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An approach to a generalized synthesis for 2-halo-1,1-diarylalkenes

Cheryll R. Roberts

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AN APPROACH TO A GENERALIZED SYNTHESIS FOR 2-HALO-1,1-DIARYLALKENES

A Thesis Presented to the Department of Chemistry at
Marshall University in Partial Fulfillment of the
Requirements for the Degree of
Master of Science

By

Cheryll R. Roberts

Marshall University

May, 1997

MARSHALL UNIVERSITY

DEPARTMENT OF CHEMISTRY

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AS MEETING THE RESEARCH REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

Gary D. Anderson

Advisor, Department of Chemistry

James E. Douglass

Member, Department of Chemistry

Member, Department of Chemistry

Leonard J. Deutsch

Dean, Graduate School

To my husband, Erik Roberts, for his
encouragement, help, and love.

To my parents, Winfred and Oretha Baker,
for all that you have taught me.

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I would like to thank Dr. Anderson for being an excellent mentor. He has been both teacher and friend. I appreciate the guidance he has given me in my course work and research. I thank the Chemistry Department for all the assistance given while working on this degree. A special thanks is extended to Dr. Larson, Dr. Norton, and Dr. Douglas.

I would like to thank my parents for their constant support and encouragement. Thank you to my husband, Erik, who is a truly wonderful and patient person. He has had to compromise many hours in order to help me during my graduate studies. I would also like to thank God for giving me strength to continue on when I was tired and wanted to quit. Without Him this project would not have become a reality.

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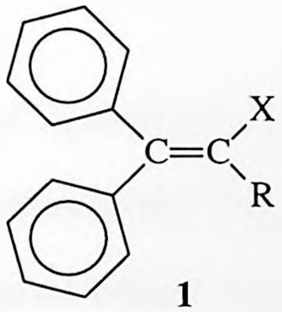
ABSTRACT

This study was concerned with the development of a generalized synthesis of halogenated 1,1-diarylalkenes. The alkylation of 1,1-diphenylethylene was carried out by the addition of organolithium compounds (CH_3Li, PhLi, *t*-BuLi, *n*-BuLi). N-bromo-succinimide (NBS) was used for bromination. The reaction forming triphenylbromo-ethylene gave the largest percent yield (93.6%). The reaction forming 2-bromo-3,3-dimethyl-1,1-diphenyl-1-butene resulted in a 38.1% yield. Each product structure was confirmed by proton and carbon-13 nuclear magnetic resonance, and infrared spectroscopy.

INTRODUCTION

In conjunction with a project aimed at the synthesis of highly substituted butadienes, we had a need for preparing a variety of halides with general structure **1**, by a simple high yield method.[1] The intention was to use these halides as intermediates in coupling reactions. The dienes are expected to exhibit chirality due to restricted rotation around the C2-C3 bond.

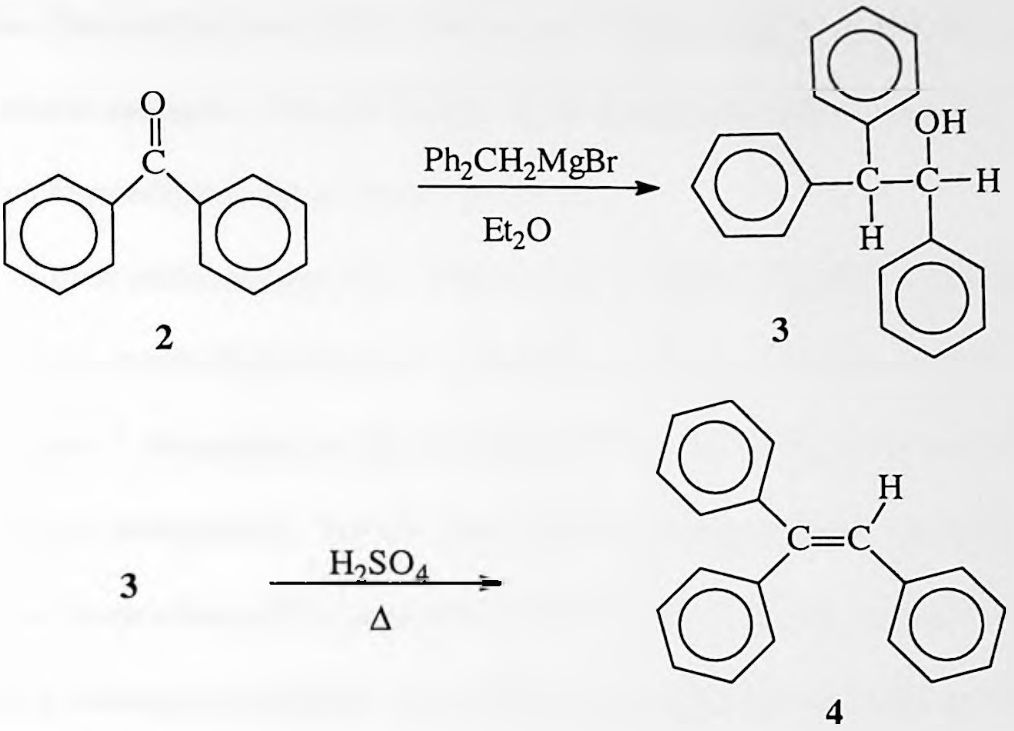


1

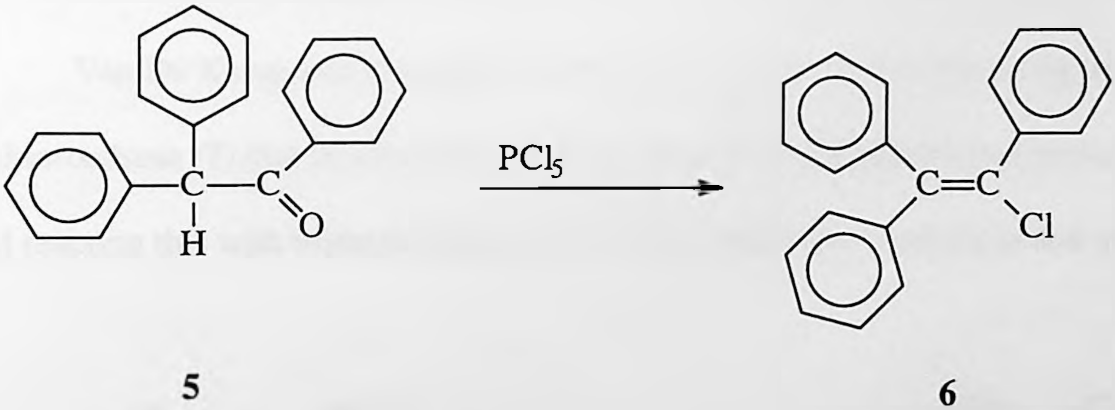
R=CH_3, *n*-butyl, *t*-butyl, phenyl
X=Cl, Br, I

While some compounds of this type had been synthesized previously and some are even commercially available,[2] no general synthetic procedure currently exists. Currently known methods are limited to the synthesis of a specific compound, rather than of many compounds of similar structure.

The synthesis of triphenylethylene as developed by Adkins and Zartman was reported in *Organic Synthesis*.[3] Their method involves the Grignard reaction of benzophenone (**2**) with benzylmagnesium chloride to produce triphenylethanol (**3**). This was then dehydrated with hot sulfuric acid to yield triphenylethylene (**4**). They reported a yield of 54-59% after vacuum-distillation, and recrystallization from hot ethanol.[3]



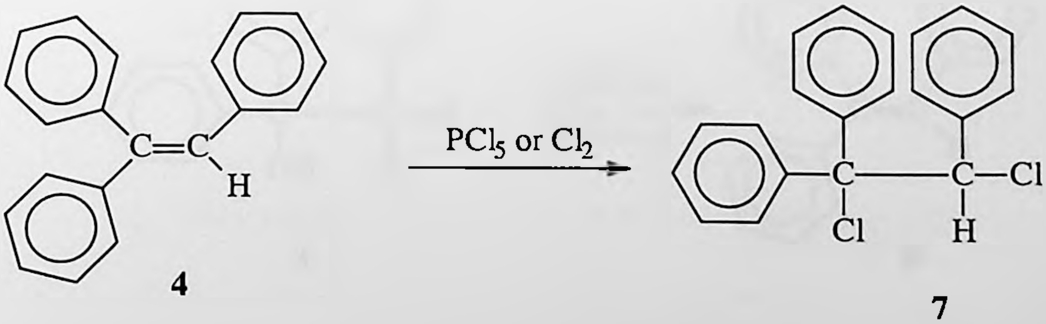
Gardeur[4] reported a method of preparing triphenylchloroethylene (**6**) beginning with triphenylethanone (**5**). The reaction (shown below) involves adding phosphorus pentachloride to the ketone. A 58% yield was obtained when the reaction was carried out at 150°C.

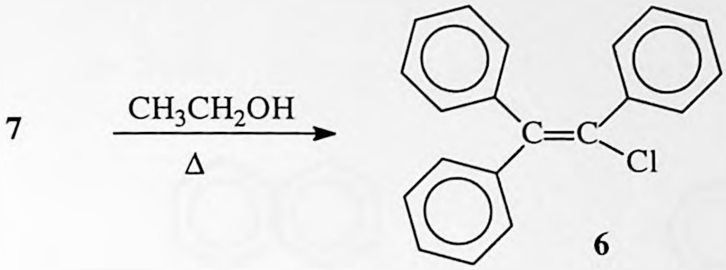


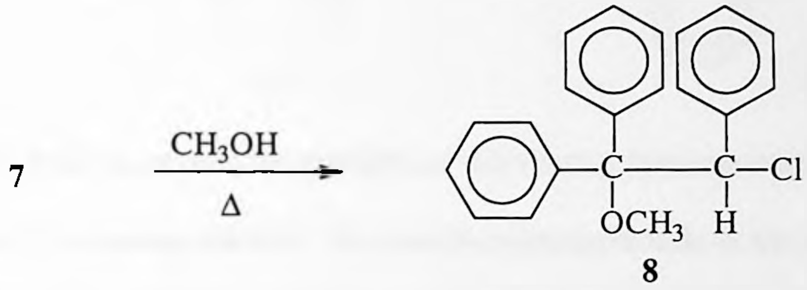
Compound **6** [Triphenylchloroethylene **1**, (R=phenyl, X=Cl)] was also prepared by Van De Kamp and Sletzinger in 1941.[4] They were interested in an efficient synthesis of this compound because it had been shown to simulate estrogenic hormones,[5] however, this compound is not currently being used for this purpose. When massive doses were used, the effects of triphenylchloroethylene were much longer lasting than many natural and synthetic estrogens. Van De Kamp and Sletzinger attempted to synthesize triphenylchloroethylene (**6**) in several ways.

In their initial attempt they followed the procedure reported by Bergmann and Bondi, which involved the treatment of triphenylethylene (**4**) with phosphorus pentachloride.[6] Bergmann and Bondi reported formation of the desired product but did not give yield information. Van De Kamp and Sletzinger reported formation of triphenyldichloroethane (**7**) in approximately 50% yield.[4] It was necessary for Van De Kamp and Sletzinger to modify the conditions described by Bergmann and Bondi in order to get the desired triphenylchloroethylene. When triphenyldichloroethane (**7**) was refluxed with methanol, triphenylchloromethoxyethane (**8**) was formed. However, refluxing the triphenyldichloroethane (**7**) with ethanol provided the desired triphenylchloroethylene (**6**).[4] This suggested that Bergmann and Bondi's product may have been a mixture of triphenylchloroethylene and triphenylchloromethoxyethane.

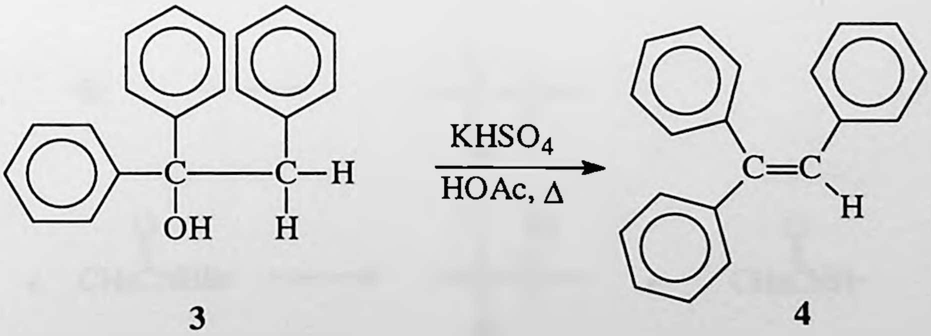
Van De Kamp and Sletzinger also reported a method of synthesizing triphenyldichloroethane (**7**) that involved substituting chlorine for the phosphorus pentachloride and reacting this with triphenylethylene (**4**) This method also resulted in low yield.[4]

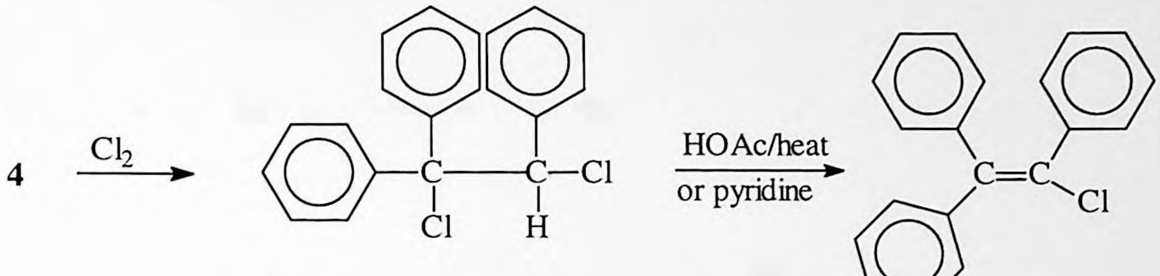






The most successful method of synthesizing triphenylchloroethylene reported by Van De Kamp and Sletzinger involved first making triphenylethylene. This was done by refluxing triphenylethanol (**3**) with potassium bisulfate in glacial acetic acid. Chlorine was then bubbled into the acetic acid solution forming triphenyldichloroethane (**7**) Heating the resulting solution caused the loss of hydrogen chloride, forming triphenylchloroethylene (**6**) in 87.3% yield. They also reported that isolating the triphenyldichloroethane and then refluxing in pyridine gave triphenylchloroethylene in 65% yield.[4]





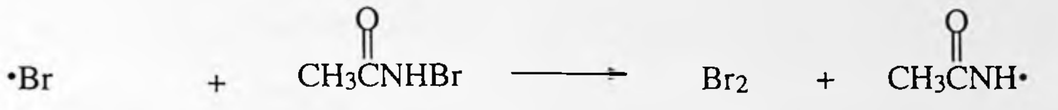
7 6

In 1949, Buckles studied the synthesis of dibromides from unsaturated compounds by reaction with N-bromoacetamide.[7] He used N-bromoacetamide as the sole source of bromine and determined that the reaction process involved a free radical mechanism. As shown in the mechanism below, initially the N-bromoacetamide forms bromine atoms through a photochemical process. The bromine atom attacks the alkene, leaving a radical which can react with N-bromoacetamide to form a dibromide. Steps 4, 5, and 6 were thought to occur when a bromine color was present.

$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}NHBr} + h\nu \longrightarrow \mathrm{CH_3\overset{\overset{O}{\|}}{C}NH\cdot} + \cdot\mathrm{Br} \qquad (1)$$

(2)

(3)

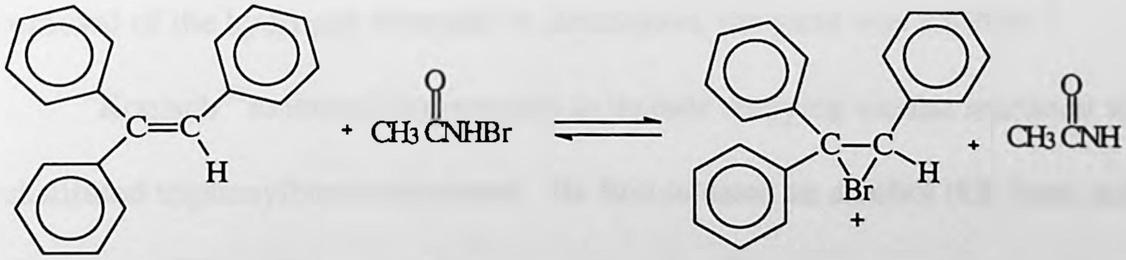


$$\cdot Br + CH_3\overset{O}{\overset{\|}{C}}NHBr \longrightarrow Br_2 + CH_3\overset{O}{\overset{\|}{C}}NH\cdot \qquad (4)$$

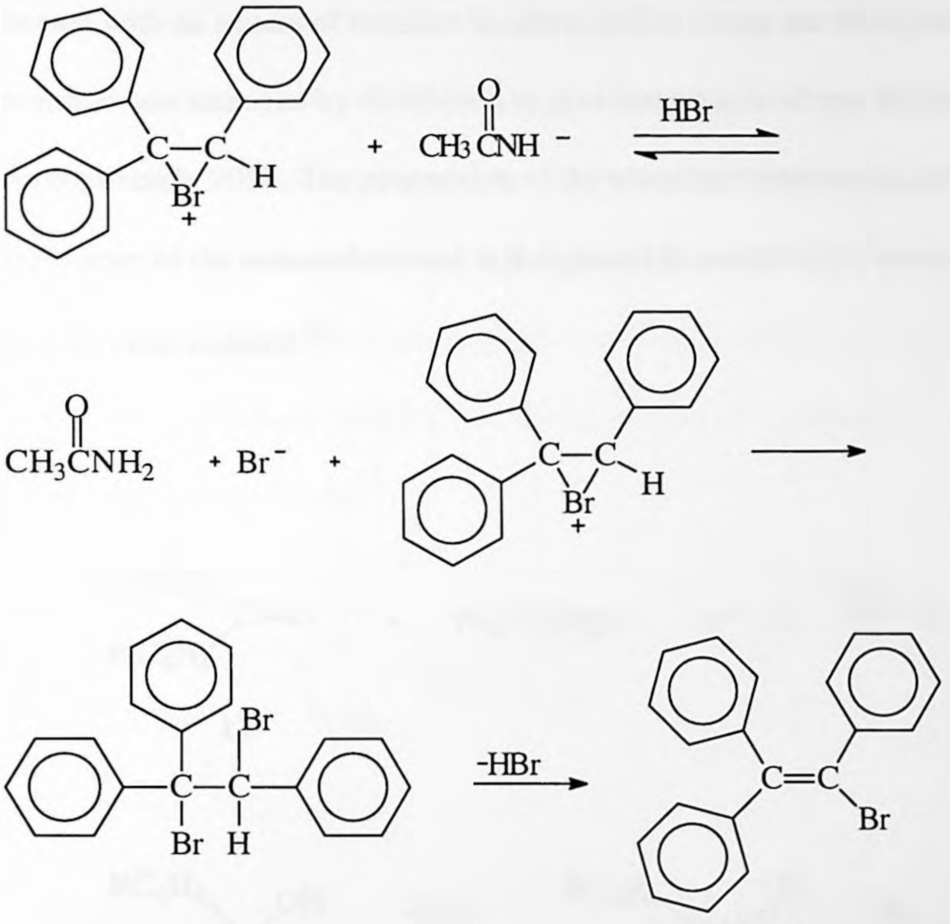
$$Br_2 + h\nu \longrightarrow 2\ \cdot Br \qquad (5)$$

$$Br_2 + -\underset{Br}{\overset{|}{C}}-\overset{\cdot}{\underset{|}{C}}- \longrightarrow -\underset{Br}{\overset{|}{C}}-\overset{Br}{\underset{|}{C}}- + \cdot Br \qquad (6)$$

Buckles[7] reported that the reaction of an alkene with N-bromoacetamide in the presence of hydrogen bromide occurs via a bridged bromonium ion. Roberts and Kimball[8] showed that the reaction of an alkene with bromine formed the *trans* halogenation product in more than 80% yield. The *trans* stereochemistry was due to the bromonium ion intermediate. Buckles reported the formation of triphenylbromoethylene (**1**, R=phenyl, X=Br) from triphenylethylene (**4**) and N-bromoacetamide (**9**) in excess hydrogen bromide. One of the intermediates was 1,2-dibromo-1,1,2-triphenylethane (**10**). After loss of the hydrogen bromide, the crude triphenylbromoethylene (**11**) was obtained in 99% yield.[7]



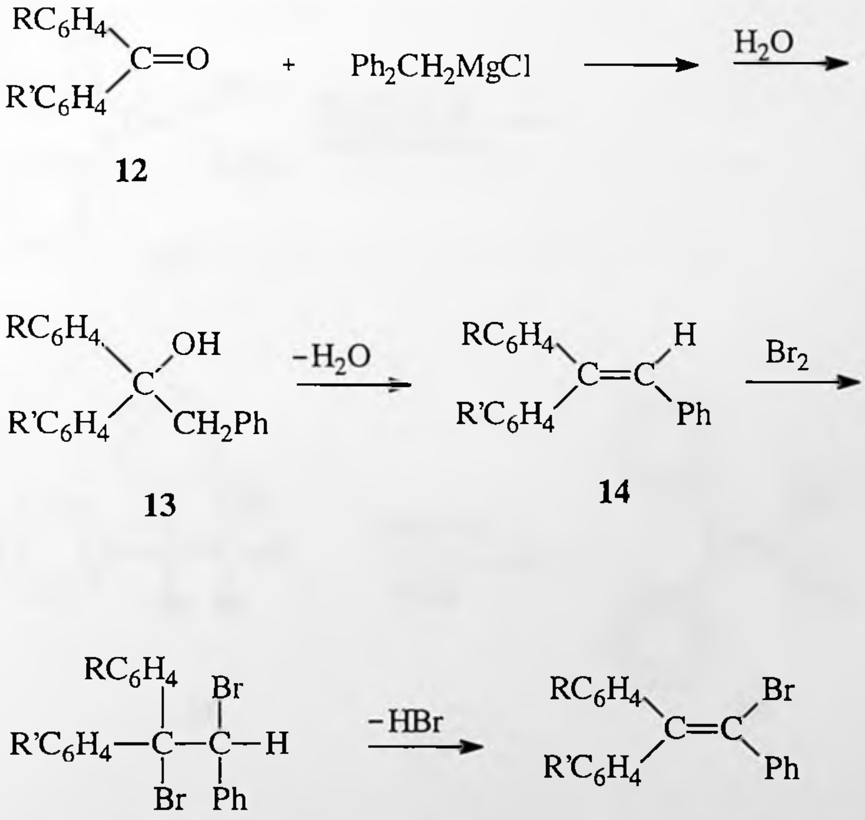
4 **9**



10 **11**

Triphenylbromoethylene (**1**, R=phenyl, X=Br) was synthesized by Koelsch[9] by allowing triphenylethylene (**1**, R=phenyl, X=H) to react with bromine in glacial acetic acid. The reaction mixture was cooled to keep the temperature below 40°C. After removal of the hydrogen bromide by distillation, the yield was 95-98%.[9]

Koelsch[10] extended his research to include studying similar reactions with certain substituted triphenylbromoethylenes. He first isolated an alcohol (**13**) from the reaction of a ketone (**12**) with benzylmagnesium chloride. This was accomplished using ammonium chloride to decompose the intermediate ROMgX. The alcohol was dehydrated to the alkene (**14**) by distillation under reduced pressure. The alkene was then treated with an excess of bromine in acetic acid to obtain the dibromide (**15**). Hydrogen bromide was removed by distillation to give compounds of type **16** in yields of approximately 90%. The preparation of the triarylbromoethylenes, showed that only the *cis* isomer of the monosubstituted α,β-diphenyl-β–*p*-tolylvinyl bromide (**16**, R'=H and R=CH_3) was isolated.[10]



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13

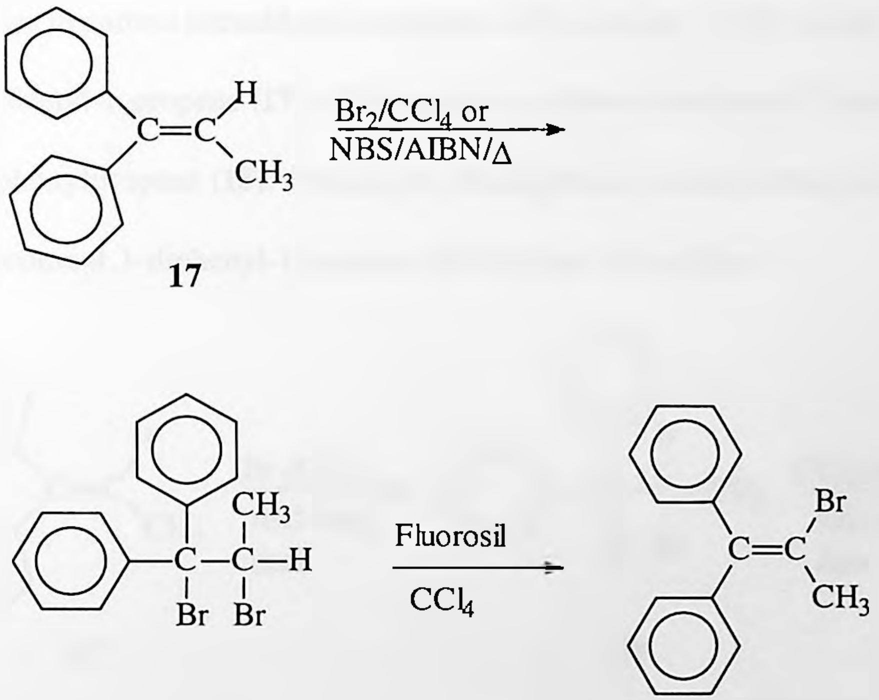
14

15

16

R=R'=CH_3 or R=H and R'=CH_3

The formation of 2-bromo-1,1-diphenyl-1-propene (**19**) was reported by Incremona and Martin[11] in 1970. They treated 1,1-diphenyl-1-propene (**17**) with an excess of molecular bromine in carbon tetrachloride. The resulting dihaloalkane (**18**), 1,2-dibromo-1,1-diphenylpropane, was then passed through a column of Fluorosil in carbon tetrachloride causing dehydrohalogenation to 2-bromo-1,1-diphenylpropene (**19**) in 56% yield. Incremona and Martin also reported forming the dihaloalkane **18** by the reaction of 1,1-diphenylpropene (**17**) with a solution of N-bromosuccinimide at 80°C using AIBN as an initiator.[11]



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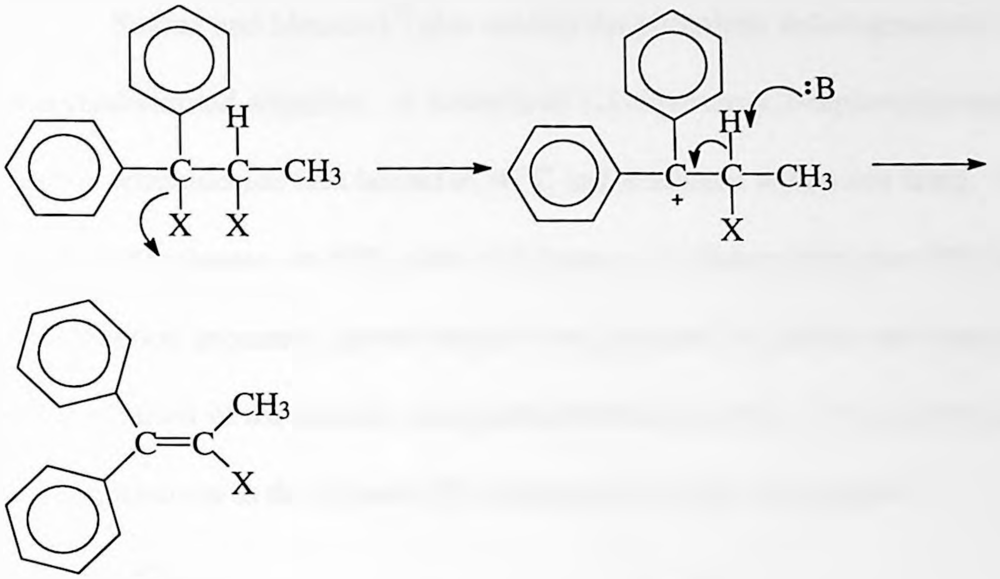
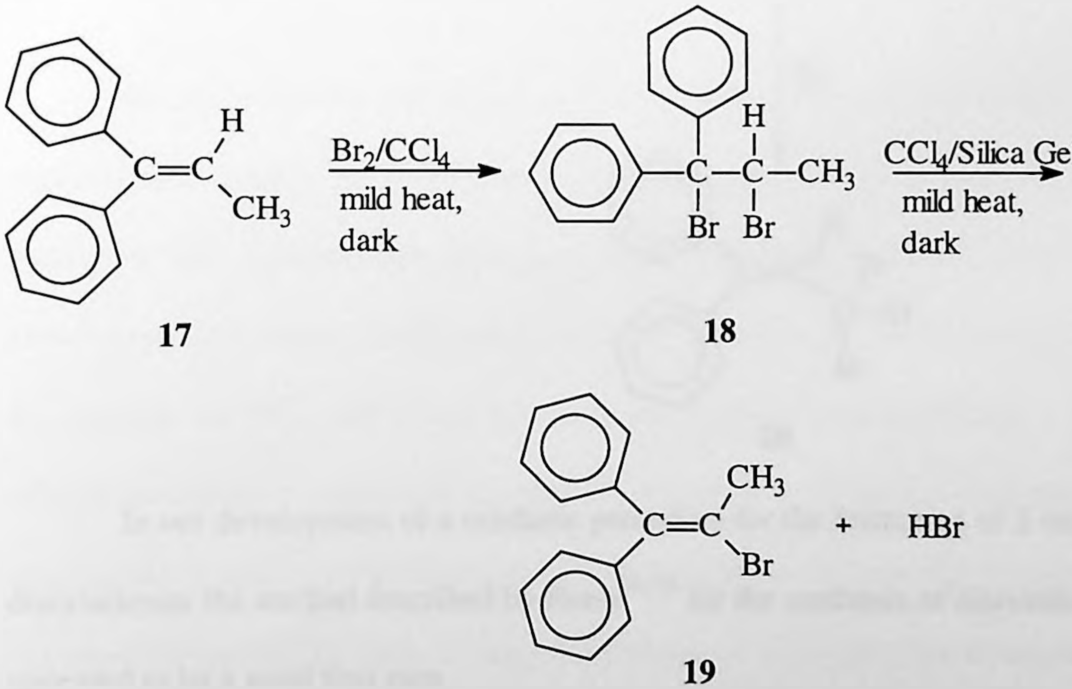
Another approach to the synthesis of 2-bromo-1,1-diphenylpropene was gas-phase dehydrohalogenation using silica gel as a catalyst at temperatures of 200-500°C. The mechanism, as shown in equation 7, is considered to be E1 like. Suárez and Mazzieri[12] extended this method to study the structural changes of 1,1-diarylsubstituted



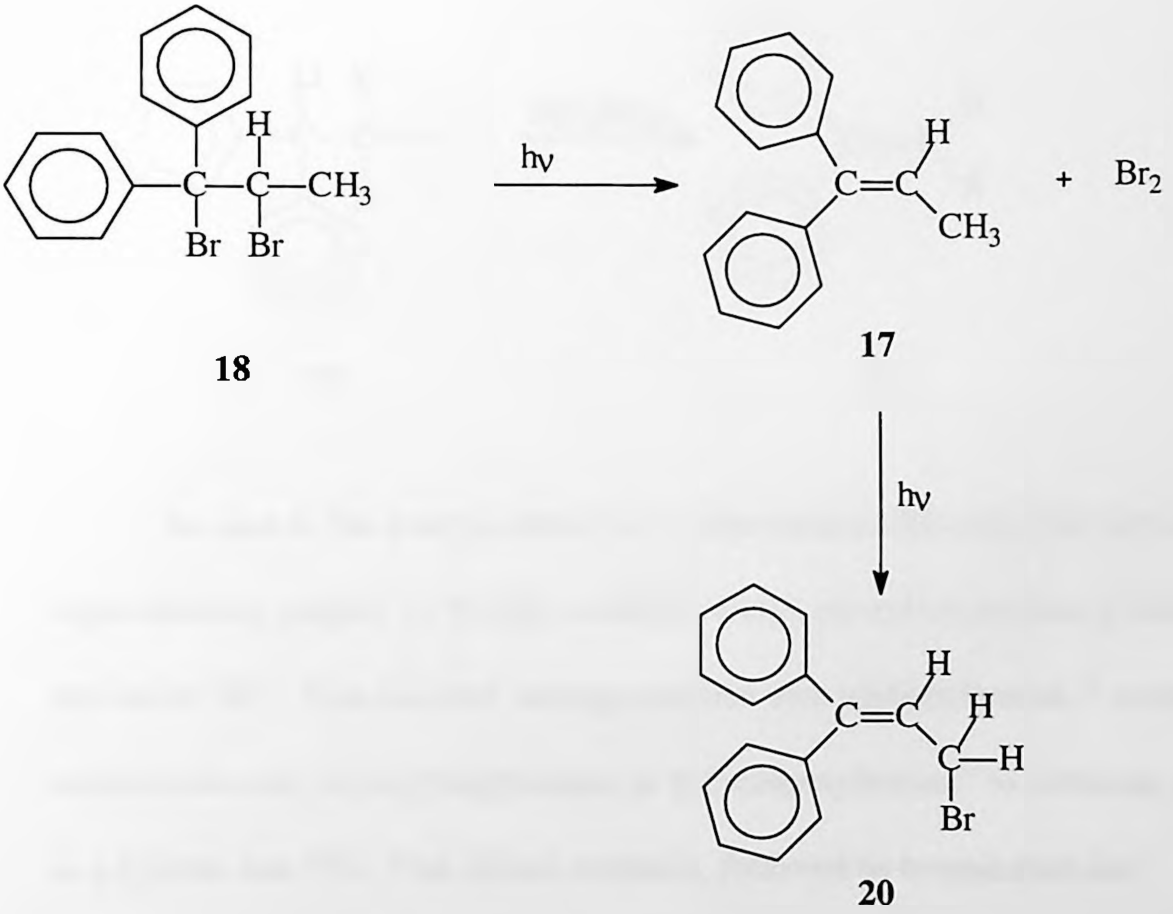
(7)

dihalides in carbon tetrachloride solutions with silica gel at 80°C in the dark. The reaction of 1,1-diphenyl-1-propene (**17**) with bromine in carbon tetrachloride formed 1,2-dibromo-1,1-diphenylpropane (**18**). Passing the dihaloalkane through silica gel afforded a 95% yield of 2-bromo-1,1-diphenyl-1-propene (**19**) in about 30 minutes.

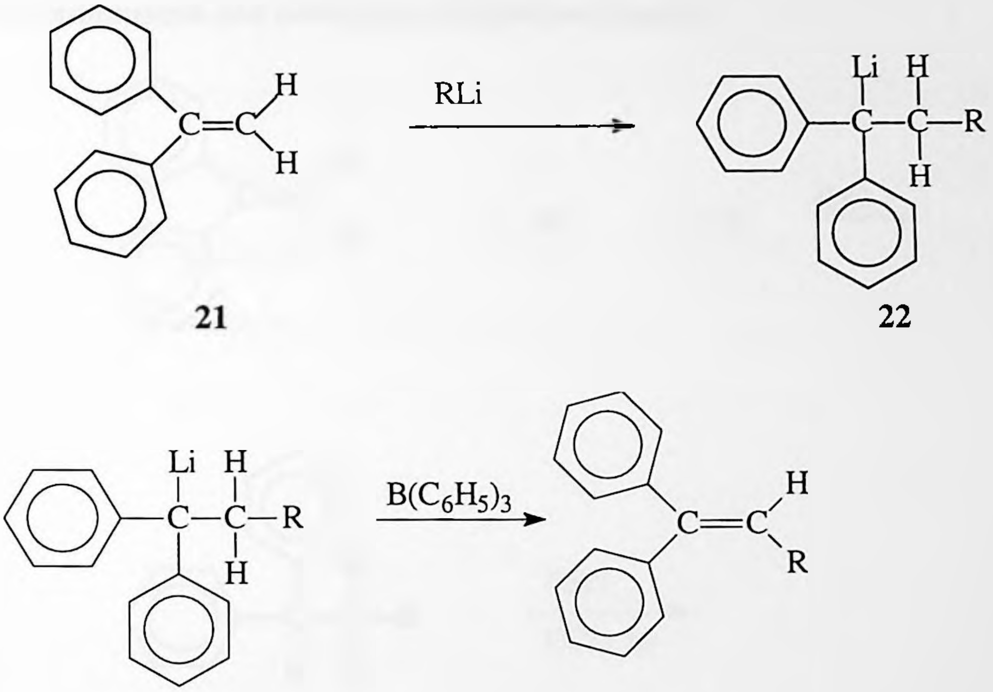


17 **18** **19**

Suárez and Mazzieri[13] also studied the photolytic dehalogenation of 1,1-diarylsubstituted dihalides. A solution of 1,2-dibromo-1,1-diphenylpropane (**18**) in carbon tetrachloride was heated at 80°C and irradiated with a sun lamp. After a reaction time of 90 minutes, an 83% yield of 3-bromo-1,1-diphenylpropene (**20**) was obtained. The reaction sequence (shown below) was proposed by Suárez and Mazzieri to explain the formation of the product via a photochemical process. The reaction involves dehalogenation to the alkene (**17**), followed by allylic bromination.[13]



In our development of a synthetic procedure for the formation of 2-halo-1,1-diarylalkenes the method described by Reetz[14, 15] for the synthesis of diarylalkenes appeared to be a good first step.

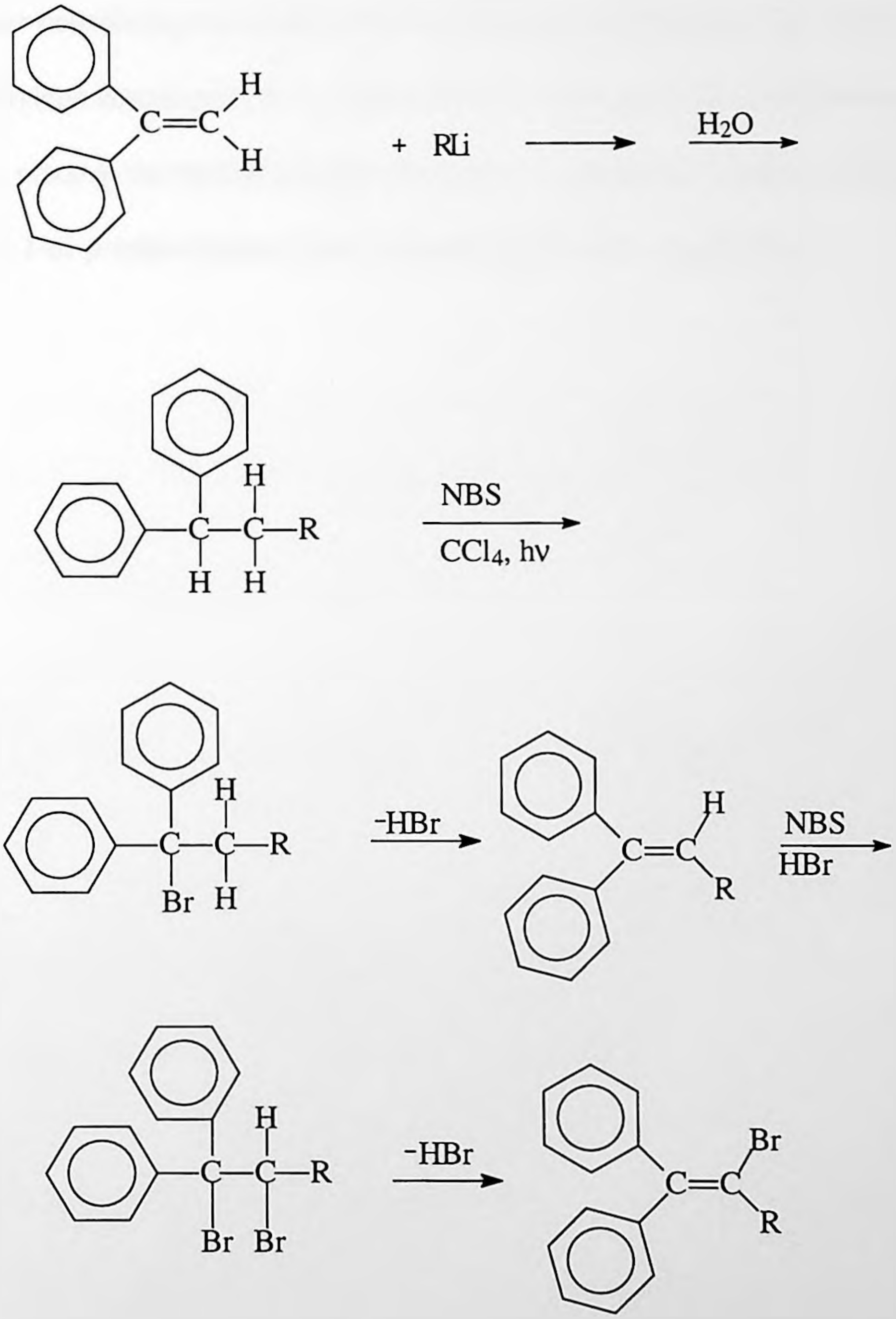


21 **22**

22 **23**

As seen in the reaction above, a 1,1-diarylalkene (**21**) can react with an organolithium reagent (**1**, R=CH_3, *n*-butyl, *t*-butyl, phenyl) to produce a lithium derivative (**22**). This can then undergo reaction with triphenylborane,[14] triphenylmethyl tetrafluoroborate, tri(sec-butyl)borane, or tricyclohexylborane[15] to eliminate a ß hydrogen as a hydride ion (**23**). This alkene synthesis, followed by bromination and dehydrobromination looked like a promising approach. Preliminary experiments[16] showed that it was very difficult to get the desired alkene without also getting side reactions giving Ph_2CHCH_2R. Even minute traces of water gave rise to the saturated product and separation was very difficult.

This led us to consider the approach shown below. Addition of the alkyllithium was still used as the first step, but the hydride elimination step was replaced by free radical bromination and subsequent dehydrobromination.



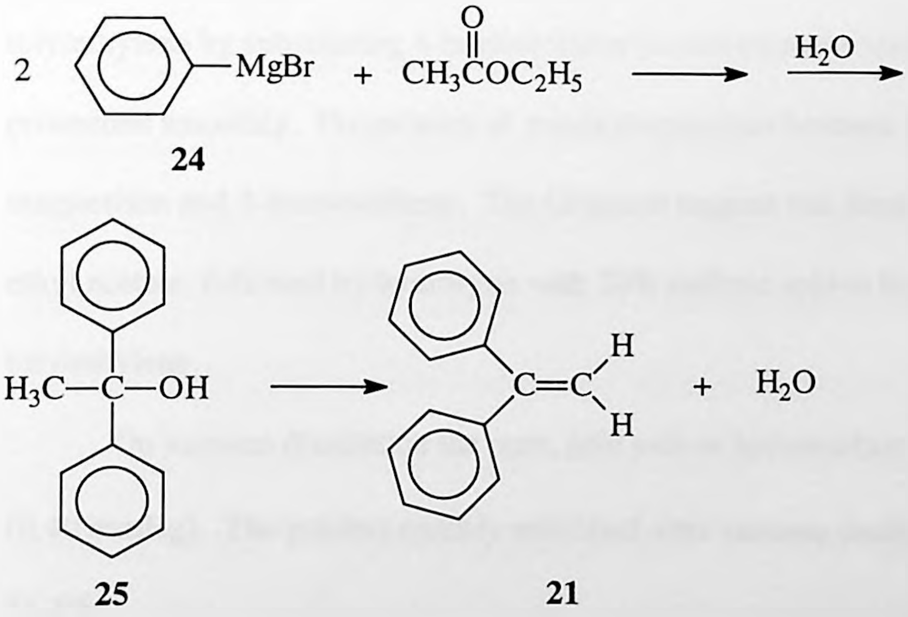
Preliminary work was done by preparing 1,1-diphenylethylene and 1,1-di-*p*-tolylethylene with the intent of comparing the relative reactivities of the two alkenes. We decided to explore the alkylation reactions between these two alkenes with methyllithium, phenyllithium, *t*-butyllithium, and *n*-butyllithium. Bromination of each of these alkenes was then done using N-bromosuccinimide.

After considering the results of the bromination reaction involving the 1,1-diphenylethylene compounds, it was determined that too much free radical bromination would take place at the methyl group of the *p*-tolyl compounds. Further reactions involving 1,1-di-*p*-tolylethylene were thus eliminated from consideration.

RESULTS AND DISCUSSION

A. Synthesis of 1,1-Diphenylethylene (21)

Diphenylethylene was prepared by the method described by Allen and Converse in *Organic Synthesis.*[17] This two-step reaction sequence involved the reaction of phenyl magnesium bromide (**24**) with ethyl acetate, followed by hydrolysis to give 2,2-diphenylethanol (**25**). The alcohol was then dehydrated using 20% sulfuric acid to 1,1-diphenylethene (**21**).



24

25

21

The product is a colorless liquid. On vacuum distillation, the pure hydrocarbon boiled at 84-85°C (0.15 mmHg). The yield was 55.0%.

The IR spectrum (Figure 1 in the Appendix) shows bands at 3029, 3057, and 3079 cm^{-1} due to C-H stretching. The bands at 1601 and 1610 cm^{-1} indicate the carbon-carbon double bond and aromatic ring. The bands at 1444 and 1495 cm^{-1} are characteristic of the phenyl groups. The proton NMR spectrum (Figure 2 in the Appendix) shows a singlet at δ 5.4 and a multiplet at δ 7.15-7.40, with integrated intensities of 1:5, respectively. The singlet would represent the two methylene hydrogens. The multiplet would correspond to the phenyl hydrogens. The decoupled carbon-13 NMR (Figure 3 in the Appendix) has a peak at δ 114 which corresponds to the alkene carbons. The group of peaks between δ 127 and 129 are due to the ten carbons of the phenyl groups.

B. Synthesis of 1,1-Di-*p*-tolylethylene

The method used to prepare 1,1-diphenylethylene was adapted to prepare 1,1-di-*p*-tolylethylene by substituting 4-bromotoluene for the bromobenzene. The reaction proceeded smoothly. Preparation of *p*-tolylmagnesium bromide was carried out using magnesium and 4-bromotoluene. The Grignard reagent was then allowed to react with ethyl acetate, followed by hydrolysis with 20% sulfuric acid to form 2,2-di-*p*-tolylethylene.

On vacuum distillation the pure, pale yellow hydrocarbon boiled at 126-127°C (0.40 mmHg). The product quickly solidified after vacuum distillation. The yield was 55.5%.

The IR spectrum (Figure 4 in the Appendix) shows bands at 3097 and 3118 cm^{-1} due to the aromatic C-H stretching modes. The bands at 1550, 1609 and 1630 cm^{-1}

indicate the carbon-carbon double bond and aromatic ring. The proton NMR spectrum (Figure 5 in the Appendix) shows a singlet at δ 2.35 which indicates the six hydrogens from the methyl groups. The singlet at δ 5.39 is due to the two methylene hydrogens. The multiplet from δ 7.08-7.29 is due to the eight aryl hydrogens. The decoupled carbon-13 NMR (Figure 6 in the Appendix) has a peak at δ 21.7 due to the methyl carbons. The peak at δ 113 is due to the methylene carbon. The group of peaks between δ 127-129 are due to the carbons of the aromatic groups.

C. Alkylation and Bromination of 1,1-Diphenylethylene (21)

1. Synthesis of 2-Bromo-1,1-diphenyl-1-propene (19)

The reaction of 1,1-diphenylethylene with methyllithium in tetrahydrofuran proceeded smoothly. Quenching the resulting bright red solution with water gave crude 1,1-diphenylpropane. The proton NMR showed that the vinyl hydrogens had disappeared. The crude product was then heated with a two fold excess of N-bromo-succinimide in carbon tetrachloride while being irradiated with a 300 W lamp for one week. The crude product solution was filtered through six inches of silica gel with pentane to remove all polar materials. The solvent was removed on a rotary evaporator leaving a 90.4% yield of crude 2-bromo-1,1-diphenyl-1-propene.

The IR spectrum shows bands at 3032 and 3061 cm^{-1} due to the aromatic C-H stretching modes. The band at 1588 cm^{-1} is due to the carbon-carbon double bond and aromatic ring. The proton NMR shows a peak at δ 1.15 with a relative intensity of three due to the methyl group. A multiplet which ranges from δ 7.1-7.5 with an intensity of ten is due to the phenyl groups. The decoupled carbon NMR shows a single methyl peak at δ 30 and a group of peaks from δ 128-133 that correspond to the phenyl groups.

2. Synthesis of Triphenylbromoethylene (11)

The reaction of 1,1-diphenylethylene with a slight excess of phenyllithium was very mild, as compared to the previous reaction which required methyllithium. Quenching the red solution with water and removal of the solvent left crude 1,1,2-triphenylethane. The proton NMR showed no vinyl hydrogens. The crude product was then heated with a two fold excess of N-bromosuccinimide in carbon tetrachloride while being irradiated with a 300 W lamp for four days. Filtration through silica gel with pentane, followed by removal of solvent on the rotary evaporator left a pale orange solid product in 93.6% yield.

The IR spectrum shows three bands at 3032, 3055, and 3078 cm^{-1} due to aromatic C-H stretching. The band at 1599 cm^{-1} is due to the carbon-carbon double bond and aromatic ring. The proton NMR shows a multiplet from δ 6.64-7.32 due to the three phenyl groups. The decoupled carbon-13 NMR shows a single peak at δ 143 due to the alkene carbons. The multiplet from δ 126-132 corresponds to the phenyl groups.

3. Synthesis of 2-Bromo-3,3-dimethyl-1,1-diphenyl-1-butene

The reaction of 1,1-diphenylethylene with *t*-butyllithium in tetrahydrofuran was vigorous. Quenching the resulting bright red solution with water gave crude 3,3-dimethyl-1,1-diphenylbutane. The proton NMR showed no vinyl hydrogens. The crude product was then heated with a two fold excess of N-bromosuccinimide in carbon tetrachloride while being irradiated with a 300 W lamp for one week. The mixture was filtered through 8 inches of silica gel, which was washed with pentane, to remove the succinimide. The solvent was removed on the rotary evaporator leaving a pale yellow solid in 38.4% yield.

The IR spectrum (Figure 7 in the Appendix) shows bands at 3061 and 3085 cm^{-1} due to the aromatic C-H stretching modes. The bands at 2874, 2909, and 2932 cm^{-1} are due to the alkane C-H stretching. The bands at 1599 and 1617 cm^{-1} are due to the carbon-carbon double bond of the aromatic ring and alkene, respectively. The proton NMR (Figure 8 in the Appendix) shows a singlet at δ1.25 with a relative intensity of nine due to the methyl groups from the *t*-butyl. There is a multiplet from δ 7.1-7.5 with an intensity of ten which corresponds to the ten phenyl hydrogens. The decoupled carbon-13 NMR (Figure 9 in the Appendix) shows a singlet at δ 32, corresponding to the *t*-butyl carbons. There is a singlet at δ 42 from the center carbon of the *t*-butyl group. There are peaks at δ 140 and δ 142 due to the alkene carbons. There is a multiplet from δ 126-129 due to the two phenyl groups.

4. Synthesis of 2-Bromo-1,1-diphenyl-1-hexene

The reaction of 1,1-diphenylethylene with *n*-butyllithium produced a dull red solution. Quenching the resulting solution with water gave crude 1,1-diphenylhexane. Proton NMR showed that the vinyl hydrogens had disappeared. The crude product was then heated with a two fold excess of N-bromosuccinimide in carbon tetrachloride while being irradiated with a 300 W lamp for five days. The crude product was filtered through 8 inches of silica gel, which was washed with pentane. The solvent was removed on the rotary evaporator, leaving a dark oil in 71.1% yield. The proton and carbon-13 NMR show a mixture of several components. Thin layer chromatography also showed a mixture of several components. One of these had approximately the same R_f as the *t*-butyl isomer and was likely to be the desired product. The additional products presumably arose from a free radical reaction at the allylic CH_2 group.

Conclusions and Suggestions for Further Study

The sequence of alkylation, followed by bromination, and subsequent dehydrobromination afforded a 38.4% yield of 2-bromo-3,3-dimethyl-1,1-diphenyl-1-butene. Further attempts should be made to increase the yield of this compound by increasing the reaction time of the bromination step.

The reaction appears to proceed as expected, when no additional allylic and benzyllic positions are available for bromination. It would seem to be worthwhile to further explore this reaction by using other alkyllithium compounds and aryl groups. Methoxy substituted aryl groups would be an example of an aryl group other than phenyl which could keep benzylic bromination from interfering in the reaction sequence. Compounds of this type could be used to make Grignard reagents. One useful application of a Grignard reagent of this structure would be possible coupling to form hexasubstituted butadienes. The potential chirality of the butadiene could then be explored by attempting to resolve the enantiomers.

EXPERIMENTAL

A. Analytical Methods

Infrared spectra were determined on a Nicolet 20DXB Fourier Transform Infrared Spectrometer. The computer software used was OMNIC 1.1 and ran on a 486DX 66. The standard sampling technique was 16 scans on autogain with an aperture of 18. The scans covered a range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1}. The data was displayed in absorbance format. A background was collected and correction for the background was made. The spectra were typically obtained as thin films on sodium chloride plates.

The proton and carbon-13 nuclear magnetic resonance spectra were obtained on a Varian XL-200 NMR spectrometer. The computer software was XL-200 5.1. The standard sampling technique was to obtain spectra at room temperature with the number of transients for proton spectra at 16. The number of transients for the carbon-13 spectra was set to the maximum. A receiver power of 30x6 was used for carbon spectra and 10x0 was used for proton spectra. All samples were dissolved in $CDCl_3$. Tetramethylsilane was used as an internal standard.

Thin layer chromatography was performed in 10% ethyl acetate/hexane using precoated Whatman silica gel plates. These plates had polyester backing with a 250 µm layer of silica gel prepared for ultraviolet fluorescence.

Halogenation experiments were carried out in a 100-mL pyrex flask equipped with a Friedrich condenser. A Drierite tube was placed on top of the condenser. A 300 W tungsten lamp was used to irradiate the reaction mixture.

B. Materials

Magnesium turnings (Fisher Scientific)

Bromobenzene (Fisher Scientific)

Ammonium chloride (MCB Manufacturing Chemists, Inc.)

Sulfuric acid (Fisher Scientific)

4-Bromotoluene (ACROS)

Anhydrous sodium sulfate (Fisher Scientific)

Pentane (ACROS)

Anhydrous ether (Fisher Scientific)

Carbon tetrachloride (Fisher Scientific)

Ethyl Acetate (Aldrich)

Silica Gel (Sigma Chemical Company)

Chloroform-d 99.8% (Aldrich)

Tetramethylsilane (Aldrich)

Methyllithium, 1.6M in diethylether (ACROS)

Phenyllithium, 1.8M in cyclohexane-ether (Aldrich)

n-Butyllithium, 1.6M in hexane (ACROS)

tert-Butyllithium, 1.7M in pentane (Aldrich)

Tetrahydrofuran (Aldrich)

N-bromosuccinimide (Fisher Scientific)

2,2'-Azobis-(-2-methylpropionitrile): AIBN (Aldrich)

C. Synthesis of 1,1-Diphenylethylene (21)

1,1-Diphenylethylene was prepared using the method of Allen and Converse as outlined in *Organic Synthesis.*[17] Magnesium turnings (27.0 g) were placed in a 2-L, three-necked flask equipped with a reflux condenser and addition funnel. The magnesium was mixed with 20.1 mL bromobenzene in 70.0 mL dry ether. It was necessary to add a little magnesium, ether, and iodobutane mixed in a test tube to initiate the Grignard reaction. An additional 101.3 mL bromobenzene in 380. mL dry ether was added over 1.5 hr. Then 48.8 mL dry ethyl acetate was added with stirring over 20-30 minutes. Ammonium chloride (50.0 g) was dissolved in 150 mL distilled water at room temperature and added to the flask over 20-30 minutes. The mixture was allowed to stand overnight at room temperature. The ether layer was decanted into an addition funnel along with a 50 mL ether extract of the pasty residue. The ether was removed by adding the solution dropwise into a warm 500-mL round-bottomed flask attached to a Claisen-head condenser. The residue was allowed to cool. The Claisen-head condenser was replaced with a Friedrichs condenser and the contents were refluxed for one hour with 100 mL of 20% sulfuric acid. The aqueous layer was removed and the oil was distilled at aspirator pressure. Further separation was accomplished using vacuum distillation. The light yellow product, 1,1-diphenylethylene (49.47g, 55.0%) was collected between 84-85°C and 0.15 mmHg (lit.[17] b.p. 113°C and 2 mmHg); IR 3029, 3057, and 3079 cm^{-1} (-CH-), 1601 and 1610 cm^{-1} (C=C), 1444 and 1495 cm^{-1} (ArH); ^{1}H NMR ($CDCl_3$) δ 5.4 (s, 2H, CH_2), δ 7.15-7.40 (m, 10H, ArH); ^{13}C NMR δ 114, δ 127-129.

D. Synthesis of 1,1-Di-*p*-tolylethylene

The method of preparation for 1,1-diphenylethylene was adapted to prepare 1,1-di-*p*-tolylethylene by substitution of 4-bromotoluene for the bromobenzene in the original Grignard process. Magnesium turnings (25.3 g) were placed in a 2-L, three-necked flask, equipped with a reflux condenser and addition funnel. The magnesium was mixed with 17.9 mL of 4-bromotoluene in 58.3 mL of dry ether. It was necessary to add a little magnesium, ether, and iodobutane mixed in a test tube to initiate the Grignard reaction. An additional 93.5 mL of 4-bromotoluene in 327 mL dry ether was slowly added with stirring over 1.5 hr. The flask was cooled in an ice bath and 41.5 mL dry ethyl acetate in 41.5 mL dry ether was added over a period of 20-30 minutes. When the reaction flask cooled again, a solution prepared from 42.5 g ammonium chloride in 128 mL distilled water was slowly added over a 20 minute time period. A pasty solid separated and the reaction mixture was left overnight. The ether was removed by adding the solution dropwise into a warm 500-mL round-bottomed flask attached to a Claisen-head condenser. The residue was allowed to cool. The Claisen-head condenser was replaced with a Friedrichs condenser and the contents were refluxed for one hour with 100 mL of 20% sulfuric acid. The aqueous layer was separated and the remaining oil was distilled at aspirator pressure. Further separation was accomplished using vacuum distillation. The light yellow crystals of 1,1-di-*p*-tolylethylene (20.75 g, 55.5 %) were collected between 126-127°C and 0.40mmHg; IR 3097 and 3118 cm^{-1} (-CH-), 1550, 1609, and 1630 cm^{-1} (C=C), 1460 cm^{-1} (ArH); ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 6H, CH_3), δ 5.39 (s, 2H, CH_2), δ 7.08-7.29 (m, 8H, ArH); ^{13}C NMR δ 21.7 (CH_3), δ 113 (=CH_2), δ 127-129 (Ar).

E. Alkylation and Bromination of 1,1-Diphenylethylene (21)

1. Synthesis of 2-Bromo-1,1-diphenyl-1-propene (19)

A solution of 3.6 g (0.02 mol) 1,1-diphenyl-ethylene in 50 mL of dry tetrahydrofuran was placed in a 100-mL three-necked round-bottomed flask. The reaction flask was equipped with a condenser and a 30-mL pressure equalizing addition funnel. The reaction was carried out under a nitrogen atmosphere. The flask was cooled in an ice bath and 20.0 mL of 1.6 M methyllithium in ether was added dropwise with stirring. The alkyllithium was transferred into the dropping funnel using a 30-mL syringe. The solution was initially orange but turned to a dark wine red before the addition was complete. This took approximately 5 minutes. The ice bath was left in place, and the solution was stirred at room temperature for 2.5 hours. The reaction was quenched with 50 mL distilled water. The first few drops reacted vigorously; thus, slow addition was required.

The two layers were separated and the aqueous layer was washed two times with 50 mL ether. The combined organic extracts were washed two times with 15 mL portions of distilled water and then dried over anhydrous sodium sulfate. Removal of the solvent on the rotary evaporator left 1,1-diphenylpropane. Its proton NMR showed no vinyl hydrogens, and this was consistent with the expected product, 1,1-diphenylpropane.

The crude 1,1-diphenylpropane was placed in a 100-mL round-bottomed flask with 50 mL carbon tetrachloride. The flask was fitted with a Friedrich condenser and a Drierite tube was placed on top of the condenser. N-Bromosuccinimide (9.05 g, 0.051 mol) was added and the resulting mixture was heated to reflux. Just before reflux started, a spatula tip of AIBN was added and a 300 W lamp was directed on the flask.

The reaction mixture was allowed to proceed for one week. Thin layer chromatography showed an incomplete reaction so heating was stopped and 16.5 g (0.0938 mol) of N-bromosuccinimide was added to restart the reaction. The reaction was stopped again after one week and the mixture was filtered through six inches of silica gel. The silica gel was washed with 300 mL pentane. Evaporation of the pentane on the rotary evaporator left a light yellowish oil (3.25 g, 90.4%); IR 3032 and 3061 cm^{-1} (-CH-), 1588 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 3H, CH_3), δ 7.1-7.5 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$) δ 30, δ 128-133.

2. Synthesis of Triphenylbromoethylene (11)

A solution of 3.6 g (0.02 mol) 1,1-diphenylethylene in 50 mL dry tetrahydrofuran was placed in a 100 mL three-necked round-bottomed flask. The reaction flask was equipped with a condenser and a 30 mL equalizing addition funnel. The reaction was carried out under a nitrogen atmosphere. The flask was cooled in an ice bath and 19.0 mL of 1.8 M phenyllithium in cyclohexane-ether was added dropwise. The alkyllithium was transferred into the dropping funnel using a 30-mL syringe. The mixture was stirred magnetically during the addition process, which took approximately 5 minutes. The first few drops were added slowly, but once the mixture turned dark red, the remaining phenyllithium was added quickly. After the addition was complete, the ice bath was removed and the mixture was allowed to stand overnight. The proton NMR spectrum of the crude product showed no methylene peak, indicating complete conversion to the triphenylethane. The bromination was then started using 16.52 g (0.09386 mol) N-bromosuccinimide and AIBN in 50 mL carbon tetrachloride, with a 300 W lamp directed on the flask. After four days the reaction was stopped and the product was filtered through 8 inches of silica gel with pentane to remove the succinimide. Removal of the solvent on the rotary evaporator left a pale orange solid (3.37 g, 93.6%); IR 3032, 3055, 3078 cm^{-1} (ArH), 1599 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 6.64-7.32 (m, ArH); ^{13}C NMR ($CDCl_3$) δ 141 and δ 143 (s, C=C), δ 126-132 (m, Ar).

3. Synthesis of 2-Bromo-3,3-dimethyl-1,1-diphenyl-1-butene

A solution of 3.6 g (0.02 mol) 1,1-diphenylethylene in 50.0 mL dry tetrahydrofuran was placed in a 100-mL three-necked round-bottomed flask. The reaction flask was equipped with a reflux condenser and 30-mL equalizing addition funnel. The reaction was carried out under a nitrogen atmosphere. The flask was cooled in an ice bath and 15.0 mL of 1.7 M *t*-butyllithium in pentane was added dropwise. The alkyllithium was transferred into the dropping funnel using a 30-mL syringe. The mixture was stirred magnetically and turned to a dark red color after a small amount of the *t*-butyllithium was added. The addition took approximately 5 minutes and then the ice bath was removed. The alkylation reaction ran for 1.25 hours. After workup the crude product ^1H NMR showed no unreacted 1,1-diphenylethylene. The bromination reaction was started with 16.5 g (0.0938 mol) N-bromosuccinimide in 50 mL carbon tetrachloride, with a spatula tip of AIBN. A 300 W lamp was directed on the reaction flask. After seven days the reaction was stopped and the product was filtered through 8 inches of silica gel to remove the succinimide. The silica gel was washed with 300 mL of pentane. The solvent was removed on the rotary evaporator, leaving a light yellow solid (1.38 g, 38.4%); IR 3061, 3085 cm^{-1} (ArH), 2874, 2909, 2932 cm^{-1} (C-H), 1599 cm^{-1} (Ar C=C), 1617 cm^{-1} (alkene C=C); ^1H NMR ($CDCl_3$) δ 1.25 (s, CH_3), δ 7.1-7.5 (ArH);

^{13}C NMR ($CDCl_3$) δ 32 (s, CH_3), δ 42 (s, tertiary C), δ 140 and 142 (s, alkene C=C), δ 126-129 (m, Ar).

4. Synthesis of 2-Bromo-1,1-diphenyl-1-hexene

A solution of 3.6g (0.02 mol) 1,1-diphenylethylene in 50 mL dry tetrahydrofuran was placed in a 100-mL three-necked round-bottomed flask. The reaction flask was equipped with a condenser and a 30-mL equalizing addition funnel. The reaction was carried out under a nitrogen atmosphere. The flask was cooled in an ice bath and 20. mL of 1.6 M *n*-butyllithium in hexane was added dropwise. The alkyllithium was transferred into the dropping funnel using a 30-mL syringe. The mixture was stirred magnetically and turned a dark red color after the addition of 3.0 mL of *n*-butyllithium. This was a very mild reaction and passed through the colors of yellow and green before turning red. The remaining *n*-butyllithium was added quickly and the ice bath was removed. The mixture was allowed to react approximately 3 hours. Distilled water (50 mL) was added to quench the reaction. The first few drops must be added slowly. Upon separation of the organic layer with ether, and removal of the solvent on the rotary evaporator, the proton NMR showed no signs of the 1,1-diphenylethylene methylene peak. The bromination was started with 16.5 g (0.0938 mol) N-bromosuccinimide and 50 mL carbon tetrachloride. A scoopula tip of AIBN was added as the mixture began to reflux. A 300 W lamp was directed on the reaction flask. After five days the reaction was stopped and the product was filtered through 8 inches of silica gel to remove the succinimide. The silica gel was washed with 300 mL of pentane and the solvent was removed on the rotary evaporator, leaving a dark oily product (2.56 g, 71.1%). Thin layer chromatography and NMR indicated a product mixture of several components.

APPENDIX

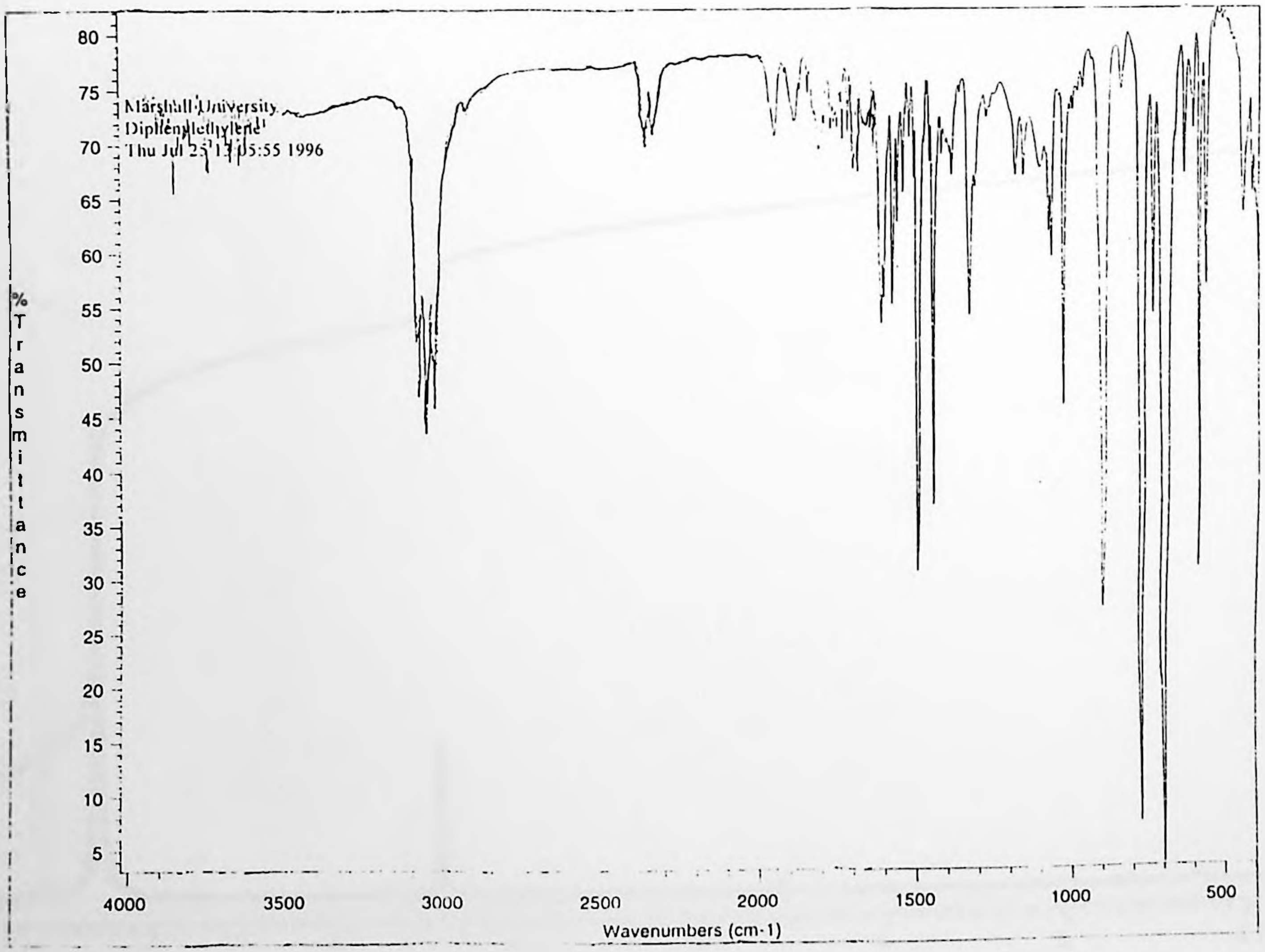


Figure 1. IR Spectrum of
1,1-Diphenylethylene

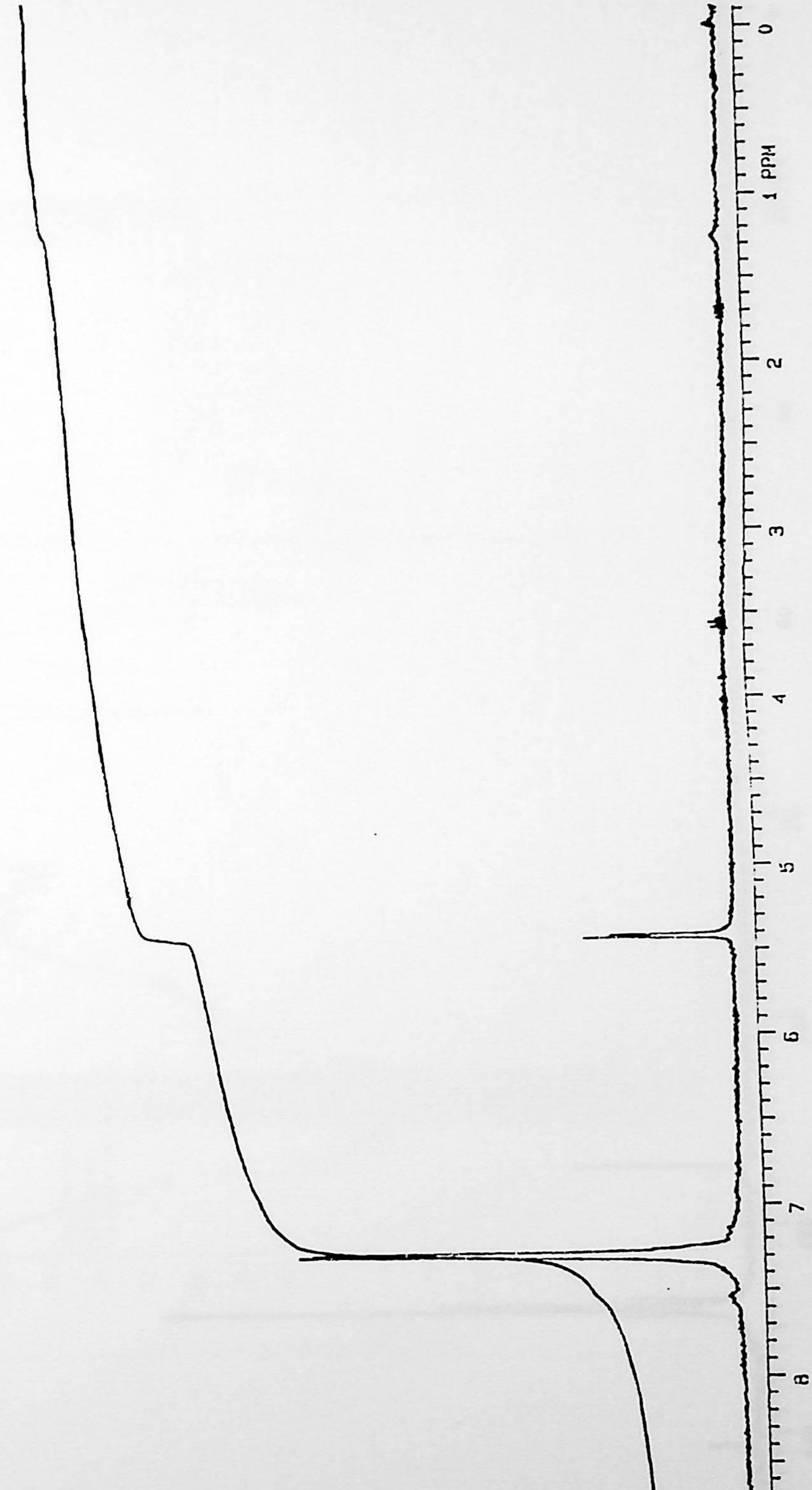


Figure 2. ^{1}H NMR Spectrum of
1,1-Diphenylethylene

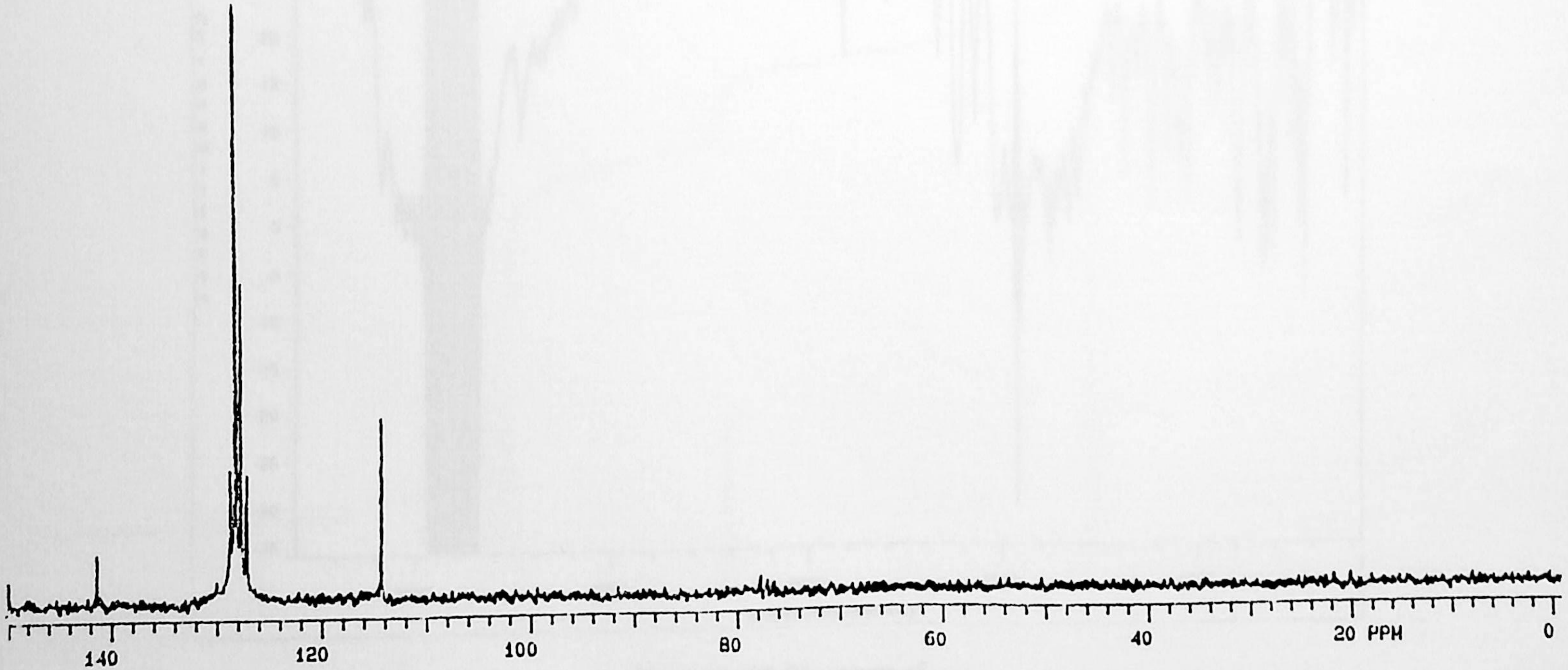


Figure 3. ^{13}C NMR Spectrum of
1,1-Diphenylethylene

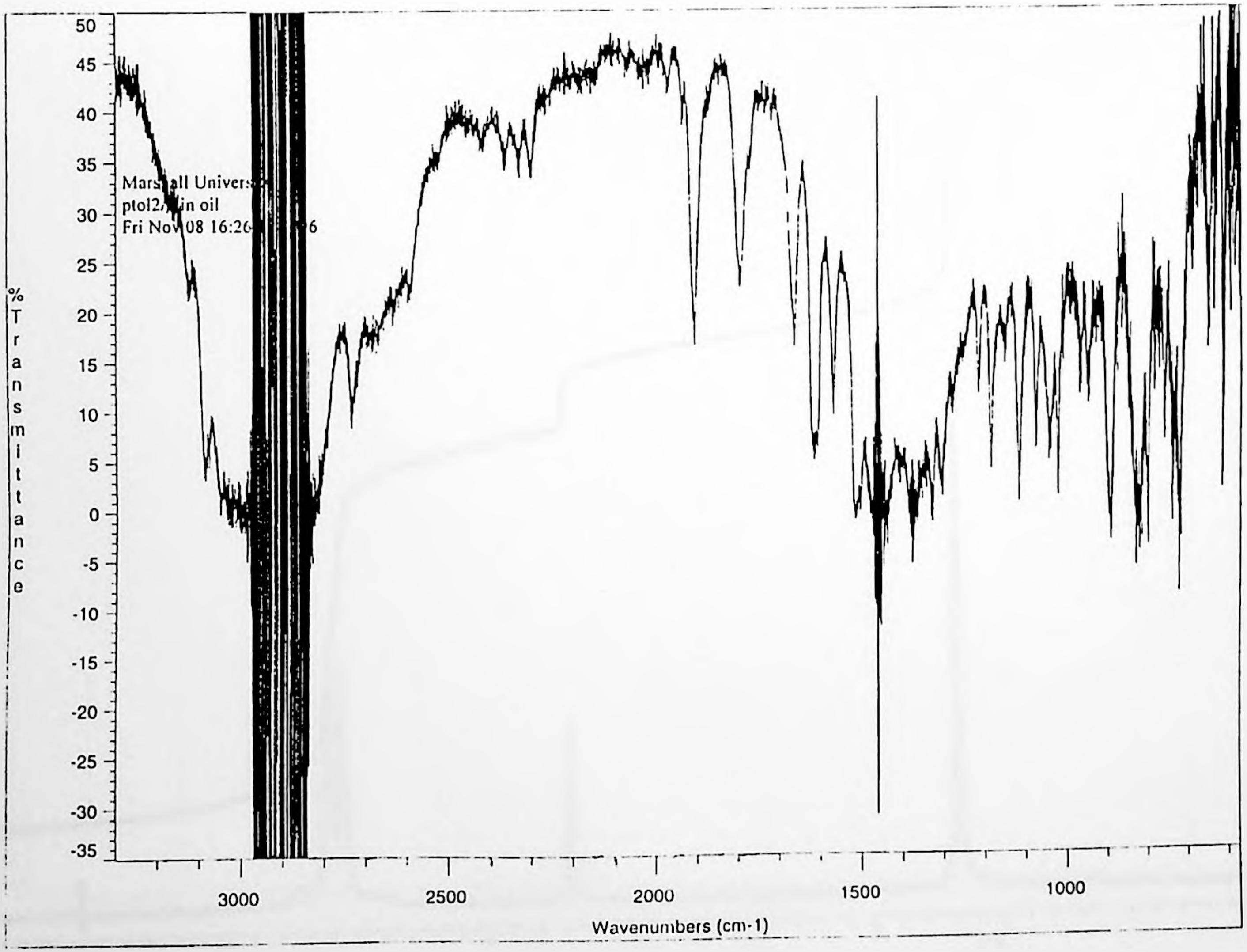


Figure 4. IR Spectrum of
1,1-Di-*p*-tolylethylene

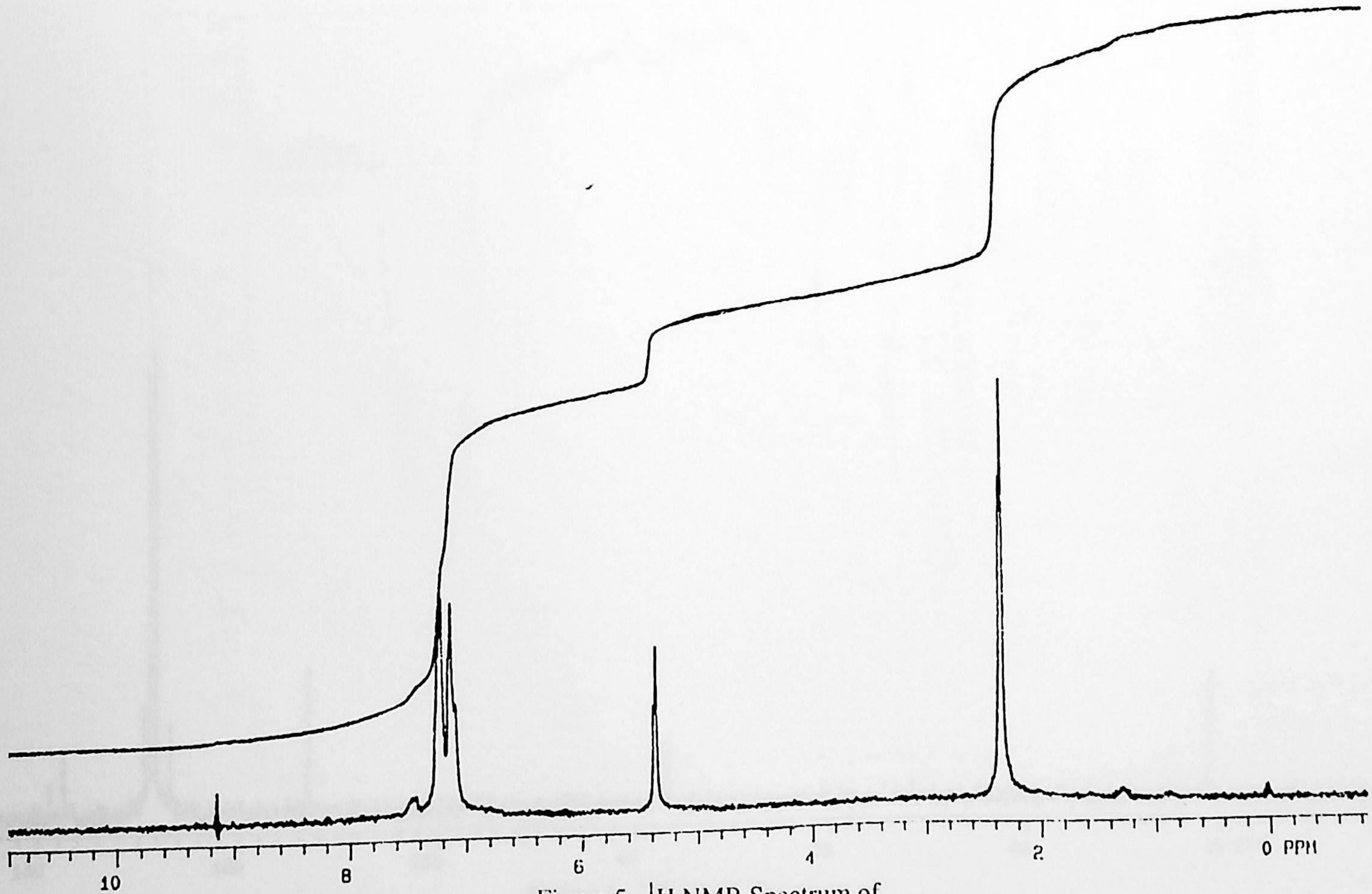


Figure 5. ^{1}H NMR Spectrum of 1,1-Di-*p*-tolylethylene

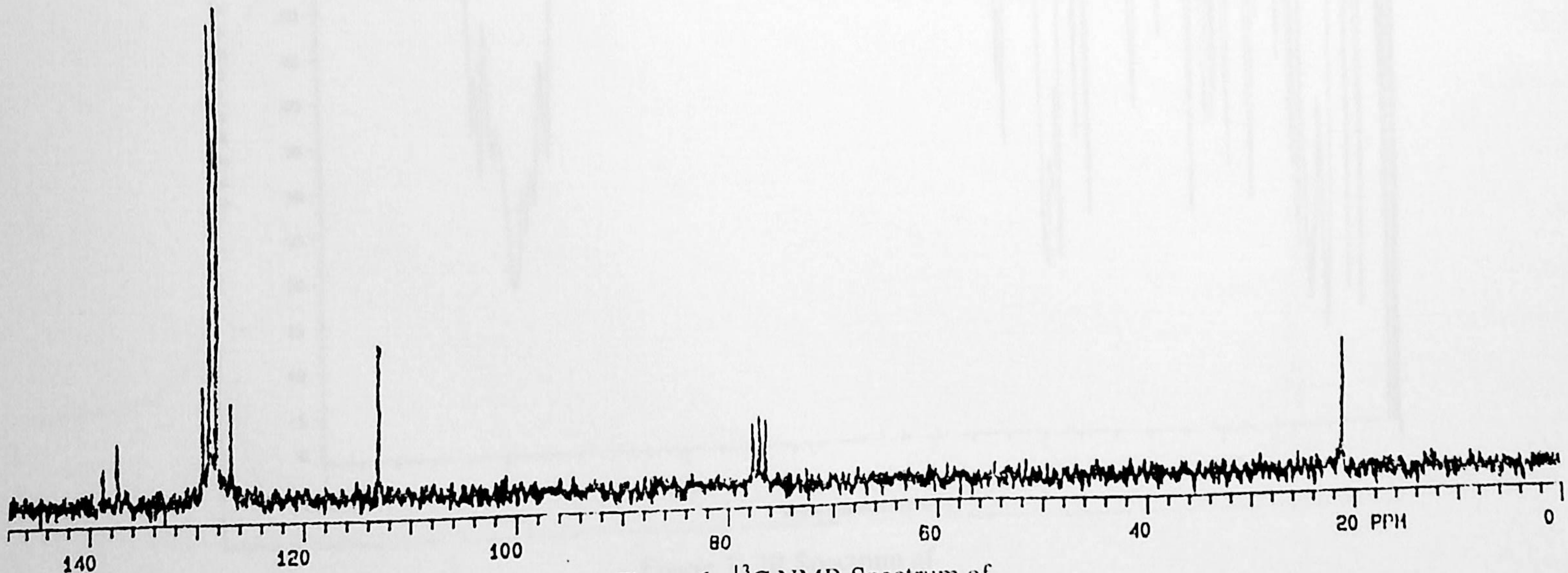


Figure 6. ^{13}C NMR Spectrum of
1,1-Di-*p*-tolylethylene

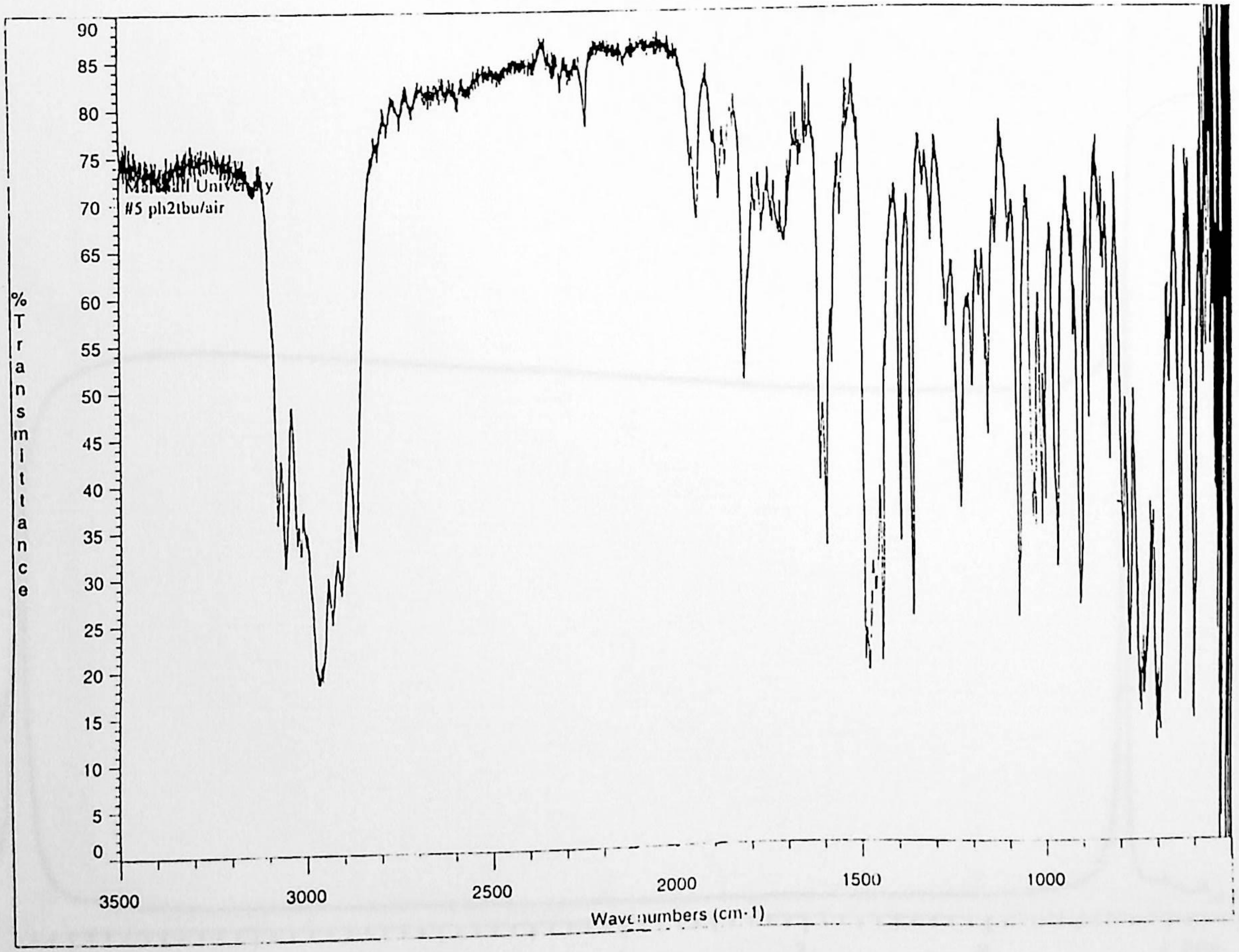


Figure 7. IR Spectrum of
2-Bromo-3,3-dimethyl-1,1-diphenyl-1-butene

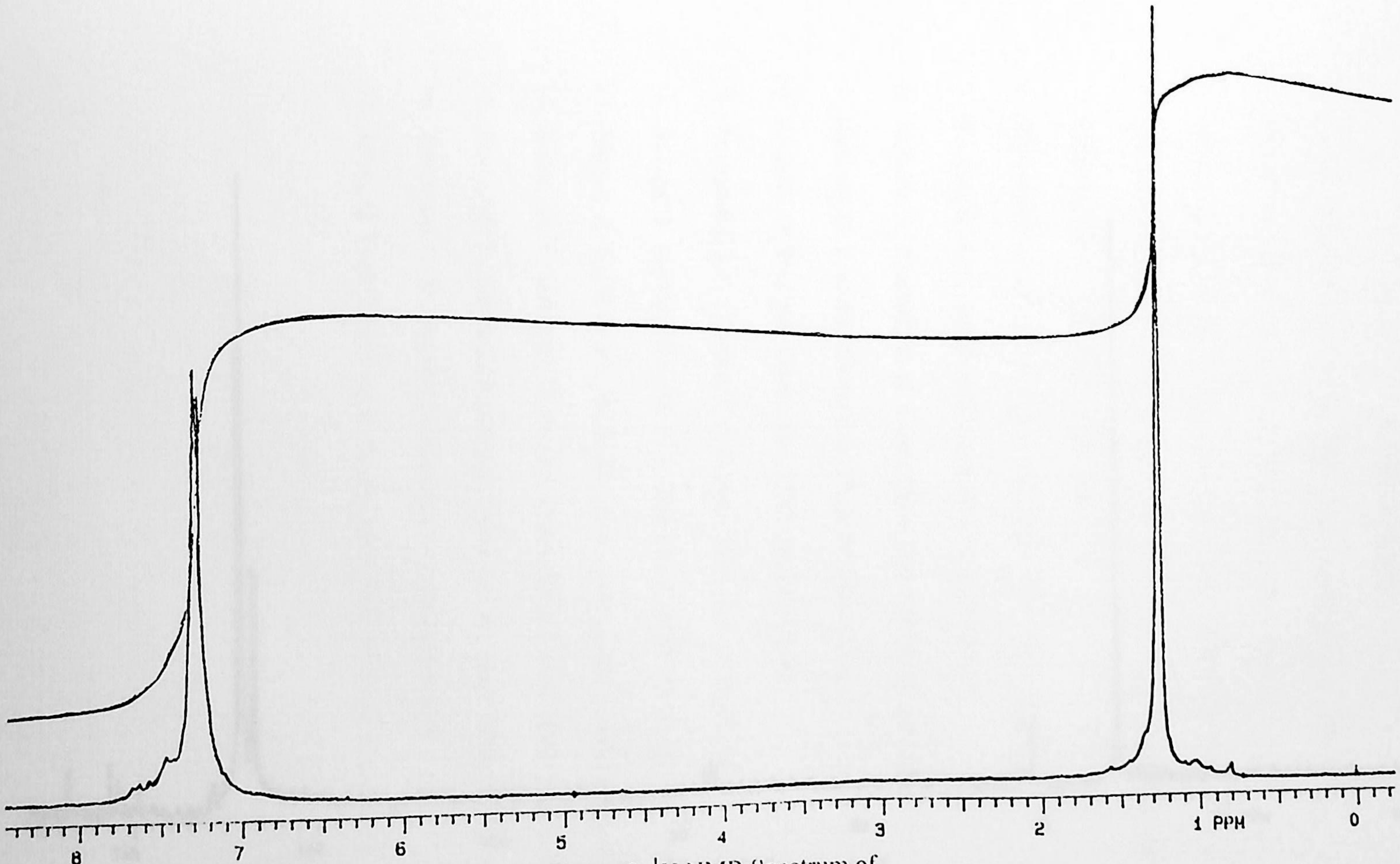


Figure 8. ^{1}H NMR Spectrum of
2-Bromo-3,3-dimethyl-1,1-diphenyl-1-butene

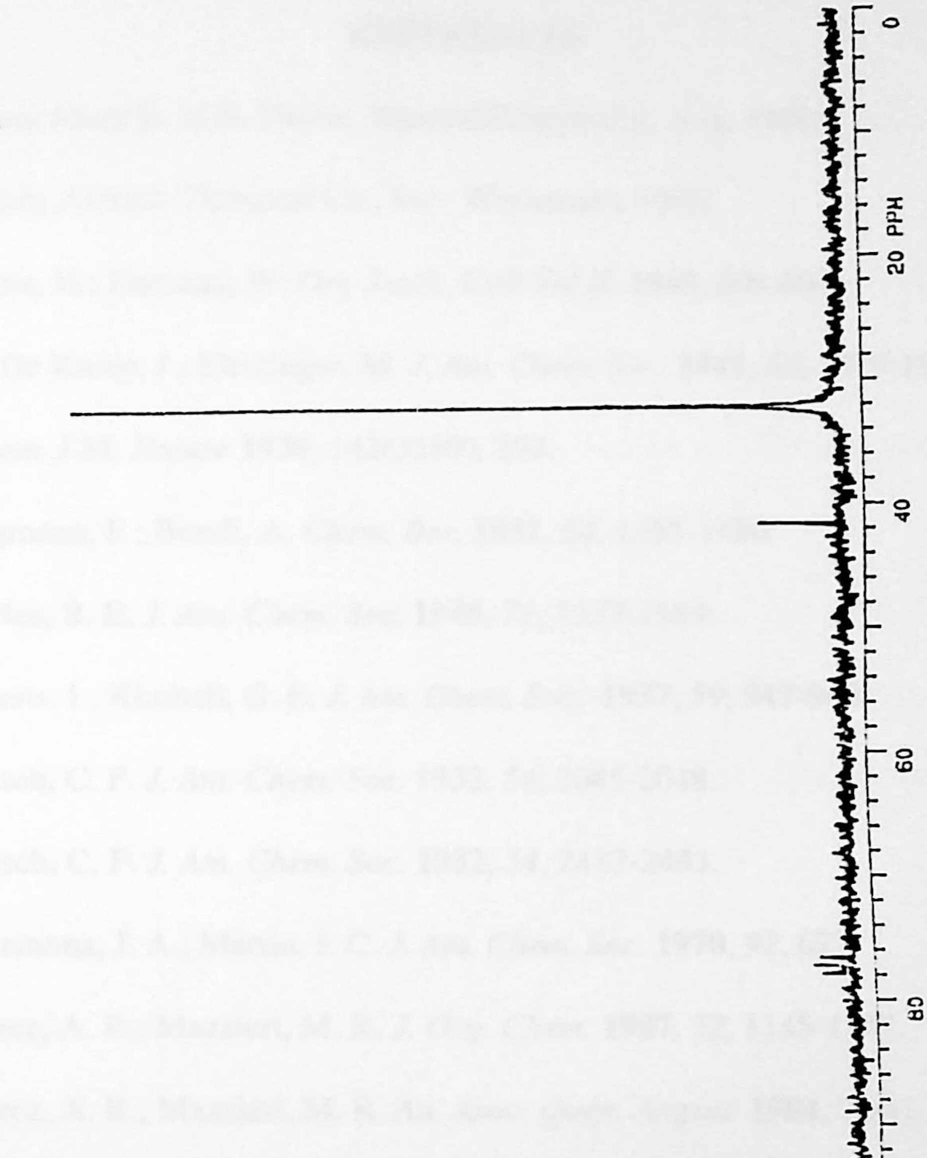


Figure 9. ^{13}C NMR Spectrum of
2-Bromo-3,3-dimethyl-1,1-diphenyl-1-butene

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VITA

The author was born on October 8, 1969, in Charleston, West Virginia. She attended Chapmanville High School.

She began her undergraduate studies at Southern WV Community College in August, 1987, and then transferred to Marshall University in August, 1988. She received her Bachelor of Arts Degree in Education, with certification in Chemistry and Physics, in May, 1992.

She began her graduate studies at Marshall University in June 1992. Throughout her graduate studies she held a teaching position at Poca High School, and a position as a Graduate Teaching Assistant. She received her Master of Science Degree from Marshall University in May, 1997.