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I. Gas Phas Thermal Reactions of Aromatic Ethers.
II. Generation of p-xylylene and its Derivative by Zinc Induced Dehalogenation

by

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EXPLANATION OF THESIS FORMAT

Each part is in the form of a full paper, suitable for publication in a professional journal. As such, each part has its own numbering system and references. The research described in the results and experimental sections was done by the author.

GENERAL INTRODUCTION

For several years, work in Trahanovsky's group has focused on gas phase thermal reactions of some aromatic ethers and generation of p-xylylene and derivatives by flash vacuum pyrolysis techniques. These studies involve synthesis of a series of aromatic ethers and some precursors of p-xylylene derivatives.

This thesis is divided into two parts. Part I of this thesis presents a preliminary investigation of mechanistic studies of aromatic ethers. The studies involved deuterium labelling, product analysis, and low temperature isolation.

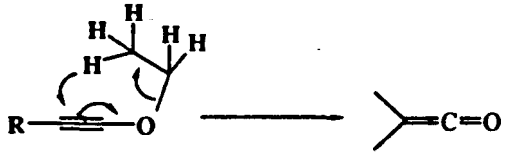
In Part II of this thesis, a new methodology to synthesize p-xylylene and to attempt to synthesize α,α'-di-t-butyl-p-xylylene is presented in detail. In these studies, the preparation of α,α'-dichloro-α,α'-di-t-butyl-p-xylene is described.

PART I. GAS PHASE THERMAL REACTIONS OF AROMATIC ETHERS

INTRODUCTION

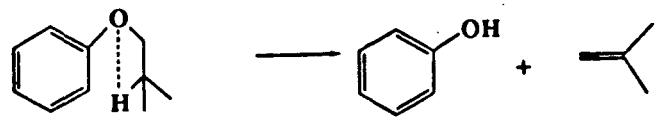
Thermal decomposition reactions of aromatic ethers are of considerable current interest in part because they are thermally labile constitutions of lignin. Lignin is a major, refractory constituent of woody biomass. Insights into thermolysis or aromatic ethers should, therefore, be directly applicable to thermal processing of biomass and low and medium rank coals.

During the past four decades, a number of aliphatic ethers has been studied,[1,2,3,4] and a first order, concerted mechanism was proposed as the general mechanism of decomposition. The major products are alkenes and corresponding alcohols. Recently, the thermolysis of 1-ethoxyethyne was reported to undergo a reaction involving a concerted six-center transition state. The major products were ketene and olefins (eq. 1).[5]



(1)

A group of aromatic ethers was also studied. The gas phase pyrolysis of 2-methyl-2-phenoxypropane was found to proceed through a four-center ring transition state (eq. 2).[6] Gas phase pyrolysis of phenetole and allyl phenyl



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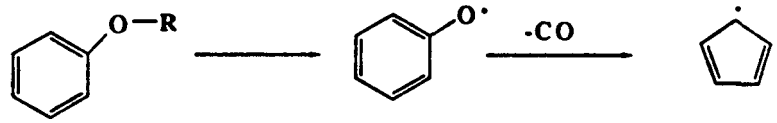
ether was found to undergo C-O bond homolysis to produce the phenoxy radical, and phenoxy radical could generate a cyclopentadienyl radical and carbon monoxide above 1000 K[7] (eq. 3). Recently low pressure pyrolysis of hydroxy and



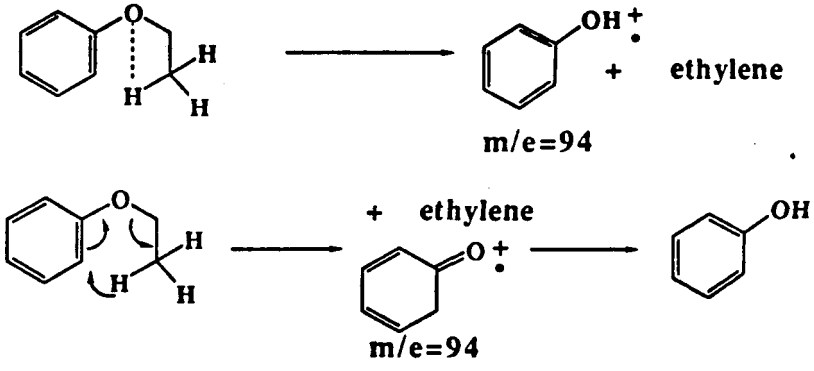
(3)

methoxy-substituted anisoles and phenetole was reported[8,9] to show a large bond-weaking effect by those substituents. Thermal decomposition of aromatic ethers in the liquid phase was also reported. For example, Gilbert and Gajewski reported that the thermal decomposition of phenethyl phenyl ether in the neat liquid phase involved a radical chain process.[10,11] However, Virk reported that in the thermolysis of phenethyl phenyl ether in tetralin there was no radical that could be trapped.[12] It is not clear why this disagreement exists.

Mass spectroscopy can be a useful way to provide some indirect information about the gas phase thermal behavior of certain molecules. Because of its low pressure, bimolecular

reactions are unlikely. The mass spectrum of phenetole gives a strong peak of m/e = 94 (no m/e = 93 could be found).[13] This indicates that a proton is transferred to oxygen or to the benzene ring (Scheme 1). This observation

Scheme 1



motivated us to reexamine the gas phase thermal decomposition of phenetole. Since iso-phenol is a very reactive molecule, which has been detected by IR and UV at -196 °C.[14,15] we decided to probe the reaction mechanism by isotropic labelling experiments. We can easily monitor the deuterium by ^{2}H NMR to see whether the deuterium will be transferred to the ortho-position of phenol. Moreover, if we assume that the pyrolysis of naphthyl ethyl ether would react via a six-center transition state, the intermediate iso-naphthanol should be much more stable than iso-phenol, and possibly detectable by ^{1}H NMR techniques. If this is

true, it may give some indirect evidence for the mechanism of the phenetole pyrolysis. We also studied the pyrolysis of phenethyl phenyl ether in order to determine how the leaving group will affect the reaction pathway.

RESULTS

The FVP of Phenetole

It was found the composition of the product mixtures could be changed with oven temperature, pressure, and sample head temperature. The results are summarized in Table 1. The temperature of the pyrolysis of phenetole ranged from 529 °C ~ 804 °C and the pressure ranged from 0.1 ~ 0.15 mmHg. Under 800 °C, phenol (93.6%), azulene (3.4%), and naphthalene (2.9%) could be detected by GC. Since the GC peak of cyclopentadiene overlapped with the solvent peak, we were unable to obtain a percentage yield of cyclopentadiene, but it could be detected as a major product by ^{1}H NMR (Figure I, Appendix). When the pyrolysis proceeded at low temperature, such as at 529 °C, a quantity of 5% of phenol and 90% of starting material were detected by GC; no cyclopentadiene was detected by ^{1}H NMR.

The Large Scale Pyrolysis of Phenetole

The large scale pyrolysis of phenetole (716.4 mg, 5.8 mmole) at relative higher sample head temperatures (-5 °C ~ -11 °C), gave about 63% of phenol and 13% of a bimolecular reaction product. The bimolecular product has not been fully identified yet.

Table 1. The products of pyrolysis of phenetole under different conditions

Conditions			products %[a]				
Oven temp, °C	System pressure, torr	Sample head, °C	phenol	phenetole	cyclopentadiene	azulene	naphthalene
529-535	0.15-0.1	25	5	90	Neg[b]	0	0
744-750	0.15-0.2	-20	23.96	65.5	Pos[c]	0	0
804-810	0.15-0.1	-20	93.6	0	Pos	3.4	2.9

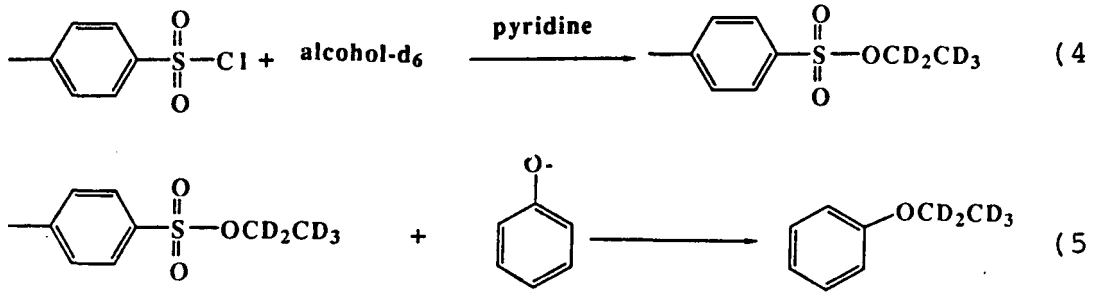
[a]The ratio of the products detected by GC.

[b]Non-detectable by ^{1}H NMR.

[c]Detectable by ^{1}H NMR as a major product.

Pyrolysis of Phenetole-d_5

Phenetole-d_5 was synthesized by a two-step sequence (eq. 4 and 5). The purity of the deuterated phenetole, analyzed



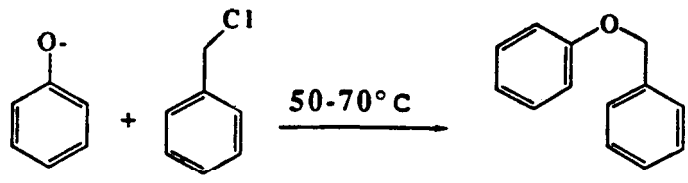
(4)

(5)

by GC mass spectrum was 95% d_5. The pyrolysis of phenetole was carried out at an oven temperature of 820 °C, under 0.3 torr pressure with the sample head temperature at -15 ~ -20 °C. The ^2H NMR was obtained at -78 °C (Figure 2, Appendix). In this spectrum, there is a strong deuterium signal at δ = 6.85 ppm which corresponds to -D on the ortho-position of the phenol. There are two signals at δ 6.5 ppm and 6.55 ppm which come from cyclopentadiene. There are two additional signals. A signal at 7.4 ppm which comes from -OD and a signal at δ 4.2 which corresponds to ethylene.

Pyrolysis of Phenyl Benzyl Ether

Phenyl benzyl ether was synthesized by a simple SN_2 reaction. The yield of this reaction was 75% (eq. 6).

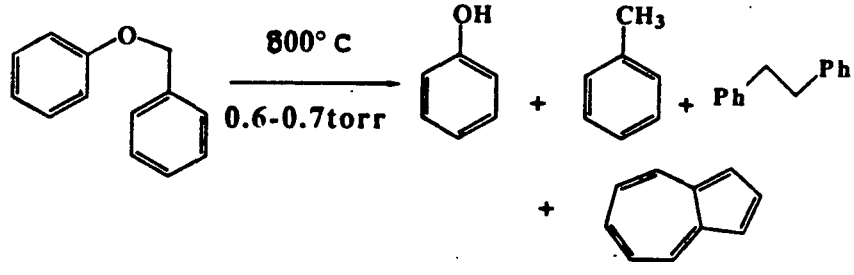


(6)

Pure phenyl benzyl ether was obtained by a flash column chromatographic separation.

The pyrolysis of phenyl benzyl ether was carried out under the following conditions: oven temperature, ~ 800 °C; pressure, ~ 0.6 mmHg; sample head temperature, -10 °C. Only phenol (28.5%), 1,2-diphenylethane (35.2%), and toluene (11.7%) were detected as major products. Azulene (0.9%) was detected (Scheme 2). The ^{1}H NMR spectrum indicated no cyclopentadiene (Figure 3, Appendix).

Scheme 2



Pyrolysis of Phenol

The pyrolysis of phenol was carried out under the following conditions; oven temperature, 800 °C; pressure, 0.6-0.7 mmHg; sample head temperature, -15 °C. The products

were analyzed by ^{1}H NMR (Figure 4, Appendix) and GC. ^{1}H NMR and GC analysis of the pyrolysis products indicated that azulene (blue color) was the only major product in 3~5% yield.

Pyrolysis of Naphthyl Ethyl Ether

The pyrolysis of naphthyl ethyl ether was carried out under different conditions and the results are summarized in Table 2. No iso-naphthanol was detected at -78 °C from any of the pyrolyses (Figure 5, Appendix). As the temperature was increased, indene increased. As the resonance time increased (for example, by increasing the pressure, entry 4), indene was detected as a major product. As indicated in entry 3, 4, and 5, four isomers were detected. They had the same molecular ion peak, which corresponds to $C_{11}H_{12}$, and the same mass spectrum pattern. An exact mass obtained by a GC-mass spectrum supported the $C_{11}H_{22}$ formula. On the basis of their mass spectra (Figures 6, 7, 8, 9, Appendix), structures $\underset{\sim}{1}$, $\underset{\sim}{2}$, $\underset{\sim}{3}$, and $\underset{\sim}{4}$ (in Scheme 5) were proposed for them. In addition, in entry 4, 5, naphthalene and 1,2-dihydronaphthalene were detected.

Pyrolysis of Phenethyl Naphthyl Ether

Phenethyl naphthyl ether was synthesized by a two-step sequence (Scheme 3). The pyrolysis of phenethyl naphthyl

Table 2. The products of pyrolysis of naphthyl ethyl ether under different conditions

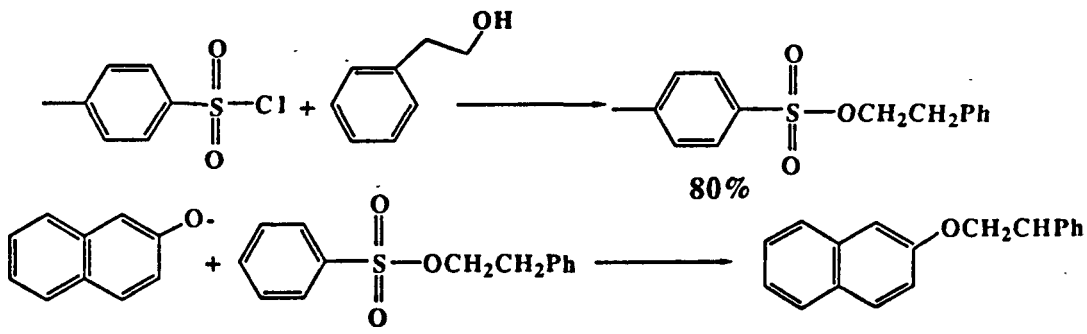
Conditions				
Entry	Oven temp, °C	System pressure, torr	Sample head temp, °C	naphthanol
1	616-620	3.5×10^{-5}	24-26	34.7
2	660-670	0.15-0.2	12-14	10
3	694-700	0.15-0.2	35	12.8
4	750-755	0.6-0.7	63-80	0
5	642-650	0.6-0.7	49-75	0.5

[a]Products ratio detected by GC.

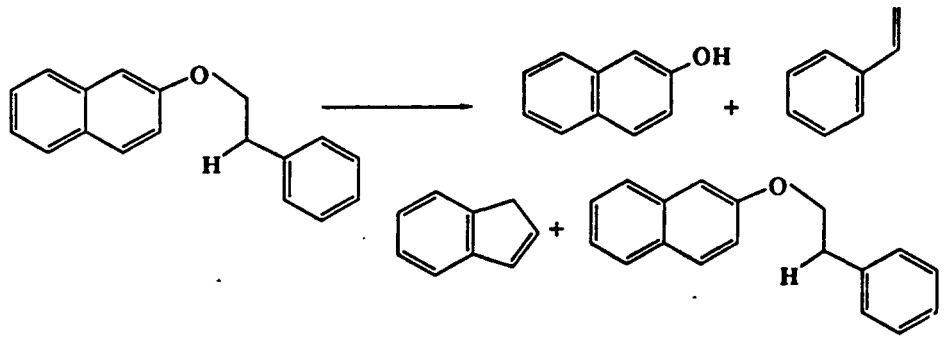
[b]Four hydrocarbon isomers shown in Scheme 5.

Products, %[a]				
Naphthyl ethyl ether	Indene	1+2+3+4[b]	Naphthalene	1,2-dihydro naphthalene
64	0	0.5	0	0
43	3.6	0	0	0
5.3	13.4	38.09	0	0
0	47	6.197	17.27	18.95
64.5	2.6	10.48	3.7	2.8

Scheme 3



ether was carried out under different conditions and the products were identified by ^{1}H NMR (Figure 11, Appendix) and GC (eq. 7). The results of the pyrolysis under different conditions are summarized in Table 3.



(7)

Table 3. The products of pyrolysis of phenethyl naphthyl ether under different conditions

Conditions			Products, %[a]			
Oven temp, °C	System pressure, torr	Sample head temp, °C	naphthanol	styrene	indene	phenethyl phenyl ether
600-620	2.5×10^{-5}	35	32	22	0	49
700-710	5×10^{-5}	40	47	43.3	1.9	4

[a]The ratio of the products detected by GC.

DISCUSSION

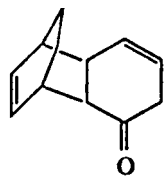
The Mechanism of Gas Phase Thermal Decomposition of Phenetole

In the pyrolysis of phenetole, as the pyrolysis temperature increased a relatively large amount of cyclopentadiene was detected. This indicates that the loss of carbon monoxide from iso-phenol is a higher energy process when compare to the 1,3-H shift (Scheme 5). The ^{2}H NMR spectrum of the pyrolysis products of phenetole-d_5 indicates that the signal at δ 6.89 is from the ortho-position of phenol. Another interesting signal, δ 4.2, corresponds to ethylene. This is the first time we detected that signal probably because ethylene is very volatile and the sample transferring techniques may have resulted in its loss.

Even though previous publications reported that the gas phase thermal decomposition of phenoxy radical[7] and phenol[16,17,18] can generate cyclopentadiene and carbon monoxide, in the pyrolysis of benzyl phenyl ether, using the same pyrolysis conditions as used for phenetole, no cyclopentadiene was detected. From the analysis of the above products, we also can not find any product which comes from the cyclopentadienyl radical. Pyrolysis of phenol using the same conditions as those for the pyrolysis of

phenetole and benzyl phenyl ether led to only a 3% yield of azulene, and again it did not give cyclopentadiene.

Detecting a bimolecular adduct with molecular ion peak (m/e = 160) was an interesting thing for us. When we used a large quantity of starting material (700 mg phenetole) and pyrolyzed it at a higher sample head temperature, we detected a bimolecular reaction adduct (13%). Apparently, these conditions led to an increasing amount of phenetole in the hot zone and bimolecular reactions occurred. The GC mass spectroscopy indicated that loss of CHO was facile. Also, the peaks of m/e = 65 and m/e = 94 were detected. These indicate [4+2] adduct may be produced. But, GC FT-IR

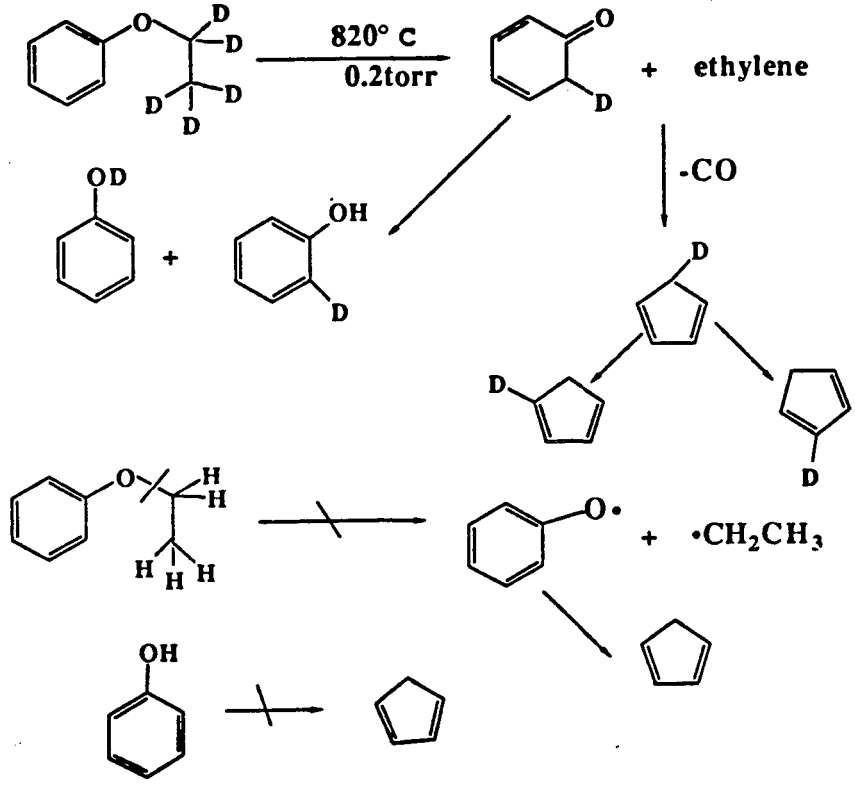


[4+2] adduct

indicated no carbonyl absorptions. This eliminates the above possibility. Detecting an OH peak in GC FT-IR indicates that the bimolecular adduct may be a rearrangement product from the [4+2]adduct. All of the above results are consistent with each other, and indicate that the pyrolysis of phenetole does not undergo a C-O bond homolytic cleavage or a four center ring transition state. Instead of that, it undergoes a six center ring transition state. So far, we do

not have enough evidence to explain why a small amount of azulene is generated in each pyrolysis and what the structure of the bimolecular reaction adduct is. From the studies of the gas phase pyrolysis of phenetole, benzyl ethyl ether and phenol, we summarize the results in Scheme 4.

Scheme 4



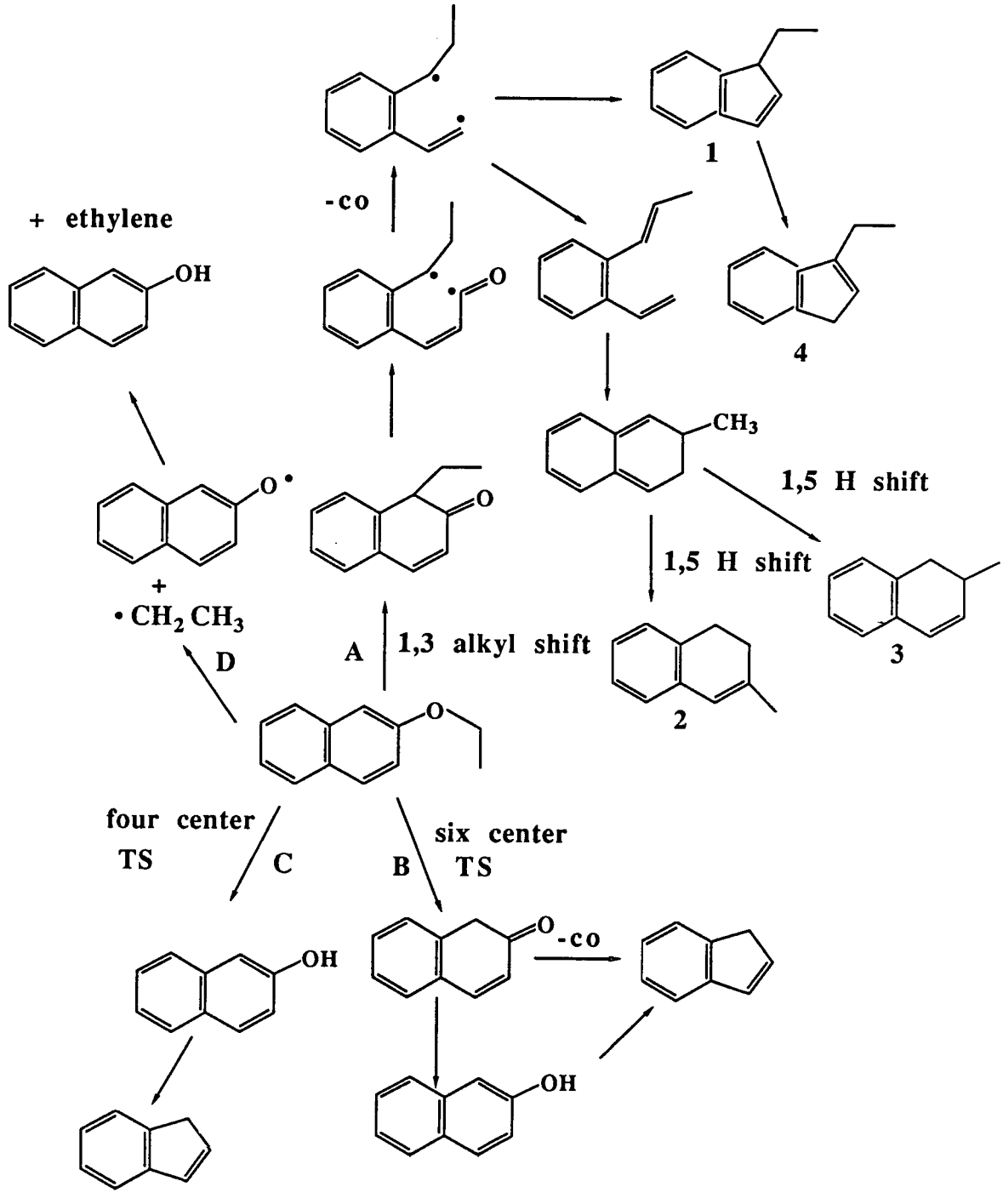
The Mechanism of Gas Phase Thermal Decomposition of Naphthyl Ethyl Ether

2-Naphthanol and indene were detected as the major products in the pyrolysis of naphthyl ethyl ether. Since we have not proven whether 2-naphthanol will give indene and naphthalene under our pyrolysis condition, the logical deduction from the Shaden, Bredael, Cypres' reports,[19-21] is that the indene could be a secondary product of 2-naphthanol. However, it could be generated from elimination of CO from iso-naphthanol. From entries 3, 4, and 5 in Table 2, several isomers were detected. The exact mass spectrum indicates these isomers are hydrocarbons with the same fragmentation pattern (m/e = 144, m/e = 129, m/e = 115). Therefore, we propose the mechanisms shown in Scheme 5 to account for these isomers. The mechanism of the gas phase thermolysis of naphthyl ethyl ether is very complicated and may involve several competitive processes (Scheme 5). So far no further evidence has been obtained which indicates which one of the paths, B, C, or D, is involved in the reaction. The four isomers were only isolated by GC chromatograph.

The Mechanism of The Pyrolysis of Phenethyl Naphthyl Ether

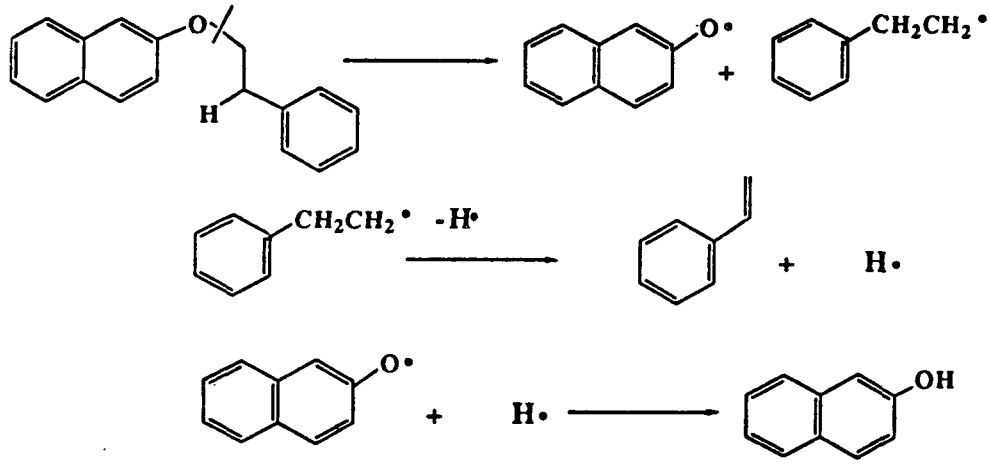
The bonding energy of a benzylic proton is 85 kcal/mole[22] and the C-O bond energy is 79 kcal/mole.[22]

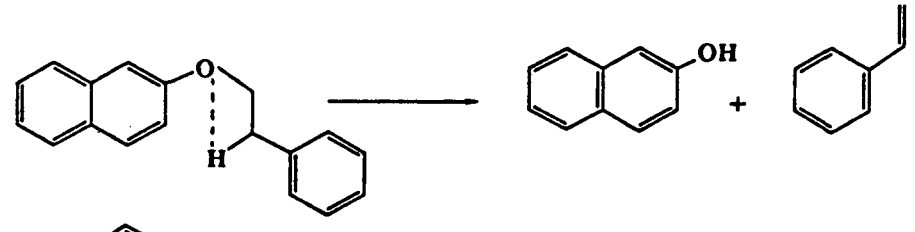
Scheme 5


+ ethylene
OH
-co
O
1
4
CH3
1,5 H shift
1,5 H shift
3
2
O•
+
• CH2 CH3
D
A
1,3 alkyl shift
O
four center
TS
C
B
six center
TS
O
-co
OH
OH

Therefore, the mechanism of pyrolysis of phenethyl ethyl ether may undergo either a C-O bond homolytic cleavage (Scheme 6), transfer of a benzylic proton to oxygen (eq. 8), or a six center ring transition state (eq. 9).

Scheme 6





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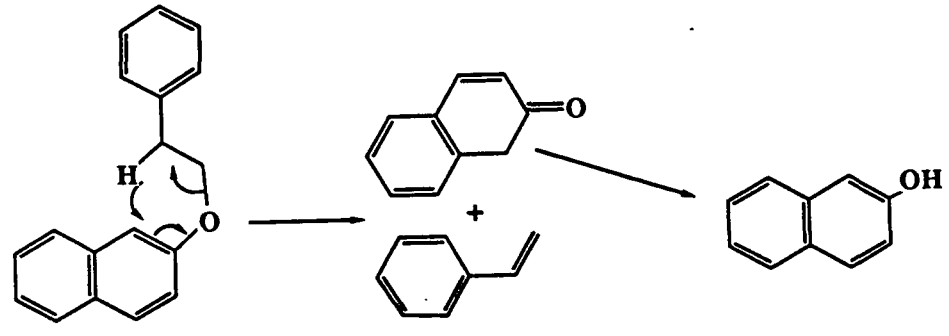
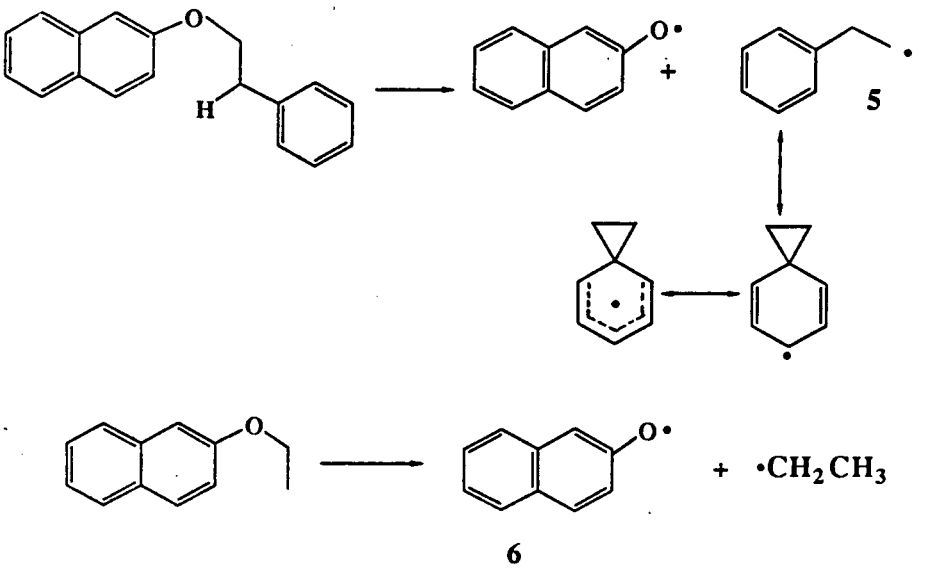


(9)

Since all of the pathways lead to the same products, it is difficult to eliminate any of the mechanisms proposed above. However, the important difference between the pyrolysis of naphthyl ethyl ether and phenethyl naphthyl ether at the same temperature is they produce different amounts of indene. This implies that the indene produced in the pyrolysis of naphthyl ethyl ether may not come from 2-naphthanol but from iso-naphthanol.

In the studies of naphthyl ethyl ether and phenethyl naphthyl ether, the elimination of ethylene is much more unlikely than the elimination of styrene because of the thermal stability. Possibly the homolytic cleavage of the C-O bond of the naphthyl ethyl ether is more difficult than the cleavage of C-O bond of phenethyl phenyl ether because of the following reasons. In Scheme 7, radical $\underset{\sim}{5}$ could be stabilized by benzene ring participation, whereas, radical $\underset{\sim}{6}$ could not. On the other hand, phenethyl naphthyl ether is more difficult to reach the conformations of the six member ring and four member ring transition state than naphthyl ethyl ether. From these points, phenethyl naphthyl ether may favor a radical chain mechanism.

Scheme 7



EXPERIMENTAL SECTION

Methods and Materials

^{1}H NMR spectra were recorded on Nicolet-300 spectrometer. ^{2}H NMR and low temperature ^{1}H NMR spectra were recorded on WM-300 spectrometer. Chemical shifts are reported in ppm. Coupling constants (J) are reported in hertz. Infrared and GC-IR were measured on MBN FT-IR 98. High resolution mass spectra were measured with an Associated Electronic Industries MS-902 Instrument at 70 eV. Gas chromatograph/mass spectral analyses (GC/MS) were performed by using a Finnigan 4000 instrument and an INCOS data system. GC analyses were performed by using a Hewlett Packard HP 5840A instrument equipped with a 25 meters, DB-1 capillary column. Melting points were measured by Hoover capillary melting point apparatus. Deuterated alcohol-d_6, naphthyl ethyl ether, phenetole, and phenol were available from Aldrich Chemical Company. The pyrolysis apparatus is indicated in Figure 11 (Appendix).

Synthesis of Phenetole-d_5

Preparation of ethyl-d_5 tosylate

A solution of 1 g (0.0217 mole) of the d_6-alcohol in 16 ml of dry pyridine in 125-ml glass-stopped Erlenmeyer flask was kept at room temperature and treated with 5 g of tosyl chloride. The mixture was kept in the refrigerator for 4-5

hours. The reaction can be followed by separation of pyridine hydrochloride as long needles. When no more crystals formed, the reaction was judged to be completed. The entire mixture was poured into 100 g of ice water, and white crystals formed after five min. The solid compound was removed by filtration. A quantity of 3.5 g (0.0171 mole) of ethyl tosylate (m.p. 29-31 °C) was obtained in 78.8% yield.

Preparation of phenetole-d_5

A quantity of 1.6 g (0.017 mole) of pure phenol (98%) has placed in a three-necked flask. Sodium hydroxide (0.699 g, 0.0175 mole) in 6-7 ml of water was dropped into it and the mixture was stirred for 10 min. Then, a quantity of 3.5 g (0.0673 mole) of ethyl-d_5 tosylate was added to the flask and the mixture was stirred vigorously at 80-90 °C for 28 hours. When the reaction was finished, H_2O (7 ml) was added to the flask and the organic layer was separated. The organic layer was extracted with 20 ml ether. The solvent was removed by rotary evaporator. The reaction mixture was purified by hickman still distillation. A quantity of 1.74 g (0.0137 mole) of phentole-d_5 was obtained in 80% yield. For phenetole: ^1H NMR ($CDCl_3$) δ 7.25 (m, 3 H), 6.9 (d, J = 9, 2 H); ^2H NMR ($CDCl_3$) δ 3.9 (s, 2 D), 1.3 (s, 3 D); purity of the phenetole-d_5 was analyzed by GCMS to be 95% d_5, 5% d_4; GCMS: m/e = 127, m/e = 95, m/e = 67.

The mass spectral data for non-deuterated phenetole and deuterated phenetole are listed as follows:

m/e	Peak intensity of non-deuterated phenetole	Peak intensity of phenetole-d_5	d_3	d_4	d_5	d_6
121	1.434 (M-1)					
122	100.00 (M)					
123	8.94 (M+1)					
124	0.58 (M+2)					
125	<0.01	<0.01				
126		5.27		5.27		
127		100.00		0.47	99.53	
128		9.18		0.03	8.96	0.19
129		0.49			0.57	

Depends on above data, we can calculate the percent yield

$$d_5\% = \frac{99.53}{5.27 + 99.53 + 0.19} \times 100\% = \frac{99.53}{104.99} \times 100\% = 95\%$$

$$d_4\% = \frac{5.27}{5.27 + 99.53 + 0.19} \times 100\% = \frac{5.27}{104.99} \times 100\% = 5\%$$

Preparation of Benzyl Phenyl Ether[10]

A mixture of 4 g (0.0416 mole) of phenol, 5.37 g (0.0416 mole) of benzyl chloride and 5.88 g (0.0416 mole) of potassium carbonate in acetone (10-20 ml) were added to a three-necked flask. The reaction mixture was stirred at 50-75 °C for 16 hours. The mixture was extracted with ether. The solvent was removed by rotary evaporator. The crude product (5.65 g) with purity (75%) was obtained. The crude product was purified by a flash column chromatographic

separation. For benzyl phenyl ether: ^1H NMR ($CDCl_3$) δ 7.6-7.35 (m, 10 H), 7.01 (d, J = 9.5, 2 H), 5.2 (s, 2 H).

Synthesis of Phenethyl Naphthyl Ether[10]

Preparation of phenethyl tosylate

A quantity of 2.65 g (0.0217 mole) of pure phenethyl alcohol was added to 16 ml of dry pyridine, and tosyl chloride (5 g, 0.026 mole) was added to the solution at room temperature. When the solid tosyl chloride dissolved completely, the mixture was kept in a refrigerator for 12 hours. A beautiful pyridine salt formed. The pyridine salt was separated. The solution was kept in a refrigerator again until no more crystals were formed. The solution was poured into 20 g ice. Crystals formed soon which were separated by filtration and were dried by air. A quantity of 4.6 g (0.0174 mole) of tosylate was obtained in 80% yield.

Preparation of phenethyl naphthyl ether

A quantity of phenethyl tosylate (4.6 g, 0.0174 mole) was added to a mixture of naphthanol (5.0 g, 0.0347 mole) and NaOH (1.4 g, 0.0347 mole) in H_2O (12 ml). The mixture was heated to 70 - 80 °C, and refluxed for 20 hours. When the reaction was finished, H_2O (10 ~ 15 ml) was added to the mixture. After a few minutes, the red oil-like product solidified. The solution phase was extracted by ether. The

solvent was removed. The purification was done by recrystallization with hexane. A quantity of 3.5 g (0.0141 mole) phenethyl naphthyl ether was obtained in 81% yield with high purity (92%). For phenethyl naphthyl ether: ^{1}H NMR ($CDCl_3$) δ 7.87-7.3 (m, 6 H), 7.29 (m, 5 H), 7.20 (d, J = 7, 1 H), 4.39 (t, 2 H), 3.2 (t, 2 H). IR (thin film): 3028, 2853, 1630, 1601, 1454, 1377, 1267, 1258, 1180, 1010, 837, 744, 719. Exact mass: Measured m/z: 248.12055, Calculated: 248.1202, error: +1.7 ppm.

General Pyrolysis Procedure

The pyrolysis apparatus is indicated in Figure 11, Appendix. The furnace was maintained at a temperature ranging between 520-820 °C. A sample of the starting material in a pyrex boat was placed into the sample chamber and the system was evacuated to 0.6-5.4 x 10^{-5} torr. The sample chamber was heated or cooled during the pyrolysis to the appropriate temperature depending on the starting material used. After the pyrolysis was completed, the appropriate amount of the solvent (CS_2:$CDCl_3$ = 1:1) was transferred to the trap. Then, the liquid-nitrogen cooled trap was warmed to -78 °C. After transferring the product solution to the NMR tubes at -78 °C, the NMR tubes were stored in an acetone-Dry Ice bath. It should be noted that the solvent (CS_2 + $CDCl_3$) was deoxygenated.

Pyrolysis of phenetole

A quantity of about 100 mg (0.8197 mmoles) of phenetole was pyrolyzed each time under different pyrolysis conditions (Table 1). The pyrolysate was collected in 3-5 ml of the solvent (1:1 $CS_2/CDCl_3$) from the liquid-nitrogen-cooled trap and ^1H NMR spectral data were recorded either at low temperature or room temperature. For cyclopentadiene: ^1H NMR (1:1 $CS_2/CDCl_3$) δ 6.5 (d, J = 5.0 Hz, 2 H), 6.4 (d, J = 5.1 Hz, 2 H), 2.9 (d, J = 2 Hz, 2 H); phenol: ^1H NMR (1:1 $CS_2/CDCl_3$) δ 7.4 (s, 1 H), 7.3 (t, J = 8.5 Hz, 2 H), 6.9 (t, J = 9 Hz, 1 H), 6.8 (d, J = 8.9 Hz, 2 H); azulene: GCMS m/e = 128.1, m/e = 102.1, m/e = 75.0, m/e = 64.2, m/e = 51.1.

Large scale pyrolysis of phenetole

A quantity of phenetole (716.4 mg, 5.87 mmole) was pyrolyzed under the following conditions: oven temperature, 795~801 °C; system pressure, 0.3~0.5 mmHz; sample head temperature, -5~-11 °C. The reaction was finished after 1.5 hours. The products were analyzed by GC mass spectroscopy. Phenol (63%) and a bimolecular adduct (13%) were obtained. For bimolecular reaction adduct: GC/MS m/e = 160, m/e = 145, m/e = 131.1, m/e = 127, m/e = 115, m/e = 94, m/e = 91, m/e = 77, m/e = 65, m/e = 57.9, m/e = 43.0, m/e = 39.0. GCFT-IR: 3653, 3549, 3067, 2936, 2666, 1585, 1488, 1327, 1250, 1196, 740.

Pyrolysis of phenetole-d_5

A quantity of 40 mg (0.315 mmoles) of phenetole-d_5 was pryolyzed under the following conditions: oven temperature, 804-819 °C; system pressure, 0.3 mmHg; sample head temperature, -20 °C. The reaction was completed after two hours. The pyrolysate was collected in 1.5 ml of 1:1 $CS_2/CDCl_3$ from the liquid-nitrogen cooled trap and ^2H NMR spectral data were recorded at low temperature (-78 °C) for cyclopentadiene: ^2H NMR (1:1 $CS_2/CDCl_3$) δ 6.55 (s, 1 H), δ 6.48 (s, 1 H), 2.3 (s, 2 H); phenol: ^2H NMR (1:1 $CS_2/CDCl_3$) δ 7.45 (s, 1 D), 6.85 (s, 1 D); ethylene: ^2H NMR δ 4.6 (s, 4 D).

Pyrolysis of benzyl phenyl ether

A quantity of 50 mg (0.272 mmoles) of benzyl phenyl ether was pyrolyzed under the following conditions: oven temperature, 800 °C; system pressure, 0.6 mmHg; sample head temperature, -10 °C. The reaction was finished after three hours. The pyrolysate was collected in 2 ml of 1:1 $CS_2/CDCl_3$ from the liquid-nitrogen-cooled trap. The sample was transferred to an NMR tube cooled to -78 °C. The spectrum was recorded at room temperature (Figure 3, Appendix). For 1,2-diphenylethane: ^1H NMR (1:1 $CS_2/CDCl_3$) δ 7.35 (m, 10 H), 3.0 (s, 4 H), GCMS: m/e = 187.0, m/e = 168.1, m/e = 91.2, m/e = 65.1. Phenol: ^1H NMR (1:1 $CS_2/CDCl_3$) 7.4 (s, 1 H), 7.3 (t, J = 8.5, 2 H), 6.9 (t, J =

9, 1 H); 6.8 (d, J = 8.9, 2 H). GCMS: m/e = 94, m/e = 66, m/e = 39. Toluene: ^{1}H NMR (1:1 $CS_2/CDCl_3$) δ 7.15 (m, 5 H), 2.4 (s, 3 H), GCMS: m/e = 92, m/e = 65.1; m/e = 39.1. Azulene: GCMS: m/e = 128.1, m/e = 102.1, m/e = 75.0, m/e = 64.2, m/e = 51.1.

Pyrolysis of phenol

A quantity of 50 mg (0.532 mmole) of phenol was pyrolyzed under the following conditions: oven temperature, 800 °C; system pressure, 0.6 mmHg; sample head temperature, -17 °C - -15 °C. The reaction was finished after 2.5 hours. The pyrolysate was collected in 2 ml of 1:1 $CS_2/CDCl_3$ from the liquid-nitrogen-cooled trap. The sample was transferred to a NMR tube cooled to -78 °C. The spectrum was recorded at room temperature (Figure 4, Appendix).

The mixture solution was a blue color. GC mass indicated azulene (3%) and phenol (90%) in the mixture.

Pyrolysis of naphthyl ethyl ether

A quantity of about 100 mg (0.5814 mmole) of naphthyl ethyl ether was pyrolyzed each time, under the appropriate pyrolysis conditions (Table 2). The pyrolysate was collected in 3.0~5.0 ml of 1:1 $CS_2/CDCl_3$ from the liquid-nitrogen-cooled trap and ^{1}H NMR spectral data were recorded at low temperature and room temperature (Figure 5, Appendix). The products were identified by comparing the

GCMS with those of standard products. GCMS for indene: m/e = 116.1, m/e = 89, m/e = 63, m/e = 58; for naphthanol: m/e = 144.0, m/e = 115, m/e = 89, m/e = 72, m/e = 57.9; for naphthalene: m/e = 128.2, m/e = 102, m/e = 75.1, m/e = 64.1, m/e = 51.0; for 1,2-dihydronaphthalene: m/e = 130, m/e = 115, m/e = 102, m/e = 89, m/e = 77.0, m/e = 64.0, m/e = 51.0, m/e = 39.0; for naphthyl ethyl ether: m/e = 172.1, m/e = 144.1, m/e = 115.1; for four hydrocarbon isomers: GCMS m/e = 144.1, m/e = 129.1, m/e = 115.1 (see Appendix).

Pyrolysis of phenethyl naphthyl ether

A quantity of about 100 mg (0.4032 mmoles) of phenethyl phenyl ether was pyrolyzed each time under the appropriate conditions (Table 3). The pyrolysate was collected in 3-5 ml of acetone from the liquid-nitrogen-cooled trap and the sample was transferred to a NMR tube under -78 °C. The ^{1}H NMR spectral data were recorded at room temperature (Figure 10, Appendix). For styrene: ^{1}H NMR (acetone) δ 7.25 (m, 5 H), 6.6 (d of d, J = 16,5, J = 10, 1 H), 5.7 (d, J = 16, J = 2, 1 H), 5.2 (d, J = 10, J = 2, 1 H). For naphthanol: ^{1}H NMR (acetone) δ 7.8-7.25 (m, 6 H), 7.2 (d, 1 H), 2.5 (s, 1 H). The products were identified by both ^{1}H NMR and GCMS with standard products (Table 3).

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APPENDIX

Figure 1. ^{1}H NMR (WM-300 Hz) spectra of the products of the pyrolysis of phenetole, recorded at -78 °C (a) and 25 °C (b) in 1:1 $CS_2/CDCl_3$

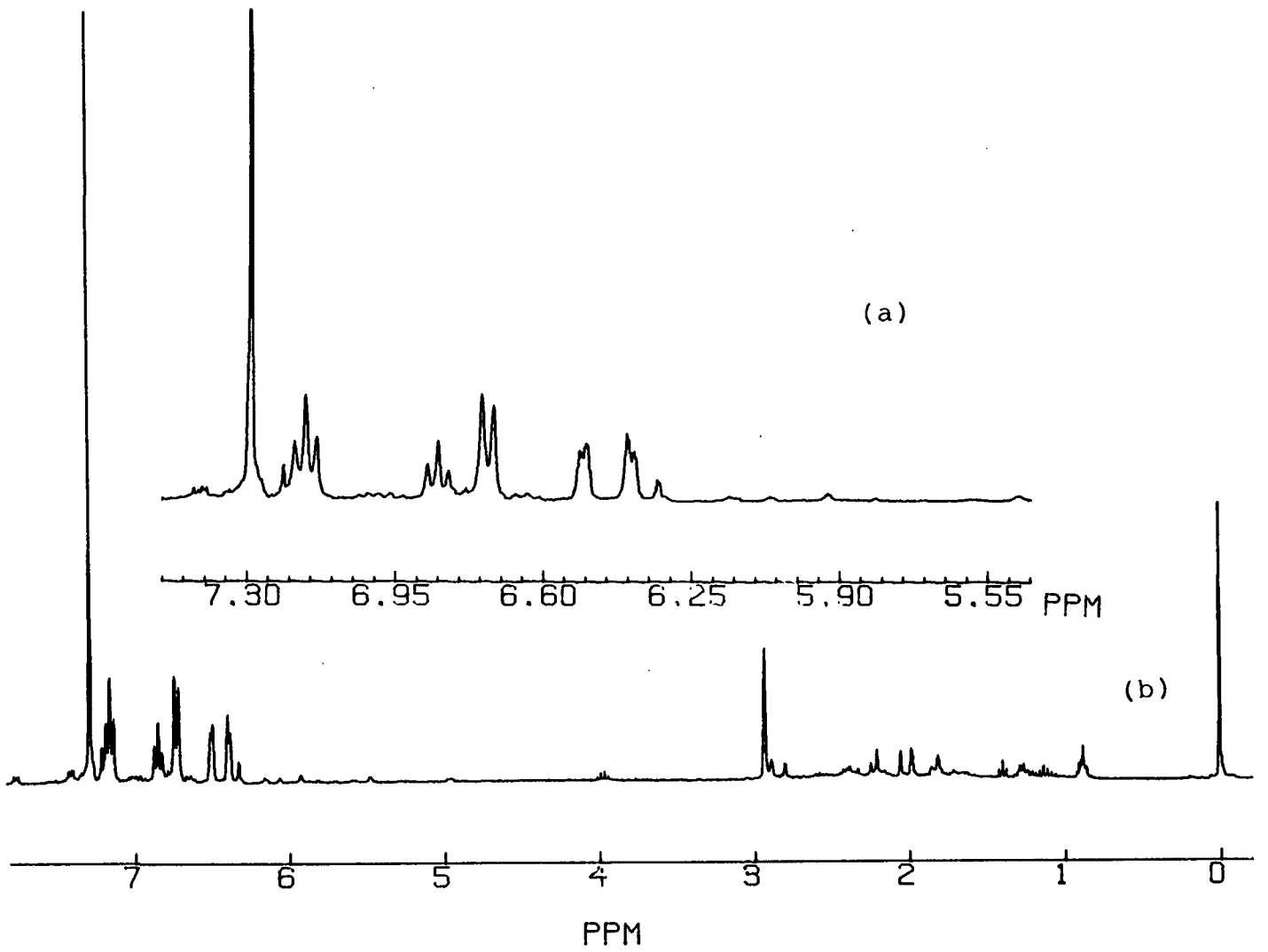

(a)
7.30
6.95
6.60
6.25
5.90
5.55
PPM
(b)
7
6
5
4
3
2
1
0
PPM

Figure 2. ^{2}H NMR (WM-300 Hz) spectrum of the products of the pyrolysis of phenetole-d_5, recorded at -78 °C in 1:1 $CS_2/CDCl_3$

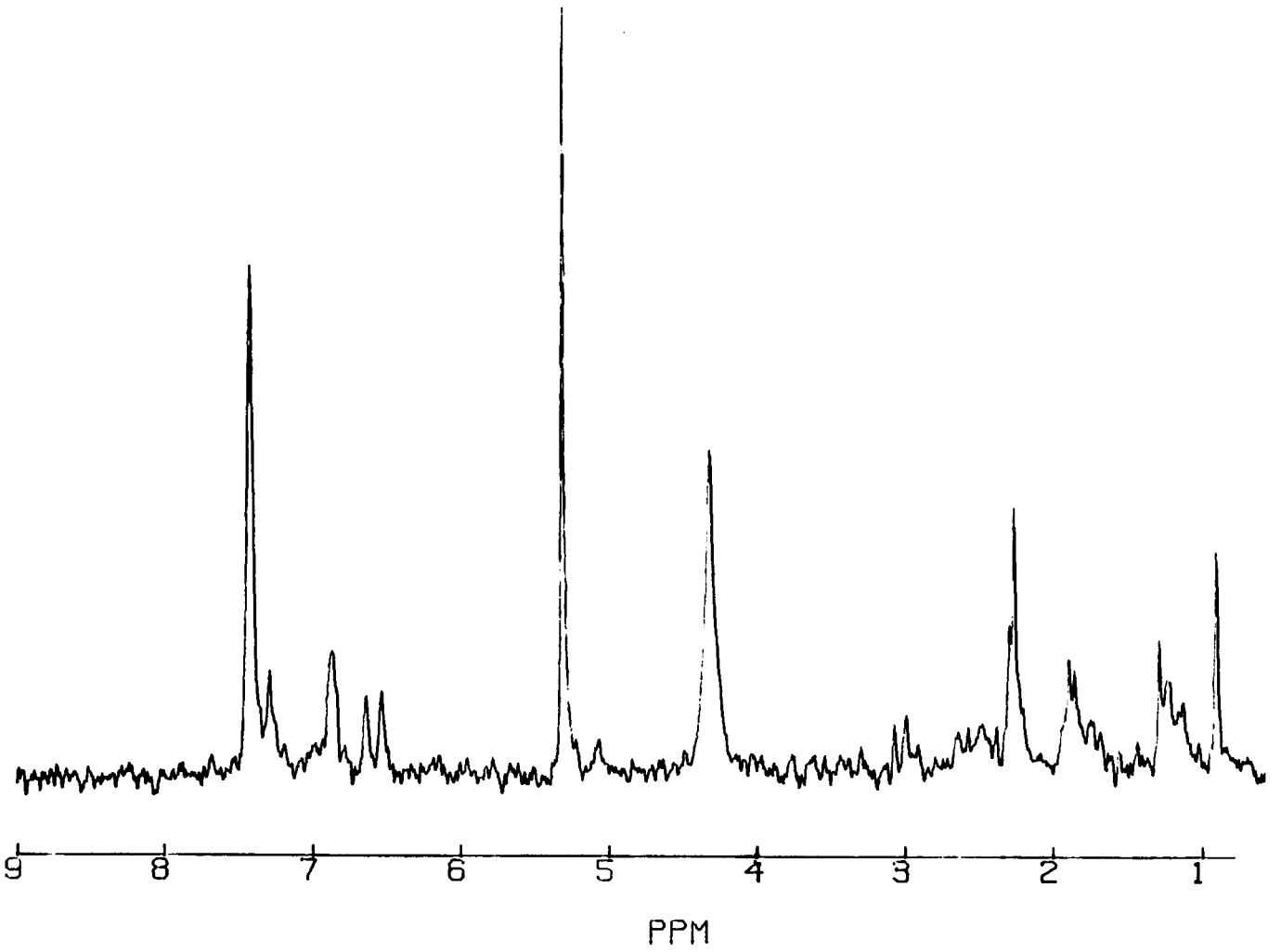

9
8
7
6
5
4
3
2
1
PPM

Figure 3. ^{1}H NMR (300 Hz) spectrum of the products of the pyrolysis of phenyl benzyl ether, recorded at 25 °C in 1:1 $CS_2/CDCl_3$

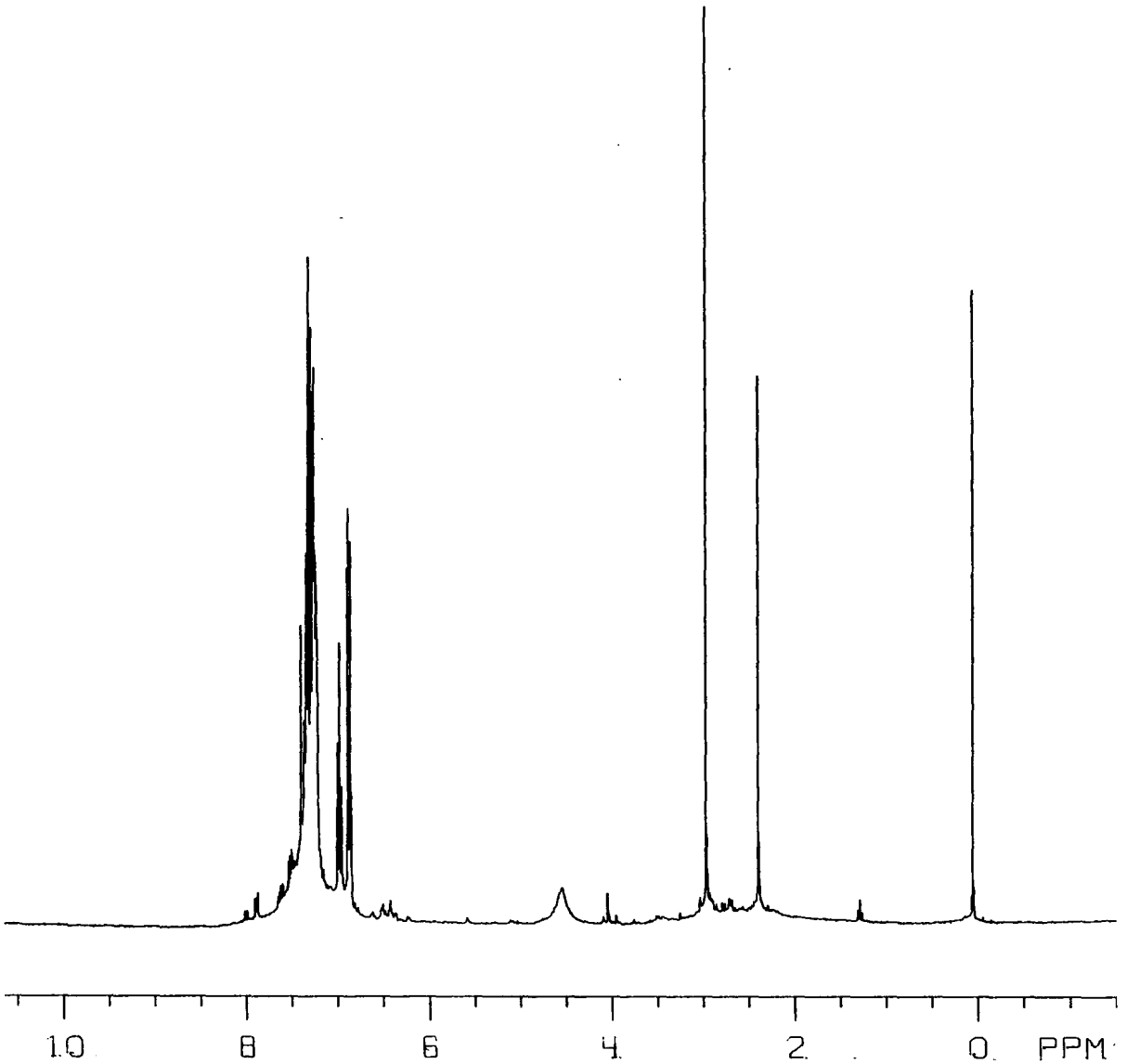

10
8
6
4
2
0
PPM

Figure 4. ^{1}H NMR (300 Hz) spectrum of the products of the pyrolysis of phenol, recorded at 25 °C in 1:1 $CS_2/CDCl_3$

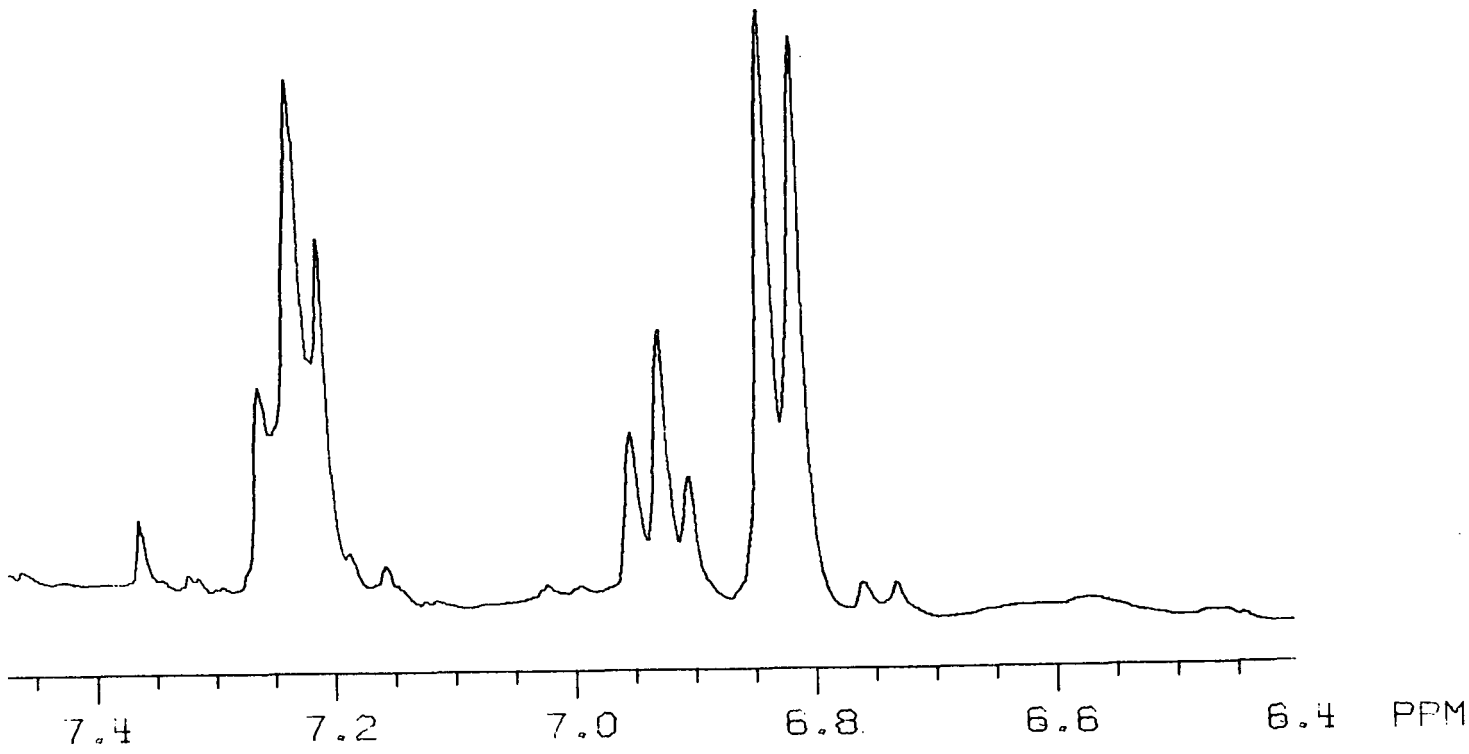

7.4
7.2
7.0
6.8
6.6
6.4
PPM

Figure 5. ^{1}H NMR spectra (WM-300) of the products of pyrolysis of naphthyl ethyl ether, recorded at various temperatures in 1:1 $CS_2/CDCl_3$

1. Temperature = -78 °C
2. Temperature = -40 °C
3. Temperature = -20 °C
4. Temperature = 25 °C after three days

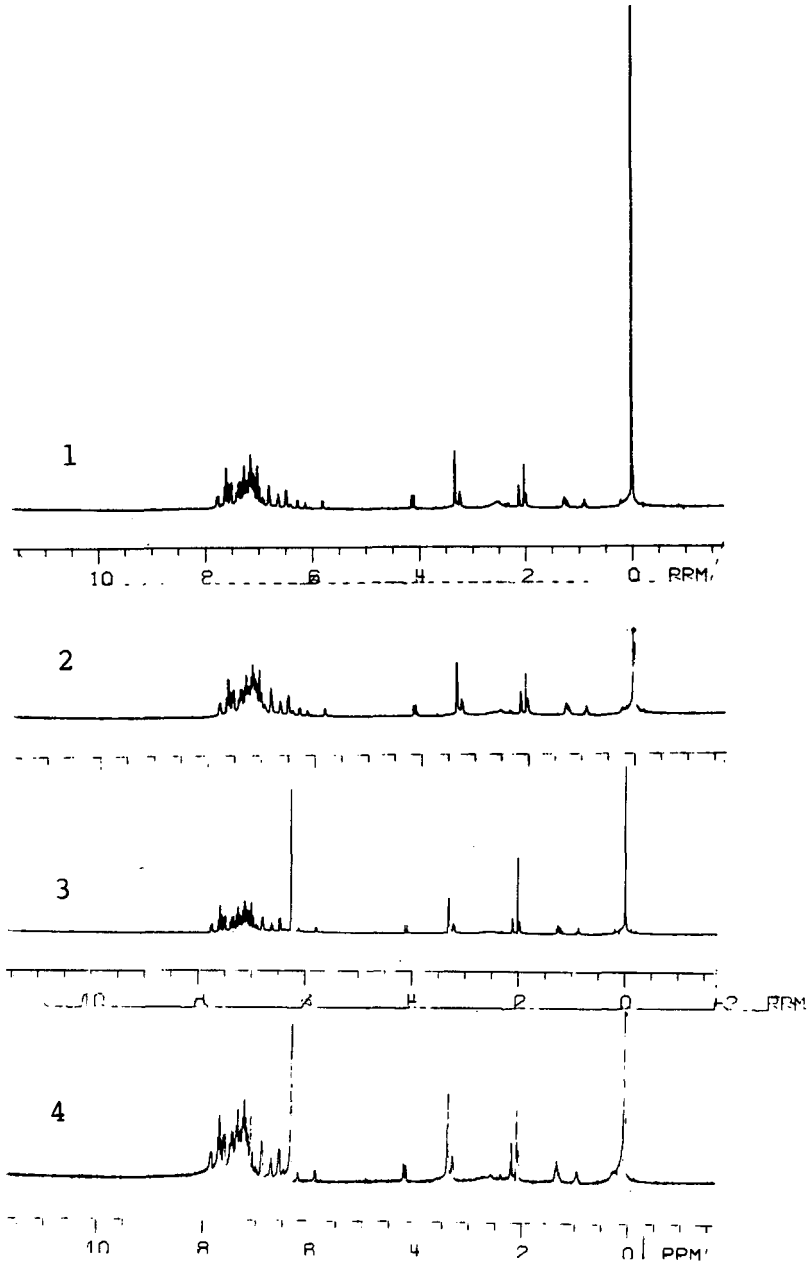

1
10
8
6
4
2
0
PPM
2
3
4
10
8
6
4
2
0
PPM

Figure 6. The GC mass spectrum of the first of the four hydrocarbon isomers

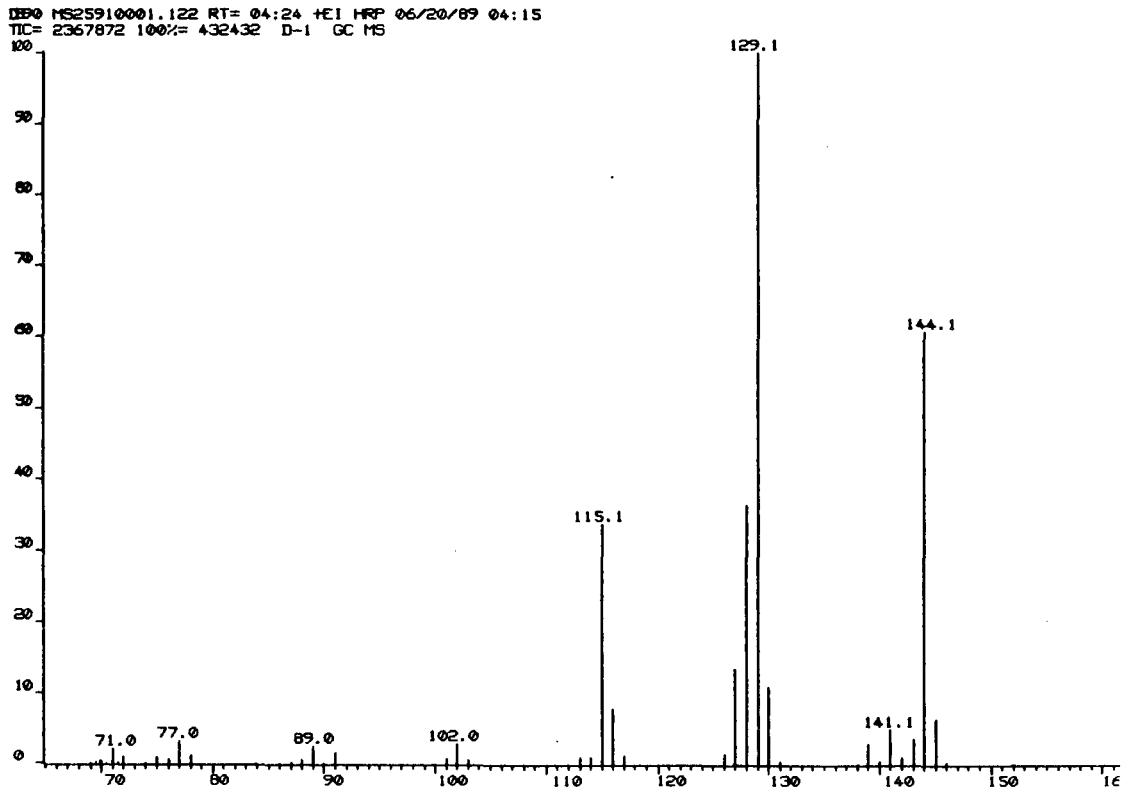

DB0 MS25910001.122 RT= 04:24 +EI HRP 06/20/89 04:15
TIC= 2367872 100%= 432432 D-1 GC MS
100
90
80
70
60
50
40
30
20
10
0
129.1
144.1
115.1
71.0
77.0
89.0
102.0
141.1
70
80
90
100
110
120
130
140
150

Figure 7. The GC mass spectrum of the second of the four hydrocarbon isomers

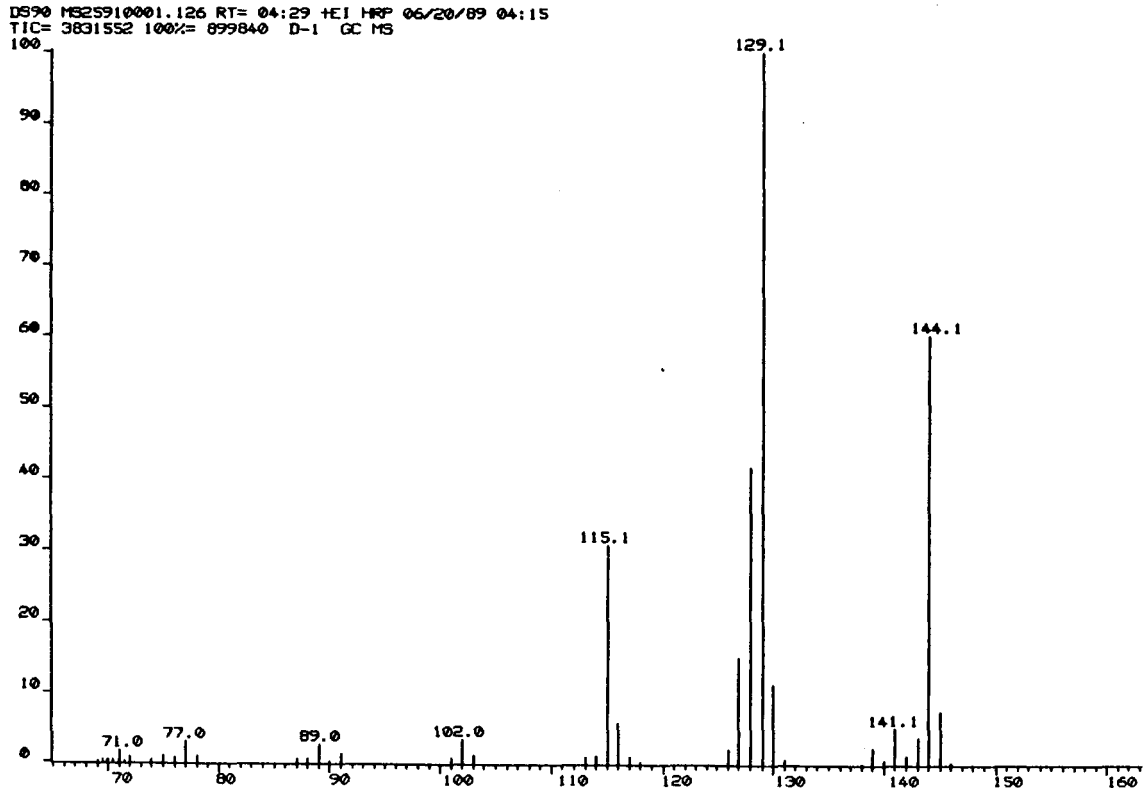

D890 MS25910001.126 RT= 04:29 +EI HRP 06/20/89 04:15
TIC= 3831552 100%= 899840 D-1 GC MS
129.1
144.1
115.1
71.0
77.0
89.0
102.0
141.1

Figure 8. The GC mass spectrum of the third of the four hydrocarbon isomers

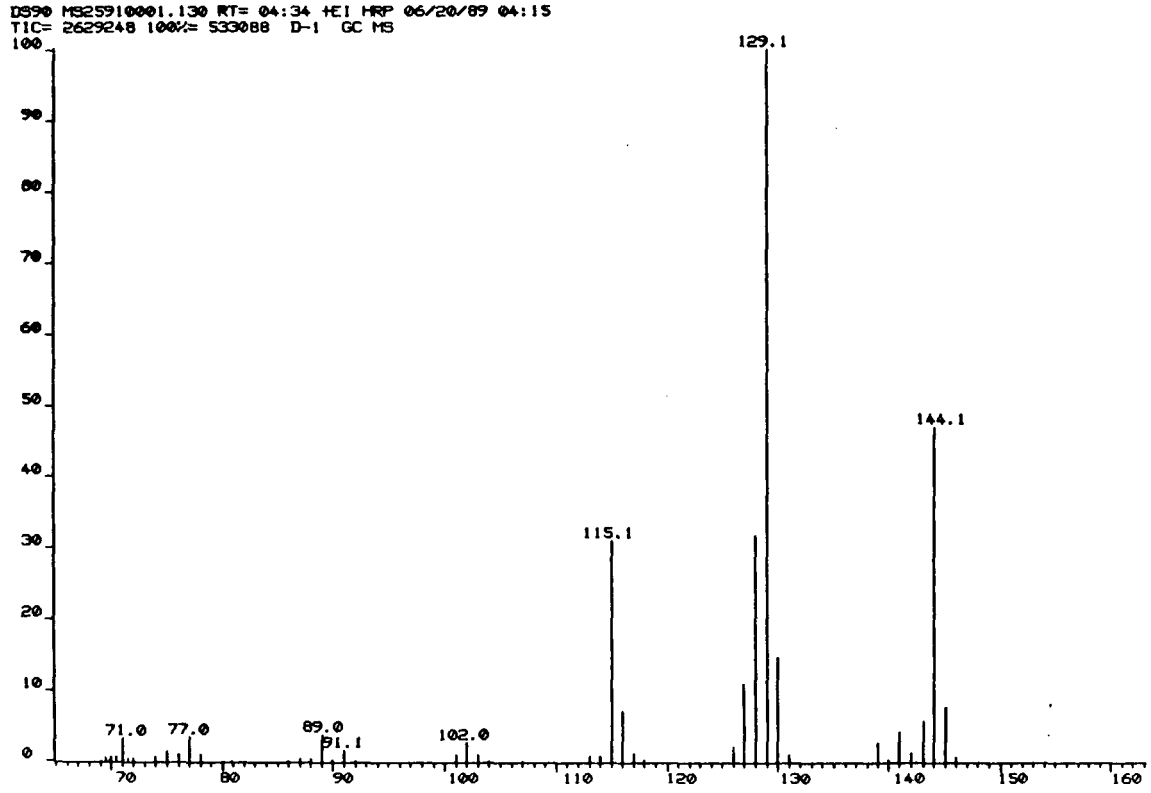

D890 MS25910001.130 RT= 04:34 +EI HRP 06/20/89 04:15
TIC= 2629248 100%= 533088 D-1 GC MS
129.1
144.1
115.1
71.0
77.0
89.0
91.1
102.0

Figure 9. The GC mass spectrum of the fourth of the four hydrocarbon isomers

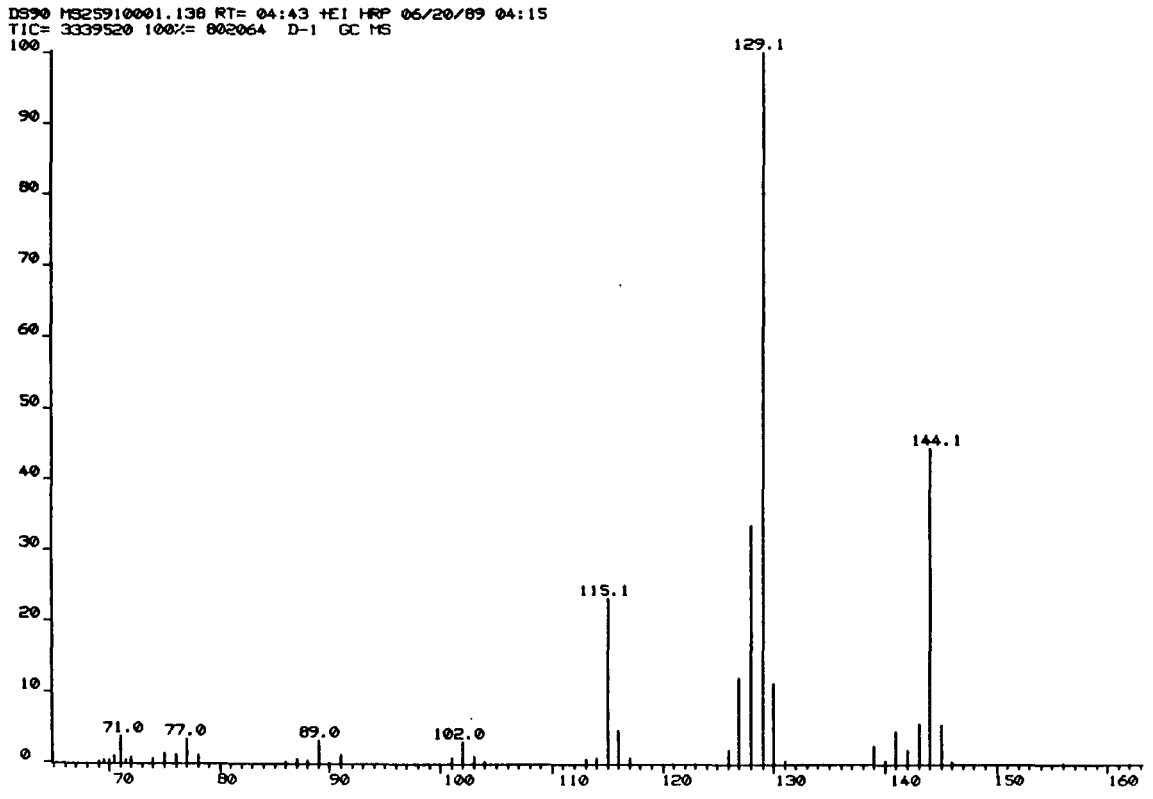

DS90 MS25910001.138 RT= 04:43 +EI HRP 06/20/89 04:15
TIC= 3339520 100%= 802064 D-1 GC MS
129.1
144.1
115.1
71.0
77.0
89.0
102.0

Figure 10. ^{1}H NMR (WM-300 Hz) spectrum of the products of pyrolysis of phenethyl naphthyl ether, recorded at -78 °C in acetone-d_6

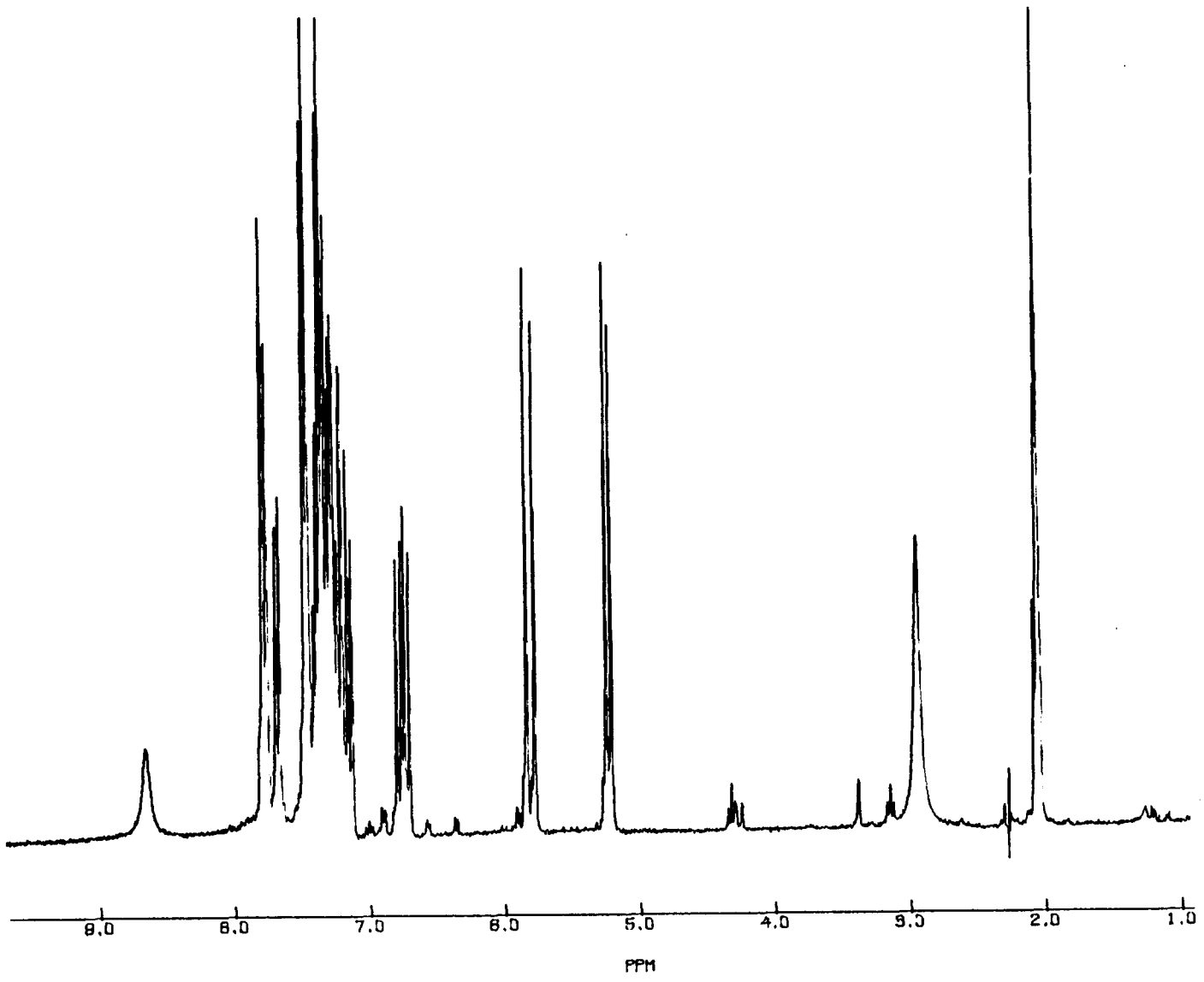
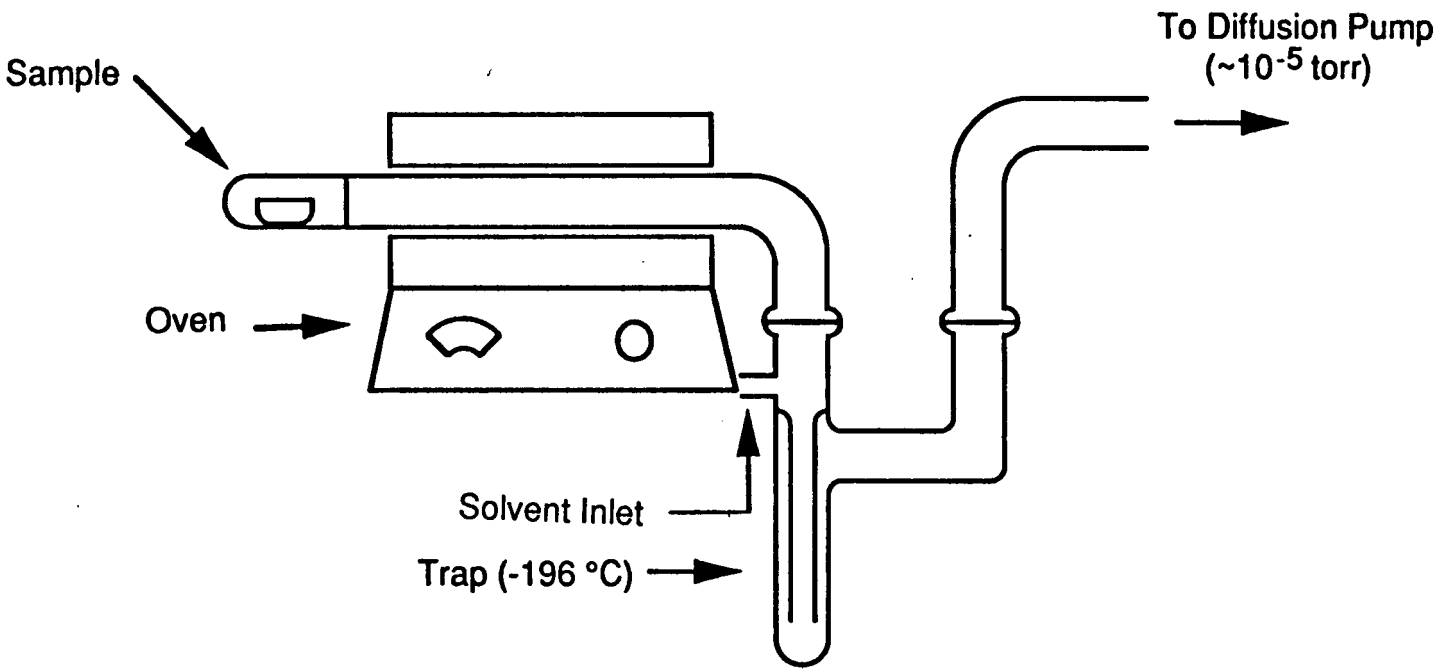

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
PPM

Figure 11. Schematic diagram of the pyrolysis apparatus

Flash Vacuum Pyrolysis



PART II. GENERATION OF p-XYLYLENE AND ITS DERIVATIVES BY ZINC INDUCED DEHALOGENATION

INTRODUCTION

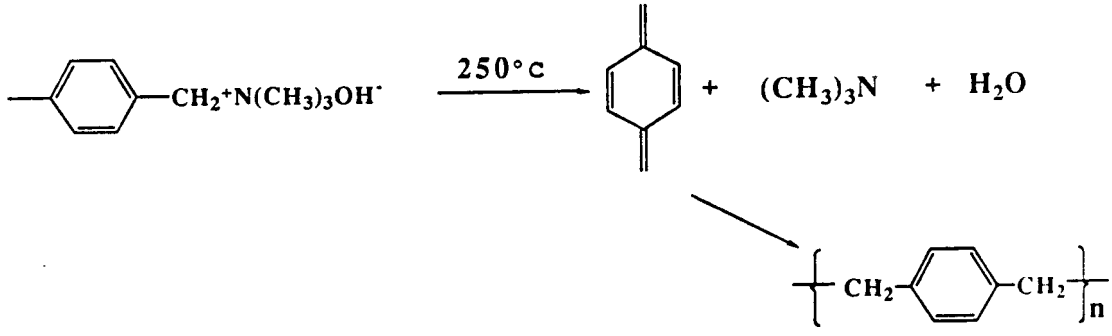
o-Quinodimethane (o-xylylene) and p-quinodimethane (p-xylylene) have been used extensively as reactive intermediates in organic synthesis.

In 1947, Szwarc was the first to observe that the fast flow pyrolysis of p-xylene at low pressure leads to the formation of a white polymeric material having the postulated structure poly p-xylylene.[1] The polymer is formed via a series of gas phase reactions whereby a C-H bond of p-xylene is cleaved thermally to give p-xylyl radicals that disproportionate on collision to produce p-xylene and p-xylylene, which subsequently polymerizes on condensation.

It is postulated that p-xylylene exists in the gas phase and that polymerization occurs at the moment of condensation even at -190 °C.[2] Theoretical calculations indicate that p-xylylene is diamagnetic at low temperature.[3] p-Xylylene is a very reactive molecule even at -78 °C. It reacts readily with monoradicals, halogen molecules,[4,5] and PCl_3.[6,7,8,9] Poly-p-xylene peroxide is formed in almost 100% yield when a vigorous stream of oxygen is bubbled through a solution of p-xylyene at -78 °C. p-Xylylene is particularly prone to undergo homopolymerization even at -78 °C to afford linear poly-p-xylylene.[10] The polymerization is first order with respect to monomer and has an activation

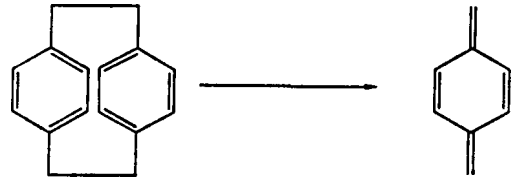
energy of about 9 kcal/mole. The half-life of a p-xylyene solution was observed to be about 22 hours at -78 °C and about 22 minutes at -36 °C.

There are a number of methods that can be used to generate p-xylyene. In 1960, Errede reported that the Hofmann degradation of p-methylbenzyltrimethylammonium hydroxide at low pressure in a modified flow system is a convenient method for generating p-xylylene[11] (eq. 1)



(1)

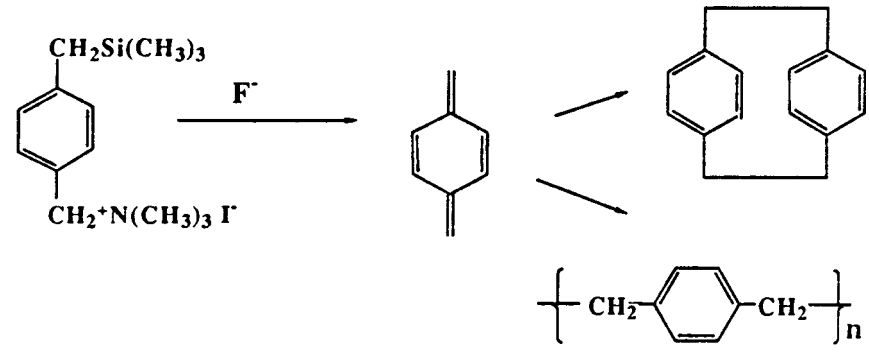
In 1963, Cram and coworkers reported that pyrolysis of paracyclophanes generates p-xylylene[12] (eq. 2).



(2)

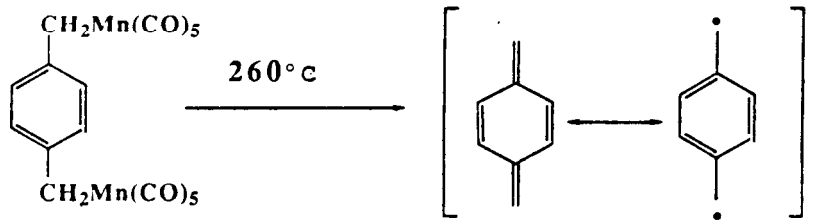
In 1970, Koch and coworkers first observed p-xylylene by ^{1}H NMR at -78 °C.[13]

In 1981, Ito and coworkers reported that the fluoride anion induced 1,6-elimination of $^{\alpha}$-[(trimethylsilyl)methyl]-benzyltrimethylammonium iodide could provide a convenient method for preparation of p-xylylene. In this situation p-xylylene dimerizes or polymerizes to [2,2]-paracyclophane and poly-p-xylylene[14] (eq. 3).



(3)

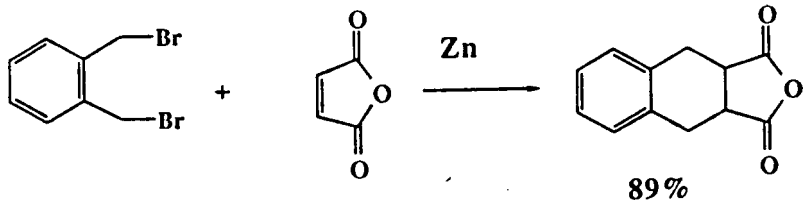
In 1985, Parker and coworkers reported that flash vacuum pyrolysis of organomanganese pentacarbonyl compounds 1 is a reasonably efficient, low temperature (260 °C) gas-phase source of p-xylylene[15] (eq. 4).



(4)

In 1982, Han and coworkers reported[16] that α,α'-dibromo-o-xylene and zinc powder react smoothly in the presence of

dienophiles and sonic waves to give high yields of cycloaddition products of o-xylylene (eq. 5).



(5)

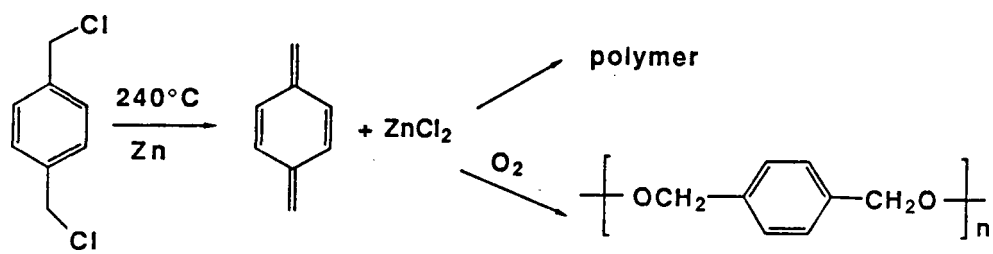
In 1904, Thiele had used 1,4-bis(diphenylbromomethyl)-benzene with zinc to generate α,α'-tetraphenyl-p-xylylene.[17] It is not difficult to find the examples of reduction of α,α'-dibromo-o-xylene and α,α'-dibromo-p-xylene with zinc in the solution phase, but reduction of α,α'-dichloro-p-xylene in the gas phase by solid zinc has not been reported to date. In this part, we will report the attempts to prepare p-xylylene and its derivatives by this method.

RESULTS

The Generation of p-xylylene

p-Xylylene was prepared by reduction of α,α'-dichloro-p-xylene 2 with zinc under oven temperature ~240 °C, system pressure ~ 0.15 mmHg. p-Xylylene was trapped by condensing it in a trap which was placed in liquid nitrogen (see Figures 1 and 3, Appendix). After the pyrolysis trap was warmed to -78 °C, p-xylylene (7%) was detected. The rest of the monomer was polymerized (except for p-xylylene and its polymer, no other products were detected). A white polymer film could be observed. In the solution phase, p-xylylene reacted with oxygen to form poly-p-xylylene peroxide (see Figure 2) (Scheme 1).

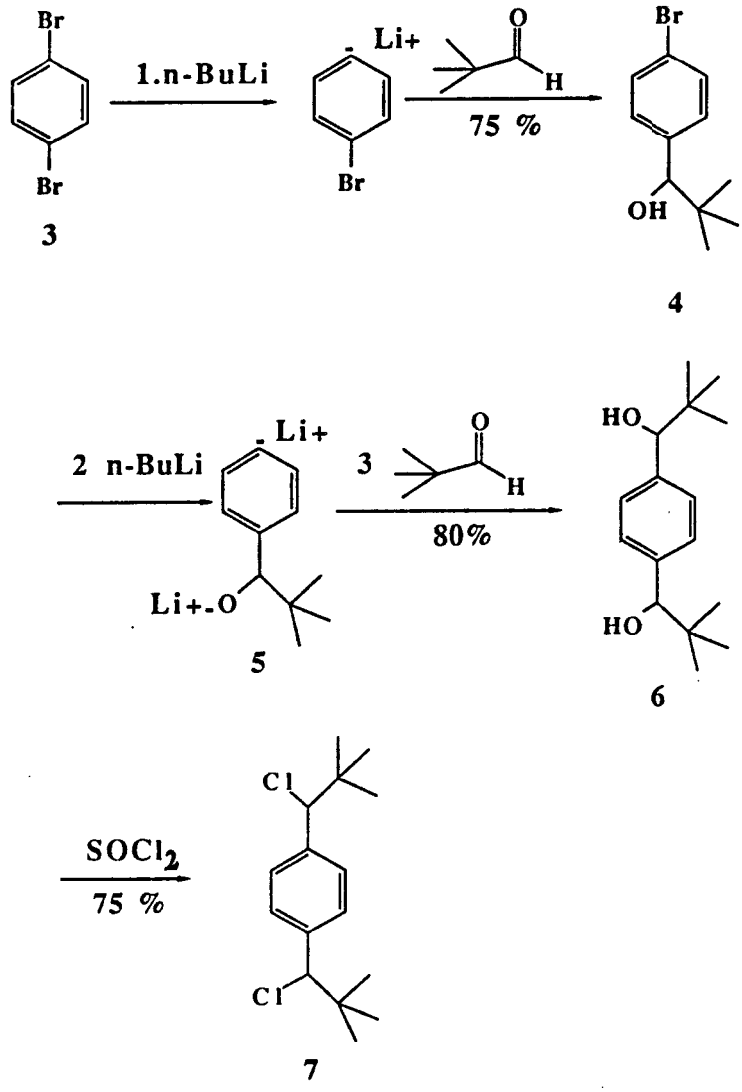
Scheme 1



Preparation of α,α'-Dichloro-α,α'-di-t-butyl-p-xylene (7) (a mixture of diastereomers)

α,α'-Dichloro-α,α'-di-t-butyl-p-xylene (as a mixture of two diastereomers) was prepared as indicated in Scheme 1. Diol 6 (a mixture of diastereomers) was prepared simply

Scheme 2


Br
Br
1.n-BuLi
Li+
Br
O
H
75 %
Br
OH
3
4
2 n-BuLi
Li+
Li+-O
3
O
H
80%
HO
HO
5
6
SOCl2
75 %
Cl
Cl
7

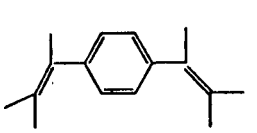
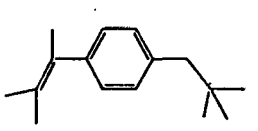
by treating compound 4 with two moles of n-butyl lithium, followed by addition of a two molar excess of trimethylacetaldehyde. Compound 4 was prepared by reaction of 4,4-dibromobenzene (1 mole) and n-butyl lithium (1 mole), followed by addition of a two molar excess of trimethyl-acetaldehyde.

Reaction of α,α'-Dichloro-α,α'-di-t-butyl-p-xylene (7) (a mixture of diastereomers) with Zinc

The reduction of 7 (a mixture of diastereomers) with mossy zinc was carried out at different temperatures. A drawing of the pyrolysis apparatus is presented in the Appendix (Figure 4). The mossy zinc was packed in the pyrolysis tube as a packing material.

It was found that it is important to control the amount of dichloride. Since the zinc takes part in the reaction, the $ZnCl_2$ produced during the reaction may deposit on the zinc surface and limit the effective zinc surface. Therefore, large amounts of dichloride will not be able to react with the zinc. The products of the reaction of 7 at different temperatures were analyzed by ^1H NMR (Figures 5, 6, Appendix) and GCMS and are summarized in Table 1.

Table 1. The products of the gas phase reduction of 7 (a mixture of two diastereomers) by zinc

Conditions				Products, %[a]		
						
Entry	Oven Temp, °C	System Pressure, torr	Sample head Temp, °C	8	9	x[b]
1	340~350	0.3	70~80	62.8	1.39	27
2	140~150	0.3	70~80	51	6	30
3	290~300	0.3	70~80	49.7	4	27
4	230~240	0.1	60~70	47	0	24

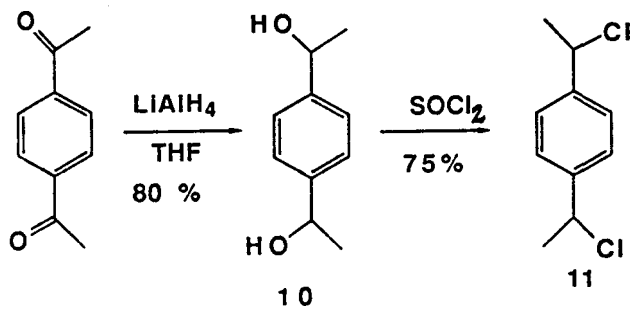
[a]The ratio of the products detected by GC.

[b]This compound has not been identified.

Preparation of α,α'-Dichloro-α,α'-dimethyl-p-xylene (11)
(a mixture of diastereomers)

α,α'-Dichloro-α,α'-dimethyl-p-xylene (11) (a mixture of diastereomers) was synthesized by a two step sequence (Scheme 3).

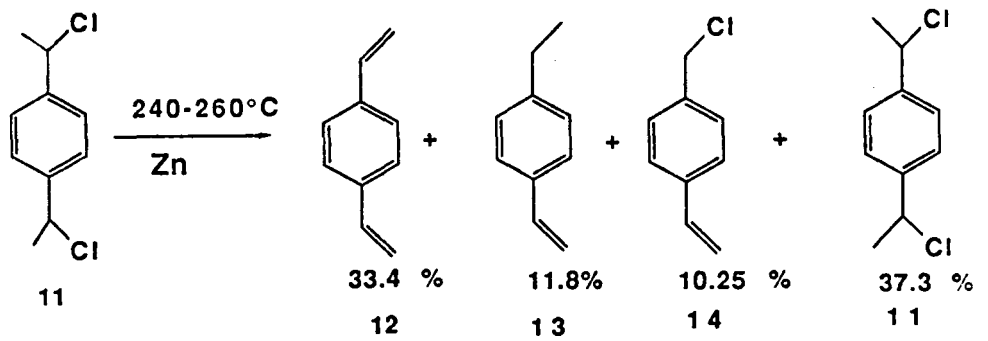
Scheme 3



Diol 10 (as a mixture of diastereomers) could be synthesized by reduction of 1,4-diacetobenzene with lithium aluminum hydride. Dichloride 11 (as a mixture of diastereomers) was synthesized by treatment of diol 10 with thionyl chloride.

The Reaction of α,α'-Dichloro-α,α'-dimethyl-p-xylene 11
(a mixture of diastereomers) with Zinc

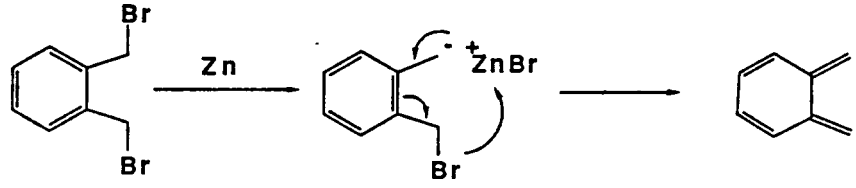
Reduction of 11 (a mixture of diastereomers) was carried out under the same conditions as used for the reduction of 7. The products were analyzed by ^{1}H NMR and GCMS (eq. 6).



(6)

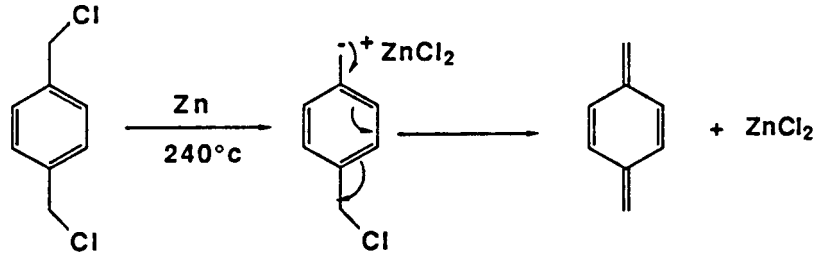
DISCUSSION AND CONCLUSION

Even though this is a unique method for generating p-xylylene, it has some limitations such as the method does not give the desired products (a,a'-dimethyl-p-xylylene). Instead, some rearrangement products were produced. Dehalogenations to generate the quinodimethane in the solution phase are well studied[16,17] (eq. 7).

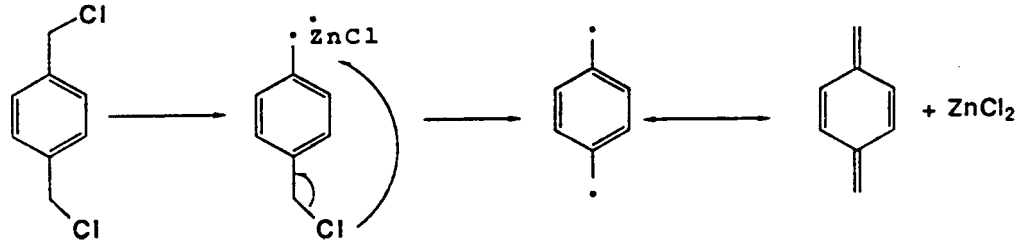


(7)

Since our reaction temperature is very high (240 f 260 °C) the general mechanisms for the formation of p-xylylene are shown in equations 8 and 9. Either mechanism may be used to



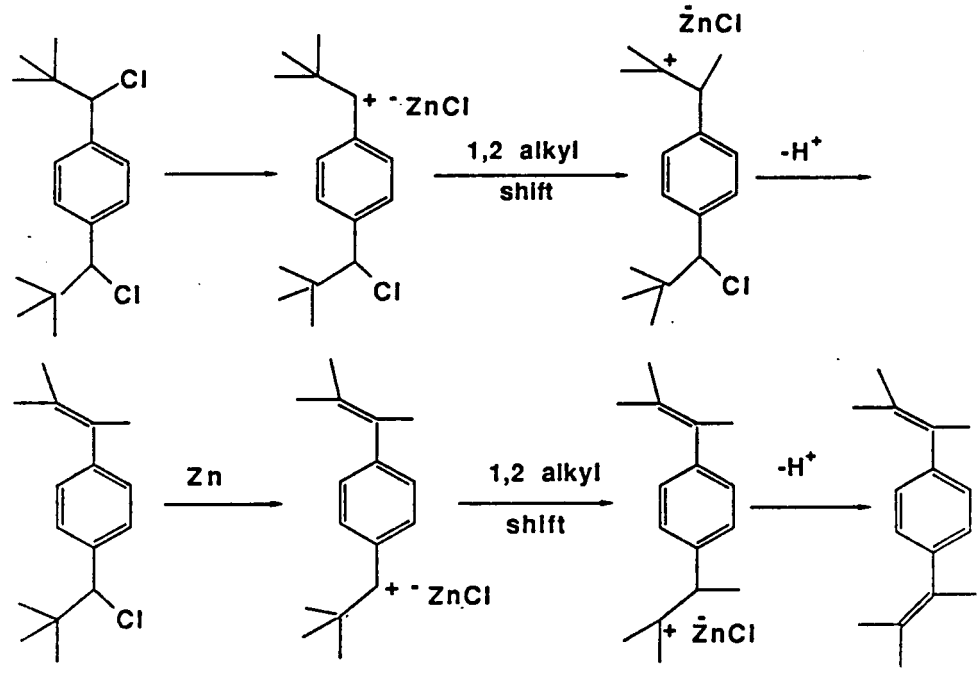
(8)



(9)

explain our experimental results for the parent system, but neither mechanism can be used to explain the results of the dehalogenation of α,α-di-t-butyl-α,α'-dichloro-p-xylene (7) (a mixture of diastereomser) with zinc. Because neither carbanions nor radicals undergo rapid 1,2-alkyl shifts, the mechanism in Scheme 4 is proposed.

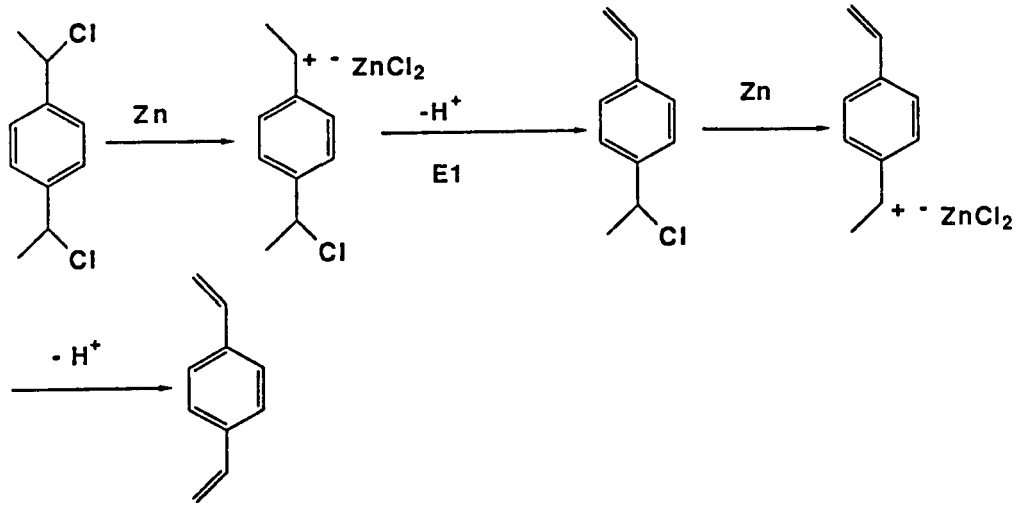
Scheme 4



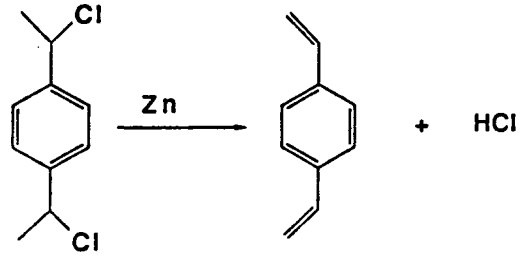
Carbocations are invoked because they undergo 1,2-alkyl shifts readily.

For the reaction of 11 under the same conditions used for 7, the same type of the mechanism may be operating (Scheme 5).

Scheme 5



It is also possible that a zinc-catalyzed concerted elimination of HCl is occurring (eq. 10).



(10)

Reduction of α,α'-dichloro-p-xylene with zinc in the gas phase generates p-xylylene in high yield, but only about 7% of p-xylylene could be trapped at -78 °C. The rest of the monomer polymerized at -78 °C or even -190 °C. To prevent the polymerization, condensation of the monomer directly into a solvent, or using some carrier gas may be beneficial.

EXPERIMENTAL

Methods and Materials

The reaction apparatus is a pyrolysis apparatus which has been previously described.[18] ^{1}H NMR spectra were recorded on WM-300, Nicolet-300 spectrometers. Chemical shifts are reported in parts per million (ppm) from tetramethylsilane (TMS). Coupling constants (J) are reported in Hertz. Gas chromatography/ mass spectral analyses (GC/MS) were performed using a Finnigan 4000 instrument and an INCOS data system. All of the chemicals used in the experiments are available from Aldrich Chemical Company.

Synthesis of α-Hydroxy-α-t-butyl-4-bromo-toluene (4)

A quantity of 4 g (0.01695 mole) of 1,4-dibromobenzene and dried THF (40-50 ml) were added to a round-bottomed flask which was kept at -78 °C. A quantity of 10.6 ml (0.0625 mole) of n-butyl lithium in hexane was transferred to the flask. The reaction mixture was stirred about 50 min at -78 °C. A white precipitate formed during this period. The solution was then transferred to a three-necked flask fitted with a condenser and mechanical stirrer (the three-necked flask was placed in an acetone-Dry Ice bath during the addition). After the addition was finished, the mixture was stirred for 30 min and then heated to 50 °C - 60

°C for five hours. The reaction mixture was washed with NH_4Cl solution. The organic layer was separated, dried with $MgSO_4$, and concentrated. A 75% yield of the crude product (2.88 g, 0.0127 mole) was obtained: ^1H NMR ($CDCl_3$) δ 7.48 (d, J = 8.9, 2 H), 7.25 (d, J = 8.5, 2 H), 4.49 (s, 1 H), 3.4 (s, 1 H), 1.01 (s, 9 H).

The Mixture of Diastereomers of
α,α'-Dihydroxy-α,α'-di-t-butyl-p-xylene (6)

A quantity of 0.23 g (0.00095 mole) of 4 and 5 ml of dried THF were added to a 25-ml three-necked flask. n-Butyllithium in hexane (1.2 ml, 0.00175 mole/1.1 ml, tiltrated concentration) was added to the three-necked flask with mechanical stirrer; the flask was cooled by an acetone-Dry Ice bath. After 50 min (dianion 5 was generated), trimethylacetaldehyde (0.33 g, 0.00383 moles, four time excess) was added to the three-necked flask. After the mixture was cooled in an acetone-Dry Ice bath and stirred for 40 min, it was warmed to 60 °C and heated to reflux for 7 hours. The reaction mixture was then washed with an ammonium chloride solution three times. The aqueous layer was extracted with 10 ml of ether and the organic layers were combined and dried with $MgSO_4$. The solvent was removed to yield 80% of the diastereomers 6 (190 mg, 0.76 mmole) ^1H NMR ($CDCl_3$) δ 7.25 (s, 4 H), 4.9 (s, 2 H), 3.75

(s, 2 H), 1 (s, 18 H). IR (thin film) 3410, 2953, 2926, 1478, 1466, 1394, 1366, 1047, 1005, 845, 756. GCMS: m/e = 166, m/e = 131, m/e = 115, m/e = 91, m/e = 77.

α,α'-Dichloro-α,α'-di-t-butyl-p-xylene (7)

(mixture of the diastereomers)

A quantity of 0.1 g (0.0004 mole) of compound 6 and 0.07 ml of dry pyridine were added to a flask fitted with a condenser and magnetic stirrer. $SOCl_2$ (0.286 g, 2.4×10^{-3} mole) was added to the flask. The mixture was heated to reflux for 6.5 hours during which it became dark brown. Water (2 ml) was then carefully added to the reaction mixture with stirring. The mixture was then extracted with 5 ml of ether and the ether layer was washed with 5% NaOH solution once and with water twice, dried by $MgSO_4$, and concentrated. Orange crystals (0.087 g, 0.0003 mole) were obtained in 75% yield. ^1H NMR ($CDCl_3$) 57.25 (s, 4 H), 4.7 (s, 2 H), 1 (s, 18 H). GCMS: m/e = 202, m/e = 167, m/e = 131, m/e = 117, m/e = 105, m/e = 91, m/e = 77, m/e = 63. Exact mass: measured m/z 286.12582. Calculated ~ 286.12551, error ~ +1.1 ppm.

α,α'-Dihydroxy-α,α'-dimethyl-p-xylene (10)

(mixture of diastereomers)

To a stirred solution of $LiAlH_4$ (0.95 g, 0.0247 mole) in dry THF (20 ml) at 0 °C was added a solution of

1,4-diacetobenzene (2 g, 0.012 mole) in dry THF (30 ml). The mixture was stirred at room temperature for 8 hours, and standard work up[19] gave 1.9 g (0.0115 mole) of the mixture of diastereomers of 10 in 93% yield: ^{1}H NMR ($CDCl_3$) δ 7.4 (s, 4 H), 4.9 (s, 2 H), 3.75 (m, 2 H), 1.5 (d, J = 6.5, 6 H).

α,α'-Dichloro-α,α'-dimethyl-p-xylene (11)

(mixture of diastereomers)

A quantity of 10 (2 g, 0.0125 mole) and dry pyridine (1.91 g, 0.025 mole) were added to a flask. $SOCl_2$ (8.6 g, 0.0703 mole) was carefully added to the mixture and it was heated to reflux at 60 °C - 70 °C for 5 hours. Water (3 ml) was then carefully added to the reaction mixture. The reaction mixture was extracted with 20 ml of ether and the ether layer was washed by 5% NaOH solution and twice with water. The organic layer was dried and concentrated to give a mixture of diastereomers of 11 (1.77 g, 8.75×10^{-3} mole) in 70% yield: ^{1}H NMR ($CDCl_3$) δ 7.49 (s, 4 H), 5.1 (q, 2 H), 1.9 (d, J = 6.5, 6 H); high resolution mass spectrum, calculated for $C_{10}H_{12}Cl_2$ 202.03161, measured 202.03187.

General Procedure for Gas Phase Zinc Reactions

The pyrolysis furnace was maintained at temperatures ranging between 140 °C - 290 °C. A sample of the dihalide in a pyrex boat was placed into the sample chamber and the

system was evacuated to 0.6 ~ 0.1 torr. The sample chamber was heated to 80-90 °C during the reaction. The tube which was packed by mossy zinc is shown in Figure 4, Appendix. The pyrolysis tube was 27 cm long and the diameter was 5.5 cm. The liquid-nitrogen-cooled trap was used to collect the products. After the reaction, solvent (3-5 ml) (CS_2:$CDCl_3$=1:1) was used to rinse the products from the cooled trap. To determine the yield, a known amount of tetrachloroethane was used as an internal standard. After transferring the product solutions to an NMR tube at -78 °C, the NMR tubes were stored in an acetone-Dry Ice bath. It is important that the solvents (CS_2 and $CDCl_3$) are deoxygenated. The packing material zinc must be activated by 10% HCl solution for 5-10 min and then rinsed with a large amount of water and then thoroughly dried under vacuum.

The Reaction of α,α'-Dichloro-p-xylene with Zinc in Gas Phase

A quantity of 200 mg (1.14 mmoles) of α,α'-dichloro-p-xylene was reacted at an oven temperature of 240~260 °C, a system pressure of 0.1~0.3 mHg, a sample head temperature of 60-70 °C. The products were collected in 3.0~5.0 ml of 1:1 $CS_2/CDCl_3$ and ^1H NMR spectral data were recorded at low temperature (-78 °C). For p-xylylene: ^1H NMR (1:1 $CS_2/CDCl_3$) δ 6.4 (s, 4 H), 5.10 (s, 4 H). Quantitative ^1H

NMR analysis with standard ($Cl_2CHCHCl_2$) indicated that pyrolysis gave 7% yield of p-xylylene. p-Xylylene reacted with O_2 inside the tube produced poly-p-xylene peroxide: ^1H NMR (1:1 $CS_2/CDCl_3$) δ 7.3 (s, 4 H), 4.5 (s, 4).

The Reaction of α,α-Dichloro-α,α'-Di-t-butyl-p-xylene 7 (a mixture of diastereomers) with Zinc in Gas Phase

A quantity of 50 mg (0.1742 mmole) of compound 7 was reacted under appropriate conditions (Table 1). The products were collected in 3.0~5.0 ml solvent (1:1 $CS_2/CDCl_3$) and the ^1H NMR spectra data were recorded at room temperature (Appendix). The products were identified by both ^1H NMR and GCMS. For product 8: ^1H NMR (1:1 $CS_2/CDCl_3$) δ 7.05 (s, 4 H), 2.0 (d, J = 1 Hz, 3 H), 1.9 (s, 3 H), 1.7 (d, J = 1 Hz, 3 H). GCMS: m/e = 214.2, m/e = 199, m/e = 171.1, m/e = 157.1, m/e = 145, m/e = 129.1, m/e = 115.1, m/e = 91.1, m/e = 77, m/e = 69.1, m/e = 57. For product 9: GCMS: m/e = 216.2, m/e = 201, m/e = 173.1, m/e = 160.2, m/e = 145.1, m/e = 128.1, m/e = 115.1, m/e = 91.1, m/e = 57.1 (Base peak), m/e = 41.1. For product x: m/e = 216.2, m/e = 201.1, m/e = 159, m/e = 145.1, m/e = 129.1, m/e = 115.1, m/e = 105.1, m/e = 91.1, m/e = 77.1, m/e = 69.1, m/e = 57.1, m/e = 41.1.

The Reaction of α,α'-Dichloro-α,α'-Dimethyl-p-xylene 11 (a mixture of diastereomers) with Zinc in Gas Phase

A quantity of 50 mg (0.286 mole) of compound 11 was reacted at an oven temperature of 240 °C~260 °C, a system pressure of 0.2-0.7 mmHg, a sample head temperature of 60 °C. The products were collected by 2~3 ml solvent (1:1 $CS_2/CDCl_3$), the ^1H NMR spectral data were recorded at room temperature (Appendix) the products were identified by ^1H NMR and GCMS. For compound 12: ^1H NMR (1:1 $CS_2/CDCl_3$) δ 7.49 (s, 4 H), 6.7 (d of d, J = 17 Hz, J = 10 Hz, 1 H), 5.75 (d, J = 17 Hz, J = 2, 1 H), 5.23 (d, J = 10 Hz, J = 2, 1 H). GCMS: m/e = 130.1, m/e = 115.0, m/e = 103.0, m/e = 77.0, m/e = 62.9, m/e = 50.8, m/e = 38.7. For compound 11: ^1H NMR (1:1 $CS_2/CDCl_3$) δ 7.495 (s, 4 H), 5.05 (q, J = 6.5, 1 H), 1.8 (d, J = 6.5, 6 H). GCMS: m/e = 202.0, m/e = 167.1, m/e = 131.1, m/e = 117.1, m/e = 105.0, m/e = 91, m/e = 77, m/e = 62.9, m/e = 50.8, m/e = 38.8. For compound 13: ^1H NMR δ 2.6 (q, J = 6.5, 1 H), 1.2 (t, J = 6.5, 3 H). GCMS: m/e = 132.1, m/e = 117.1, m/e = 91, m/e = 77, m/e = 64.9, m/e = 50.8, m/e = 38.7. For compound 14: ^1H NMR overlapped with 12 and 11. GCMS: m/e = 166.0, m/e = 131.1, m/e = 115.0, m/e = 103.0, m/e = 91.0, m/e = 77.0, m/e = 62.9, m/e = 50.8, m/e = 38.7.

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APPENDIX

Figure 1. ^{1}H NMR (WM-300) spectrum of reaction products of α,α'-dichloro-p-xylene with zinc in the gas phase, recorded at -78 °C in 1:1 $CS_2/CDCl_3$

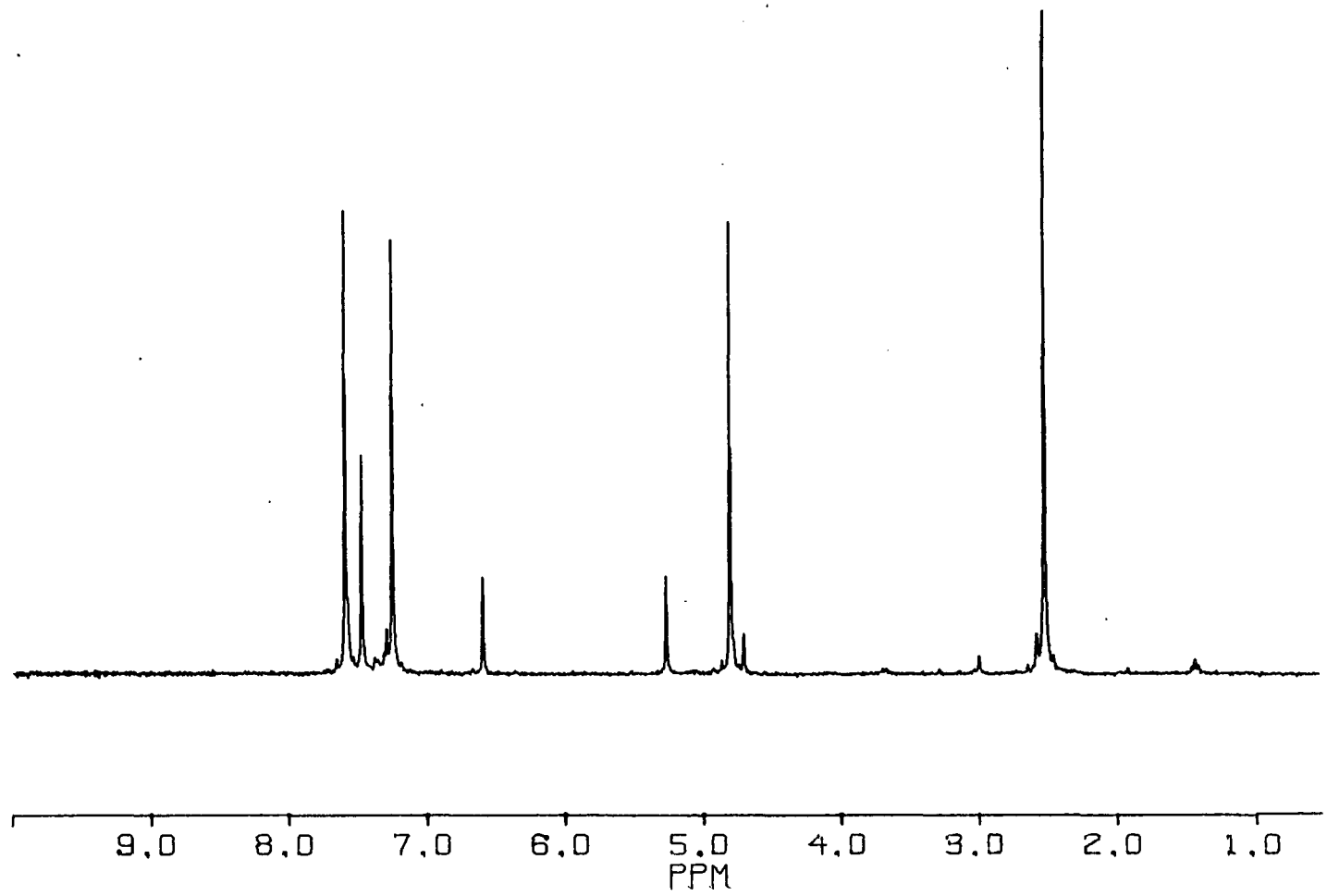

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
PPM

Figure 2. ^{1}H NMR (300 Hz) spectrum of reaction products of α,α'-dichloro-p-xylene with zinc in the gas phase, recorded at 25 °C in 1:1 $CS_2/CDCl_3$

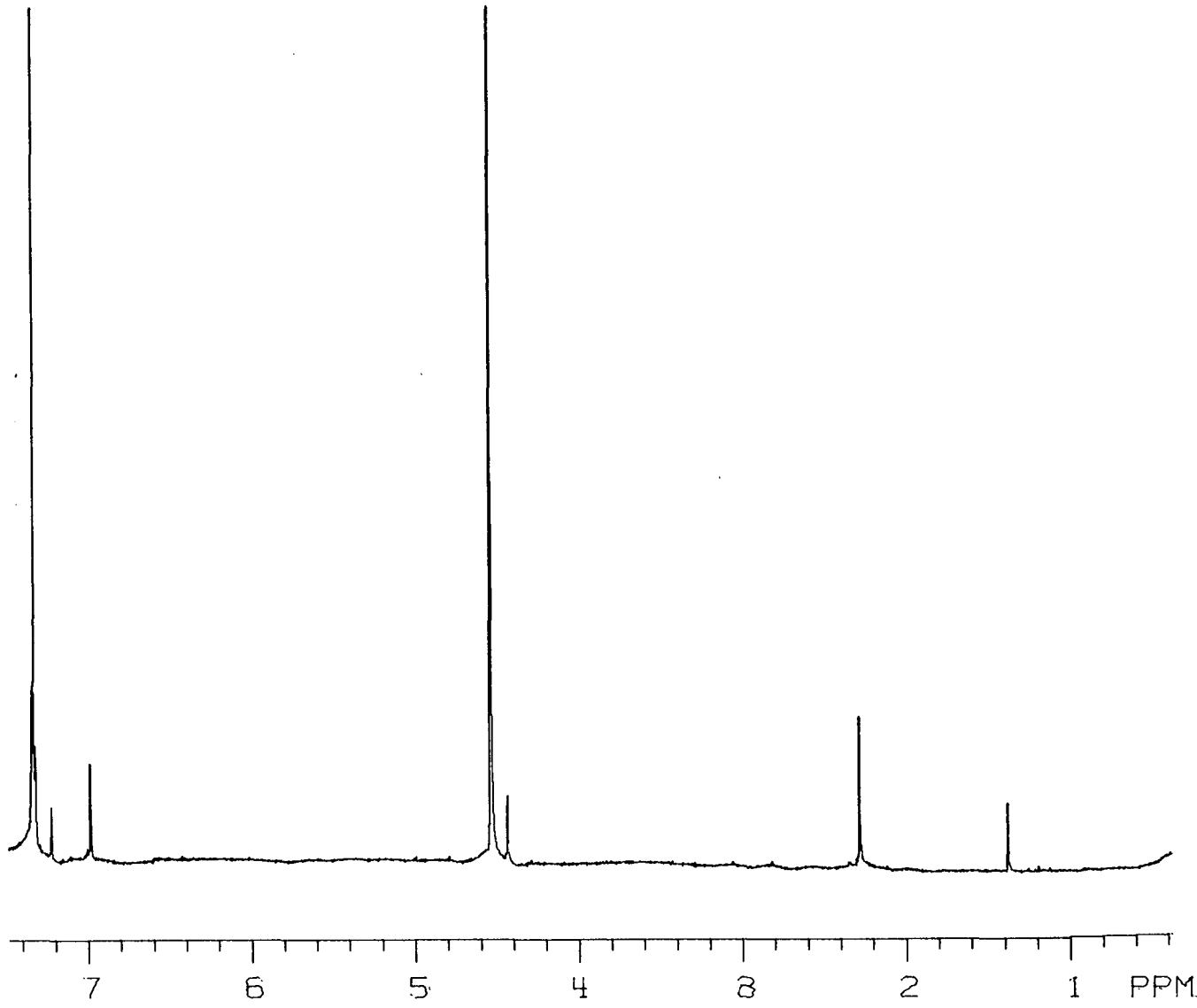

7
6
5
4
3
2
1
PPM.

Figure 3. ^{1}H NMR (WM-300 Hz) spectrum of reaction products of α,α-dichloro-p-xylene with zinc in the gas phase with a standard ($CHCl_2CHCl_2$), recorded at -78 °C in 1:1 $CS_2/CDCl_3$

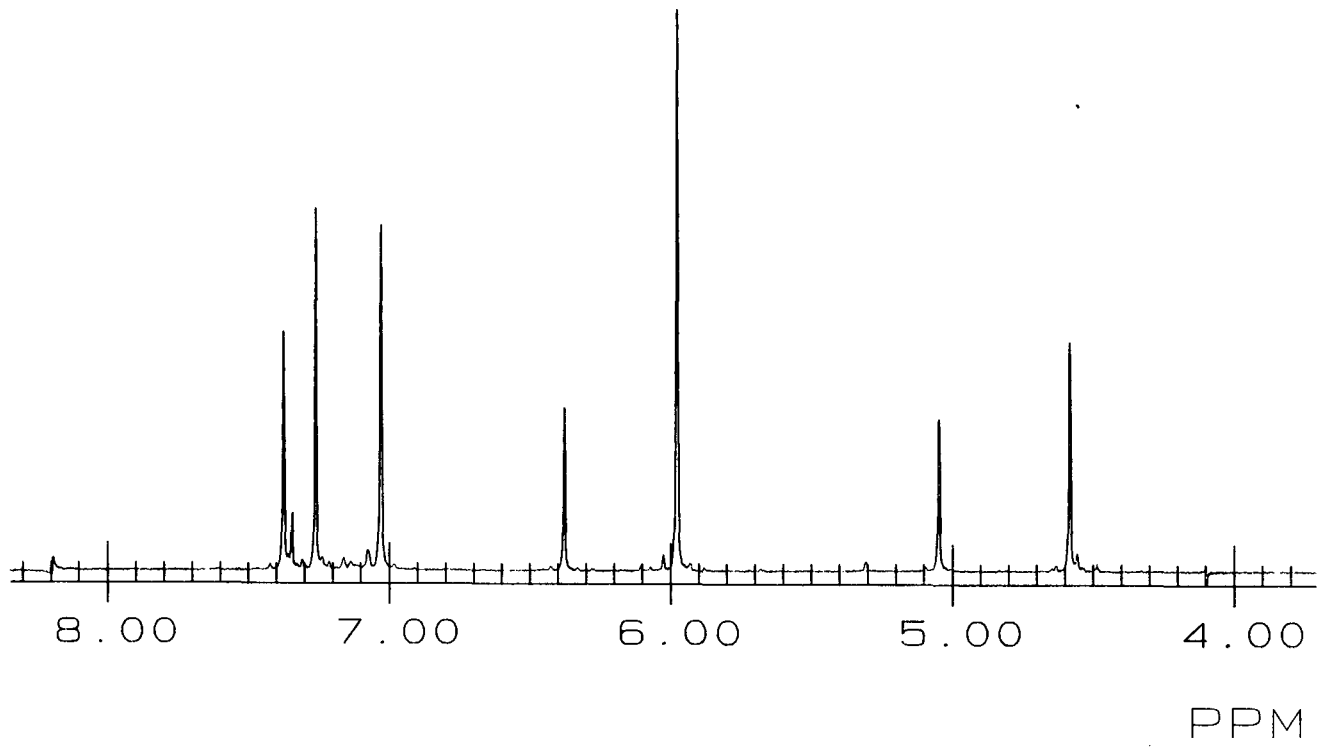

8.00
7.00
6.00
5.00
4.00
PPM

Figure 4. The schematic diagram of reaction apparatus

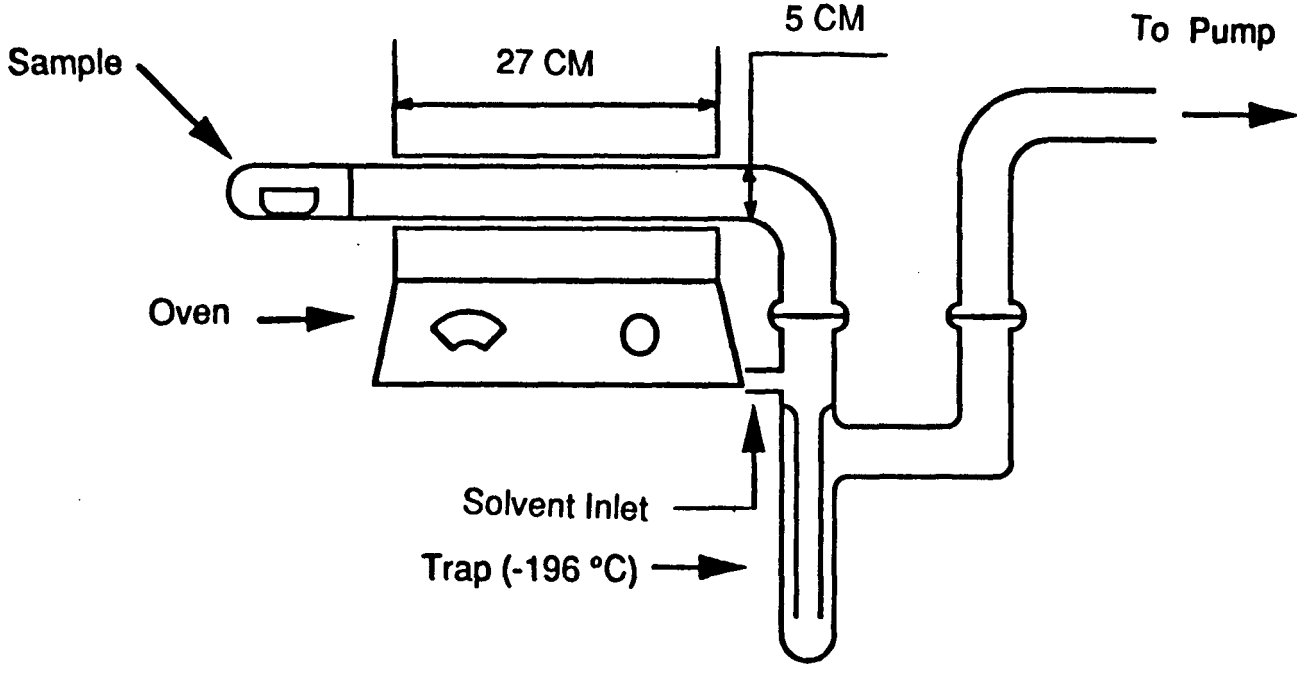

Sample
27 CM
5 CM
To Pump
Oven
Solvent Inlet
Trap (-196 °C)

Figure 5. ^{1}H NMR spectrum of the reaction products of α,α'-dichloro-α,α'-di-t-butyl-p-xylene (7) (a mixture of diastereomers) with zinc at 350 °C in gas phase, recorded at 25 °C in 1:1 $CS_2/CDCl_3$

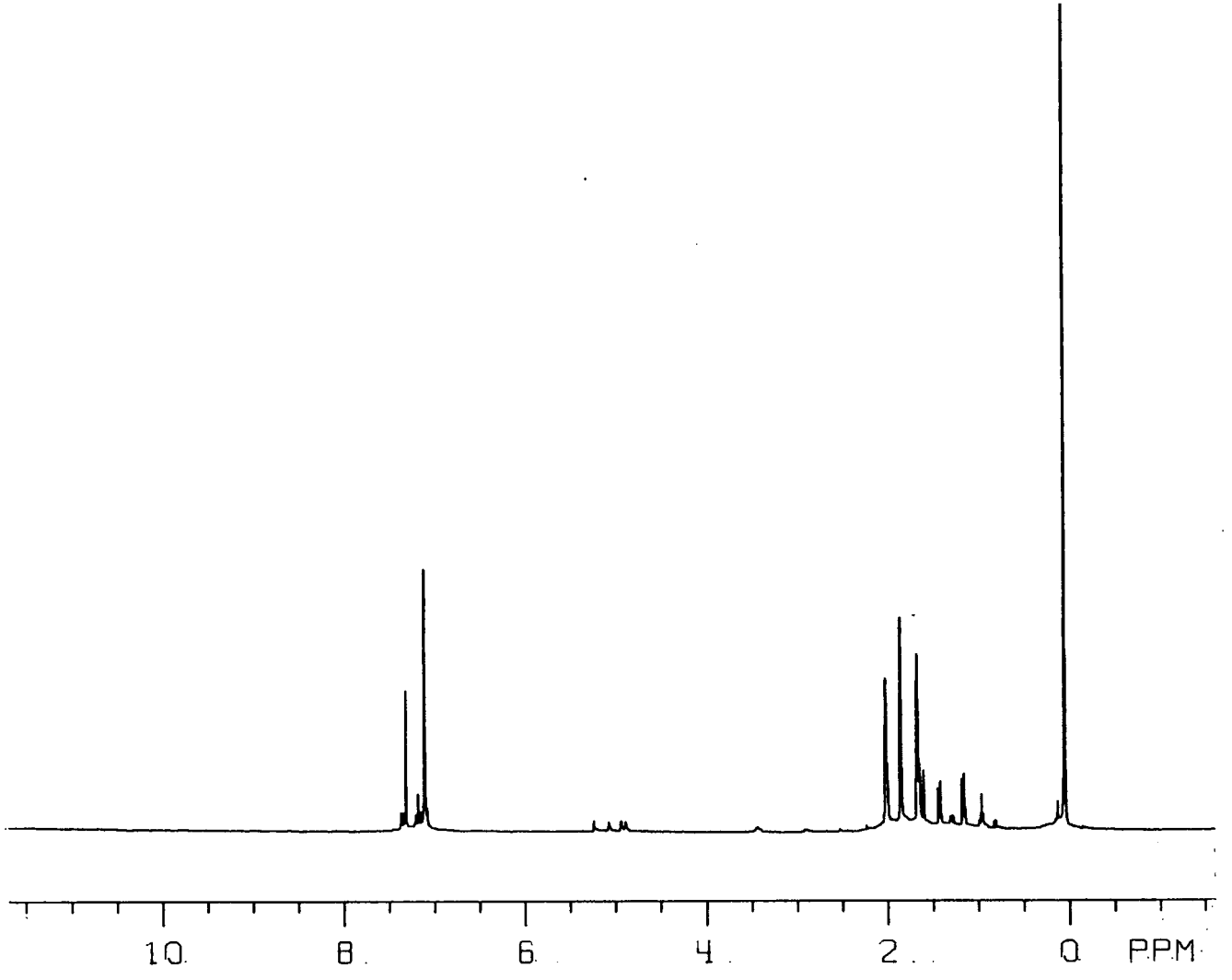

10
8
6
4
2
0
PPM

Figure 6. ^{1}H NMR (300 Hz) spectrum of the reaction products of α,α'-dichloro-α,α'-di-t-butyl-p-xylene (7) (a mixture of diastereomers) with zinc at 140 °C, recorded at 25 °C in 1:1 $CS_2/CDCl_3$

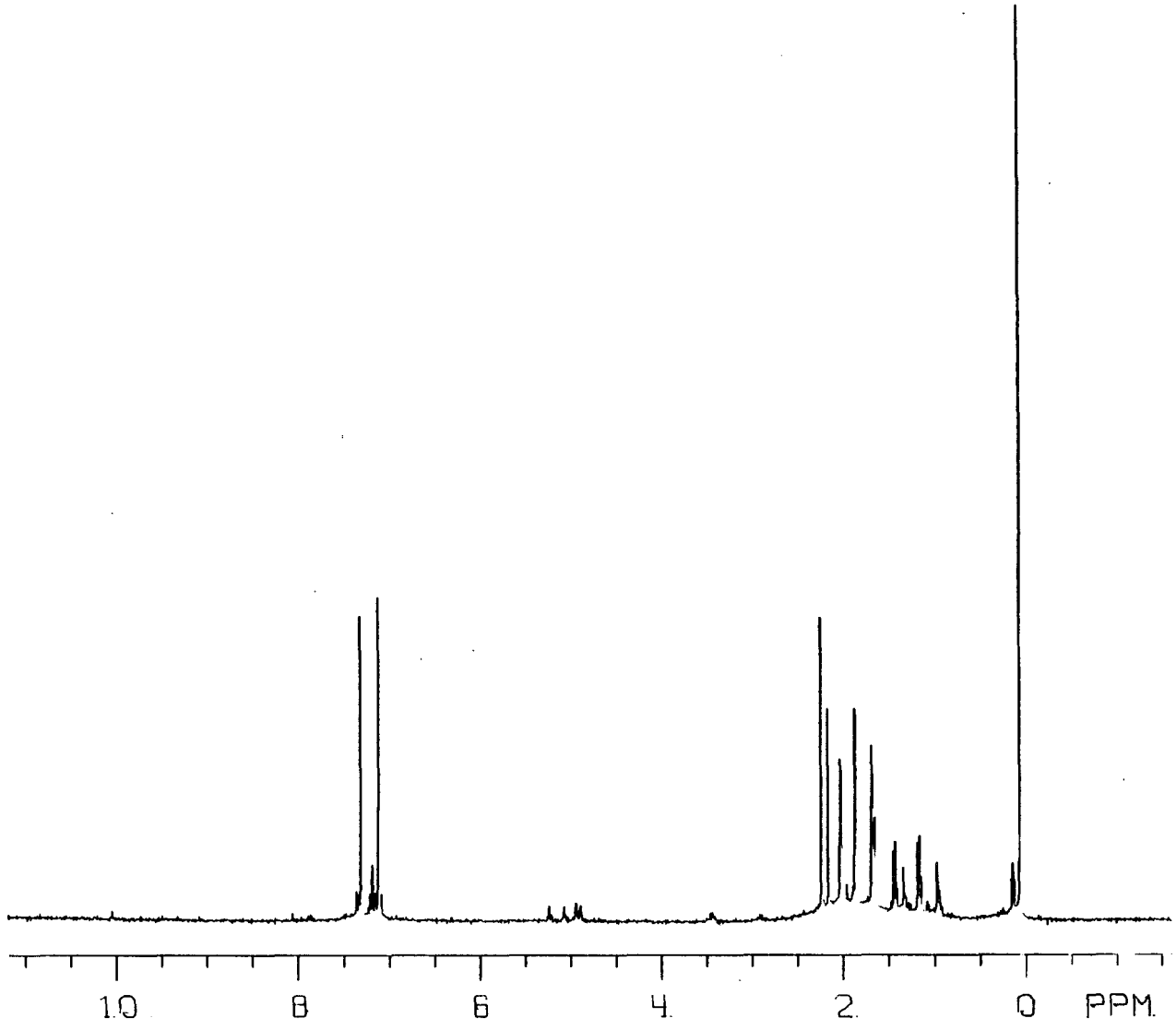
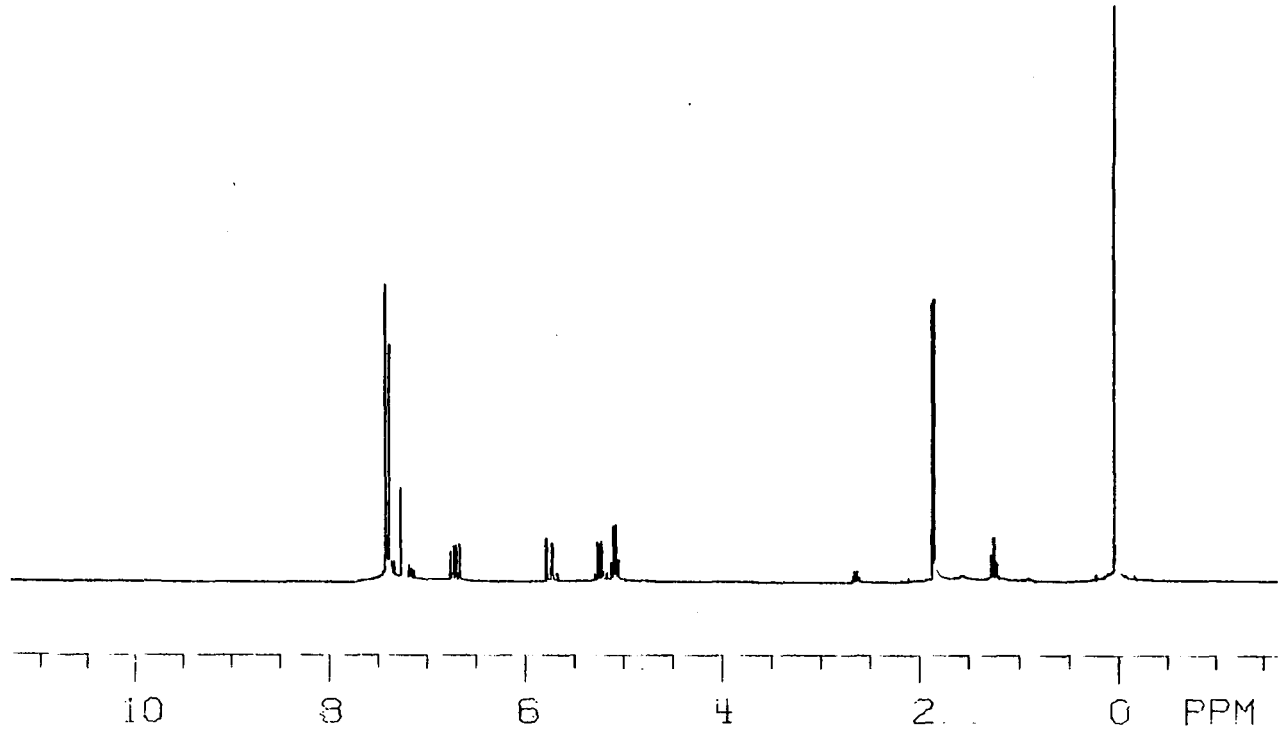

10
8
6
4
2
0
PPM.

Figure 7. ^{1}H NMR (300 Hz) spectrum of the reaction products of α,α'-dichloro-α,α'-dimethyl-p-xylene (11) (a mixture of diastereomers) with zinc at 240 °C, recorded at 25 °C in 1:1 $CS_2/CDCl_3$


10
8
6
4
2
0
PPM

GENERAL SUMMARY

The mechanism of the thermal decomposition of aromatic ethers is the subject of Part I. The results of product studies of the gas phase pyrolysis of phenetole, perdeutero-ethyl phenetole, phenyl benzyl ether, phenol, naphthyl ethyl ether and phenethyl naphthyl ether are presented. On the basis of these studies, it is concluded that the thermal decomposition of aromatic ethers proceeds primarily by a one-step concerted mechanism involving a six-membered ring transition state.

In Part II, a new methodology to synthesize p-xylylene is presented. The new methodology involves gas-phase zinc-induced dehalogenation. Results of studies of substituted systems are presented and these define some of the limitation of the new methodology.

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