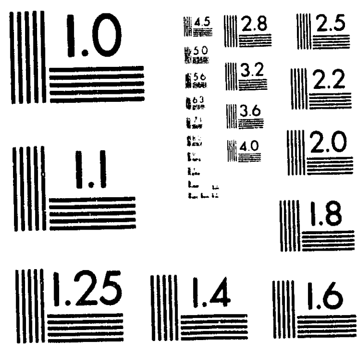
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IS-T 1602

Thermally-generated reactive intermediates: Trapping of the Parent Ferrocene-based o-quinodimethane and Reactions of Diradicals generated by Hydrogen-atom Transfers

by

Ferguson, J. M.

PHD Thesis submitted to Iowa State University

Ames Laboratory, U.S. DOE

Iowa State University

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Thermally-generated reactive intermediates: Trapping of the parent ferrocene-based *o*-quinodimethane and reactions of diradicals generated by hydrogen-atom transfers

John Michael Ferguson

Under the Supervision of Walter S. Trahanovsky
From the Department of Chemistry
Iowa State University

The first part of this dissertation addresses the thermal reactions of ferrocene-based reactive intermediates. Ferrocenocyclobutene is prepared by the flash vacuum pyrolysis (FVP) of the N-amino-2-phenylaziridine hydrazone of 2-methylferrocenealdehyde. We propose that FVP of the hydrazone gives 2-methylferrocenyl carbene which rearranges to ferrocenocyclobutene by C-H insertion. Heating ferrocenocyclobutene and N-phenylmaleimide (NPMI) in phenyl ether at 200 °C for 30 h gives two stereoisomeric 1 : 1 adducts of NPMI and the parent ferrocene-based *o*-quinodimethane, which is generated by ring opening of ferrocenocyclobutene.

In the second section of this dissertation, we have observed a series of novel hydrocarbon rearrangements. For example, the FVP of *o*-allyltoluene at 0.1 Torr (700-900 °C) gives 2-methylindan and indene as the major products, accompanied by *o*-propenyltoluene. We propose that these products are formed by intramolecular hydrogen-atom transfer occurs generating a diradical intermediate which undergoes coupling (2-methylindan) or intramolecular disproportionation (*o*-propenyltoluene). Indene is formed by secondary

pyrolysis of 2-methylindan. Similarly, FVP of *o*-methallyltoluene under similar conditions gives 2,2-dimethylindan as the primary product. $\Delta H^{\ddagger}$ values for formation of the diradical intermediates were estimated to be *ca.* 39-47 kcal mol^{-1}. Solution-phase thermolysis of *o*-methallyltoluene leads primarily to 1-(*o*-tolyl)-2-methylpropene, probably by a radical-chain mechanism.

FVP of 2-methyl-2'-vinylbiphenyl affords 9-methyl-9,10-dihydrophenanthrene, which fits our proposed mechanism. However, FVP of 2-(*o*-methylbenzyl)styrene gives mainly anthracene and 1-methylanthracene, possibly through an *o*-quinodimethane intermediate. Extension of this cyclization reaction to phenol derivatives is successful with *o*-allylphenol and *o*-(2-methylallyl)phenol, which afford dihydrobenzofuran derivatives, presumably by the hydrogen transfer/diradical coupling mechanism we have proposed.

Thermally-generated reactive intermediates: Trapping of the parent ferrocene-based *o*-quinodimethane and reactions of diradicals generated by hydrogen-atom transfers

by

John Michael Ferguson

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For the Graduate College

Iowa State University
Ames, Iowa

1993

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GENERAL INTRODUCTION

For several years, workers in the Trahanovsky research group have been studying various reactive molecules such as carbenes and *o*-quinodimethanes (*o*-QDM's) derived from benzene, furan, and thiophene. *o*-QDM's have been shown to be reactive intermediates in a number of reactions, and have been used in organic synthesis. We desired to attempt generation of a reactive organometallic *o*-QDM based on ferrocene, a well-known aromatic organometallic system.

In addition, studies have been directed toward the understanding of the gas-phase thermal reactions of simple organic molecules such as tetralin and benzocyclobutene. During FVP of *o*-allyltoluene, we observed a rearrangement that appears to involve intramolecular hydrogen-atom transfer, followed by intramolecular coupling or disproportionation of the resulting diradical intermediates. Papers 2 through 4 describe our studies concerning the pyrolytic rearrangements of a number of alkylaryl olefins and allylphenols.

The first section of this dissertation (Paper 1) concerns the preparation of ferrocenocyclobutene as well as the generation and trapping of the parent ferrocene-based *o*-quinodimethane.

The second section of this dissertation consists of three separate papers, each addressing a different aspect of research concerning the hydrogen-atom transfer/diradical coupling reactions and rearrangements of aryl olefins under FVP conditions. In paper 2, the FVP reactions of *o*-allyltoluene and several derivatives are discussed. A mechanism consisting of intramolecular hydrogen-atom transfers to generate diradicals is proposed. Three of the seven systems studied in paper 2 are part of the Ph.D dissertation of James L. Malandra (Iowa State University, 1993). In paper 3, the FVP reactions of two aryl-substituted styrene deriviatives are examined in terms of the mechanism proposed in paper 2. Additional mechanisms for formation of the products observed are suggested. Paper 4 presents the extension of this mechanism to the rearrangement of *o*-allylphenols under FVP conditions.

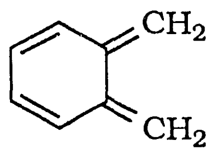
Explanation of Dissertation Format

This dissertation consists of four complete papers in the style suitable for publication in journals published by the American Chemical Society. As such, each section has its own numbering system and reference section following the text. The research described in the results and experimental sections was done by the author unless otherwise indicated. Detailed analytical data and/or spectra are contained in appendices following each section. Paper 1 has been previously published as a communication in *Organometallics* (Vol. 11, pp. 2006-7). Paper 2 is the result of a collaborative project as described above. The material in paper 2 that is part of the Ph.D. dissertation of James L. Malandra (Iowa State University, 1993) is indicated with a footnote. A general summary follows the final paper.

PAPER 1. GENERATION AND TRAPPING OF η^3-(4,5-DIMETHYLENECYCLOPENTENYL)-η^5-CYCLOPENTADIENYL-IRON, THE PARENT FERROCENE-BASED *o*-QUINODIMETHANE

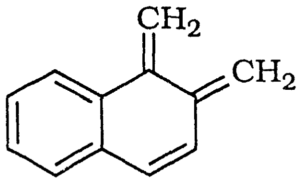
INTRODUCTION

The reactive molecule *o*-xylylene (**1**) is the parent benzene-based



1

member of the large and important class of reactive molecules called *o*-quinodimethanes (*o*-QDM's). *o*-QDM's have been shown to be transient intermediates in many reactions[1,2] and have been used extensively as dienes in several organic syntheses.[1k,m-o,s,t,v,x,z] Many *o*-QDM's based on aromatic systems other than benzene are known. Examples of these are the *o*-QDM's which are derivatives of naphthalene (**2**)[3] and furan (**3**).[2b,4] In general,*o*-QDM's readily undergo reac-



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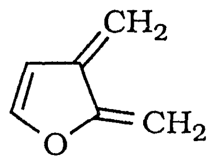
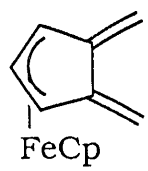


3

tions such as dimerizations and Diels-Alder reactions which generate the aromatic system on which they are based.[1-4]

Although many *o*-QDM's have been prepared and studied, only a few organometallic *o*-QDM's are known. A number of *o*-xylylene derivatives with a metal coordinated to the exocyclic diene moiety have been synthesized,[5] but these compounds lack the high reactivity characteristic of free *o*-xylylenes. Kündig[6] and Butenschön[7] have recently reported the syntheses of substituted tricarbonylchromium-benzocyclobutene complexes which, when heated in the presence of a dienophile, exhibited chemical behavior similar to that of the uncomplexed analogs. Apparently the chromium-complexed substituted benzocyclobutenes undergo ring opening to give the corresponding complexed substituted *o*-xylylenes which react with the dienophile at a slightly slower rate than the uncomplexed species.[6,7] Also, Butenschön has recently reported generation of a η^3-(4,5-dimethylenecyclopentenyl)cobalt complex that appears to exhibit *o*-QDM-like reactivity.[8] In this study, we present evidence for the generation and trapping of the parent ferrocene-based *o*-QDM (**4**) by the electrocyclic ring opening of ferrocenocyclobutene (**5**).



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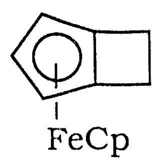
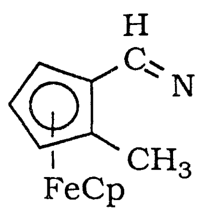


5

Cp = η^5- C_5H_5

RESULTS

FVP of 2-methylferrocenecarboxaldehyde N-amino-2-phenylaziridine hydrazone (**6**) at *ca.* 6 x 10^{-5} torr (380 °C) gave ferrocenocyclobutene (**5**) in 30-35% yield. Thermolysis of **5** in phenyl ether in the presence of N-phenyl maleimide (**7**) gave a pair of 1 : 1 adducts in a 11 : 1 ratio. The major product was purified by recrystallization and identified as adduct **8**, which was obtained in 13% isolated yield. The minor product was not isolated, but analysis of ^{1}H NMR provided substantial evidence that the minor component was compound **9**, a stereoisomer of **8**.



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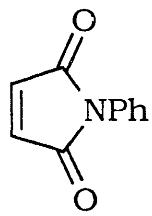

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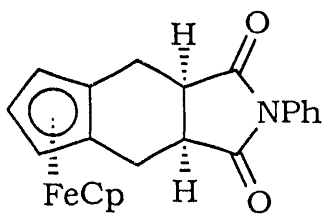

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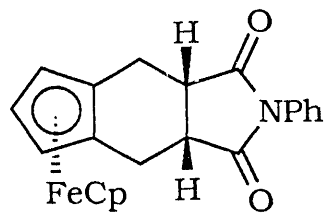
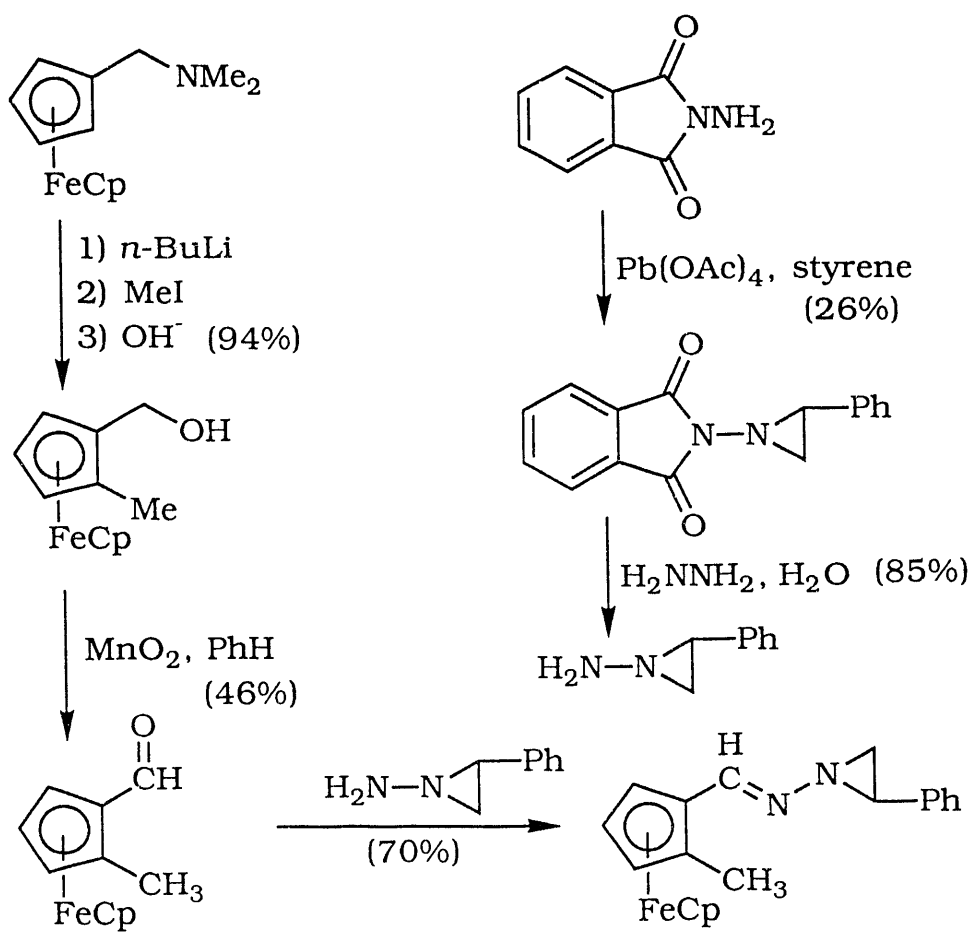


9

DISCUSSION

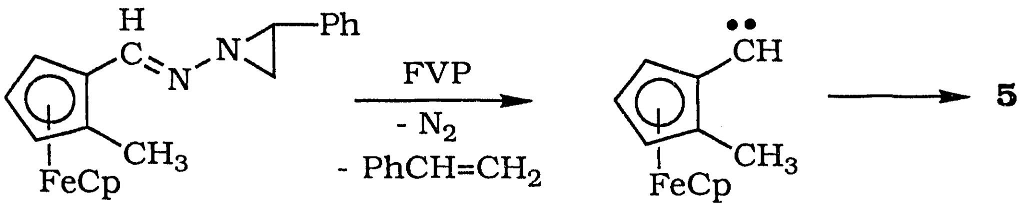
It has been shown that carbenes can be conveniently and efficiently generated by the decomposition of N-amino-2-phenylaziridine hydrazones.[9] We predicted that 2-methylferrocenylcarbene (**10**), if it could be generated, would likely undergo C-H insertion to give **5**. Hydrazone **6** was judged to be a suitable precursor to **5**. Compound **6** was prepared as shown in Scheme I.

Scheme I



6

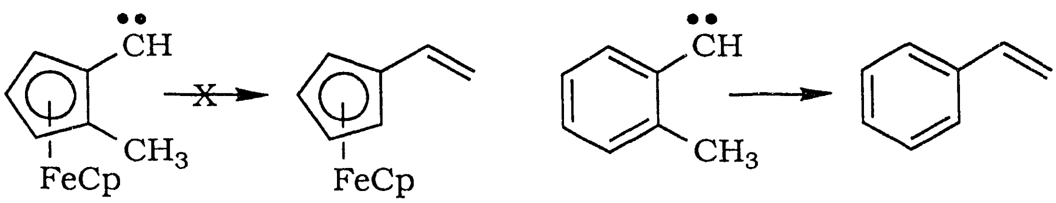
FVP of **6** presumably gives molecular nitrogen, styrene, and 2-methylferrocenyl carbene (**10**) which rearranges to **5** by C-H insertion.



6 **10**

Compound **5** was obtained in relatively high purity (>95%; the rest of the material was ferrocene, methylferrocene, 1,2-dimethylferrocene, and an unidentified ferrocene derivative, probably 2-methylferrocenylcarbonitrile) but in only fair yields (30-35%).

We had speculated that **10** could undergo rearrangement to give vinylferrocene (**11**) in analogous fashion to that of *o*-tolylcarbene (**12**) to give styrene (**13**).[10] No vinylferrocene was detected, which indicates that carbene **10** does not readily undergo a rearrangement analogous to that of **12**.



10 **11** **12** **13**

Evidence for ring opening of **5** to *o*-QDM **4** was obtained from a trapping experiment analogous to the one used to provide evidence for the production of *o*-xylylene by the ring opening of benzocyclobutene.[1c,11] Compound **5** was heated in the presence of N-phenylmaleimide (NPMI) in phenyl ether at 200 °C for 30 h. Compounds **8** and **9**, the Diels-Alder adducts of **4** and NPMI, were formed in an 11:1 ratio as determined by ^{1}H NMR. Compound **8** was separated from this mixture in pure form in 13% yield; **9** was not isolated in pure form. The stereochemistry of **8** was established based on work by Bitterwolf, which has shown that the chemical shifts of hydrogens *syn* to the iron atom are deshielded relative to the *anti* hydrogens.[12] The tertiary hydrogens in the major isomer were 0.32 ppm downfield relative to the analogous hydrogens in the minor isomer. Based on this chemical shift difference the major isomer was assigned as shown **8** and the minor isomer was assigned structure **9**. The stereochemistry of **8** is consistent with *endo* addition of **7** to *o*-QDM **4**. Production of these adducts provides strong evidence for the conversion of **5** to **4** under these conditions. The conversion of **5** to **4** is an example of a ring-slippage reaction[13] with the hapticity of the reacting ligand changing from η^5 to η^3. It is uncertain whether a molecule of solvent coordinates with the iron atom of intermediate **4** to retain the inert gas electronic configuration or whether **4**, which is coordinately unsaturated, remains intact long enough to react with NPMI. Reaction of **4** with NPMI to produce **8** and **9** involves changing the hapticity of the reacting ligand from η^3 to η^5, which also regenerates the aromatic ferrocene system.

CONCLUSION

FVP of 2-methylferrocenecarboxaldehyde N-amino-2-phenylaziridine hydrazone (**6**) affords ferrocenocyclobutene (**5**) in moderate yield. Thermolysis of **5** at 250 °C is believed to generate the parent ferrocene-based *o*-QDM (**4**), which is trapped NPMI to give a pair of 1 : 1 adducts in a 11 : 1 ratio. The major product was isolated in 13% yield and identified as compound **8**, whose structure was consistent with *endo*-addition of NPMI to the parent ferrocene-based *o*-QDM (**5**).

EXPERIMENTAL

Methods and materials

The pyrolysis apparatus has been previously described.[14] Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. ^1H NMR spectra were obtained on Nicolet NT-300 and Varian VXR-300 instruments. ^{13}C NMR spectra were obtained on a Varian VXR-300 instrument. Chemical shifts are relative to the accepted chemical shift of the solvent peak unless otherwise noted. GCMS was performed on a Finnegan 4500 spectrophotometer with 70-eV EI after separation on a DB-1 capillary column. Exact mass determinations were performed on a Kratos 50 spectrophotometer. Capillary GC was performed on a Hewlett-Packard 5840A instrument using a DB-1 capillary column. All reactions were carried out under an argon atomsphere unless stated otherwise. Diethyl ether was distilled from Na/benzophenone ketyl. Methylene chloride was distilled from P_2O_5. Other reagents were purchased as reagent grade and used as received.

2-Methylferrocenylmethanol. *n*-Butyllithium in hexanes (2.3 M, 14 mL, 0.0320 mol) was added to a stirred solution of (dimethylamino)methylferrocene (4.0 mL, 4.86 g, 0.020 mol) in ether (12 mL) at 28 °C over 15 min. The red color of the solution deepened somewhat during lithiation. After 4 h, methyl iodide (10 ml, 0.160 mol) was added slowly and the mixture was stirred for at 16 h. The ether, hexanes, and excess methyl iodide were evaporated by warming of the flask to *ca.* 40 °C, coupled with blowing argon through the flask. The remaining orange paste of 2-methyl(dimethylamino)methylferrocene methiodide was added to aqueous NaOH (1.0 M, 150 mL), and the mixture was refluxed for 3 h under argon. After cooling, the mixture was extracted with ether (3 x 30 mL). The combined ether portions were washed with water (20 mL portions) until the aqueous layer was neutral to litmus. The ether solution was then washed with brine (3 x 30 mL), then dried (Na_2SO_4). Filtration, followed by removal of the solvent under reduced pressure gave (2-methylferrocenyl)methanol (2.1690 g, 94%). ^{1}H NMR (300 MHz, C_6D_6) δ 4.26 (dd, J_d = 23.2, J_d = 12.0 Hz, 2 H), 4.07-4.03 (m, 1 H), 3.93-3.90 (m, 1 H) 3.88 (s, 5 H), 3.85 (t, J = 2.1 Hz, 1 H), 2.36 (br. s, 1 H), 1.86 (s, 3 H).

2-Methylferrocenecarboxaldehyde. Preparation was based on the method of Sokolov.[15] (2-Methylferrocenyl)methanol (1.91 g, 0.0082 mol) was dissolved in chloroform (80 mL) and then MnO_2 (5.31 g, 0.061 mol) was added. The mixture was stirred for 3 d and then filtered through a medium frit. The filtrate was concentrated under reduced pressure and then chromatographed on neutral alumina with 10% EtOAc in hexanes. The first major product fraction was collected and the solvent was removed under reduced pressure to give a dark red oil. GC and ^{1}H NMR revealed a small amount of ferrocenecarboxaldehyde was present, but this was removed by a second chromatography column. After removal of solvent under reduced pressure, 2-methylferrocenecarboxaldehyde was obtained as a dark red oil (0.86 g, 0.0038 mol, 46%). The ^{1}H NMR spectrum was in excellent agreement with the one reported by Sololov: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.10 (s, 1 H), 4.71-4.68 (m, 1 H), 4.51-4.49 (m, 1 H), 4.47 (t, J = 2.5 Hz, 1 H), 4.20 (s, 5 H), 2.25 (s. 3 H).

N-Phthalimidyl-2-phenylaziridine. Eschenmoser's method of preparation was used.[16] N-Aminophthalimide (8.10 g, 50 mmol) was added to a solution of styrene (67 mL, 0.580 mol) in CH_2Cl_2 (300 mL). This mixture was stirred vigorously and lead tetraacetate (26.06 g, 0.059 mol) was added gradually by powder addition funnel over 1 h. After the addition was complete, the mixture was stirred for 2 h, and then basic alumina (100 g) was added. The suspension was swirled and filtered through a pad of Celite. The solvent was removed and then ether (500 mL) was added. The salts were removed by extraction with water (3 x 50 mL), and then the organic layer was concentrated under reduced pressure. The product was chromatographed on silica gel (200 g) with CH_2Cl_2. Removal of the solvent followed by two recrystallizations from $CHCl_3$/pentane gave pale yellow needles of N-phthalimidyl-2-phenylaziridine (3.42 g, 0.013 mol, 26%): mp 147.9-149.8° C (lit.[23] mp 152° C). The ^{1}H NMR spectrum agreed well with that reported by Eschenmoser, although he used $CDCl_3$ as solvent: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.80-7.70 (m, 4 H), 7.46-7.34 (m, 5 H), 3.56 (dd, J_d = 8.0, J_d = 5.9 Hz, 1 H), 2.90 (dd, J_d = 8.0, J_d = 2.5 Hz, 1 H), 2.75 (dd, J_d = 5.9, J_d = 2.5 Hz, 1 H).

N-Amino-2-phenylaziridine. This was prepared as described by Eschenmoser.[16] To a mixture of pentane (67 mL), hydrazine hydrate (16.7 mL), and water (1.7 mL), N-phthalimidyl-2-phenylaziridine

(1.7710 g, 0.00670 mol) was added. The suspension was stirred for 3 h. Care was taken during stirring to avoid formation of an emulsion. The pentane layer was removed by pipet and saved. The aqueous layer was extracted with pentane (3 x 15 mL). The pentane portions were combined, dried (K_2CO_3), filtered and concentrated under reduced pressure to give N-Amino-2-phenylaziridine (0.7672 g 0.00572 mol, 85%) as a colorless oil. The ^1H NMR spectrum agreed well with that reported by Eschenmoser, although he used $CDCl_3$ as solvent: ^1H NMR (300 MHz, CD_2Cl_2) δ 7.34-7.18 (m, 5 H), 3.70 (br. s, 2 H), 2.58 (dd, J = 7.8, 4.6 Hz, 1 H), 1.99 (d, J = 4.6 Hz, 1 H), 1.97 (d, J = 7.8 Hz, 1 H).

2-Methylferrocenecarboxaldehyde N-(2-Phenylaziridine) Hydrazone (6). A modification of Eschenmoser's procedure was used.[16] N-amino-2-phenylaziridine (0.1921 g, 0.00143 mol) was added to a solution of 2-methylferrocenecarboxaldehyde (0.150 g, 0.00066 mol) in benzene (15 mL). The mixture was stirred for 30 h. The solvent was removed and the resulting dark red oil was chromatographed on neutral alumina with 8% EtOAc in hexanes. The first major fraction was saved and the solvent was removed to give the hydrazone (0.1569 g, 0.00046 mol, 70%) as a dark red oil. The product was isolated as a pair of diastereomers with very similar NMR chemical shifts. While some of the chemical shifts of these diastereomers coincided, others differed slightly. ^1H NMR (300 MHz CD_2Cl_2) δ 8.55, 8.54 (two s, 1 H), 7.51-7.31 (m, 5 H), 4.57-4.55 (m, 1 H), 4.32-4.30 (m, 1 H), 4.26 (t, J = 2.4

Hz, 1 H), 4.14, 4.13 (two s, 5 H), 3.07-3.01 (two dd, 1 H), 2.51-2.47 (two dd, 1 H), 2.40-2.37 (two dd, 1 H), 2.15, 2.14 (two s, 3 H).

Ferrocenocyclobutene (5). A typical procedure for the pyrolysis of **6** is as follows: A sample of **6** (*ca.* 75 mg, 0.00022 mol) was placed in a Pyrex sample boat and the boat was placed in the sample head. The sample head joint was greased and then attached to the pyrolysis tube which was preheated to 380° C. After evacuation of the apparatus to *ca.* 6 x 10^{-5} torr, the sample head was heated to 65° C and then gradually increased to 95° C over 4-6 hours. After the pyrolysis was completed, the system was restored to atmospheric pressure with nitrogen, and the cold trap was removed. The lower white band (styrene) was dissolved in CS_2 and the solution was removed from the trap by pipet and discarded. The yellow-orange upper band containing crude product was then removed in a similar manner, concentrated under reduced pressure, and chromatographed on neutral alumina with hexanes. The first major fraction was collected, and the solvent was removed under reduced pressure giving ferrocenocyclobutene (**5**) in 30-35% yield. Analysis by GC, GC/MS, and NMR confirmed the presence of small amounts of ferrocene (*ca.* 1.5%), methylferrocene (*ca.* 0.5%), 1,2-dimethylferrocene (*ca.* 0.9%), and an unidentified ferrocene derivative with a molecular weight of 225 which is probably 1-cyano-2-methylferrocene (*ca.* 2%), but as these impurities were judged to be unreactive under thermolysis conditions, the product mixture was used for trapping experiments without additional purification: m.p. 51.1-59.7° C.: m.p. 51.1-59.7 °C; ^{1}H NMR (300 MHz,

C_6D_6) δ 3.99 (d, J = 2.1 Hz, 2 H), 3.94 (s, 5 H), 3.70 (t, J = 2.1 Hz, 1 H), 2.93-2.83 (AA'BB' m, 2 H), 2.71-2.61 (AA'BB' m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 92.381, 70.114, 65.688, 61.976, 29.207; MS m/z (relative intensity), 212 (M^+, 100), 184 (6.1), 134 (37), 121 (72), 91 (14), 56 (53); HRMS m/z for $C_{12}H_{12}Fe(M^+)$ calcd. 212.02884, found 212.02934.

Ferrocenocyclobutene–N-phenylmaleimide Adducts (8, 9). Ferrocenocyclobutene (8.9 mg, 0.000042 mol), N-phenylmaleimide (15.1 g, 0.0000872 mol), and 0.5 mL of phenyl ether were mixed in a thick-walled tube. The contents were subjected to four freeze-thaw cycles (-78° C to 30° C) under vacuum. The tube was sealed, immersed in a heating bath at 200° C for 30 hours, and then allowed to cool. A thin brown band, possibly due to decomposition products, and a small amount of orange precipitate were visible in the orange solution. The tube was opened and the orange solution was removed and saved. The orange precipitate from the tube was dissolved in methylene chloride and removed. The ^1H NMR spectrum indicated that the precipitate contained two products in a 11:1 ratio. The solution from the tube was chromatographed on neutral alumina with hexanes in order to remove the phenyl ether. Acetone was used to elute the ferrocene products. Upon removal of solvent an orange powder was obtained. This orange powder was combined with the precipate product mixture and the combined mixture was recrystallized from toluene/hexane to give 2.1 mg (0.0000055 mol, 13%) of orange needles which darkened at 185° C. The ^1H NMR spectrum of the recrystallized product showed it to be the major component of the 11:1 mixture. Comparison of the ^1H NMR spectrum of the recrystallized product with that of the crude mixture made it possible to assign the stereochemistry of the cycloaddition. The minor (exo) product was not isolated. The only detectable differences in the ^1H NMR spectrum were in the alkyl region. Integration shows the multiplets from the alkyl protons to be in a 1:1:1 ratio: **8**: ^1H NMR (300 MHz, CD_2Cl_2) δ 7.53-7.43 (m, 2 H), 7.43-7.37 (m, 1 H), 7.21-7.17 (m, 2 H) 4.15 (d, J = 2.4 Hz, 2 H), 4.14 (s, 5 H), 4.03 (t, J = 2.4 Hz, 1 H), 3.59-3.49 (ABC m, 2 H), 3.03-2.95 (ABC m, 2 H), 2.57-2.49 (ABC m, 2 H); ^{13}C NMR (75 MHz, C_6H_6) δ 178.912, 132.556, 129.358, 128.864, 127.008, 83.183, 69.263, 66.545, 65.464, 41.028, 24.170; MS m/z (relative intensity), 385 (M^+, 100), 172 (15), 121 (6.9), 121 (6.1), 113 (37), 103 (3.7), 101 (5.6), 56 (5.6); HRMS m/z for $C_{22}H_{19}FeNO_2$ (M^+) calcd. 385.07648, found 385.07654. **9**: ^1H NMR (300 MHz, CD_2Cl_2) δ (phenyl and ferrocenyl proton signals are obscured by the absorptions of **8**) 3.34-3.28 (m), 3.30-2.95 (m), 2.57-2.49 (m).

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APPENDIX

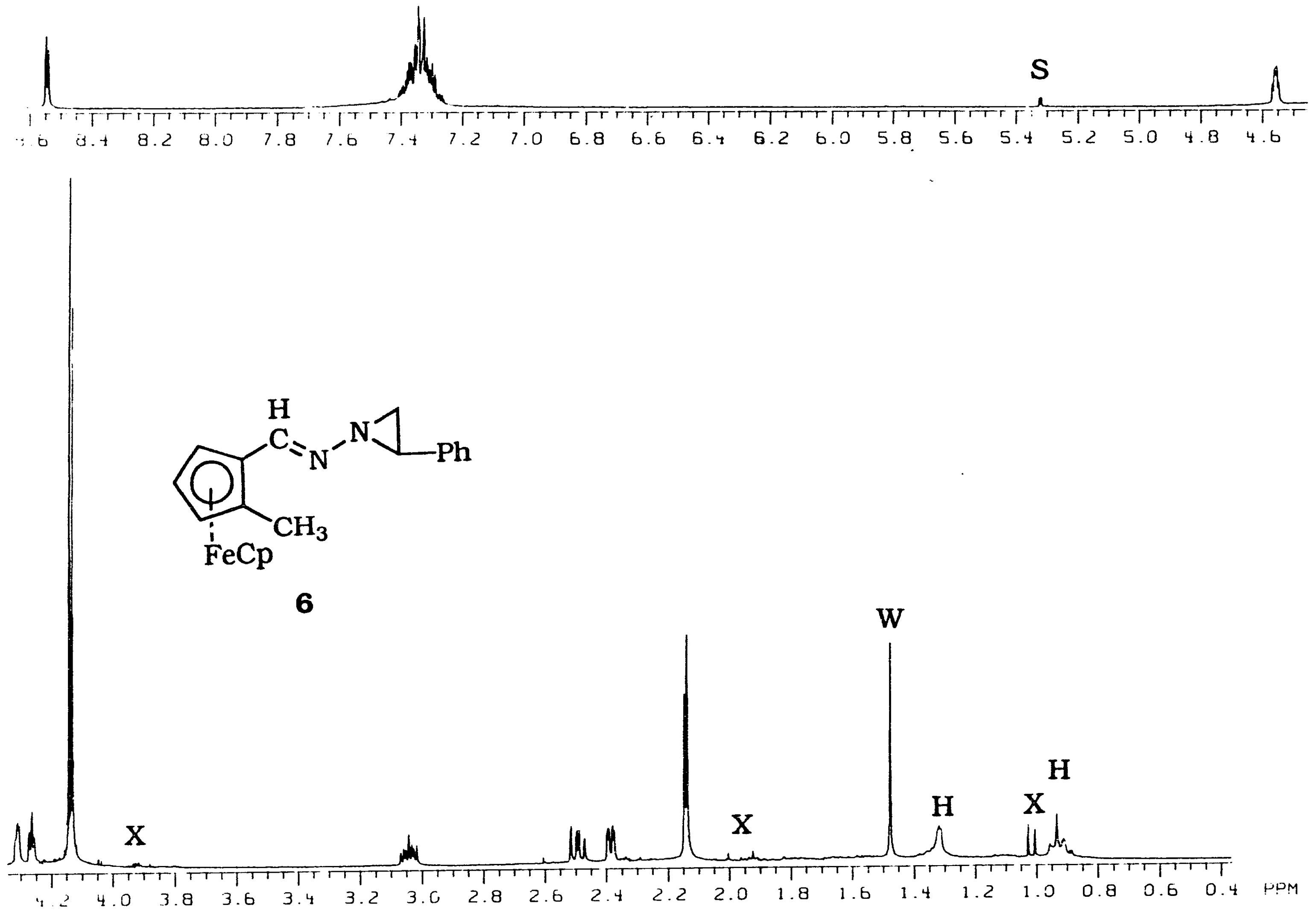

Figure A-1. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of N-amino-2-phenylaziridine hydrazone (**6**) (S: $CHDCl_2$, W: H_2O, H: high-boiling residue from hexanes, X: unidentified impurity).

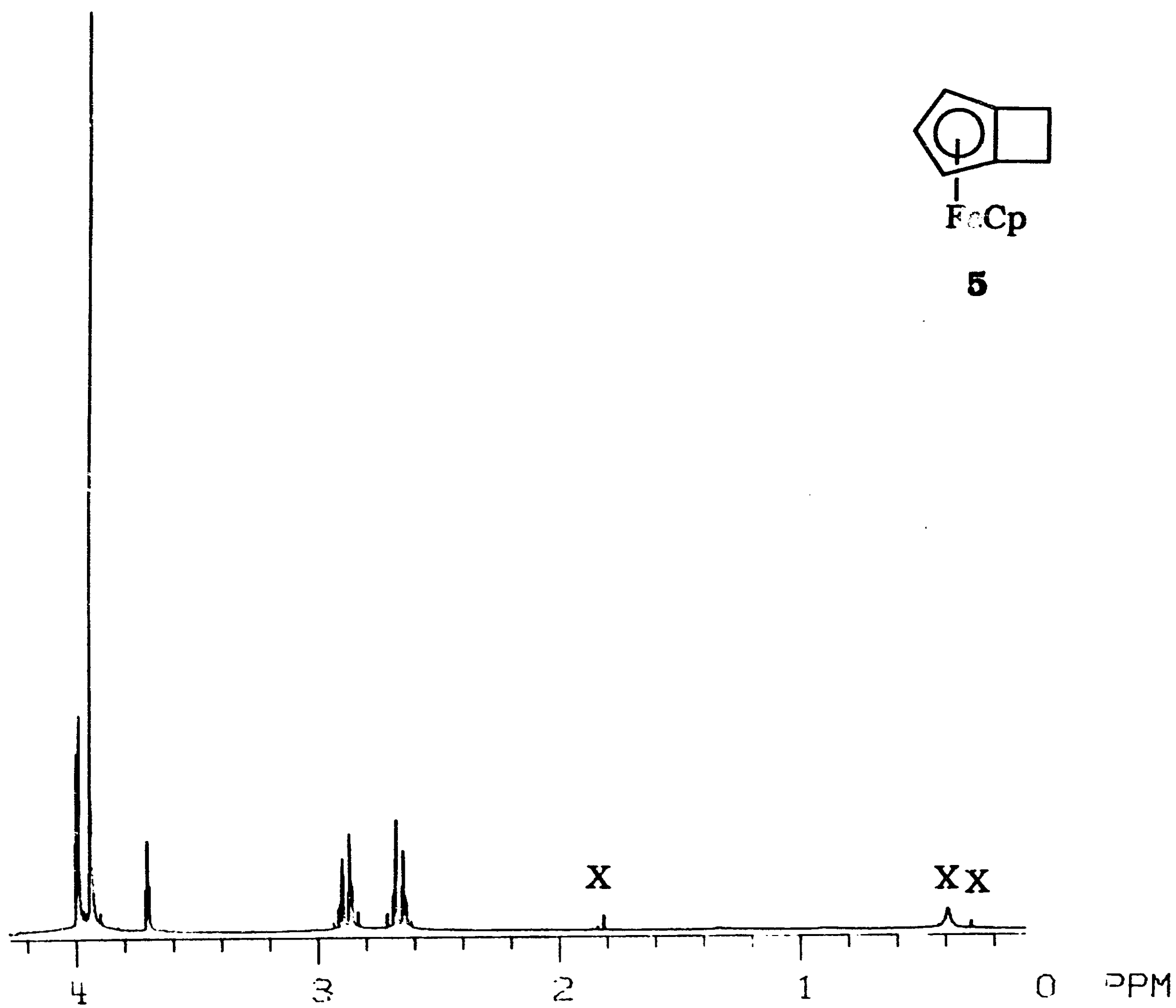

Figure A-2. ^{1}H NMR spectrum (300 MHz, C_6D_6) of ferrocenocyclobutene (**5**) (X: unidentified impurity).

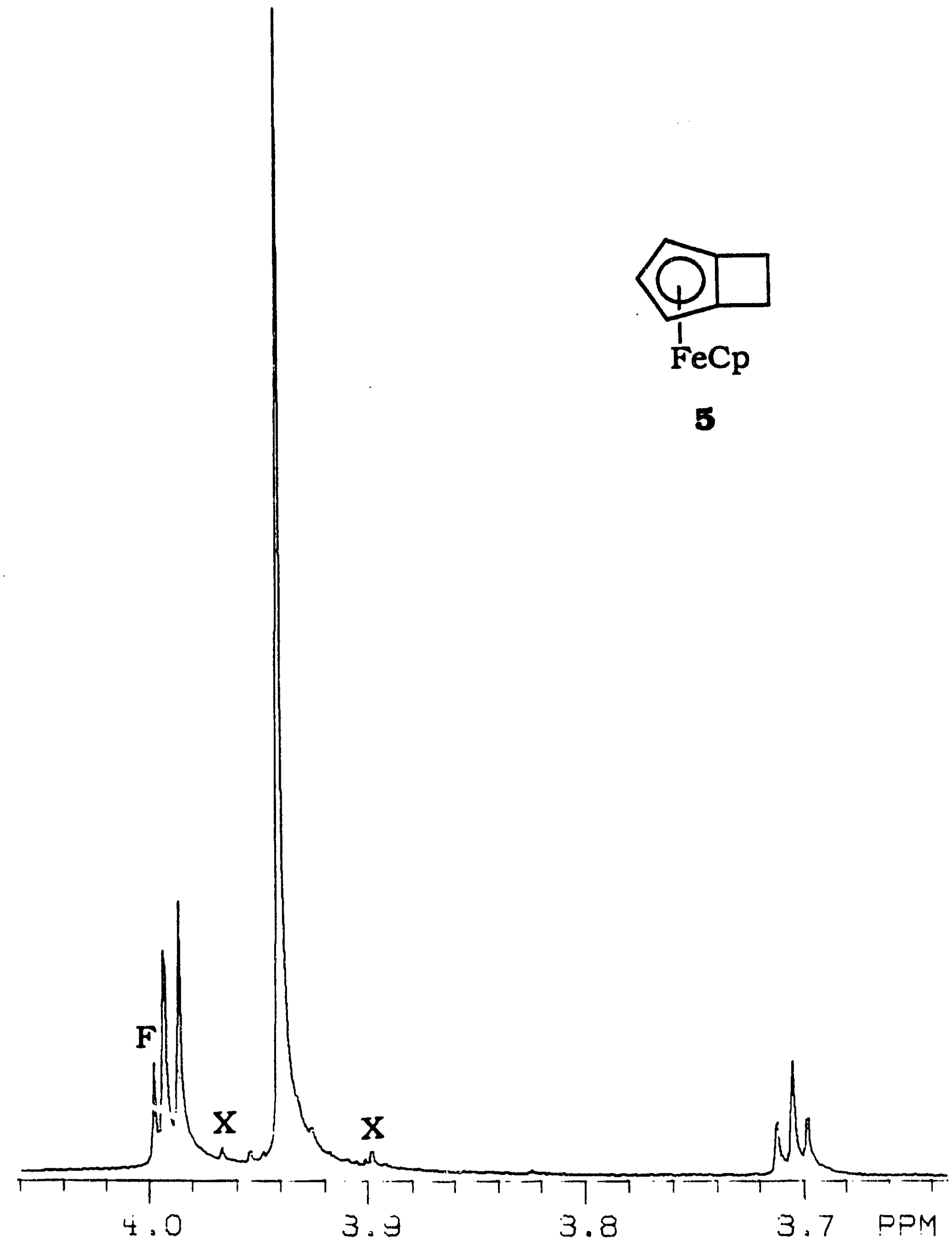

Figure A-3. ^1H NMR spectrum (300 MHz, C_6D_6) of the ferrocenyl protons of ferrocenocyclobutene (**5**) (F: ferrocene, X: unidentified impurity).

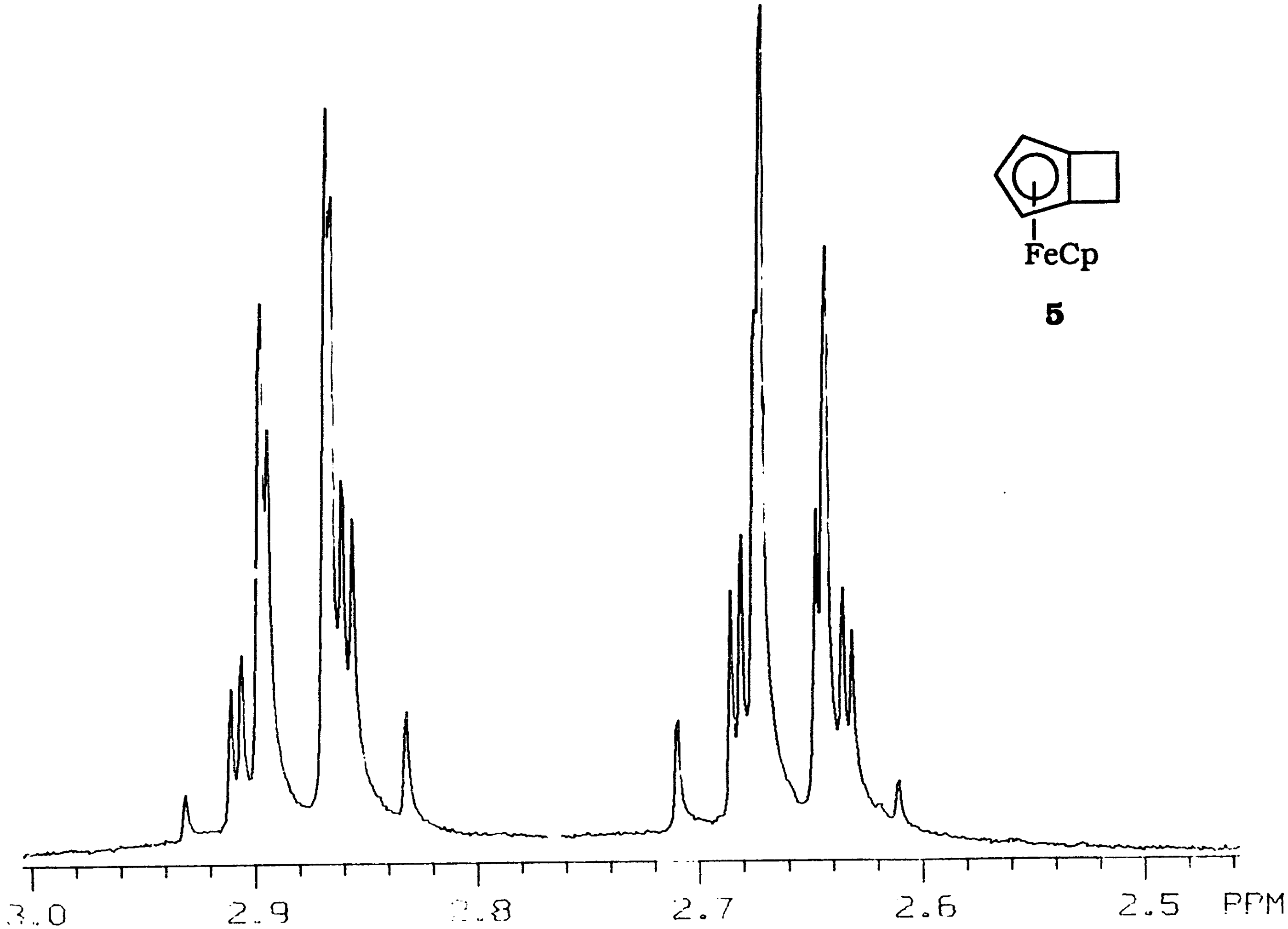

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Figure A-4. ^1H NMR spectrum (300 MHz, C_6D_6) of the AA'BB' quartet caused by the methylene protons of ferrocenocyclobutene (**5**).

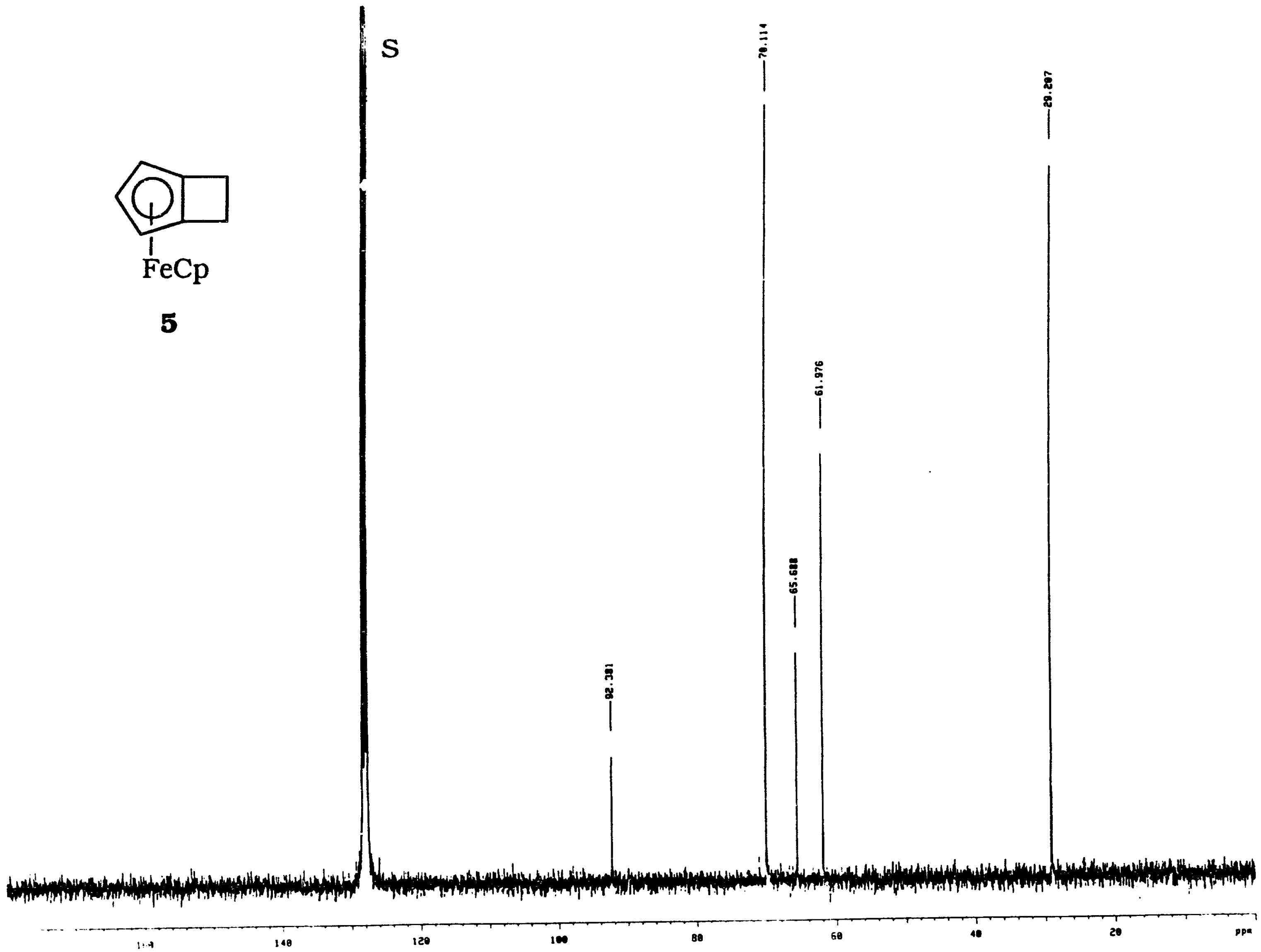
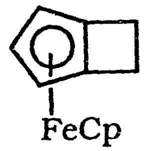


Figure A-5. ^{13}C NMR spectrum (75.5 MHz, C_6D_6) of ferrocenocyclobutene (**5**) (S: solvent).



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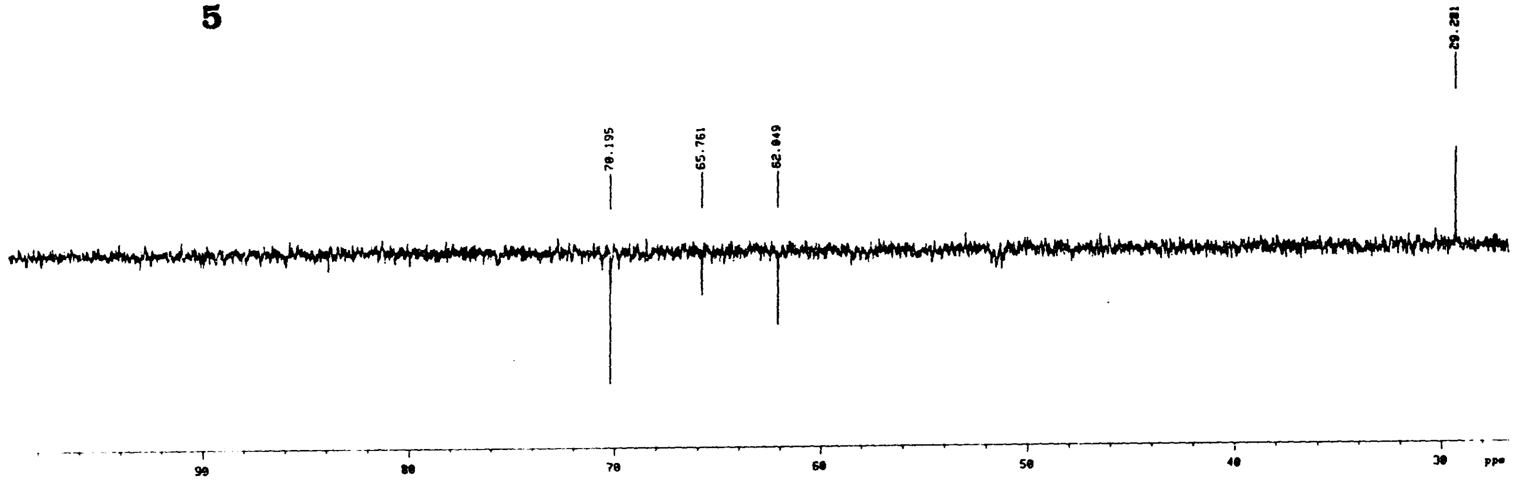


Figure A-6. ^{13}C NMR Attached Proton Test (APT) spectrum (75.5 MHz, C_6D_6) of ferroceno-cyclobutene (**5**) (positive peaks indicate CH_2 groups, negative peaks indicate aromatic CH groups or quaternary carbons; quaternary carbon at *ca.* 92 ppm could not be observed, due to its low sensitivity to APT).

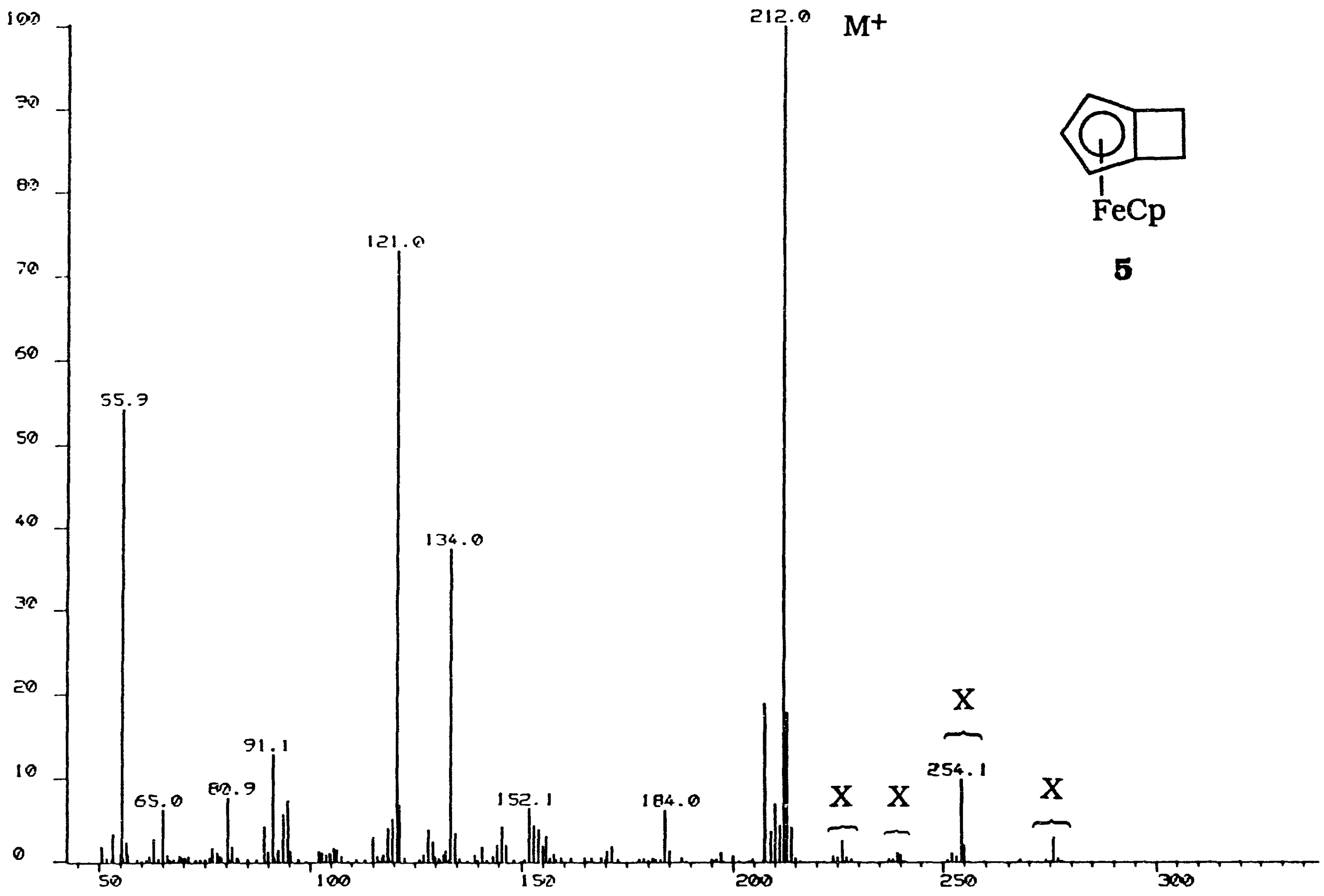
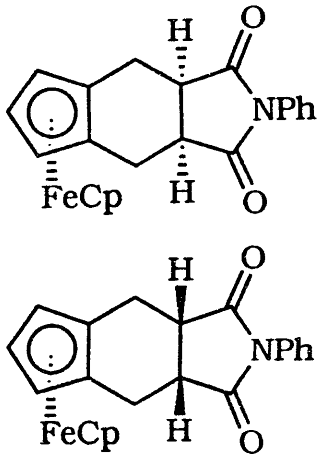


Figure A-7. HRMS of ferrocenocyclobutene (**5**) (M^+: molecular ion, X: unidentified impurity).



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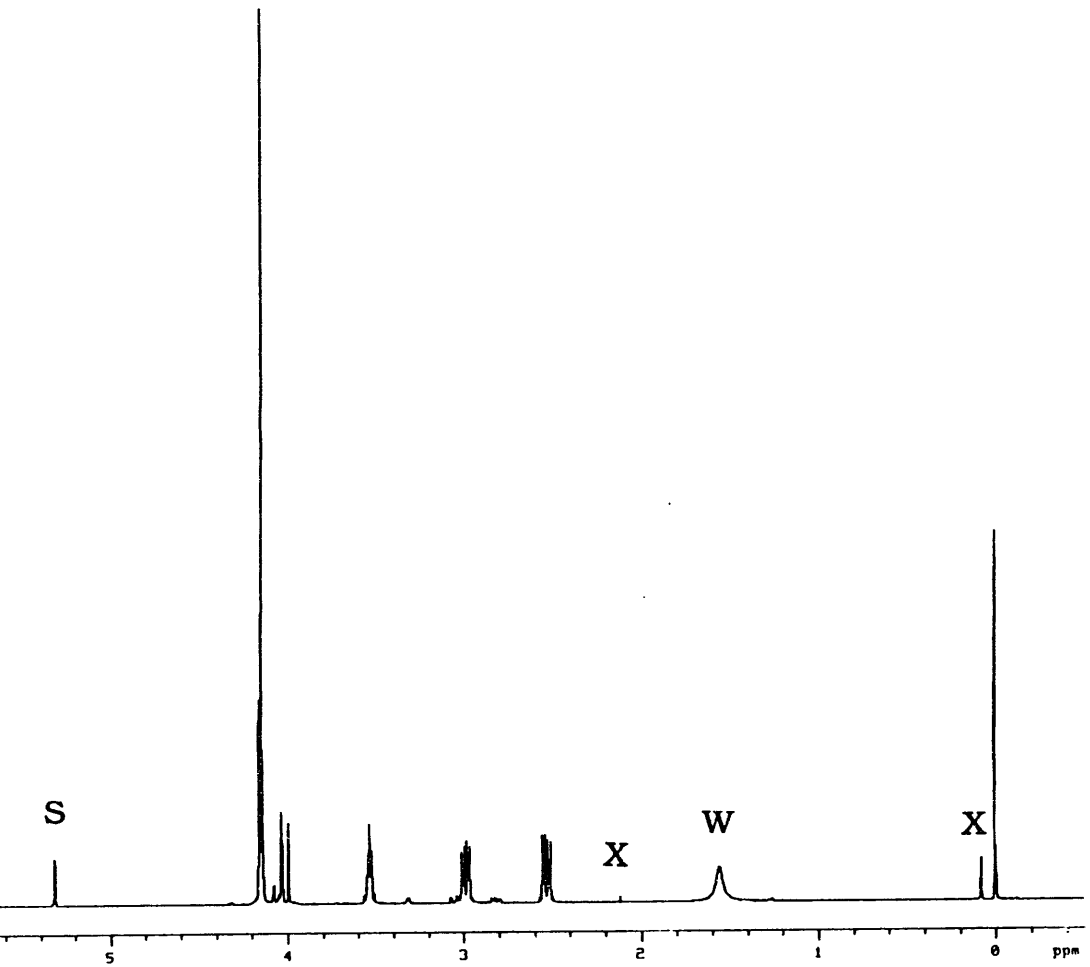


Figure A-8. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the crude adduct of ferrocenocyclobutene and NPMI (**8** and **9**) (S: $CHDCl_2$, W: H_2O, T: tetramethylsilane, X: unidentified impurity).

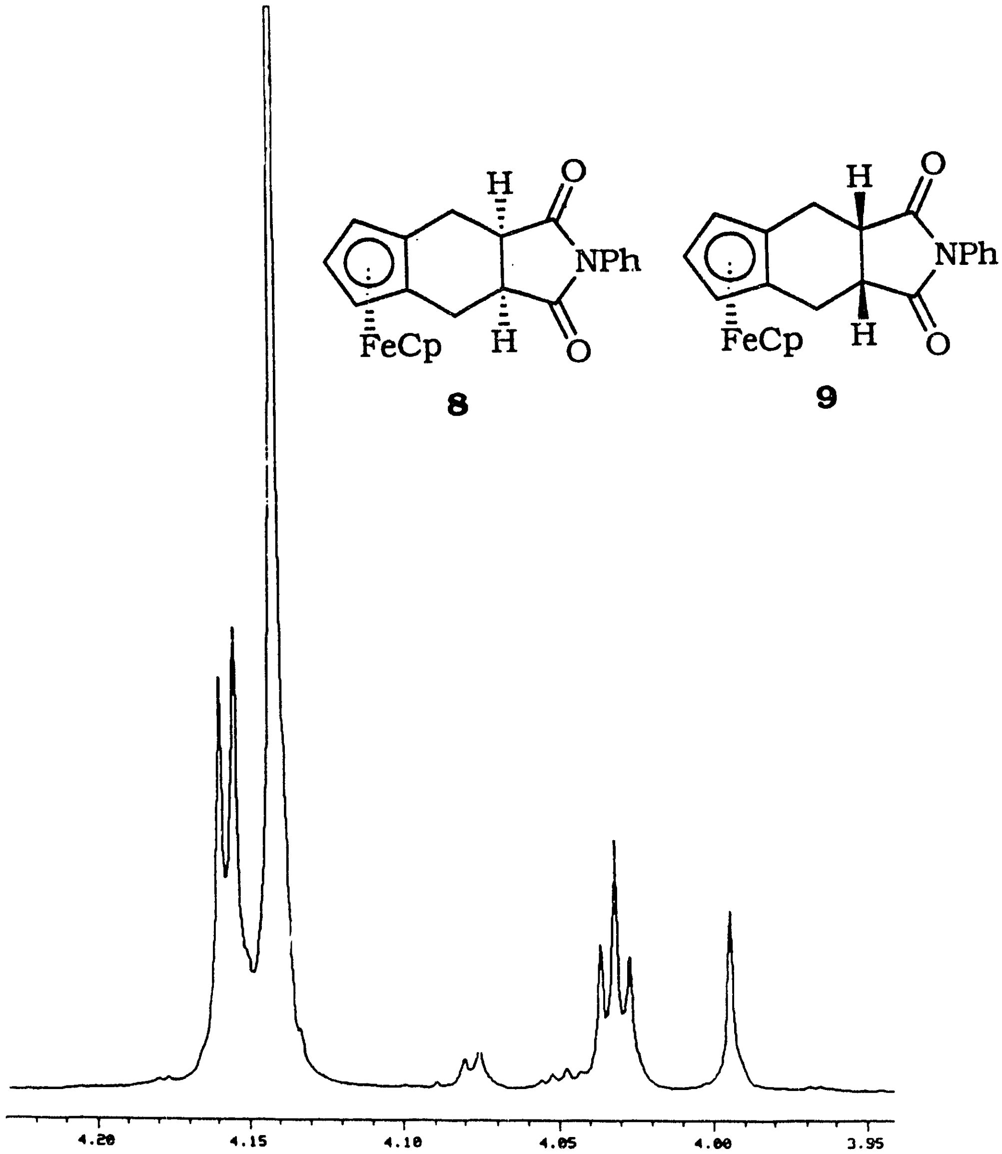


Figure A-9. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of the ferrocenyl region of the crude adduct of ferrocenocyclobutene and NPMI (**8** and **9**).

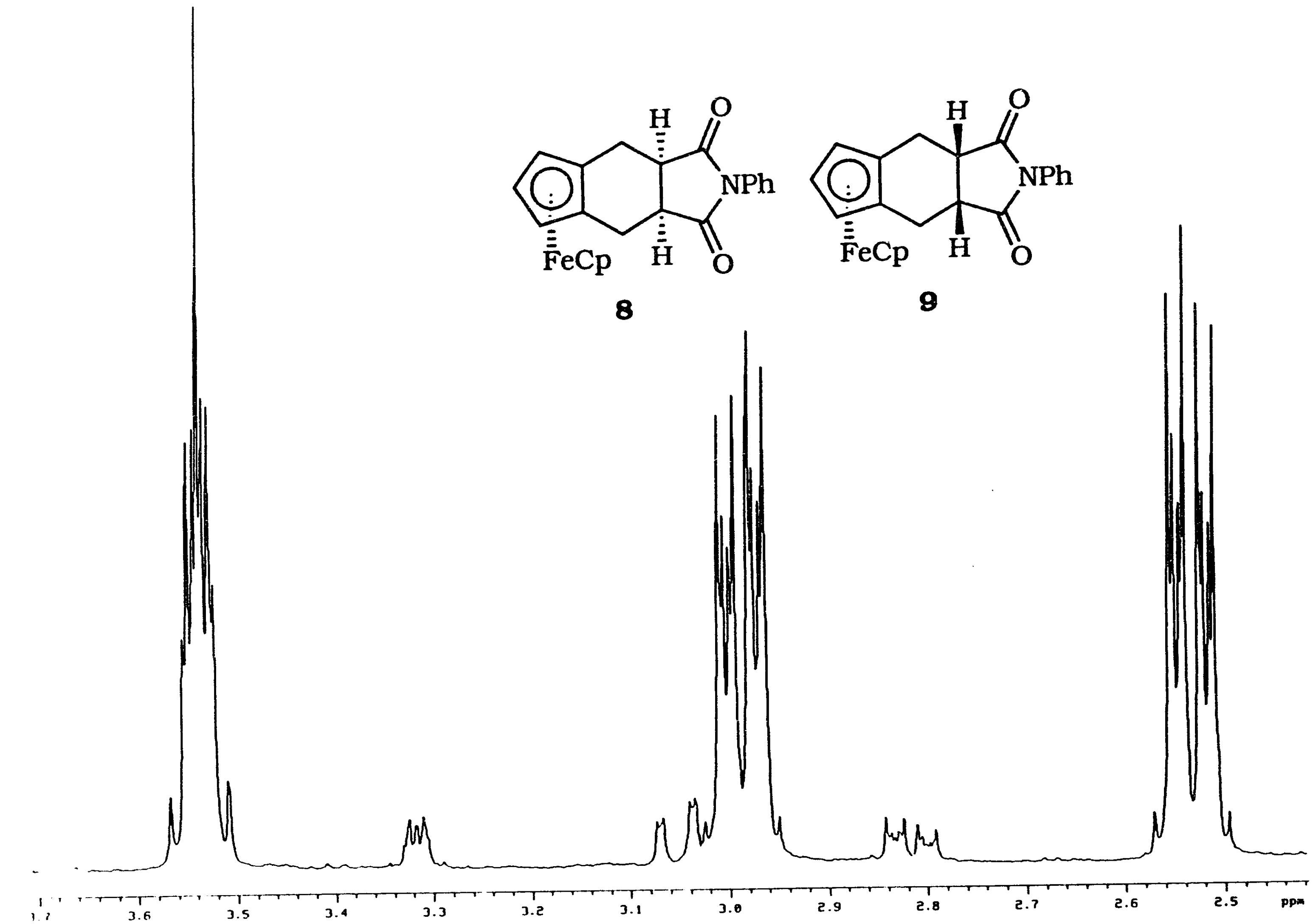


Figure A-10. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of the aliphatic region of the crude adduct of ferrocenocyclobutene and NPMI (**8** and **9**).

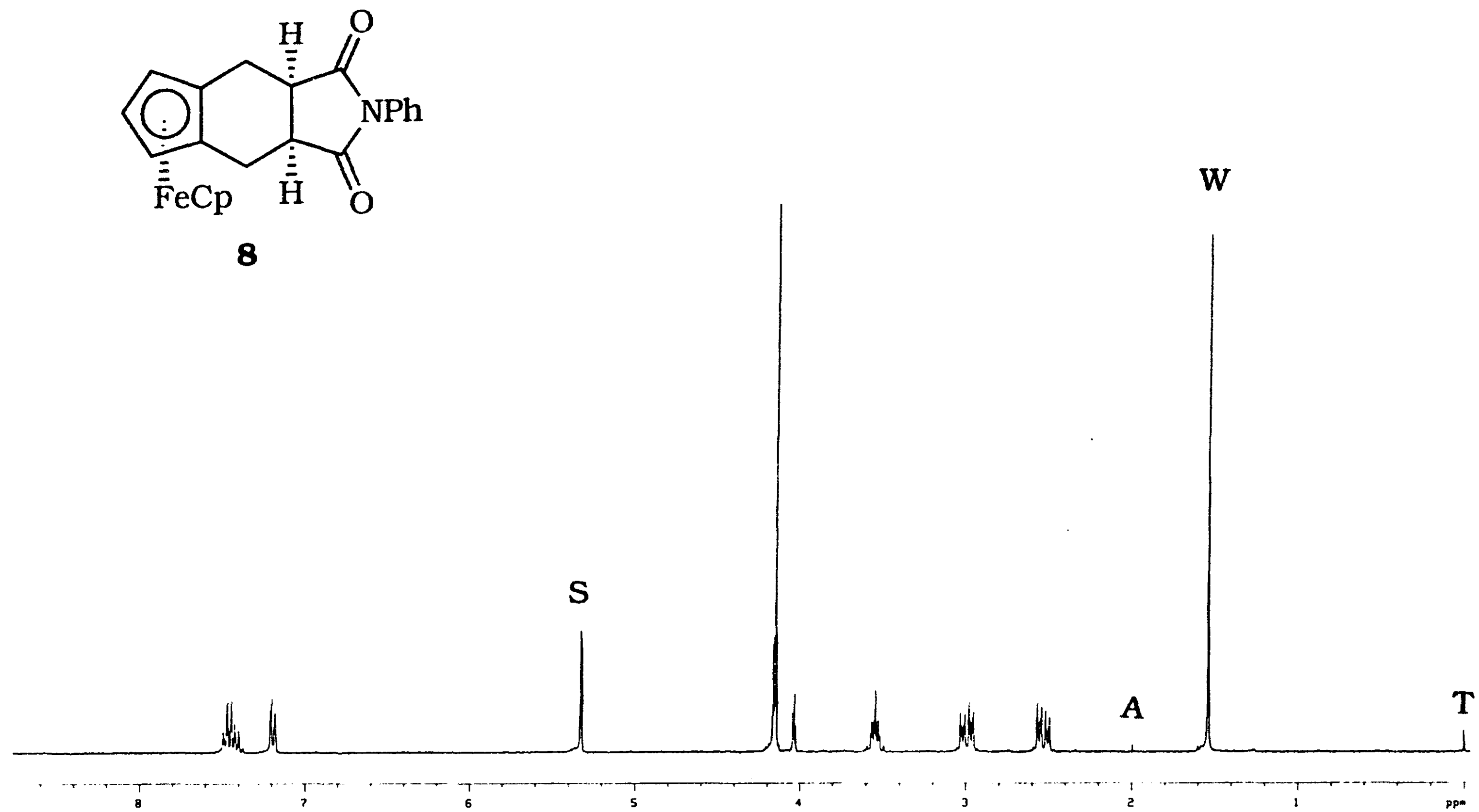


Figure A-11. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the purified major adduct of ferrocenocyclobutene and NPMI (**8**) (S: $CHDCl_2$, W: H_2O, T: tetramethylsilane, A: acetone).

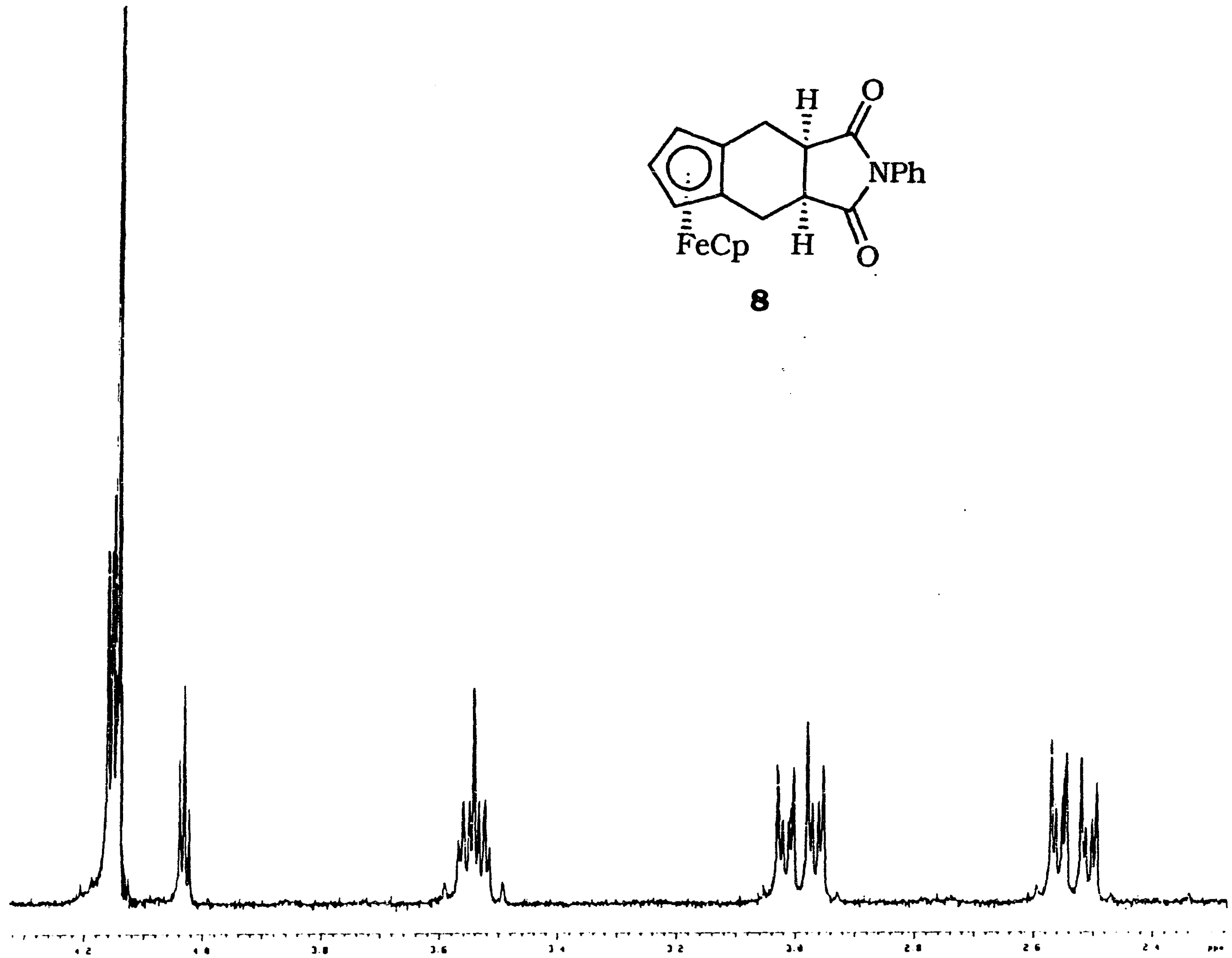


Figure A-12. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the ferrocenyl and aliphatic regions of the major adduct of ferrocenocyclobutene and NPMI (**8**).

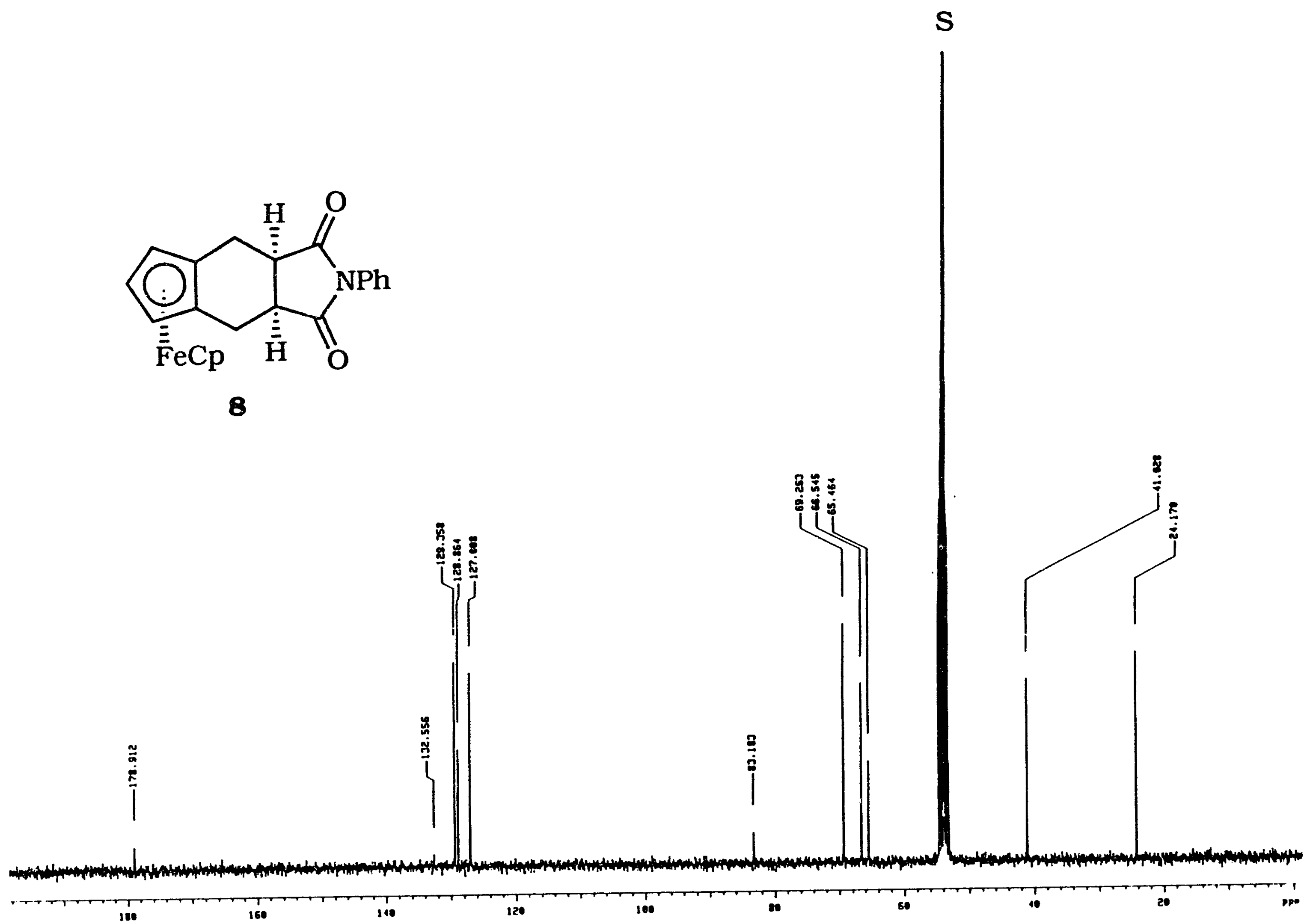
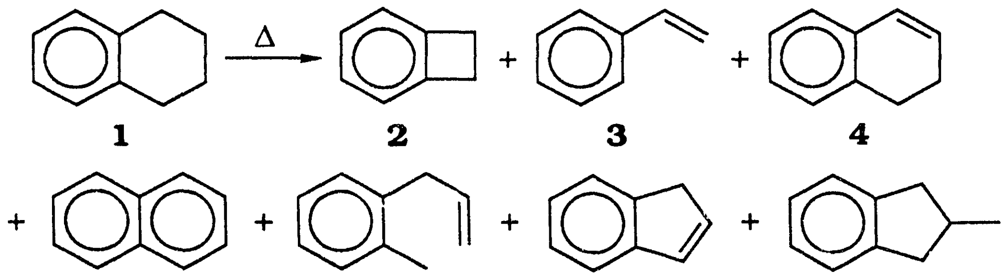


Figure A-13. ^{13}C NMR spectrum (75.5 MHz, CD_2Cl_2) of the major adduct of ferrocenocyclobutene and NPMI (**8**), (S: $CHDCl_2$).

PAPER 2. COUPLING OF DIRADICALS GENERATED BY THERMAL INTRAMOLECULAR HYDROGEN-ATOM TRANSFERS: CYCLIZATION OF *o*-ALLYLTOLUENE DERIVATIVES

INTRODUCTION

The gas-phase pyrolysis of tetralin (**1**) involves two major decomposition pathways: (a) loss of ethylene to give benzocyclobutene (**2**) and styrene (**3**) and (b) loss of hydrogen to give 1,2-dihydronaphthalene (**4**) and naphthalene (**5**).[1,2] In addition to these major products there are many other minor products including *o*-allyltoluene (**6**) and indene (**7**),[1,2] and 2-methylindan (**8**).[1]

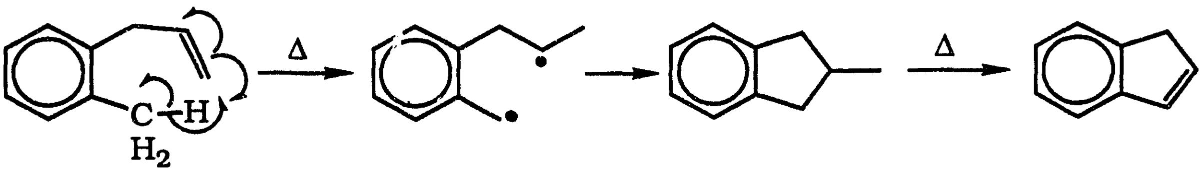


1 **2** **3** **4**

5 **6** **7** **8**

While studying the effects of pyrolysis temperature on the yields of products obtained by the flash vacuum pyrolysis (FVP) of tetralin (**1**), we noted that as the pyrolysis temperature increases, the yield of *o*-allyltoluene (**6**) decreases but the yield of indene (**7**) increases. To check the possibility that **6** was the source of **7** we studied the FVP of **6** itself.[3] We found that at *ca.* 700-800 °C, 2-methylindan (**8**) is the major product, which differs from results previously reported for the gas-phase reactions of **6**.[4,5] At higher temperatures (900 °C), **7** is the major product, presumably arising by secondary pyrolysis of **8**.

We propose that **8** is produced by a two-step mechanism involving diradical **9** which is formed by an *intramolecular* thermal hydrogen

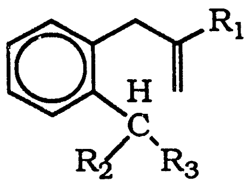


6 **9** **8** **7**

atom transfer, a novel hydrocarbon reaction. To date, the only examples of formation of diradicals or radical pairs by transfer of a hydrogen atom

have been intramolecular photochemical[6] reactions and a few intermolecular thermal reactions.[7,8,9] There is only one report which presents evidence for the formation of a diradical by thermally-induced transfer of a hydrogen atom and this is for the cyclization of an organosilicon compound.[10]

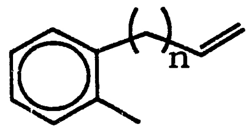
In this study, we carried out the FVP of *o*-allyltoluene (**6**) in order to investigate the conversion to **7** and **8** and to examine the product mixture for products that would offer support for the existence of diradical **9**. We also pyrolyzed a number of substituted derivatives of **6** containing methyl groups on the double bond or the benzylic methyl group (**A**), with the anticipation that increased substitution would lead to formation of by-products that could offer additional support for existence of diradical intermediates. We also expected the methyl groups to accelerate the reaction by leading to more stable radicals. In addition, we explored the effect of chain length (**B**) on the reaction to



A

R_1 = Me and R_2 = R_3 = H

or R_2 and/or R_3 = Me, R_1 = H



B

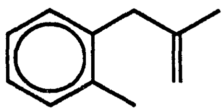
n= 2, 3

determine more about the scope and limitations of the hydrogen transfer/diradical coupling reaction. We also carried out the thermolysis of *o*-methallyltoluene (**10**) in solution in order to its solution-phase chemistry.

RESULTS

A summary of the product studies of the flash vacuum pyrolysis FVP of *o*-allyltoluene (**6**) at 0.10 torr (700–900 °C) is given in Table I.[3] The major products are 2-methylindan (**8**) and indene (**7**). Small amounts of *o*-(1-propenyl)toluene (**11**) are produced at 800-900 °C. Low yields of tetralin (**1**), 1,2-dihydronaphthalene (**4**), and naphthalene (**5**) are also produced.

o-Methallyltoluene (**10**) was pyrolyzed under conditions similar to those for used **6**. It was expected that the tertiary radical site of the proposed diradical intermediate (**12**) would enhance the stability of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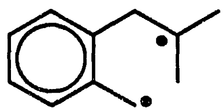
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the intermediate, resulting in a more facile reaction. The product studies of the FVP of **10** are summarized in Table II. The major product at 700-850 °C is 2,2-dimethylindan (**13**). Small amounts of 1-(*o*-tolyl)-2-methylpropene (**14**), 2-methylindene (**15**) and 3-methylindene (**16**), **5**, and **7** are formed. At 900 °C, the major products are **5** and **7**, accompanied by small amounts (*ca.* 4–10 %) of **8** and **13-16**.

2,2-Dimethylindan (**13**) was pyrolyzed in order to determine which products from the FVP of **10** are due to secondary pyrolysis of **13**. The FVP of **13** at 900 °C affords products (Table III) similar to the mixture produced by the FVP of **10** at 900 °C; the major products are **5** and **7**, along with low yields (*ca.* 5–11 %) of **8** and **13-16**.

Table I. Products and recovered starting material from the FVP of *o*-allyltoluene (**6**) at various temperatures [a,b]

entry	yield, % [c]		
	700 °C	800 °C	900 °C
o-allyltoluene (**6**) [d]	90.9	45.4	6.6
2-methylindan (**8**)	4.1	25.3	14.1
indene (**7**)	0.8	6.9	32.0
1,2-dihydronaphthalene (**4**)	0.6	1.4	1.1
tetralin (**1**)	0.3	2.7	3.3
o-(1-propenyl)toluene (**11**)	—	3.1	3.7
naphthalene (**5**)	—	1.0	8.1
other products	3.3 [e]	14.2 [e]	31.1 [e]
recovery [f]	83.3	88.8	72.8
conversion [g]	9.1	54.6	93.4

[a] FVP conditions: system pressure = 0.10 torr, sample temperature = 0 °C. [b] Amounts determined by GC with a known quantity of biphenyl added as standard. Data represent the average of triplicate runs. Products identified by comparison with authentic samples by retention time and GCMS are indicated by name. Products identified by GCMS only are indicated by code: **X**Y-nnn, where '**X**' corresponds to the system where first observed (**T** = **1**,[1] **A** = **6**, **M** = **10**, **E** = **17**, **C** = **21**, 'Y' to the individual unknown product (A, B, C, etc.), and 'nnn' to the nominal mass. [c] Moles of product divided by total moles of recovered material. [d] Starting material (yield, %): *o*-allyltoluene (96.5), *m*/*p*-allyltoluene (1.9), toluene (0.6), unidentified product **TL**-128 with formula $C_{10}H_8$ (0.4), naphthalene (0.4), 2,2'-dimethylbiphenyl (0.2). [e] See Table A-I in Appendix 2 of Paper 2, this dissertation, for a more detailed analysis. [f] Total moles of recovered material divided by moles of starting material used. [g] Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material.

Table II. Products and recovered starting material from the FVP of *o*-methallyltoluene (**10**) at various temperatures [a,b]

entry	yield, % [c]			
	700°C	800 °C	850 °C	900 °C
o-methallyltoluene (**10**) [d]	89.6	30.2	22.2	6.2
2,2-dimethylindan (**13**)	4.0	31.7	24.1	9.8
1-(*o*-tolyl)-2-methylpropene (**14**)	0.7	6.0	6.6	4.7
2-methylindene (**15**)	0.4	3.5	4.4	4.0
3-methylindene (**16**)	0.2	3.3	4.5	5.2
naphthalene (**5**)	0.1	4.1	6.6	18.8
indene (**7**)	—	2.7	5.9	16.6
other products	4.5 [e]	15.6 [e]	20.9 [e]	23.3 [e]
recovery [f]	89.0	83.8	81.0	67.3
conversion [g]	10.4	69.8	77.8	93.8

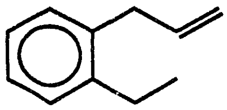
[a] See Table I, note *a*. [b] See Table I, note *b*. [c] See Table I, note *c*. [d] Starting material (GC assay, mol %): *o*-methallyltoluene (94.5) toluene (3.3), unidentified product **MM**-146 with formula $C_{11}H_{14}$ (1.4), unidentified product **ME**-146 with formula $C_{11}H_{14}$ (0.2), 2,2'-dimethylbiphenyl (0.2). 1-methyl-1-phenylpropene (0.2), propylbenzene (0.1), other minor impurities (total of 0.1). [e] See Table A-II in Appendix 2 of Paper 2, this dissertation, for a more detailed analysis. [f] See Table I, note *f*. [g] See Table I, note *g*.

Table III. Products and recovered starting material from the FVP of 2,2-dimethylindan (**13**) at 900 °C [a,b,]

entry	yield,%[c]
naphthalene (**5**)	24.0
indene (**7**)	21.7
2,2-dimethylindan (**13**) [d]	10.7
3-methylindene (**16**)	7.4
2-methylindene (**15**)	5.4
1-(*o*-tolyl)-2-methylpropene (**14**)	5.4
o-methallyltoluene (**10**)	4.8
other products	26.0 [e]
recovery [f]	60.4
conversion [g]	89.3

[a] See Table I, note *a*. [b] See Table I, note *b*. [c] See Table I, note *c*. [d] Starting material (GC assay, area %): 2,2-dimethylindan (97.2), unidentified minor impurities, none of which are present in the pyrolysis product mixtures (2.8). [e] See Table A-III in Appendix II-2 of Paper 2, this dissertation, for a more detailed analysis. [f] See Table I, footnote *f*. [g] See Table I, footnote *g*.

The FVP reactions of *o*-allylethylbenzene (**17**) were also explored. We believed that the methyl group would stabilize the benzylic radical site of the predicted diradical intermediate (**18**) thus favoring the reaction at lower temperatures.



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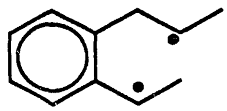

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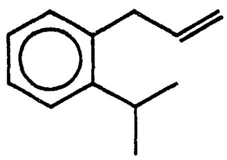
Pyrolysis of **17** was carried out at 0.1 torr (700-800 °C). At 700 °C, **15**, **16**, and E-(*o*-propenyl)ethylbenzene (**19**), as well as small amounts of **ED**-146 (see Table I, note *b* for explanation of nomenclature) are produced. At 750-800 °C, the major products are **8** and **5**. Compounds **15**, **16**, and **19**, *o*-propylstyrene (**20**), and many minor products are also produced. These results are presented in Table IV.

In addition, we pyrolyzed *o*-allylcumene (**21**), anticipating that the predicted diradical intermediate (**22**) would be sufficiently



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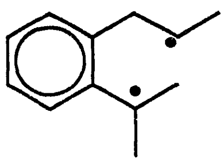


22

stabilized to allow reaction at even lower temperatures than **17**. FVP of **21** was carried out at 0.10 torr (700-750 °C). At 700 °C, low yields of **5**, **7**, and **16** are obtained, along with small amounts of compounds **CC**-160, **CG**-160 (see Table I, note *b* for explanation of nomenclature). At 750 °C, larger amounts of **5**, **7**, **16**, and many minor compounds are formed. These results are presented in Table V.

Table IV. Products and recovered starting material from the FVP of *o*-allylethylbenzene (**17**) at various temperatures [a,b]

entry	yield, %[c]		
	700 °C	750 °C	800 °C
o-allylethylbenzene (**17**) [d]	74.2	48.5	14.6
AED-146 [$C_{11}H_{14}$]	3.9	3.6	2.6
indene (**7**)	1.9	6.9	22.8
3-methylindene (**16**)	1.8	4.7	6.7
naphthalene (**5**)	1.6	5.7	19.3
2-methylindene (**15**)	1.2	3.6	4.5
E-(*o*-propenyl)ethylbenzene (**19**)	1.4	2.2	2.1
o-propylstyrene (**20**)	—	1.7	3.6
other products	9.8 [e]	16.9 [e]	19.8 [e]
recovery [f]	78.5	78.7	70.7
conversion [g]	25.8	51.8	85.4

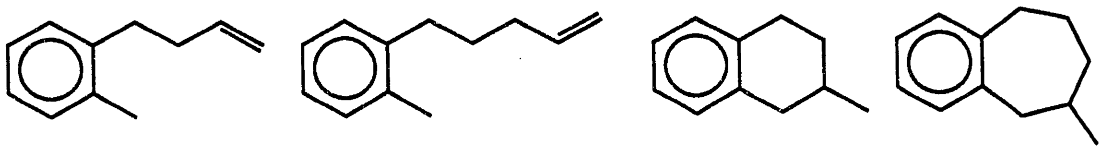
[a] See Table A-I, note *a*. [b] See Table I, footnote *b*. [c] See Table I, note *c*. [d] Starting material (GC assay, area%): *o*-allylethylbenzene (96.5), unidentified product **EL** (1.3), 2,2'-diethylbiphenyl (1.2), ethylbenzene (0.8), unidentified product **EI** (0.5), *o*-bromoethylbenzene (0.4). [e] See Table A-IV in Appendix 2 of Paper 2, this dissertation, for a more detailed analysis. [f] See Table I, footnote *f*. [g] See Table I, footnote *g*.

Table V. Products and recovered starting material from the FVP of from the FVP of *o*-allylcumene (**21**) at various temperatures [a,b]

	yield,% [c]	
entry	700 °C	750 °C
o-allylcumene (**21**) [d]	53.5	19.9
naphthalene (**5**)	5.1	17.7
CC-160 [C12H16]	4.4	3.4
3-methylindene (**16**)	3.6	8.2
CG-160 [C12H16]	2.5	5.1
indene (**7**)	1.7	6.6
other products	29.8 [e]	39.1 [e]
recovery [f]	83.4	73.2
conversion [g]	46.5	80.1

[a] Amounts determined by GC with a known quantity of biphenyl added as standard. [b] Amounts determined by GC with a known quantity of biphenyl added as standard. Data for 700 °C represent the average of duplicate runs. Data for 750 °C represent the average of triplicate runs. [c] See Table I, note *c*. [d] Starting material (GC assay, area%): *o*-allylcumene (91.8), 2,2'-diisopropylbiphenyl (3.2), unidentified product **C**P (1.8), cumene (0.7), unidentified product **C**J (0.6), unidentified product **C**F-160 with formula $C_{12}H_{16}$ (0.5), unidentified product **C**R (0.5), unidentified product **C**R-160 with formula $C_{12}H_{16}$ (0.4), unidentified product **C**S (0.2), unidentified product **C**I-144 with formula $C_{11}H_{12}$ (0.2). [e] See Table A-V in Appendix 2 of Paper 2, this dissertation, for a more detailed analysis. [f] See Table I, footnote *f*. [g] See Table I, footnote *g*.

The effect of the length of the alkyl chain connecting the double bond and the aromatic ring on the ease of hydrogen-atom transfer was explored through pyrolysis of *o*-(3-butenyl)toluene (**23**) and *o*-(4-pentenyl)toluene (**24**). Hydrogen-atom transfer and diradical coupling occurred should produce 2-methyltetralin (**25**) and β-methylbenzosuberane (**26**), respectively.



23 **24** **25** **26**

The FVP of *o*-(3-butenyl)toluene[3] (**23**) at 0.1 torr (700-900 °C) produces good yields (*ca.* 40%) of 1,2-di(*o*-tolyl)ethane (**27**) at 700–800 °C. At 900 °C, significant amounts (*ca.* 10–20%) of *o*-xylene (**28**), benzocyclobutene (**2**), *o*-ethyltoluene (**29**), and styrene (**3**) are formed. No 2-methyltetralin (**25**) was detected. These results are presented in Table VI.

FVP of *o*-(4-pentenyl)toluene[3] (**24**) was carried out at 0.01 torr (600–800 °C). The major product at 700–800 °C is *o*-methylstyrene (**30**). Numerous side products, each produced in small amounts, are formed at high conversion (900 °C). No β-methylbenzosuberane (**26**) was detected. These results are presented in Table VII. In addition to our studies of gas-phase reactions of these compounds, we explored the solution-phase reactions of **10**.

The results of the thermolysis of **10** in phenyl ether (240 min, 400°C) are presented in Table VIII. At a higher starting concentration

Table VI. Products and recovered starting material from the FVP of *o*-(3-butenyl)toluene (**23**) at various oven temperatures [a,b]

entry	yield, % [c]		
	700 °C	800 °C	900 °C
o-(3-butenyl)toluene (**23**) [d]	64.2	41.7	15.9
1,2-di(*o*-tolyl)ethane (**27**)	34.4	39.4	7.6
o-xylene (**28**)	0.4	4.7	18.6
benzocyclobutene (**2**)	0.4	3.5	15.2
o-ethyltoluene (**29**)	—	3.0	10.4
styrene (**3**)	—	0.5	6.8
other products	0.6 [e]	7.3 [e]	25.5 [e]
recovery [f]	97.8	88.7	110.0
conversion [g]	35.8	58.3	84.1

[a] See Table I, note *a*. [b] See Table I, note *b*. [c] See Table I, note *c*. [d] Starting material (yield, %): *o*-(3-butenyl)toluene (100.0). [e] See Table A-VI in Appendix 2 of Paper 2, this dissertation, for a more detailed analysis. [f] See Table I, note *f*. [g] See Table I, note *g*.

Table VII. Products and recovered starting material from the FVP of *o*-(4-pentenyl)toluene (**24**) at various oven temperatures [a,b]

entry	yield, % [c] 600 °C	700 °C	800 °C
o-(4-pentenyl)toluene (**24**) [d]	90.4	52.9	3.0
o-methylstyrene (**30**)	1.5	30.6	59.8
other products	8.1 [e]	16.5 [e]	37.0 [e]
recovery [f]	96.2	86.6	70.4
conversion [g]	9.6	47.1	97.0

[a] FVP conditions: see Table I, note *a*. [b] See Table I, note *b*. [c] See Table I, note *c*. [d] Starting material (yield, %): *o*-(4-pentenyl)toluene (92.4), 2,2'-dimethylbiphenyl (7.6), unidentified impurity PC which constitutes <0.35% total area by GC. [e] See Table A-VII in Appendix 2 of Paper 2, this dissertation, for a more detailed analysis. [f] See Table I, note *f*. [g] See Table I, note *g*.

of **10**, the major product is **14**, the double-bond isomer of **10**. Small amounts of **5**, **13**, **15**, and **16** are also formed. When the initial concentration of **10** is lowered five-fold, the conversion to **14** is lower. The dependence of conversion upon concentration suggests that a chain mechanism is responsible for the conversion from **10** to **14**. The percentages of **5**, **13**, **15**, and **16** do not change significantly.

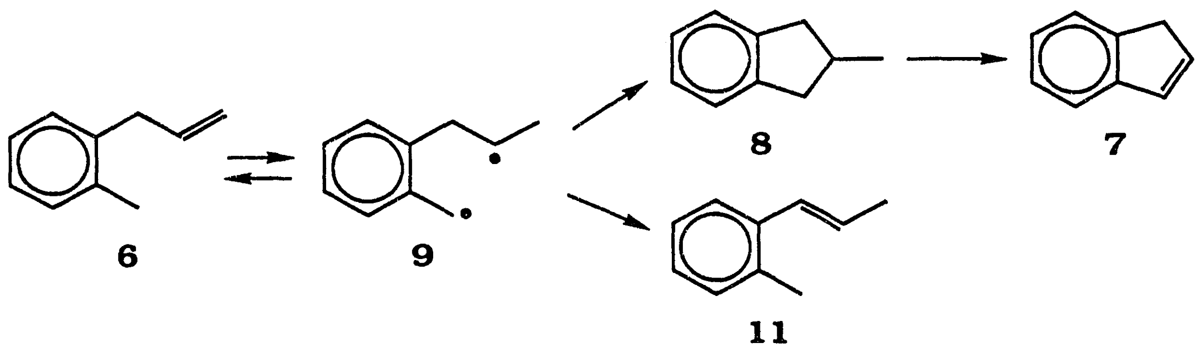
Table VIII. Products and recovered starting material from the solution-phase thermolysis of *o*-methallyltoluene (**10**) in phenyl ether (240 min, 400 °C) at various concentrations [a]

entry	yield, %[c]	
	0.0724 mol L^{-1}	0.0145 mol L^{-1}
1-(*o*-tolyl)-2-methylpropene (**14**)	57.7	26.7
o-methallyltoluene (**10**) [b]	14.0	50.0
3-methylindene (**16**)	6.1	7.3
2-methylindene (**15**)	4.5	2.2
naphthalene (**5**)	4.7	1.2
2,2-dimethylindan (**13**)	3.6	3.9
other products	9.4 [c]	8.7 [c]

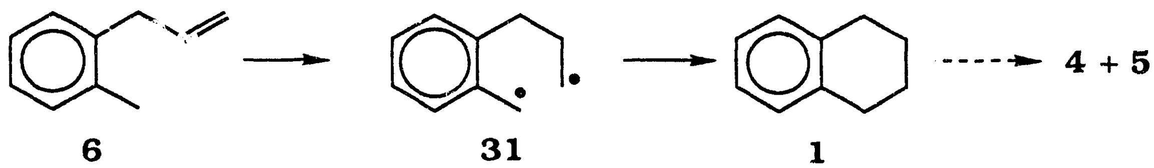
[a] Thermolysis conditions: 0.5 mL of degassed phenyl ether solution was sealed in a glass tube, and then is heated to 400 °C for 240 minutes. [b] Starting material (GC assay, mol%): *o*-methallyltoluene (94.5) toluene (3.3), unidentified product **TM**-146 with formula $C_{11}H_{14}$ (1.4), unidentified product **TE**-146 with formula $C_{11}H_{14}$ (0.2), 2,2'-dimethylbiphenyl (0.2). 1-methyl-1-phenylpropene (0.2), propylbenzene (0.1), other minor impurites (total of 0.1). [c] See Table A-VIII in Appendix 2 of Paper 2, this dissertation, for a more detailed analysis.

DISCUSSION

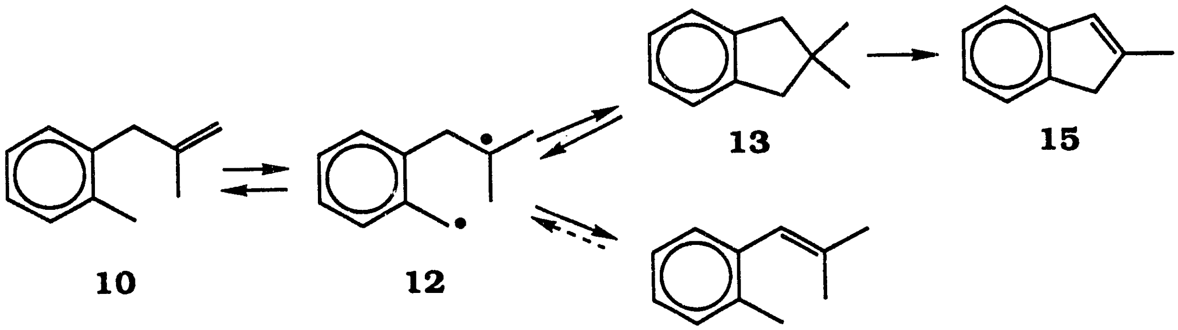
The products of the FVP of *o*-allyltoluene (**6**), *o*-methallyltoluene (**10**), 2,2-dimethylindan (**13**), and *o*-allylethylbenzene (**17**) offer considerable support for the existence of diradical intermediates during pyrolysis of these hydrocarbons. FVP of **6** affords 2-methylindan (**8**) whose formation can be explained by the coupling of **9**, the predicted diradical intermediate resulting from hydrogen-atom transfer. *o*-(1-Propenyl)toluene (**11**), which could arise by intramolecular disproportionation of **9**, is also observed.[5,11] Indene (**7**) probably arises by loss of the methyl group from **8**, followed by loss of a β-hydrogen.



The formation of tetralin (**1**), which is formed in low yields, also offers support for the proposed mechanism. Hydrogen transfer to the internal carbon of the double bond would give diradical **31**, which could undergo coupling to give **1**. The formation of 1,2-dihydronaphthalene (**4**), and naphthalene (**5**) is probably at least partially due to secondary pyrolysis of **1**.

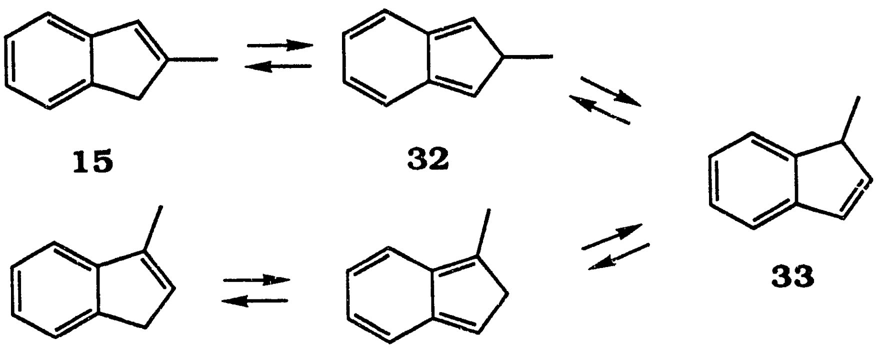


Further evidence for the existence of diradical intermediates was obtained through the FVP of **10** (Table II). 2,2-Dimethylindan (**13**), the major product of FVP of **10**, is believed to arise from coupling of diradical intermediate **12**. Intramolecular disproportionation of **12** would lead to either starting material or to 1-(*o*-tolyl)-2-methylpropene (**14**).



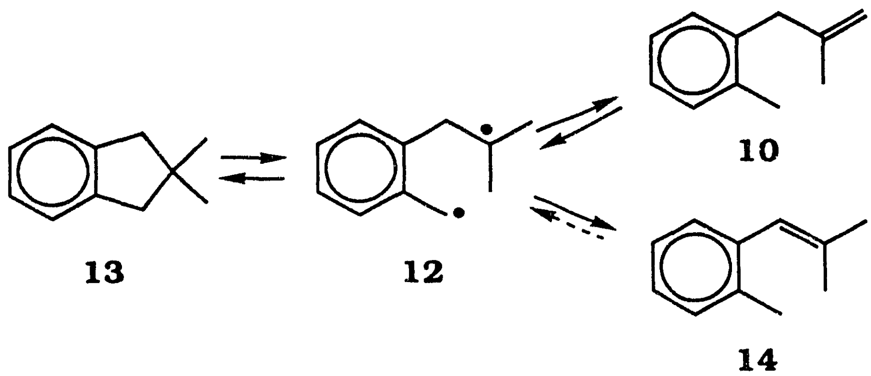
10 **12** **13** **15** **14**

The formation 2-methy..ndene (**15**) can be explained by loss of a methyl group and a β-hydrogen from **13**. 3-Methylindene (**16**) is probably formed from **15** by a series of 1,5 hydrogen and 1,5 methyl shifts involving intermediates **32-34**, which is reasonable based on the known interconversion of phenyl substituted indenes.[12]

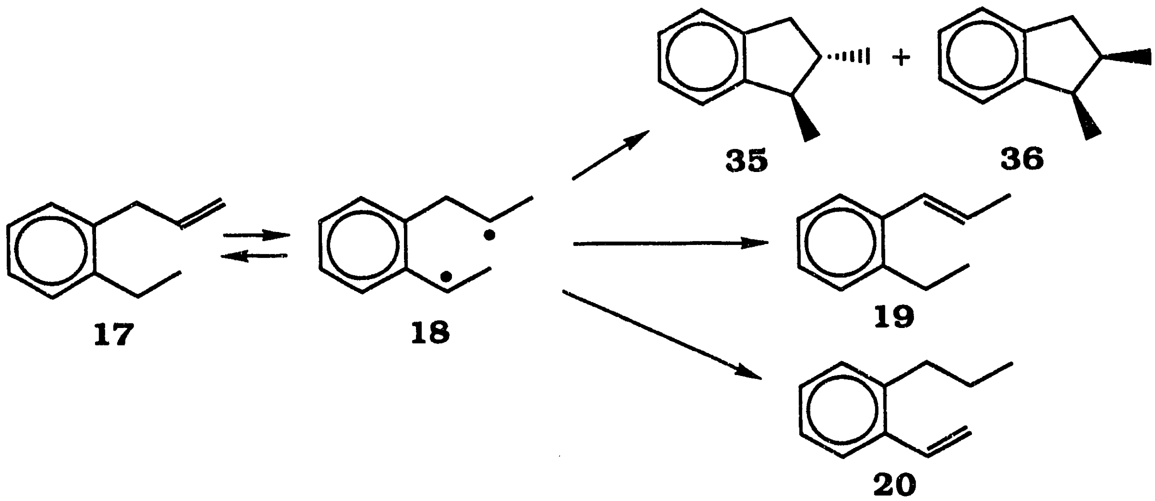


15 **32** **33** **16** **34**

The FVP of dimethylindan (**13**) at 900 °C gives **10** and **14** as minor products, with **5**, **7**, **15**, and **16** being formed in larger amounts. The formation of **10** and **14** can be explained by cleavage of the Cα-Cβ bond, affording diradical **12**, which then undergoes intramolecular disproportionation to give **10** and **14**. The reversibility of the conversion of **10** from **13** further supports the existence of diradical **12**.

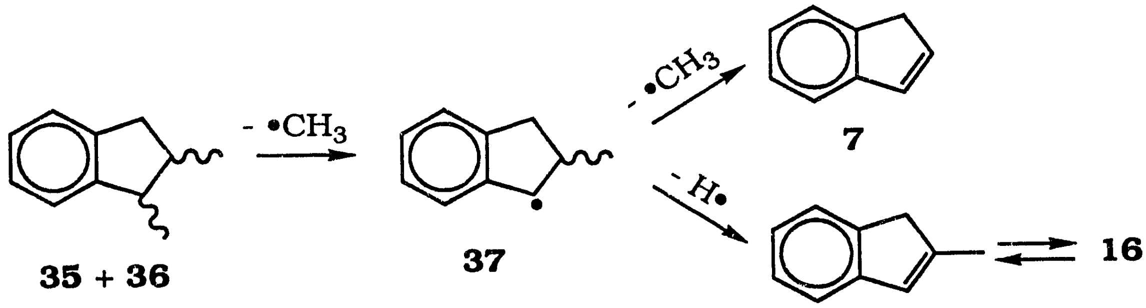


The FVP of *o*-allylethylbenzene (**17**) produces several compounds that are consistent with the generation of diradical intermediate **18**. Once formed by hydrogen-atom transfer, diradical **18** could undergo four reactions affording distinct products: coupling to give *cis*- and *trans*- 2,3-dimethylindans (**35** and **36**, respectively), or three intramolecular disproportionation reactions to give either starting material (**17**), E-(*o*-propenyl)ethylbenzene (**19**), or *o*-propylstyrene (**20**).



Analysis by GC (Table IV), GCMS, and ^{1}H NMR clearly shows compounds **19** and **20**[13] are formed during the FVP of **17**. Intramolecular disproportionation of **18** readily explains their formation. The presence of dimethylindans **35** and **36** could not be firmly established, but it is possible that some minor products, such as ED-146, could be **35** or **36**. Unfortunately, these minor products are formed in such small amounts that they could not be clearly identified by GC or ^{1}H NMR, although GCMS shows that these products are isomeric with **17**.

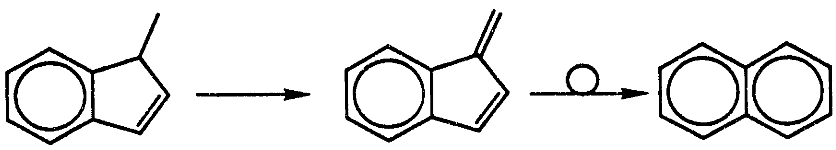
The high yield of **7** and the substantial amounts of **15** and **16** that are formed can be explained by loss of the α-methyl group to give radical **37** followed by loss of either the β-methyl group to give **7** or the β-hydrogen to give **15**, which can then isomerize to **16**, as previously indicated. The loss of the α-methyl group should be relatively facile, which could explain the lack of readily identifiable amounts of **35** and/or **36** in the product mixtures.



35 + 36 37 7 16 15

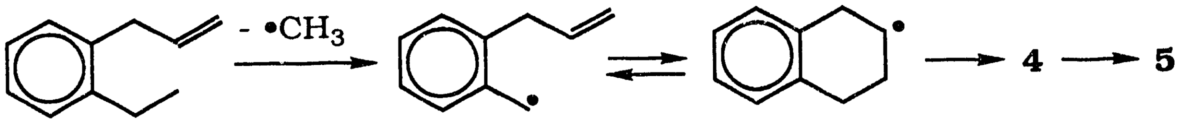
In addition to products that support the existence of diradical intermediates, formation of naphthalene (**5**) and indene (**7**) is prominent in most of these pyrolyses, particularly at higher temperatures. Therefore, consideration has been given to their formation. Likely routes to **5** and **7** are described below.

The formation of **5** during the FVP of **6** is probably partially due to secondary pyrolysis of **1**. The route from **10** to **5** could involve benzofulvene (**38**), which is detected in the pyrolysis mixture (*ca.* 1%). The interconversion of 2-methylindene (**15**) and 3-methylindene (**16**), is believed to proceed through 1-methylindene (**33**). Loss of hydrogen would give **38**, which rearranges to naphthalene.[14]



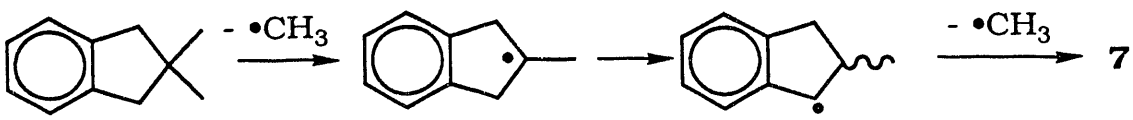
15 **38** **5**

Formation of **5** during the FVP of **17** could also be by way of benzofulvene, but it is also possible that **5** could arise as a result of α-fragmentation of **17**. Compound **17** would give *o*-allylbenzyl radical (**39**) which could cyclize, giving the 2-tetryl radical (**40**). Loss of a β-hydrogen to give **4** followed by further dehydrogenation gives **5**.[15]



17 **18** **39**

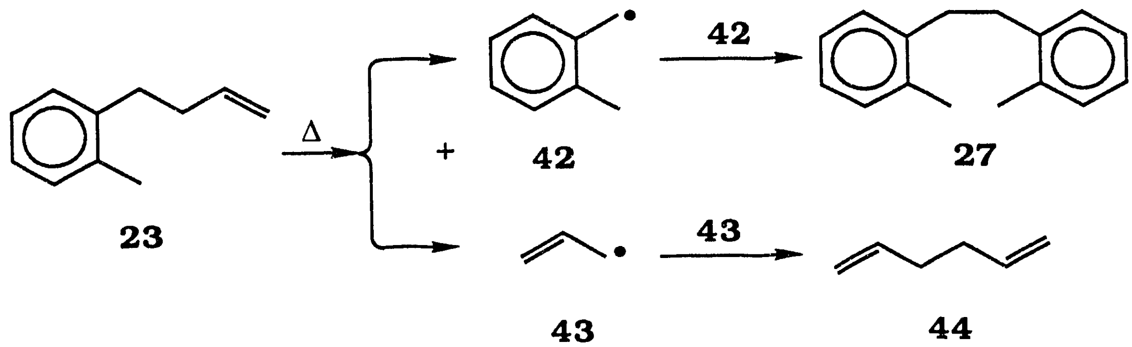
Indene (**7**) is another major product from the FVP of **6**, **10**, **17**, and **21** at high temperatures. Some possible routes to **7** have been described above. The route from **13** to **7** is more uncertain, but a possible route involves stepwise loss of a methyl group, followed by a 1,2 hydrogen shift to give radical **37** and then loss of the β-methyl group from **37** to give **7**.



13 **41** **37**

Both naphthalene and indene are major products formed in the FVP of *o*-allylcumene **21** (Table V). Unfortunately, the large amount of lower molecular-weight products resulting from α-fragmentation observed during pyrolyis makes it difficult to determine which products result from α-fragmentation and which, if any, result from secondary reactions of cyclized products resulting from hydrogen-atom transfer. Brown has observed formation of **5** and **7** during pyrolyses which result in formation of polymethylated indenes,[16] so formation of **5** and **7** during the pyrolysis of **21** is not unexpected. The pyrolysis of **17** and **21** clearly showed that α-fragmentation is a major pathway if α-methyl groups are present.

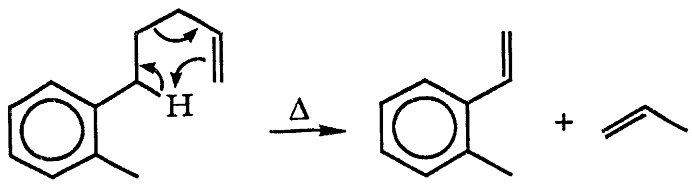
We investigated the effect of chain length on the hydrogen-atom transfer reaction and cyclization. *o*-(3-Butenyl)toluene (**23**) and *o*-(4-pentenyl)toluene (**24**) were pyrolyzed. In the FVP of **23**, the main reaction is homolytic cleavage of the weak benzylic-allylic carbon-carbon bond (Table VI). The dimerization of the *o*-methylbenzyl radical (**41**) which is produced from this bond cleavage, results in the formation of 1,2-di(*o*-tolyl)ethane (**27**). The allyl radicals (**42**) should dimerize to form biallyl (**43**), but none was detected. At 900 °C, the major



products are benzocyclobutene (**2**), styrene (**3**), and *o*-xylene (**28**), *o*-ethyltoluene (**29**). Analogous results for the FVP of 4-phenylbutene (**44**) were observed by Ondruschka and co-workers.[17] It is likely that **2** is formed by closure of *o*-xylylene (**45**), which would result from the loss of a hydrogen atom from **42**. Rearrangement of **2** leads to formation of styrene.[18] Compound **28** is probably formed by hydrogen abstraction by **42**, and the route to **29** is uncertain. ΔH values

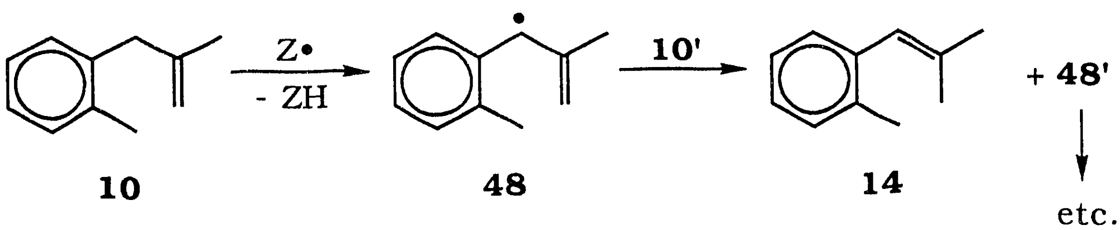
The main product from the pyrolysis of *o*-(4-pentenyl)toluene (**24**) (Table VII) is *o*-methylstyrene (**30**) which is probably formed, along with propene (**46**), by a retro-ene reaction. Analogous results for the

FVP of 4-phenylpentene (**47**) were observed by Ondruschka and co-workers.[17]



24 **30** **46**

In addition to FVP studies, we investigated the solution-phase reactions of **10**. It is clear that the solution-phase chemistry of **10** at 400 °C (See Table Table VIII) differs markedly from its gas-phase reactions. At a starting concentration of **10** of 0.0724 mol L^{-1}, the major product is double-bond isomer **14.** Some cyclized product, 2,2-dimethylindan (**13**) as well as its secondary products such as 2-methyl- (**15**) and 3-methylindene (**16**) were also formed. At a starting concentration of **10** of 0.0142 mol L^{-1}, the yield of **14** is considerably lower, and the yield of **13** is slightly higher. The dependence of the formation of **14** on the concentration of **10** shows that the reaction is not unimolecular in nature. We propose that a radical chain mechanism is responsible for this isomerization.



10 **48** **14**

ΔH values for the conversions of **6**, **10**, **17**, and **21** into their respective diradicals were calculated using Benson's method.[19] The

ΔH values for the conversions of **6** to **9**, **10** to **12**, **17** to **18**, and **21** to **22** were estimated to be 45.0, 44.0, 41.5, and 37.9 kcal mol^{-1}, respectively. Assuming that these calculated ΔH values lie within 2-3 kcal mol^{-1} of their corresponding $\Delta H^{\ddagger}$ values, which is reasonable, given the high energy of the diradical intermediates, the range of $\Delta H^{\ddagger}$ values is *ca.* 40-47 kcal mol^{-1}. This range of $\Delta H^{\ddagger}$ is readily accessible at 700-900 °C.

We also attempted to estimate $\Delta G^{\ddagger}$ values for these conversions these approximations through use of Scheiss'[20] method. By plotting % conversion *vs.* temperature using the data in Tables I, II, and IV-VII, the temperature of 50% conversion ($T_{50\%}$) was determined for **6**, **10**, **17**, **21**, **23**, and **24** to be 794, 783, 720, 705, 761, and 697 °C, respectively. (See Appendix 3 for details) $\Delta G^{\ddagger}$ values for bond cleavage of **23** was estimated from activation parameters obtained for homolytic cleavage of biallyl[21], and $\Delta G^{\ddagger}$ for the retro-ene reaction of **24** was estimated from activation parameters obtained in the retro-ene reaction of 1,6-heptadiene.[22] The $\Delta G^{\ddagger}$ values for conversion of **23** and **24** were calculated to be inversely related to their respective $T_{50\%}$ value, rather than the direct relation that is expected. The discrepancy is probably due to uncertainties in the calculations, as well as variance of the oven temperature throughout the heating zone. However, the trends in the $T_{50\%}$ values for the conversions of **6**, **10**, **17**, and **21** are reasonable, considering the increasing substitution and stability of the diradicals being formed.

CONCLUSION

Flash vacuum pyrolysis (FVP) of *o*-allyltoluene (**6**), *o*-methallyltoluene (**10**), and *o*-allylethylbenzene (**17**) give a number of products whose formation is consistent with the existence of diradical intermediates produced by intramolecular hydrogen-atom transfers. $\Delta H^{\ddagger}$ values for the diradical intermediates are estimated to be *ca.* 40-47 kcal mol^{-1}, which are easily accessible at *ca.* 700 °C.

Some substantial limitations to the hydrogen-atom transfer reaction were revealed during the course of this study. The presence of methyl groups in the benzylic position, such as in *o*-allylethylbenzene (**17**) and *o*-allylcumene (**21**), causes α-fragmentation to become competitive with hydrogen-atom transfer.

The role of chain length in these cyclizations is critical, as well. FVP of *o*-(3-butenyl)toluene (**23**) affords products resulting from cleavage of the weak Cα-Cβ bond, and FVP of *o*-(4-pentenyl)toluene (**24**) appears to result in a retro-ene reaction rather than the hydrogen-atom transfer.

In solution phase, **10** undergoes rearrangement to **12**, instead of cyclization. A radical chain mechanism is proposed for the rearrangement.

EXPERIMENTAL

Methods and materials.

Some general methods[1] and the pyrolysis apparatus[23] have been described previously. ^{1}H NMR spectra were obtained on a Nicolet NT-300 instrument. ^{13}C NMR spectra were obtained on a Varian VXR-300 instrument. Chemical shifts are relative to tetramethylsilane or the accepted chemical shift of the solvent. IR spectra were obtained on a Digilab FTS-7 spectrophotometer. GCMS was performed on a Finnegan 4500 spectrophotometer with 70-eV EI after separation on a DB-1701 capillary column or on a Finnegan Magnum spectrophotometer with 70-eV EI after separation on a DB-5 capillary column. Exact mass determinations were performed on a Kratos 50 spectrophotometer. Combustion analyses were performed by Galbraith Laboratories, Inc.

***o*-Allyltoluene (6).**[3] *o*-Allyltoluene (**6**) was prepared by a previously published procedure.[5] ^{1}H NMR ($CDCl_3$) δ 7.12 (s, 4 H), 5.94 (qt, J_q = 10.3 Hz, J_t = 6.4 Hz, 1 H), 5.04 (dq, J_d = 10.1 Hz, J_q = 1.6 Hz, 1 H), 4.98 (dq, J_d = 17.0 Hz, J_q = 1.7 Hz, 1 H), 3.36 (dq, J_d = 6.3 Hz, J_t = 1.6 Hz, 2 H), 2.28 (s, 3 H) [lit.[2b] ^{1}H NMR (CCl_4) δ 6.94 (s, 4 H), 5.79 (qt, J_q = 11.3 Hz, J_t = 6.5 Hz, 1 H), 4.93 (m, 1 H), 4.79 (dq, J_d = 11.3 Hz, J_q = 2.1 Hz, 1 H), 3.24 (dt, J_d = 6.0 Hz, J_t = 1.8 Hz, 2 H), 2.20 (s, 3 H)]; GCMS *m/e* (% base peak) 132 (77.5), 117 (100), 115 (42.3), 91 (35.6), 65 (31.6) [lit.[2b] MS (50 eV) *m/e* 132 (parent), 117 (base)].

***o*-Methallyltoluene (10).** o-Methallyltoluene (**10**) was prepared in 26% yield from o-tolylmagnesium bromide and methallyl chloride by a method patterned after Hurd's procedure:[22] ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.18-7.10 (m, 4 H), 4.84-4.80 (m, 1 H)), 4.52-4.50 (m, 1 H)), 3.32 (s, 2 H), 2.27 (s, 3 H), 1.74 (s, 3 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 144.9, 138.3, 137.3, 130.4, 130.1, 126.6, 126.1, 111.5, 42.0, 22.8, 19.5; IR (thin film) ν 3075, 3019, 2970, 2916, 1650, 1494, 1446, 1375, 891 cm^{-1}; GCMS (70 eV) *m/e* (% base peak) 146 (57.6), 131 (100), 129 (16.1), 128 (17.3), 116 (14.5), 115 (24.0), 105 (11.4), 91 (35.0), 77 (10.4); HRMS *m/z* for $C_{11}H_{14}$ (M^+) calcd. 146.10955, found 146.10932.

2,2-Dimethylindan-1-one. This was prepared based on the previously published procedure.[24] ^{1}H NMR δ 7.69-7.60 (m, 2 H), 7.54-7.47 (m, 1 H), 7.45-7.36 (1 H, m), 3.02 (s, 2 H), 1.17 (s, 6 H)

2,2-Dimethylindan (13). Preparation was based on the previously published procedure.[25] ^{1}H NMR δ 7.16-7.02 (m, 4 H), 2.69 (s, 4 H), 1.12 (s, 6 H); GCMS (70 eV) *m/e* (% base peak) 146 (43.1), 131 (100), 115 (15.2), 91 (26.3).

***o*-Allylethylbenzene (17).** o-Allylethylbenzene (**17**) was prepared in 31% yield by a method patterned after Hurd's procedure:[22] ^{1}H NMR δ 7.19-7.09 (m, 4 H), 5.97 (ddt, J_d = 16.9 Hz, J_d = 10.3 Hz, J_t = 6.5 Hz, 1 H), 5.03-4.91 (m , 2 H), 3.41 (dt, J_d = 7.31 Hz, J_t = 1.5 Hz, 2 H), 2.65 (q, J = 7.5 Hz, 2 H), 1.18 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 142.7, 138.0, 137.9, 129.8, 128.7, 126.8, 126.2, 115.6, 37.3, 25.9, 15.4; IR (thin film) ν 3060, 3014, 2965, 2930, 2870, 1640, 1600, 1485, 1450, 1430, 990, 912 cm^{-1}; GCMS (70 eV) *m/e* (% base peak) 146 (24.1), 145 (16.1), 131 (100), 129 (15.0), 128 (12.1), 117 (41.7), 116 (21.5), 115 (35.0), 91 (5.4), 89 (5.2); HRMS *m/z* for $C_{11}H_{14}$ (M^+) calcd. 146.10955, found 146.10926. Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 88.99; H, 9.66

1-(*o*-Propylphenyl)ethanol. Preparation was patterned after Seebach's method,[26] employing propyl bromide as the electrophile. 1-(*o*-Propylphenyl)ethanol was obtained in 3% yield as a clear oil: ^{1}H NMR δ 7.55-7.47 (m, 1 H), 7.19-7.07 (m, 3 H), 5.16-5.05 (m, 1 H), 3.974 (d, *J* = 3.9 Hz, 1 H), 2.65-2.56 (m, 2 H), 1.73-1.53 (m, 2 H), 1.37 (d, *J* = 6.4 Hz, 3 H), 0.96 (t, *J* = 7.3 Hz, 3 H)

1-(*o*-Propylphenyl)ethyl acetate. Treatment of 1-(*o*-propylphenyl)ethanol with acetyl chloride in ether and triethylamine gave 1-(*o*-propylphenyl)ethyl acetate as a clear oil in 55% yield. ^{1}H NMR δ 7.44-7.36 (m, 1 H), 7.22-7.11 (m, 3 H), 6.09 (q, *J* = 6.5 Hz, 1 H), 2.75-2.55 (m, 2 H), 1.99 (s, 3 H), 1.73-1.53 (m, 2 H), 1.67 (d, *J* = 6.6 Hz, 3 H), 0.97 (t, *J* = 7.3 Hz, 3 H)

***o*-Propylstyrene (20).** 1-(*o*-Propylphenyl)ethyl acetate was pyrolyzed at 600° C and 0.1 torr. The pyrolysate was dissolved in acetone-d6 and neutralized. ^{1}H NMR spectroscopy showed peaks that were consistent with formation of *o*-propylstyrene (**20**) and E-2-(1-propenyl)-toluene (**19**) in a ratio of about 4 : 1. Comparison of the GC retention times and GCMS fragmentation patterns of **19** and **20** clearly established that both are produced during the FVP of **17**. Compound **20** was also identified by comparision of ^{1}H NMR spectra:[27] E-2-(1-propenyl)-toluene (**19**): ^{1}H NMR δ (aryl protons and methylene protons are obscured due to overlap) 6.68 (dt, J_d = 15.5 Hz, J_t = 1.5 Hz, 1 H), 6.13 (qd, J_d = 15.5 Hz, J_q = 7.6 Hz, 1 H), 1.87 (dd, J_d = 7.6 Hz, J_d = 1.7 Hz, 3 H), 0.93 (t, J = 7.6 Hz, 3 H); *o*-propylstyrene (**20**): ^{1}H NMR δ (aryl protons of **19** and **20** overlap) 7.34 (dd, J_d = 17.0 Hz, J_d = 11.0 Hz, 1 H), 5.57 (dd, J_d = 17.0 Hz, J_d = 1.5 Hz, 1 H), 5.26 (dd, J_d = 11.0 Hz, J_d = 1.5 Hz, 1 H), 2.66 (t, J = 7.7 Hz, 2 H), 1.58 (m, 2 H), 0.93 (t, J = 7.3 Hz, 3 H); [lit.[26] ^{1}H NMR ($CDCl_3$) δ 7.2 (m, 4 H), 7.06 (dd, J_d = 17 Hz, J_d = 12 Hz, 1 H), 5.66 (d, J = 17 Hz, 1 H), 5.30 (d, J = 12 Hz, 1 H), 2.67 (t, 2 H), 1.60 (m, 2 H), 1.14 (t, J = 8 Hz, 3 H)];

***o*-Allylcumene (21).** *o*-Allylcumene (**21**) was formed in 31% yield by the addition of allyl bromide to *o*-cumylmagnesium bromide in a method patterned after Hurd's procedure:[22] ^{1}H NMR (CD_2Cl_2) δ 7.31-7.24 (m, 1 H), 7.22-7.15 (m, 1 H), 7.13-7.07 (m, 2 H), 6.00 (ddt, J = 16.9, 10.3, 6.2 Hz, 1 H), 5.03-4.90 (m, 2 H), 3.43 (dt, J = 5.5, 1.5 Hz. 2 H), 3.19 (septet, J = 6.9 Hz, 1 H), 1.20 (s, J = 7.1 Hz, 6 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 147.4, 138.3, 137.1, 130.0, 127.0, 126.0, 125.6, 115.5, 37.1, 29.1, 24.0; Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06; IR (thin film) ν 3066, 3018, 2962, 2926, 2867, 1636, 1600, 1488, 1449, 1430, 1033, 993, 913 cm^{-1}; HRMS *m/z* for $C_{12}H_{16}$ (M^+) calcd. 160.12520, found 160.12530. Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.10; H, 9.80.

***o*-(3-Butenyl)toluene (23).**[3] *o*-(3-Butenyl)toluene (**23**) was prepared in 64% yield by the addition of allylmagnesium bromide to α-chloro-*o*-xylene: ^{1}H NMR ($CDCl_3$) δ 7.17–7.07 (m, 4 H), 5.84 (qt, J_q = 10.2 Hz, J_t = 6.6 Hz, 1 H), 5.04 (dq, J_d = 17.1 Hz, J_q = 1.5 Hz, 1 H), 4.98 (ddt, J_d = 10.2 Hz, J_d = 1.8 Hz, J_t = 1.2 Hz, 1 H), 2.73–2.65 (m, 2 H), 2.37–2.27 (m, J = 7 Hz, 2 H), 2.31 (s, 3 H); [lit.[28] ^{1}H NMR ($CDCl_3$) δ 7.08 (4 H, broad), 6.2-4.8 (4 H, broad), 2.25 (3 H, s)]; GCMS (70 eV) *m/e* (% base peak) 146 (15.4), 105 (100), 91 (3.1), 77 (10.9) [lit.[26] 146, 105 (base peak), 91].

o-(4-Pentenyl)toluene (24).[3] Preparation was based on the procedure reported by Nishimura and co-workers.[29] Reaction of *o*-tolylmagnesium bromide and 5-bromo-1-pentene afforded *o*-(4-pentenyl)toluene in 40 % yield: ^{1}H NMR ($CDCl_3$) δ 7.15–7.05 (m, 4 H), 5.85 (qt, J_q = 10.2 Hz, J_t = 6.7 Hz, 1 H), 5.04 (dq, J_d = 17.1 Hz, J_q = 1.7 Hz, 1 H), 4.98 (ddt, J_d = 10.2 Hz, J_d = 2.2 Hz, J_t = 1.2 Hz, 1 H), 2.64–2.55 (m, 2 H), 2.30 (s, 3 H), 2.19–2.11 (m, 2 H), 1.71–1.65 (m, 2 H) [lit.[30] ^{1}H NMR ($CDCl_3$) δ 7.08 (4 H), 5.88 (1 H), 5.05 (2 H), 2.60 (2 H), 2.28 (3 H), 2.6–1.3 (4 H)]; GCMS (70 eV) *m/e* (% base peak) 160 (16.4), 118 (78.4), 106 (33.8), 105 (100), 91 (40.7), 77 (26.7).

Flash vacuum pyrolysis. Flash vacuum pyrolysis (FVP) was performed as described by Malandra.[1]

Product analysis. FVP reaction mixtures were analyzed by capillary gas chromatography on Hewlett-Packard HP5840A and HP5890 gas chromatographs equipped with a 30-m (0.25-μm film thickness) DB-1701 capillary column and a flame ionization detector. The temperature program on the HP5840A was set at 80 °C for 10 min, followed by heating at 3 °C min^{-1} to a final temperature of 250

The temperature program on the HP5840A was set at 80 °C for 10 min, followed by heating at 3 °C min^{-1} to a final temperature of 250 °C. The temperature program on the HP5890 was set at 70 °C for 10 min, followed by heating at 3 °C min^{-1} to a final temperature of 250 °C.

GC analysis was performed by injecting 1 μL of the pyrolysate/biphenyl solution. Triplicate pyrolyses were performed, with the exception of FVP of **21** at 700 °C, for which duplicate analysis was performed. Peaks not appearing in all GC traces for a series of pyrolysis runs were discarded. For most major compounds, FID response factors were calculated (**1-7**, **10**, **13**, **28-30**, toluene, ethylbenzene, *m/p*-xylenes, 1-methylnaphthalene, and 2-methylnaphthalene). Other compounds were assigned a response factor equal to biphenyl. Except where noted, percentages are for moles of product relative to total moles of starting material. Identification of products was based on GC retention time of authentic samples or those samples whose identity could be clearly established by NMR or GCMS. GCMS was used to determine the molecular weights of minor products where possible.

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APPENDIX 1

SPECTRA

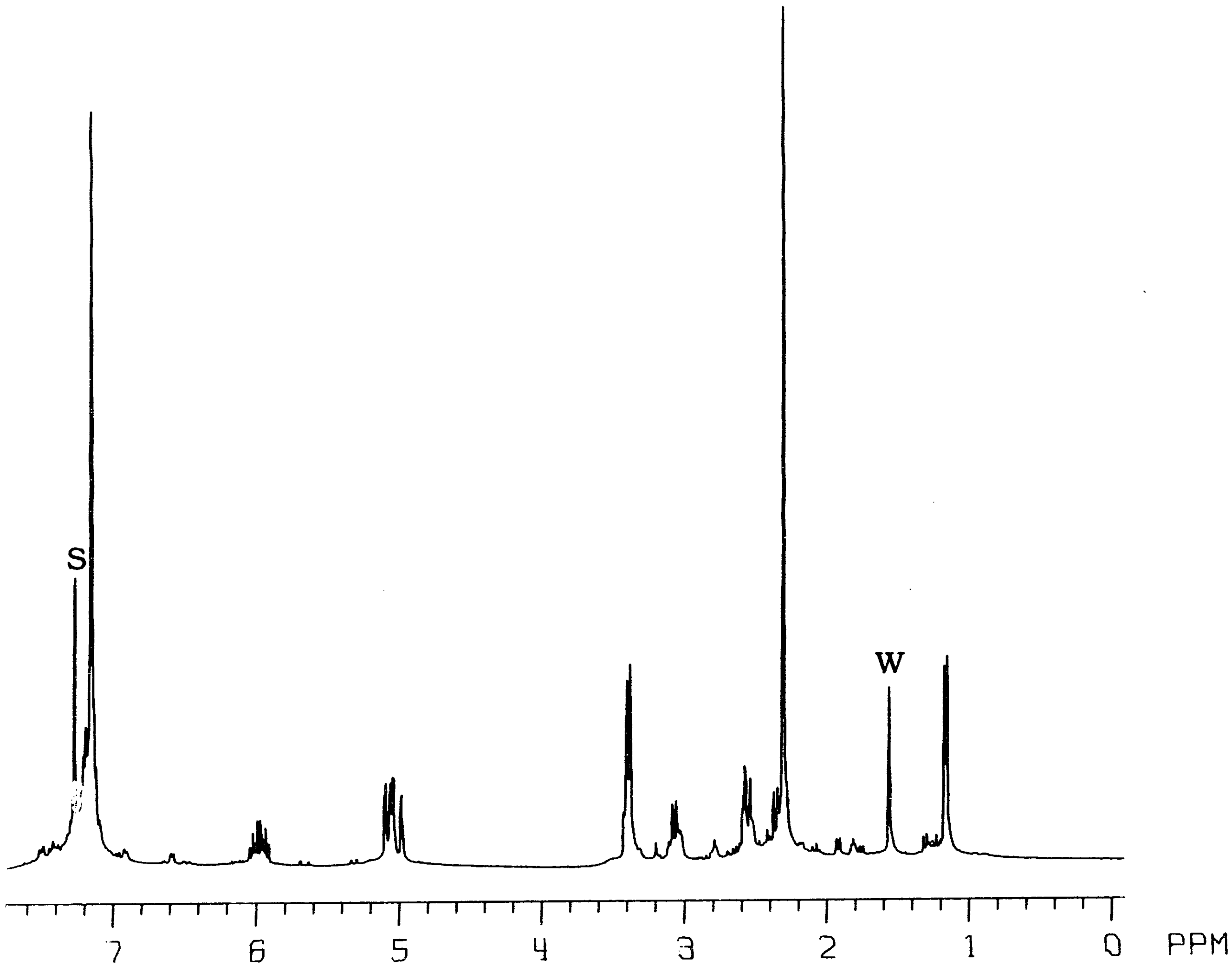


Figure A-1. ^1H NMR spectrum (300 MHz, $CDCl_3$) of the pyrolysis mixture from the FVP at 800 °C of *o*-allyltoluene (**6**) (S: chloroform, W: H_2O).

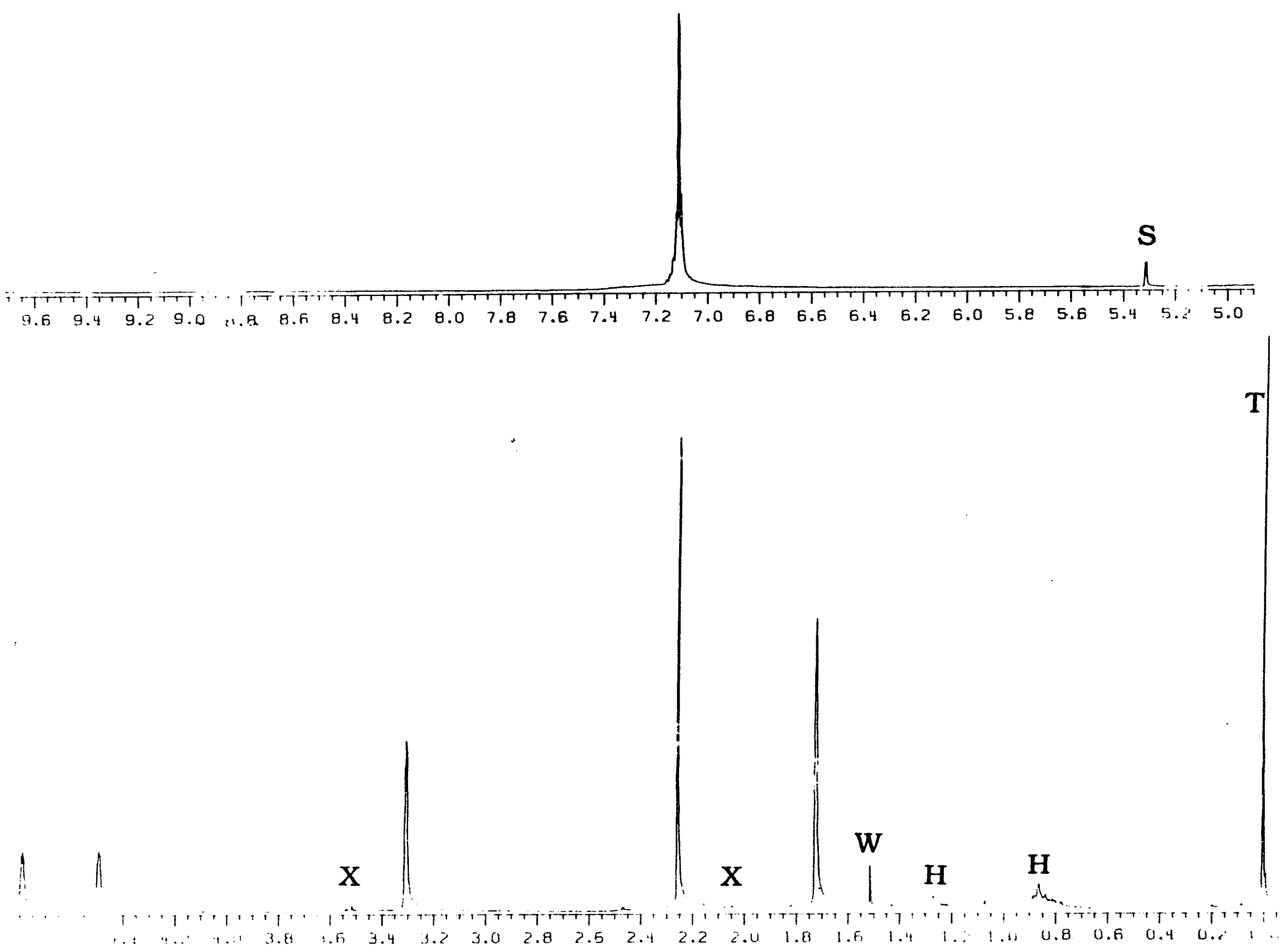


Figure A-2A. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of *o*-methallyltoluene (**10**) (S: $CHDCl_2$, W: H_2O, T: tetramethylsilane, H: high-boiling residue from hexanes, X: unidentified impurity).

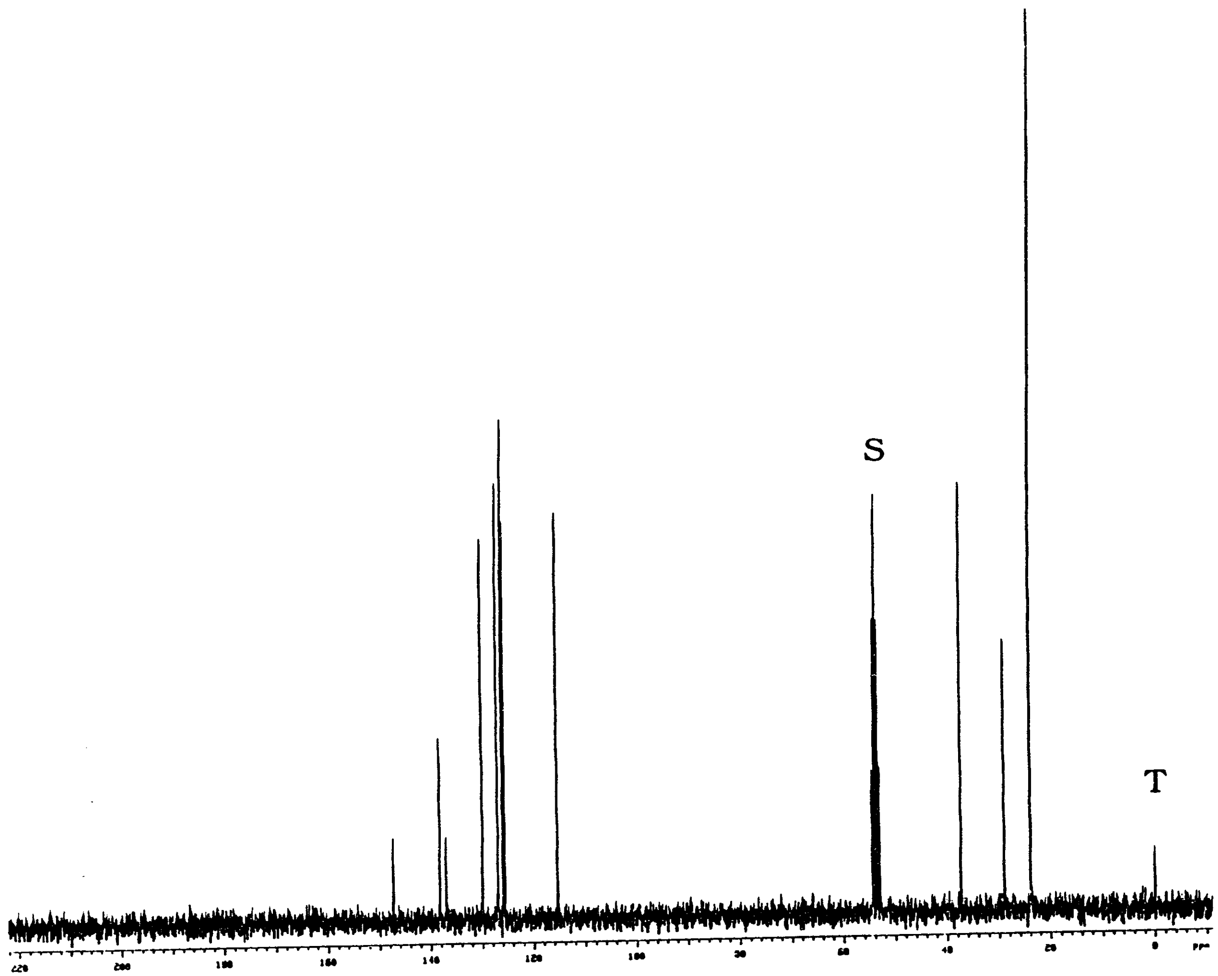


Figure A-2B. ^{13}C NMR spectrum (75.5 MHz, CD_2Cl_2) of *o*-methallyltoluene **(10)** (S: CD_2Cl_2, T: tetramethylsilane).

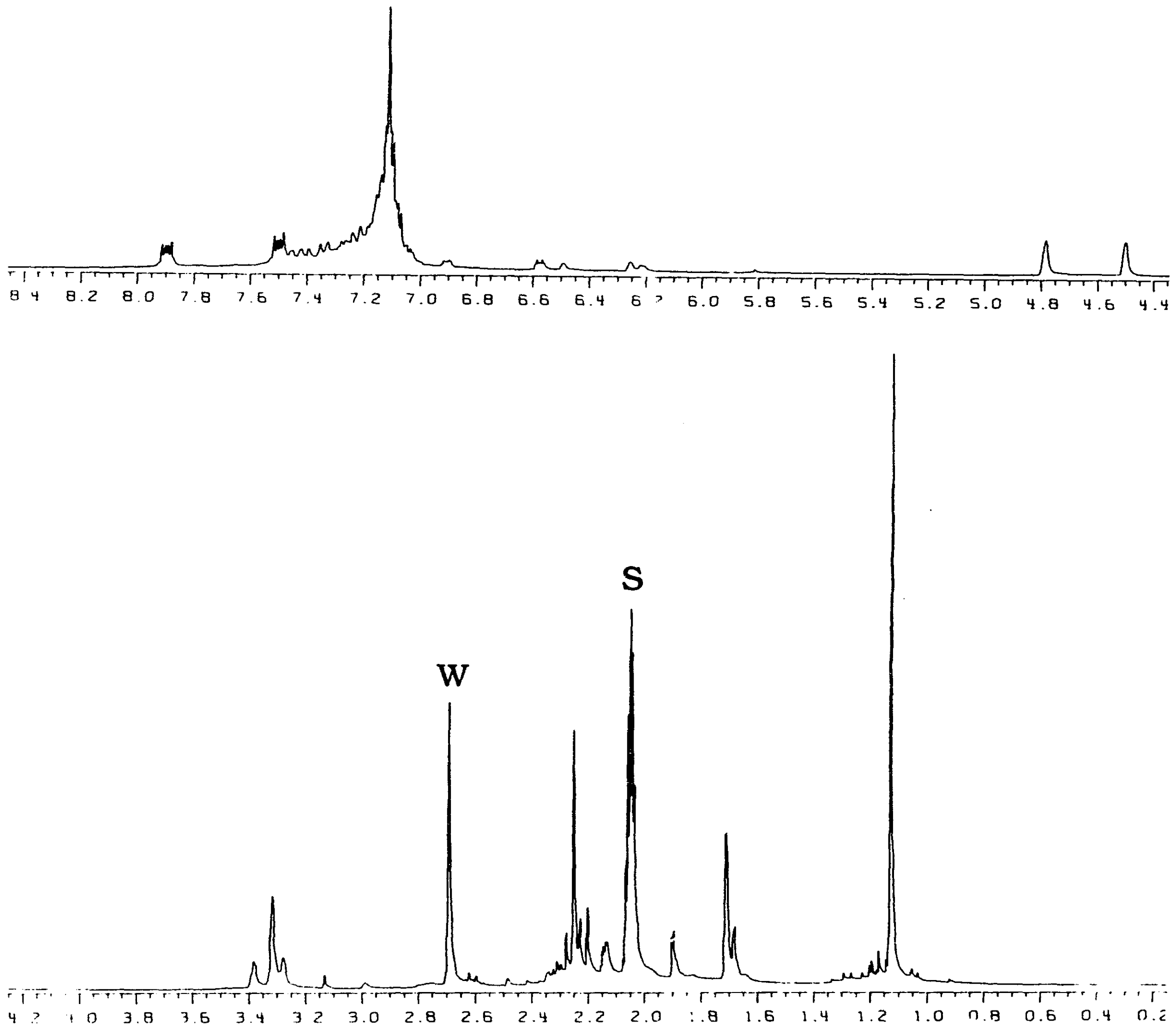


Figure A-3. ^{1}H NMR spectrum (300 MHz, acetone-d_6) of the pyrolysis mixture from the FVP at 850 °C of *o*-methallyltoluene (**10**) (S: acetone-d_5, W: H_2O).

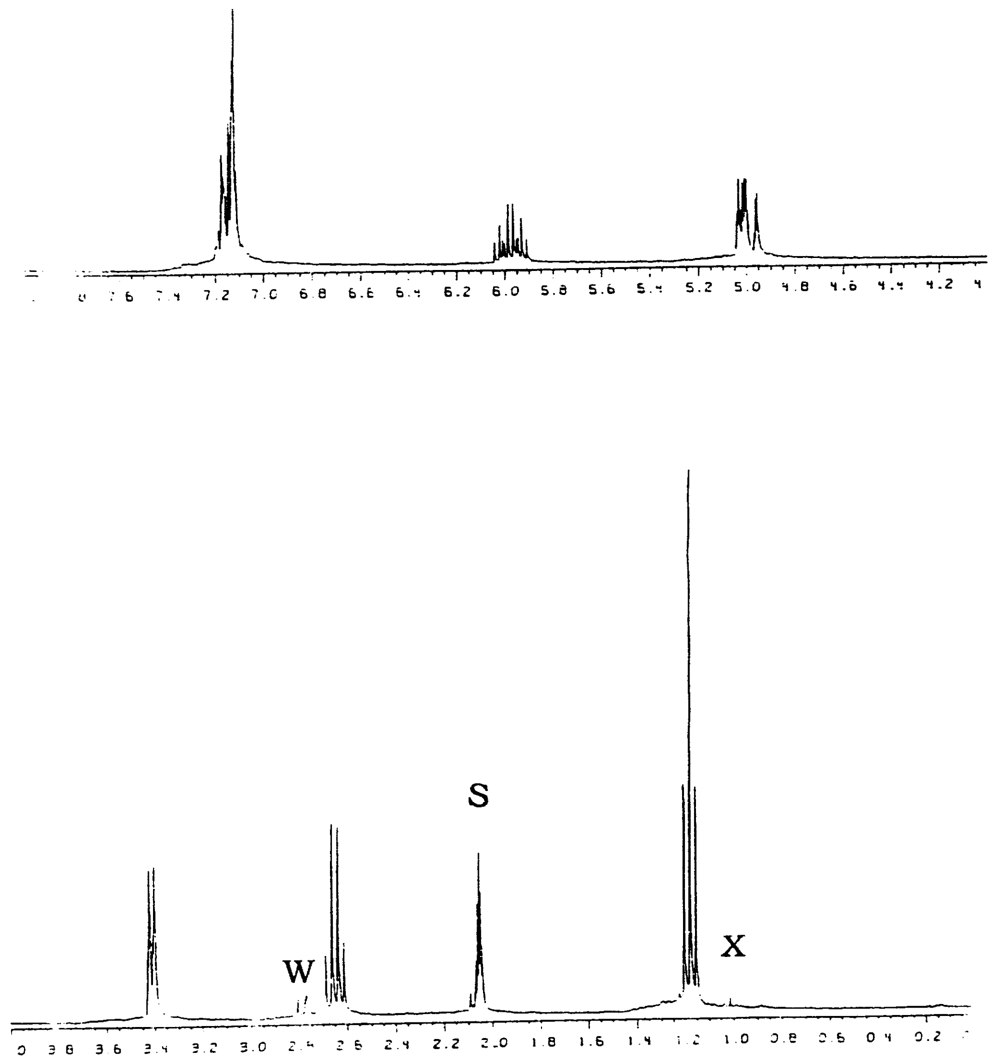


Figure A-4A. ^1H NMR spectrum (300 MHz, acetone-d_6) of *o*-allylethylbenzene (**17**) (S: acetone-d_5, W: H_2O, X: unidentified impurity).

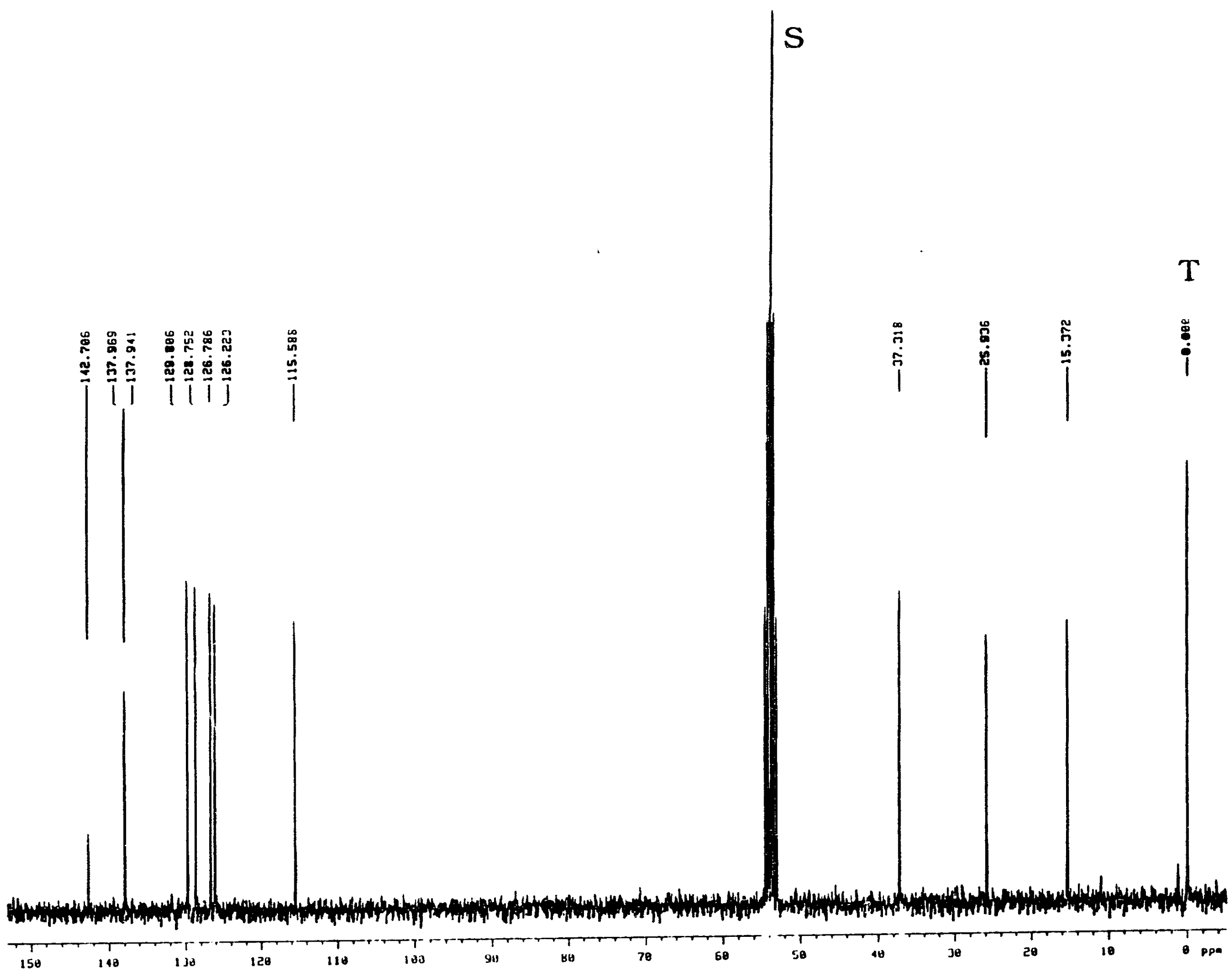


Figure A-4B. ^{13}C NMR spectrum (75.5 MHz, CD_2Cl_2) of *o*-allylethylbenzene (**17**) (S: CD_2Cl_2, T: tetramethylsilane).

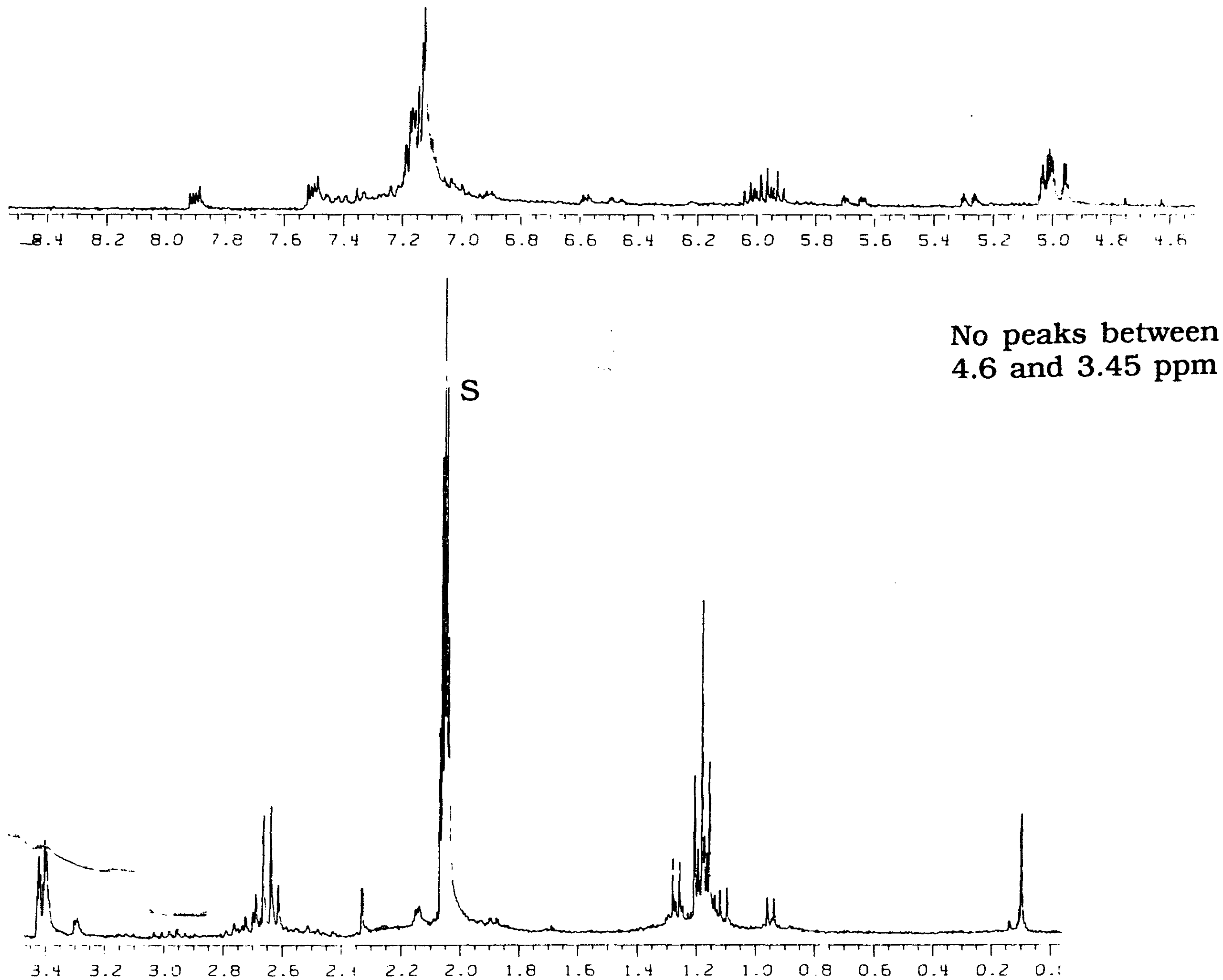
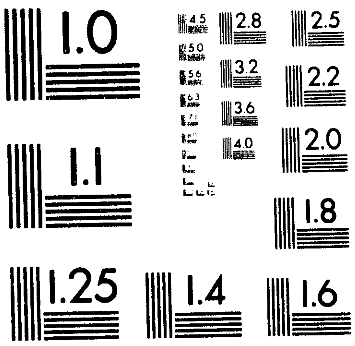


Figure A-5. ^{1}H NMR spectrum (300 MHz, acetone-d_6) of the pyrolysis mixture from the FVP at 750 °C of *o*-allylethylbenzene (**17**) (S: acetone-d_5).


1.0
2.8
2.5
3.2
2.2
3.6
2.0
4.0
1.1
1.8
1.25
1.4
1.6

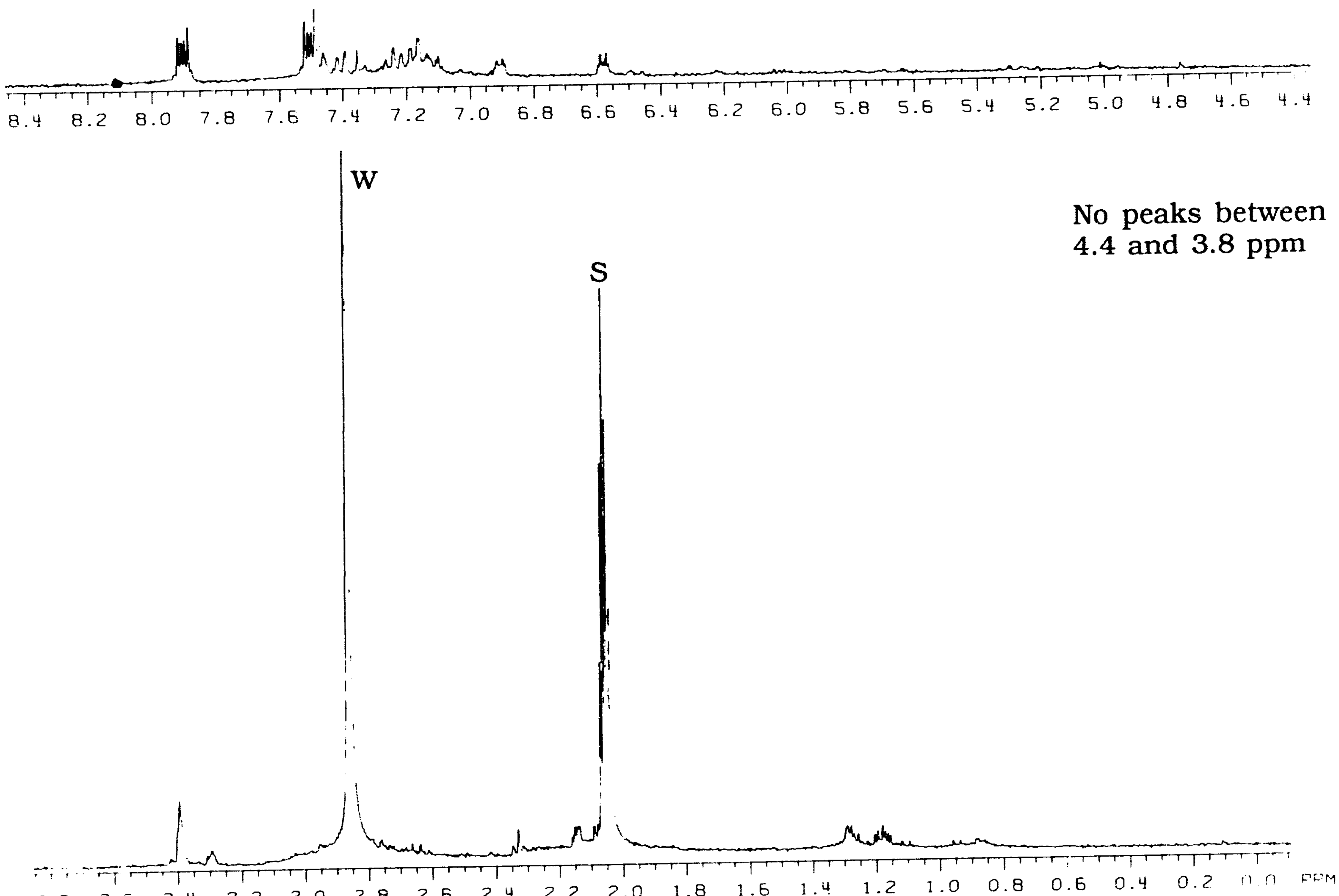


Figure A-6. ^{1}H. NMR spectrum (300 MHz, acetone-*d6*) of the pyrolysis mixture from the FVP of *o*-allylethylbenzene (**17**) at 800 °C (S: acetone-*d5*, W: H_2O).

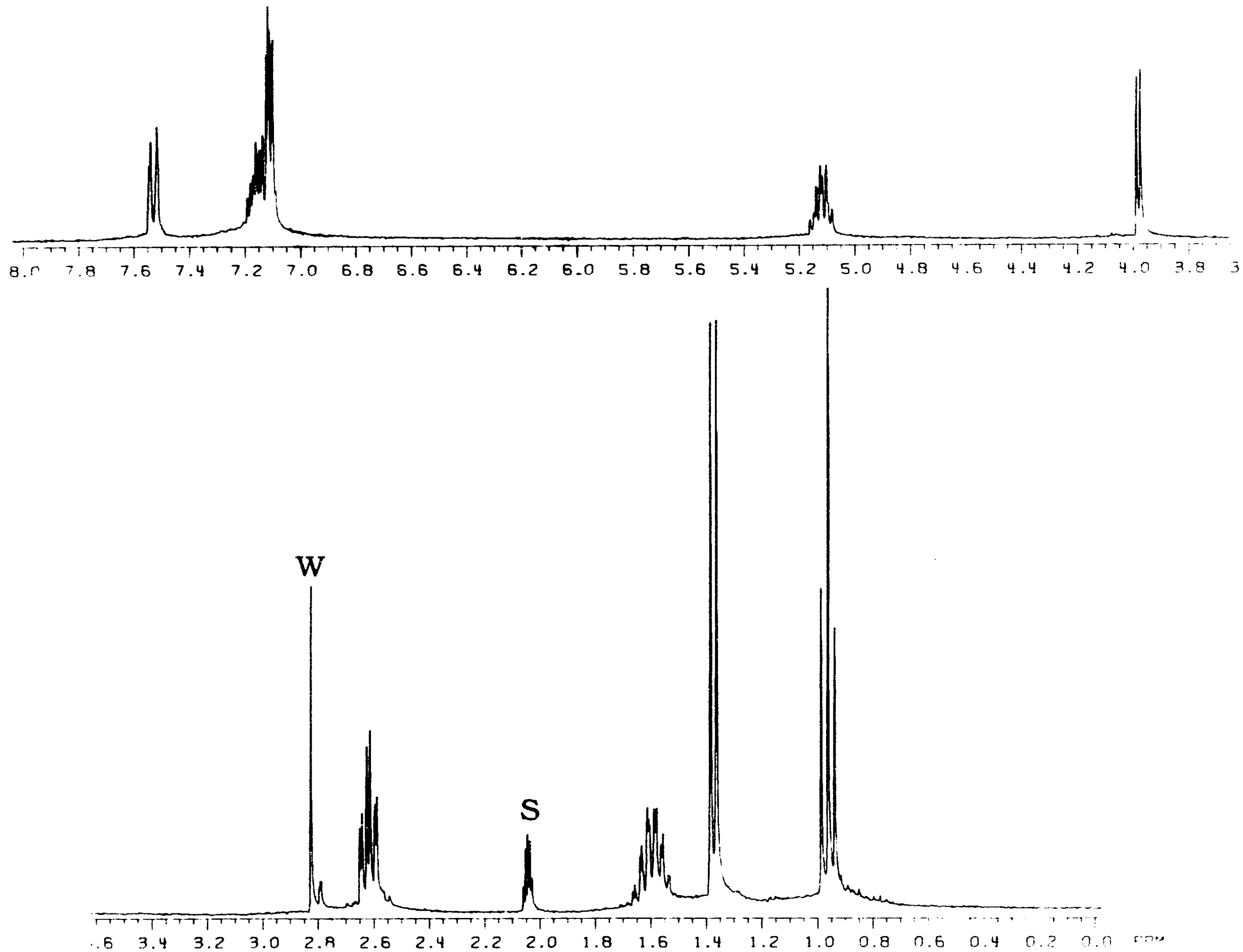


Figure A-7. ^{1}H NMR spectrum (300 MHz, acetone-*d*6) of 1-(*o*-propylphenyl)ethanol (S: acetone-*d*5, W: H_2O).

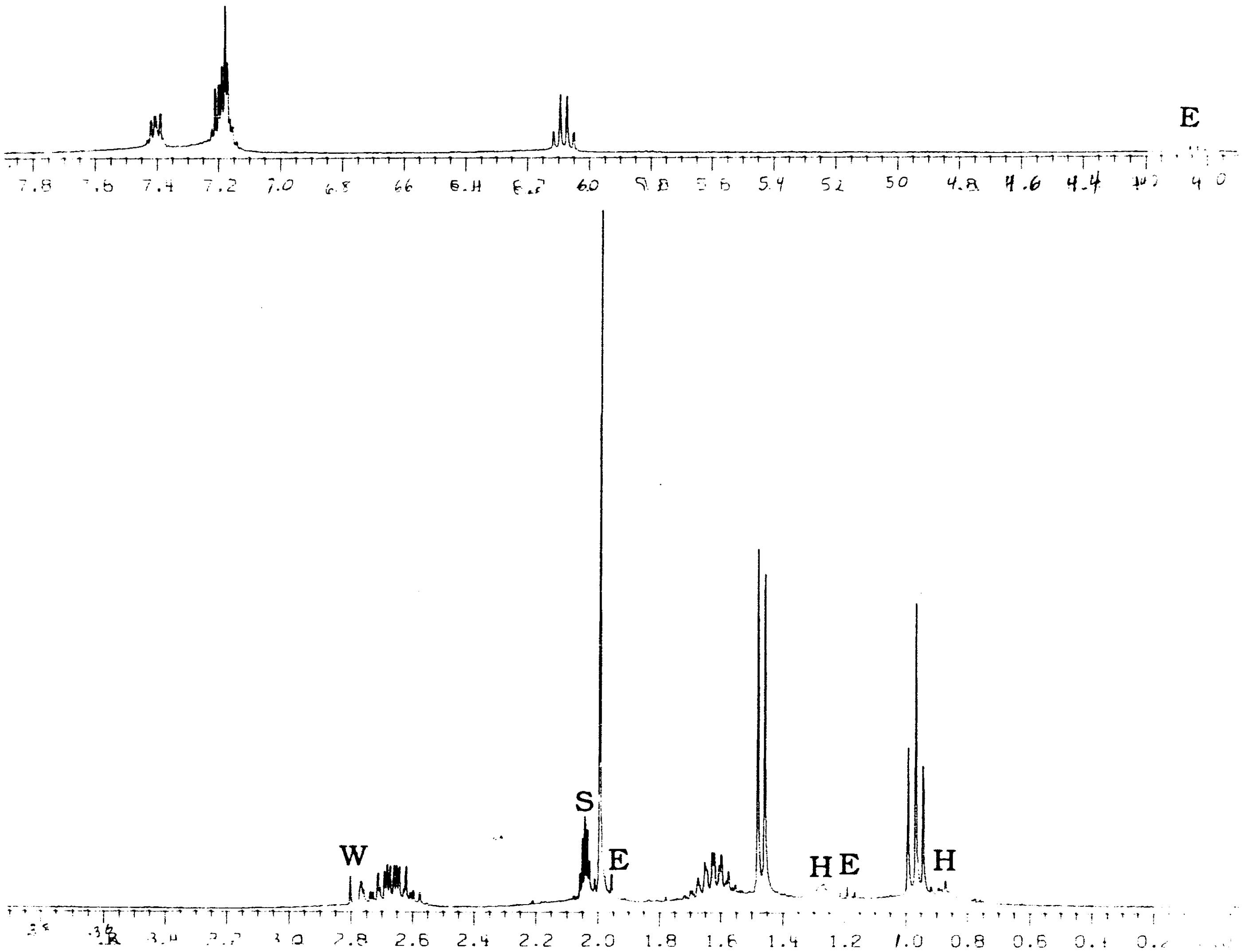


Figure A-8. ^1H NMR spectrum (300 MHz, acetone-d_6) of 1-(o-propylphenyl)ethyl acetate (S: acetone-d_5, W: H_2O, H: high-boiling residue from hexanes, E: ethyl acetate).

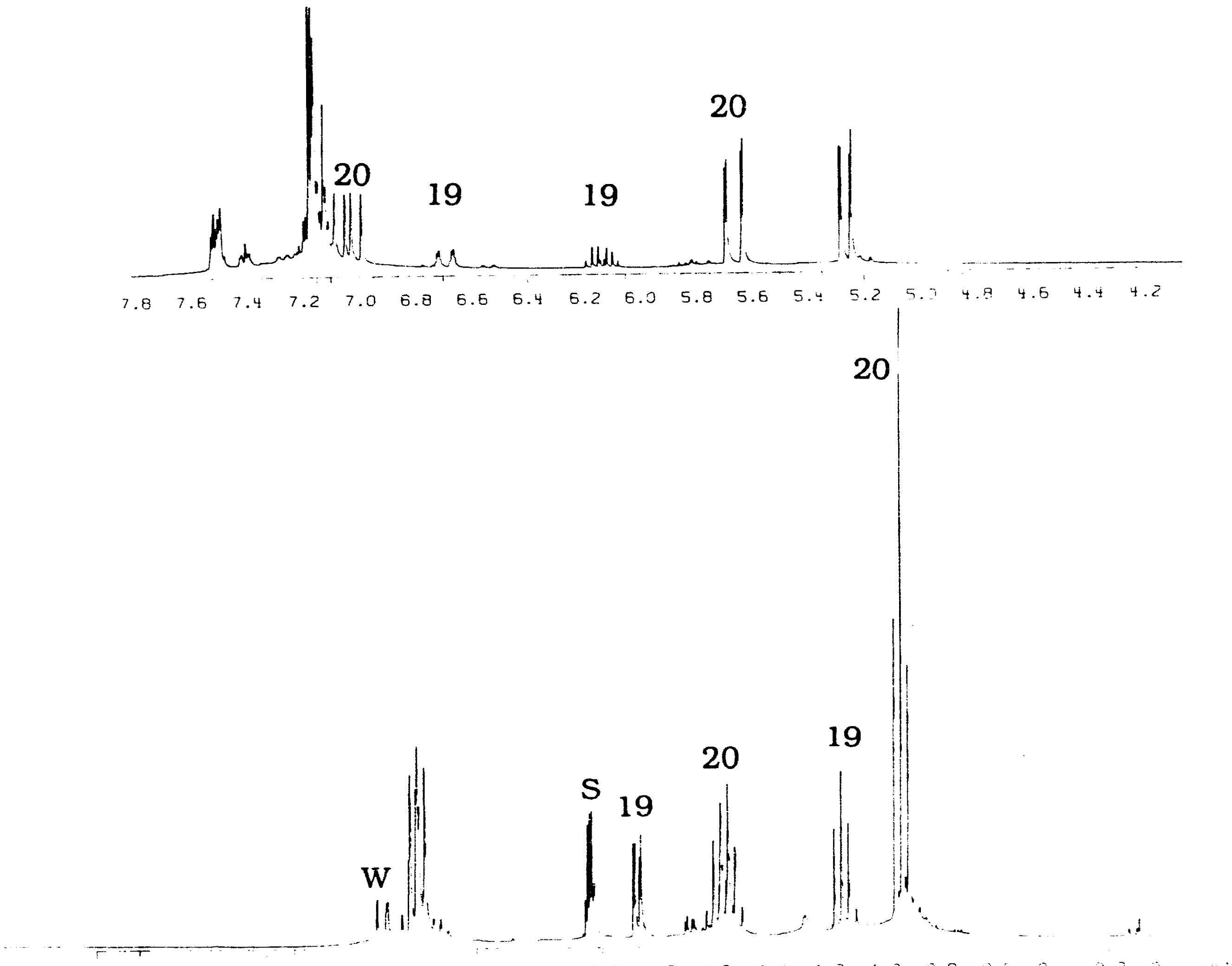


Figure A-9. ^1H NMR spectrum (300 MHz, acetone-d_6) of the pyrolysis mixture from the FVP of 1-(o-propylphenyl)ethyl acetate, showing E-2-(1-propenyl)-toluene (**19**), and *o*-propylstyrene (**20**) (19: Compound **19**, 20: Compound **20**, S: acetone-d_5, W: H_2O).

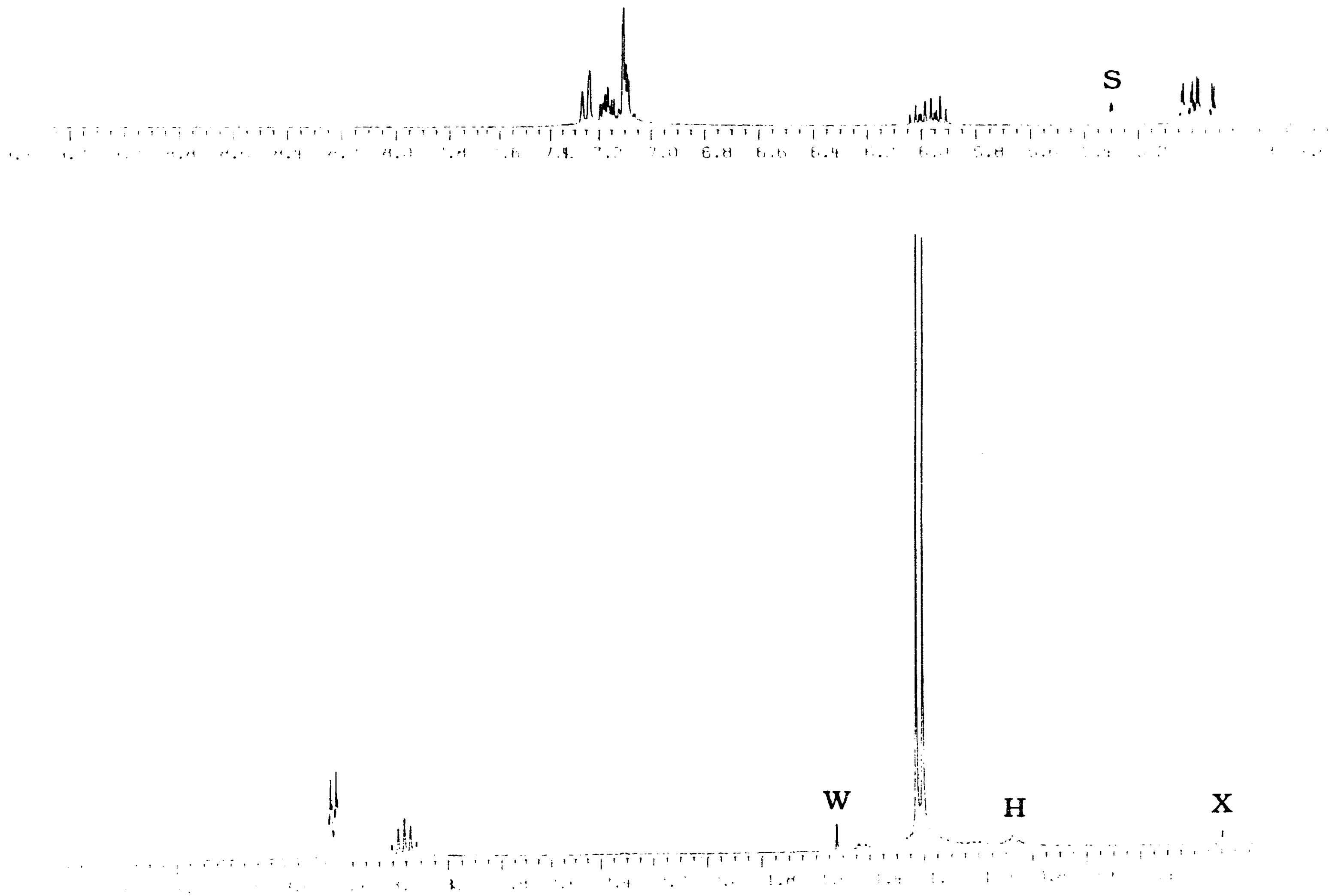


Figure A-10A. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of *o*-allylcumene (**21**) (S: $CHDCl_2$, W: H_2O, H: high-boiling residue from hexanes, X: unidentified impurity).

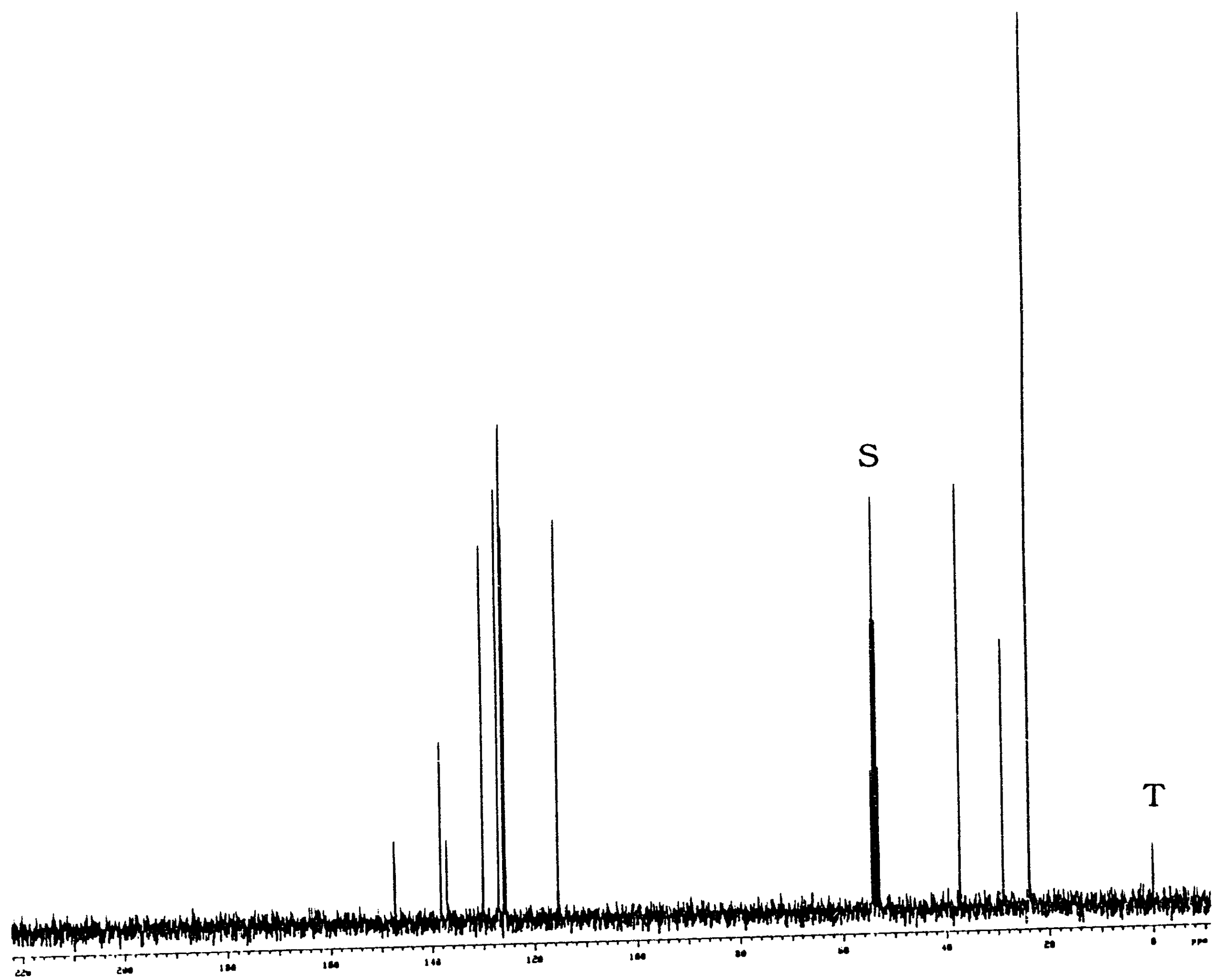


Figure A-10B. ^{13}C NMR spectrum (75.5 MHz, CD_2Cl_2) of *o*-allylcumene (**21**) (S: CD_2Cl_2, T: tetramethylsilane).

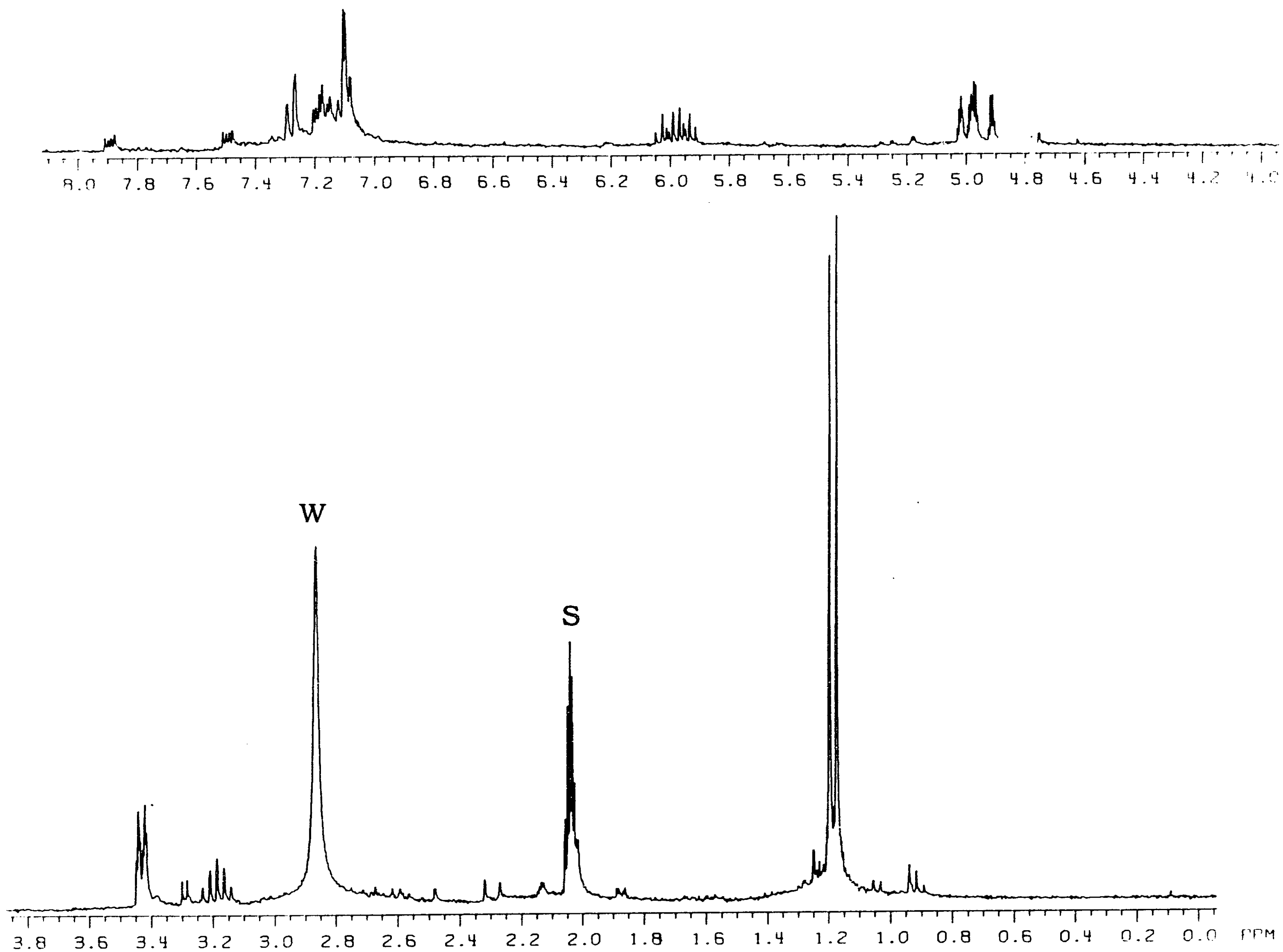


Figure A-11. ^1H NMR spectrum (300 MHz, acetone-*d6*) of the pyrolysis mixture from the FVP at 700 °C of *o*-allylcumene (**2i**) (S: acetone-*d5* W: H_2O).

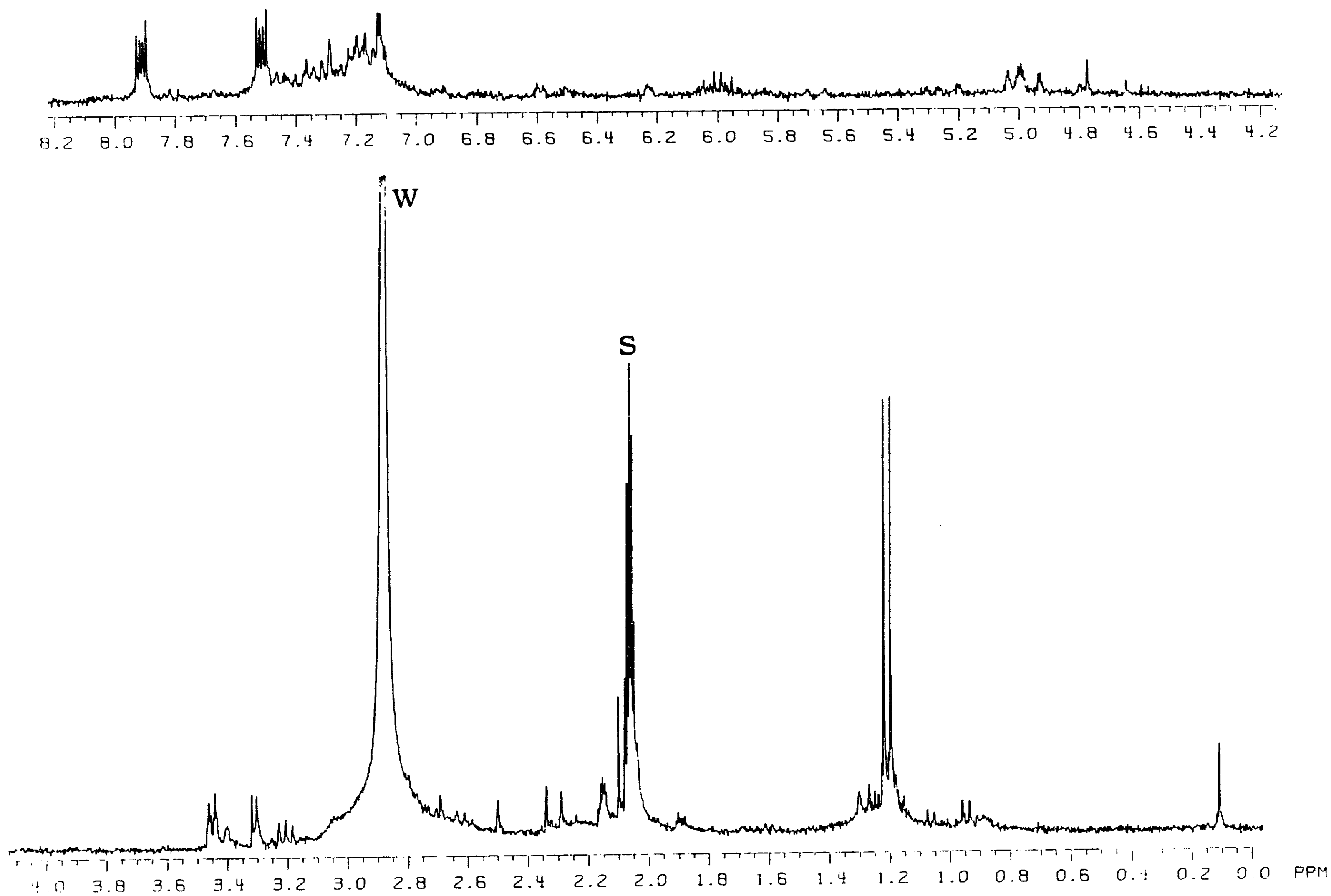


Figure A-12. ^1H NMR spectrum (300 MHz, acetone-d_6) of the pyrolysis mixture from the FVP at 750 °C of *o*-allylcumene (**21**) (S: acetone-d_5 W: H_2O).

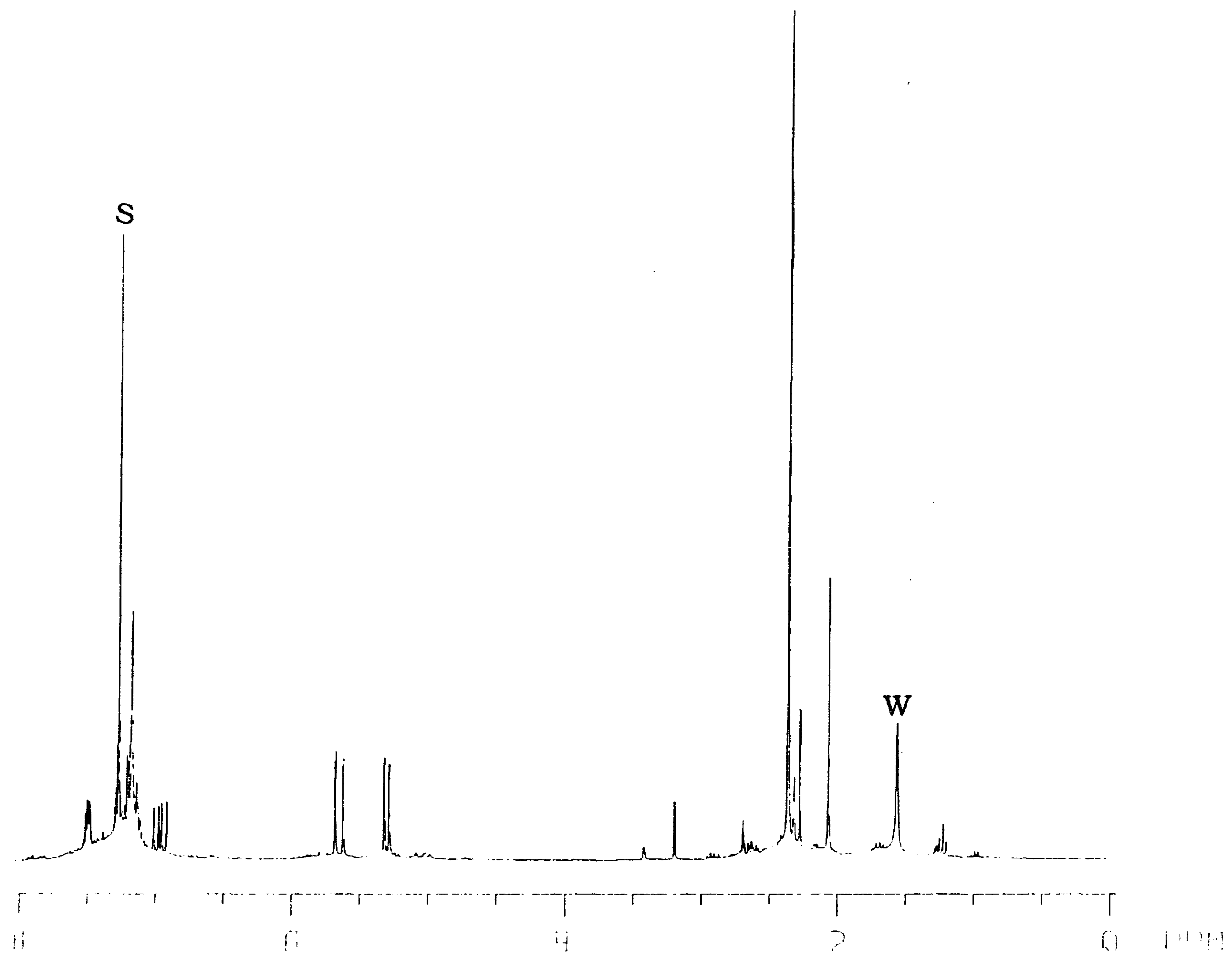


Figure A-13. ^1H NMR spectrum (300 MHz, $CDCl_3$) of the pyrolysis mixture from the FVP at 800 °C of *o*-(4-pentenyl)toluene (**24**) (S: chloroform, W: H_2O).

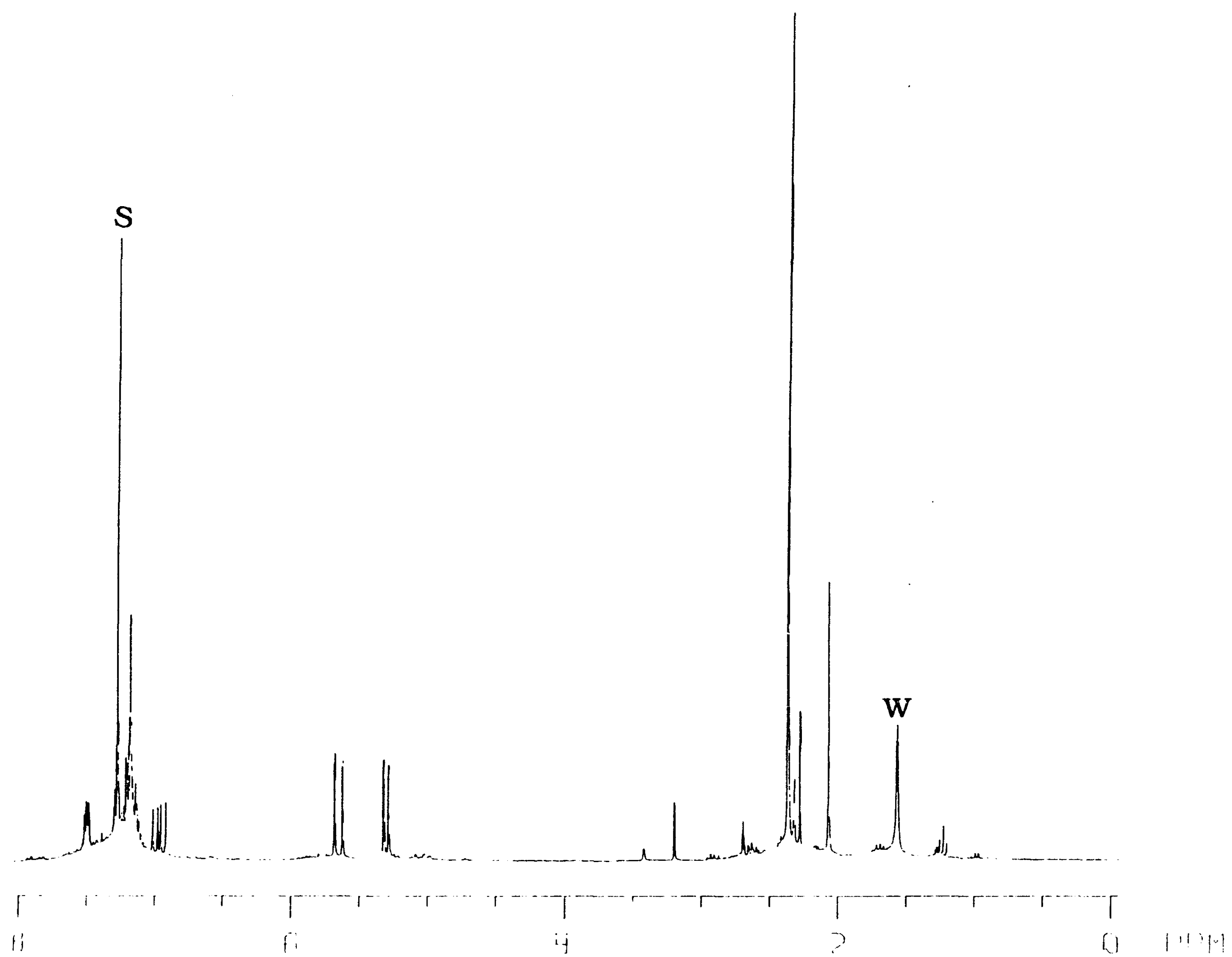


Figure A-13. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the pyrolysis mixture from the FVP at 800 °C of *o*-(4-pentenyl)toluene (**24**) (S: chloroform, W: H_2O).

APPENDIX 2

SUPPLEMENTARY DATA TABLES

Table A-I. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-allyltoluene (**6**) at various temperatures [a, b]

	yield, % [c]			
entry	RT [d]	700 °C	800 °C	900 °C
toluene	0.57	—	1.05	3.03
ethylbenzene	—	—	0.55	1.92
m/*p*-xylene	—	—	0.51	0.18
o-xylene (**28**)	—	—	0.23	1.92
styrene (**3**)	—	—	0.75	3.45
benzocyclobutene (**2**)	—	—	0.35	1.19
allylbenzene	—	—	—	0.26
propylbenzene	—	—	—	0.12
o-ethyltoluene (**29**)	—	—	1.46	0.94
AA-118 [C_9H_{10}]	—	—	—	0.09
o-methylstyrene (**30**)	—	1.02	3.18	5.52
AB-118 [C_9H_{10}]	—	—	—	0.29
benzaldehyde	—	—	—	0.17
indan	—	—	—	0.68
trans-ß-methylstyrene	—	—	—	0.11
m/*p*-allyltoluene	1.94	1.97	1.76	0.79
o-allyltoluene (**6**)	96.47	90.94	45.35	6.56

Table A-I continues on next page

Table A-I. Continued

entry	yield, % [c]			
	RT [d]	700 °C	800 °C	900 °C
indene (**7**)	—	0.83	6.86	31.98
2-methylindan (**8**)	—	4.09	25.34	14.08
1-methylindan	—	—	1.43	0.60
TD-130 [$C_{10}H_{10}$]	—	—	0.14	0.92
TE-130 [$C_{10}H_{10}$]	—	—	—	0.11
o-methylbenzaldehyde	—	—	0.28	0.15
o-(1-propenyl)toluene (**11**)	—	—	3.05	3.68
TH-130 [$C_{10}H_{10}$]	—	—	—	0.18
3-methylindene (**16**)	—	—	0.72	3.47
tetralin (**1**)	—	0.32	2.74	3.28
2-methylindene (**15**)	—	—	0.42	0.73
TK-130 [$C_{10}H_{10}$]	—	—	1.20	2.43
1,2-dihydronaphthalene (**4**)	—	0.55	1.42	1.10
TL-128 [$C_{10}H_8$]	0.40	—	—	0.98
naphthalene (**5**)	0.39	—	0.96	8.10
TN	—	—	—	*e*
TO-148 [$C_{11}H_{16}$]	—	—	—	0.10
2-methylnapthalene	—	—	—	0.17
1-methylnapthalene	—	—	—	0.24
2,2'-dimethylbiphenyl	0.24	0.27	0.25	0.39
AC-182 [$C_{14}H_{14}$]	—	—	—	0.10

Table A-I continues on next page

Table A-I. Continued

entry	yield, % [c]			
	RT [d]	700 °C	800 °C	900 °C
recovery [f]	94.62	83.28	88.78	72.79
conversion [g]	d	9.06	54.65	93.44

[a] FVP conditions: system pressure = 0.10 torr, sample temperature = 0 °C. [b] Amounts determined by GC with a known quantity of biphenyl added as standard. Data represent the average of triplicate runs. Products identified by comparison with authentic samples by retention time and GCMS are indicated by name. Products that were identified by GCMS only are indicated by code: **X**Y-nnn, where '**X**' corresponds to the system where first observed (**T** = **1**, **A** = **6**, **M** = **10**, **E** = **17**, **C** = **21**, **B** = **23**, **P** = **24**, 'Y' to the individual unknown product (A, B, C, etc.), and 'nnn' to the nominal mass. [c] Moles of product divided by total moles of recovered material. [d] Starting material purity assay. [e] Unidentified product which constitutes ≤0.25% total area by GC. [f] Total moles of recovered material divided by moles of starting material used. [g] Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material.

Table A-II. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-methallyltoluene (**10**) at various temperatures [a,b]

	yield, % [c]				
entry	RT [d]	700°C	800 °C	850 °C	900 °C
toluene	3.28	0.27	0.68	1.93	3.73
ethylbenzene	0.01	—	1.03	2.53	3.18
m/*p*-xylene	—	—	0.75	0.15	—
o-xylene (**28**)	—	—	0.41	1.71	4.26
styrene (**3**)	—	—	—	1.10	4.96
benzocyclobutene (**2**)	0.03	0.13	0.80	1.13	1.43
propylbenzene	0.07	—	—	0.21	—
o-ethyltoluene (**29**)	—	0.27	4.24	4.49	2.73
o-methylstyrene (**30**)	—	0.29	0.92	1.45	1.82
methallylbenzene	0.03	—	0.41	0.28	—
MA	—	—	*e*	—	—
1-methylpropenylbenzene	0.23	0.12	0.67	0.64	—
indene (**7**)	—	—	2.71	5.92	16.64
MB	—	—	*e*	*e*	—
MC	—	—	—	*e*	—
2,2-dimethylindan (**13**)	—	4.03	31.71	24.08	9.76
MD-130 [$C_{10}H_{10}$]	—	—	1.02	1.17	1.49
ME-146 [$C_{11}H_{14}$]	0.24	1.08	0.35	0.62	—
MF	—	*e*	—	—	—
o-methallyltoluene (**10**)	94.54	89.57	30.15	22.22	6.21
MG	—	*e*	—	—	—

Table A-II continues on next page

Table A-II. Continued

entry	yield, % [c]				
	RT [d]	700 °C	800 °C	850 °C	900 °C
1-(*o*-tolyl)-2-methylpropene (**14**)	—	0.70	5.99	6.58	4.68
MH	—	*e*	*e*	*e*	—
3-methylindene (**16**)	—	0.18	3.28	4.50	5.23
MI-130 [$C_{10}H_{10}$]	—	—	0.34	0.77	1.10
MJ	—	—	*e*	*e*	—
MK-130 [$C_{10}H_{10}$]	—	—	—	0.76	3.68
2-methylindene (**15**)	—	0.42	3.47	4.35	4.00
ML-128 [C_8H_{10}]	—	0.16	0.63	0.69	2.12
MM-146 [$C_{11}H_{14}$]	1.40	0.26	1.02	1.22	—
benzofulvene (**38**)	—	—	1.30	1.08	—
naphthalene (**5**)	—	0.08	4.12	6.56	18.80
MN-144 [$C_{11}H_{12}$]	—	0.20	—	—	—
MO	—	—	*e*	—	—
MP-144 [$C_{11}H_{12}$]	—	0.50	0.29	0.23	—
MQ-144 [$C_{11}H_{12}$]	—	0.34	0.36	0.39	—
MR-144 [$C_{11}H_{12}$]	—	0.26	0.25	—	—
MS-144 [$C_{11}H_{12}$]	—	—	—	0.17	—
2-methylnaphthalene	—	—	0.94	1.13	1.61
1-methylnaphthalene	—	0.23	0.35	0.47	0.86
2,2'-dimethylbiphenyl	0.16	0.93	1.79	1.42	1.72

Table A-II continues on next page

Table A-II. Continued

	yield, % [c]				
entry	RT [d]	700 °C	800 °C	850 °C	900 °C
recovery [f]	100.00	89.00	83.81	80.97	67.31
conversion [g]	*d*	10.43	69.85	77.78	93.78

[a] FVP conditions: system pressure = 0.10 torr, sample temperature = 0 °C. [b] See Table A-I, note *b*. [c] Moles of product divided by total moles of recovered material. [d] Starting material purity assay. [e] Unidentified product which constitutes ≤0.43% total area by GC. [f] Total moles of recovered material divided by moles of starting material used. [g] Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material.

Table A-III. Products and recovered starting material, total recovery of material, and conversion from the FVP of 2,2-dimethylindan (**13**) at 900 °C [a,b]

entry	yield,% [c]
toluene	3.12
DA	*e*
DB	*f*
DC	*e*
ethylbenzene	4.08
o-xylene (**28**)	0.90
benzocyclobutene (**2**)	0.26
propylbenzene	1.39
o-ethyltoluene (**29**)	1.22
o-methylstyrene (**30**)	0.17
DD	*e*
DE	*e*
indene (**7**)	21.67
DF	*e*
DG	*e*
2,2-dimethylindan (**13**) [d]	10.67
DH	*f*
o-methallyltoluene (**10**)	4.78
1-(*o*-tolyl)-2-methylpropene (**14**)	5.01
3-methylindene (**16**)	7.41
MI-130 [C10H10]	1.93
MJ-130 [C10H10]	1.55

Table A-III continues on next page

Table A-III. Continued

entry	yield,%c
2-methylindene (**15**)	5.38
benzofulvene (**38**)	3.11
naphthalene (**5**)	24.01
DI-144 [C11H12]	0.21
MP-144 [C11H12]	0.14
MS-144 [C11H12]	0.13
2-methylnaphthalene	1.81
1-methylnaphthalene	0.98
2,2'-dimethylbiphenyl	0.08
DJ	*e*
DK	*e*
recovery *g*	60.35
conversion *h*	88.33

[a] See Table A-I, note *a*. [b] See Table A-I, note *b*. [c] See Table A-I, note *c*. [d] Assay of starting material in relative area percent: (2,2-dimethylindan (97.2), unidentified impurities, none of which are detected in the product mixtures (2.8) [e] Unidentified product which constitutes ≤0.35% total area by GC. [f] Unidentified product which constitutes ≤1.82% total area by GC. [g] See Table A-I, note *f*. [h] See Table A-I, note *g*.

Table A-IV. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-allylethylbenzene (**17**) at various temperatures [a,b]

entry	yield, % [c]			
	RT [d]	700 °C	750 °C	800 °C
ethylbenzene	0.84	0.78	1.31	2.02
o-xylene (**29**)	—	—	—	0.70
styrene (**3**)	—	0.60	1.73	3.64
allylbenzene	—	0.28	0.52	0.42
o-ethylstyrene (**30**)	—	2.62	5.24	5.47
EA	—	—	—	*e*
indene (**7**)	—	1.90	6.91	22.84
2-methylindan (**8**)	—	4.16	6.21	4.02
MD-130 [$C_{10}H_{10}$]	—	0.37	0.78	0.34
EB-146 [$C_{11}H_{14}$]	—	1.14	0.33	1.03
o-bromoethylbenzene	0.35	0.44	0.98	0.70
o-allylethylbenzene (**17**)	95.84	74.17	48.49	14.62
EC-146 [$C_{11}H_{14}$]	—	0.21	0.29	—
ED-146 [$C_{11}H_{14}$]	—	3.91	3.58	2.56
EE-146 [$C_{11}H_{14}$]	—	0.66	—	—
3-methylindene (**16**)	—	1.83	4.70	6.72
EF-146 [$C_{11}H_{14}$]	—	—	—	0.58
o-propylstyrene (**20**)	—	—	1.70	3.55
2-methylindene (**15**)	—	1.76	4.56	6.37
ML-128 [$C_{10}H_8$]	—	—	0.27	—
E-(*o*-propenyl)ethylbenzene (**19**)	—	1.36	2.22	2.10

Table A-IV continues on next page

Table A-IV. Continued

entry	yield, % [c] RT [d]	700 °C	800 °C	900 °C
EG	—	—	*e*	—
EH	0.47	—	—	—
naphthalene (**5**)	—	1.57	5.72	19.28
EI-146 [$C_{11}H_{14}$]	—	1.43	2.01	1.01
EJ-144 [$C_{11}H_{12}$]	—	0.37	0.19	—
MP-144 [$C_{11}H_{12}$]	—	—	0.25	—
EK	1.33			
MQ-144 [$C_{11}H_{12}$]	—	—	0.23	—
EL-144 [$C_{11}H_{12}$]	—	—	0.76	0.59
2-methylnaphthalene	—	—	0.39	0.62
1-methylnaphthalene	—	—	0.60	0.81
2,2'-diethylbiphenyl	1.17	0.31	—	—
recovery [f]	100.00	78.45	78.67	70.68
conversion [g]		41.81	61.85	89.67

[a] See Table A-I, note *a*. [b] See Table A-I, note *b*. [c] See Table A-I, note *c*. [d] Assay of starting material. Percentages given are of relative area by GC. [e] Unidentified product which constitutes ≤0.22% total area by GC. [f] See Table A-I, note *f*. [g] See Table A-I, note *g*.

Table A-V. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-allylcumene (**21**) at various temperatures [a,b]

	yield, % [c]		
entry	RT [d]	700 °C [e]	750 °C
ethylbenzene	—	—	0.96
o-xylene (**28**)	—	—	0.75
styrene (**3**)	—	0.67	2.36
cumene	0.74	1.21	1.11
allylbenzene	—	0.41	0.57
o-ethyltoluene (**29**)	—	2.21	3.29
o-ethylstyrene (**30**)	—	2.81	3.67
indene (**7**)	—	1.74	6.60
CA-146 [C11H14]	—	2.79	3.41
MD-130 [C10H10]	—	0.66	1.45
CB-146 [C11H14]	—	1.19	1.18
CC-160 [C12H16]	—	4.35	3.37
CD	—	*f*	—
3-methylindene (**16**)	—	3.56	8.19
CE-146 [C11H14]	—	1.02	0.81
o-allylcumene (**21**)	91.84	53.51	19.88
CF-160 [C12H16]	0.52	0.68	2.58
CG-160 [C12H16]	—	2.50	5.10
CH-160 [C12H16]	—	2.28	—
CI-144 [C11H12]	0.15	0.68	0.72
ML-128 [C_8H_{10}]	—	1.95	3.09

Table A-V continues on next page

Table A-V. Continued

entry	yield, % [c]		
	RT [d]	700 °C	750 °C
CJ	0.59	—	—
CK-146 [C11H14]	—	0.52	0.55
naphthalene (**5**)	—	5.10	17.69
CL-144 [C11H12]	—	0.98	1.07
CM-160 [C12H16]	—	2.10	1.35
CN-160 [C12H16]	0.39	0.83	0.54
CO	0.13	—	—
MP-144 [C11H12]	—	0.47	0.61
CP	1.79	—	—
EL-144 [C11H12]	—	2.15	2.63
MS-144 [C11H12	—	0.34	—
CQ	—	*f*	—
CR	0.48	—	—
CS	0.20	—	—
2-methylnaphthalene	—	2.17	3.78
1-methylnaphthalene	—	1.12	2.69
2,2'-diisopropylbiphenyl	3.18	—	—
recovery [g]	100.00	83.43	73.22
conversion [h]	*d*	46.49	80.04

[a] See Table A-I, note *a*. [b] See Table A-I, note *b*. [c] See Table A-I, note *c*. [d] Assay of starting material. Percentages are of relative area by GC. [e] Duplicate runs performed, rather than triplicate runs. [f] Unidentified product which constitutes ≤0.52% total area by GC. [g] See Table A-I, note *f*. [h] See Table A-I, note *g*.

Table A-VI. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-(3-butenyl)toluene (**23**) at various temperatures [a,b],

entry	yield, % [c]			
	RT [d]	700 °C	800 °C	900 °C
toluene	—	—	—	2.29
ethylbenzene	—	—	—	1.59
m/*p*-xylene	—	—	—	0.75
o-xylene (**28**)	—	0.40	4.70	18.58
styrene (**3**)	—	—	0.46	6.80
benzocyclobutene (**2**)	—	0.36	3.51	15.24
allylbenzene	—	—	—	0.23
propylbenzene	—	—	—	0.32
o-ethyltoluene (**29**)	—	—	2.97	10.37
o-methylstyrene (**30**)	—	—	0.51	2.14
indan	—	—	—	0.13
m/*p*-allyltoluene	—	—	0.95	3.83
o-allyltoluene (**6**)	—	—	0.21	0.40
BA	—	—	*e*	—
indene (**7**)	—	—	0.34	1.64
2-methylindan (**8**)	—	—	—	0.22
o-methylbenzaldehyde	—	0.33	0.39	0.21
o-(1-propenyl)toluene (**11**)	—	—	—	0.15
BB-146 [$C_{11}H_{14}$]	—	—	0.16	0.43
BC-146 [$C_{11}H_{14}$]	—	—	0.16	0.22

Table A-VI continues on next page

Table A-VI. Continued

entry	yield, % [c]			
	RT [d]	700 °C	800 °C	900 °C
o-(3-butenyl)toluene (**23**)	100.0	64.20	41.73	15.87
BD-146 [$C_{11}H_{14}$]		0.32	0.25	0.12
2-methylindene (**15**)	—	—	0.23	0.10
TK-130 [$C_{10}H_{10}$]	—	—	—	0.14
1,2-dihydronaphthalene (**4**)	—	—	0.30	0.30
TM	—	—	*e*	*e*
naphthalene (**5**)	—	—	0.45	1.38
BE-146 [$C_{11}H_{14}$]	—	—	0.20	0.12
BF-156 [$C_{12}H_{12}$]	—	—	—	0.20
2-methylnapthalene	—	—	—	0.10
1-methylnapthalene	—	—	—	0.18
BG-182 [$C_{14}H_{14}$]	—	—	—	0.46
BH-182 [$C_{14}H_{14}$]	—	—	—	0.47
BI-196 [$C_{15}H_{16}$]	—	—	—	0.29
BJ-196 [$C_{15}H_{16}$]	—	—	2.15	4.24
BK-210 [$C_{16}H_{18}$]	—	—	0.37	0.49
1,2-di(*o*-tolyl)ethane (**27**)	—	34.38	39.36	7.59
BL-178 [$C_{14}H_{10}$]	—	—	0.63	1.46
BM-208 [$C_{16}H_{16}$]	—	—	—	0.46
BN-192 [$C_{15}H_{12}$]	—	—	—	0.47
recovery [f]	102.4	97.77	88.72	110.0

Table A-VI continues on next page

Table A-VI. Continued

entry	yield, % *c*			
	RT *d*	700 °C	800 °C	900 °C
conversion *g*	*d*	35.80	58.27	84.13

[a] FVP conditions: system pressure = 0.010 torr, sample temperature = 0 °C. [b] Amounts determined by GC with a known quantity of biphenyl added as standard. Data for 700 °C represent the average of duplicate runs. Data for 750 °C represent the average of triplicate runs. See Table A-I, note *b* for notation.[c] See Table A-I, note *c*. [d] See Table A-I, note *d*. [e] See Table A-I, note *e*. [f] See Table A-I, note *f*. [g] See Table A-I, note *g*.

Table A-VI. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-(4-pentenyl)toluene (**24**) at various temperatures [a,b]

entry	yield, % [c]			
	RT [d]	600 °C	700 °C	800 °C
toluene	—	—	0.26	3.24
ethylbenzene	—	—	—	1.32
o-xylene (**28**)	—	—	1.00	5.65
styrene (**3**)	—	—	—	2.54
benzocyclobutene (**2**)	—	—	0.92	3.24
o-ethyltoluene (**29**)	—		0.88	3.15
o-methylstyrene (**30**)	—	1.52	30.62	59.78
benzaldehyde	—	—	0.21	1.33
indan	—	—	—	1.07
m/*p*-allyltoluene	—	0.31	0.26	0.51
o-allyltoluene (**6**)	—	—	0.20	—
indene (**7**)	—	—	0.34	2.29
o-methylbenzaldehyde	—	—	1.67	2.56
PA	—	—	*e*	—
PB-146 [$C_{11}H_{14}$]	—	—	0.82	0.98
naphthalene (**5**)	—	—	0.11	0.52
PC	*e*	*e*	*e*	—
PD	—	—	*e*	—
2-(4-pentenyl)toluene (**24**)	92.42	90.40	52.92	2.97
PE-160 [$C_{12}H_{16}$]	—	—	0.58	0.52

Table A-VII continues on next page

Table A-VII. Continued

entry	yield, % [c]			
	RT [d]	600 °C	700 °C	800 °C
PF	—	—	*e*	—
PG-160 [$C_{12}H_{16}$]	—	—	0.97	1.10
2,2'-dimethylbiphenyl	7.58	7.77	8.23	7.22
recovery [e]	97.85	96.20	86.59	70.36
conversion [f]	*d*	9.60	47.08	97.03

[a] See Table A-II, note *a*. [b] See Table A-I, note *b*. [c] See Table A-I, note *c*. [d] See Table A-I, note *d*. [e] Unidentified product which constitutes ≤0.35% total area by GC. [f] See Table A-I, note *f*. [g] See Table A-I, note *g*.

Table A-VIII. Products and recovered starting material from the solution-phase thermolysis of *o*-methallyltoluene (**10**) in phenyl ether (240 min, 400 °C) at various concentrations [a]

entry	yield,%c	
	0.0724 M	0.0145 M
ethylbenzene	1.06	1.15
styrene (**3**)	3.30	0.93
o-methylstyrene (**30**)	1.45	1.30
2,2-dimethylindan (**13**)	3.58	3.89
o-methallyltoluene (**10**) [c]	14.03	49.97
1-(*o*-tolyl)-2-methylpropene (**14**)	57.73	26.67
3-methylindene (**16**)	6.11	7.72
2-methylindene (**15**)	4.50	2.20
napthalene (**5**)	4.65	1.22
MP-144 [C11H12]	0.56	0.72
MQ-144 [C11H12]	2.21	1.57
1-methylnapthalene	0.83	2.65

[a] Thermolysis conditions: 0.5 mL of phenyl ether solution is degassed and sealed in a glass tube, and then is heated to 400 °C for 240 minutes, then allowed to cool to RT. [b] See Table A-I, note *b*. [c] See Table A-II for starting material assay.

APPENDIX 3
SUPPLEMENTARY CALCULATIONS AND GRAPHS

Calculation of $T_{50\%}$ was performed by plotting the % conversion for conversion of **23** and **24** *vs.* temperature (Figure A-14). Similar calculations gave the $T_{50\%}$ values for the conversions of **6**, **10**, **17**, and **21** (Figure A-15). The resulting $T_{50\%}$ values are given, along with their calculated ΔH values, in Table A-IX.

Schiess' method[20] was used to attempt to estimate $\Delta G^{\ddagger}$ values for the conversions of **23** and **24** in order to construct a calibration curve. Literature values for activation parameters were obtained from model systems. The homolytic cleavage of biallyl at 700 °C[21] was the model for **23**. The activation parameters are E_a = 54.5 kcal mol^{-1} and log A = 13.4. The model system for **24** was the retro-ene reaction of 1,6-heptadiene at 700 °C, with E_a = 46.9 kcal mol^{-1} and log A = 11.3.[22] The $\Delta S^{\ddagger}$ values for **23** and **24** were assumed to be the same as their respective model systems. In addition, we assumed that differences in ΔH_f values used in corrections were the same as the differences in the $\Delta H^{\ddagger}$.

The ΔH for conversion of propene to an allyl radical is 3 kcal mol^{-1} greater than ΔH for conversion of *o*-xylene to the 2-methylbenzyl radical. This results in a calculated $\Delta H^{\ddagger}$ of 52 kcal mol^{-1}, and a $\Delta G^{\ddagger}$ of 53 kcal mol^{-1} at its $T_{50\%}$. Similarly, 0.4 kcal mol^{-1} was subtracted from the calculated $\Delta H^{\ddagger}$ for conversion of 1,6-hexadiene in order to give an approximate $\Delta H^{\ddagger}$ value for conversion of **24**. $\Delta G^{\ddagger}$ is then calculated to be approximately 57 kcal mol^{-1} at its T50%

The values of T50% for **23** and **24** were plotted against their respective $\Delta G^{\ddagger}$ values to make a calibration curve. The slope of the line was negative, rather than the expected positive slope. This is probably the result of two main causes: the crude nature of the approximations of $\Delta H^{\ddagger}$ in these reactions, along with the fact that the temperature in the pyrolysis oven is not constant throughout its length, and the thermocouple only measures the temperature in the middle of the oven.

However, if one considers the T50% values for all of these compounds, it is apparent that all of the compounds have similar T50% values, and should therefore have reasonably similar $\Delta G^{\ddagger}$ values. The decrease in T50% values in **6**, **10**, **17**, and **21** as substitution at the radical sites increases is reasonable. A decrease in $\Delta G^{\ddagger}$ with increasing substitution is expected. However, it is possible that the values for conversion of **17** and **21** reflect α-fragmentation reactions rather than hydrogen transfer to give diradicals.

Table A-IX. Estimated ΔH values for diradical formation from *o*-allyltoluene (**6**), *o*-methallyltoluene (**10**), *o*-allylethylbenzene (**17**), and *o*-allylcumene (**21**) and T50% values for the conversion of **6**, **10**, **17**, **21**, *o*-(3-butenyl)toluene (**23**), and *o*-(4-pentenyl)toluene (**24**)

entry	Calculated[a] ΔH, kcal mol^{-1}	T50%,°C
o-allyltoluene (**6**)	45.0	794
o-methallyltoluene (**10**)	44.0	783 [b]
o-allylethylbenzene (**17**)	41.5	720
o-allylcumene (**21**)	37.9	705 [c]
o-(3-butenyl)toluene (**23**)	—	761
o-(4-pentenyl)toluene (**24**)	—	697

[a] See ref. 19. [b] Pyrolysis of **10** was carried out at 4 temperatures. [c] Pyrolysis of **21** was carried out at only 2 temperatures.

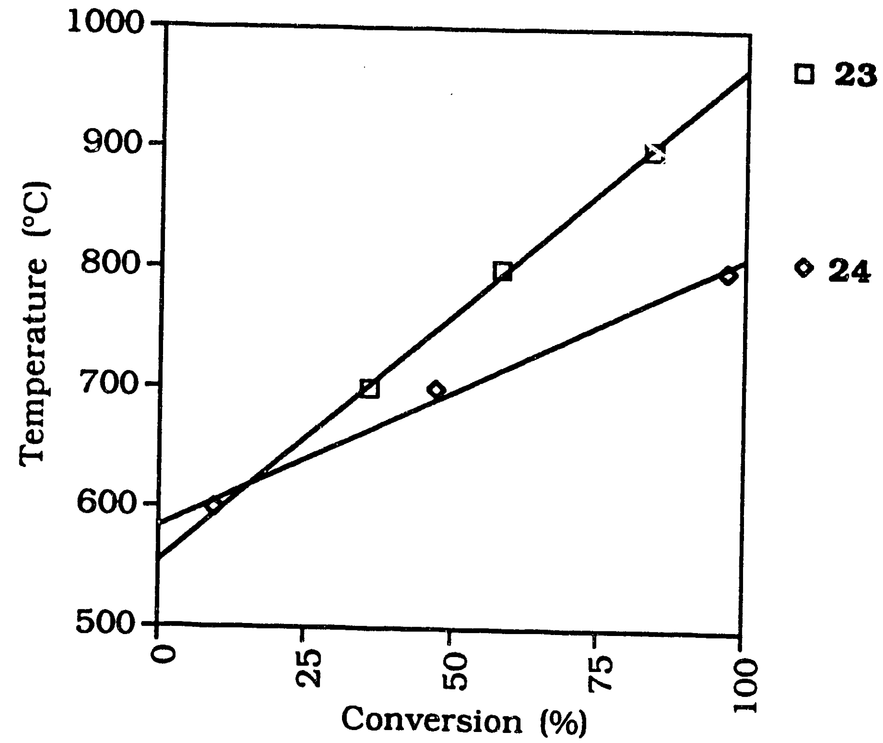


Figure A-14. Plot of temperature *vs.* conversion for the FVP of *o*-(3-butenyl)toluene (**23**) and *o*-(4-pentenyl)toluene (**24**).

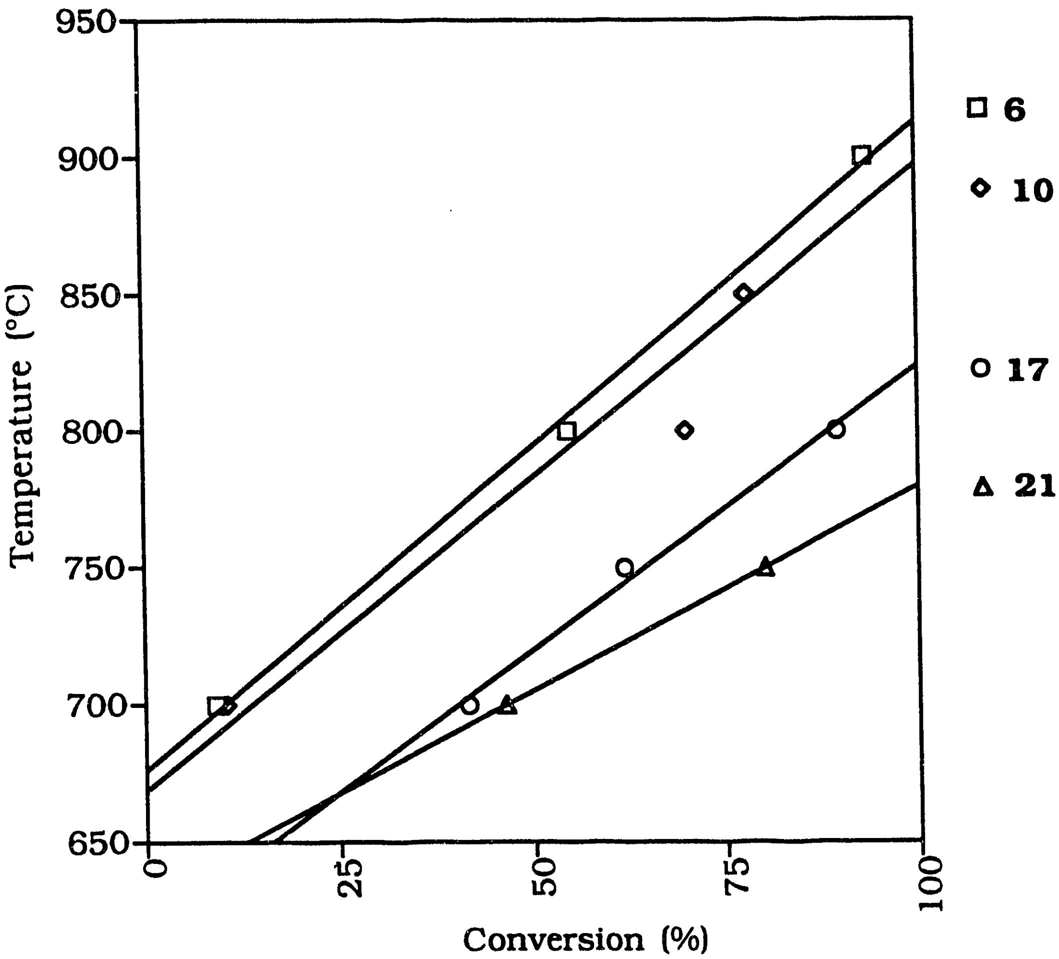


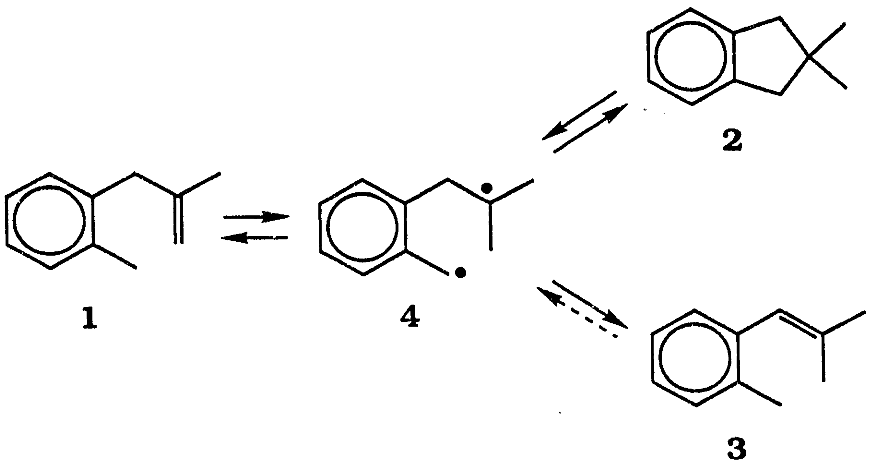
Figure A-15. Plot of temperature *vs.* conversion for the FVP of *o*-allyltoluene (**10**), *o*-methallyltoluene (**10**), *o*-allylethylbenzene (**17**), and *o*-allylcumene (**21**).

PAPER 3. COUPLING OF DIRADICALS GENERATED BY INTRAMOLECULAR HYDROGEN-ATOM TRANSFERS: CYCLIZATION REACTIONS OF ARYL STYRENE DERIVATIVES

INTRODUCTION

We recently reported findings concerning a novel thermally-induced hydrocarbon cyclization reaction.[1] Flash vacuum pyrolysis (FVP) of *o*-methallyltoluene (**1**) at 700-900 °C gives moderate yields of 2,2-dimethylindan (**2**) along with small amounts of *o*-(2-methylpropenyl)toluene (**3**). We postulate that an intramolecular hydrogen-atom transfer occurs to give a diradical intermediate (**4**) which then undergoes coupling to give **2** or intramolecular disproportionation to give either **1** or **3** as shown in Scheme I.

Scheme I

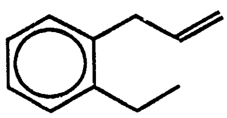


To date, the only examples of formations of diradicals or a pair of radicals by transfer of a hydrogen atom

$$\mathrm{RH}\quad \mathrm{R'H} \longrightarrow \mathrm{R}\bullet \quad \bullet\mathrm{R'H_2}$$

have been intramolecular photochemical[2] reactions and a few intermolecular thermal reactions.[3,4,5] There is only one other report which presents evidence for the formation of a diradical by thermally-induced transfer of a hydrogen atom and this is for the cyclization of an organosilicon compound.[6]

As part of our previous study, we investigated the FVP behavior of other derivatives including *o*-allylethylbenzene (**5**) and *o*-allylcumene (**6**). We had believed that the relative stability of predicted diradical intermediates **7** and **8**, respectively, would allow investigation



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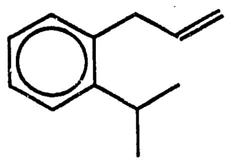

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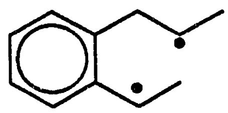

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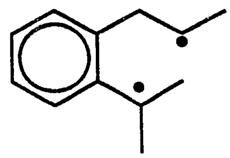

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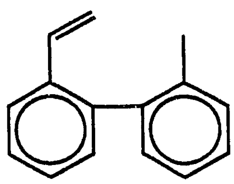
of the hydrogen atom transfer reaction at lower temperatures. Unfortunately, compounds **5** and **6**, particularly **6**, undergo competetive α-fragmentation to give a large number of products. We also observed that in solution, **1** largely isomerizes to **3**; only a small amount of **2** is formed, and then only at high temperatures.

In this chapter, we report the results of the study of the products of the FVP of 2-methyl-2'-vinylbiphenyl (**9**), which was expected to be more resistant to fragmentation reactions than **5** or **6**. The results from the FVP of **9** could be explained by other mechanisms besides hydrogen transfer/diradical coupling. Therefore we investigated the pyrolysis of 2-(*o*-methylbenzyl)styrene (**10**), which contains a methylene bridge between the aryl rings to act as an 'insulator' to eliminate some alternative mechanisms.



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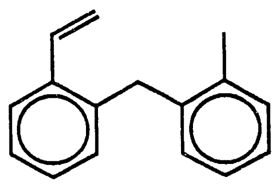

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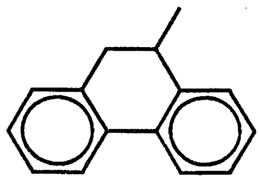
RESULTS

A summary of the product study of the FVP of 2-methyl-2'-vinylbiphenyl (**9**) at 0.10 torr (600-800 °C) is presented in Table I. At 600 °C, small amounts of 9-methyl-9,10-dihydrophenanthrene (**11**), **B**M-194 (See Table I, note *b* for an explanation of nomenclature), and phenanthrene (**12**) are formed. At 700 °C, the amounts of **11** and



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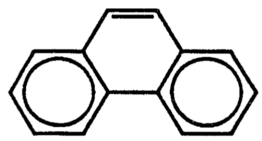

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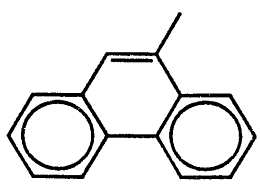
BM-194 have increased. Phenanthrene is now a significant component of the mixture, and a small amount of 9-methylphenanthrene (**13**) is detected. At 800 °C, no starting material can be detected, and the major product is **12**. The amount of **11** is much lower, and the amounts of **B**M-194 and **13** are slightly higher. Fluorene (**14**), a significant product at 800 °C, is probably formed by secondary pyrolysis of primary products.



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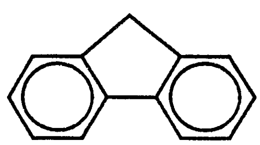

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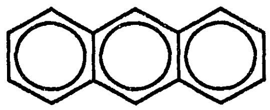
A summary of the product study of the FVP of 2-(*o*-methylbenzyl)styrene (**10**) at 0.10 torr (600-800 °C) is presented in Table II. At 600 °C, the most abundant products are compound **S**N-208 (See Table

I, note *b* for an explanation of nomenclature) and anthracene (**15**), and **S**T-208 are also produced in low yields. At 700 °C, **15** makes up over 45 % of the product mixture, and 1-Methylanthracene (**16**) is produced in *ca.* 7.2 % yield.



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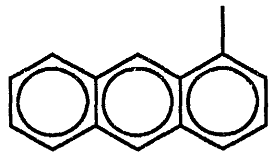

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At 700 °C, the yield of **S**N-208 drops substantially, and the yields of **S**T-208 and **S**EE-208 increase slightly. Two other products, **S**K-208 and **S**NN-206, are formed in low yield. At 800 °C, starting material is almost completely consumed, and **15** makes up over 60 % of the product mixture. 1-Methylanthracene accounts for nearly 12 % of the products, and compounds **S**N-208, **S**T-208, **S**K-208, and **S**NN-206 are formed in low yields (*ca.* 0.5-4.0%).

Table I. Products and recovered starting material, total recovery of material, and conversion from the FVP of 2-methyl-2'-vinylbiphenyl (**9**) at various temperatures [a,b]

entry	yield, % [c] 600°C	700 °C	800 °C
2-methyl-2'-vinylbiphenyl (**9**) [d]	93.0	44.0	—
9-methyl-9,10-dihydrophenanthrene (**11**)	4.6	27.2	6.8
BM-194 [$C_{15}H_{14}$]	1.4	9.8	10.3
phenanthrene (**12**)	0.4	10.0	57.9
9H-fluorene (**14**)	0.1	1.2	8.2
9-methylphenanthrene (**13**)	—	3.0	3.9
other products	0.5 [e]	7.8 [e]	16.8 [e]
recovery [f]	85.8	69.5	50.2
conversion [g]	7.0	56.1	100.0

[a] FVP conditions: system pressure = 0.10 torr, sample temperature = 50-60 °C. [b] Amounts determined by GC with a known quantity of biphenyl added as standard. Data represent the average of triplicate runs. Products identified by comparison with authentic samples or by retention time and GCMS are indicated by name. Products identified by GCMS only are indicated by code: **X**Y-nnn, where '**X**' represents the experiment where first observed (**B** = 2-methyl-2'-vinylbiphenyl, **S** = 2-(*o*-methylbenzyl)styrene, 'Y' the individual unknown product (A, B, C, etc.), and 'nnn' the nominal mass. [c] Moles of product divided by total moles of recovered material. [d] Starting material assay (GC, mole %): 2-methyl-2'-vinylbiphenyl (99.2), unidentified compounds **B**B (0.3), **B**C (0.1) **B**G-180 with formula $C_{14}H_{12}$ (0.1), **B**Q (0.1), **B**S-192 with formula $C_{15}H_{12}$ (0.1), **B**E-194 with formula $C_{15}H_{14}$ and **B**O-194 with formula $C_{15}H_{14}$ (total of 0.1). [e] See Table A-I in the Appendix of Paper

Table I. continued on next page

Table I. Continued

3, this dissertation, for a more detailed analysis. [f]Total moles of recovered material divided by moles of starting material used. [g]Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material.

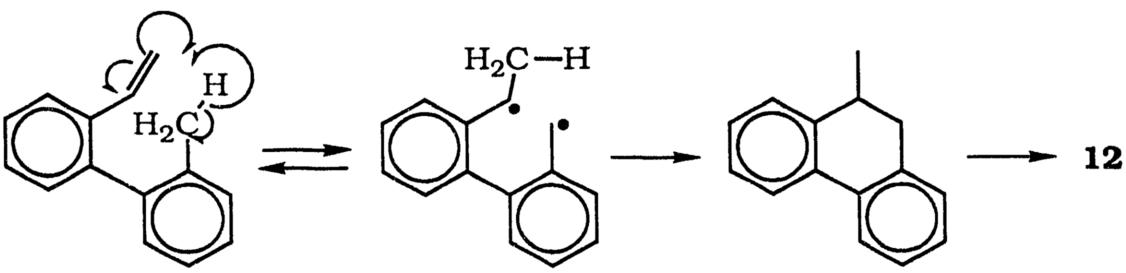
Table II. Products and recovered starting material, total recovery of material, and conversion from the FVP of 2-(*o*-methylbenzyl)styrene (**10**) at various temperatures [a,b]

	yield, % [c]		
entry	600°C	700 °C	800 °C
2-(*o*-methylbenzyl)styrene (**10**) [d]	65.7	13.2	1.2
SN-208 [$C_{16}H_{16}$]	12.1	5.1	0.6
anthracene (**15**)	7.2	45.3	62.6
ST-208 [$C_{16}H_{16}$]	1.1	6.6	4.4
1-methylanthracene (**16**)	—	7.2	11.8
SK-208 [$C_{16}H_{16}$]	—	4.3	3.2
SNN-206 [$C_{16}H_{14}$]	—	2.6	1.6
other products	14.0 [e]	15.7[e]	14.9 [e]
recovery [f]	75.2	58.5	59.3
conversion [g]	34.3	86.8	98.8

[a] See Table A-I, note *a*. [b] See Table I, note *b*. [c] See Table I, note *c*. [d] Starting material (GC assay, relative area%): 2-(*o*-methylbenzyl)styrene (93.5), 2-benzylethylbenzene (1.1), unidentified products **S**W-208 with formula $C_{16}H_{16}$ (1.6), **S**J-206 with formula $C_{16}H_{14}$ (1.4), **S**S-208 with formula $C_{16}H_{16}$ (1.3), **S**P-208 with formula $C_{16}H_{16}$ (0.7), **S**N-208 with formula $C_{16}H_{16}$ (0.4), **S**E-206 with formula $C_{16}H_{14}$ (0.2). [e] See Table A-II in the Appendix of Paper 3, this dissertation, for a more detailed analysis. [f] See Table I, note *f*. [g] See Table I, note *g*.

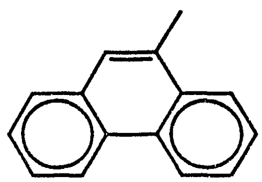
DISCUSSION

The products produced by the FVP of 2-methyl-2'-vinylbiphenyl (**9**) are consistent with intramolecular hydrogen-atom transfer followed by coupling of the resulting diradical intermediate. Hydrogen-atom transfer from the methyl group of **9** would afford diradical intermediate **17**, which upon coupling would give 9-methyl-9,10-dihydrophenanthrene (**11**). Subsequent loss of the methyl group and a β-hydrogen would give phenanthrene (**12**). The identity of **11** was es-



9 **17** **11**

tablished by comparison to the reported ^1H NMR spectrum of **11**[7] as well as by analysis of ^1H NMR and GCMS data. In addition to **11** and **12**, 9-methyl-phenanthrene (**13**) is formed in *ca.* 3 % yield. ^1H NMR and GCMS data are consistent with reported literature values[8] for **13**.



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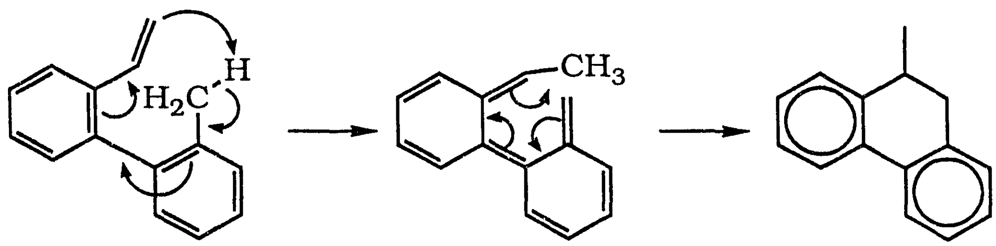
There are a number of possible mechanisms for formation of **11** from **9** in addition to the one described above. This mechanism does require generation of **17**, a relatively high energy species, but both radical sites are resonance stabilized. The ΔH_f for **17** is calculated[9] to lie *ca.* ~35 kcal mol^{-1} higher than **9**. If the transition state lies only a few kcal mol^{-1} above **17**, it would still be accessible at *ca.* 700 °C.

A second mechanism for the formation of **11** involves a 1,7 sigmatropic hydrogen-atom shift[10] to give polyene **18**, which then affords **11** by electrocyclic ring closure.[10] Movement of the hydrogen

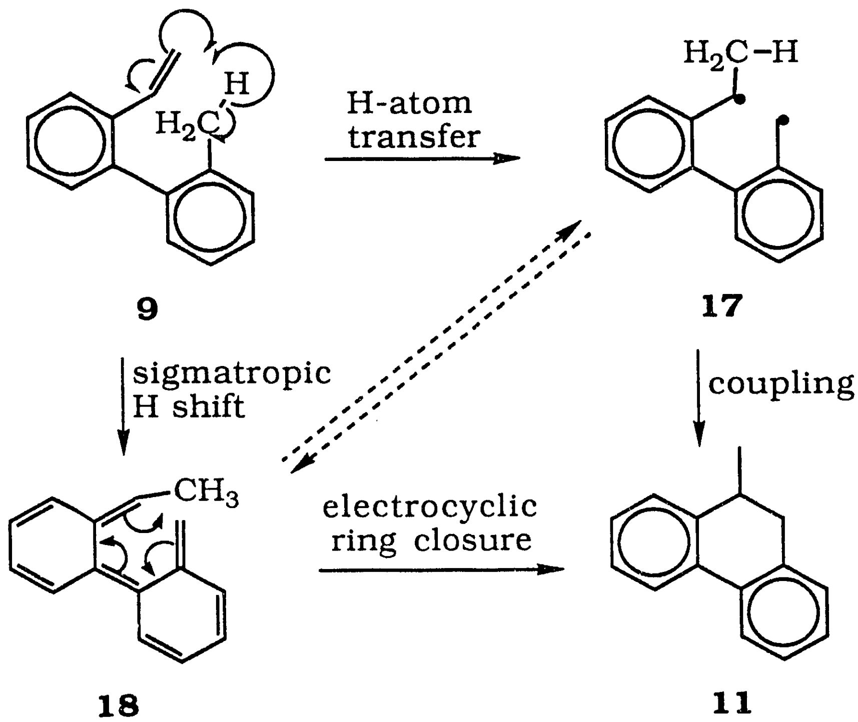


9 **18** **11**

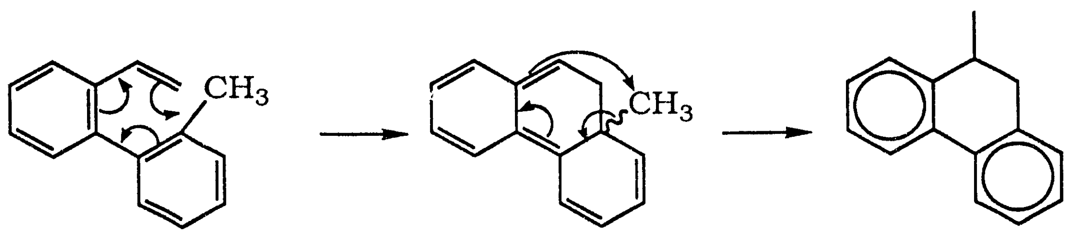
is the same as in the first mechanism, but the intermediate in this mechanism is a polyene rather than a diradical. A significant drawback to this mechanism is that it requires disruption of both aromatic rings, resulting in a loss of *ca.* 40 kcal mol^{-1} in resonance energy.[11]

If **18** is formed, twisting of the aryl rings would result in breaking the aryl-aryl π-bond to give **17**, which could then couple rapidly. It is also possible that the actual mechanism involves a combination of both of these mechanisms. These possibilities are shown in Scheme II.

Scheme II

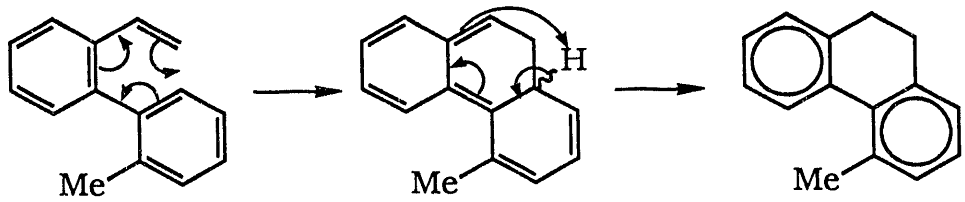


Another possible mechanism involves electrocyclic ring closure of **9** to give **19**, followed by a 1,5 methyl shift[10] to give **11**. However,



9 **19** **11**

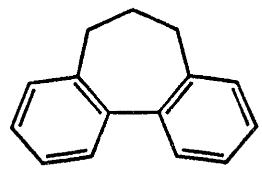
this mechanism would require disruption of both aromatic rings in addition to severe steric interaction between the methyl group and the vinyl group. Further, if ring closure did occur, one would expect reaction to occur at the unsubstituted carbon, giving **20**, which would then give 4-methyl-9,10-dihydrophenanthrene (**21**). The presence of **21** could not be established by analysis of the ^{1}H NMR[12] and GCMS



9 **20** **21**

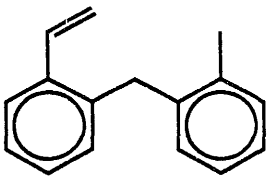
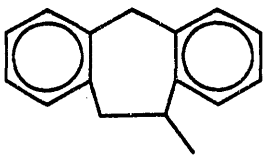
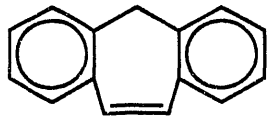
data. This mechanism is further discredited by the fact that pyrolysis conditions (700 °C) where 2-vinylbiphenyl (**23**) is produced do not result in formation of 9,10-dihydrophenanthrene (**24**) and/or **12**.[13]

There are a number of compounds formed which could not be identified, the most abundant of these being **B**M-194. Some of these intermediates could represent primary products which undergo secondary pyrolysis, possibly giving **11**, **12**, or fluorene (**14**). The increase in production of **B**M-194 at higher temperatures suggests that it is resistant to secondary pyrolysis. A possible structure for **B**M-194 is dibenzosuberane **25**, but no there is convincing spectroscopic evidence for its identity.

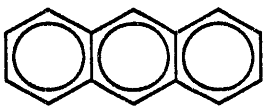
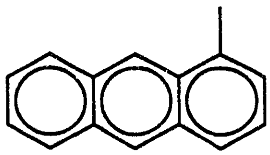


25

We decided that incorporation of a methylene group between the aromatic rings would act as an "insulator" and eliminate the 1,7 sigmatropic shift, allowing us to obtain clearer support for the hydrogen-atom transfer mechanism. 2-(*o*-methylbenzyl)styrene (**10**) was pyrolyzed, in anticipation of formation of 1-methyldibenzosuberane **26** and dibenzosuberene (**27**). Instead, we obtained anthracene (**15**) in good yields, accompanied by small amounts of 1-methylanthracene (**16**). Examination of ^{1}H NMR and GCMS data provided no clear evi-

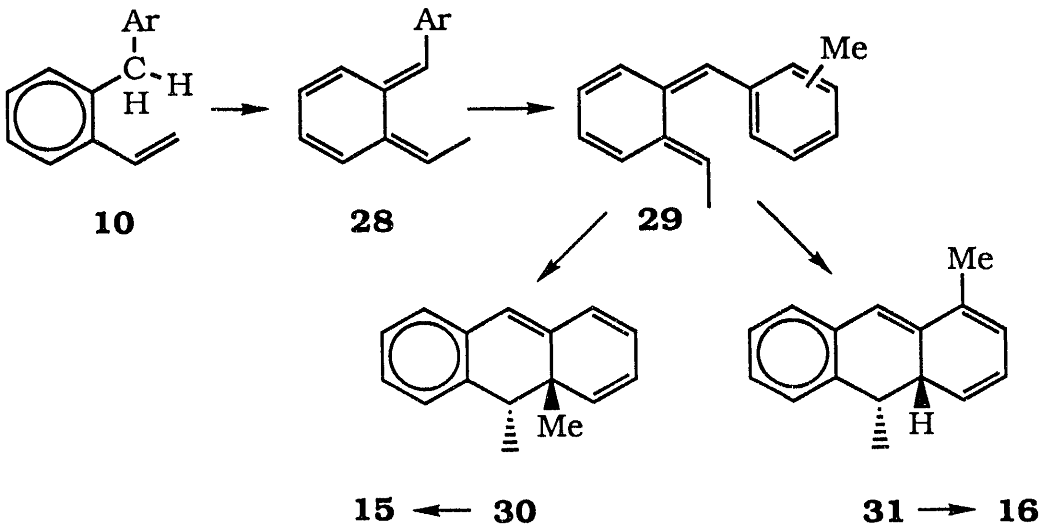
10 **26** **27**

15 **16**

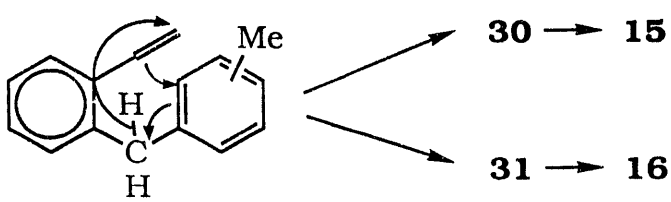
dence for the formation of **26**. Comparison with an authentic sample clearly showed that **27**, the predicted product of the secondary pyrolysis of **26**, is not formed. In other systems we have examined,[1] the loss of methyl groups from primary products is observed; therefore the failure to detect **27** argues against the formation of **26**.

It is uncertain how **15** and **16** are formed, but a reasonable mechanism involves a 1,5 sigmatropic hydrogen shift[10] to afford *o*-quinodimethane (*o*-QDM) derivative **28**. Isomerization of the double bonds would give *o*-QDM **29**, which would be followed by electrocyclic ring closure to give **30** and/or **31**.[14] Secondary pyrolysis of **30** and **31** would afford **15** and **16**, respectively. The trends in the yields of **SN**-208, **ST**-208, or **SEE**-208 respect to temperature suggest that they undergo secondary pyrolysis and could be **30** or **31**.



A possible drawback to this mechanism is that steric considerations would suggest more **31** would be formed, leading to **16**, but it is possible that electronic effects favor formation of **30**, leading to **15**.

A second possible mechanism for formation of **15** and **16** involves an ene reaction[10,15] to give compound **30** and **31** directly, followed by secondary pyrolysis to give **15** and **16** as described above. However,



the required conformation for proper orbital overlap for the ene reaction cannot be readily achieved due to the shortness of the chain length between the reacting centers. The effect of chain length in *o*-allylstyrene (**32**) on the ene reaction has been discussed by

Lambert.[16] Compound **10** can be viewed as an analog of **32** and should therefore suffer similar restrictions on the ene reaction.

CONCLUSION

Flash vacuum pyrolysis (FVP) of 2-methyl-2'-vinylbiphenyl (**9**) at 0.10 torr (600-800 °C) results in a mixture of products that are consistent with hydrogen-atom transfer from the methyl group in **9** to the double bond, followed by coupling of the resulting diradical intermediate. However, a sigmatropic hydrogen shift, followed by an electrocyclic ring closure could also explain the products that are observed.

FVP of 2-(*o*-methylbenzyl)styrene (**10**) resulted in the formation of anthracene (**15**) and 1-methylanthracene (**16**). The route leading to formation of **15** and **16** is uncertain, but we believe a likely mechanism for formation of **15** and **16** involves a sequential 1,5 hydrogen shift, electrocyclic ring closure of the resulting *o*-quinodimethane intermediate, and subsequent secondary pyrolysis. We were unable to obtain any clear evidence for products resulting from hydrogen transfer/diradical coupling.

EXPERIMENTAL

General Procedures

Methods and materials.

The pyrolysis apparatus has been described previously.[17] NMR spectra were obtained in d_6-methylene chloride solution and chemical shifts are relative to tetramethylsilane. Spectral techniques and general preparatory procedures have been previously described.[1] 2-iodobromobenzene, and 2-bromostyrene were purified by passing themthrough neutral alumina immediately prior to use. Other reagents were purchased as reagent grade and used as received.

1-[2-(*o*-Methylphenyl)phenyl]ethanol. A modification of Hart's method was used.[18] Two equivalents of *o*-tolylmagnesium was allowed to react with 2-iodobromobenzene. Addition of acetaldehyde followed by workup and column chromatography on silica gel using 10% ethyl acetate in hexanes afforded 1-[2-(*o*-Methylphenyl)phenyl]ethanol in 32 % yield. 1-Phenylethanol was also present, but it did not affect the next step.

2-methyl-2'-vinylbiphenyl (9). A modification of Hanzlik's procedure for the preparation of 4-vinylbiphenyl was used.[19] Dehydration of 1-[2-(*o*-tolyl)phenyl]ethanol) with $KHSO_4$ in DMSO and hydroquinone gave 2-methyl-2'-vinylbiphenyl (**9**) as a colorless oil in 73 % yield: ^{1}H NMR (CD_2Cl_2) δ 7.68-7.65 (dd, J_d = 7.5 Hz, J_d = 1.5 Hz., 1 H), 7.37-7.17 (m, 5 H), 7.15-7.08 (m, 2H), 6.39 (dd, J_d = 17.6 Hz, J_d = 11.0 Hz., 1 H), 5.66 (dd, J_d = 17.6 Hz, J_d = 1.2 Hz., 1 H), 5.09 (dd, J_d

= 11.0 Hz, J_d = 1.1 Hz.,1 H), 2.03 (s, 3 H) [lit.[20] ^{1}H NMR δ 7.66 (dd, J_d = 7.3 Hz, J_d = 2.0 Hz., 1 H), 7.40-7.08 (m, 7 H), 6.40 (dd, J = 17.5, 11.0 Hz., 1 H), 5.66 (dd, J = 17.6, 1.2 Hz., 1 H), 5.08 (dd, J = 11.0, 1.2 Hz., 1 H), 2.05 (s, 3 H)];^{13}C NMR (CD_2Cl_2) δ 140.56, 140.48, 136.11, 135.63, 134.84, 129.66, 129.57, 129.52, 127.31, 127.21 (2 carbons), 125.28, 124.48, 114.06, 19.58; GCMS (70 eV) *m/e* (% base peak) 194 (41.8), 180 (14.5), 179 (100), 178 (48.9), 165 (10.8).

2-(*o*-Methylbenzyl)styrene (10). α-Bromo-*o*-xylene was added to 2-styrylmagnesium bromide in a procedure patterned after that used for the preparation of *o*-(3-butenyl)toluene.[1] Workup and chromatography gave 2-(*o*-methylbenzyl)styrene in 8% yield: ^{1}H NMR (CD_2Cl_2) δ 7.55 (dd, J_d = 7.4 Hz, J_d =1.6 Hz, 1 H), 7.28-7.02 (m, 5 H), 6.98-6.76 (m, 3 H), 5.66 (dd, J = 17.3 Hz, J_d = 1.3 Hz., 1 H), 5.25 (dd, J_d = 10.9 Hz, J_d =1.3 Hz, 1 H), 4.00 (s, 2 H), 2.27 (s, 3 H); ^{13}C NMR (CD_2Cl_2) δ 138.5, 137.3, 139.9, 136.3, 134.4, 129.8, 129.6, 128.9, 127.7, 126.3, 126.0, 125.8, 125.5, 115.3, 36.1, 19.2; GCMS (70 eV) *m/e* (% base peak) 208 (29.7), 194 (15.1), 193 (100), 179 (15.5), 178 (77.6), 165 (16.9), 115 (33.3), 91 (18.1), 89 (19.4); Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.07; H, 7.53.

Flash vacuum pyrolysis. Flash vacuum pyrolysis was performed as previously described.[21]

Product analysis. FVP mixtures were analyzed as previously described.[21] FID response factors were calculated for **12** and **15**. Other compounds were assigned a response factor equal to biphenyl.

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APPENDIX 1

SPECTRA

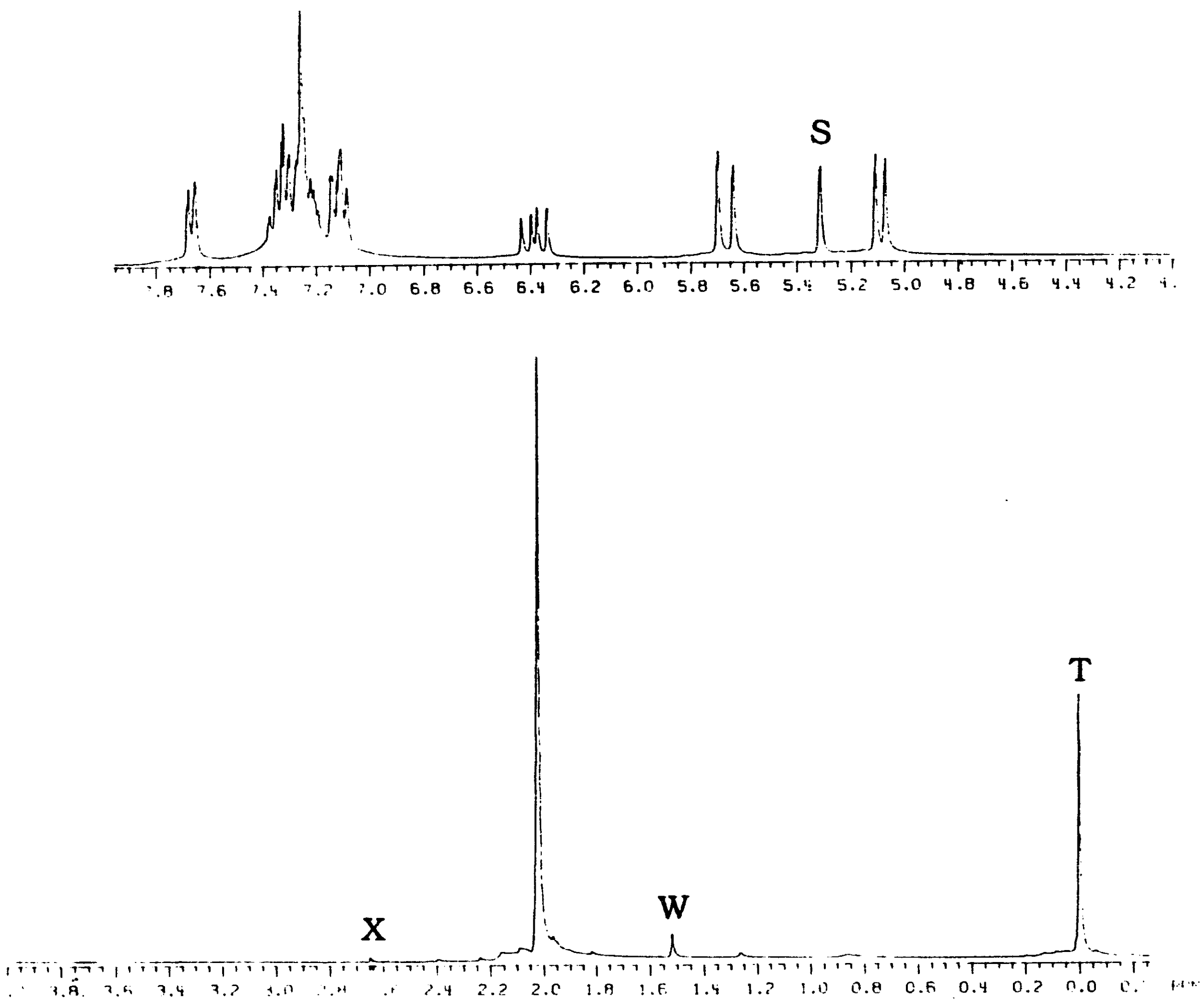


Figure A-1. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of 2-methyl-2-vinylbiphenyl (**9**) (S: $CHDCl_2$, W: H_2O, T: tetramethylsilane, X: unidentified impurity).

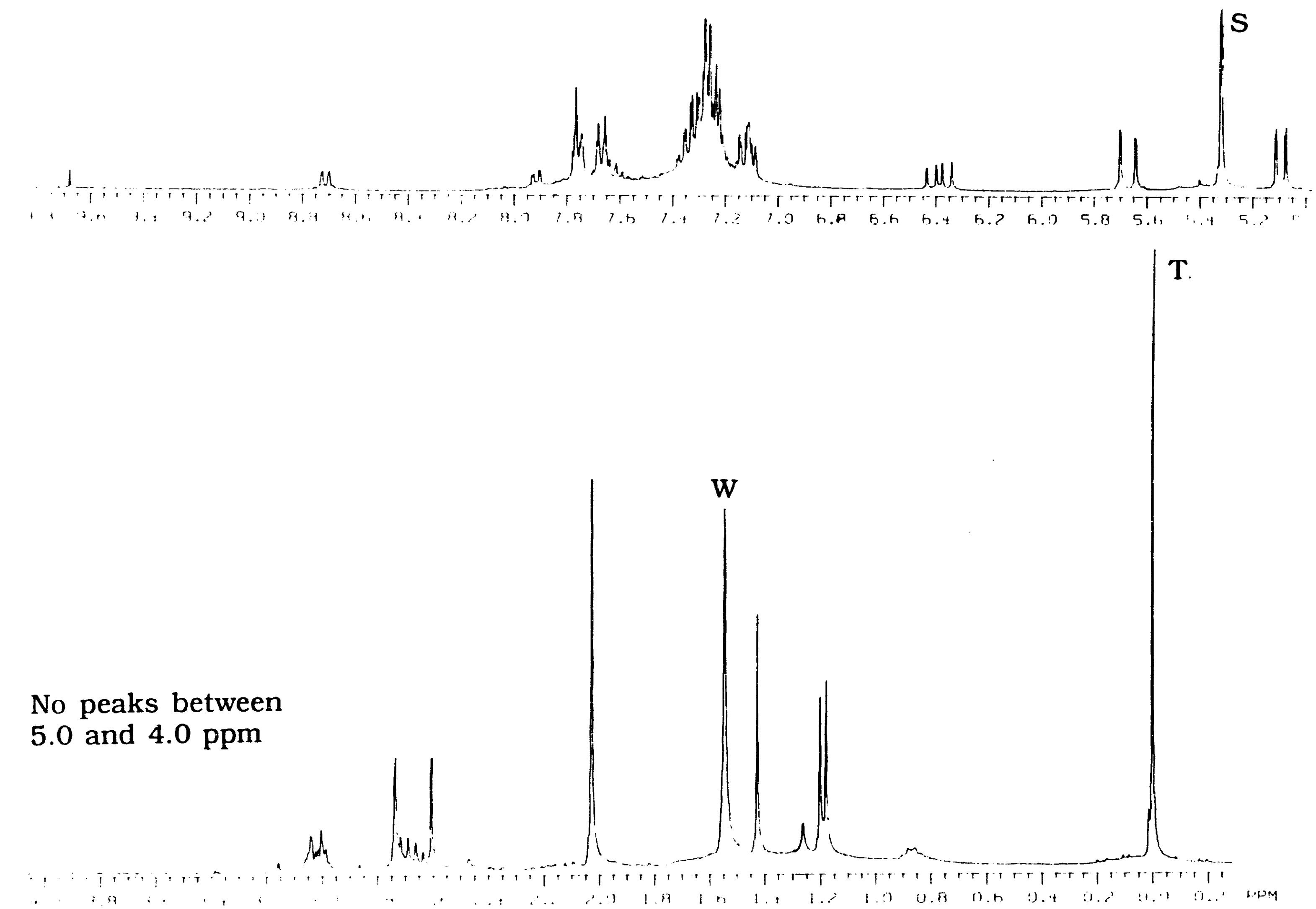


Figure A-2. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 700 °C of 2-methyl-2-vinylbiphenyl (**9**) (S: $CHDCl_2$, W: H_2O).

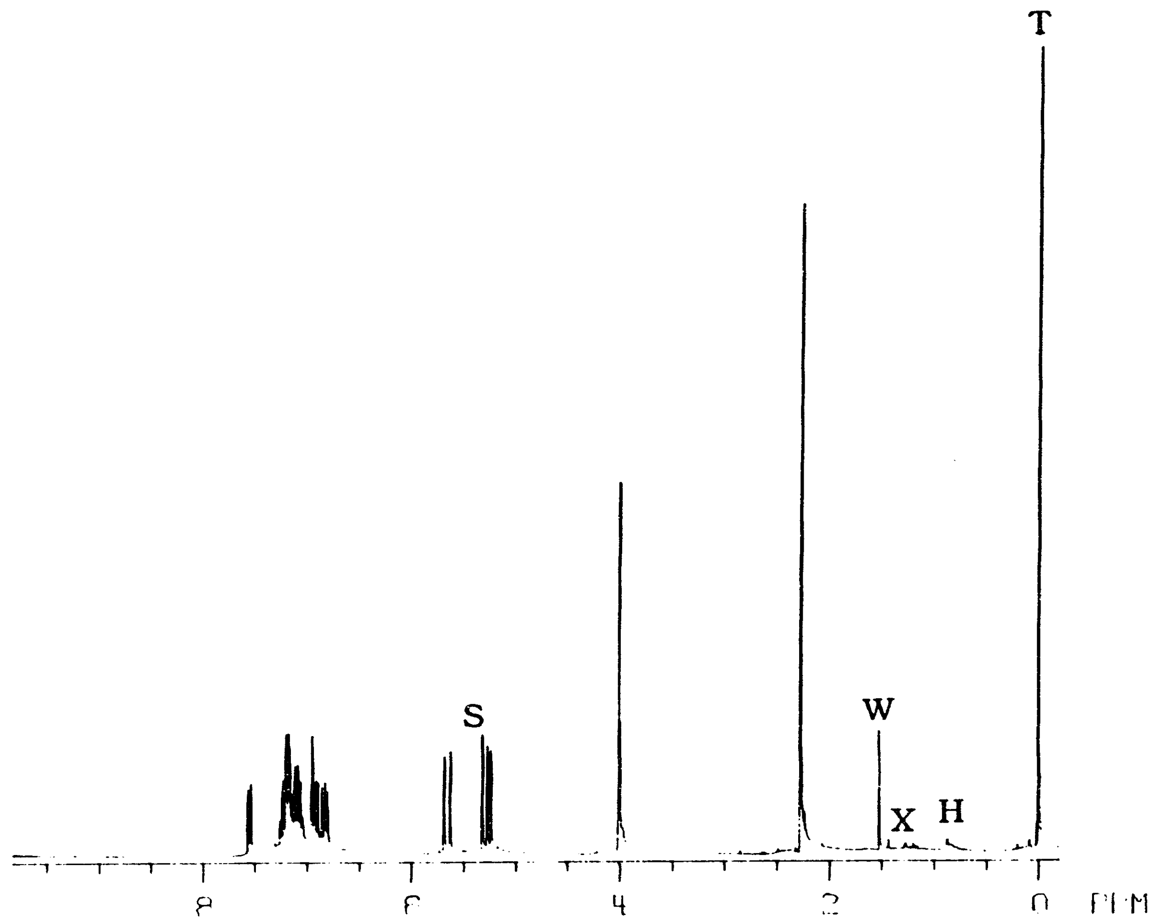


Figure A-3A. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of 2-(*o*-methylbenzyl)styrene **(10)** (S: $CHDCl_2$, W: H_2O, T: tetramethylsilane, H: high-boiling residue from hexanes, X: unidentified impurity).

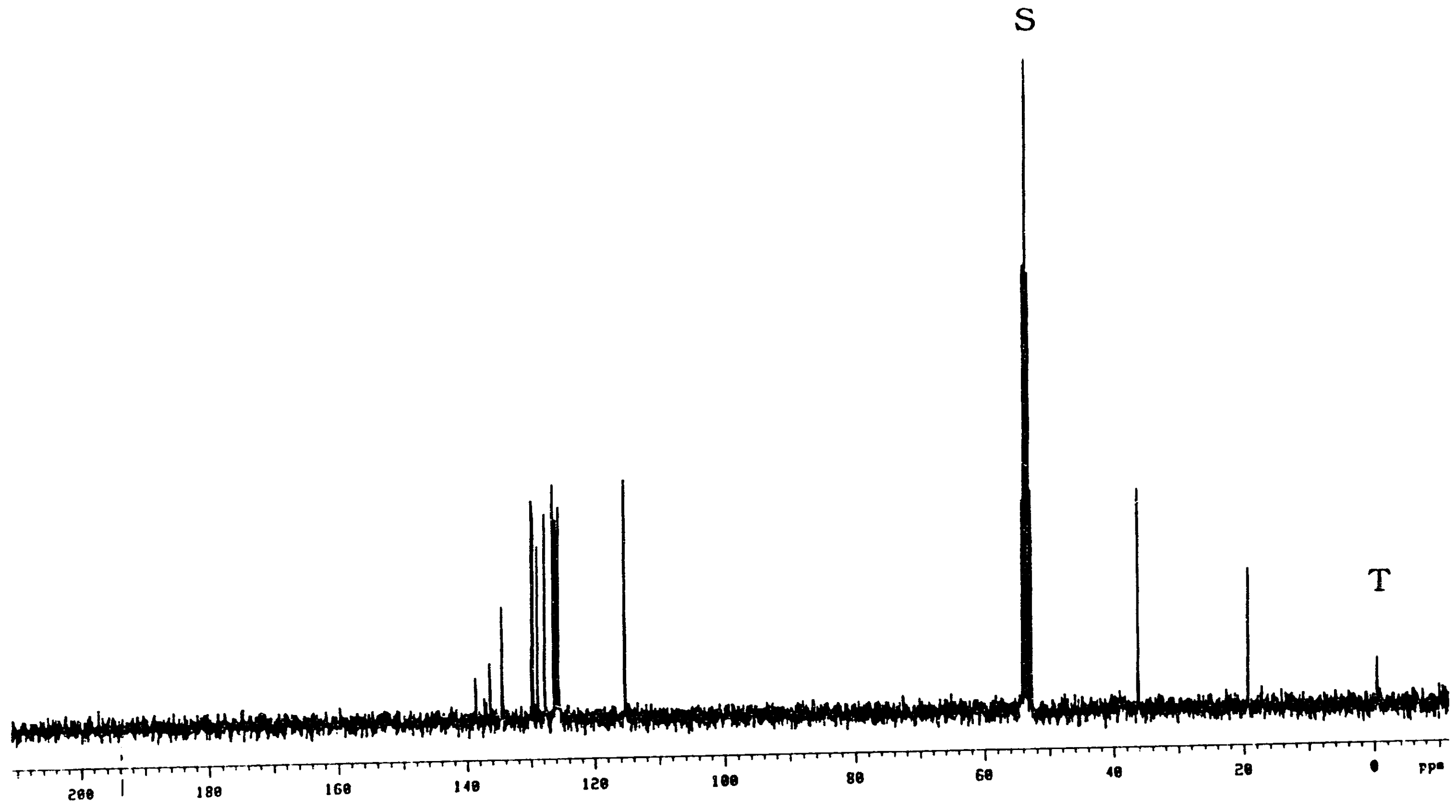


Figure A-3B. ^{13}C NMR spectrum (75.5 Hz, CD_2Cl_2) of *o*-[(2-methyl)phenylmethyl)styrene (**10**) (S: CD_2Cl_2, T: tetramethylsilane).

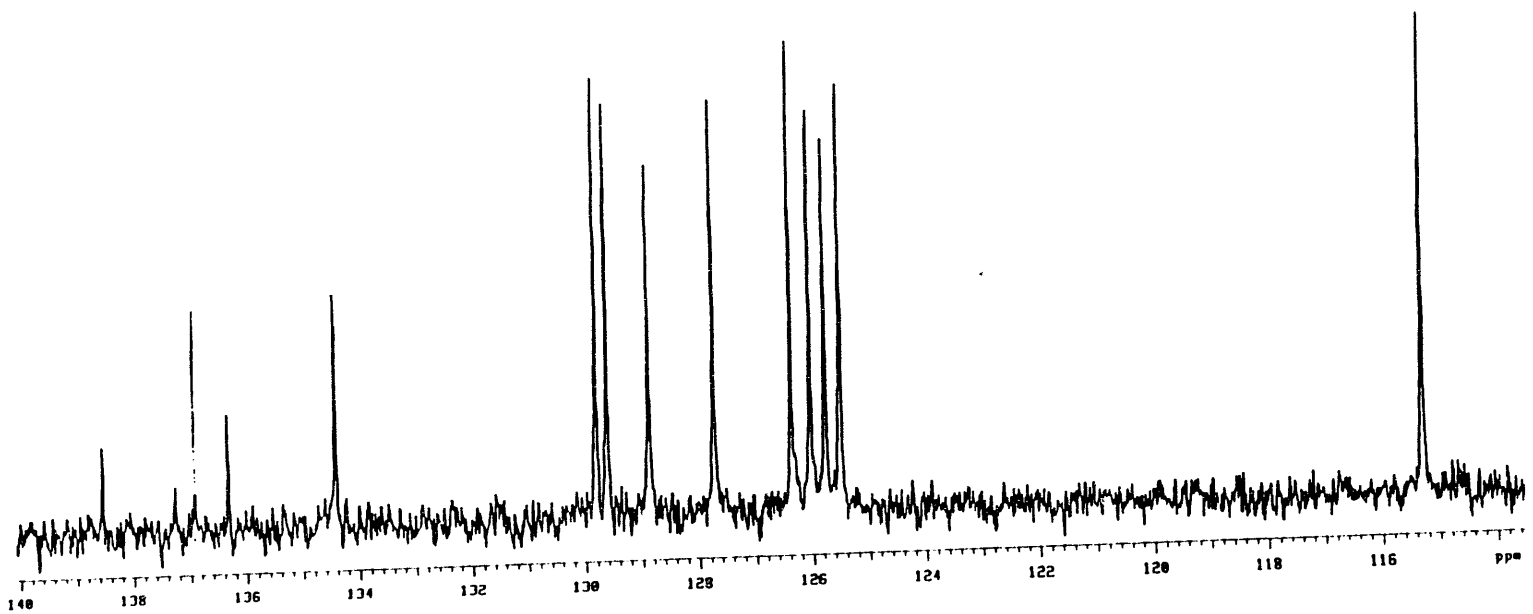


Figure A-3C. ^{13}C NMR spectrum (75.5 Hz, CD_2Cl_2) of the downfield region of *o*-[(2-methyl)phenylmethyl)styrene (**10**).

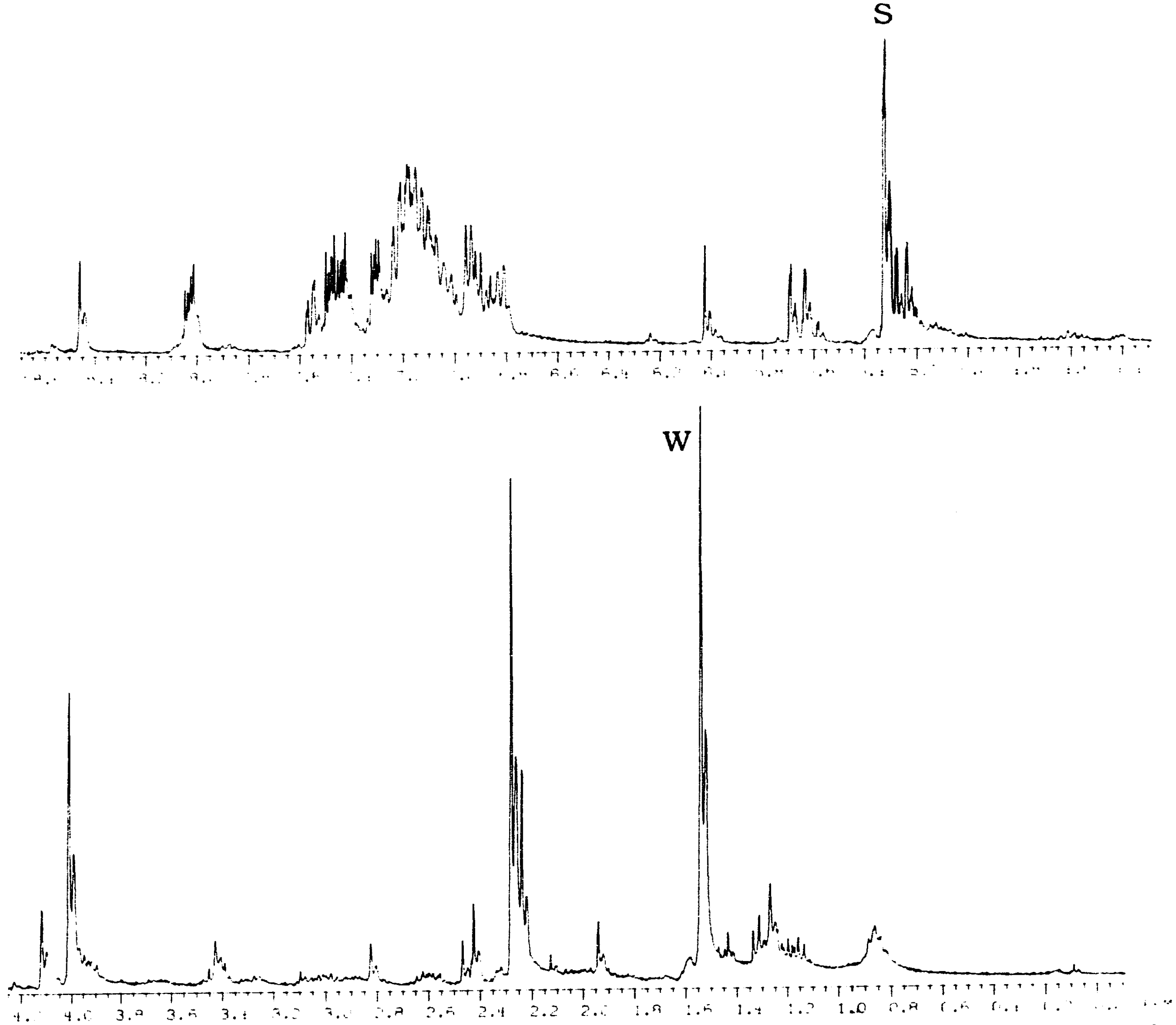


Figure A-4. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 700 °C of 2-(*o*-methylbenzyl)styrene (**10**) (S: $CHDCl_2$, W: H_2O).

APPENDIX 2

SUPPLEMENTARY DATA TABLES

Table A-I. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-2-methyl-2'-vinylbiphenyl (**9**) at various temperatures [a,b]

	yield, % [c]			
entry	RT [d]	600°C	700 °C	800 °C
naphthalene	—	0.12	—	—
BA-180 [$C_{14}H_{12}$]	—	—	—	2.67
2-methyl-2'-vinylbiphenyl (**9**)	99.37	92.95	43.99	—
BB-194 [$C_{15}H_{14}$]	0.28	—	—	—
9H-fluorene (**14**)	—	0.08	1.22	8.21
BC-208 [$C_{16}H_{16}$]	0.10	—	—	—
BD-180 [$C_{14}H_{12}$]	—	0.14	1.88	1.62
BE-194 [$C_{15}H_{14}$]	0.03	0.08	0.94	1.60
BF-196 [$C_{15}H_{16}$]	—	0.06	0.28	—
BG-180 [$C_{14}H_{12}$]	0.05	0.03	0.88	2.45
BH-180 [$C_{14}H_{12}$]	—	—	—	0.53
9,10-dihydro-9-methylphenanthrene (**11**)	—	4.59	27.16	6.75
BJ-180 [$C_{14}H_{12}$]	—	—	—	0.65
BK-194 [$C_{15}H_{14}$]	—	—	—	1.56
BL-194 [$C_{15}H_{14}$]	—	0.05	0.51	0.46

Table A-I continues on next page

Table A-I. Continued

entry	yield, % ^{c}			
	RT ^{d}	600 °C	700 °C	800 °C
BM-194 [$C_{15}H_{14}$]	—	1.38	9.75	10.28
BN-194 [$C_{15}H_{14}$]	—	—	—	0.39
BO-194 [$C_{15}H_{12}$]	0.03	—	0.42	—
phenanthrene (**12**)	—	0.44	10.02	57.93
BP-192 [$C_{15}H_{12}$]	—	—	—	0.60
BQ-192 [$C_{15}H_{12}$]	0.14	0.09	—	0.35
9-methylphenanthrene (**13**)	—	—	2.96	3.92
recovery ^{f}		85.76	69.54	50.21
conversion ^{g}	^{d}	6.97	56.05	100.00

^{a} FVP conditions: system pressure = 0.10 torr, sample temperature = 50-60 °C. ^{b} Amounts determined by GC with a known quantity of biphenyl added as standard. Data represent the average of triplicate runs. Products identified by comparison with authentic samples or those that could be identified by retention time and GCMS are indicated by name. Products that were identified by GCMS only are indicated by code: **X**Y-nnn, where '**X**' corresponds to the system first observed (**B** = 2-methyl-2'-vinylbiphenyl, **S** = *o*-((2-methyl)phenylmethyl)styrene, 'Y' to the individual unknown product (A, B, C, etc.), and 'nnn' to the nominal mass. ^{c} Moles of product divided by total moles of recovered material. ^{d} Starting material purity assay. ^{e} Unidentified product which constitutes ≤0.25% total area by GC. ^{f} Total moles of recovered material divided by moles of starting material used. ^{g} Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material.

Table A-II. Products and recovered starting material, total recovery of material, and conversion from the FVP of 2-(*o*-methylbenzyl)styrene (**10**) at various temperatures [a,b]

entry	yield, % [c]			
	RT [d]	600°C	700 °C	800 °C
ethylbenzene	—	—	—	0.40
styrene	—	—	—	0.41
o-ethyltoluene	—	—	—	0.25
o-methylstyrene	—	—	—	0.39
indene	—	—	0.56	1.04
naphthalene	—	—	—	0.58
o-benzyltoluene	—	0.14	0.46	0.39
fluorene (**14**)	—	—	—	0.32
SA-196 [$C_{15}H_{16}$]	—	0.16	—	—
o-benzylethylbenzene	1.06	1.05	0.70	0.39
SB-194 [$C_{15}H_{14}$]	—	—	0.40	—
SC-196 [$C_{15}H_{14}$]	—	—	0.22	0.29
SD-208 [$C_{16}H_{16}$]	—	—	—	0.16
SE-206 [$C_{16}H_{14}$]	0.17	—	—	—
SF-180 [$C_{14}H_{12}$]	—	—	0.33	—
SG-194 [$C_{15}H_{14}$]	—	0.14	—	0.19
SH-208 [$C_{16}H_{16}$]	—	0.55	—	—

Table A-II continues on next page

Table A-II. Continued

entry	yield, % [c]			
	RT [d]	600 °C	700 °C	800 °C
SI-208 [$C_{16}H_{16}$]	—	—	—	—
SJ-206 [$C_{16}H_{14}$]	1.36	1.25	—	—
SK-208 [$C_{16}H_{16}$]	—	—	4.32	3.17
SL-208 [$C_{16}H_{16}$]	—	—	1.01	—
SM-196 [$C_{15}H_{14}$]	—	0.98	1.22	—
SN-208 [$C_{16}H_{16}$]	0.41	12.13	5.12	0.29
SO-208 [$C_{16}H_{16}$]	—	0.31	—	—
2-(*o*-methylbenzyl)styrene (**10**)	93.54	65.69	13.22	1.24
SP-208 [$C_{16}H_{16}$]	0.67		—	—
SQ-210 [$C_{16}H_{18}$]	—	0.50	0.41	0.21
SR-208 [$C_{16}H_{16}$]	—	0.31	—	—
SS-208 [$C_{16}H_{16}$]	1.26	—	—	—
ST-208 [$C_{16}H_{16}$]	—	1.09	6.56	4.44
SU-208 [$C_{16}H_{16}$]	—	1.09	1.04	—
SV-206 [$C_{16}H_{14}$]	—	0.30	—	0.43
SW-208 [$C_{16}H_{16}$]	1.55	0.10	—	—
SX	—	—	*e*	—
SY-208 [$C_{16}H_{16}$]	—	1.24	1.40	1.57
SZ-208 [$C_{16}H_{16}$]	—	0.11	0.23	—
SAA-208 [$C_{16}H_{16}$]	—	—	0.25	—
SBB-206 [$C_{16}H_{14}$]	—	—	—	0.28

Table A-II continues on next page

Table A-II. Continued

entry	yield, % [c]			
	RT [d]	600 °C	700 °C	800 °C
SCC-208 [$C_{16}H_{16}$]	—	0.45	1.35	1.44
SDD-208 [$C_{16}H_{16}$]	—	0.94	—	—
anthracene (**15**)	—	7.24	45.29	62.58
SEE-208 [$C_{16}H_{16}$]	—	1.07	3.05	0.42
SFF-208 [$C_{16}H_{16}$]	—	0.15	—	—
SGG-208 [$C_{16}H_{16}$]	—	0.23	0.83	0.59
SHH-208 [$C_{16}H_{16}$]	—	0.46	0.37	—
SII-192 [$C_{15}H_{12}$]	—	—	—	0.36
SJJ-208 [$C_{16}H_{16}$]	—	—	0.41	0.53
SKK-206 [$C_{16}H_{14}$]	—	—	0.14	—
SLL-192 [$C_{15}H_{12}$]	—	—	0.35	1.24
1-methylanthracene (**16**)	—	—	7.20	11.78
9-methylanthracene	—	1.26	1.26	0.85
SMM-206 [$C_{16}H_{14}$]	—	0.18	—	0.23
SNN-206 [$C_{16}H_{14}$]	—	—	2.55	1.57
SOO-206 [$C_{16}H_{14}$]	—	0.63	—	0.22
SPP-204 [$C_{16}H_{12}$]	—	0.22	—	0.45
SQQ-206 [$C_{16}H_{14}$]	—	—	0.38	0.30
SRR-206 [$C_{16}H_{14}$]	—	—	—	0.41
recovery [f]	100.00	75.24	58.45	59.28
conversion [g]	d	51.02	85.34	93.91

Table A-II continues on next page

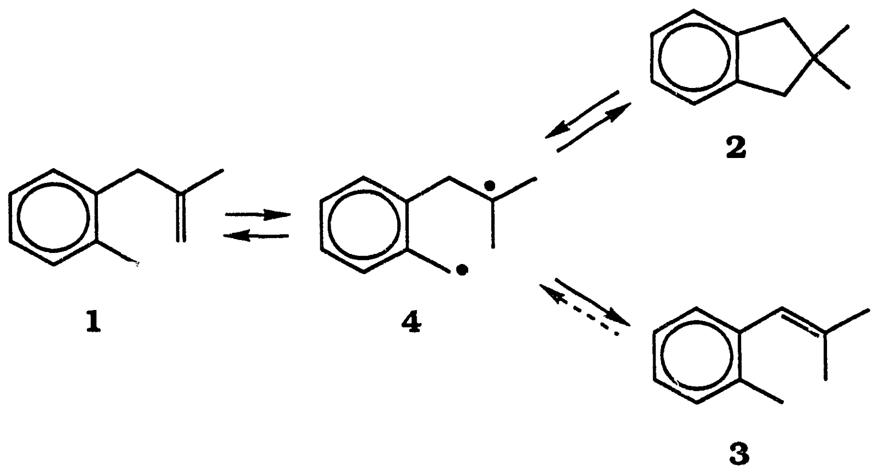
Table A-II. Continued

[a] FVP conditions: system pressure = 0.10 torr, sample temperature = 50-60 °C. [b] See Table I, note *b*. [c] See Table I, note *c*. [d] Assay of starting material by GC in area percentages. [e] Unidentified product which constitutes ≤0.25% total area by GC. [f] See Table I, note *f*. [g] See Table I, note *g*.

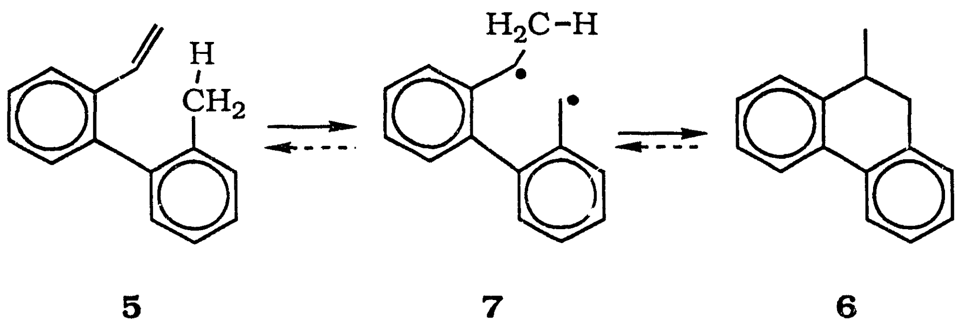
PAPER 4. COUPLING OF DIRADICALS GENERATED BY INTRAMOLECULAR HYDROGEN-ATOM TRANSFERS: CYCLIZATION REACTIONS OF ALLYLPHENOLS

INTRODUCTION

We have recently reported findings concerning the conversion of *o*-methallyltoluene (**1**) to 2,2-dimethylindan (**2**) and *o*-(2-methyl-propenyl)toluene (**3**) under flash vacuum pyrolysis (FVP) conditions.[1] We postulate that an intramolecular hydrogen-atom transfer occurs to give a diradical intermediate (**4**) which then undergoes coupling or intramolecular disproportionation. We have also reported that FVP of



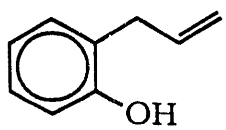
2-methyl-2'-vinylbiphenyl (**5**) at 600-800 °C, gives 9-methyl-9,10-dihydrophenanthrene (**6**), presumably through diradical intermediate **7**.[2]



While there are several examples of formation of diradicals or a pair of radicals by transfer of a hydrogen atom

by intramolecular photochemical reactions[3] or intermolecular thermal reactions[4,5,6], there has been only one other report which presents evidence for the formation of a diradical by transfer of a hydrogen atom and this is for the cyclization of an organosilicon compound.[7]

We investigated the FVP reactions of *o*-allylphenol (**8**), and *o*-[(1-methylallyl)phenol (**9**) to determine whether these compounds undergo cyclization in the same manner as **1** and **5**.



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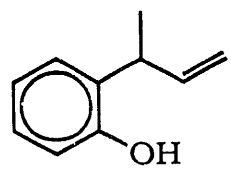

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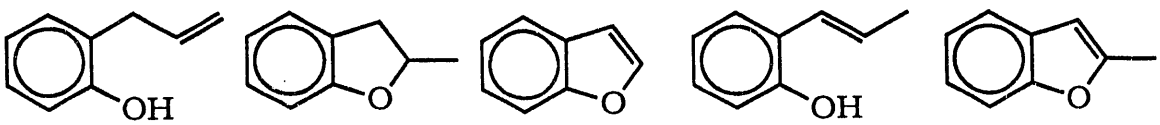
RESULTS

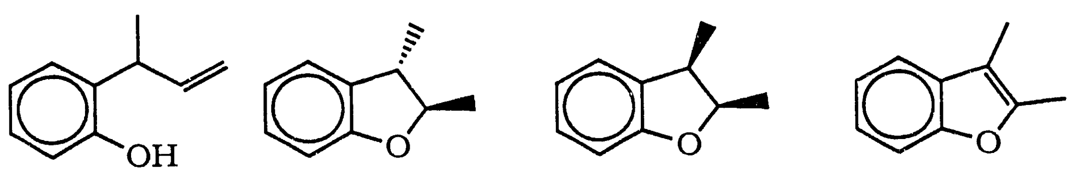
A summary of the product studies of the flash vacuum pyrolysis (FVP) of 2-allylphenol (**8**) at 0.10 torr (600-800 °C) are presented in Table I. At 600 °C, the major product is 2,3-dihydro-2-methylbenzofuran (**10**). Smaller amounts of benzofuran (**11**), E-(*o*-1-propenyl)phenol (**12**), and 2-methylbenzofuran (**13**) are produced. At 700 °C, the



8 **10** **11** **12** **13**

amounts of **10-13** increase. At 800 °C, **11** makes up nearly half of the product mixture, and the amount of **10** drops. Starting material is nearly completely consumed, and **12** is obtained in greater than 10 % yield.

A summary of the product studies of the FVP of 2-(1-methylallyl)phenol (**9**) at 0.10 torr (600-800 °C) are presented in Table II. At 600 °C, the major product is *trans*-2,3-dihydro-2,3-dimethylbenzofuran (**14**). The *cis* isomer (**15**) makes up *ca.* 18 % of the product. 2,3-Dimethylbenzofuran (**16**), **13**, and **11** are also formed. At 700 °C,



9 **14** **15** **16**

11 is now the predominant product, and the yield of **13** is much higher. The yields of **14** and **15** drop somewhat, a At 800 °C, **11** makes up over 70 % of the product mixture, and most of the remainder is **13**. No other compound represents more than *ca.* 2.9 % of the mixture.

Table I. Products and recovered starting material, total recovery of material, and conversion from the FVP of 2-allylphenol (**8**) at various temperatures [a,b]

entry	yield, % [c]		
	600°C	700 °C	800 °C
2-allylphenol (**8**) [d]	49.0	18.1	6.1
2,3-dihydro-2-methylbenzofuran (**10**)	27.0	37.4	11.1
benzofuran (**11**)	10.2	20.6	48.4
E-(*o*-1-propenyl)phenol (**12**)	3.7	6.9	10.1
2-methylbenzofuran (**13**)	1.4	4.1	7.2
AD-134 [$C_9H_{10}O$]	0.9	2.8	1.6
other products	8.7 [e]	13.0 [e]	17.1 [e]
recovery [f]	93.6	81.0	58.5
conversion [g]	51.0	81.9	93.9

[a] FVP conditions: system pressure = 0.10 torr, sample temperature = 0 °C. [b] Amounts determined by GC with a known quantity of biphenyl added as standard. Data represent the average of triplicate runs. Products identified by comparison with authentic samples or by retention time and GCMS are indicated by name. Products identified by GCMS only are indicated by code: **X**Y-nnn, where '**X**' represents the experiment where first observed (**A** = 2-allylphenol, **M** = 2-(1-methylallyl)phenol, 'Y' the individual unknown product (A, B, C, etc.), and 'nnn' the nominal mass. [c] Moles of product divided by total moles of recovered material. [d] Starting material assay (GC, mole %): *o*-allylphenol (96.4), 2,3-dihydro-2-methylbenzofuran (3.6). [e] See Table A-I in the Appendix of Paper 3, this dissertation, for a more detailed analysis. [f] Total moles of recovered material divided by moles of starting material used. [g] Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material.

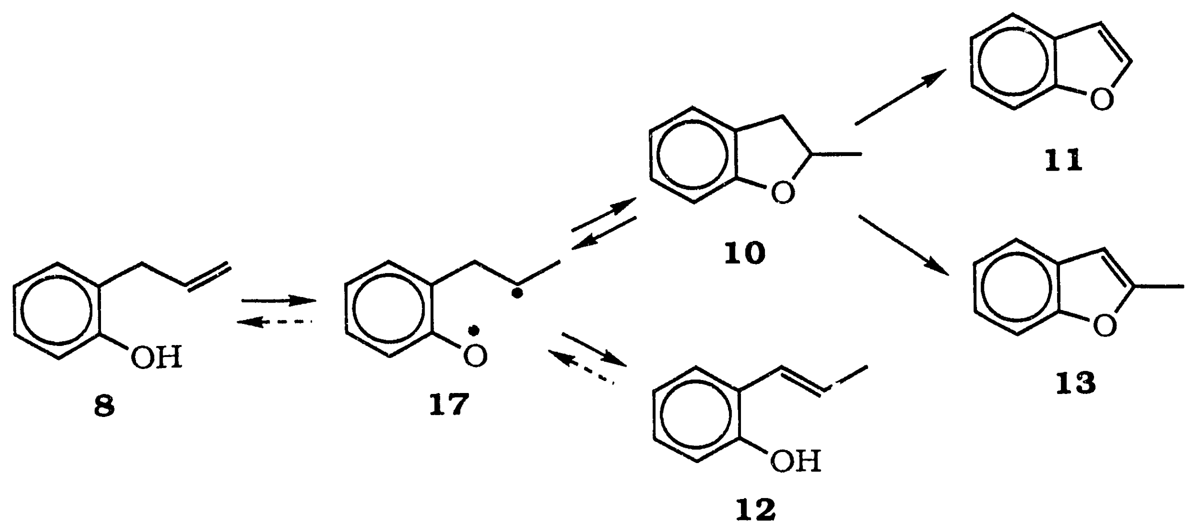
Table II. Products and recovered starting material, total recovery of material, and conversion from the FVP of 2-(1-methylallyl)phenol (**9**) at various oven temperatures [a,b]

entry	yield, % [c]		
	600°C	700 °C	800 °C
trans-2,3-dihydro-2,3-dimethyl-benzofuran (**14**)	40.7	25.6	1.7
cis-2,3-dihydro-2,3-dimethylbenzofuran (**15**)	18.1	9.1	1.0
2-(1-methylallyl)phenol (**9**) [d]	13.7	—	—
2-methylbenzofuran (**13**)	9.3	21.1	14.5
2,3-dimethylbenzofuran (**16**)	3.1	4.8	2.9
benzofuran (**11**)	3.0	26.3	71.1
other products[e]	12.0	13.1	8.8
recovery [f]	73.1	65.4	64.9
conversion [g]	86.3	100.0	100.0

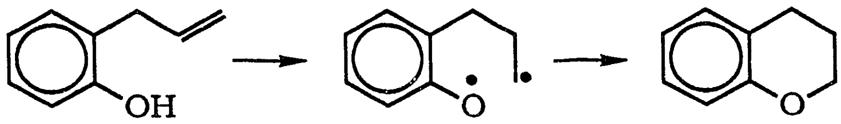
[a] See Table A-I, note *a*. [b] See Table I, note *b*. [c] See Table I, note *c*. [d] Starting material (GC assay, relative area%): 2-(1-methylallyl)phenol (98.5), **M**Y-148 (0.8), **M**P-148 (0.7). [e] See Table A-II in the Appendix of Paper 3, this dissertation, for a more detailed analysis. [f] See Table I, note *f*. [g] See Table I, note *g*.

DISCUSSION

The formation of the major products of the FVP of *o*-allylphenol (**8**) and *o*-[(1-methylallyl)phenol (**9**) are explained by the intramolecular hydrogen-atom transfer/diradical coupling mechanism we have proposed. At low temperatures, FVP of **8** affords 2,3-dihydro-2-methylbenzofuran (**10**) as the major component, and small amounts of E-(*o*-1-propenyl)phenol (**11**) are also formed. The formation of **10** and **11** can be explained by intramolecular hydrogen-atom transfer of the phenolic hydrogen the end of the double bond to give diradical **17**.[8] Coupling of **17** would give **10**, and disproportionation would give either starting material or **12**. Secondary pyrolysis of **10** is probably responsible for the formation of compounds **11** and **13**.



Analysis of GCMS and NMR data strongly suggested the production of chroman (**18**), although its presence could not be definitely established. The likely route to **18** is by hydrogen transfer to the internal carbon of the double bond followed by coupling of the resulting diradical (**19**)

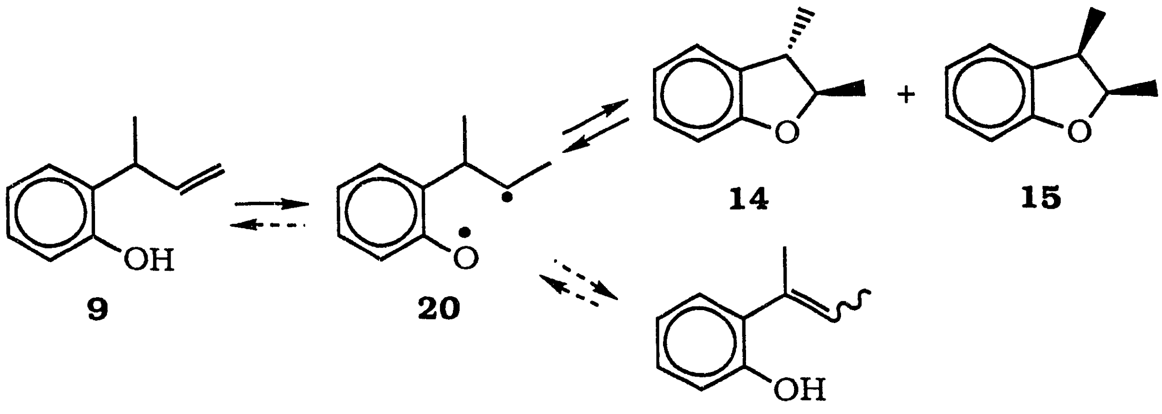


8 **19** **18**

The cyclization of **8** to **10** under acid-catalyzed[12] conditions has been previously observed. In addition, photolysis of **8** is known to afford **10** and **19**.[13] The ratio of **10** : **18** we observe at 800 °C resembles that reported by Miranda,[13i] which adds some support to our identification of chroman.

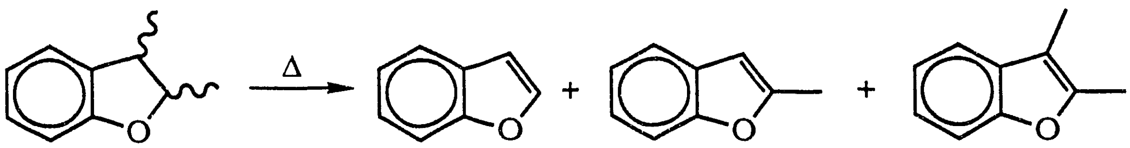
Recent work by Li[14] in our laboratory indicates that the cyclization of **10** is reversible. Secondary pyrolysis of **10**, which is produced from a different precursor, results in the production of substantial amounts of **10** and **12**, although **11** was the major product. We have previously observed that the cyclization of 2,2-dimethylindan (**2**) is reversible,[1] and Li's results are consistent with a hydrogen transfer/diradical intermediate mechanism for **8**.

FVP of *o*-[(1-methylallyl)phenol (**9**) gives good yields of both the *trans*- and *cis*- isomers of 2,3-dihydro-2,3-dimethylbenzofuran (**14** and **15**, respectively) as the major products at low temperatures. **14** and **15** were identified based on analysis of the GCMS and ^{1}H NMR data, including comparison to the ^{1}H NMR reported in the literature.[15] Formation of **14** and **15** is consistent with formation and coupling of diradical **20**. Double bond isomer **21**, the anticipated product of dis



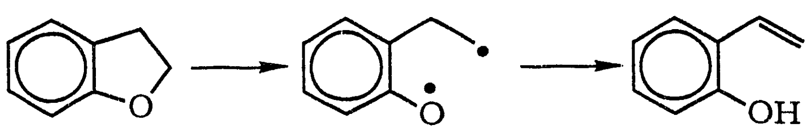
9 **20** **14** **15** **21**

proportionation of **20**, was not found, but it is possible that the presence of the α-methyl group leads to fragmentation reactions.[1] Compounds **11**, **13**, and **16** are probably the products of secondary pyrolysis of **14** and **15**.



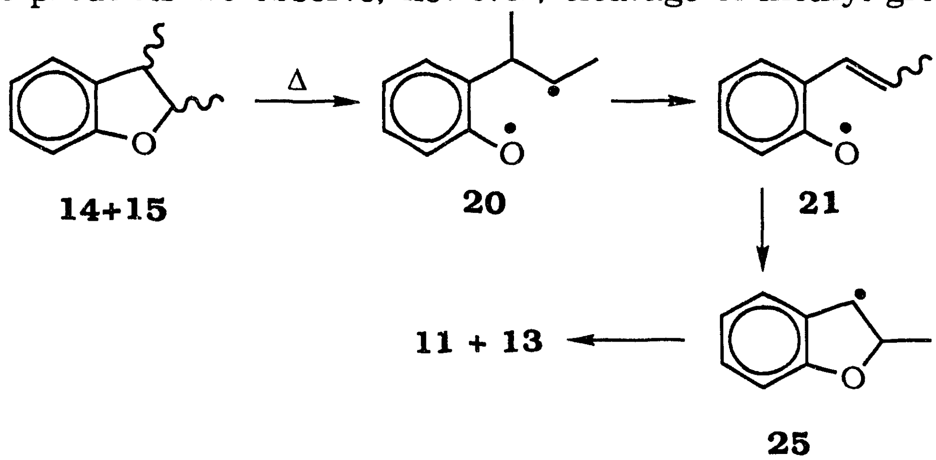
14+15 **11** **13** **16**

A related study concerning the flow pyrolysis behavior of dihydrobenzofuran derivatives has been recently published.[16] When dihydrobenzofuran (**22**) is pyrolyzed in a toluene/N_2 mixture at 700-750 °C, *o*-vinylphenol (**23**), and **11** are formed in a 1 : 1 ratio. They propose that **23** arises by C-O cleavage to give diradical **24**, followed by disproportionation of **24**.



22 **24** **23**

In addition, pyrolysis of a mixture of **14** and **15** under similar conditions affords **11** and **13** in a 5 : 1 ratio, which is close to the ratio we observed at 800 °C. They propose that ring opening of **14/15** occurs to afford diradical **20**, which then loses the α-methyl group to give **25**. Cyclization of **25** would be followed by loss of either the β-methyl group to give **11** or the or β-hydrogen to afford **13**. This series of reactions could explain formation of some of the secondary pyrolysis products we observe, however, cleavage of methyl groups



from **14** and **15** directly without ring opening is also possible. Their results are consistent with our findings in several respects: high yields of **11**, formation of **12**, and no **21** observed. However, they did not report finding any **16**. It is possible that the pyrolysis conditions they employed disfavored formation of **21**.

CONCLUSION

The flash vacuum pyrolysis (FVP) of 2-allylphenol (**8**) at 0.10 torr (600-800 °C) gives 2,3-dihydro-2-methylbenzofuran (**10**), as the main primary product, along with low yields of E-(*o*-1-propenyl)phenol (**12**). Benzofuran (**11**) and 2-methylbenzofuran (**13**) are produced by secondary pyrolysis of **8**.

Likewise, FVP of 2-(1-methylallyl)phenol (**9**) under similar conditions gives fair yields of 2,3-dihydro-2,3-dimethylbenzofuran (**14** and **15**) as a mixture of cis- and *trans*- isomers. Secondary pyrolysis of **14** and **15** affords **11**, **13**, and 2,3-dimethylbenzofuran (**16**). The formation of **10** and **12** from **8** and of **14** and **15** from **9** are consistent with hydrogen-atom transfer reactions to afford diradical intermediates (**14** and **19**) which then undergo coupling or intramolecular disproportionation.

EXPERIMENTAL

Methods and materials.

The pyrolysis apparatus has been described previously.[1] Unless otherwise noted, NMR spectra were obtained in d_6-methylene chloride solution and chemical shifts are relative to tetramethylsilane. ^1H NMR spectra were recorded on a Nicolet NT-300 spectrometer. GCMS was performed on Finnegan 4500 spectrophotometer with 70-eV EI after separation on a DB-1701 capillary column or on a Finnegan Magnum quadrapole ion-trap spectrophotomer with 70-eV EI after separation on a DB-5 capillary column. *o*-Allylphenol was purchased from Aldrich and purified by colum chromatography prior to use.

Phenyl crotyl ether. Phenyl crotyl ether was prepared by Claisen's method:[9a] ^1H NMR (CD_2Cl_2) δ 7.31–7.19 (m, 2 H), 6.95–6.81 (m, 2 H), 5.93-5.62 (m, 2 H), 4.42 (dd, J_d = 5.8 Hz, J_d = 0.8 Hz, 2 H), 1.73 (dd, J_d = 6.1 Hz, J_d = 1.1 Hz, 3 H).

***o*-(1-Methylallyl)phenol (9).** *o*-(1-methylallyl)phenol (**9**) was prepared by Claisen's method:[9a] ^1H NMR (CD_2Cl_2) δ 7.20–7.02 (m, 2 H), 6.89 (t, J_t = 7.5 Hz, 1 H), 6.77 (d, J = 6.8 Hz, 1 H), 6.14-5.97 (m, 1 H), 5.21–5.04 (m, 3 H), 3.80–3.64 (m, 1 H), 1.36 (d, J = 7.2 Hz, 1 H); [lit.[17] ^1H NMR (CCl_4) δ 7.20-6.55 (m, 4 H), 6.33-5.78 (m, 1 H), 5.30-4.90 (m, 3 H), 3.93-3.40 (m, 1 H), 1.36 (d, 3 H)].

Flash vacuum pyrolysis. Flash vacuum pyrolysis (FVP) was performed as previously described.[18]

Product analysis. FVP reaction mixtures were analyzed by capillary gas chromatography as previously described.[15] Flame ionization detector response factors were calculated for **8**, **10**, and **11**. Compounds **9** and **12** were assumed to have response factors equal to **8**. Compounds **13** and **16** were assumed to have response factors equal to **11**. Compounds **14** and **15** were assumed to have response factors equal to **10**. Other compounds were assigned response factors equal to biphenyl.

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(8) The possibility of the cyclization proceding by proton transfer and coupling of the resulting zwitterion can be eliminated by examination of the heats of formation of the two pathways. While the heat of formation of the phenoxy anion[9] is *ca.* 50 kcal mol^{-1} lower than that of the phenoxy radical[10], the heat of formation of the secondary cation[9] site is *ca.* 170 kcal mol^{-1} higher than

that of the radical.[11] Therefore, the zwitterionic mechanism is *ca.* 120 kcal mol^{-1} higher than the diradical mechanism, and the energy required is prohibitively high.

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APPENDIX 1

SPECTRA

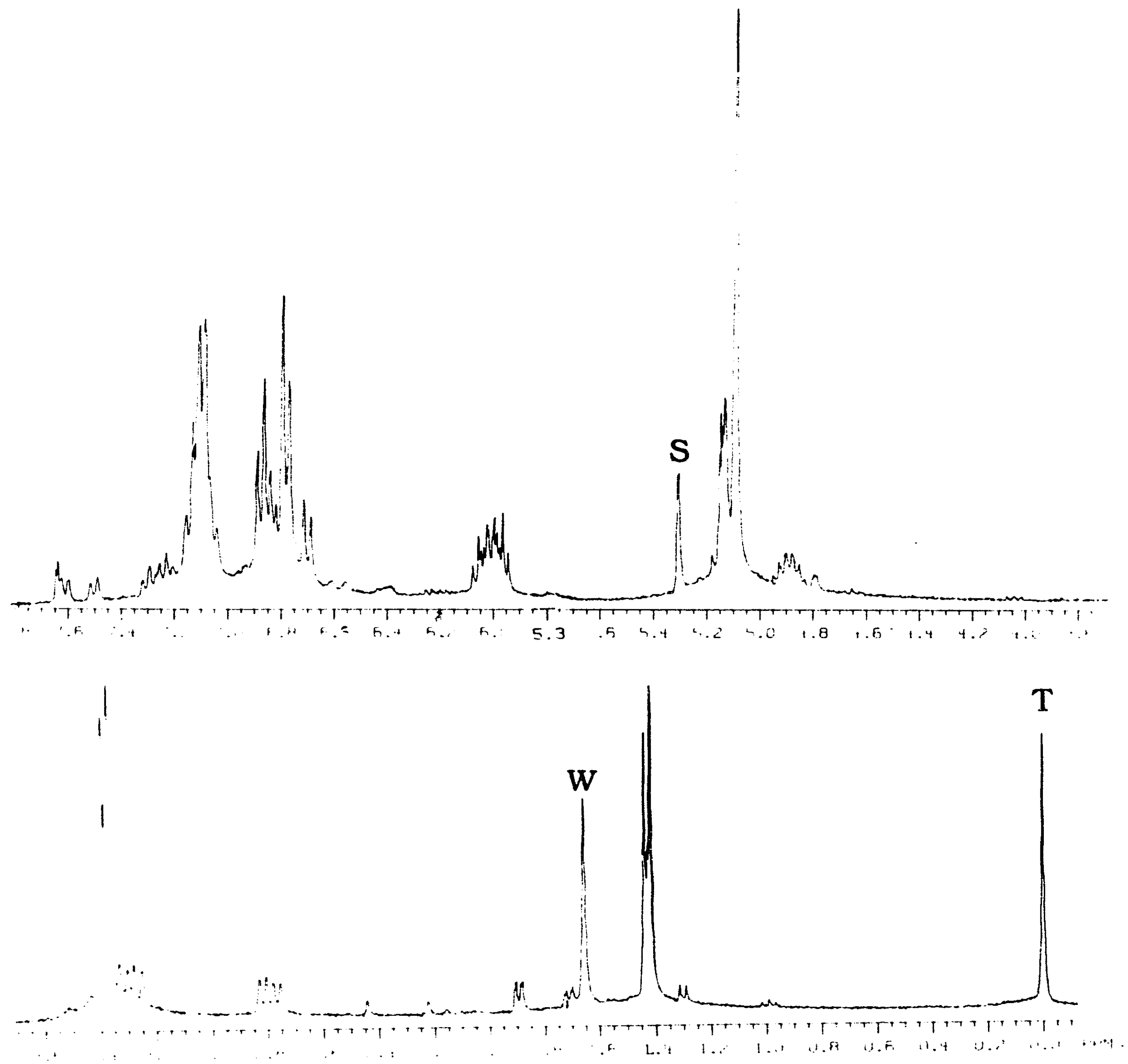

Figure A-1. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 700 °C of *o*-allylphenol (**8**) (S: $CHDCl_2$, W: H_2O, T: tetramethylsilane).

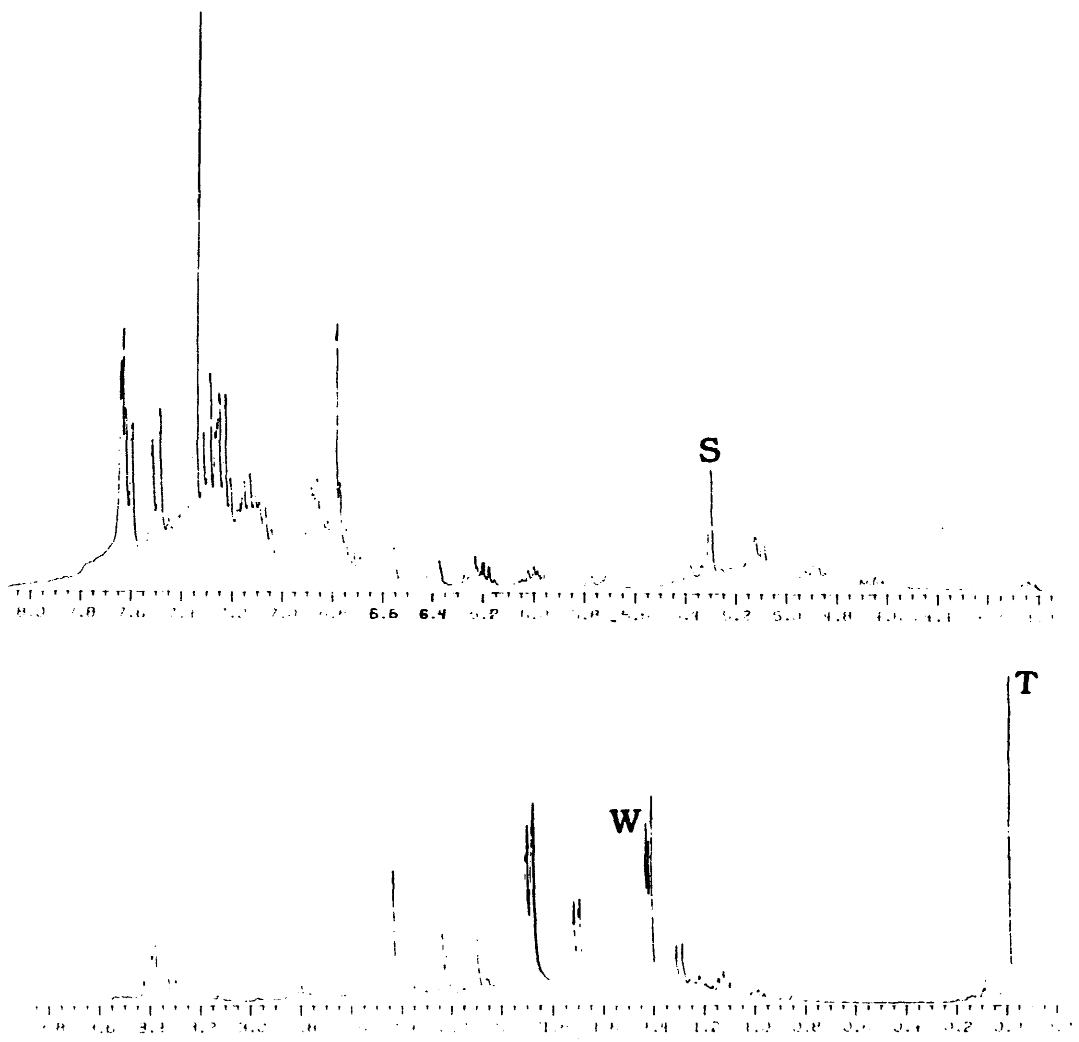

Figure A-2. ^1H NMR spectrum (300 Hz, CD_2Cl_2) of the pyrolysis mixture from the FVP of *o*-allylphenol (**8**) at 800 °C (S: $CHDCl_2$, W: H_2O, T: tetramethylsilane).

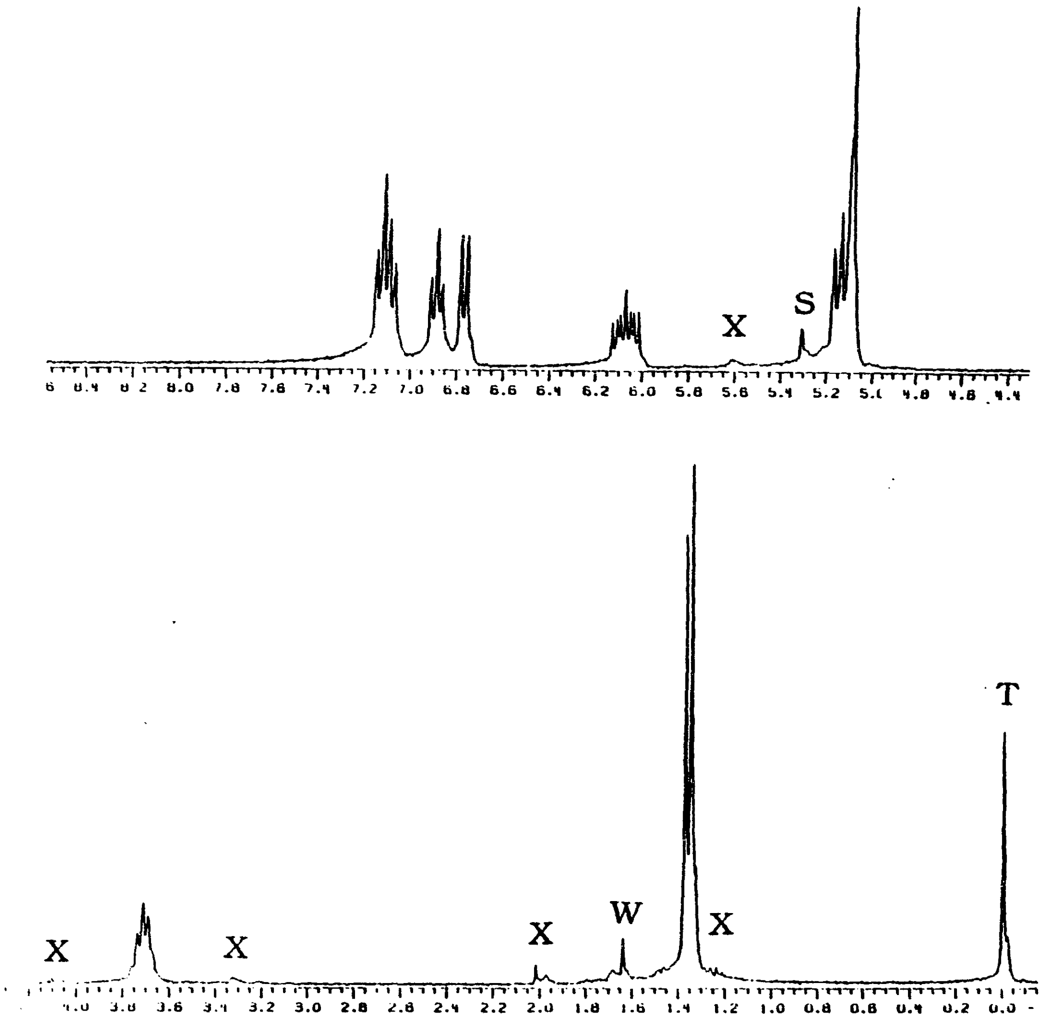

Figure A-3. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of *o*-(1-methylallyl)phenol **(9)** (S: $CHDCl_2$, W: H_2O, T: tetramethylsilane, X: unidentified impurity)

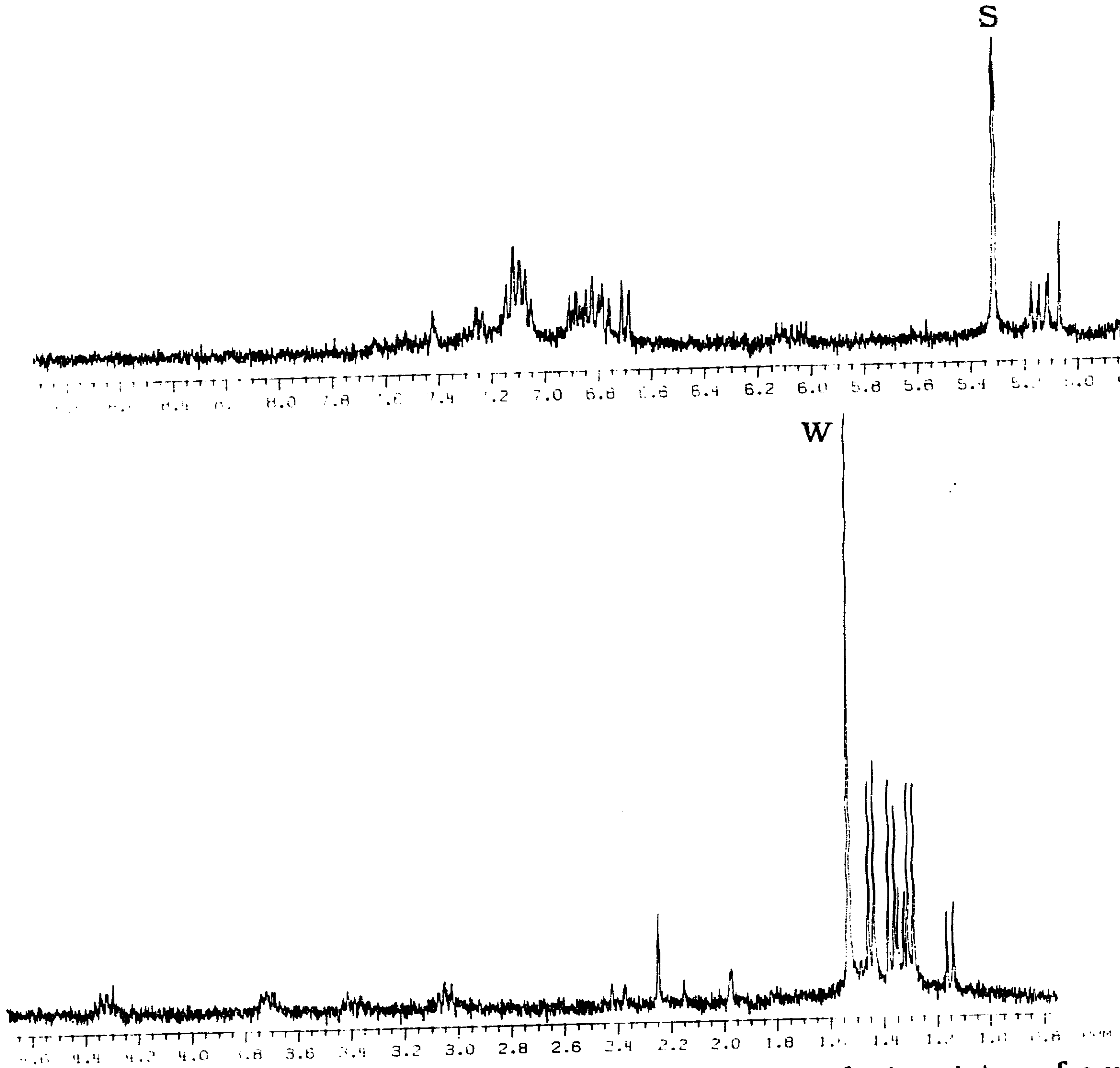

Figure A-4. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 800 °C of *o*-(1-methylallyl)phenol (**9**) (S: $CHDCl_2$, W: H_2O, T: tetramethylsilane)

APPENDIX 2

SUPPLEMENTARY DATA TABLES

Table A-I. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-allylphenol (**8**) at various temperatures [a,b]

entry	yield, % [c]			
	RT [d]	600°C	700 °C	800 °C
ethylbenzene	—	—	—	0.29
m/*p*-xylene	—	—	—	0.14
phenylacetylene	—	—	0.10	0.35
styrene	—	—	0.18	0.77
benzofuran (**11**)	—	10.17	20.56	48.39
indene	—	—	0.22	1.12
1-phenylpropyne	—	—	—	0.16
AA-130 [$C_{10}H_{10}$]	—	—	0.09	0.12
AB-132 [C_9H_8O]	—	0.05	—	0.26
2-methylbenzofuran (**13**)	—	1.41	4.08	7.18
AC-134 [$C_9H_{10}O$]	—	—	—	1.37
2,3-dihydro-2-methylbenzofuran (**10**)	3.58	26.99	37.41	11.12
chroman (**19**)	—	0.86	2.84	1.56
AE-132 [C_9H_8O]	—	—	0.16	0.23
AF-130 [$C_{10}H_{10}$]	—	0.78	1.88	1.58
AG-132 [C_9H_8O]	—	0.22	0.50	1.43
o-cresol	—	5.16	3.61	1.88

Table A-I continues on next page

Table A-I. Continued

entry	yield, % [c]			
	RT [d]	600 °C	700 °C	800 °C
AH	—	—	*e*	—
AI-146 [$C_{10}H_{12}O$]	—	0.04	0.13	0.15
AJ-134 [$C_9H_{10}O$]	—	1.30	—	4.02
AK-146 [$C_{10}H_{12}O$]	—	—	0.30	0.10
AL-120 [C_8H_8O]	—	0.28	0.30	0.92
o-allylphenol (**8**)	96.42	48.98	18.10	6.09
AM	—	*e*	—	—
AN-132 [C_9H_8O]	—	—	—	0.11
AO-132 [C_9H_8O]	—	0.06	0.39	0.50
E-(*o*-1-propenyl)phenol (**12**)	—	3.71	6.94	10.12
recovery [f]		93.59	80.98	58.52
conversion [g]	*d*	51.02	81.90	93.91

[a] FVP conditions: system pressure = 0.10 torr, sample temperature = 50-60 °C. [b] Amounts determined by GC with a known quantity of biphenyl added as standard. Data represent the average of triplicate runs. Products identified by comparison with authentic samples or those that could be identified by retention time and GCMS are indicated by name. Products that were identified by GCMS only are indicated by code: **XY**-nnn, where '**X**' corresponds to the system first observed (**A** = *o*-allylphenol, **M** = *o*-(α-methylallyl)phenol, 'Y' to the individual unknown product (A, B, C, etc.), and 'nnn' to the nominal mass. [c] Moles of product divided by total moles of recovered material. [d] Starting material purity assay. [e] Unidentified product which constitutes ≤0.13% total area by GC. [f] Total moles of recovered material divided by moles of starting material used. [g] Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material.

Table A-II. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-(1-methylallyl)phenol (**9**) at various temperatures [a,b]

entry	yield, % [c]			
	RT [d]	600°C	700 °C	800 °C
toluene	—	—	2.58	0.70
MA	—	—	*e*	—
MB	—	—	—	*f*
phenylacetylene	—	—	0.36	1.33
styrene	—	—	0.43	0.62
MC	—	*e*	—	—
MD-148 [$C_{10}H_{12}O$]	—	—	—	—
ME	—	—	—	*e*
MF	—	—	*e*	*e*
benzofuran (**11**)	—	3.04	26.33	71.11
indene	—	—	0.15	0.50
MG-132 [C_9H_8O]		—	0.38	—
MH-148 [$C_{10}H_{12}O$]	—	—	—	0.11
MI-148 [$C_{10}H_{12}O$]	—	—	—	0.11
MJ-148 [$C_{10}H_{12}O$]	—	—	—	2.32
2-methylbenzofuran (**13**)	—	9.35	21.10	14.45
MK-148 [$C_{10}H_{12}O$]	—	0.86	—	—
ML	—	—	*e*	—
trans-2,3-dimethyl-2,3-dihydrobenzofuran (**14**)	—	40.72	25.63	1.72

Table A-II continues on next page

Table A-II. Continued

entry	yield, % [c]			
	RT [d]	600 °C	700 °C	800 °C
MM-148 [$C_{10}H_{12}O$]	—	—	0.68	0.53
MN-132 [C_9H_8O]	—	—	0.17	—
MO-136 [C9H12O]	—	—	—	0.38
cis-2,3-dimethyl-2,3-dihydrobenzofuran (**15**)	—	18.12	9.07	1.03
MP-148 [$C_{10}H_{12}O$]	—	1.00	1.23	0.71
MQ-148 [$C_{10}H_{12}O$]	—	3.60	0.90	0.48
MR-146 [$C_{10}H_{10}O$]	—	0.18	0.97	0.24
MS-146 [$C_{10}H_{10}O$]	—	0.38	—	—
MT-146 [$C_{10}H_{10}O$]	—	0.46	—	—
2,3-dimethylbenzofuran (**16**)	—	3.08	4.79	2.85
MU-148 [$C_{10}H_{12}O$]	—	0.82	1.70	0.24
MV-144 [$C_{10}H_8O$]	—	1.34	0.40	0.32
MW-160 [$C_{11}H_{10}O$]	—	1.21	0.42	—
MX-146 [$C_{10}H_{10}O$]	—	—	0.73	—
MY-148 [$C_{10}H_{12}O$]	—	2.18	—	—
MZ	—	*e*	—	—
MAA	—	—	—	*e*
MBB	—	—	—	*e*
o-(1-methylallyl)phenol (**9**)	100.00	13.67	—	—
MCC-136 [$C_9H_{12}O$]	—	—	2.35	0.13

Table A-II continues on next page

Table A-II. Continued

entry	yield, % [c]			
	RT [d]	600 °C	700 °C	800 °C
recovery [g]	100.00	73.08	65.35	64.92
conversion [h]	*d*	86.33	100.00	100.00

[a] FVP conditions: system pressure = 0.10 torr, sample temperature = 0 °C. [b] See Table I, note *b*. [c] See Table I, note *c*. [d] Assay of starting material by GC in area percentages. [e] Unidentified product which constitutes ≤0.18% total area by GC. [f] Unidentified product which constitutes ≤0.43% total area by GC. [g] See Table I, note *f*. [h] See Table I, note *g*.

GENERAL SUMMARY

In the first section of this dissertation, two novel thermal reactions of ferrocene derivatives have been reported. Flash vacuum pyrolysis (FVP) has been used to prepare ferrocenocyclobutene from the N-amino-2-phenylaziridine hydrazone of 2-methylferrocenealdehyde. Heating of the hydrazone results in formation of 2-methylferrocenylcarbene which closes to give ferrocenocyclobutene. Heating of ferrocenocyclobutene and N-phenylmaleimide (NPMI) in phenyl ether at 200 °C for 30 h gives two stereoisomeric compounds which correspond to 1 : 1 adducts of NPMI and the parent ferrocene-based *o*-quinodimethane. The major product, corresponding to endo-addition of NPMI to the organometallic *o*-quinodimethane derivative, is isolated in 13% yield. Unfortunately, the low yields for the FVP and trapping steps suggest that this approach is not feasable for development into a synthetic method for preparation of fused-ring compounds.

Paper 2 concerns the FVP reactions of *o*-allyltoluene and some related compounds. We propose that these reactions take place by thermally-induced intramolecular hydrogen-atom transfers which generate diradical intermediates. The diradicals can either couple or undergo intramolecular disproportionation reactions. Calculated ΔH values for formation of some of the proposed diradicals indicate that diradical formation is reasonable at the temperatures of pyrolysis (700-900 °C). This reaction has no precedent in hydrocarbon

chemistry and could represent a novel means of creating fused-ring carbocyclic compounds.

In Paper 3, we reported that the FVP of 2-methyl-2'-vinylbiphenyl affords 9-methyl-9,10-dihydrophenanthrene. The formation of this compound fits our proposed mechanism, although other mechanisms can be proposed for this cyclization. In contrast, the FVP of 2-(o-methylbenzyl)styrene does not give products consistent with hydrogen transfer/diradical coupling. Instead, anthracene and 1-methylanthracene are the major products. While the means of their formation is uncertain, a reasonable mechanism involving an o-quinodimethane intermediate has been proposed. It is possible that the cyclizations of 2-methyl-2'-vinylbiphenyl and 2-(o-methylbenzyl)styrene could be reasonable models for the formation of phenanthrene and anthracene substructures found in high-rank coals.

Paper 4 reports the successful application of this hydrogen-atom transfer/diradical coupling reaction to the preparation of benzofuran derivatives by the FVP of *o*-allylphenol and *o*-(1-methylallyl)phenol. This hydrogen-atom transfer/diradical coupling reaction offers considerable possibilities for future research, including synthesis of carbocyclic and heterocyclic fused-ring systems.

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