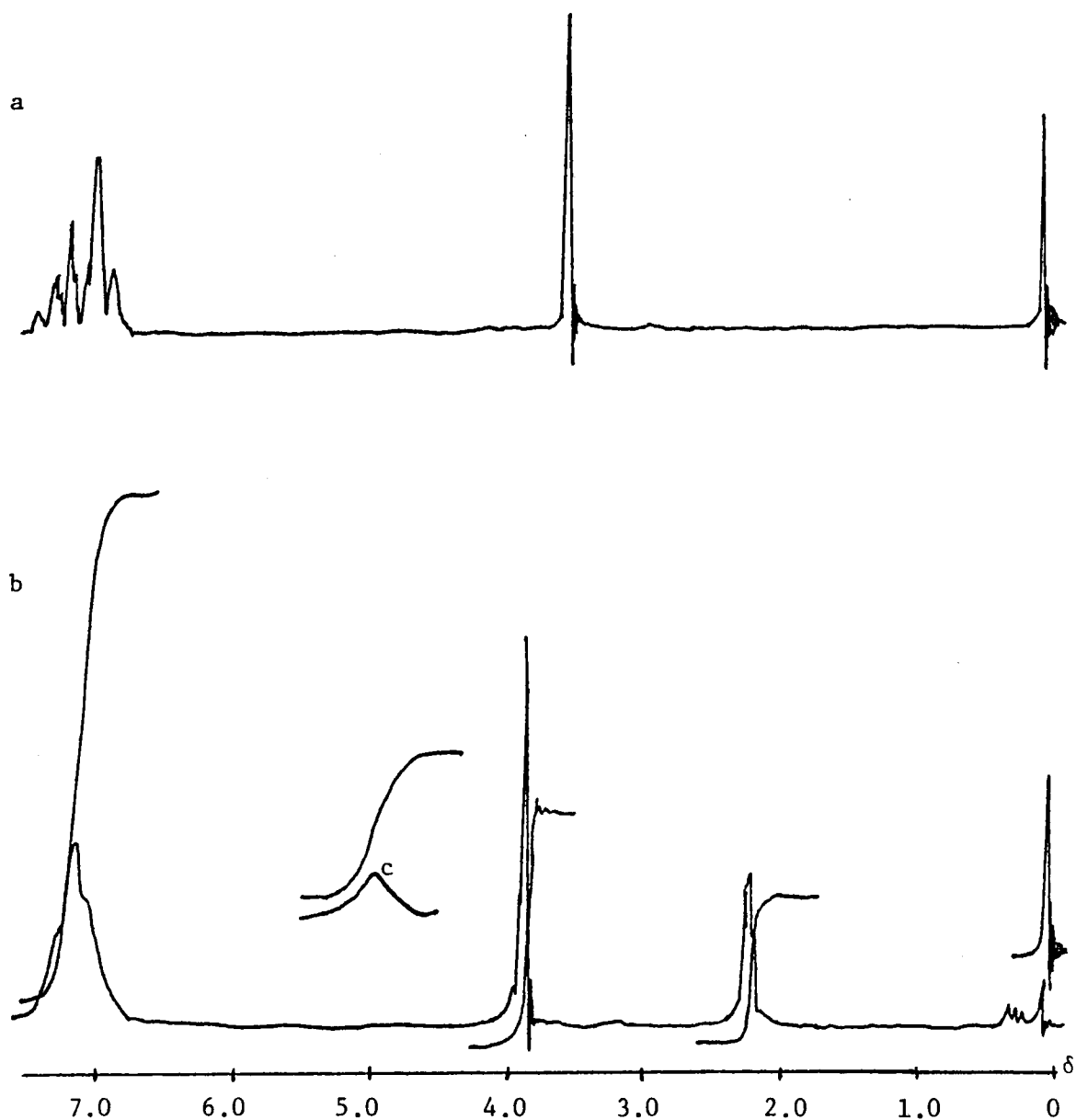


Figure 8.  $^1\text{H}$  NMR spectra showing rearrangement. (a) pure anisole, (b) a sample from 10 ml of anisole complex and 5 drops of water after 4 days showing a phenol looking peak, (c) peak offset 220 Hz. (TMS was external and chemical shifts may or may not be exact.)

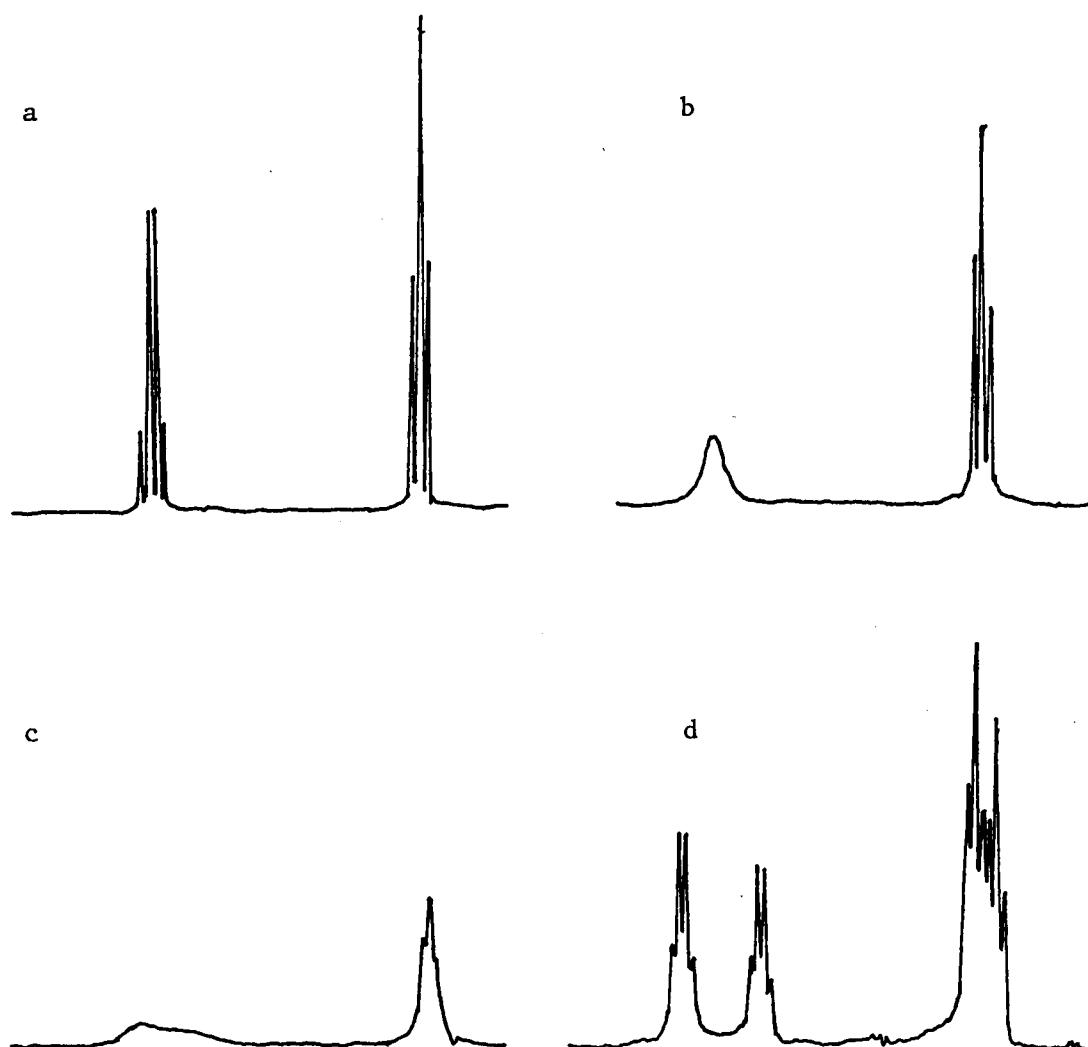


Figure 9.  $^1\text{H}$  NMR of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  at 100MHz and different temperatures. (a)  $\text{Et}_2\text{O} \cdot \text{BF}_3$  at  $27^\circ\text{C}$ , (b)  $\text{Et}_2\text{O} \cdot \text{BF}_3$  at  $-17^\circ\text{C}$ , (c)  $\text{Et}_2\text{O} \cdot \text{BF}_3$  at  $-27^\circ\text{C}$  showing separation of resonance peaks, (d)  $\text{Et}_2\text{O} \cdot \text{BF}_3$  at  $-57^\circ\text{C}$  showing complete separation of  $\text{Et}_2\text{O}$  and  $\text{Et}_2\text{O} \cdot \text{BF}_3$  resonance peaks.

## E. The Study of Polymer Compounds

### 1. Sources of Poly(p-methoxystyrene)

a. Vandergriff. One source of poly(p-methoxystyrene) was from research done by C. Vandergriff, Jr.<sup>57</sup> The contents of two bottles of monomer left by Vandergriff were noticed to be extremely viscous, showing some polymerization had taken place. To separate the polymer and the monomer, the mixture was added dropwise to hexane. The percentage of monomer/polymer solution to hexane was about 10%. Complete transferal of monomer and polymer was insured by thorough rinsing of all vessels by benzene. The addition was made slowly and with much stirring. The precipitated polymer was isolated by filtration, air dried for two days, dried in a vacuum for 6 hr, then at 40°C under vacuum for 6 hr more. The excess monomer was recovered by use of a Rotovac and was then placed over molecular sieves to dry.

b. Polymerization of monomer. The second source of polymer was polymerization of monomer purchased from Aldrich Chemical Company. Polymerization of the monomer was done free radically using AIBN. The following procedure was the one commonly used. A 100-ml, 3-necked, round-bottomed flask was thoroughly cleaned, dried and equipped with a stirring bar, a reflux column, and a pressure equalizing dropping funnel. Fifty grams of molecular sieves were then dried in the oven at 250°C. Using 1/4 of the molecular sieves, 30 ml of benzene was dried for 3 hr with stirring and heating. The monomer was washed with 10% NaOH until the wash remained relatively colorless, showing removal of all inhibitors. The monomer was then dried. To the

reaction flask which had been flushed with argon while heating, was added approximately 20 ml of benzene which was heated to reflux temperature. Once reflux temperature was achieved, the monomer solution, which contained 5 ml of monomer, 20 ml of benzene and 0.2769 g of AIBN, was added dropwise to the reaction flask via the dropping funnel. The preheating time was about 2 hr and the addition time was about 15 min. The reaction time for the polymerization was a total of 18 hr after the monomer addition. After the polymerization was over, the reaction mixture was added dropwise to hexane to precipitate all polymer. Once precipitated, the polymer was air dried for 1 day, vacuum dried for 12 hr, and then dried an additional 6 hr under vacuum at 40°C. The yield was calculated at approximately 50%. The unreacted monomer was saved by stripping off all hexane and benzene with a Rotovac. The recovered monomer was then placed in a 2-oz bottle over 4 Å molecular sieves and allowed to polymerize. Once the molecular sieve polymerization had taken place, it gave about 70% yield of polymer. (Note: Monomer was found to polymerize readily over molecular sieves at room temperature with a good yield and what seemed to be a high molecular weight.) An  $^1\text{H}$  NMR was then run of the polymer (see Figure 10).

## 2. Complexation of the Polymer

Once the polymer was dried thoroughly, it was complexed with  $\text{BF}_3$ . The procedure first used called for a 3-necked, 100-ml, round-bottomed flask equipped with a gas inlet tube, a vacuum line, and a rubber septum. Also used with the flask were an icebath and a magnetic stirrer. For the first polymer complexation, 2.7867 g ( $2.077 \times 10^{-2}$

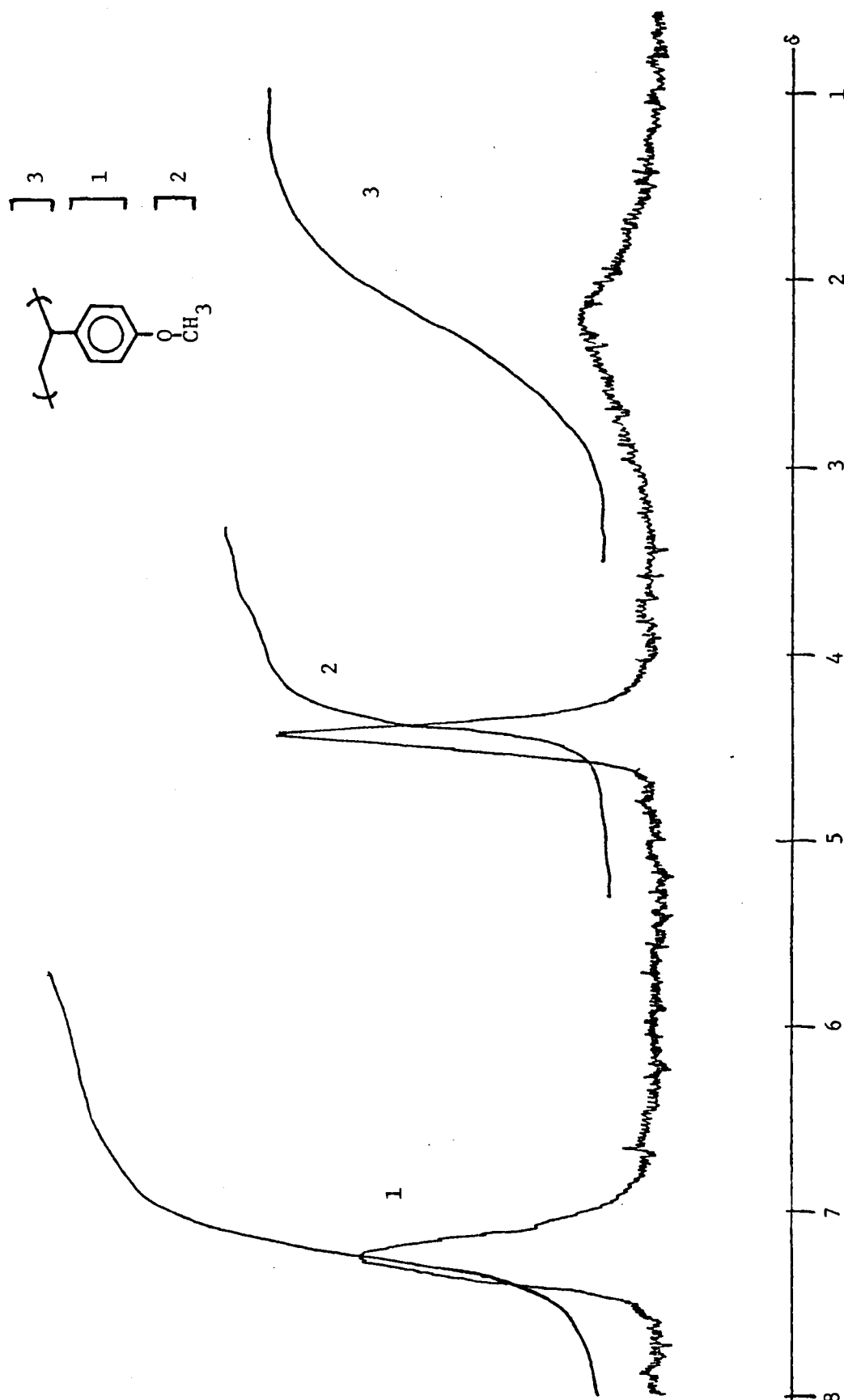


Figure 10.  $^1\text{H}$  NMR spectrum of poly(p-methoxystyrene). The sample was run in  $\text{CDCl}_3$  at 60 MHz, at  $25^\circ\text{C}$  and TMS was not added because it made the polymer precipitate.

mole repeat units) of polymer was dissolved in 46.3 ml of benzene. Once dissolved, the polymer-benzene solution was poured into the reaction flask. Complete transferal was aided by benzene washes of all vessels used. After the washes and apparatus rinses, a total of 66.6 ml of benzene had been used. Once the benzene-polymer solution was placed into the reaction flask, it was closed completely. In setting up this apparatus,  $\text{BF}_3$  resistant grease, Fluorolube<sup>R</sup>, and Fluron<sup>R</sup> tubing were used to prevent stopcock freezing and  $\text{BF}_3$  leakage through glass joints, respectively. After the system was closed, the benzene-polymer solution was frozen in a Dry Ice-acetone bath and the system evacuated to remove all air in the lines. After the system was depressurized (1.5 mm pressure) the reaction mixture was warmed to  $0^\circ\text{C}$  and  $\text{BF}_3$  was then added slowly to the system. Instantaneously, reddish-brown rubbery looking bubbles appeared as the  $\text{BF}_3$  came up through the solution. As the polymer was complexed with  $\text{BF}_3$ , it became insoluble in benzene. This and other problems with the system as described were confronted. Since subsequent work was not contingent upon them, the problems and methods used to overcome them are described in the Appendix, Section B.

### 3. Solvents for the Polymer Complex

It would be very desirable to be able to dissolve the polymer  $\text{BF}_3$  complex. Nitrobenzene was a good solvent but it's aromatic group gave a spectrum that covered up the polymer aromatic group. Deuterated nitrobenzene cost \$100.00 for 10 g - too much to justify. Solubility effects for eleven different solvents were observed (see Table IV). (Note: It was much easier to dissolve the polymer and then make the complex than to take the precipitated complex and redissolve it.)

TABLE IV  
SOLUBILITY TESTS ON POLY(p-METHOXYSTYRENE) · BF<sub>3</sub> COMPLEX

| Solvent      | Observations                                                                           | Solubility    |
|--------------|----------------------------------------------------------------------------------------|---------------|
| Nitrobenzene | color stayed deep red                                                                  | fair          |
| Nitromethane | solution turned red, polymer turned white around the edges                             | fair          |
| Acetone      | clear solution, polymer is light pink, polymer looks more like powder than a jelly now | some          |
| Bromobenzene | polymer dark red, solution cloudied with BF <sub>3</sub>                               | little        |
| THF          | solution clear                                                                         | very little   |
| DMSO         | polymer white, solution clear                                                          | very little   |
| Formaldehyde | solution is clear, polymer is faded purple                                             | none apparent |
| Dioxane      | polymer looks like mold and mildew, white with dark green spots, solution is clear     | none apparent |
| Acetonitrile | polymer red and rubbery, solution is pink                                              | very little   |
| Anisole      | solution is pink, polymer red jelly                                                    | fair          |
| Benzene      | solution is cloudy white, polymer is dark red                                          | none apparent |

#### 4. Titration of the Polymer Complex

The general procedure for titration was performed in the manner of the anisole complex titrations. In the first polymer titration, 0.2054 g of complex was refluxed for one hour in a solution of 20 ml ethanol and 10 ml of 20%  $\text{CaCl}_2$ . The reflux column was rinsed with 10 ml of distilled water and the entire solution was placed into a 250-ml beaker with a stirring bar. (Note: After refluxing for 1 hr the polymer looked like bits of fine tobacco leaf.) Approximately 101.5 ml of  $2.654 \times 10^{-2}$  M base was used to titrate the polymer to the first equivalence point. A blank titration took 18.53 ml. The difference between the 1st equivalence point and the second was 26.0 ml. When the blank was subtracted, it gave approximately 70% complexed (see Figure 11). Subsequent titrations gave data which followed closely the type of titration accuracy and reproducibility shown in the anisole  $\text{BF}_3$  complex titrations (see Table V). The percentage of complexation (which is defined as the percentage of methoxy units complexed with  $\text{BF}_3$  out of the total number of methoxy units) was calculated as before except that the molecular weight of anisole was replaced with the molecular weight of a *p*-methoxystyrene repeat unit.

#### F. Reactions with the Polymer Complex

##### 1. Octene Rearrangements

Once the polymer complex was made and after the amount of  $\text{BF}_3$  was determined by titrations, reactions were run to test its catalytic activity. The first reaction was the isomerization of 1-octene to 2-octene (NMR spectra of each shown in Figure 12). Several reactions

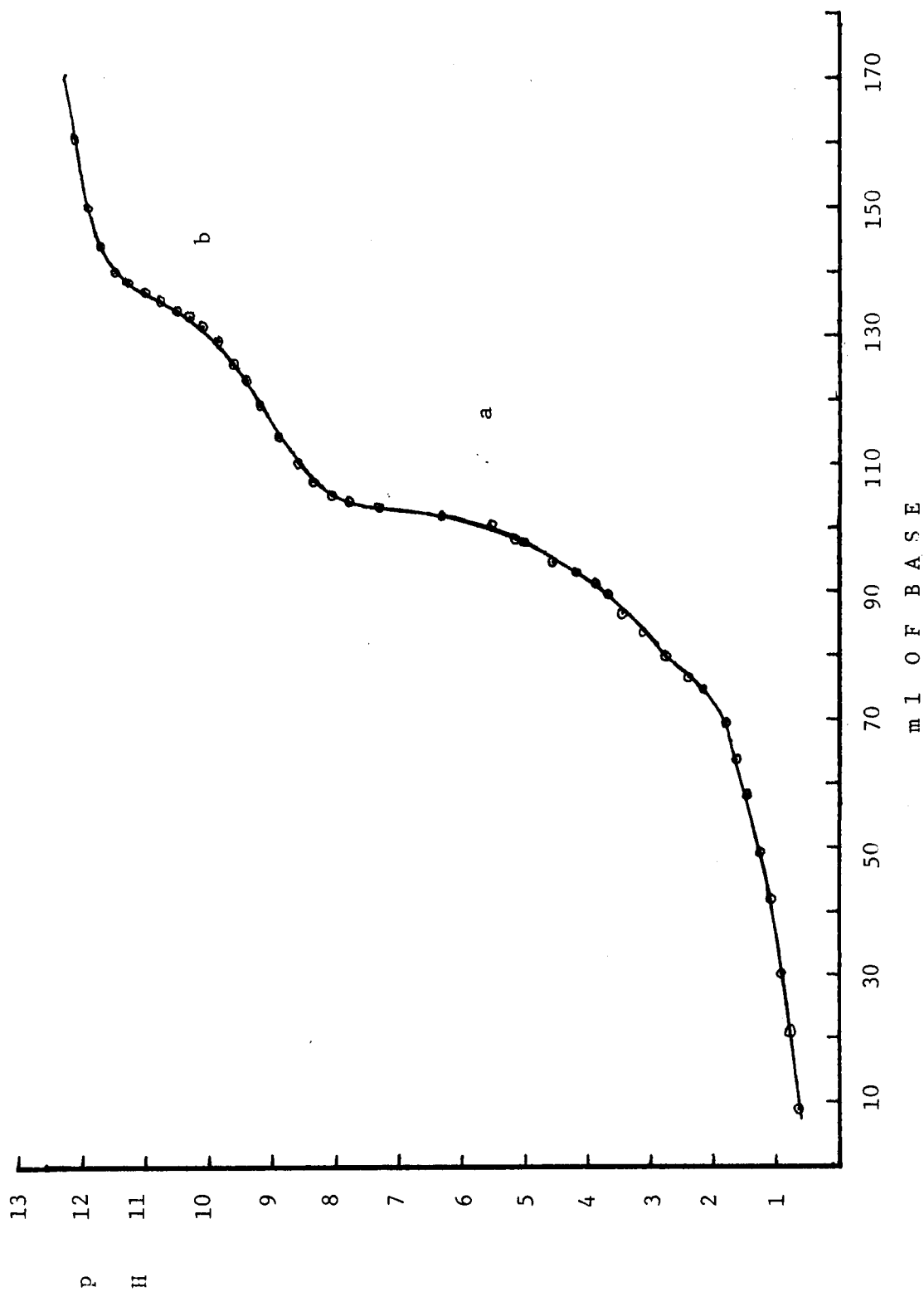


Figure 11. Titration curve for the polymer  $\text{BF}_3$  complex. Two equivalence points are shown (a) equivalence point for  $\text{F}^{-1}$  titration and (b) equivalence point for  $\text{B}(\text{OH})_3$  titration.

TABLE V  
TITRATIONS OF POLYMER COMPLEX

| Sample No.       | Weight | ml Base | Moles $\text{F}^{-1} \times 10^3$ | Moles $\text{BF}_3 \times 10^4$ | G $\text{BF}_3 \times 10$ | G Polymer $\times 10^1$ | Moles Polymer $\times 10^3$ | Percent Complexed |
|------------------|--------|---------|-----------------------------------|---------------------------------|---------------------------|-------------------------|-----------------------------|-------------------|
| 1 <sup>a</sup>   | 0.2054 | 82.97   | 2.20                              | 7.34                            | 4.97                      | 1.55                    | 1.16                        | 63.3              |
| 2 <sup>a</sup>   | 0.4124 | 151.50  | 4.02                              | 13.4                            | 9.09                      | 3.21                    | 2.39                        | 56.1              |
| 3 <sup>b</sup>   | 0.3711 | 24.24   | 4.46                              | 14.8                            | 10.0                      | 2.71                    | 2.02                        | 73.3              |
| 4 <sup>b</sup>   | 0.2527 | 15.94   | 2.93                              | 9.77                            | 6.62                      | 1.86                    | 1.39                        | 70.3              |
| 5 <sup>b,c</sup> | 0.7819 | 30.35   | 5.58                              | 17.6                            | 11.9                      | 6.63                    | 4.94                        | 35.6              |
| 6 <sup>b,c</sup> | 1.0800 | 25.80   | 4.75                              | 15.8                            | 10.7                      | 9.73                    | 7.25                        | 21.8              |
| 7 <sup>d</sup>   | 0.7700 | 62.40   | 1.16                              | 38.6                            | 26.2                      | 5.08                    | 3.79                        | 102.              |
| 8 <sup>d</sup>   | 0.8515 | 71.80   | 1.31                              | 44.3                            | 30.0                      | 5.511                   | 4.10                        | 108.              |
| 9 <sup>e</sup>   | 0.2238 | 0.33    | .0021                             | .207                            | .140                      | 2.22                    | 1.65                        | 1.25              |
| 10 <sup>e</sup>  | 0.3106 | 0.55    | .102                              | .340                            | .230                      | 3.08                    | 2.30                        | 1.50              |

<sup>a</sup>  $2.654 \times 10^{-2}$  M base run at least 2 days after complex preparation.

<sup>b</sup>  $0.84 \times 10^{-2}$  M base run at least 2 days after complex preparation.

<sup>c</sup>  $0.84 \times 10^{-2}$  M base titration,  $\text{BF}_3$  ran out in complex preparation.

<sup>d</sup>  $0.1855 \times 10^{-2}$  M base run just after the complex was made.

<sup>e</sup>  $0.1855 \times 10^{-2}$  M base titration run after using complex in reaction.

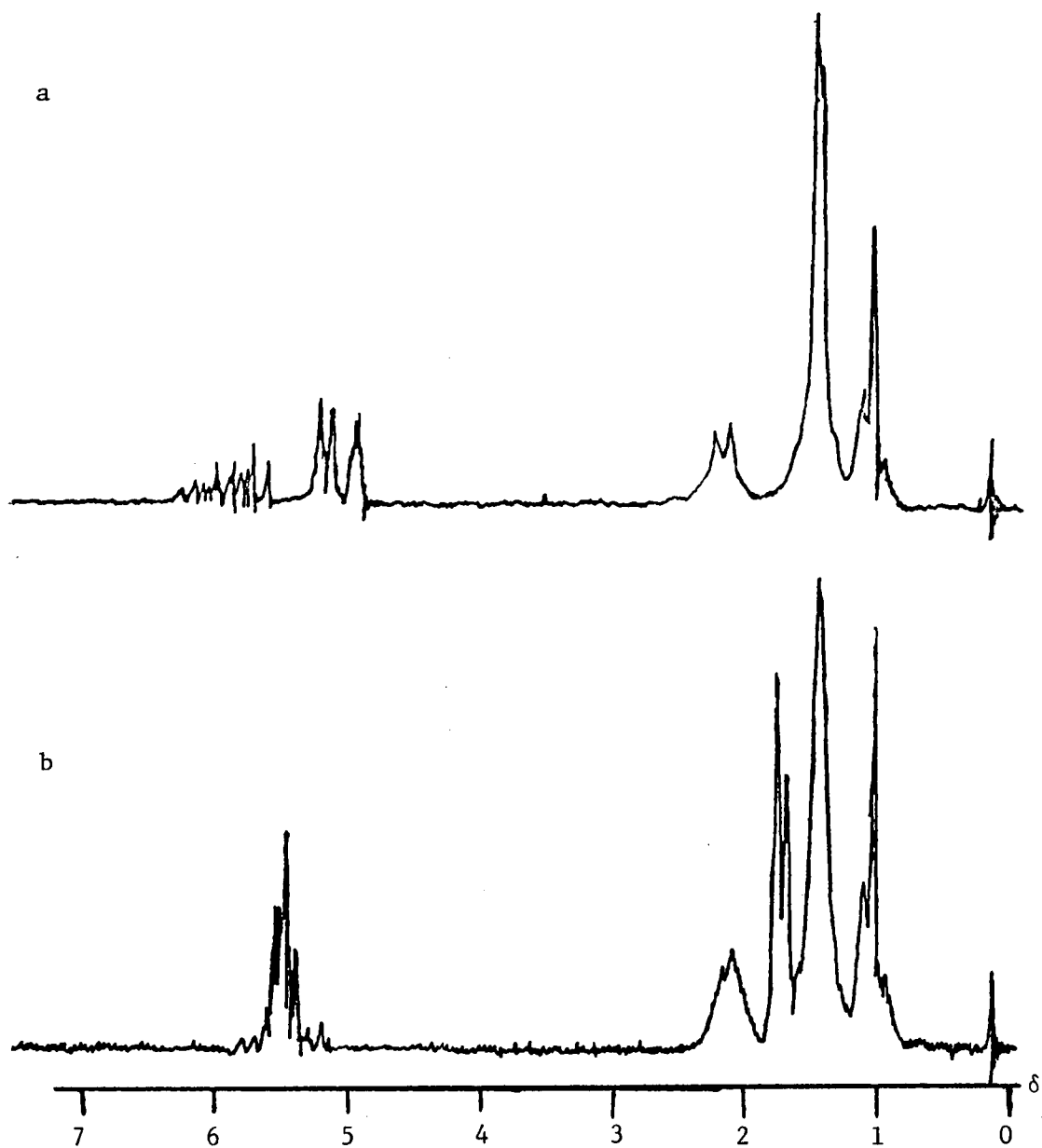


Figure 12.  $^1\text{H}$  NMR spectra for 1-Octene and 2-Octene. Shown, respectively, as (a) and (b) taken at 60 MHz and 25°C.

were used during the experiment to determine the temperature and the amount of catalyst necessary to achieve the octene isomerization. The temperature used was approximately 75°C. This temperature was determined by mixing the polymer complex with 1-octene and varying the temperature of the reaction. By checking products with  $^1\text{H}$  NMR, the lowest temperature to give products in a relatively short time (4 hr) was identified.

The procedure most used is demonstrated by the example below. A 3.5 ml sample of 1-octene ( $4.04 \times 10^{-2}$  mole) was placed in a 3-necked 100-ml round-bottomed flask. The flask was equipped with a magnetic stirrer, a rubber septum for removing samples, and an oil bath for temperature control. The system was then heated for 16 hr with stirring at 74°C. At the end of 16 hr no rearrangement was noticed, as shown by NMR, and so, 1.380 g ( $6.83 \times 10^{-3}$  mole) of complex was added to the 1-octene. The mole ratio used was 6 moles of octene to 1 mole of complex, even though the literature recommended a 1:1 mole ratio. Products and percentage yields are discussed in the next chapter, and data for some of the octene reactions are given in Table VI.

## 2. Limonene Epoxide Reactions

From the literature,<sup>58</sup> it was found that limonene epoxide could rearrange to form a series of products. It was also noted that  $\text{BF}_3$  could be used to cause rearrangement and so limonene epoxide was prepared to test the catalytic activity of the complex.

a. Preparation of limonene epoxide. Following the procedure used by Royals and Harrell,<sup>59</sup> 150 g of phthalic anhydride was mixed with 250 ml of 30%  $\text{H}_2\text{O}_2$ , and 100 ml of ether. The solution was

TABLE VI  
REACTIONS OF 1-OCTENE AND POLYMER COMPLEX

| Sample No.     | 1-Octene |                       | Polymer Complex |                       |
|----------------|----------|-----------------------|-----------------|-----------------------|
|                | ml       | Moles                 | Grams           | Moles                 |
| 1 <sup>a</sup> | 12.55    | $1.45 \times 10^{-1}$ | .1457           | $7.2 \times 10^{-4}$  |
| 2 <sup>b</sup> | 5.0      | $3.18 \times 10^{-2}$ | 1.026           | $5.96 \times 10^{-3}$ |
| 3 <sup>c</sup> | 10.0     | $6.37 \times 10^{-2}$ | .6264           | $3.64 \times 10^{-3}$ |
| 4 <sup>d</sup> | 19.5     | $1.25 \times 10^{-2}$ | 1.1433          | $6.23 \times 10^{-3}$ |
| 5 <sup>e</sup> | 3.5      | $4.04 \times 10^{-2}$ | 0               | 0                     |
| 6 <sup>f</sup> | 3.5      | $4.04 \times 10^{-2}$ | 1.38            | $6.83 \times 10^{-3}$ |

<sup>a</sup>Ran NMR every 2 hr, polymer was 63% complexed, 320:1 mole ratio (defined as moles of  $\text{BF}_3$  to moles of alkene).

<sup>b</sup>Temperature gradually increased, noticeable rate of reaction at 75°C polymer was 56% complexed, 5:1 mole ratio.

<sup>c</sup>Used low temperature and 3 ml of nitrobenzene as solvent. Noticed no reaction, 18:1 mole ratio.

<sup>d</sup>No reaction after 2 days. 20:1 mole ratio.

<sup>e</sup>No catalyst added. No reaction after 19 hr.

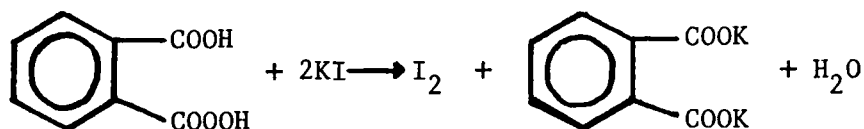
<sup>f</sup>Reaction complete after 4 hr. 6:1 mole ratio.

stirred at a moderate rate for 24 hr at room temperature. Once the reaction to prepare peroxyphthalic acid was completed, the two layers were separated. The aqueous layer was extracted twice with 500 ml ether washes. The total ether solution was then washed with three 175 ml portions of 40% ammonium sulfate, dried with 80 g of sodium sulfate (anhydrous), and stored over Drierite.

To check the product yield of peroxy acid, titrations of the acid-ether solution were done using a 20% KI solution and an  $8.54 \times 10^{-2}$  M  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The procedure used was to take 2 ml of ether-acid solution added to 20 ml of KI and titrate with the  $\text{Na}_2\text{S}_2\text{O}_3$  after 10 minutes of stirring. According to Skoog and West,<sup>60</sup> the thiosulfate iodometric titration follows the equation.



and when mixed with peracid the KI equation is:



From these equations, it can be seen that 1 mole of peracid gives one mole of  $\text{I}_2$  which needs 2 moles of  $\text{Na}_2\text{S}_2\text{O}_3$  to titrate it, so that the moles of peroxyacid will be one half that of the  $\text{Na}_2\text{S}_2\text{O}_3$ . The titration solutions were made as follows: 1.3507 g of  $\text{Na}_2\text{S}_2\text{O}_3$  was dissolved in 100.0 ml of water (pipette). The KI solution was prepared by mixing 20.05 g of KI in 100 ml of water (graduated cylinder). Titration data can be seen in Table VII.

Once the acid was prepared and analysed, the limonene epoxide could be prepared. The method used was to add limonene dropwise to the ether solution with stirring at  $0^\circ\text{C}$ . The reaction calls for a 20% excess of acid, and so the volumes of ether-acid solution to be used were

TABLE VII

TITRATION DATA USED FOR THE DETERMINATION OF PEROXYACID CONCENTRATION  
IN THE LIMONENE EPOXIDE SYNTHESIS

| Sample<br>No. | Vol. of<br>Ether Soln,<br>ml | Amount of<br>$\text{Na}_2\text{S}_2\text{O}_3$ , l | Moles<br>$\text{Na}_2\text{S}_2\text{O}_3$<br>$\times 10^3$ | Moles<br>$\text{I}_2$<br>$\times 10^3$ | Conc. <sup>a</sup><br>of $\text{I}_2$ ,<br>g/l |
|---------------|------------------------------|----------------------------------------------------|-------------------------------------------------------------|----------------------------------------|------------------------------------------------|
| 1             | 2                            | .03041                                             | 2.59                                                        | 1.29                                   | .648                                           |
| 2             | 2                            | .03352                                             | 2.86                                                        | 1.43                                   | .715                                           |
| 3             | .952                         | .01560                                             | 1.33                                                        | .667                                   | .699                                           |

<sup>a</sup> Average concentration of acid was .687 mole/l which showed a 85.02% yield.

multiplied by concentration and then by 80%. The number of moles of acid thus calculated was converted to ml of limonene to be added to the ether using the literature values of 136.24 g/mole and 0.8411 g/ml as the molecular weight and density, respectively.<sup>45</sup> As the addition was made, it was noticed that a white solid appeared in the solution which was assumed to be phthalic acid, which has a low solubility in ether.

Once the addition of the limonene was completed, the reaction mixture was allowed to stir for approximately 24 hr at room temperature, and then filtered to remove the phthalic acid. The filtered acid was washed with 3-20 ml portions of ether and all the ether solutions were combined. The ethereal solution was then washed with a 10%  $\text{Na}_2\text{CO}_3$  solution to remove excess acid since limonene epoxide is acid sensitive. Once all acid was removed, the ether and water layers were separated and the water layers were washed with ether to remove all epoxide. Then the majority of the ether was stripped off by Rotovac and the resulting solution was distilled under pressure. The distillation at 1 mm pressure gave two fractions; the first was limonene which came off at 35°C (literature 123:760 mm). The  $^1\text{H}$  NMR and I.R. spectra taken of the limonene epoxide which came over at 75°C matches well that given in the literature<sup>61,62</sup> (see Figure 13).

b. Limonene epoxide reactions. The procedure commonly used for the reaction of limonene epoxide and polymer complex called for 2-3 ml of epoxide in a 25-ml round-bottomed flask, equipped with a condenser column, a magnetic stirring bar, and an oil bath. Hexane

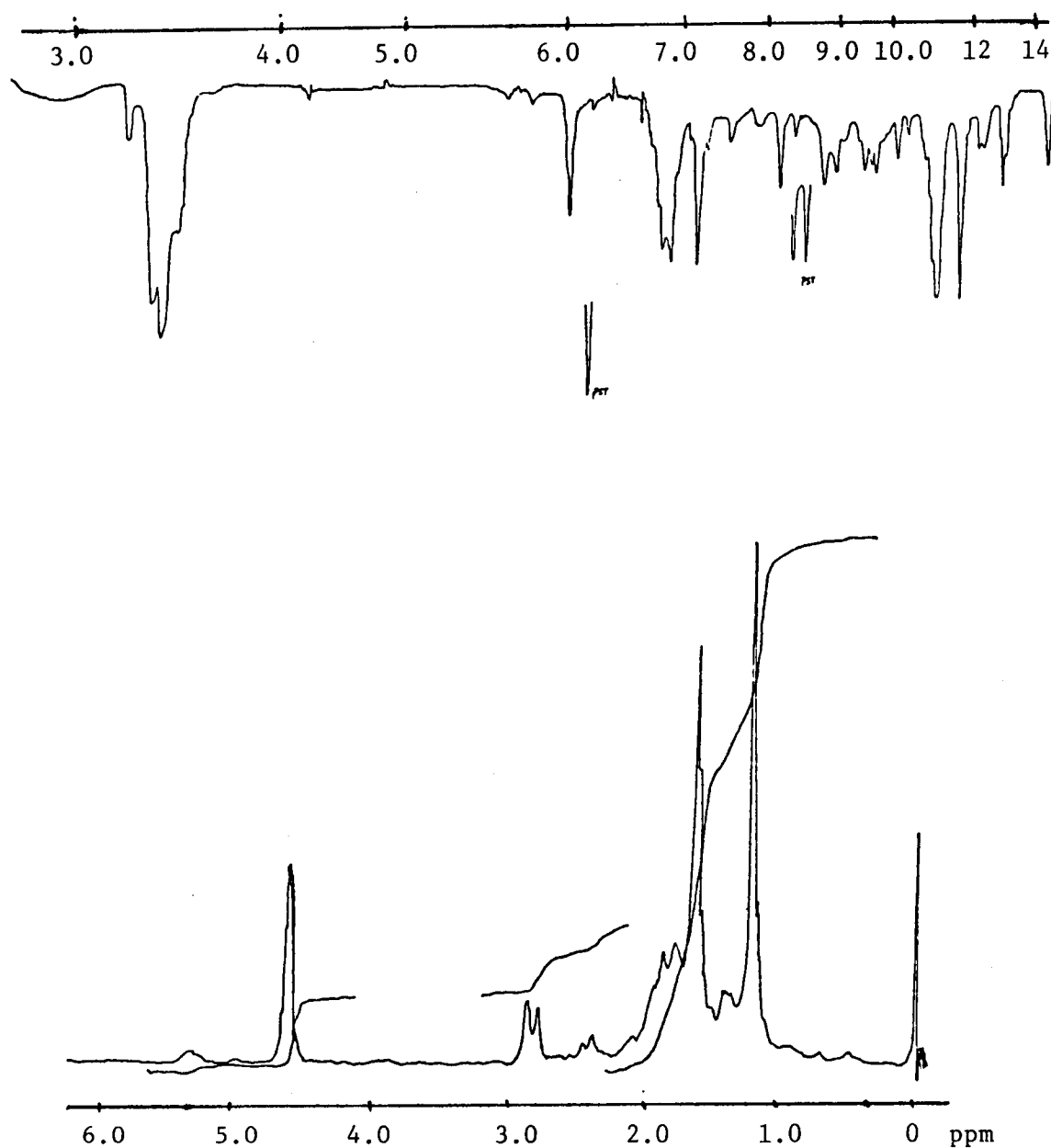


Figure 13. Spectra of limonene epoxide. Spectrum (a) I.R. absorbance (literature<sup>61</sup>,  $\mu$  3.37, 6.06, 5.90, 7.23, 8.27, 8.93, 9.12, 9.78, 9.88, 10.31, 10.91, 11.25, 11.88, 13.17) and (b) NMR resonance peaks (literature<sup>62</sup>,  $\delta$  1.27, 3H, s; 1.72, 3H, s; 2.93, 1H, dist; 4.75, 2H, s).

was used as solvent in 5-10 ml portions for reducing viscosity only. After heating the reaction mixture to approximately 85°C as monitored by oil bath temperature, from 1-7 g of polymer complex was added. Reaction times ranged from 9-12 hr and then the products were separated by G.C. analysis (see Appendix, section C-2) and identified by  $^1\text{H}$  NMR, I.R. and mass spectroscopy. Products from the reaction are discussed in the next chapter, and data for other limonene reactions are given in Table VIII.

### 3. Dicyclopropyl Carbinol Reactions

Following the method of Neckers, et al.,<sup>15</sup> dicyclopropylcarbinol was reacted with polymer complex to give di(dicyclopropylcarbiny) ether. Dicyclopropylcarbinol was prepared from dicyclopropyl ketone as follows or it was bought from Pfaltz and Bauer.

a. Preparation of dicyclopropyl carbinol. According to the method of Hart and Curtis<sup>63</sup> approximately 15 ml of ketone and 30 ml of ether were mixed together and placed in a beaker. A suspension of LAH and ether was placed in a 100-ml round-bottomed flask. The flask was equipped with magnetic stirrer, an ice bath, and a reflux column. The ketone was then added dropwise to the LAH suspension. Once the reaction had refluxed for 1 hr, the reaction was stopped. The LAH was then killed using a strong NaOH solution to separate the ether and water layers. To wash the water layer methylene chloride was used since ether would remove the product from water. Once the ether layer was separated the solvent was stripped off by a Rotovac and the resulting organic solution was distilled under pressure. The alcohol was recovered at 38°C and 1 mm pressure,

TABLE VIII  
REACTIONS OF LIMONENE EPOXIDE WITH POLYMER COMPLEX

| Sample No.       | Limonene ml | Epoxide moles          | Polymer Grams | Complex Moles         | Mole Ratio | Percent <sup>h</sup> Complexed |
|------------------|-------------|------------------------|---------------|-----------------------|------------|--------------------------------|
| 1 <sup>a,c</sup> | 30          | $2.055 \times 10^{-2}$ | 1.201         | $6.56 \times 10^{-3}$ | 3:1        | 73                             |
| 2 <sup>a,d</sup> | 30          | $2.055 \times 10^{-2}$ | 1.3925        | $7.59 \times 10^{-3}$ | 3:1        | 73                             |
| 3 <sup>a,e</sup> | 5           | $3.4 \times 10^{-3}$   | .9156         | $5.00 \times 10^{-3}$ | 1:1        | 73                             |
| 4 <sup>a,f</sup> | 11.5        | $7.88 \times 10^{-3}$  | 1.953         | $1.02 \times 10^{-2}$ | 1:1        | 85                             |
| 5 <sup>b</sup>   | 5           | $4.79 \times 10^{-2}$  | 1.501         | $7.88 \times 10^{-3}$ | 6:1        | 85                             |
| 6 <sup>b,g</sup> | 7.6         | $7.28 \times 10^{-2}$  | 7.621         | $3.99 \times 10^{-2}$ | 2:1        | 85                             |

<sup>a</sup>Limonene epoxide solution used without purification.

<sup>b</sup>Pure limonene epoxide

<sup>c</sup>Reaction takes place immediately as shown by boiling ether.

<sup>d</sup>Products were inseparable by alumina column.

<sup>e</sup>Hexane used as solvent to lower viscosity.

<sup>f</sup>Immediate reaction, steam distillation did not help purify products.

<sup>g</sup>Reaction ran at room temperature. Products separated by G.C.

<sup>h</sup>Percent of poly(p-methoxystyrene) methoxy groups with  $\text{BF}_3$  complexed to them.

uncorrected, (literature, 48°C at 3mm).<sup>63</sup> From the 2nd and 3rd alcohol preparations, a total of 20 ml was obtained giving good NMR and I.R. spectra (see Figure 14).

b. Reaction using dicyclopropyl carbinol and polymer complex.

The typical reaction was much like that of limonene epoxide with 0.4417 g of alcohol being placed in a 25-ml round-bottomed flask equipped with a reflux column, a magnetic stirrer, and an oil bath. Approximately 5-10 ml of hexane was added to reduce viscosity, and the solution was then heated with stirring to 65°C. At this point, 1.0934 g of polymer complex was added and the reaction was heated for another hour. After the reaction was stopped, the hexane was stripped off using a Rotovac and then the products were separated by gas chromatography (G.C.) and identified by NMR, I.R. and mass spectrometry. Data for other carbinol reactions can be seen in Table IX.

G. Studies of a Catalytic Gel

1. Preparation of the Gel

A polymer gel was prepared in order to examine any differences of catalytic properties due to crosslinking and/or higher molecular weight. A sample of p-methoxystyrene was freed from inhibitor by 3 successive 10% NaOH washes and dried with Na<sub>2</sub>SO<sub>4</sub>. The monomer, 5.001 g ( $3.73 \times 10^{-2}$  mole), was then placed into a 100-ml round-bottomed flask equipped with a gas inlet tube, a reflux condenser, a heating mantle, and a magnetic stirrer. To the monomer was added a solution of benzene, 0.0585 g of AIBN, and approximately 0.05 g of divinylbenzene. The solution was allowed to reflux for 24 hr at which time the heat was turned off and the polymer gel precipitated in hexane.

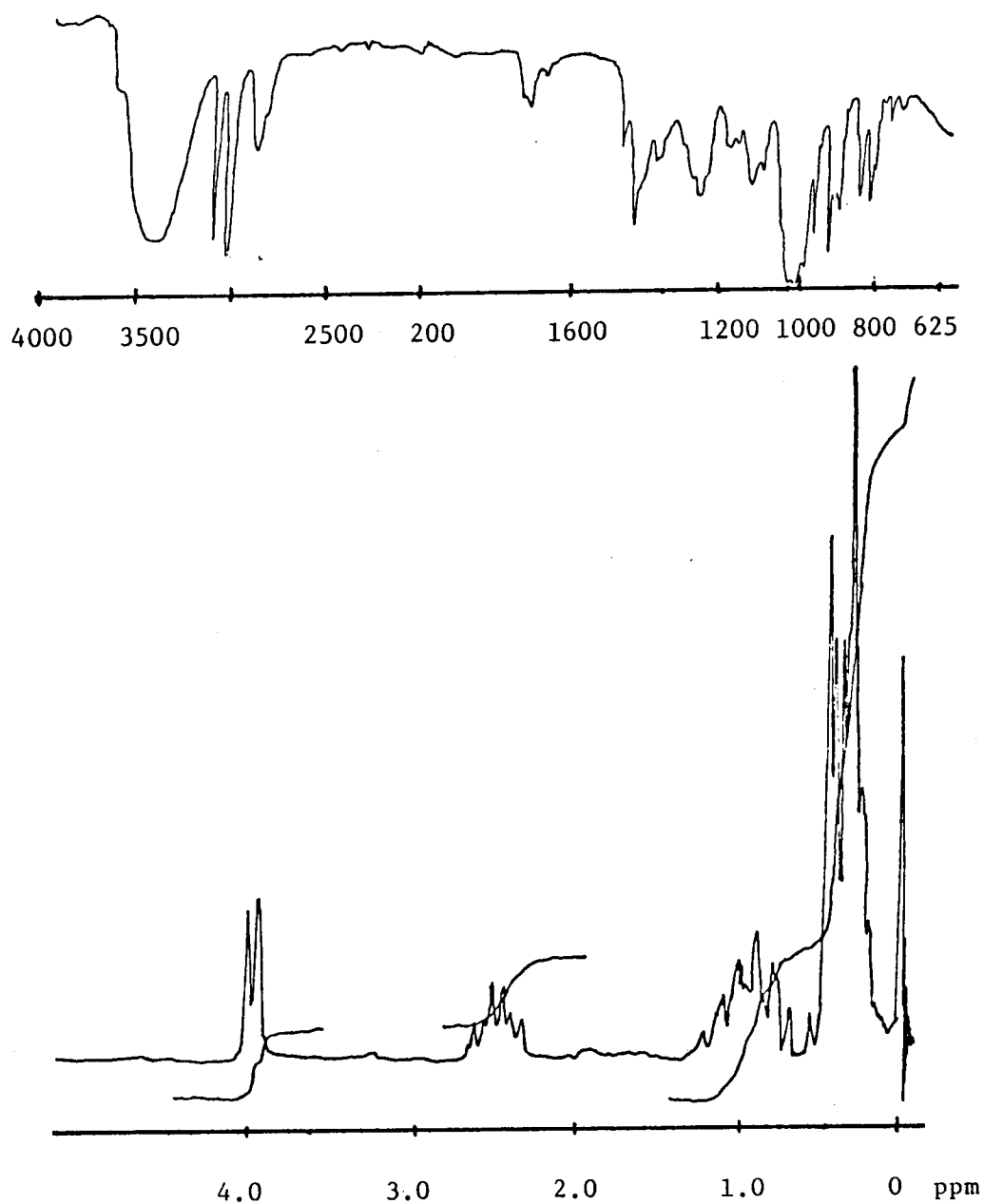


Figure 14. Spectra of dicyclopropylcarbinol. Spectra (a) I.R. absorbances (literature<sup>63</sup>, 3650m, 3500m, 3110s, 3040s, 2890s, 1470m, 1437s, 1385m, 1350w, 1288m, 1260m, 1194m, 1172m, 1137s, 1107s, 1040s, 1021s, 997s, 970m, 931s, 909m, 853m) and (b)  $^1\text{H}$  NMR resonance.

TABLE IX

REACTIONS OF DICYCLOPROPYLCARBINOL (DCPC) WITH POLYMER COMPLEX

| Sample No.     | DCPC  |                       | Polymer Complex |                       | Percent Complexed |
|----------------|-------|-----------------------|-----------------|-----------------------|-------------------|
|                | Grams | Moles                 | Grams           | Moles                 |                   |
| 1 <sup>a</sup> | 14.02 | $1.25 \times 10^{-1}$ | 1.0934          | $5.97 \times 10^{-3}$ | 73                |
| 2 <sup>b</sup> | 1.46  | $1.30 \times 10^{-2}$ | 2.3011          | $1.26 \times 10^{-2}$ | 73                |
| 3 <sup>c</sup> | 8.9   | $7.89 \times 10^{-2}$ | 3.0179          | $1.59 \times 10^{-2}$ | 82                |
| 4 <sup>d</sup> | 3.97  | $3.54 \times 10^{-2}$ | 1.1567          | $6.12 \times 10^{-3}$ | 82                |

<sup>a</sup>Reactions run at 55°C. Products could not be separated by alumina column.

<sup>b</sup>Solvent used was hexane.

<sup>c</sup>Reaction was tried over a catalyst gel and methanol was used as solvent.

<sup>d</sup>Products were separated by G.C.

## 2. Complexation of the Gel

The polymer gel was complexed with  $\text{BF}_3$  in the manner previously mentioned. No new techniques or characteristics were tried or noticed.

## 3. Reactions with the Polymer Gel

Only one reaction was tried using the polymer gel; i.e., the preparation of a symmetrical ether from dicyclopropylcarbinol. In doing this reaction it was desired that a column of polymer should be made and the reaction solution poured through the column. The reaction temperature to be used was  $50^\circ\text{C}$ . However, this posed a problem; i.e., the difficulty of heating a column. To overcome this problem, an oil bath heating coil was straightened out and then recoiled between the glass liners of a refluxing column; i.e., the coiled wire was placed in the space in which water is run to cause condensation. Once the heating coil was in place, the rest of the space was filled with mineral oil to allow better heat transferal and surface area contact. The oil bath coil was then connected via alligator clips to a variable transformer which when turned on gave an oil bath heated column with which one could use varying temperatures to do column work.

Once the heating column was prepared, a stopcock was attached with rubber tubing. A small piece of glass wool was then placed over the stopcock, followed by sand and then followed by the crushed polymer gel catalyst. Reactions were run at  $50^\circ\text{C}$  by pouring a mixture of alcohols and hexane (solvent) over the polymer support and allowing it to flow through the column. Elution times were approximately 30 minutes and were regulated by the stopcock. Conclusions follow in the next chapter.

## H. Complex Rejuvenation

If this catalyst were used commercially, it would be very desirable to be able to rejuvenate the  $\text{BF}_3$  supply on the backbone after a reaction. Tests were run to determine the feasibility of complex rejuvenation.

In one polymer complex preparation, 3.9915 g of polymer was complexed in the usual manner with a  $\text{BF}_3$  addition time of 5 hr. The complex appeared very rubbery, so a titration was done on two samples, one of 0.7819 g ( $3.87 \times 10^{-3}$  mole) and one of 1.0800 g ( $5.35 \times 10^{-3}$  mole) of complex. The first gave a titration showing 44% complexed and the second gave 35% complexed. The remaining polymer was then dissolved over a period of 24 hr in 50 ml nitrobenzene and another  $\text{BF}_3$  addition was made. This time the polymer came out as was expected and a titration of the polymer complex started 5 minutes after complex precipitations showed that the polymer was approximately 100% complexed (Note: Instead of drying the polymer for a couple of days over paraffin chips, the complex was placed into a beaker and dried in an oven at  $250^\circ\text{C}$  for 2-3 minutes).

In a second attempt at rejuvenation, two samples of polymer were used. One had been used in a chemical reaction and the other sample was from a titration done to determine  $\text{BF}_3$  concentration. Each had been thoroughly dried. In trying to dissolve the polymer so that it could again be complexed, no solvent was found that would work.. A number of solvents were tried, including hexane, concentrated  $\text{HCl}$  THF, acetone, and DMSO. Some solvents were tried for periods of up to two weeks with stirring and showed only slight swelling of the polymer.

The only solvent that would work was "Magic Acid" and it appeared to drastically decompose the polymer.

## CHAPTER III

## RESULTS AND CONCLUSIONS

A. Stability of the Anisole and Polymer  $\text{BF}_3$  Complexes

Literature sources state that anisole and  $\text{BF}_3$  form a one-to-one mole complex but that the complex is not stable enough to distill under any conditions.<sup>64</sup> Due to the use of  $\text{A} \cdot \text{BF}_3$  in boron isotope separation other characteristics and data have been determined.

Palko et al.,<sup>49</sup> calculated the heat of formation of the  $\text{A} \cdot \text{BF}_3$  complex as  $-12.1 \text{ kcal mole}^{-1}$ , and noticed a 5% solvent decomposition after 30 days. The dissociation constants for  $\text{A} \cdot \text{BF}_3$  at various temperatures were given by Katal'nikov.<sup>65</sup> Topchii and Borovikov listed the dielectric permittivity (39.3), the electric susceptibility ( $.24 \times 10^{-4}$ ), the refractive index (1.442), the density (1.219), the dipole moment (5.4D) and the bond strength (4D), but without units.<sup>66</sup>

The properties of  $\text{A} \cdot \text{BF}_3$  and the stability, or lack thereof, in the  $\text{A} \cdot \text{BF}_3$  complex derive from three major reasons. Firstly, the anisole molecule is known to have a  $p-\pi$  conjugation between the oxygen atom and the benzene ring.<sup>67</sup> This is what causes the splitting of the aromatic group in the 7 ppm region. In forming the  $\text{A} \cdot \text{BF}_3$  complex, the  $p-\pi$  conjugation is broken, as can be seen in the room temperature  $^1\text{H}$  NMR spectrum of 100%  $\text{A} \cdot \text{BF}_3$  where the aromatic peak is displayed as a benzene-like singlet. Breaking the conjugation requires energy. Secondly, to form a complex, the planar molecule of  $\text{BF}_3$  must assume a pyramidal structure at a cost of energy;  $\Delta G = 34.2 \text{ kcal mole}^{-1}$ .<sup>68</sup> Thirdly, the rapid exchange between Lewis acid and available Lewis

base sites, which is characteristic in the  $A \cdot BF_3$  complex, would suggest that the bonding in the complex is predominantly of an ionic type of bond. That is, the bonding is of an electrostatic type with no electron transfer.<sup>53</sup>

A hint of the polymer complex's stability can be derived from titration data seen earlier. When a complex was allowed to dry over paraffin chips for 24 hr or longer, the titration data indicated a 75% complexed polymer. When the polymer was titrated directly after complexation, with very little time allowed for drying, the titration data seemed to indicate 100% complexation. In view of these facts, and information in the literature,<sup>69</sup> it would appear that the  $BF_3$  on the surface of the polymer is being hydrated by water in the air. Once the surface is hydrated, no further deterioration of the  $BF_3$  concentration is noticeable.

It should also be noted, however, that the polymer is not so stable that it will not react. Titrations of polymer complexes, after reactions, showed less than 1% of the  $BF_3$  left in the polymer matrix. Also, the reactivity of the polymer complex (discussed later) seems to come mainly from the weakness of the bonding shown between the methoxy group and  $BF_3$  and the ease with which  $BF_3$  attacks other Lewis bases.

In fact, stability problems of the polymer complex are not found in the polymer  $BF_3$  bonding but in the polymer's ability to withstand rearrangement brought on by the  $BF_3$ . In the polymer complex, after handling and use, which allows exposure to water vapor in the air, the polymer backbone seems to form an insoluble cross-linked matrix. In view of the phenol type  $^1H$  NMR peaks displayed by model

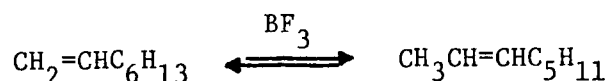
compound complexes when reacted with minute quantities of water, and looking at the literature concerning  $\text{BF}_3$  induced rearrangement of aryl ethers, phenols, and xylenes,<sup>44</sup> one could imagine some type of cross linking occurring due to any acidic proton that might enter the system. Further supporting this idea is the deep red color displayed by polymer and anisole complex alike which can be caused by the formation of cations. Further, the  $\text{BF}_3$  gas was used as received, without removing any HF that might have been present. Since  $\text{BF}_3$  is highly hygroscopic and since it forms HF when reacted with water, there is a very good chance that HF entered the polymer matrix along with  $\text{BF}_3$ . This cross linking prevents polymer complex rejuvenation as it negates the solubility needed to put the polymer back into solution. It should be noted here that the only rejuvenation accomplished was done with a polymer complex right after its preparation and while it was still 30% complexed with  $\text{BF}_3$ . Tests were not run to check the time dependence on the amount of crosslinking. It could be that the 30%  $\text{BF}_3$  complex was not allowed to sit long enough to crosslink, whereas the other polymer complex, since it was prepared properly at first, was allowed to sit from 2 days to 2 months before being used in a reaction. Or it could be that rejuvenation cannot be accomplished if the polymeric complex has been "bled" of  $\text{BF}_3$  to below 30% complexed.

It should be mentioned that the possibility of polymer backbone rearrangement or worsening of the rearrangements prevents one from using the complex in many reactions. Excluded, for example, are reactions such as esterifications, alkylations, nitrations, sulphonations, condensations, or polymerizations where an acidic species is used.<sup>44</sup>

## B. Reaction Products and Yields

### 1. 1-Octene to 2-Octene Isomerization

The reaction studied was a straight forward rearrangement reaction from which one or more isomers may have been expected. The reaction is as follows.



The products of the 1-octene rearrangement were studied by  $^1\text{H}$  NMR. For the reaction in which  $4.04 \times 10^{-2}$  moles of 1-octene was mixed with  $6.83 \times 10^{-3}$  moles of polymer complex (56% complexed) the products appeared to be a mixture of isomers (see Figure 15). Intergration of the  $^1\text{H}$  NMR spectrum shows a quantitative conversion of reaction materials, at least 90%. The small size of the peak at 1.7 $\delta$ , which is due to  $\text{CH}_3$  resonance exclusively in 2-octene, would tend to indicate not only the presence of 2-octene, but other isomers as well. The multiplet at 5.5 $\delta$  definitely shows very little 1-octene left. A G.C. analysis of the products was not done. The fact that the rearrangement did occur was of primary interest and was clearly demonstrated by  $^1\text{H}$  NMR. Since  $\Delta H$  reaction data for the conversion of 2-octene to 3-octene and 4-octene were not studied, it is not known in what quantities they should be expected in the products. The points to be stressed are that the catalyst did aid the isomerization and that the isomerization reaction gave a very high product yield.

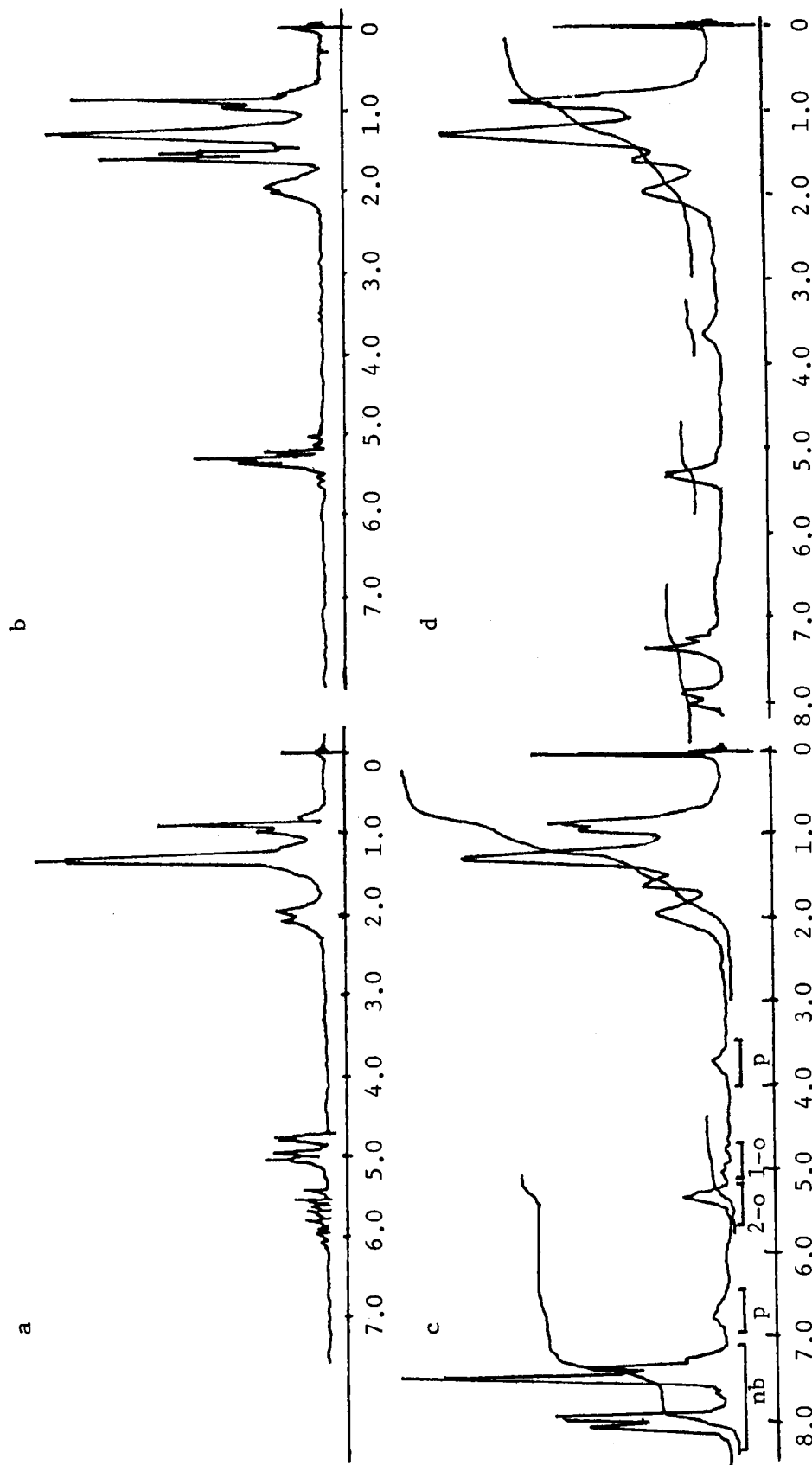
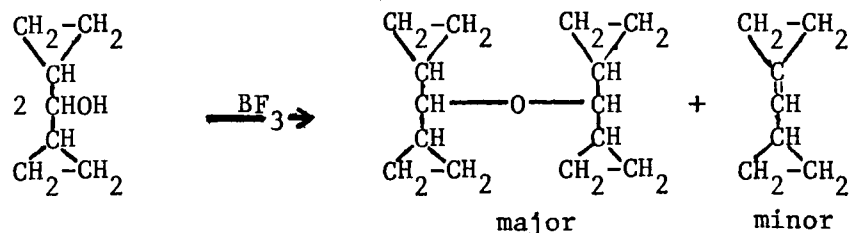


Figure 15.  $^1\text{H}$  NMR spectra showing isomerization of 1-octene. (a) 1-octene, (b) 2-octene, (c) 1-octene reaction mixture after 3 hr with polymer complex and nitrobenzene solvent, (d) 1-octene reaction mixture after 4 hr with polymer complex and nitrobenzene solvent.

$^1\text{nb}$  = nitrobenzene, p = polymer, 2-o = 2-octene, 1-o = 1-octene.

## 2. Dicyclopropylcarbinol Reaction

This second reaction was the preparation of an ether from an alcohol. The reaction is shown below.



By looking at the spectra obtained from the reaction of  $3.54 \times 10^{-2}$  moles of alcohol with  $6.12 \times 10^{-3}$  moles of polymer complex (85% complexed), one can see the reaction afforded the ether product with few side products. The products were identified by  $^1\text{H}$  NMR, I.R. and mass spectrometry after separation on a G.C. column. The sample giving peak 3, as seen in Figure 16b, was collected and its  $^1\text{H}$  NMR and I.R. spectra showed that separation of the products had not been complete.

$^1\text{H}$  NMR. By comparison with dicyclopopyl ketone (Figure 17b) and dicyclopopylcarbinol (Figure 17a), the reaction product spectrum (Figure 17c) leaves no doubt that a reaction occurred. The alcohol peak in Figure 17a, seen at  $4.0 \delta$  and identified by deuterium exchange, has completely disappeared. Instead one can now see at  $5.0\text{--}5.7 \delta$  a multiplet arriving from a  $\text{R}_2\text{C=CHR}$  proton, showing an alkene. One can also see a triplet at  $3.7$  to  $4.08$  showing a  $\text{R}_2\text{CH-OR}$  proton, definitely showing an ether. Cyclopropyl protons gave a signal at  $.2\text{--}.7$  which can also be seen, and at  $2.0\text{--}2.4$  one can see the  $\text{R}_2\text{CH-C-OR}$  proton. The two observations that do not match completely are the multiplet at  $5.2$ , it should be a singlet, and two triplets at  $3.7$  instead of one triplet.

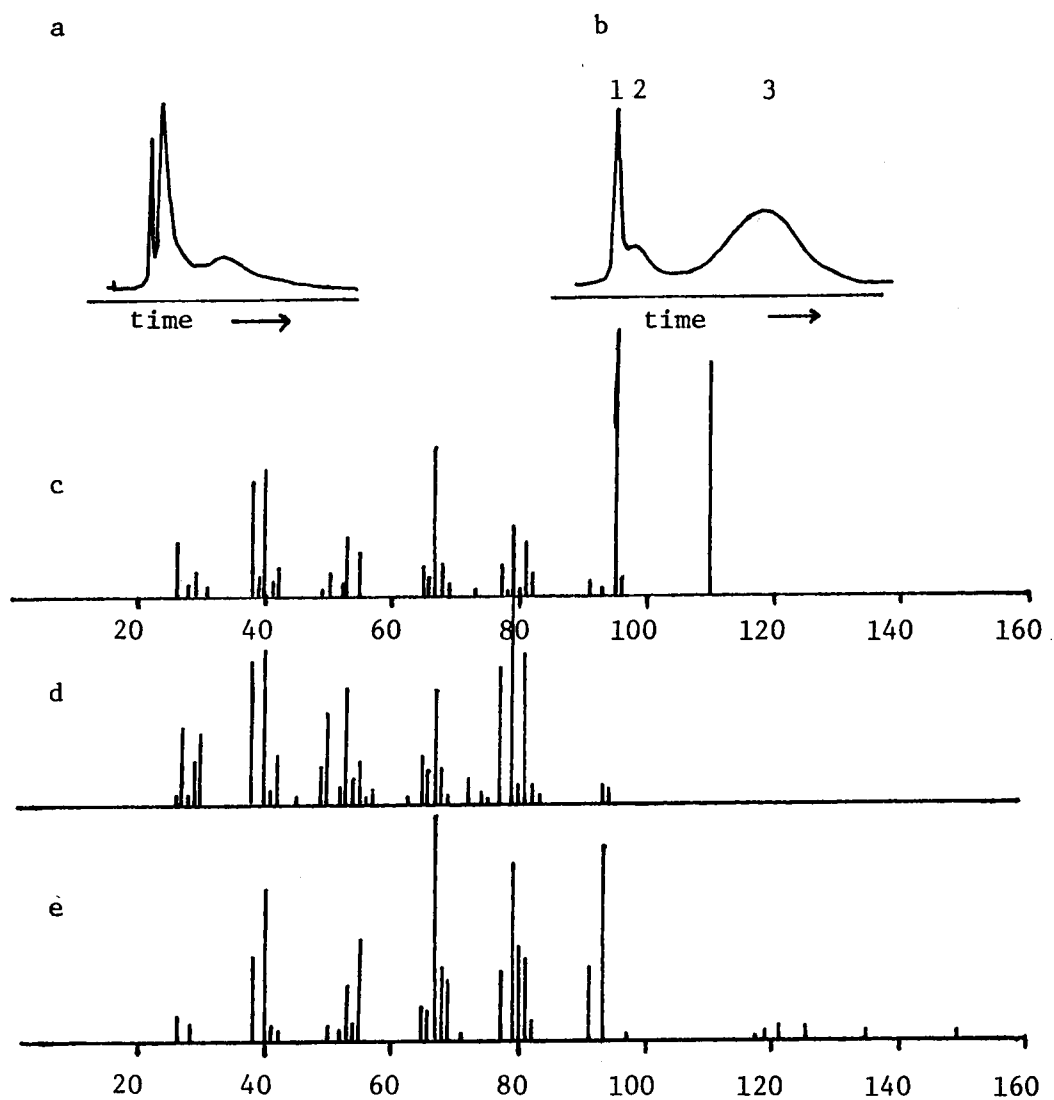


Figure 16. G.C. and mass spectral data for dicyclopropylcarbinol reaction products. (a) G.C. trace for starting materials and acetone. (b) G.C. trace for the reaction mixture products. Also shown are mass spectra of (c) dicyclopropyl ketone, (d) the alkene, and (e) the ether.

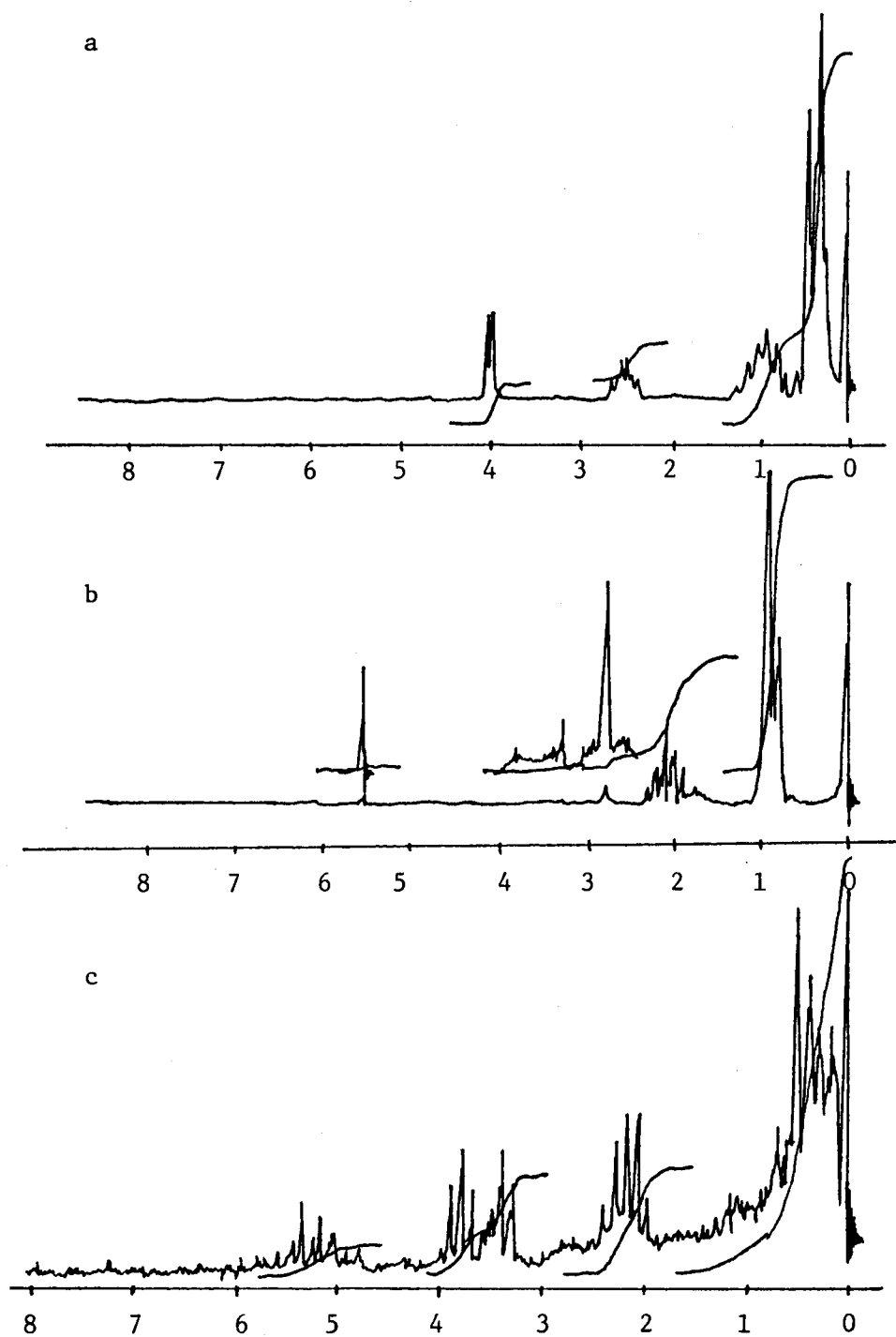


Figure 17.  $^1\text{H}$  NMR spectra for dicyclopropylcarbinol reaction. Spectra are (a) dicyclopropylcarbinol, (b) dicyclopropyl ketone and (c) peak #3 from the G.C. separation of the reaction products (taken at 60 MHz and 25°C).

I.R. Looking at and comparing I.R. Figure 18, one can see the absorption characteristics of the ketone ( $\sim 1690$ ), the alkene ( $\sim 810$ ), and the ether ( $\sim 1100$ ). One can also see a broad peak at 3500 that could derive from starting material or water that entered the sample while collecting the samples from the G.C. Comparing the dicyclopentylcarbinol spectrum and the product spectrum one can see the absorption characteristics of the dicyclopentyl methane backbone ( $\sim 3080$ , 3010, 2880, 1450, 1260, 1140, 1040, and 950). One can also see a small peak due to an alkene, meaning that the alkene could be an impurity in the starting material or that it was generated as a minor side product during the reaction.

G.C. G.C. gave 3 peaks, one of which was starting material, peak 1; one of which was unknown, peak 2; and the third one, peak 3, which was the product peak. The portion of the reaction mixture which accounted for the third peak was caught using glass coils dipped in  $N_2(l)$  which may have let  $H_2O$  get in the reaction products (Figure 18a and b).

Mass spectrometry. Looking at the total ion count graph from the mass spec one can see what appears to be five peaks (Figure 19). When comparing fragmentation data, however, one notices that peaks 3, 4, and 5 are due to the same compound, whereas peak 1 and 2 are the alkene and ketone respectively (Figure 19). This can be determined from peak 1's parent ion of 94, by peak 2's parent ion of 110, and by the similarity of ions in peaks 3, 4, and 5. Observed mass spectral peaks and their masses can be seen in Figure 18c, d, e.

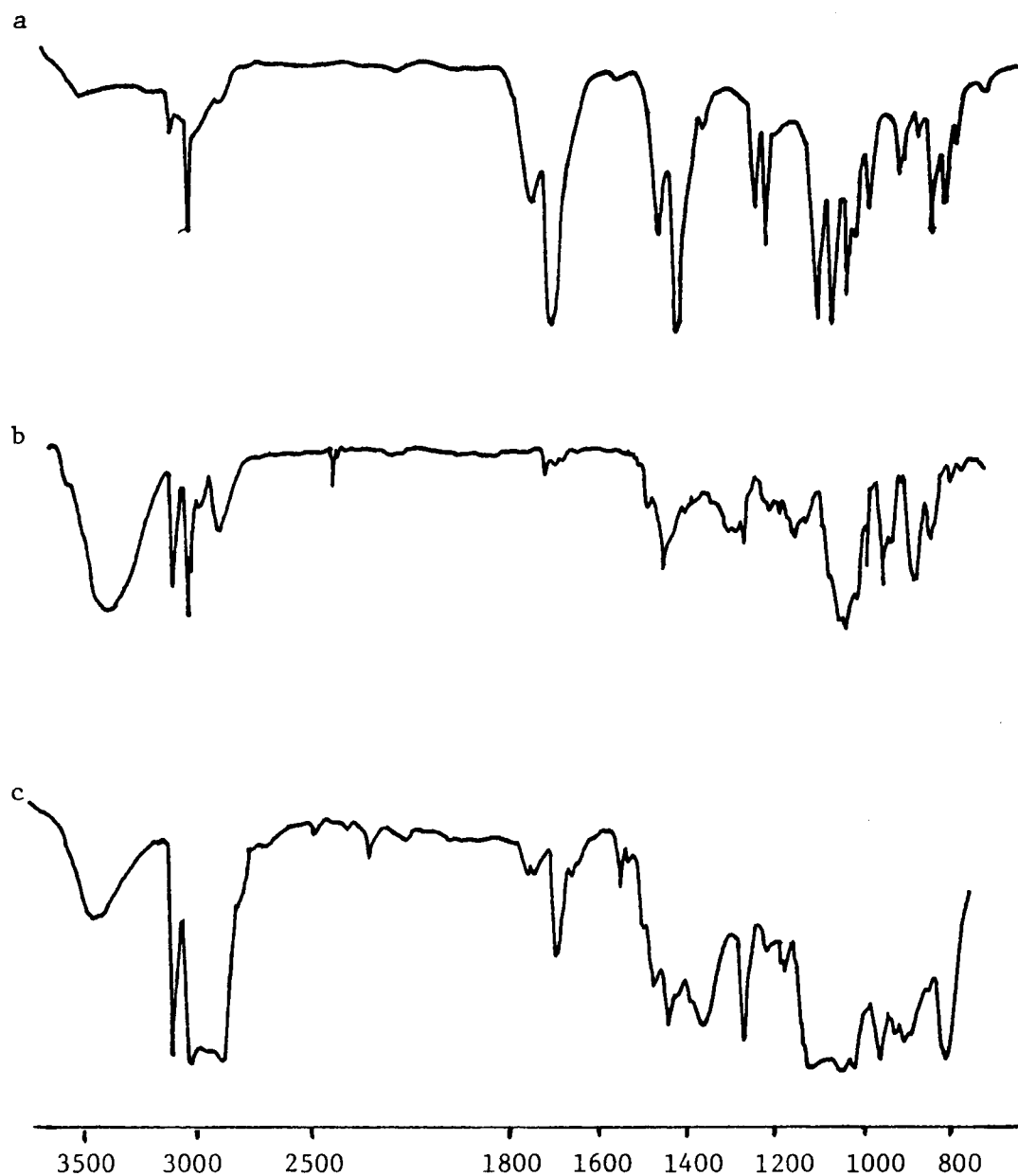


Figure 18. I.R. spectra for dicyclopropylcarbinol reaction. Spectra are (a) dicyclopropyl ketone, (b) dicyclopropylcarbinol, and (c) the reaction products isolated in G.C. peak #3 as identified in Figure 18b.

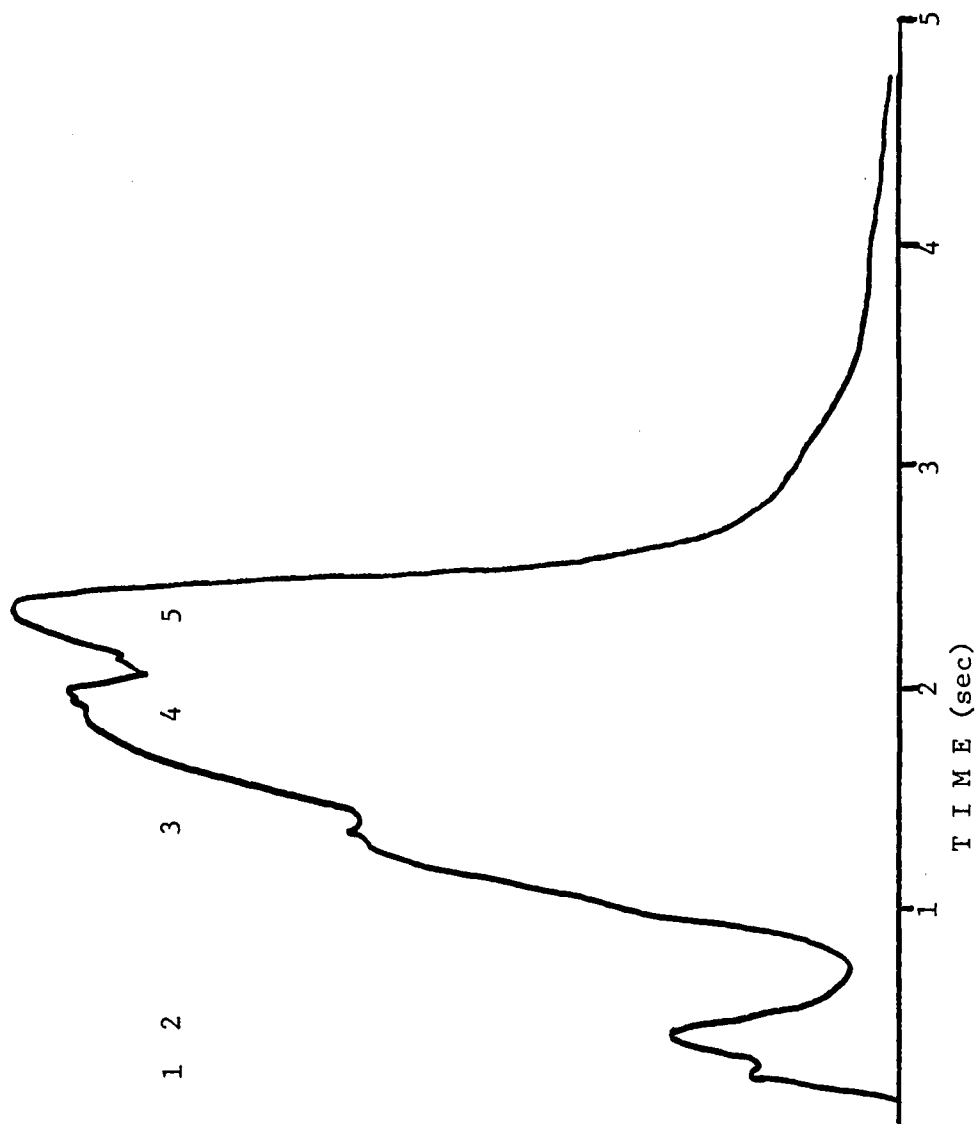


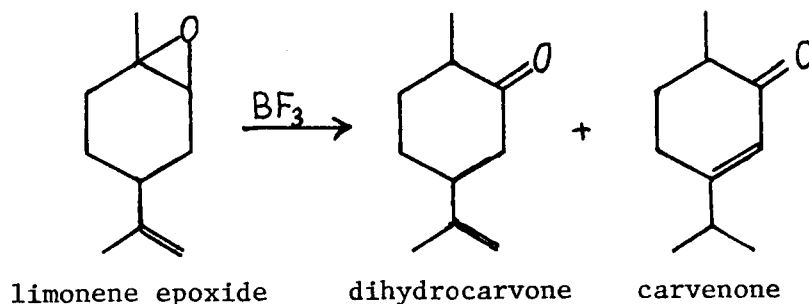
Figure 19. Mass spectral ion count of dicyclopropylcarbinol reaction.

Percent yields.  $^1\text{H}$  NMR integration of the isolated products, specifically the multiplet at 5.2 $\delta$ , the alkene, and of the multiplet at 2.3 $\delta$ , the ether, shows a 1:3 ratio meaning 75% of the separated product was ether and 25% was alkene. From the G.C. trace of the reaction mixture the percent of products, peak 3, can be calculated by weight/area to weight/area ratios as  $\sim 73.3\%$ . Combining the data would correspond to 55% ether, 20% alkene, and 25% side products and unreacted alcohol. The best Neckers<sup>15</sup> reported with his aluminum trichloride polymer catalyst was 58.5% ether with 66.5% conversion or a total of 39.5% ether for the whole reaction which is less than 3/4 of that obtained in this research.

Discussion. The type of reaction used was selected in order to stay away from proton acid media which leads to polymer backbone rearrangement. The high yields would tend to indicate the ease with which the  $\text{BF}_3$  is released from the polymer. This is indicated by the fact that the  $\text{BF}_3$  is removed from the polymer, as shown by titration, and so the increased productivity has to be a surface phenomenon or a kinetic one since the solvents channels of the polymer would increase productivity and selectivity only if the reaction occurred inside the polymer matrix. The occurrence of the reaction outside the polymer may or may not also be demonstrated by the elimination reaction to give an alkene. One could imagine that inside small polymer channels it would be hard to bring to large alcohols together to react, thus allowing for more intermolecular reactions and therefore giving more alkene. Pore size was not experimented with and so it can not be identified positively as a factor in productivity.

### 3. Limonene Epoxide Reaction

The last series of reactions in which the new catalyst was used was the rearrangement reactions of limonene epoxide to dihydrocarvone. The reaction scheme is shown below.



The limonene epoxide products from the reaction mixture of  $7.28 \times 10^{-2}$  moles of epoxide with  $3.99 \times 10^{-2}$  moles of complex (82% complexed), were separated by G.C. and matched to one obtained from the products of a control reaction conducted with equal volumes of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  and limonene epoxide. Except for a slight variation in flow rate, they compare very well (see Figure 20). From the limonene epoxide polymer G.C. trace, material producing peaks 3 and 4 was collected. From the control reaction only the material giving peak 4 was collected. Analysis was done by  $^1\text{H}$  NMR, I.R., and mass spectrometry.

$^1\text{H}$  NMR. Comparing the limonene epoxide starting material's spectrum to that of the products, one can see that a reaction has definitely occurred (Figure 21a,b,c). From the  $^1\text{H}$  NMR spectrum, peak 3 on the G.C. trace can be identified as dihydrocarvone. Peaks at approximately 1.01, .96, and 1.75 match those in the literature fairly well.<sup>70</sup> The .96 peak could come from  $\text{CH}_3\text{-R}$  protons; the 1.01 peak would be a  $\text{CH}_3\text{-C-C=O}$ , the 2.3 multiplet could easily derive from a

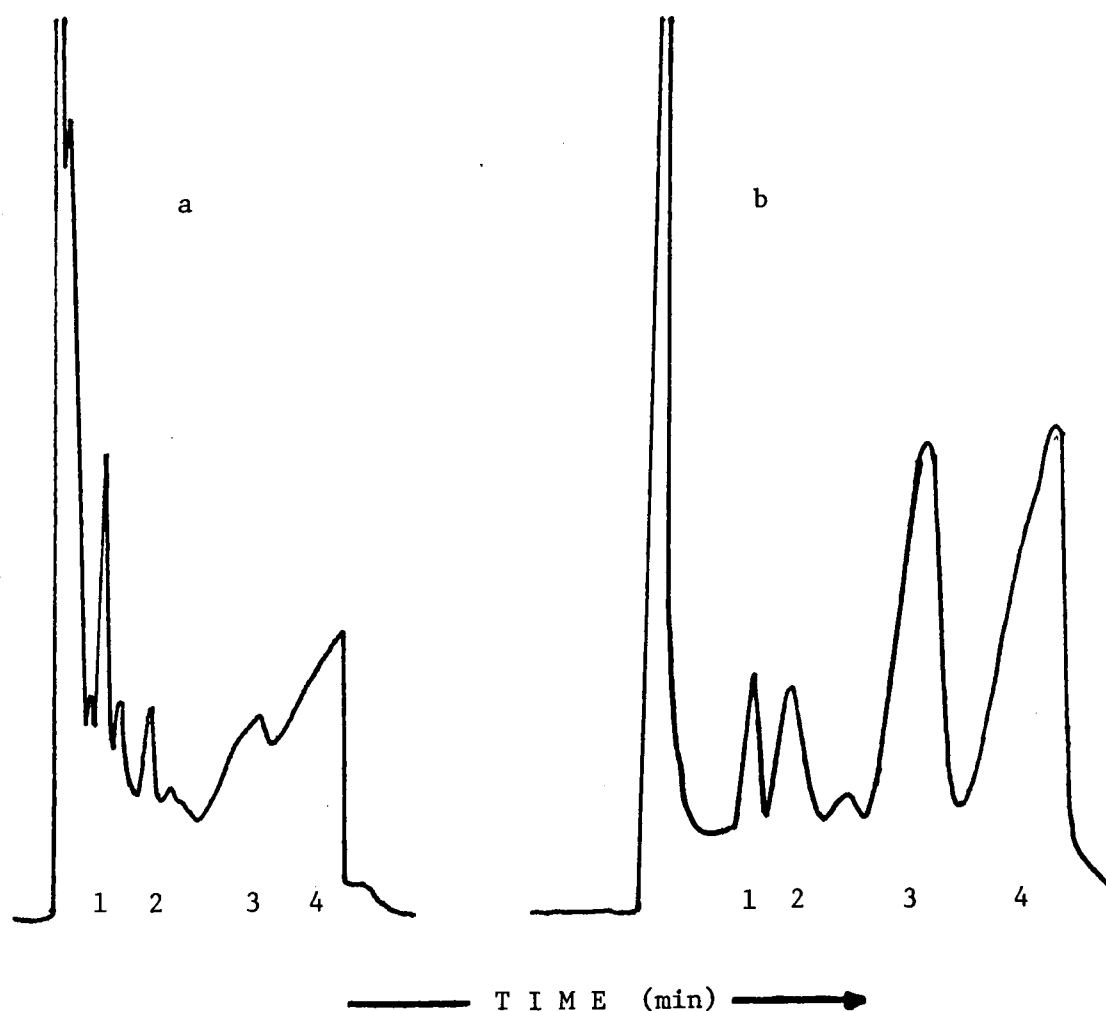


Figure 20. G.C. traces for the limonene epoxide reactions. Spectra are (a) products for the  $\text{Et}_2\text{O} \cdot \text{BF}_3$  limonene epoxide reaction and (b) the trace of the products for the limonene epoxide-polymer reaction. The G.C. traces were collected using 5  $\mu\text{l}$  samples, at 128 attenuation. Temperature settings were: column  $150^\circ\text{C}$ , detector,  $280^\circ\text{C}$ , and injector  $235^\circ\text{C}$ . The column used was a 10% OV-1 chrom W 60/80 that was 5' long and  $1/4$ " in outside diameter. Flow rates for (a) and (b) respectively, are 30 ml/min and 20 ml/min.

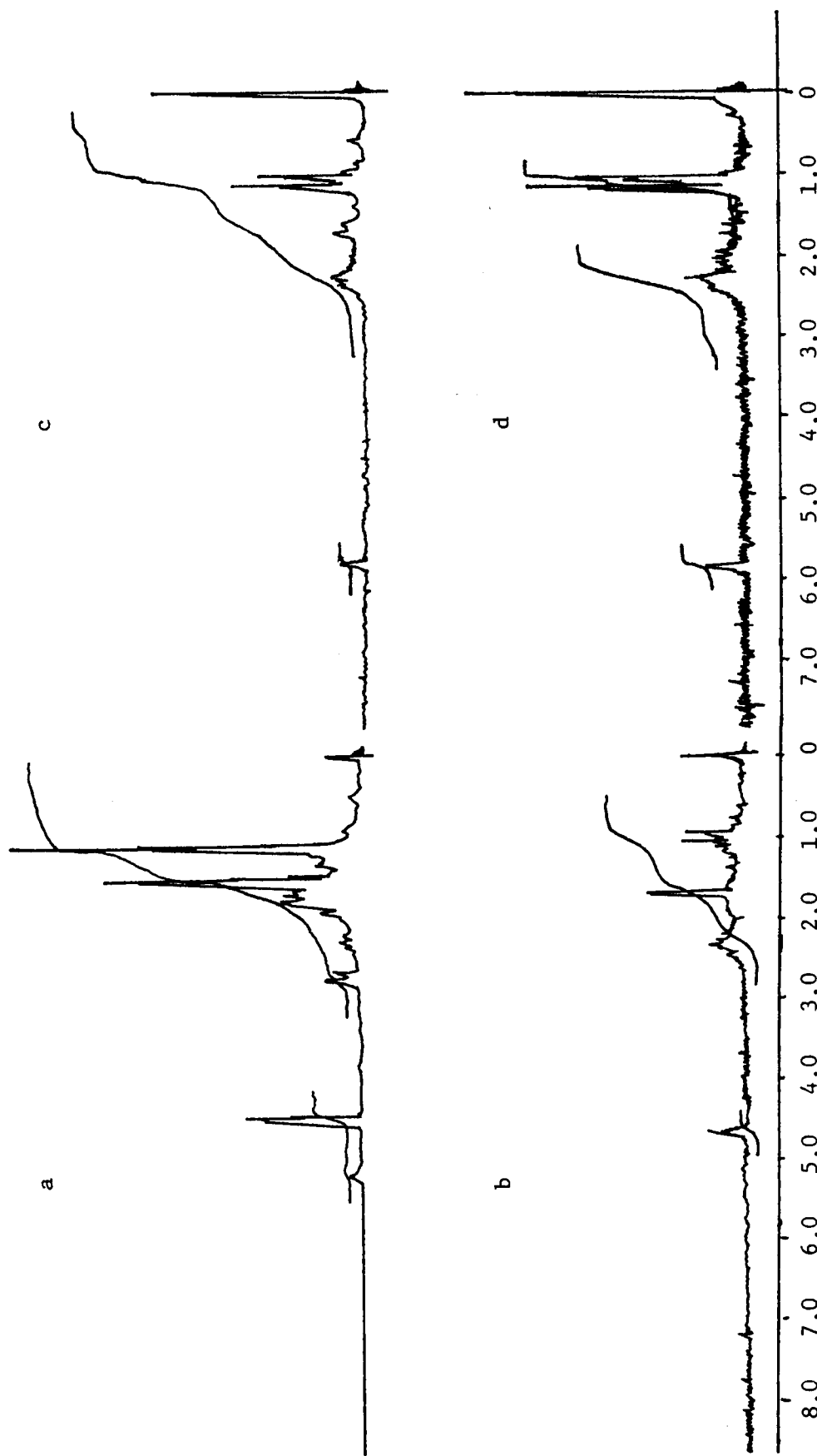


Figure 21.  $^1\text{H}$  NMR spectra for the limonene epoxide reaction. Spectra are (a) limonene epoxide starting material, (b) limonene epoxide-polymer reaction products from G.C. trace peak 3, (c) G.C. trace peak 4, and (d) limonene epoxide reaction products with  $\text{Et}_2\text{O}\cdot\text{BF}_3$  as separated on G.C.

$\text{RCH}_2\text{-CR=R}$  group and the peak at 4.7 would be a  $\text{R-C=CH}_2$  group. This matches well the spectrum that dihydrocarvone would yield. Literature values are incomplete at lower fields.

Peak 4 in the G.C. trace of the limonene epoxide-polymer reaction gives a  $^1\text{H}$  NMR spectrum that is very much like peak 3 with the only difference being the methine proton was shifted up field. This would lead one to believe that the methine proton was in a  $\text{R}_2\text{C-CHR}$  type of arrangement which would give a compound very much like carvenone. One peak that is not consistent is one that matches the  $\text{R}_2\text{C=CH}_2$  peak of dihydrocarvone at 4.7 which may be due to incomplete separation.

A  $^1\text{H}$  NMR spectrum of peak 4 in the  $\text{Et}_2\text{O}\cdot\text{BF}_3$  G.C. trace (Figure 20a) looked exactly like that from peak 4 of the G.C. trace for the limonene epoxide-polymer reaction (Figure 20b), except for the missing 4.7 peak (compare Figure 21c and d).

I.R. analysis. Peak 3, of the limonene epoxide-polymer reaction, from the G.C. trace again matched exactly what one would expect for dihydrocarvone. One can see absorptions at 3080, 2975, 1420 and  $890\text{ cm}^{-1}$  caused by the C-H stretching on a  $\text{R}_2\text{C=CH}_2$  group. At 1640 and  $1715\text{ cm}^{-1}$  one can see the C-C stretch of a  $\text{R}_2\text{C=CH}_2$  and the C=O stretch of a six membered ring unconjugated ketone, respectively. The methyl groups' C-H stretching can be seen at 2960 and  $2872\text{ cm}^{-1}$ . Peak 4 of the limonene epoxide-polymer reaction shows the methyls at 2960 and  $2872\text{ cm}^{-1}$  as well as the C-H stretch of a  $\text{CR}_3\text{-H}$  at  $2890\text{ cm}^{-1}$ . It also has a peak at 1680 showing an unsaturated ketone. Peaks that do not match the proposed spectrum are located at 880, 920, and  $1620\text{ cm}^{-1}$  which again would suggest that during product isolation one obtained incomplete

separation by G.C. Also in spectra, one can see a slight absorption at  $3500\text{ cm}^{-1}$  which may be a trace of carvenol or water. Water might be present due to insufficient G.C. separation techniques (see Figure 22).

Mass spectrometry. Comparison of the mass spectra show a definite reaction. The products of reaction give spectra quite similiar, with peak 4 of limonene epoxide-polymer reaction matching almost exactly peak 4 of the  $\text{Et}_2\text{O}\cdot\text{BF}_3$  control reaction. Peak 3 of the limonene epoxide-polymer reaction is very close in ion formation but different in relative abundances (see Figure 23).

Percent yields. Assuming peak 3 of the limonene epoxide-polymer reaction to be the compound dihydrocarvone, and calculating percentage yields by relative G.C. peak areas, one gets 32%. The literature states total yields obtained for cis and trans dihydrocarvone, endocarveol, and exocarveol, using  $\text{BF}_3$ , was 54.5 and 37.9%.<sup>58</sup> The percent yield of products based on peaks 3 and 4 together for the polymer reaction is approximately 76%. The literature also notes that carvenone is the isomerization product of dihydrocarvone.

The conclusions drawn from all of these data are that 32% of pure dihydrocarvone was prepared with a possibility of even greater yields if separation was not complete. Also this reaction gave comparable yields to the previous reaction route; i.e., 72% vs. 54% and 38% overall.

Discussion. This third reaction is the third experiment in which no protonic media was used and it is also the third reaction in which rearrangement has been noticed. Again good yields indicate the polymer complex may indeed be used as a catalyst.

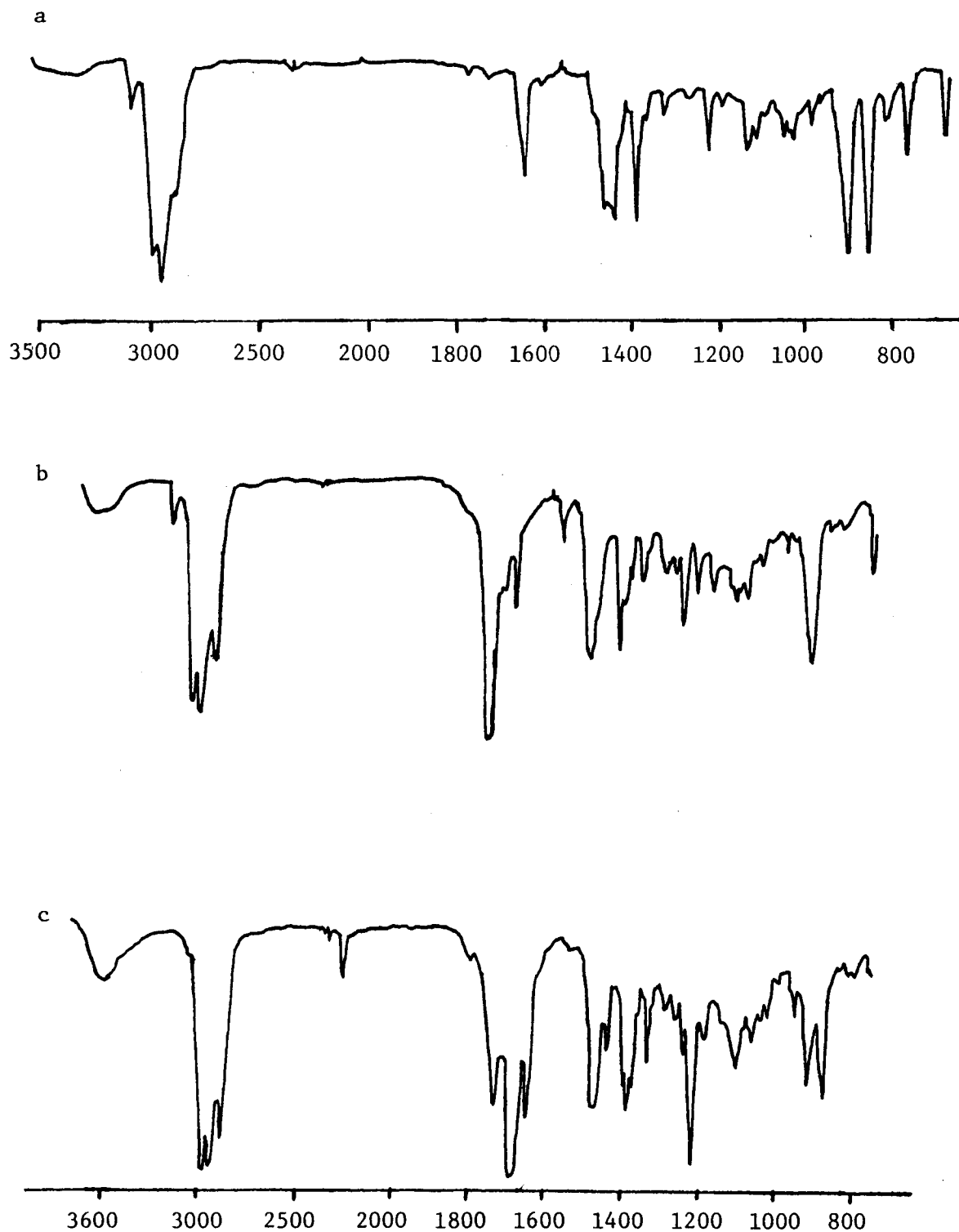


Figure 22. I.R. spectra for the limonene epoxide reaction. Spectra are (a) limonene epoxide, (b) peak 3 of limonene epoxide reaction products (Figure 20b), and (c) peak 4 of limonene epoxide reaction products (Figure 20b).

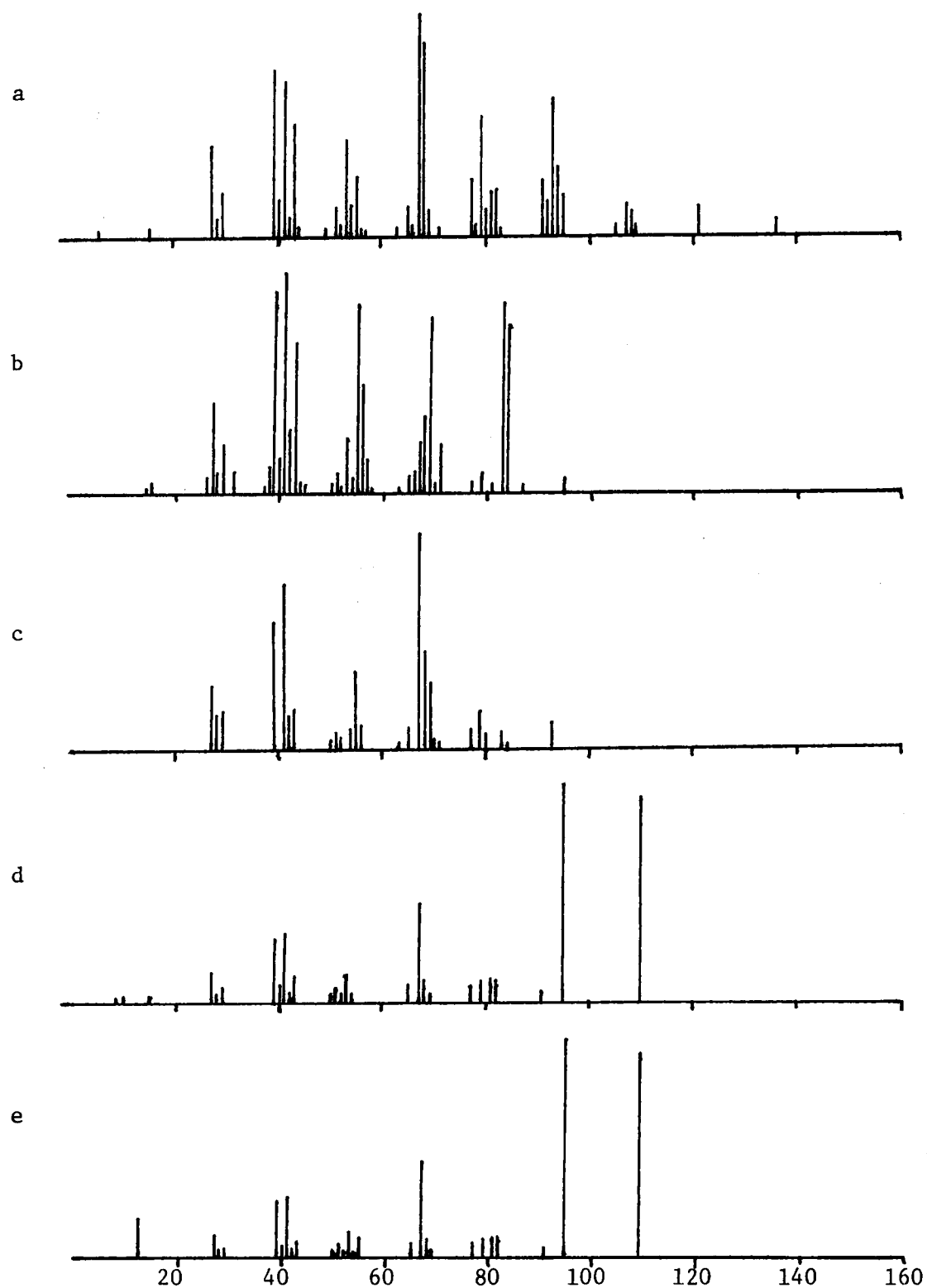


Figure 23. Mass spectral data for the limonene epoxide reaction. Spectra are (a) limonene, (b) limonene epoxide, (c) G.C. peak #3 of epoxide-polymer reaction, (d) G.C. peak 4 of epoxide-polymer reaction and (e) G.C. peak 4 of the epoxide-Et<sub>2</sub>O·BF<sub>2</sub> reaction products.

### C. Conclusions of Research

This research was proposed to develop a new catalyst and to determine its practicality. From the data gathered and produced, this end has certainly been met.

The catalyst, boron trifluoride supported by poly *p*-methoxystyrene, has never before been produced and never before been used.

In order to use this catalyst, a method of  $\text{BF}_3$  analysis was needed. It was found that potentiometric titration gave good quantitative results but took approximately 4 hr to do. It was also noted, however, that once a few titrations had been done and titration curves were set up, that a good semi-quantitative titration could be run. Using methyl red indicator and titrating the HF present, analysis requires only 2-5 min after the 1 hr sample preparation, a savings of 3 hr.

Once the catalyst had been prepared many solvent tests were run. Solvents of differing polarities were tested in order to try and find a good solvent for the polymer. A good solvent was needed if experiments on changing the state of catalyst were to be tried. That is, could one take the heterogeneous catalyst in a nonsolvent and increase the amount of good solvent until one got a purely homogeneous catalyst. If so the range of experiments and types of catalysis would be magnitudes greater. Lack of a good solvent and the presence of crosslinking prevented any experimentation in this area. Nitrobenzene was used in the octene isomerization but in small quantities only. Nitrobenzene was the best solvent available but had such a high boiling point that it interfered with product isolation.

A few experiments with a gel were done to test selectivity using smaller pore size and they seemed promising. The experiments were discontinued, however, when full attention was turned to acquiring a G.C. with which to do product isolations. Time did not permit further experimentation. It should be noted, as organic molecules were passed through the column that the eluted material got darker with successive passes. The darkening of the solution could have been caused by several things. (1) The solution was removing part of the lower molecular weight polymer molecules. (2) The solution was developing more cations, showing reaction. (3) The solution was reacting to produce product which was dark. The reaction of the material seemed promising. If the small polymer molecules were causing the effect, less accumulation of color would be noticed each time since fewer small molecules were left in the polymer to wash out. This did not seem the case as the color got successively darker each time the solution was eluted over the gel. The goal to be achieved here, if the color is from the reaction, is a very specific reaction with few side products. To maximize the yield, one would simply continue passing the solution over the column.

The higher productivity displayed by this new catalyst system may arise from several factors; i.e., 1) solvent channel size selectivity, 2) surface phenomenon, 3) ease of  $\text{BF}_3$  release, and possibly 4) polar stability for developing charges. Experiments done would neither support nor disprove pore size selectivity. All of the molecules used were sufficiently small to enter the polymer pores

and the polymer itself was not sufficiently crosslinked to have a small average pore size. The only thing which might suggest that pore size had no effect on the reaction was the removal of the  $\text{BF}_3$  from the polymer indicating the reaction occurred outside of the polymer matrix. Surface phenomena, such as organic molecules being brought into close proximity of each other for ease of reaction, was not studied. The ease of  $\text{BF}_3$  release can be predicted by  $\Delta H$  values and explained by resonance and was shown to be prevalent in reaction systems. Since  $\text{BF}_3$  maintains a vapor phase equilibrium, and since the Lewis base and the  $\text{BF}_3$  might be reacting in this vapor phase or in this phase outside of the polymer, then the easier the polymer can release the  $\text{BF}_3$  and the more "free  $\text{BF}_3$ " a Lewis base will find available to react with. This might explain the increased productivity over  $\text{Et}_2\text{O} \cdot \text{BF}_3$  since  $\text{Et}_2\text{O} \cdot \text{BF}_3$  is complexed more strongly than the polymer complex. An experiment which might give some insight into these problems would be to run reactions of the polymer  $\text{BF}_3$  complex vs one of the  $\text{A} \cdot \text{BF}_3$  complex. If the polymer catalyst and the  $\text{A} \cdot \text{BF}_3$  had the same productivity, then one would tend to believe the  $\text{A} \cdot \text{BF}_3$  bond strength was the determining factor. If the polymer complex demonstrated better yields one would tend to believe the productivity came from pore size or surface phenomenon. The fourth phenomenon, polar stability, might be proved or disproved by using microelectrodes. If the polymer holds many polar  $\text{BF}_3$  molecules close together, then the area inside the polymer would become a very polar area as compared to the outside of the polymer (depending of course on solvent systems used). This polar area would aid in the development and stabilization of the charges needed to

perform the isomerization and rearrangement reactions used in this research. Microelectrodes could measure the electric conductivity inside the polymer which could then be compared to that outside the polymer.

This new catalyst also displayed a heterogeneous property in its ease of separation from the reaction media. Simple filtration could be used to remove most of the polymer. A problem did arise in that not all of the polymer could be filtered out which could be determined by viscosity and color. This problem was caused by one or more reasons. It could have been due to the fact that in several of the experiments, low molecular weight polymer was used. The low molecular weights gave less mechanical stability and were easier for the  $\text{BF}_3$  to degrade. They were also hard to filter out. The second problem could have been that when high molecular weight polymer was used, the low molecular weight material was not thoroughly washed out, again causing filtration problems. A third problem may have been caused by polymer matrix degradation brought about by the reaction with  $\text{BF}_3$ .

The catalyst also had the property of catalytic site protection. Experiments comparing  $\text{Et}_2\text{O} \cdot \text{BF}_3$  and  $\text{A} \cdot \text{BF}_3$  to the  $\text{P} \cdot \text{BF}_3$  showed that the  $\text{P} \cdot \text{BF}_3$  had higher  $\text{BF}_3$  concentrations for equal lengths of time when exposed to similar conditions. So the property often displayed by other supported catalysts also appears in this one.

Another benefit to this particular catalyst is the ease of handling. During all the experimentation done, the polymer catalyst showed sufficient stability to be handled in air. It was weighed on a balance and placed in the reaction flask without stiffling gases or smells, and without noticeable loss of catalytic activity.

Major problems associated with the catalyst were polymer backbone rearrangements, and the loss of the ability to be rejuvenated, which was caused by backbone rearrangements. Experiments performed demonstrated a change in the ether group to that of a phenol. It was also proven that the polymer matrix becomes crosslinked. The phenol groups, the aryl substitution, the crosslinking, all change the polymer backbone so that the specific properties which it started with are lost. One way to overcome this problem would be to change poly ethers. Two directions could be taken in this process. An in chain ether such as poly(ethylene oxide) could be used or a polymer with an ether in a side group, like p-methoxystyrene, except without the aromatic group, such as poly(methoxyethylene). In either case, differences would arise, such as differences in bond strength and in the catalyst availability. A new polymer would not only change the reactivity of the catalyst, but it would affect the solvent systems one might use. This might allow for improvement of the solvents used.

In summary, the idea was good and the catalyst did work. Properties were much like those expected and could be improved by improving the polymer support. Future experiments will probably be in line with those suggested with the ultimate goal being a man-made type of enzyme where the catalyst stays indefinitely fixed within the polymer.

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## APPENDIX

## APPENDIX

A. Problems Encountered in the U. V. Analysis of  $\text{BF}_3$  Concentration1. Problems with initial  $\text{Et}_2\text{O} \cdot \text{BF}_3$  and dioxane calibration curve.

It was noted when setting up the first calibration curve that U.V. spectra could not be attained at concentrations as low as that given in the literature. In the first attempts, the minimum concentration allowable was 5 ml of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  in 25 ml of dioxane which varied from that of Pobiner by two factors of ten.

To run a check on the U.V. instrument, a Cary 17 spectrometer, various spectra were run. One was air vs. air, another was dioxane vs. dioxane, and another was ether vs. ether. All gave good baselines with no negative absorption. A second check was run using acetone. The dilutions were made as above and then as necessary to get an absorption maximum. The spectrum and concentration values allowed one to calculate a molar absorptivity somewhere between 14 and 8. The book value is given at  $14.5^{71}$  and so the problem was not the machine. Only three possible problems could be thought of, (a) the dioxane had enough water in it to destroy the  $\text{BF}_3$  active center of absorption, (b) the  $\text{BF}_3$ -diethyletherate was not pure, and (c) the original literature was incorrect. To determine what the problem was, new dioxane was purified and a new bottle of  $\text{BF}_3$ -etherate was acquired. The  $\text{BF}_3$ -etherate was the problem as apparently the first bottle was old and, part of the  $\text{BF}_3$  had been lost out of it.

Once the problem was found and corrected, dilutions were made of a stock solution and the calibration curves were set up as discussed in the Experimental section.

## 2. Anisole absorptivity

In order to try and circumvent the problem in analysis of the anisole  $\text{BF}_3$  complex, many methods were tried. One was to decompose the anisole with heat and then using a vacuum, move the  $\text{BF}_3$  through a bubble tube where it could be bubbled through ether. The resulting complex could then be diluted and a spectrum run from which one could calculate the  $\text{BF}_3$  concentration. Another method was to take copious amounts of ether and rinse the anisole complex leaching out all  $\text{BF}_3$ . Once the  $\text{BF}_3$ -etherate was complexed, one could remove by distillation the etherate from the solution. Making the proper dilutions and running a spectrum, one could calculate the  $\text{BF}_3$  concentration. The third method tried was to mix the anisole complex with ether and separate the two solutions by freezing (f. pt. anisole  $-37.5^\circ\text{C}$ ., f. pt.  $\text{BF}_3$ -etherate  $-60.4^\circ\text{C}$ , f. pt. ether  $-116.2^\circ\text{C}$ ). Neither method worked, and both were abandoned. The major reasons for dropping these procedures were that complete separation could not be achieved between the anisole and etherate and because the right kind of vacuum lines and cold traps to pursue the ideas further were not present. (Note: It was hoped that when the polymer complex was made, that the polymer could be filtered out of the etherate solution. This method did not work as some monomer and/or oligomers could not be filtered out, and were absorbing magnitudes greater than the  $\text{BF}_3$  in the spectrum.). In running the polymer spectrum, 0.7647 g of polymer complex was washed with 100.0 ml of dioxane. This was further diluted as necessary to give a final concentration of 0.382 g/l polymer or approximately 0.128 g  $\text{BF}_3$ /l of solution. The U. V. spectrum showed a maximum of 0.52 units at 275 nm but the overall maximum was at 290 nm. From the calibration

curves previously run, this gave a  $\text{BF}_3$  concentration between 7.7 g/l and 7.4 g/l. The maximum  $\text{BF}_3$  concentration possible for 100% complexed polymer weighing 0.7647 g would be 0.128 g/l. The discrepancy had to be due to the large differences in  $\epsilon$ 's for anisole, polymer, and  $\text{BF}_3$ -diethyletherate.

To overcome the problem, a method found in Fundamentals of Analytical Chemistry<sup>60</sup> was tried; the method of multiple additions. A U. V. spectrum chart from the literature,<sup>71</sup> gave a  $\epsilon$  maximum for anisole at 259 nm as 19200 and that at 275 nm as  $7.6 \times 10^3$  in units of moles/l cm.<sup>54</sup> Using U. V. data from charts run on  $\text{BF}_3$  etherate in dioxane the  $\epsilon$  maximum was calculated at  $\lambda = 259$  to be  $3.88 \times 10^{-4}$  and at  $\lambda = 275$  to be  $4.78 \times 10^{-4}$  in units of l/mole cm. Calculations were done using simultaneous equations and two different  $\text{BF}_3$ -etherate spectra absorbances to obtain anisole complex concentrations. The calculations were done several times but the results were disappointing. Apparently, the difference in  $\epsilon$ 's was just too great. So the method was dropped.

#### B. Problems Encountered with the Polymer Complexation

Problems encountered with the polymer complexation included

1. Change in solubility of the polymer which caused complex precipitation.
2. Precipitation of the polymer after it was only 30% complexed which prevented further complexing.
3. Removal of the precipitated polymer complex from the reaction flask.

4. Poor control over the great pressure differences in the system, i.e., a vacuum in the reaction flask and high pressures in the cylinder of  $\text{BF}_3$ .

5. A tendency of the cylinder valve to close due to the high pressures causing a back lash of reaction materials through the connection lines toward the  $\text{BF}_3$  cylinder.

The first three problems were corrected by using nitrobenzene as the solvent. The fourth and fifth were corrected by one of two methods. (a) A vacuum could be placed on the system and once the air was out, let air back in via a  $\text{CaCl}_2$  drying tube or, (b) one could use argon and flush all the air and water out of the system, again open to atmosphere by  $\text{CaCl}_2$  tube just before  $\text{BF}_3$  addition. Once the system was cleared of all  $\text{H}_2\text{O}$  vapor,  $\text{BF}_3$  could be bubbled through solution for a long time without worry of checking the pressure via the septum. Any extra pressure of  $\text{BF}_3$  would merely go out the drying tube into the hood. The white cloud of  $\text{BF}_3$  in air would show that the reaction should be close to over. This also allowed one to open the valve further on the  $\text{BF}_3$  cylinder preventing backlash of solution, and to make longer gas additions than those needed to reach atmospheric pressure. To further insure no backlash of reaction materials, a dead volume flask was placed in the line connecting the reaction flask and  $\text{BF}_3$  cylinder.

Once the solvent was changed to nitrobenzene, the polymer complex had to be precipitated in hexane. To do this, enough hexane was used to make the reaction mixture 10% by volume of the total

precipitation solution. When precipitating the complex, the polymer solution was added dropwise to a cooled beaker of hexane with stirring. Upon addition, the polymer formed a sludge at the bottom of the hexane beaker while the hexane itself turned reddish with a cloud of  $\text{BF}_3$  hovering over it. After sitting 1-2 hrs, all polymer settled and the hexane became fairly colorless again. The nitrobenzene and hexane were then decanted off and the complex was washed again with hexane. Once free from most of the nitrobenzene, the polymer was placed into a dessicator, filled with paraffin chips and  $\text{CaCl}_2$ . With a nitrobenzene polymer complex preparation, it should be noted that the polymer is darker and seems to be of a lot lower molecular weight, i.e., more degradation has occurred.

### C. Problems Encountered with the Limonene Epoxide Reaction

#### 1. Purification of the epoxide.

Royals and Harrell<sup>56</sup> suggested that limonene epoxide could be produced in high yields and good purity. In this reasearch, only 25 ml of epoxide would result from the 150 ml of alkene used. The  $^1\text{H}$  NMR matched that given in the literature fairly well but G.C. analysis showed a number of peaks with the epoxide comprising about 76 % of the sample. These trash peaks clutter up the NMR, I.R., and G.C. identification process but distillation was not capable of separating the compounds

#### 2. Separation of the products.

At first columns were used to separate the products of both the limonene and the carbinol reactions. The columns were made of activated

alumina and the solvents were charged in order of increasing polarity. The solvents used were hexane, ligroine, benzene, carbon tetrachloride, methylene chloride, and acetone. Approximately 150 ml of each solvent was used in trying to separate the products. The products were caught as they came off the column in 6 test tubes to give good separation of compounds. Once the products were chromatographed, the test tubes were checked using Thin Layer Chromatography (TLC) for the number of products they contained. Some separation was noticed, but the best separation effected was two compounds per test tube.  $^1\text{H}$  NMRs were run and compared to that of the reaction mixture just after the reaction was stopped. This was done to see if any of the peaks in the spectra seemed to belong to any one compound. Nothing was gained from these experiments in the way of product identification.

Separation was finally obtained by using gas chromatograph (G.C.) A column of OVI-chromosorb W 10%, 60/80, that was 5 ft in length and 1/4 in. in outside diameter was used. Flow rate for the G.C. was 29 ml/min, with a column temperature of 150°C, detector temperature at 280°C, and an injector temperature at 235°C (see G.C. spectrum 1). The peaks were caught in glass coils submerged in  $\text{N}_2(\text{L})$  that were connected to the G. C. exhaust ports. Approximately 25 - 40 injections of 25  $\mu\text{l}$  sample size were needed to separate enough products to run an  $^1\text{H}$  NMR. The solvent commonly used was  $\text{CDCl}_3$  with TMS (1%).

## D. Miscellaneous Problems

1. Nitrobenzene removal.

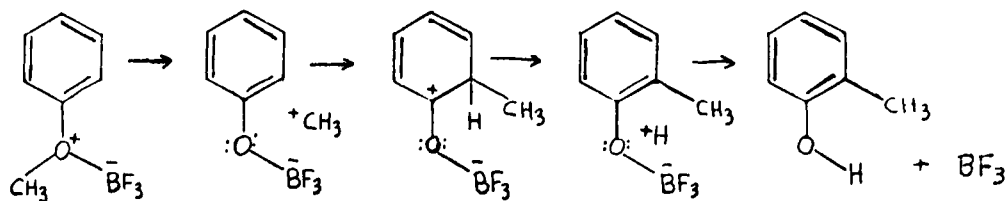
The solvent, nitrobenzene, was hard to remove from the precipitated complex. Reaction mixtures of limonene epoxide and polymer complex were separated by G.C. and the peaks were collected. One of the peaks seemed to be nitrobenzene. To remove it from the polymer, samples of the complex were placed in 25 ml of hexane, washed for 2 days and then washed again. Subsequent reaction showed less solvent than before. The problem was the high boiling point and high affinity that nitrobenzene has for the polymer.

2. Toxicity of nitrobenzene.

The toxicity of nitrobenzene is too high to use it as a common solvent. A better, less toxic solvent is needed, or a more soluble polymer is required.

## E. Reaction Proposed for Phenol Rearrangement

The reaction proposed for the anisole rearrangement to produce the phenol type peaks in  $^1\text{H}$  NMR is the following.



## VITA

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