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The Addition of Disilanes to Cumulenes

by

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DEDICATION

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GENERAL INTRODUCTION

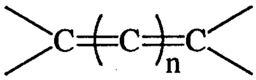
The syntheses of silicon-containing compounds and the studies of their rearrangements have been active research areas in the Barton research group. Previously, the addition of disilanes to acetylenes was studied in the group and an intramolecular [2S + 2A] mechanism has been proposed. In this thesis, the work is focused on the addition of disilanes to cumulenes. The syntheses of the precursors are discussed and the possible mechanisms for their thermal, photochemical and catalytic rearrangements are proposed.

Conjugated organic polymers have been studied in the group since 1985 because of their potential for exhibiting high electroconductivity, photoconductivity, strong non-linear optical response and intense fluorescence. In the second section of this dissertation, the synthesis and property studies of poly(phenylene vinylene) analogues are discussed.

I. THE ADDITION OF DISILANES TO CUMULENES

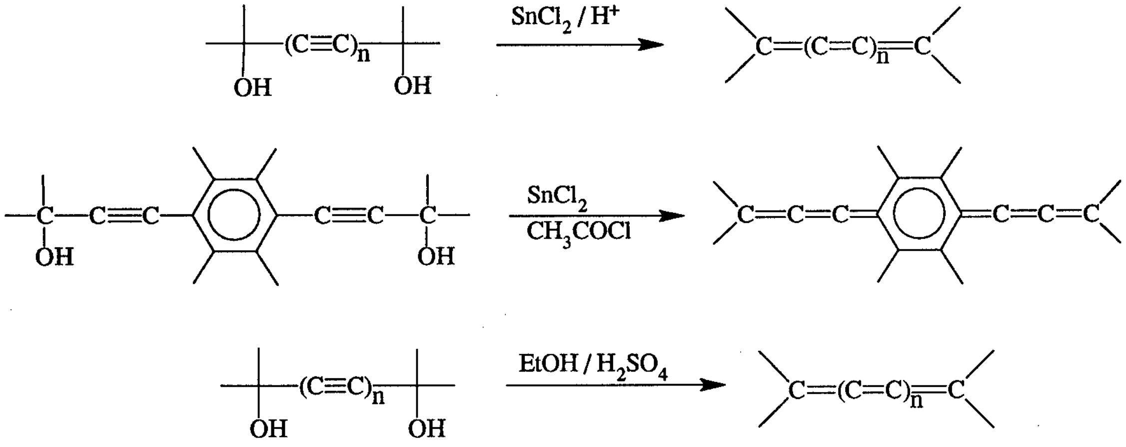
Literature Survey

Cumulenes are a special class of conjugated organic molecules, which have two sp^2-hybridized carbons separated by n sp-hybridized carbons with n+1 double bonds ($n \geqq 1$).[1]



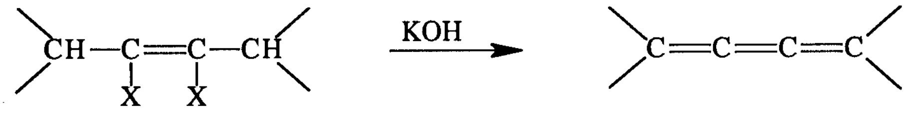
Within the cumulene backbone, two extended π-systems are perpendicular to each other. Most of the C=C bonds in cumulenes are shorter than a normal C=C bond (1.34 A) and the odd number C=C bonds are slightly longer than the even number C=C bonds.[2,3] When n is an odd number, the two end planes of the cumulene molecule are orthogonal to each other, when n is an even number, the structure would be expected to be planar, but is not so because of the steric interactions between the substituents. For instance, in tetraphenyl butatriene, the four phenyl rings make dihedral angles of 30, 28, 29 and 42°, respectively, with the plane through the butatriene system.[2]

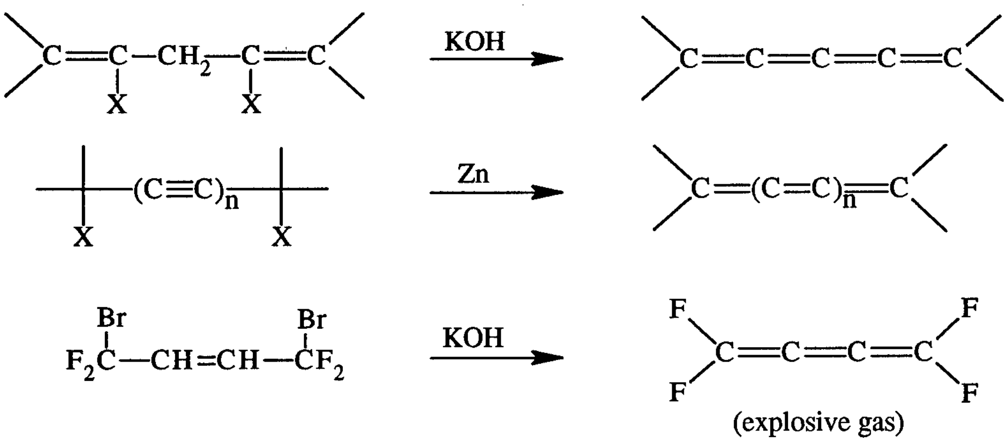
Cumulenes can be synthesized by several different routes.[4] The most common way is through elimination reactions. Among these, the simplest and the most widely used method is reductive elimination from diol precursors, reported by Chodkewicz[4-7], as shown in Scheme 1. However, only cumulenes with an even number of carbon atoms are obtained by this route. The diol precursors are usually obtained from the reactions of acetylenic Grignard or lithium reagents with the corresponding ketones and aldehydes. Tin (II) chloride functions as the reducing agent. It was also reported that the diol precursor was converted to cumulene upon heating in sulfuric acid-ethanol solution.[8] The reducing agent in this case was proposed to be the SO_2 produced by heating sulfuric acid with ethanol.



Scheme 1. Synthesis of cumulenes from reductive elimination

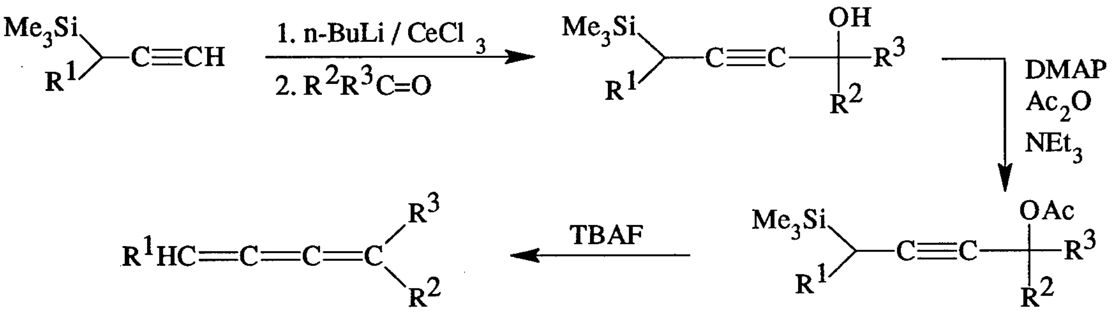
Elimination of hydrogen halide under basic conditions or of halogen by zinc from the corresponding dihalides afford cumulenes in excellent yield (Scheme 2).[4] This method is especially convenient to produce the cumulenes whose diol precursors are not available, such as tetraflurobutatriene.[1]





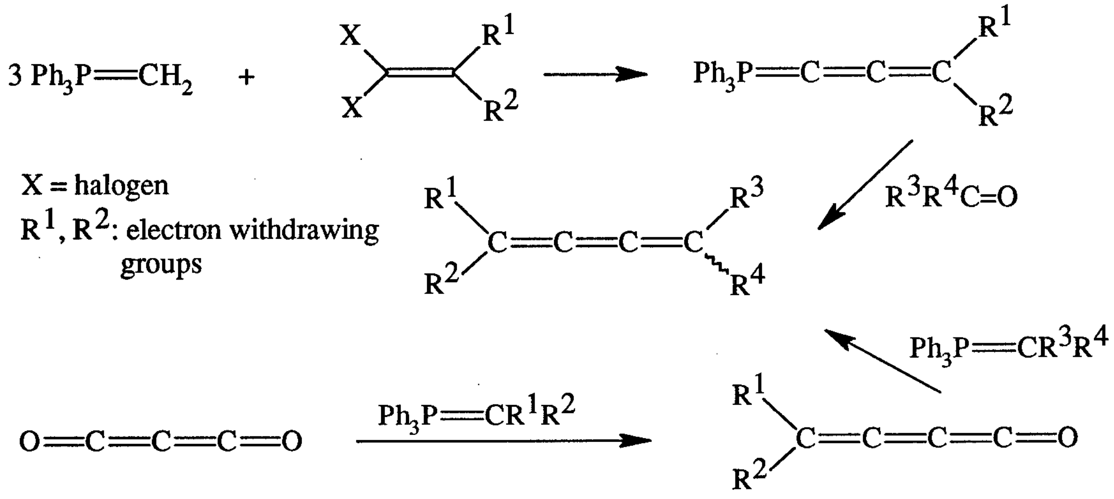
Scheme 2. Synthesis of cumulenes by elimination of halides

Fluoride-induced elimination[9] usually gives cumulenes in good yields. In the following example, silyl prop-2-ynilic alcohols, which were obtained from the reaction of silyl prop-2-ynilic cerium reagents with ketones or aldehydes, were converted into the corresponding acetates in 4-(dimethylamino) pyridine (DMAP), followed by tetrabutylammonium fluoride (TBAF)-induced 1,4-elimination to give alkyl or aryl substituted butatrienes (Scheme 3).



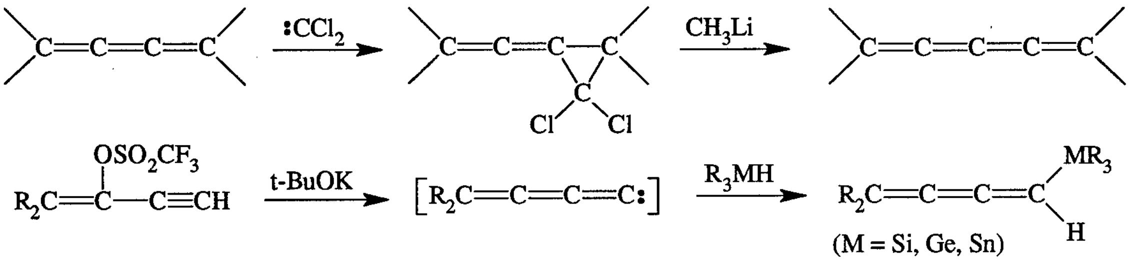
Scheme 3. Fluoride-induced elimination

Besides the above elimination reactions, Wittig reactions are also used for cumulene synthesis, as shown in Scheme 4. The first approach is to synthesize a cumulenic Wittig reagent and then couple with the corresponding ketone to give the desired cumulene.[10] In the second approach', carbon suboxide is reacted with two equivalents of Wittig reagents sequentially to give the cumulenic products.[11, 12]



Scheme 4. Preparation of cumulenes via Wittig reaction

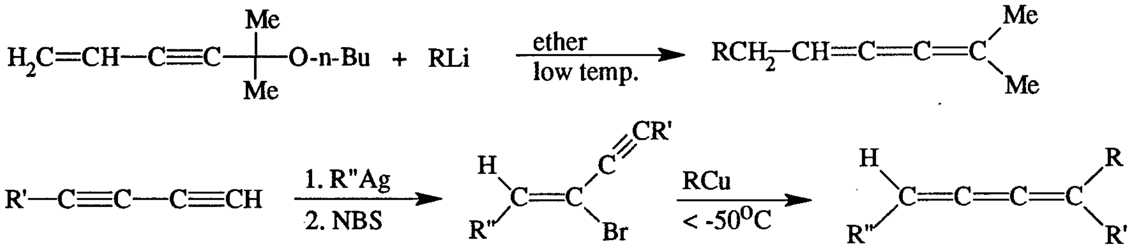
The length of a cumulene segment can be increased by one carbon atom through the carbene insertion reported by Karich and Jochims (Scheme 5).[13] This method is



Scheme 5. Synthesis of cumulenes through carbene insertion

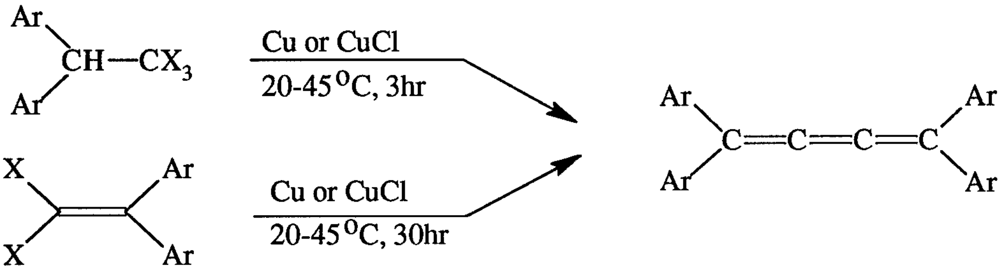
usually used to synthesize cumulenes with an odd number of carbon atoms from the easily obtained cumulenes with an even number of carbons. Silicon-, germanium- and tin-functionalized cumulenes have been synthesized by this route.[14]

Cumulenes are also obtained from S_N' reaction under appropriate reaction conditions (Scheme 6).[4c, 15]



Scheme 6. S_N' process

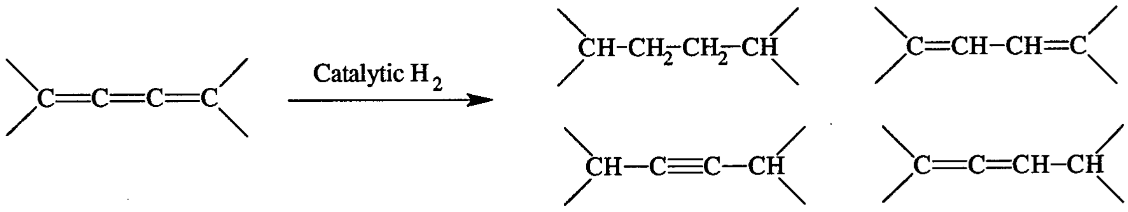
Catalytic coupling of halides with transition metal catalysts is another route to cumulenes (Scheme 7).[16]



Scheme 7. Preparation of cumulenes via catalytic coupling

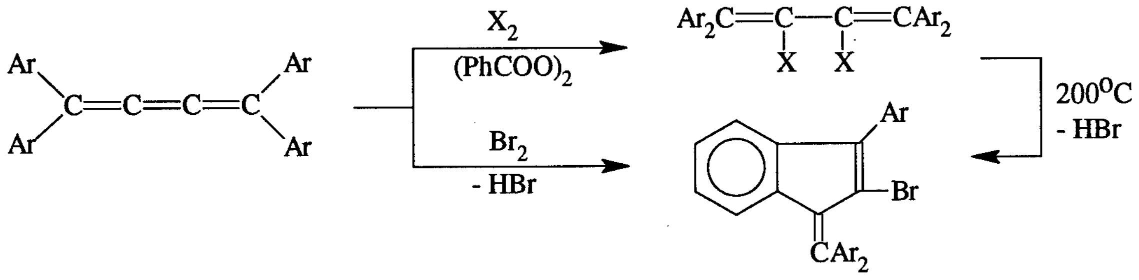
Most of the tetraaryl or tetra(*t*-butyl) substituted cumulenes are stable compounds with remarkably high melting points. The stability is decreased if one or more of the four substituents are hydrogen atoms. Thus 1,4-distyrylbutatriene can only be obtained by a very careful process of isolation [17], and butatriene itself is extremely labile.

Cumulenes have a high degree of unsaturation, therefore many reactions characteristic of unsaturated compounds can readily occur with cumulenes. For example, hydrogenation of cumulenes: the reactions afford different products with different catalysts (Scheme 8). [1]



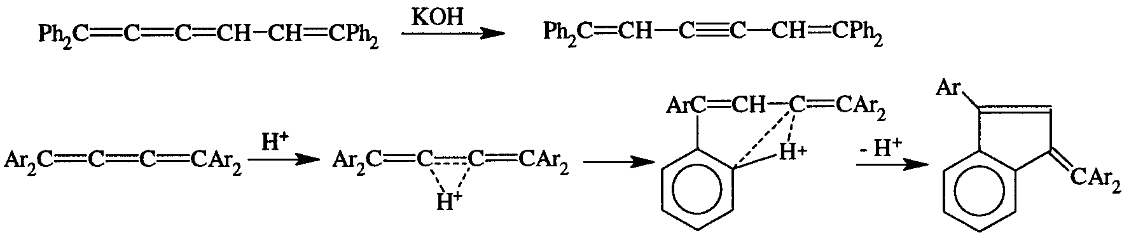
Scheme 8. Hydrogenation of cumulenes

In halogenation, butatrienes generally take up the halogen in the 2- and 3-positions and furnish 2,3-dihalo-1,3-butadienes. In the case of tetraarylbutatrienes, the yields reach 90% if dibenzoyl peroxide is used as a catalyst. Without this catalyst, however, formation of methylenebromoindenes becomes a competitive reaction (Scheme 9). [18]



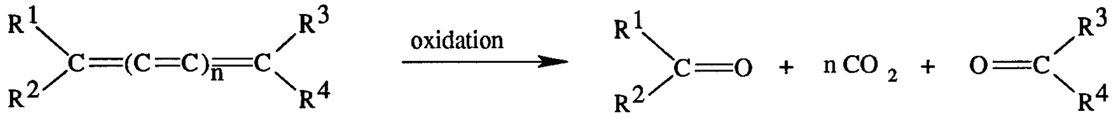
Scheme 9. Halogenation of cumulenes

Tetrasubstituted cumulenes are resistant towards basic reagents, but if at least one hydrogen is present as a substituent, then a cumulene can isomerize to an ene-yne form through a sort of retro-propargylic rearrangement.[19] Acids isomerize tetraarylbutatrienes to methyleneindenes (Scheme 10).[20]



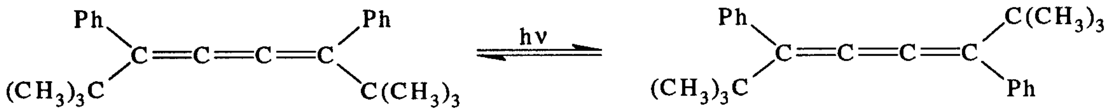
Scheme 10. Isomerizations of cumulenes

Forced oxidation by chromic acid, permanganate or ozone splits cumulenes into the corresponding carbonyl compounds and carbon dioxide, as shown in Scheme 11, a reaction which serves to prove the constitution of these cumulenes.[21]



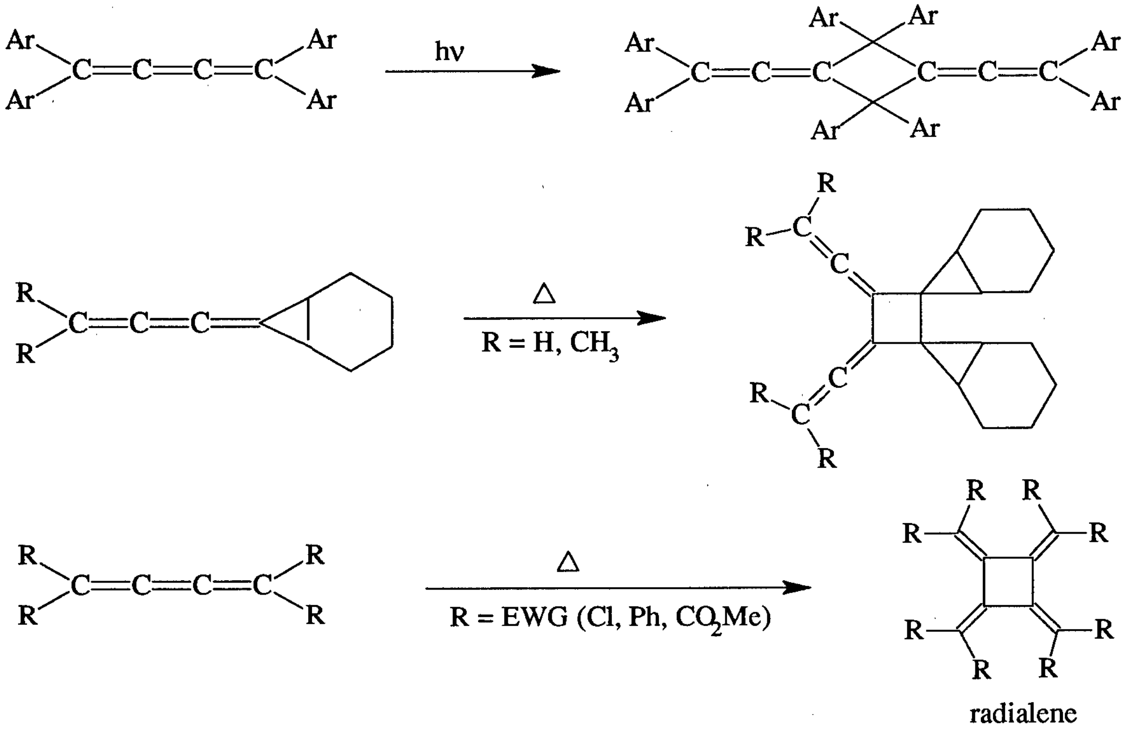
Scheme 11. Oxidation of cumulenes

The *cis-trans* isomerization (Scheme 12) of butatriene upon irradiation was first reported by Kohn and Scholler.[22] The isomers were successfully separated on alumina.



Scheme 12. *cis-trans* isomerization of the butatriene

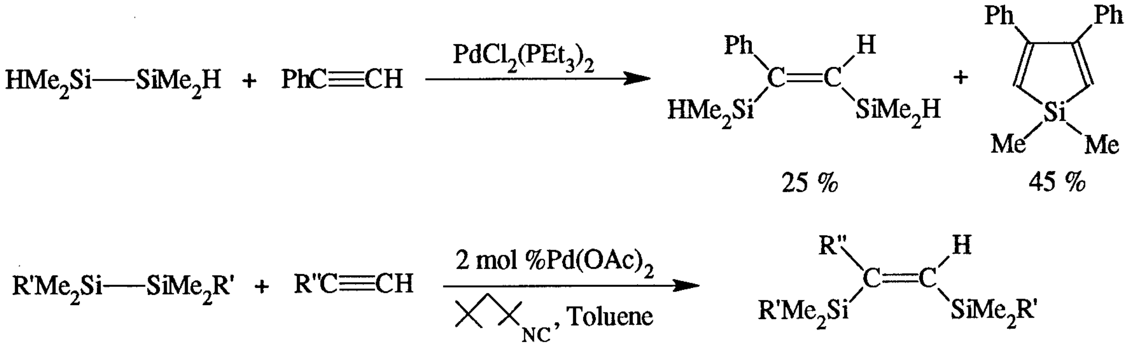
The dimerization of cumulenes was first observed by Brand.[21] Solid-state tetraphenyl butatriene dimerized on exposure to sunlight to tetramethylenecyclobutane, a [2+2] head to tail dimer of the end double bond, while butatrienes with alkyl substituents dimerize via a [2 + 2] head to head fashion.[23] Also, butatrienes with electron-withdrawing substituents dimerize to give [4] radialenes thermally, which is a very important route to radialenes (Scheme 13).[24-26]



Scheme 13. Dimerization of butatrienes

The nature of the Si-Si bond has attracted a lot of attention. Among these investigations, the transition metal catalyzed reactions of the Si-Si bond have been well studied.[83] Oxidative addition of the Si-Si bond to the metal center offers the potential for formation of bis(silyl), silyl(silylene), silylene and disilane complexes, followed by reductive elimination. A range of potential catalytic processes can be envisaged.

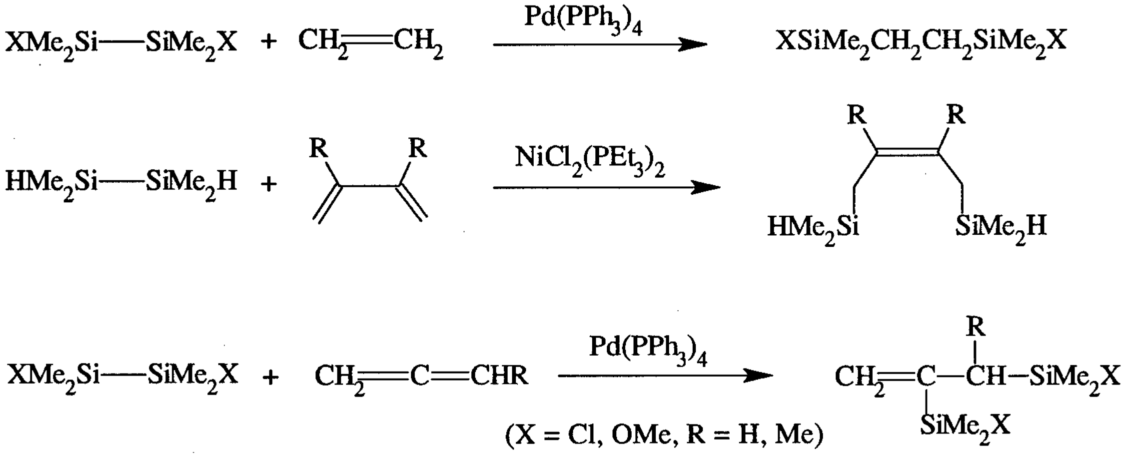
Isomerizations[27], silylene generation[28] and polymerizations [29-33] readily happen with disilanes. The aspect we are interested in is the addition of the Si-Si bond to unsaturated molecules. It is reported that acetylenes in the presence of a variety of Pd catalysts undergo bissilylation with 1,1,2,2-tetramethyl disilane (Scheme 14).[34] Also, the palladium (II) acetate/*tert*-alkyl isocyanide and $Pd(dba)_2 2P(OCH_2)_3CEt$ complexes efficiently catalyze the bissilylation of alkynes with otherwise unreactive disilanes such as hexamethyldisilane and 1,1,2,2-tetramethyl-1,2-diphenyl disilane (Scheme 14).[35,36] In general, Z isomers, which arise from the *cis* addition of the Si-Si bond to alkynes, were formed predominantly in excellent yields. Both catalysts were also successfully applied to permethylated tri- and tetrasilanes. The reactivity of organodisilanes in such addition chemistry is enhanced by electronegative substituents such as fluorine, chlorine and alkoxide.



(R' = Me, Ph; R" = H, n-Hex, Ph)

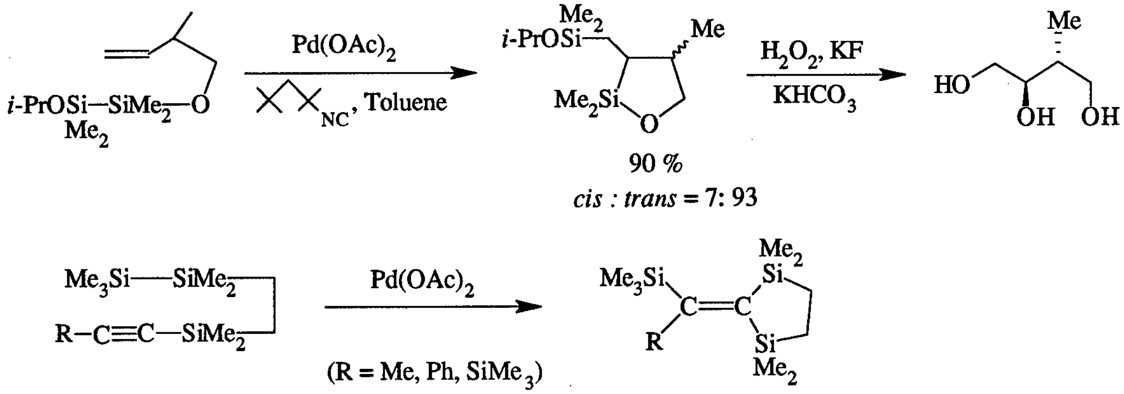
Scheme 14. Bissilylation of acetylenes

The Tanaka group reported the first successful bissilylation of ethylene with disilanes in the presence of platinum phosphine complexes to give 1,2-bis(silyl)ethanes (Scheme 15).[37] The reactivity of the disilane is considerably enhanced by the introduction of electronegative and sterically less demanding substituents on the silicon atom. The order of reactivity of the disilanes, $XSiMe_2SiMe_2X$, was X = F > OCH_3 > Cl >CH_3 > *p*-$CF_3C_6H_4$ > C_6H_5 > *p*-$CH_3C_6H_4$. The double silylation of 1,3-butadienes by 1,1,2,2-tetramethyldisilane was reported to be catalyzed by $NiCl_2(PEt_3)_2$ to give 1,4-bis(dimethylsilyl)-but-2-enes.[38] Several examples of metal-catalyzed 1,2-additions of Si-Si bonds to allenic compounds have also been reported (Scheme 15).[39,40]



Scheme 15. Bissilylation of ethylene and other olefins

Intramolecular bissilylation of C=C and C≡C is an attractive stereo- and regioselective synthesis of organosilicon compounds (Scheme 16). The intramolecular bissilylation reactions of C=C bonds led to the stereoselective synthesis of 1,2,4-triols.[41]



Scheme 16. Intramolecular bissilylation

Palladium (II) acetate/*tert*-alkyl isocyanide-catalyzed bissilylations of pentaalkyldisilyl-substituted alkynes involve intramolecular regioselective *cis* addition of the Si-Si linkage to furnish exocyclic olefins in good yields.[35,42]

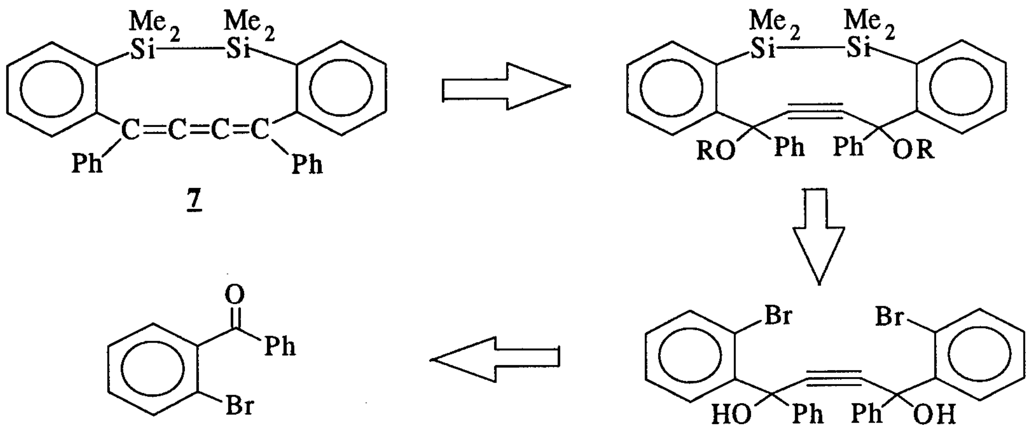
The disilane hydrosilylation[34,43], metathesis[44-46] and insertion to hetro-unsaturated molecules[47-51] were also reported and reviewed.

Results and Discussions

The additions of disilanes to acetylenes have been studied in the group.[52] Ma found that the intramolecular addition occured thermally, photochemically and catalytically. However no intermolecular reactions occur under the same conditions. For the intramolecular reaction, a [2S + 2A] mechanism was proposed. In order to extend the study of the Si-Si bond addition to *sp*C-*sp*C bonds, we chose to construct butatrienes to react intramolecularly with disilanes.

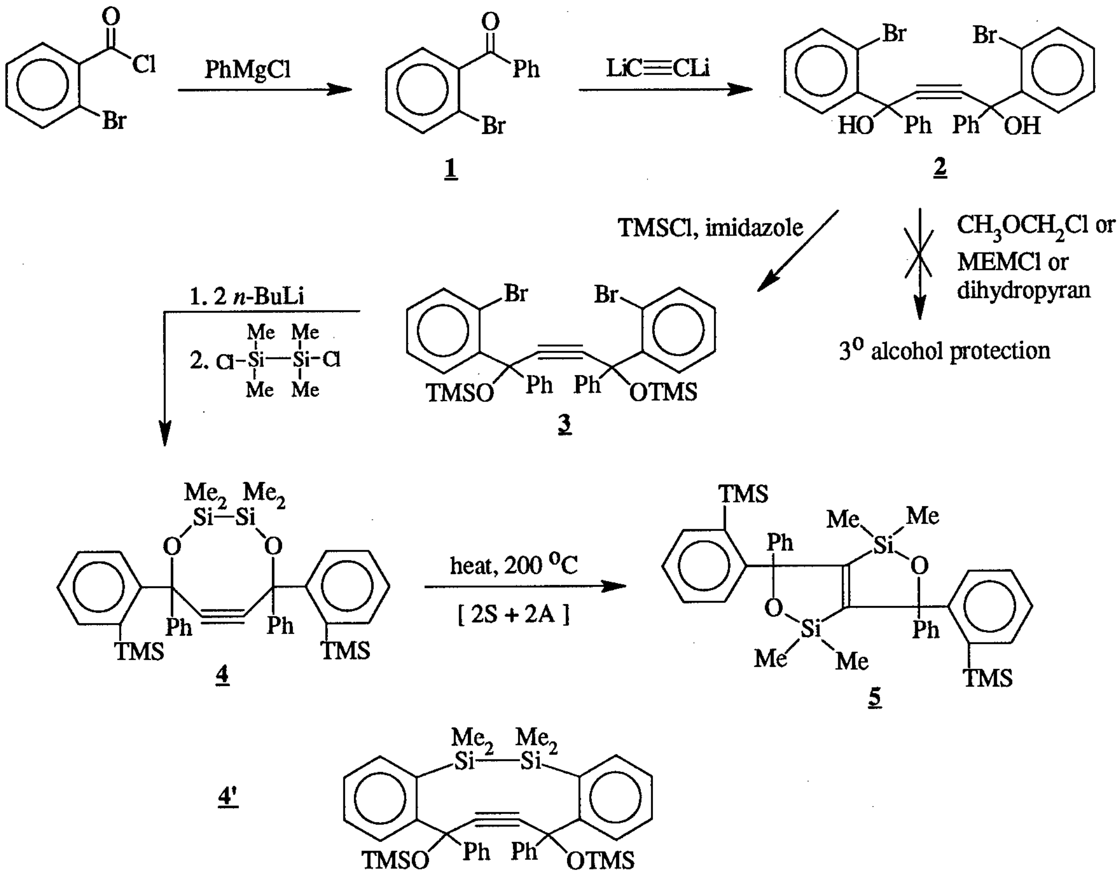
Attempted synthesis of cyclic butatriene 7

The first synthetic route designed for the target molecule-cyclic butatriene 7 is shown below (Scheme 17):



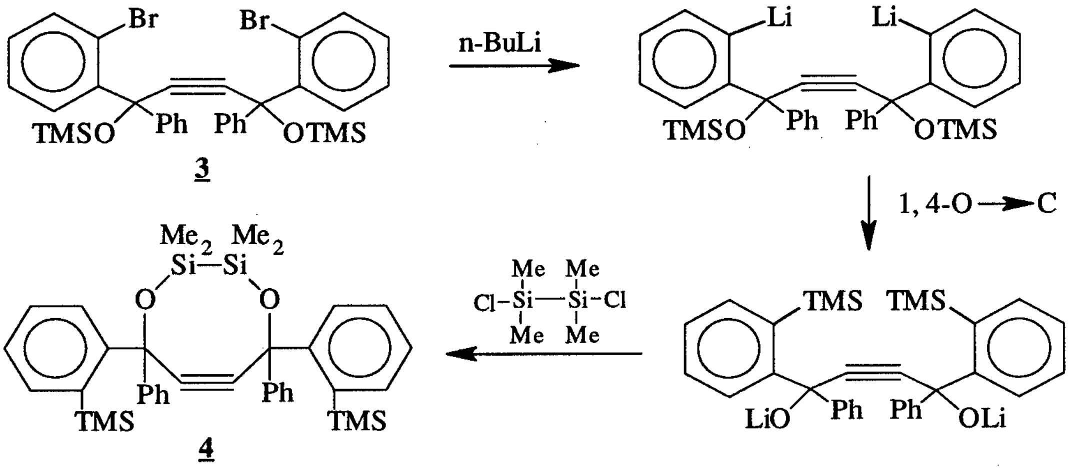
Scheme 17. Retro-synthesis of cyclic butatriene 7

The actual synthesis (Scheme 18a) started with 2-bromobenzoylchloride, which reacted with phenylmagnesium chloride to produce 2-bromobenzophenone 1 in 97% yield.[75] The treatment of dilithioacetylene[74] with 2-bromobezophenone 1 producing acetylenic diol 2, followed by the hydroxyl protection with trimethylchlorosilane afforded 3 in 65% total yield. After the lithium-halogen exchange of 3 with *n*-BuLi, dichlorotetramethyldisilane was added to the mixture to yield colorless crystals which were submitted for X-ray diffraction analysis. To our surprise, the crystal was dioxydisilacyclooctyne 4 instead of benzocyclooctyne 4', the compound we were expecting. A possible explanation is that after the lithium-halogen exchange, the trimethylsilyl groups migrate from oxygen



Scheme 18a. Attempted synthesis of cyclic butatriene

to carbon to make the oxygen dianion, which cyclized with dichlorotetramethyldisilane to give dioxydisilacyclooctyne 4 (Scheme 18b). The same phenomenon was also reported by P. Hudrlik in enolates of sily esters.[84] He found the lithium enolate of trimethylsilyl acetate underwent a 1,3-O→C migration of the trimethyl-silyl group, but the migrations did not apply to the triethylsilyl group. For this reason, the triethylsilyl and dimethyl-*t*-butylsilyl protecting groups were tried, but neither of them would attach, probably due to the steric hindrance of the acetylenic diol 2. The other protecting groups, such as methoxymethyl (MOM), tetrahydropyranyl (THP) and 2-methoxyethoxymethyl (MEM) were also tried and failed, presumably due to the same reason.



Scheme 18b. A possible explanation of the formation of 4

Dioxy cyclooctyne 4 undergoes a [2S + 2A] reaction by heating to 200°C in a sealed tube, producing the fused five membered ring compound 5 (Scheme 18a) in 31% yield. The structure of 5 was verified by single crystal X-ray crystallography (Figure 1).

Synthesis of cyclic butatriene 7

Since the attempts to protect 3° acetylenic alcohol 2 failed, we tried to make the butatriene immediately after the formation of the alcohol, followed by a cyclization reaction with dichlorotetramethyldisilane. It turned out to be a successful route: the butatriene formation from reaction of 2 with $SnCl_2$ and HCl gave 1,4-bis(2-bromophenyl)-1,4-diphenyl-1,2,3-butatriene 6 in 62% yield.[72] After 6 was reacted with *n*-BuLi and dichlorotetramethyldisilane, the desired cyclic butatriene 7 was obtained as bright yellow

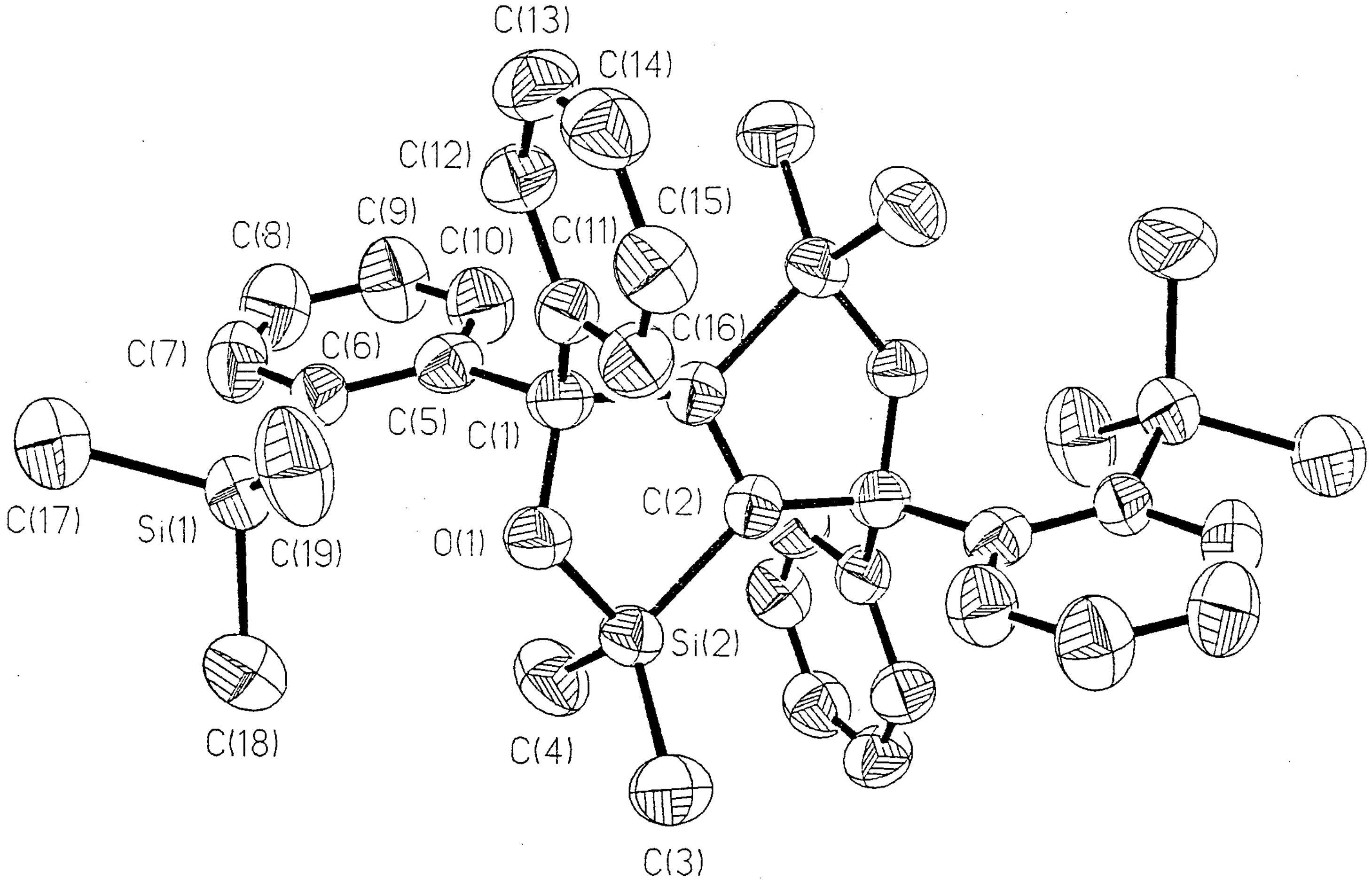
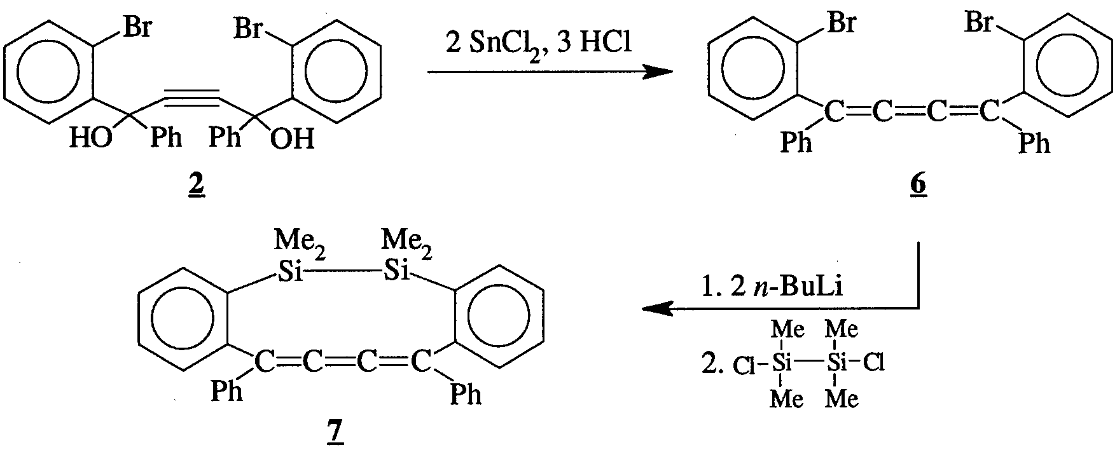


Figure 1. X ray structure of 5

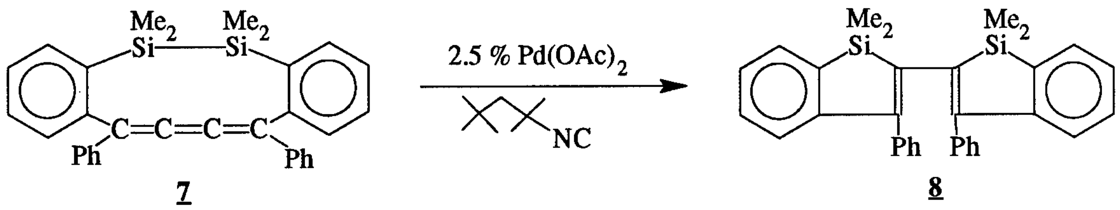
crystals in 55% yield (Scheme 19). Considering the yield we got from the cyclization reaction, the 1,4-bis(2-bromophenyl)-1,4-diphenyl-1,2,3-butatriene **6** should be a *cis*-isomer. Since the reductive elimination step does not seem to have much selectivity, we still have no idea if *cis*-**6** obtained was the only one produced in the reaction or was the only one crystallized from the solution.



Scheme 19. Synthesis of cyclic butatriene **7**

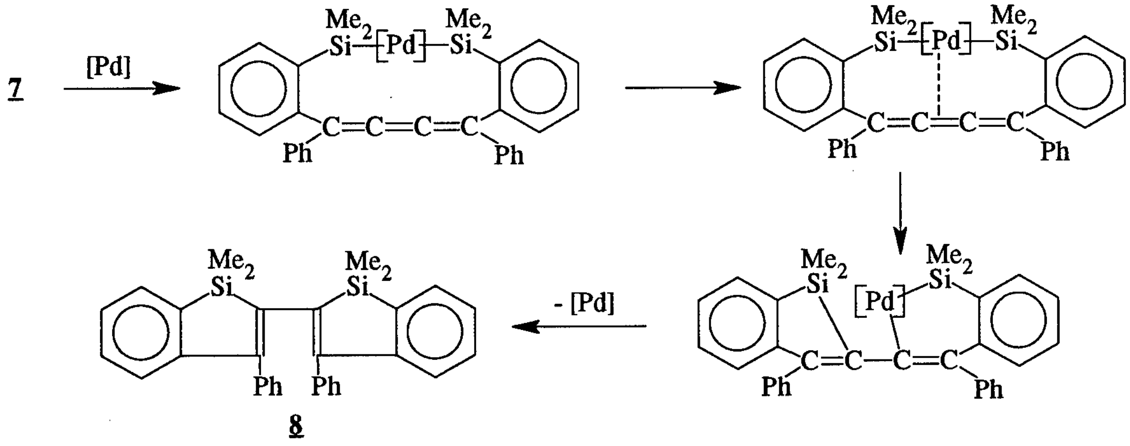
Catalytic study of cyclic butatriene 7

The literature mentioned in the previous section give a lot of examples of bissilylation of unsaturated molecules. In this investigation, butatriene **7** was stirred at room temperature in the presence of a catalytic amount of $Pd(OAc)_2$ and 1,1,3,3-tetramethylbutyl isocyanide overnight. As expected, it produced 2,2'-bis(1-phenyl-3,3-dimethyl-3-silaindene) **8** with the silicons in five-membered rings in nearly quantitative yield (Scheme 20). The structure of **8** is confirmed by crystal X-ray analysis (Figure 2).



Scheme 20. Catalytic reaction of 7

The mechanism of this reaction is envisaged as a normal [2 + 2] addition (Scheme 21), which proceeds via oxidative addition of the disilane followed by insertion of the central double-bond of butatriene into one of the resulting Si-Pd bonds and finally, reductive elimination of the product 8 from the palladium intermediate.



Scheme 21. A proposed mechanism of catalytic reaction

Thermal study of cyclic butatriene 7

The thermolysis of 7 was carried out by heating a nonane solution of 7 in a sealed tube to 175°C for 10 hours. The reaction yielded the same product 8 as the catalytic reaction (Scheme 22).

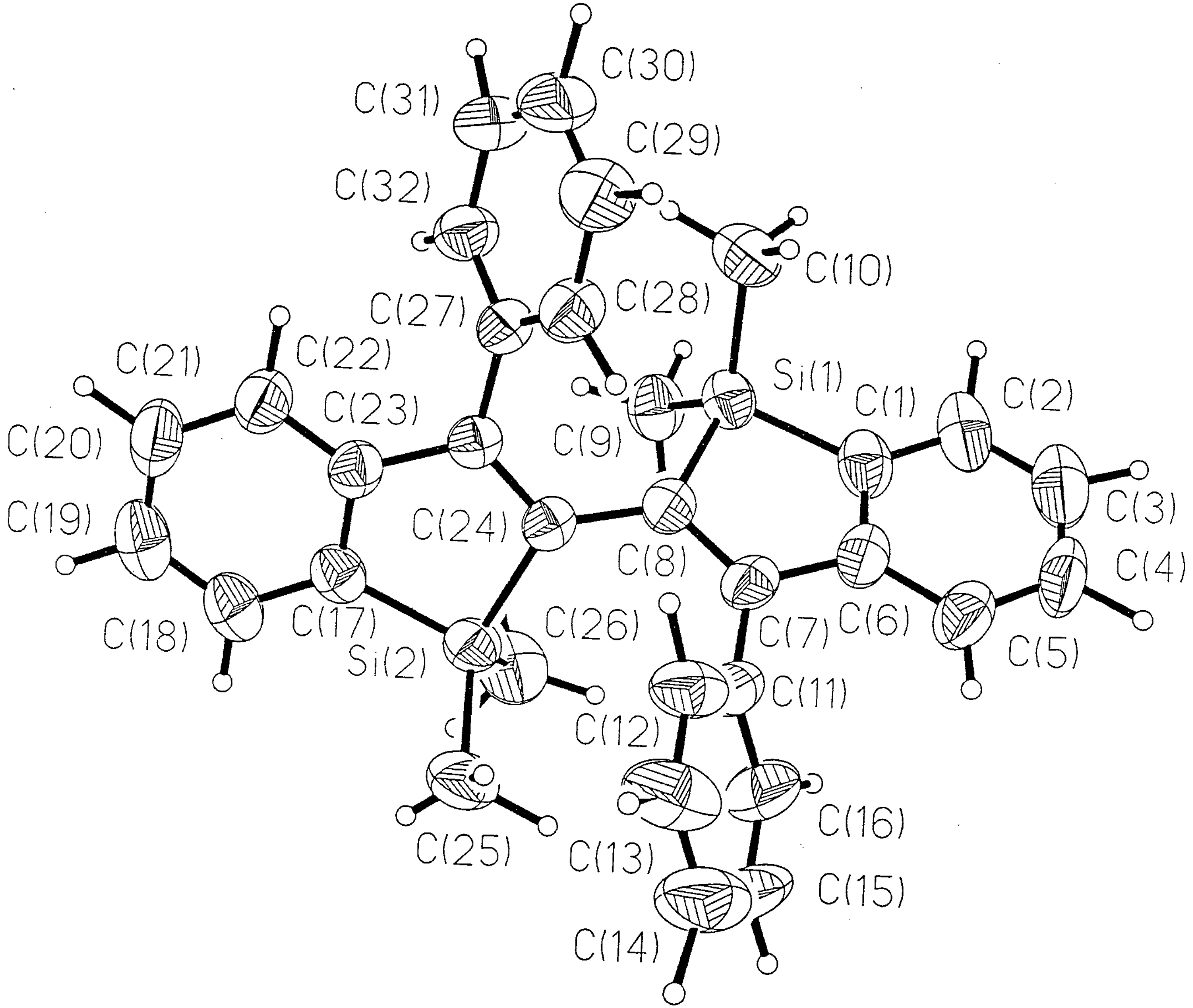
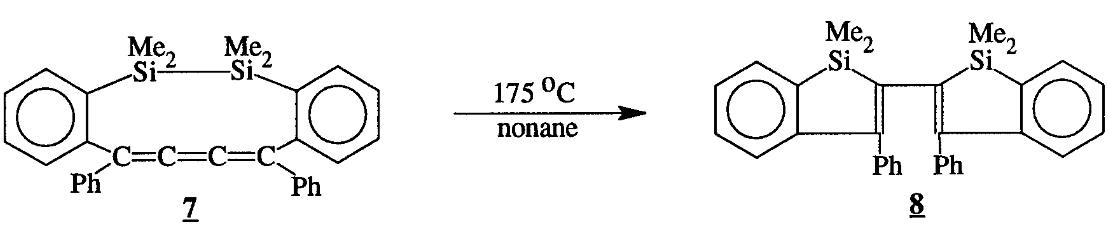
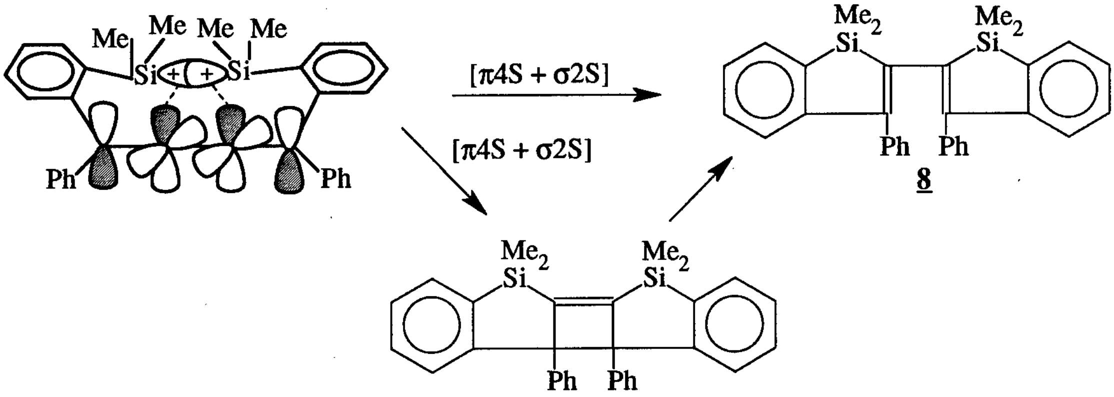


Figure 2. X-ray structure of 8



Scheme 22. Thermal reaction of 7

This result was surprising because, based on our experience with an acetylenic analog, we expected that the thermolysis would yield the product of S-A addition of the Si-Si bond across the central double bond, which would yield a completely fused tetracyclic system with the silicons each in six-membered rings. Considering the product obtained, the addition can not be [2S + 2A], but seems to be a [2S + 2S] process, which is forbidden under thermal conditions, according to the Woodward-Hoffmann rules. Another possibility is intramolecular [π4S + σ2S] thermal addition, which is an allowed reaction under the same conditions. In this case, the geometry of cyclic butatriene 7 takes a “boat” rather than planar conformation to become a symmetry-allowed reaction. Since the two orbitals of the central carbon-carbon double bond are not involved in this reaction, the butatriene orbitals are simplified as the butadiene orbitals. Reaction occurs by interaction of the LUMO of the diene (ψ_3) and σ orbital of the disilane, which can be seen from the illustration below to be allowed (Scheme 23). It is also possible that this process does not lead directly to the final product, but rather closes directly to a cyclobutene which then opens to compound 8. To get some evidence for this mechanism, we studied the low temperature ^{1}H NMR spectra of butatriene 7, in the hope of seeing two silicon

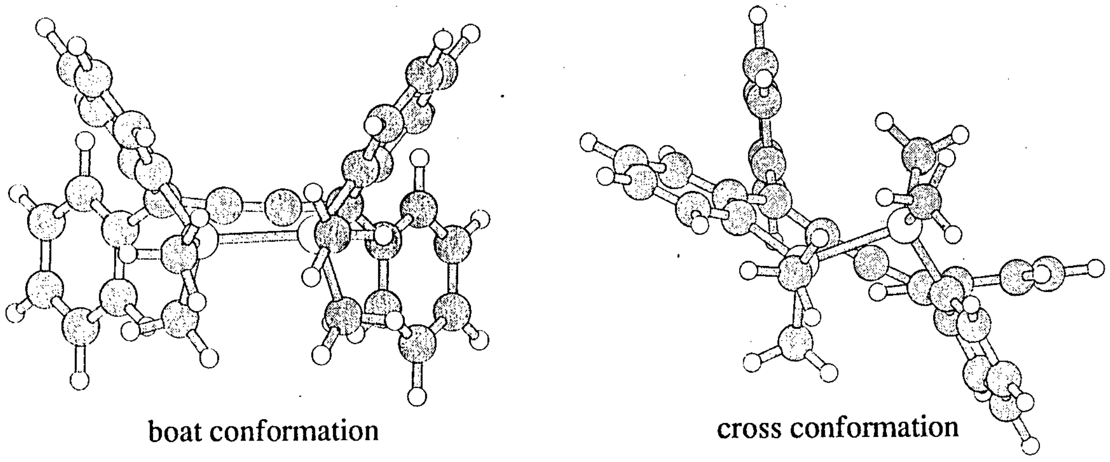


Scheme 23. A possible reaction mechanism

methyl peaks due to the boat conformation. But only one signal appeared, even at -55°C, and no obvious peak broadening was observed at that temperature. A possible explanation is that the exchange of methyls is very fast and beyond the NMR time scale. We used HyperChem version 4.5 software (Hypercube) to optimize the molecular geometries based on the molecular mechanics. Then, the further optimizations were carried out by PM3 method from the same software. From the calculation, we find that the "boat" conformation has one of the lowest energy (E = -7129 Kcal/mol), the other one being the "cross" conformation with the Si-Si bond across the central carbon-carbon double bond (E = -7125 Kcal/mol). The distances from Si atom to the central carbons are 3.33 A and 3.80 A for the boat conformation and 3.04 A and 3.34 A for the cross conformation, respectively (Figure 3).

Photochemical study of cyclic butatriene 7

Photolysis of a hexane solution and a d^6-benzene solution of 7 at 350 nm with a

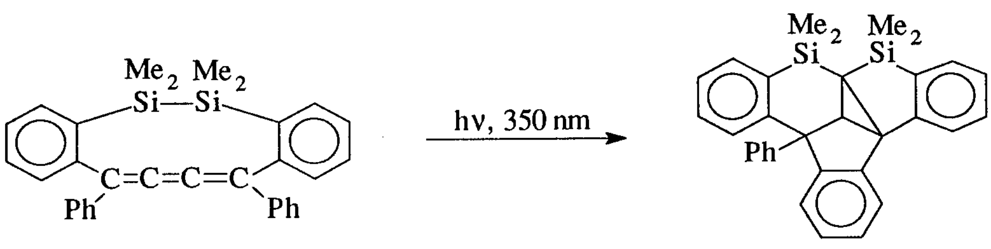


boat conformation

cross conformation

Figure 3. Conformations of cyclic butatriene 7

Rayonet photolysis apparatus both afforded 9 (Scheme 24). The product was isolated and crystallized from hexane in 50% and 47% yields, respectively. The structure of 9 was identified by NMR and X-ray diffraction (Figure 4).



7

9

Scheme 24. Photoreaction of 7 at 350 nm

A possible mechanism shown in Scheme 25 is that UV light excites 7 to form a diradical, which has several resonance structures. Then the radicals of A, which is the most favorable resonance structure, combine with each other to make six-membered ring B. After a 1,5-H shift of B, the allene C is formed, which readily goes to cyclopropylidene D due to the ring strain. The cyclopropylidene is easily trapped by disilane to give the final product E.

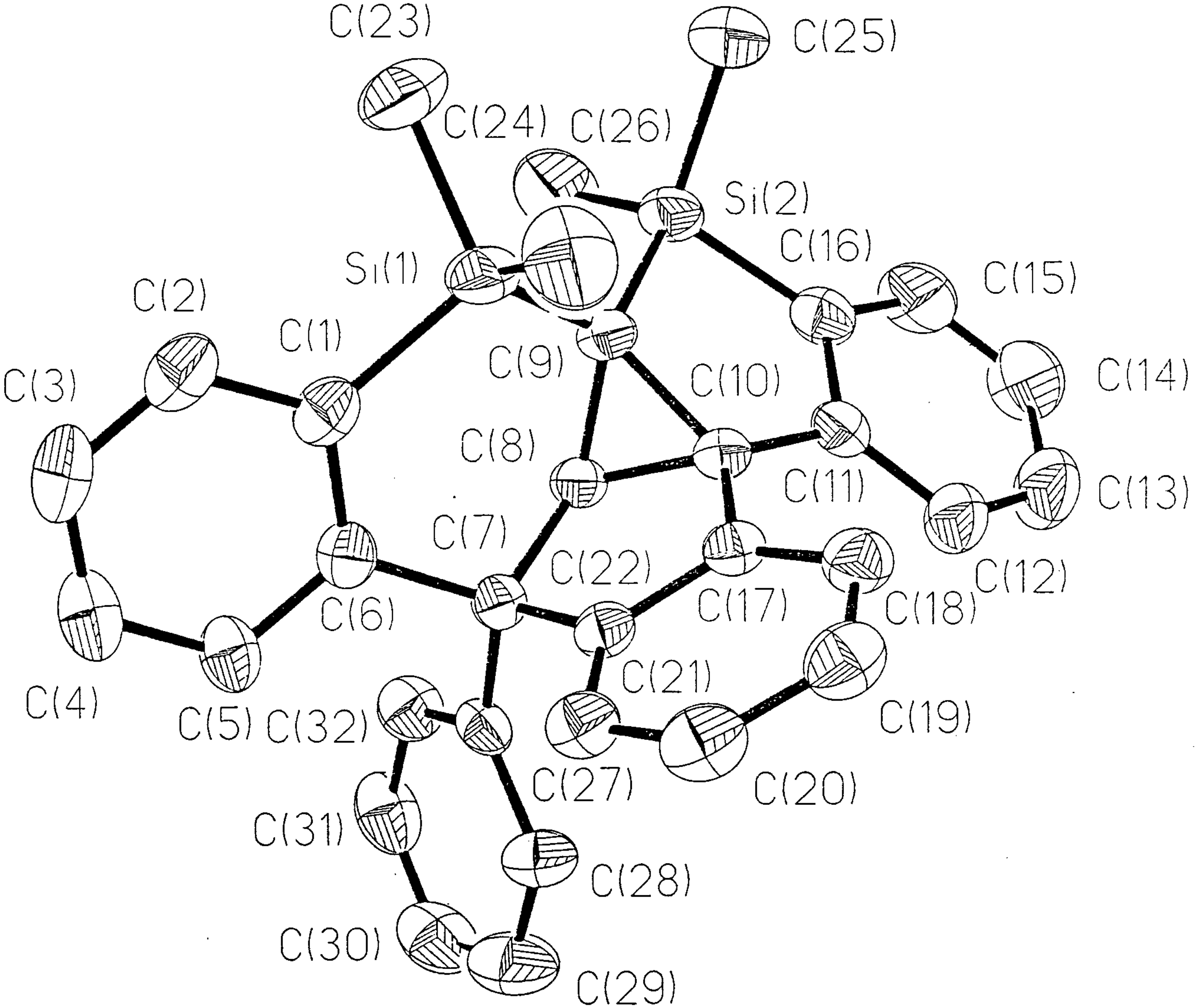
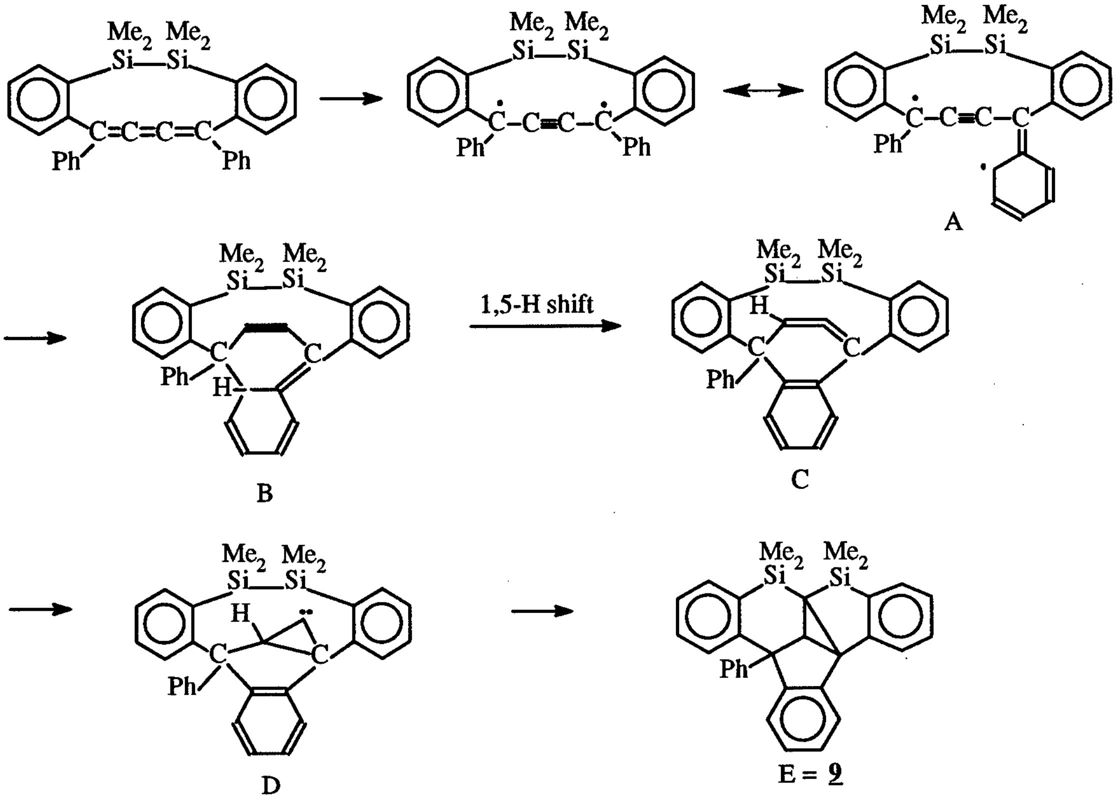
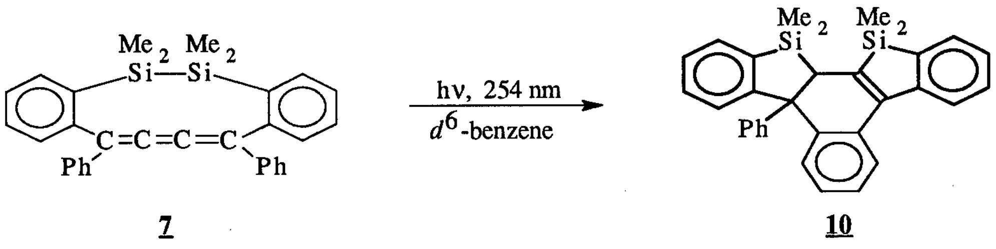


Figure 4. X-ray structure of **9**



Scheme 25. A possible mechanism for photoreaction of 7 at 350 nm

In order to see what kind of role the wavelength plays in these photochemical reactions, photolysis of 7 in d^6-benzene at 254 nm was carried out. The reaction produced 10 in 90% yield after 3 hours (Scheme 26). The product crystallized from hexane and the X-ray structure was obtained (Figure 5).



Scheme 26. Photoreaction of 7 in d^6-benzene at 254 nm

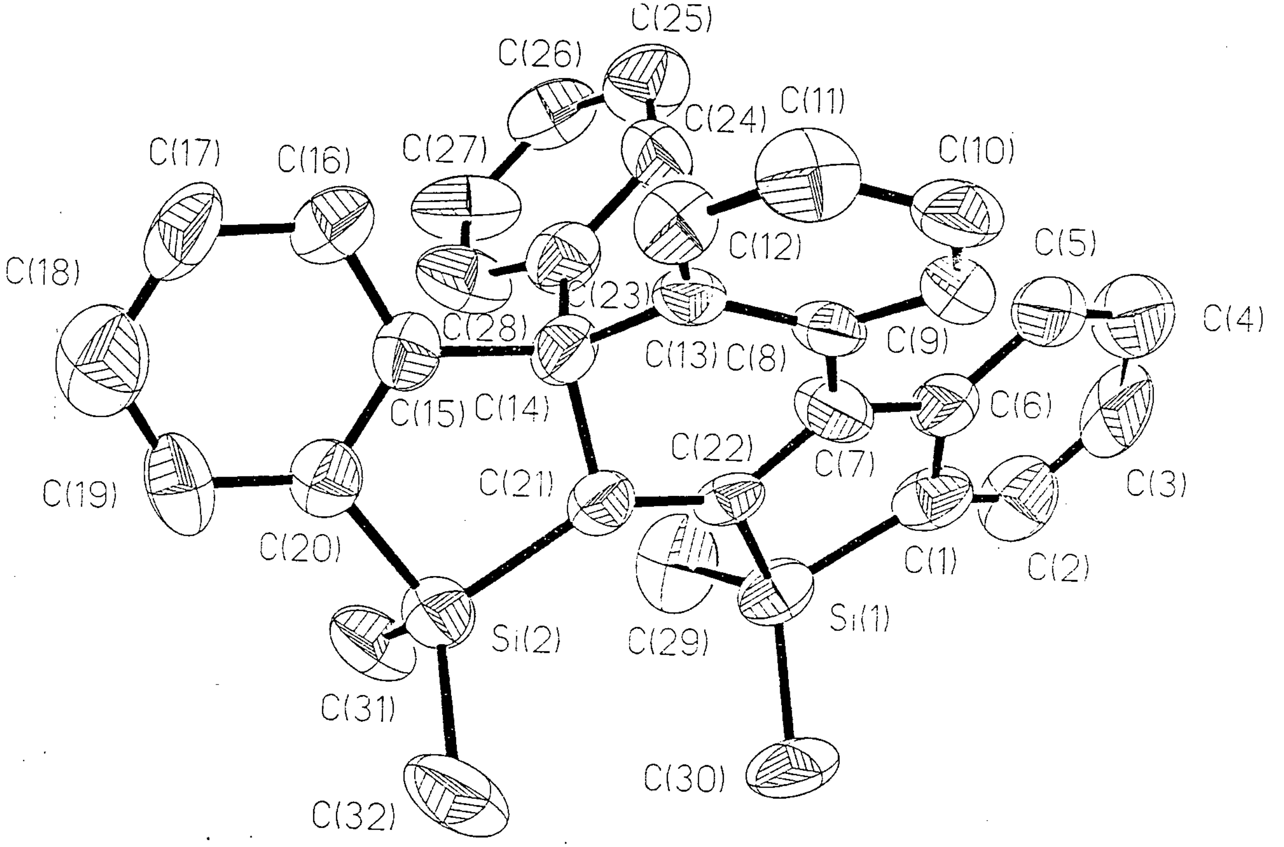
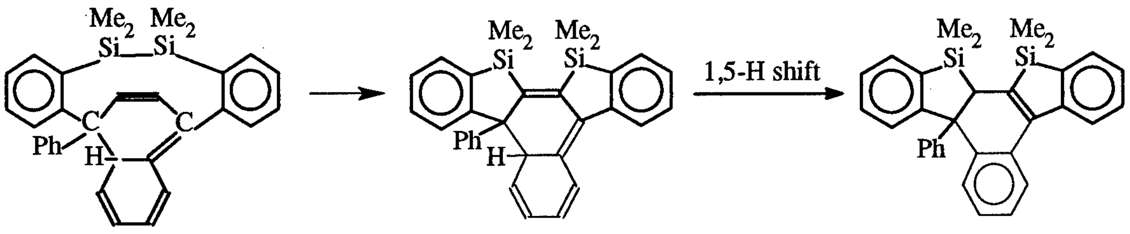


Figure 5. X-ray structure of **10**

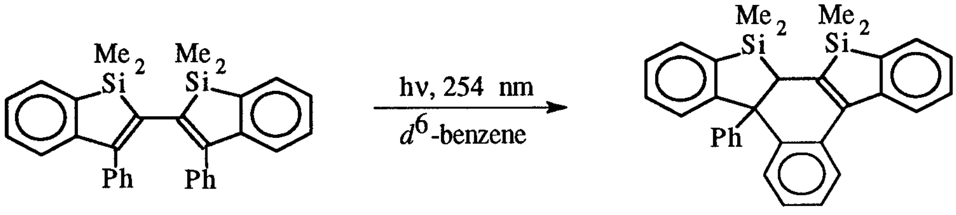
A possible mechanism is very similar to that proposed for the photoreaction at 350 nm. The UV light generates the same diradical species A, which undergoes ring formation to give intermediate B. In this case, under 254 nm radiation, the Si-Si bond adds to the acetylene first to produce F, followed by a 1,5-H shift to afford 10 (Scheme 27). Considering the possibility of transformation of compound 9 to 10, 9 was irradiated in d^6-benzene at 254 nm for 5 hours without any reaction occurred. Therefore, compound 9 is not an intermediate of isomerization from cyclic butatriene 7 to product 10.



B F G = 10

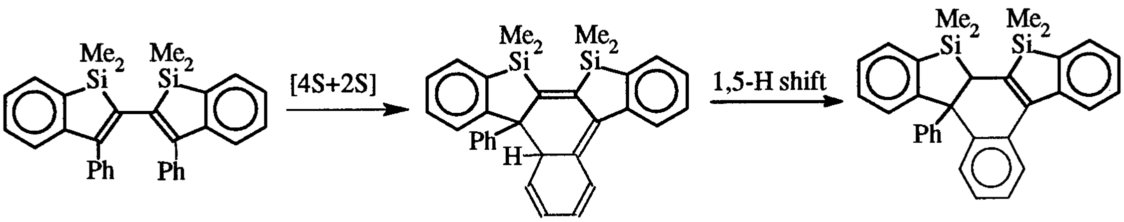
Scheme 27. A possible mechanism for photoreaction of 7 in d^6-benzene at 254 nm

Since the structure of 10 is kind of similar to that of 2,2'-bis(3,3-dimethyl-3-silaindene) 8, which is the product from the catalytic and thermal reactions of 7, we had compound 8 irradiated at 254 nm in a d^6-benzene solution. This photolysis yielded 10quantitatively after an hour's reaction, according to ^{1}H-NMR. (Scheme 28). For this



8 10

Scheme 28. Photoreaction of 8 in d^6-benzene at 254 nm reason, we checked the 254 nm reaction of 7 again. By monitoring the reaction by ^{1}H NMR every half hour till the reaction completion, we could see that compound 8 really exists as an reaction intermediate, although always as a small fraction until reaction was completed. Therefore, the photolysis of 7 really could undergo [2S + 2S] addition to give compound 8 first. The isomerization from 8 to 10 seems to be a [4S + 2S] addition, which is thermally allowed (Scheme 29). If so, the photolysis of 8 at 254 nm is really a



8

10

Scheme 29. A possible mechanism for 8 in d^6-benzene at 254 nm

photothermal reaction and the same product also should be obtained thermally. Therefore, compound 8 crystals was heated in a sealed tube at 220°C for 2 hours, but no reaction occurred.

Photolysis of 7 in hexane at 254 nm produced a new product 11 and compound 9 in 4:1 ratio, according to ^{1}H NMR integration. Although the structure of 11 is not known yet, it does have an asymmetric structure, probably very similar to that of 9 or 10 by comparing the NMR spectra of 9, 10 and 11. From ^{1}H NMR spectra (Figure 6), it is obvious to see that all three compounds have four different silicon methyl peaks and a methine proton with a chemical shift range from 2.5-3.3 ppm. In ^{13}C NMR, there are four silicon methyl carbons also and a lot of nonequivalent aromatic carbons.

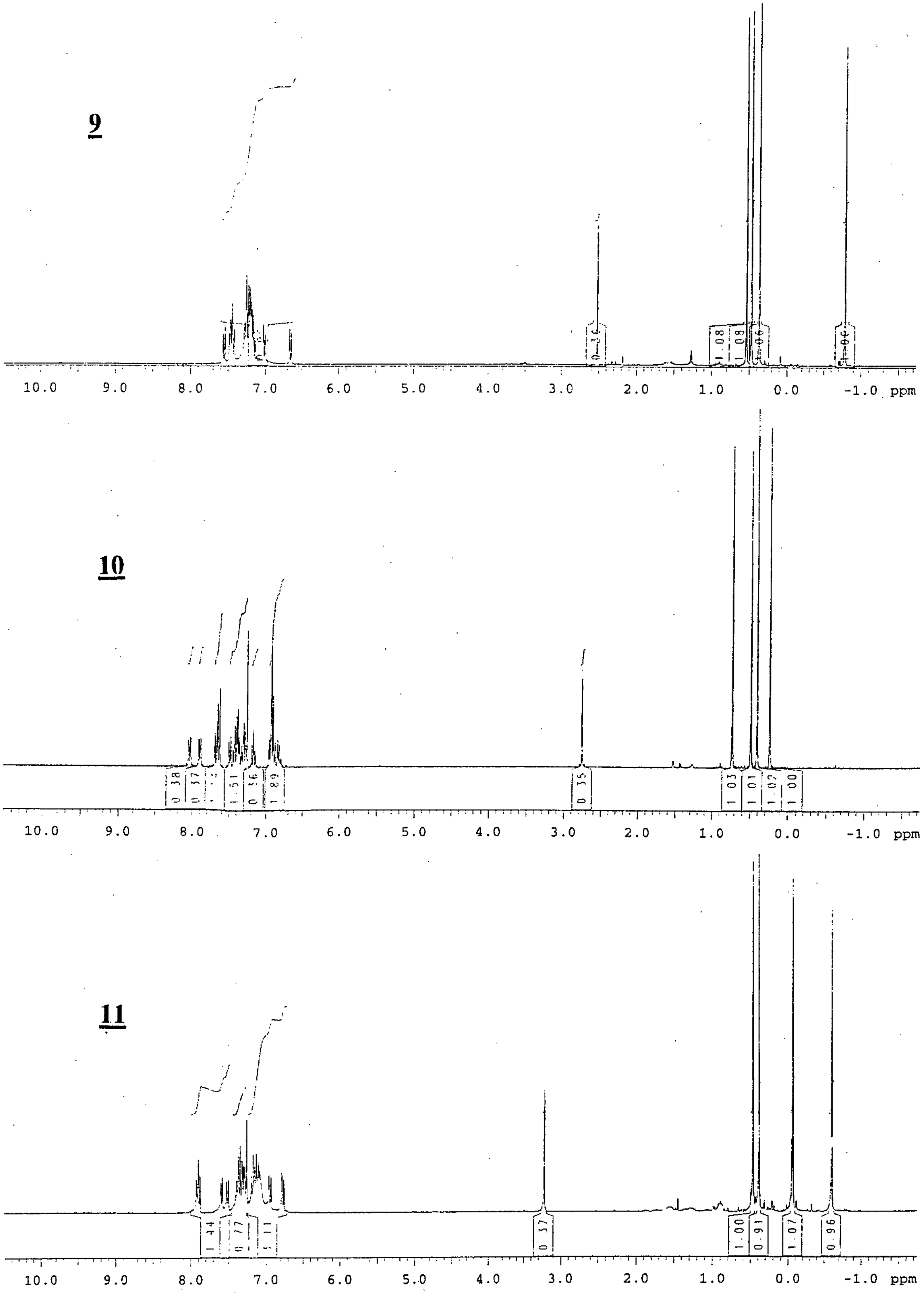


Figure 6. ^{1}H NMR spectra of **9**, **10** and **11**

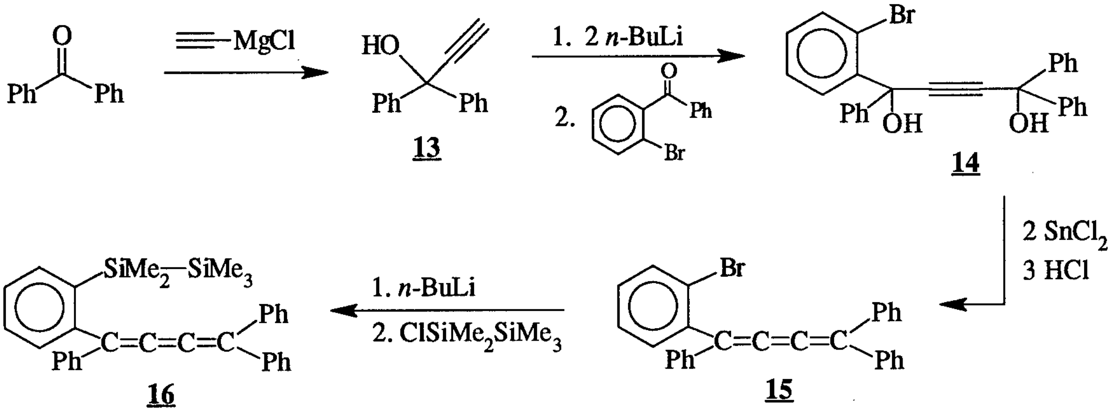
The study of intermolecular addition of Si-Si to cumulene

Since we got a plethora of interesting results from the intramolecular addition of Si-Si to cumulene, we wondered if there would be any reaction in the intermolecular addition. The intermolecular reaction was carried out by using tetraphenylbutatriene and hexamethyldisilane as reagents under the same conditions as that of the intramolecular reactions. The catalytic reaction using palladium (II) acetate as catalyst, thermolysis of nonane solution, and photolysis in hexane or benzene at 350 nm and 254 nm were tested, but no reactions occurred. The reason probably is that a lot of energy is needed to overcome the high energy barrier to make these entropy decreasing reactions happen, but under our reaction conditions, the supplied energy is not enough.

Synthesis of acyclic butatriene **16**

Since the intermolecular addition of Si-Si to cumulene gave negative results, we desired to build another system whose strucure is in between that of the disilane-containing cyclic butatriene **7** and a totally unattached disilane plus butatriene system. The molecule which came to mind is acyclic butatriene **16**, with only one Si atom attached to the phenyl group.

The synthesis started with benzophenone, which was reacted with ethynylmagnesium chloride to produce 3,3-diphenyl-1-propyne-3-ol **13** in 94% yield.[82] The treatment of **13** with *n*-BuLi followed by the reaction with 2-bromobenzophenone **1** afforded acetylenic diol **14** in 62%. The butatriene **15** was obtained as bright yellow crystals after diol **14** reacted with $SnCl_2$ and HCl. The reaction of **15** with *n*-BuLi and chloropentamethyldisilane produced acyclic butatriene **16** in 56% yield (Scheme 30).[72]

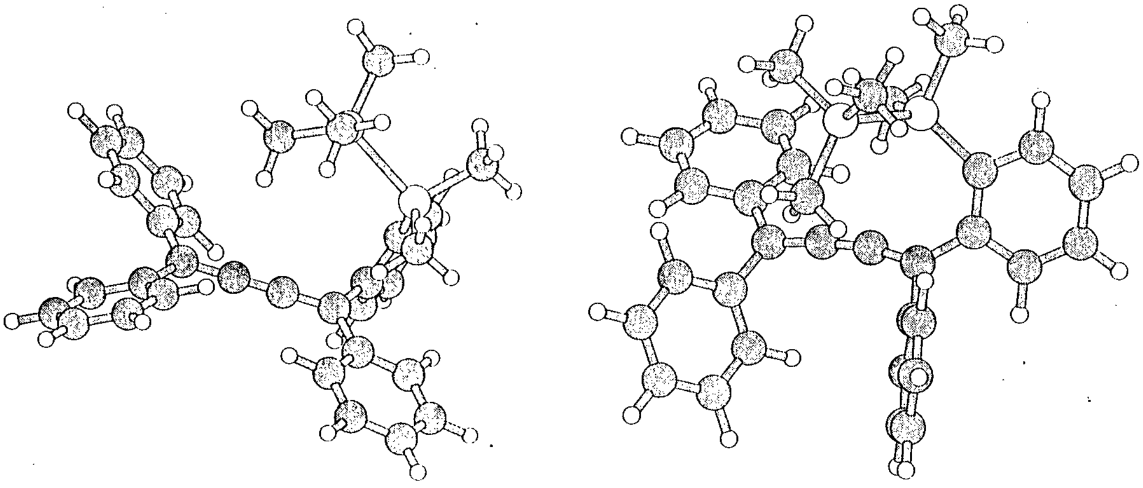


Scheme 30. Synthesis of acyclic butatriene **16**

<u>The study of acyclic butatriene 16</u>

The study of acyclic butatriene **16** was carried out just as that of cyclic butatriene **7**. The catalytic reaction of **16** in THF with the catalyst $Pd(OAc)_2$ and co-catalyst 1,1,3,3-tetramethylbutyl isocyanide overnight gave nothing but starting material. The thermal study was performed in a sealed tube with a nonane solution of **16**, which was heated at 175°C for 3 hours, then at 200°C for another 8 hours. No reaction occurred during the heating. The photolysis in hexane or benzene at both 350 nm and 254 nm were also tried without any success.

In order to know the relationshisp between the structure and reactivity, the molecular geometry studies of cyclic and acyclic systems were carried out with HyperChem version 4.5 software (Hypercube). The method used to optimize the structures is PM3. As described above, the cyclic butatriene **7** has two stable conformations, one is the "boat" conformation, the other is the "cross" conformation with the Si-Si bond across the central carbon-carbon double bond (Figure 3). The distances between one Si atom and two central carbon atoms are 3.33 A and 3.80 A for the former, and 3.04 A and 3.34 A for the latter. As for the acyclic butatriene **16**, there are also two energy minima, of which the conformations are similar to the "boat" and "cross" conformations described for the cyclic system (Figure 7). The distances from the internal Si atom to the two central carbon atoms are 4.71 A and 4.45 A for the boat conformation and 4.22 A and 3.92 A for the cross conformation. The distances from the terminal Si atom to the two central carbon atoms are 3.95 A and 4.81 A for the first, and 3.37 A and 3.99 A for the second. From this study, we can see the distances between the Si and central carbon atoms are much larger in the acyclic system than in the cyclic system.


boat conformation

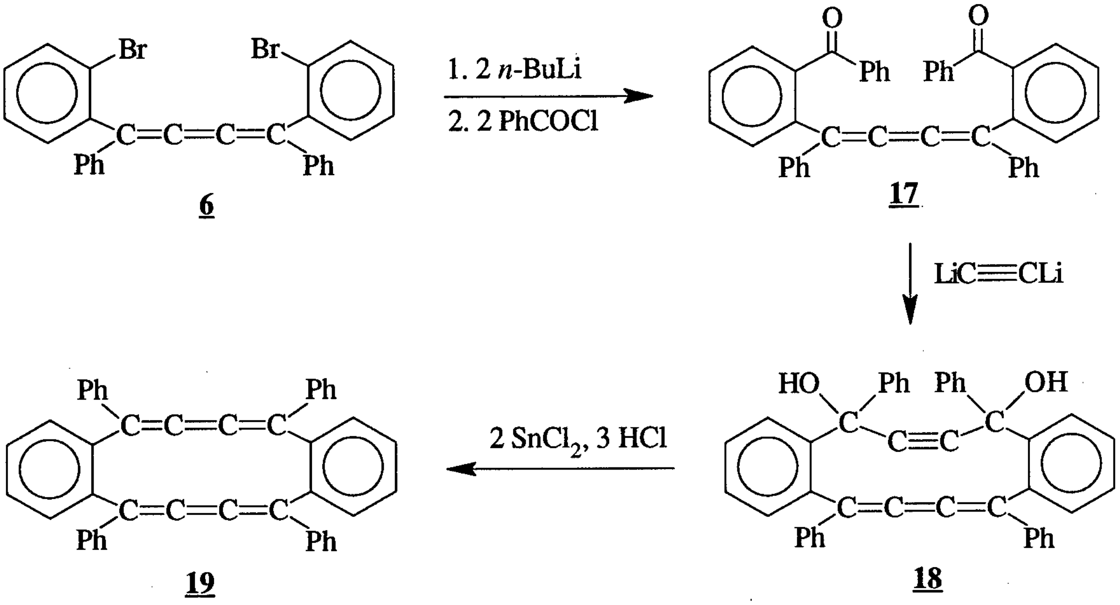
cross conformation

Figure 7. Conformations of acyclic butatriene **16**

Usually, the bond length of Si-C is 1.90 A. However, in the intramolecular addition of Si-Si to acetylene, the Si-C distances of the transition state, which is a cross conformation, are about 3.0 A. To summarize, the distances between Si and the central carbon atoms of the cyclic butatriene are larger than the cyclic acetylene, but by putting in enough energy, the reaction still occurs, while the distances of the acyclic system are too large to have the reaction occur under the given reaction conditions.

Synthesis of 1,4-(bis-2-benzoylphenyl)-1,4-diphenyl-1,2,3-butatriene 17 and future work

To further the study of cumulene compounds, 1,4-bis(2-benzoyl)-1,4-diphenyl-1,2,3-butatriene 17 was synthesized in 46% yield from 1,4-bis(2-bromophenyl)-1,4-diphenyl-1,2,3-butatriene 6 by reacting it with *n*-BuLi and benzoyl chloride. The continued reaction with dilithioacetylene, followed by reductive elimination by $SnCl_2$ will produce cyclic bisbutatriene 19 (Scheme 31).



Scheme 31. Synthesis of 17 and planned synthesis of 19

The thermolysis and photolysis of **19** is of great interests. It is hard to predict how many products would be produced and what the structures would be. Hopefully, further study will provide the answer.

Conclusions

A series of cumulene containing compounds were synthesized and characterized. The intramolecular and intermolecular additions of the Si-Si bond to cumulene were studied. Catalytic, thermal and photochemical reactions were carried out. Among the disilanes and butatrienes studied, only the intramolecular addition of the disilane-containing cyclic butatriene occured under all of the reaction conditions. Those reactions produced four isomers of cyclic butatriene, which were characterized by IR, ^{1}H NMR, ^{13}C NMR and single crystal X-ray analysis. Reaction mechanisms leading to these compounds were proposed. To my knowledge, it is the first study of the disilane addition to a cumulene unit.

Experimental

^{1}H and ^{13}C-NMR spectra were acquired on a Varian VXR-300 spectrometer. In order to assure the quantitative features of the ^{13}C-NMR spectra, the relaxation agent chromium (III) acetylacetonate was used in $CDCl_3$ with a relaxation delay of 5 seconds.

The exact masses were obtained from a Kratos MS 50 mass spectrometer with 10,000 resolution. The infrared spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer from neat sample. The UV/Vis spectra were obtained on a Hewlett Packard 8452A diode array UV/Vis spectrometer. Reactions were monitored by Hewlett Packard 5890 series II GC and Hewlett Packard tandem GC-IR-MS (5890A GC-5965A IR-5970 Series MS) parallel connected. X-ray structures were obtained at the Iowa State Molecular structure Laboratory. Refinement calculations were performed on a Digital Equipment Micro VAX 3100 computer using the SHELXTL- Plus and SHELXL-93.

THF was distilled over sodium-benzophenone and ether was distilled over CaH_2 right before use. Other reagents were used as received from Aldrich or Fisher Chemical Co. without further purification unless specified otherwise.

2-Bromobenzophenone 1. A 250 mL oven-dried round bottom flask, equipped with addition funnel and magnetic stirrer, was charged with 2-bromobenzoylchloride (21.95 g, 100 mmol) and dry THF (70 mL). Phenylmagnesium chloride (100 mmol, 2 M, 50 mL) was added dropwise at -78°C. After addition, the reaction mixture was warmed to room temperature and stirred for 3 hours before poured into a mixture of 30 mL ether and 20 mL 2.0 M HCl acid. The aqueous layer was extracted with ether (20 mL x 2) and the combined organic layer was then washed with water twice and dried over magnesium sulfate. After removal of the solvents, the crude product was purified by flash chromatography on a silica gel column eluted with a solution of hexane/ethyl acetate (v:v

= 6:1) to give 2-bromobenzophenone as colorless crystals (25.2 g, 97% yield). m.p. 40-41°C (Lit.[73] 41.5°C); GC-MS *m/z* 262(22, M+2), 260(23, M), 185(25), 183(26), 105(100), 77(68), 51(44); FTIR ν (cm^{-1}) 3028(m), 1734(m), 1672(vs), 1585(vs), 1483(m), 1430(s), 1250(s), 1154(s), 1045(s), 928(s), 800(m), 763(s), 632(s); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.30-7.82(m, 9H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 119.33(1C), 127.07(1C), 128.50(2C), 128.82(1C), 130.05(2C), 131.05(1C), 133.02(1C), 133.62(1C), 135.91(1C), 140.46(1C), 195.70(1C).

1,3-Bis(2-bromophenyl)-1,3-diphenyl-2-butyne-1,3-diol 2. To a solution of 12 mL (30 mmol, 2.5 M) of *n*-BuLi in a100 mL flask at -78°C, trichloroethylene was added dropwise. After addition, the reaction temperature was raised to room temperature and stirred for another 2 hours. A white slurry of dilithioacetylene was obtained.[74] To the recooled dilithium acetylene solution, 2-bromobenzophenone 1 (5.2 g, 20 mmol) in 20 mL dry THF was added. The reaction mixture was stirred overnight at room temperature before work-up with 3 M NH_4Cl. The reaction solution was extracted with ether (20 mL x 3) and then the combined organic layer was washed with water twice and dried over magnesium sulfate. After removal of the solvents, the residue was purified by flash chromatography with hexane/ethyl acetate (v:v = 5:1) as eluent. The desired product was obtained as white powder (3.55 g, 65% yield). m.p. 132-134°C; CI-MS *m/z* 549(10, M+2), 547(22, M), 533(51), 531(100), 529(51), 452(20), 449(20); FTIR ν (cm^{-1}) 3533(w), 3403(m), 3060(w), 3028(w), 1598(w), 1491(w), 1450(s), 1028(m), 906(s), 758(s), 734(s), 697(s); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.43(s, 2H), 7.14-7.55(m, 14H), 7.90(d, J = 3 Hz, 2H), 7.92(dd, J = Hz, J = 2.7 Hz, 2H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 74.49(2C), 87.95(2C), 121.74(2C), 126.87(6C), 127.72(2C), 127.90(4C), 128.14(2C), 134.42(2C), 141.65(2C), 142.60(2C).

1,3-Bis(2-bromophenyl)-1,3-diphenyl-1,3-ditrimethylsiloxy-2-butyne 3. A 50 mL round bottom flask, equipped with magnetic stirrer, was charged with diol **2** (4.88 g, 8.9 mmol), imidazole (2.45 g, 36 mmol) and THF (25 mL). With stirring, trimethylchlorosilane (3.9 g, 35.8 mmol) was added through a syringe. Stirring was continued for another 5 hours at room temperature and a considerable amount of white precipitate was formed. The reaction mixture was treated with 3 M NH_4Cl and extracted with ether (20 mL x 2). The resulting organic layer was washed with water twice and dried over magnesium sulfate. After removal of the solvents, the product was obtained as a white powder (6.16 g, 100% yield). m.p. 170-172°C; EI-MS *m/z* 694(53, M+2), 693(38, M+1), 692(100, M), 690(47), 677(11, M-15), 613(18), 350(22), 335(51), 333(51), 265(59), 183(33), 185(33), 176(58), 147(34), 105(46); FTIR ν (cm^{-1}) 2920(s), 2850(m), 1448(m), 1248(s), 1125(w), 1049(vs), 872(s), 841(vs), 752(vs), 696(s); ^{1}H-NMR (300 MHz, $CDCl_3$) δ -0.25(s, 18H), 7.15 (td, J = 7.5 Hz, J = 2.7 Hz, 2H), 7.23-7.26(m, H); 7.38(td, J = 7.5 Hz, J = 2.7 Hz, 2H), 7.51-7.56(m, H), 8.13(dd, J = 6 Hz, J = 3 Hz, 2H) ^{13}C-NMR (300 MHz, $CDCl_3$) δ 0.98(6C), 76.39(2C), 88.26(2C), 122.16(2C), 126.71(2C), 127.43(2C), 127.66(4C), 128.05(4C), 128.62(2C), 129.04(2C), 134.74(2C), 143.53(2C), 143.88(2C); Exact mass *m/z* 692.06134 (calc. for $C_{34}H_{36}O_2Si_2Br_2$ 692.06014).

5,5,6,6-tetramethyl-3,8-diphenyl-3,8-bis(2-trimethylsilylphenyl)-4,7-dioxy-5,6-disilyn-cyclooctyne <u>4</u>. To a solution of the protected diol 3 (2.07 g, 3 mmol) and dry THF (20 mL), 2.4 mL (6 mmol, 2.5 M) *n*-BuLi was added dropwise at -78°C and was stirred for half an hour. Then, dichlorotetramethylsilane (0.56 g, 3 mmol) was added by syringe. After addition, the reaction mixture was warmed to room temperature and stirred overnight before it was treated with 3 M NH_4Cl and extracted with ether (10 mL x 2). The combined organic layer was washed with water twice and dried over magnesium sulfate. After the removal of the solvents, a sticky liquid was obtained. Crystallization in ether and methanol afforded the desired product as fine colorless crystals (1.55 g, 85% yield). m.p. 171-173°C; EI-MS *m/z* 648(11, M), 633(3, M-15), 575(24), 501(20), 394(23), 306(26), 239(37), 147(100), 73(100); FTIR ν (cm^{-1}) 2953(s), 2894(m), 1450(w), 1247(vs), 1049(m), 1026(vs), 842(vs), 768(s), 696(m), 634(m); ^1H-NMR (300 MHz, $CDCl_3$) δ -0.08(s, 18H), 0.08(s, 6H), 0.28(s, 6H), 7.16-7.72(m, 18H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ -0.35(2C), 0.64(2C), 2.02(6C), 78.72(2C), 97.72(2C), 126.98(2C), 127.23(4C), 127.51(2C), 127.73(6C), 128.31(2C), 136.83(2C), 139.64(2C), 145.90(2C), 147.54(2C); Exact mass *m/z* 648.27404 (calc. for $C_{38}H_{48}O_2Si_4$ 648.27315).

3,3,8,8-tetramethyl-5,6-diphenyl-5,6-bis(2-trimethylsilylphenyl)-4,7-dioxy-3,8-disilyn-bicyclo[3,3,0]oct-1-ene 5. Cyclooctyne 4 (0.140 g) was heated at 200°C for two days in a sealed tube to afford product 5 (0.043 g, 31% yield) as clear crystals after recrystallization. m.p. 175-177°C; EI-MS *m/z* 648(15, M), 633(5, M-15), 499(13), 394(35), 239(23), 221(21), 147(83), 73(100); FTIR ν (cm^{-1}) 3030(w), 2954(m), 2896(m), 1489(w), 1445(m), 1253(s), 1095(m), 1013(vs), 888(vs), 838(vs), 787(vs), 698(m); ^{1}H-NMR (300 MHz, d^6 acetone) δ -0.50(s, 6H), -0.08(s, 18H), -0.07(s, 6H), 6.95-7.81(m, 18H); ^{13}C-NMR (300 MHz, CDCl$_3$) δ -1.43(2C), 1.94(6C), 2.16(2C), 92.25(2C), 126.16(2C), 126.65(4C), 126.7(2C), 127.05(2C), 127.71(6C), 136.77(2C), 140.62(2C), 148.14(2C), 151.17(2C), 168.78(2C); Single crystal X-ray analysis: 5 crystallized in the monoclinic space group P2$_1$/n with cell dimensions of a = 12.323(2) A, b = 11.538(2) A, and c = 13.304(3) A; $\alpha = 90°$, $\beta = 97.62(3)°$, $\gamma = 90°$, V = 1874.9(6) A^3, and an occupation of Z = 2 in the unit cell. Data were collected at 293(2) K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Cu K_α radiation, to a maximum $2\theta = 55°$, giving 5391 total reflections; the structure was solved by direct methods (SHELXL-93) and refined with full matrix least squares, yielding R = 0.0697, wR = 0.1505 for 4295 independent reflections with $I \geq 2\sigma(I)$; Exact mass *m/z* 648.27415 (calc. for $C_{38}H_{48}O_2Si_4$ 648.27315).

***cis*-1,4-Bis(2-bromophenyl)-1,4-diphenyl-1,2,3-butatriene 6.** In a 100 mL round bottom flask equipped with magnetic stirrer, diol 2 (2.74 g, 5 mmol), $SnCl_2 \cdot (H_2O)_2$ (2.26

g, 10 mmol), THF (15 mL) and ether (30 mL) were mixed under argon flow after which 30 mL of 1.0 M HCl in ether was injected dropwise by syringe. After stirring at room temperature for 3 hours, some yellow precipitate was formed. The precipitate was filtered and then the solvents in the filtration was removed to give a crude brown solid. The bright yellow crystals was obtained (1.58 g, 62% yield) after recrystallization in ether-hexane. m.p. 243-244°C; EI-MS *m/z* 514(44, M), 434(30), 356(100), 178(36); FTIR ν (cm^{-1}) 3056(m), 1591(m), 1488(s), 1465(s), 1025(s), 763(vs), 689(vs); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.17-7.62(m, 18H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 122.28(2C), 123.81(2C), 127.30(2C), 127.95(4C), 128.04(2C), 128.56(4C), 129.38(2C), 132.11(2C), 133.27(2C), 138.49(2C), 138.67(2C), 154.18(2C); Exact mass *m/z* 513.97357 (calc. for $C_{28}H_{18}Br_2$ 513.97561).

Cyclic 1,2,3-butatriene 7. To a solution of 1,4-bis(2-bromophenyl)-1,4-diphenyl-1,2,3-butatriene 6 (0.656 g, 1.28 mmol) in THF at -78°C, 1.02 mL (2.5 M, 2.55 mmol) *n*-BuLi was added dropwise. The reaction was maintained at that temperature for 0.5 hour before the addition of 1,2-dicholorotetramethyldisilane (0.21 mL, 1.28 mmol). The reaction was warmed to room temperature for another 5 hours followed by treatment with 3 M NH_4Cl. The resulting mixture was extracted with ether (10 mL x 2) and the organic layer was washed with water and dried over magnesium sulfate. After removal of the solvents, the desired product 7 was obtained (0.325 g, 55% yield) as bright yellow crystals by recrystallizing from ether-methanol. m.p. 217°C; EI-MS *m/z* 470(10, M), 455(5, M-15), 356(100), 276(20), 178(38); FTIR ν (cm^{-1}) 3049(m), 2950(m), 1488(s), 1246(s), 768(vs), 690(vs); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.35(s, 12H), 7.22-7.68(m, 18H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 0.047(4C), 125.38(2C), 126.95(2C), 127.88(2C), 128.12(2C), 128.56(4C), 128.60(4C), 129.09(2C), 135.75(2C), 138.43(2C), 140.90(2C), 152.07(2C); UV/Vis λ_{max} = 418 nm (THF); Exact mass *m/z* 470.18907 (calc. for $C_{32}H_{30}Si_2$ 470.18861).

Thermal reaction of 7. 0.1 M solution of **7** (40 mg) in nonane was heated in a sealed tube at 175°C overnight to give 2,2'-bis(1-phenyl-3,3-dimethyl-3-silaindene) **8**. Compound **8** was isolated in 83% yield (32.1 mg) as a light green crystal by preparative thin layer chromatography using hexane/ethyl acetate (v:v = 20:1) as developing solvents followed by recrystallization in hexane. m.p. 158°C; EI-MS *m/z* 470(100, M), 395(73), 377(50), 320(64), 135(38), 73(37); FTIR ν (cm^{-1}) 3051(m), 2955(m), 1951(w), 1582(s), 1438(s), 1246(s), 848(vs), 779(vs); ^{1}H-NMR (300 MHz, $CDCl_3$) δ -0.11(s, 12H), 7.11-7.47(m, 18H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ -3.73(4C), 123.09(2C), 126.04(2C), 127.55(2C), 128.33(4C), 129.36(2C), 130.17(4C), 131.26(2C), 138.74(2C), 139.26(2C), 144.07(2C), 150.08(2C), 152.67(2C); UV/Vis λ_{max} = 360 nm (THF); λ_e = 520 nm (THF); Single crystal X-ray analysis: **8** crystallized in the triclinic space group P1 with cell dimensions of a = 9.609(2) A, b = 10.572(2) A, and c = 15.693(3) A; α = 78.63(3)°, β = 75.28(3)°, γ = 63.68(3)°, V = 1375.5(5) A^3, and an occupation of Z = 2 in the unit cell. Data were collected at 293(2) K on a Siemens P4RA diffractometer using graphite-monochromated Cu K_α radiation, to a maximum $2\theta = 113°$, giving 4147 total reflections; the structure was solved by direct methods (SHELXL-93) and refined with full matrix least squares, yielding $R = 0.0572$, $wR = 0.1563$ for 3475 independent reflections with $I \geq 2\sigma(I)$; Exact mass *m/z* 470.18938 (calc. for $C_{32}H_{30}Si_2$ 470.18861).

Catalytic reaction of 7. To a solution of 7 (40 mg) in 20 mL THF was added 1 mg of $Pd(OAc)_2$ and 0.002 mL of 1,1,3,3-tetramethylbutyl isocyanide. The reaction mixture was stirred at room temperature overnight. Product 8 was isolated in 85% yield (34 mg) by preparative thin layer chromatography and crystallization as mentioned above. The product was characterized as previously described..

Photoreaction of 7 at 350 nm in hexanes. A solution of 7 (40 mg) in 50 mL HPLC grade hexanes was irradiated with 350 nm UV light in a Rayonet photochemical apparatus. After 5 hours of irradiation, the reaction mixture was concentrated and the product 9 was isolated in 50% yield (19.5 mg) as colorless crystals by preparative thin layer chromatography with hexanes/ethyl acetate (v:v = 20:1) as developing solvent followed by the recryastallization in hexane. m.p. 219-221°C; EI-MS *m/z* 470(100, M), 377(23), 319(44), 135(30), 73(20); FTIR ν (cm^{-1}) 3052(m), 1586(s), 1443(s), 1249(vs), 844(vs), 749(vs); ^{1}H-NMR (300 MHz, $CDCl_3$) δ -0.78(s, 3H), 0.37(s, 3H), 0.47(s, 3H), 0.54(s, 3H), 2.52(s, 1H), 6.64-7.56(m, 17H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ -3.07(1C), -2.93(1C), 0.87(1C), 1.48(1C), 17.41(1C), 52.16(1C), 56.02(1C), 61.93(1C), 123.97(1C), 124.91(1C), 125.11(1C), 125.80(1C), 126.27(1C), 126.77(1C), 126.90(1C), 127.47(1C), 128.19(1C),, 128.46(2C), 129.18(2C), 129.26(2C), 132.26(1C), 133.08(1C), 138.06(1C), 138.20(1C), 143.89(1C), 147.92(1C), 148.64(1C), 150.90(1C), 153.10(1C); Single crystal X-ray analysis: **9** crystallized in the monoclinic space group C2/c with cell dimensions of a = 27.053(5) A, b = 9.100(2) A, and c = 21.699(4) A; $\alpha = 90°$, $\beta = 97.70(3)°$, $\gamma = 90°$, V = 5293.7(18) A^3, and an occupation of Z = 8 in the unit cell. Data were collected at 293(2) K on a Siemens P4RA diffractometer using graphite-monochromated Cu K_α radiation, to a maximum $2\theta = 113°$, giving 4392 total reflections; the structure was solved by direct methods (SHELXL-93) and refined with full matrix least squares, yielding R = 0.0475, wR = 0.1270 for 3543 independent reflections with $I \geq 2\sigma(I)$; Exact mass *m/z* 470.18902 (calc. for $C_{32}H_{30}Si_2$ 470.18861).

Photoreaction of 7 at 350 nm in *d*^{6}-benzene. A solution of **7** (40 mg) in 20 mL d^6-benzene was irradiated with 350 nm UV light in a Rayonet photochemical apparatus. After 5 hours of irradiation, the solvent was removed. The product **9** was isolated in 47% yield (18 mg) by preparative thin layer chromatography and characterized as previously described.

Photoreaction of 7 at 254 nm in *d*^{6}-benzene. A solution of **7** (40 mg) in 20 mL d^6-benzene was irradiated with 254 nm UV light in a Rayonet photochemical apparatus. After 3 hours of irradiation, the solvent was removed and the product **10** was isolated in

90% yield (35.7 mg) as milky yellow crystals by preparative thin layer chromatography with hexanes/ethyl acetate (v:v = 20:1) as developing solvent followed by cryastallization in hexane. m.p. 216-218°C; EI-MS *m/z* 470(100, M), 411(14), 395(14), 377(16), 320(19), 181(28), 135(26), 73(13); FTIR ν (cm^{-1}) 3052(m), 1583(w), 1440(s), 1250(vs), 846(vs), 747(vs), 698(vs); ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.24(s, 3H), 0.41(s, 3H), 0.49(s, 3H), 0.74(s, 3H), 2.76(s, 1H), 6.83-8.05(m, 17H); ^{13}C-NMR (300 MHz, CDCl$_3$) δ -4.25(1C), -2.90(1C), 0.19(1C), 1.11(1C), 40.57(1C), 59.29(1C), 122.81(1C), 123.04(1C), 125.03(1C), 125.79(1C), 125.91(1C), 125.92(1C), 126.29(1C), 126.94(1C), 126.97(2C), 128.41(2C), 129.15(1C), 129.26(1C), 130.06(1C), 131.77(1C), 131.71(1C), 133.38(1C), 138.84(1C), 139.69(1C), 141.34(1C), 145.92(1C), 146.50(1C), 146.92(1C), 153.17(1C), 153.77(1C); Single crystal X-ray analysis: **10** crystallized in the triclinic space group P1 with cell dimensions of a = 10.039(2) A, b = 10.087(2) A, and c = 14.208(3) A; $\alpha = 84.03(3)°$, $\beta = 73.90(3)°$, $\gamma = 72.15(3)°$, V = 1315.5(5) A^3, and an occupation of Z = 2 in the unit cell. Data were collected at 293(2) K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo K$_\alpha$ radiation, to a maximum $2\theta = 50°$, giving 5476 total reflections; the structure was solved by direct methods (SHELXL-93) and refined with full matrix least squares, yielding R = 0.0892, wR = 0.1954 for 4607 independent reflections with $I \geq 2\sigma(I)$; Exact mass *m/z* 470.18913 (calc. for $C_{32}H_{30}Si_2$ 470.18861).

Photoreaction of 8 at 254 nm in d^6-benzene. A solution of **8** (15 mg) in 10 mL d^6-benzene was irradiated with 254 nm UV light in a Rayonet photochemical apparatus. After one hour of irradiation, the starting material **8** was quantitatively converted into product **10** according to ^{1}H-NMR and ^{13}C-NMR spectra. The product was characterized as above.

Photoreaction of 7 at 254 nm in hexanes. A solution of **7** (40 mg) in 50 mL HPLC grade hexanes was irradiated with 254 nm UV light in a Rayonet photochemical apparatus. After 3 hours of irradiation, the solvent was removed. Compound **9** and **11** were obtained in 1:4 ratio, according to ^{1}H-NMR integration. The total yield of this reaction was 85%. After the purification by preparative thin layer chromatography with hexanes as developing solvent, the product **11** was obtained as a slightly yellow liquid. EI-MS *m/z* 470(100, M), 393(18), 377(17), 319(20), 181(22), 135(15), 69(21); FTIR ν (cm^{-1}) 3052(m), 2952(w), 1583(m), 1439(s), 1247(s), 1130(m), 908(s), 780(s), 731(vs); ^{1}H-NMR (300 MHz, $CDCl_3$) δ -0.60(s, 3H), -0.06(s, 3H), 0.39(s, 3H), 0.47(s, 3H), 3.23(s, 1H), 6.75-7.93(m, 17H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ -4.98(1C), -4.43(1C), -4.35(1C), -1.59(1C), 47.18(1C), 58.49(1C), 121.97(1C), 123.91(1C), 125.17(1C), 125.71(1C), 125.87(1C), 126.23(1C), 127.26(1C), 127.32(1C), 127.32(1C), 128.98(1C), 129.17(1C), 129.35(1C), 130.21(1C), 131.91(1C), 132.01(1C), 133.26(1C), 138.36(1C), 140.91(1C), 141.01(1C), 143.82(1C), 145.01(1C), 146.77(1C), 147.97(1C), 158.94(1C).

1,1,4,4-Tetraphenyl-1,2,3-butatriene <u>12</u>. To a solution of 1,4-bis(2-bromophenyl)-1,4-diphenyl-1,2,3-butatriene <u>6</u> (0.656 g, 1.28 mmol) in THF at -78°C, 1.02 mL (2.5 M, 2.55 mmol) *n*-BuLi was added dropwise. The reaction was maintained at that temperature for 0.5 hour before the treatment with 3 M NH_4Cl. The resulting mixture was extracted with ether (10 mL x 2) and the organic layer was washed with water and dried over magnesium sulfate. After removal of the solvents, the desired product <u>12</u> was obtained (0.367 g, 81% yield) as bright yellow crystals by recrystallizing from ether-methanol. m.p. 237°C (Lit.[72] 240°C); EI-MS *m/z* 357(30, M+1), 356(100, M), 276(10), 178(46); FTIR ν (cm^{-1}) 3055(m), 1951(w), 1890(w), 1811(w), 1591(m), 1488(s), 1440(s), 771(vs), 692(vs); ^1H-NMR (300 MHz, $CDCl_3$) δ 7.30-7.60(m, 20H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 122.35(2C), 127.67(4C), 128.12(8C), 129.11(8C), 138.39(4C), 151.59(2C); UV/Vis λ_{max} = 419 nm (THF).

3,3-Diphenyl-1-propyne-3-ol <u>13</u>.[82] A 250 mL oven-dried round bottom flask, equipped with addition funnel and magnetic stirrer, was charged with benzophenone (3.64 g, 20 mmol) and dry THF (70 mL). Ethynylmagnesium chloride (30 mmol, 0.5 M, 60 mL) was added dropwise at -78°C. After addition, the reaction mixture was warmed to room temperature and then refluxed for 2 hours before being poured into a mixture of 30 mL ether and 20 mL 2.0 M HCl acid. The aqueous layer was extracted with ether (20 mL x 2) and the combined organic layer was then washed with water twice and dried over magnesium sulfate. After removal of the solvents, the crude product <u>13</u> was obtained as brownish liquid (3.9 g, 94% yield). GC-MS *m/z* 208(56, M), 207(66, M-1), 178(44),165(25), 131(42), 105(28), 102(32), 77(54), 53(100); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.90(s, 1H), 2.99(br, 1H), 7.30-7.68(m, 10H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 74.22(1C), 75.50(1C), 86.33(1C), 125.93(4C), 127.79(2C), 128.24(4C), 144.34(2C).

1-(2-Bromophenyl)-1,1,3-triphenyl-2-butyne-1,3-diol 14. To a solution of 3,3-diphenyl-1-propyne-3-ol **13** (1.04 g, 5 mmol) in 15 mL THF at -78°C, 4 mL (10 mmol, 2.5 M) of *n*-BuLi was added dropwise. The reaction was maintained at this temperature for 15 minutes before the addition of 2-bromobenzphenone **1** (1.3 g, 5 mmol). The reaction mixture was warmed up to room temperature and stirred for another 10 hours followed by the treatment with 2M HCl. The aqueous layer was extracted with ether (10 mL x 2) and the combined organic layer was washed with water and dried over magnesium sulfate. After removal of the solvents, the resulting product was purified by flash chromatography with hexane/ethyl acetate (v:v = 5:1) as eluent. The desired product **14** was obtained as a white powder (1.45 g, 62% yield) after recrystallization from methanol. m.p. 67-68°C (Lit.[72] 71°C); EI-MS *m/z* 451(10), 449(10), 284(28), 265(38), 183(37), 105(100), 77(31); FTIR ν (cm^{-1}) 3533(m), 3418(s), 3059(m), 1490(s), 1450(vs), 758(s), 697(vs); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.90(s, 1H), 2.99(br, 1H), 7.30-7.68(m, 10H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 74.59(1C), 74.72(1C), 87.93(1C), 90.15(1C), 121.88(1C), 126.00(2C), 126.04(2C), 126.95(2C), 127.17(1C), 127.66(2C), 128.07(1C), 128.19(2C), 128.22(2C), 128.25(2C), 128.32(1C), 129.46(1C), 134.71(1C), 141.82(1C), 142.92(1C), 144.58(1C), 144.64(1C).

1-(2-Bromophenyl)-1,4,4-triphenyl-1,2,3-butatriene 15. In a 100 mL round bottom flask equipped with magnetic stirrer, diol 14 (2.34 g, 5 mmol), $SnCl_2\cdot(H_2O)_2$ (2.26 g, 10 mmol), THF (15 mL) and ether (30 mL) were mixed under argon flow after which 30 mL of 1.0 M HCl in ether was injected dropwise via syringe. After stirring at room temperature for 3 hours, some yellow precipitate was formed. The precipitate was filtered and then filtrate was concentrated to give the crude brown solid. The bright yellow crystals was obtained (1.20 g, 55% yield) after recrystallization in ether-hexane. m.p. 144-145°C (Lit.[72] 141°C); EI-MS *m/z* 436(98, M), 434(98), 355(38), 276(76), 246(73), 178(100),169(39), 105(43); FTIR ν (cm^{-1}) 3055(m), 3016(w), 1592(m), 1488(s), 1465(s), 1027(s), 908(s), 763(vs), 691(vs); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.26-7.71(m, 19H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 120.56(1C), 123.82(1C), 124.34(1C), 127.41(1C), 127.65(1C), 127.77(2C), 128.18(1C), 128.25(1C), 128.34(2C), 128.44(2C), 128.47(2C), 129.16(2C), 129.32(1C), 129.58(2C), 132.06(1C), 133.37(1C), 138.14(1C), 138.50(1C), 138.77(1C), 139.07(1C), 152.92(1C), 153.12(1C).

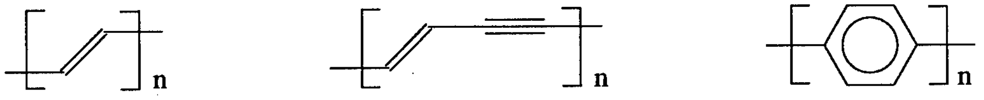
Acyclic 1,2,3-butatriene 16. To a solution of 1-(2-bromophenyl)-1,4,4-triphenyl-1,2,3-butatriene 15 (0.675 g, 1.55 mmol) in THF at -78°C, 0.62 mL (2.5 M, 1.55 mmol) *n*-BuLi was added dropwise. The reaction was maintained at that temperature for 0.5 hour before the addition of chloropentamethyldisilane (0.27 mL, 1.56 mmol). The reaction was raised to room temperature and stirred for another 10 hours, followed by the treatment with 3 M NH_4Cl. The resulting mixture was extracted with ether (10 mL x 2) and the organic layer was washed with water and dried over magnesium sulfate. After removal of the solvents, the desired product **16** was obtained as bright yellow liquid (0.421 g, 56% yield) after purified by flash chromatography using hexane as eluent. EI-MS *m/z* 486(4, M), 471(14), 470(23), 413(100),397(30), 321(21), 223(57), 167(37), 73(38); FTIR ν (cm^{-1}) 3054(w), 2952(s), 1947(w), 1595(w), 1488(s), 1441(s), 1245(s), 833(vs), 799(vs), 767(vs), 693(vs); ^1H-NMR (300 MHz, $CDCl_3$) δ -0.06(s, 9H), 0.17(s, 6H), 7.25-7.70(m, 19H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ -1.83 (1C), -1.78(1C), 122.95(1C), 123.81(1C), 126.65(1C), 127.45(1C), 127.51(1C), 127.88(1C), 128.01(1C), 128.23(2C), 128.28(2C), 128.32(1C), 128.37(2C), 128.42(2C), 129.13(2C), 129.29(2C), 130.48(1C), 135.93(1C), 138.29(1C), 139.25(1C), 139.39(1C), 140.66(1C), 152.27(1C), 154.08(1C).

1,4-(Bis-2-benzoylphenyl)-1,4-diphenyl-1,2,3-butatriene 17. To a solution of 1,4-bis(2-bromophenyl)-1,4-diphenyl-1,2,3-butatriene **6** (0.411 g, 0.8 mmol) in THF at -78°C, 0.64 mL (2.5 M, 1.6 mmol) *n*-BuLi was added dropwise. The reaction was maintained at that temperature for 0.5 hour before the addition of benzoyl chloride (0.23 g, 1.6 mmol). The reaction was raised to room temperature for another 12 hours followed by the treatment with 2 M HCl. The resulting mixture was extracted with ether (10 mL x 2) and the organic layer was washed with water and dried over magnesium sulfate. After removal of the solvents, the product **17** was obtained (0.208 g, 46% yield) as a bright yellow crystals by recrystallizing from ether-methanol. m.p. 180-181°C; EI-MS *m/z* 564(29, M), 459(47), 383(25), 294(62), 105(82), 77(100); FTIR ν (cm^{-1}) 3050(w), 1662(vs), 1595(m), 1558(m), 1285(s), 767(s), 693(vs); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.06-7.60(m, 28H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 122.41(2C), 127.74(4C), 127.98(2C), 128.10(2C), 128.18(4C), 128.30(4C), 129.41(4C), 129.95(2C), 130.66(2C), 131.19(2C), 132.41(2C), 137.61(2C), 138.38(2C), 138.65(2C), 139.33(2C), 153.33(2C), 197.28(2C).

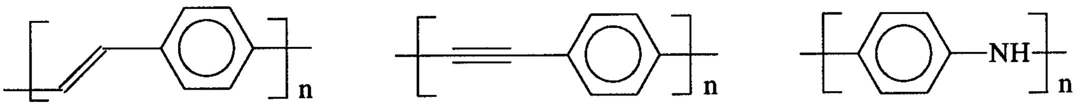
II. THE SYNTHESES OF POLY(PHENYLENE VINYLENE) ANALOGUES

Literature Survey

Conjugated polymers[53] are polymers which contain overlapping *p*-orbitals throughout the polymer main chains. These polymers have been attracting attention for more than two decades because they exhibit some unique properties such as conductivity, non-linear optical properties and fluorescence. In the past years, polyacetylene (PA)[54], polydiacetylene (PDA)[55], polyparaphenylene (PPP)[56], poly(phenylene vinylene) (PPV)[57], poly(phenylene ethynylene) (PPE)[58] and polyaniline (PANI)[54] have been extensively studied. The structure of these polymers are shown in Scheme 32. Among these polymers, poly(phenylene vinylene), hereafter referred to as PPV, is one of the most interesting.



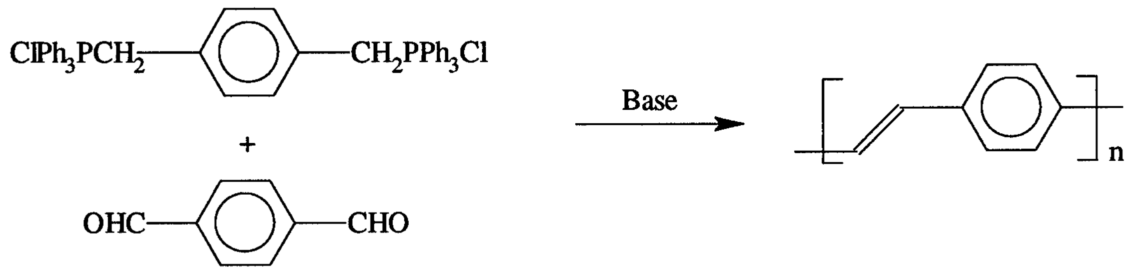
Polyacetylene (PA) Polydiacetylene (PDA) Polyparaphenylene (PPP)



Poly(phenylene vinylene) (PPV) Poly(phenylene ethynylene) (PPE) Polyaniline (PANI)

Scheme 32. The structures of conjugated polymers

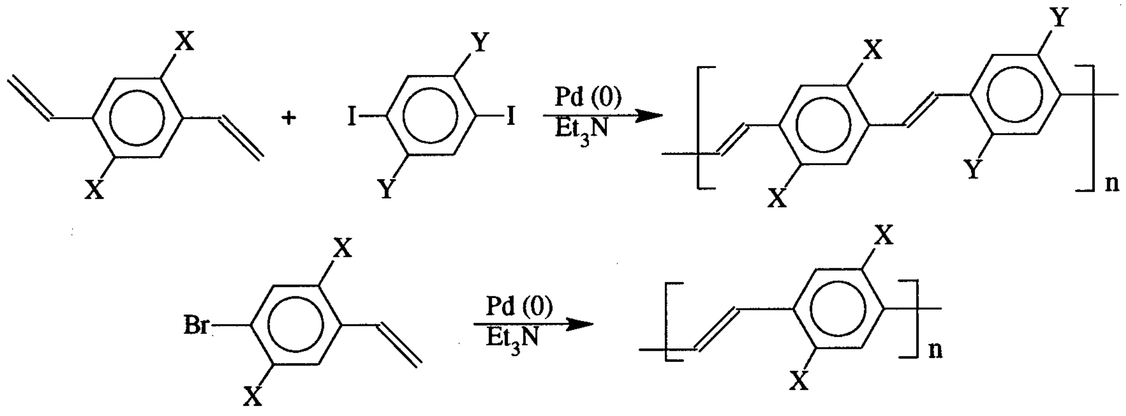
PPV and its derivatives can be synthesized by several different routes. The first synthesis was carried out by McDonald and Campbell via a Wittig reaction of *p*-xylene bis(triphenylphosphonium chloride) with terephthalaldehyde, as shown in Scheme 33.[59] However, the product is insoluble and infusible.



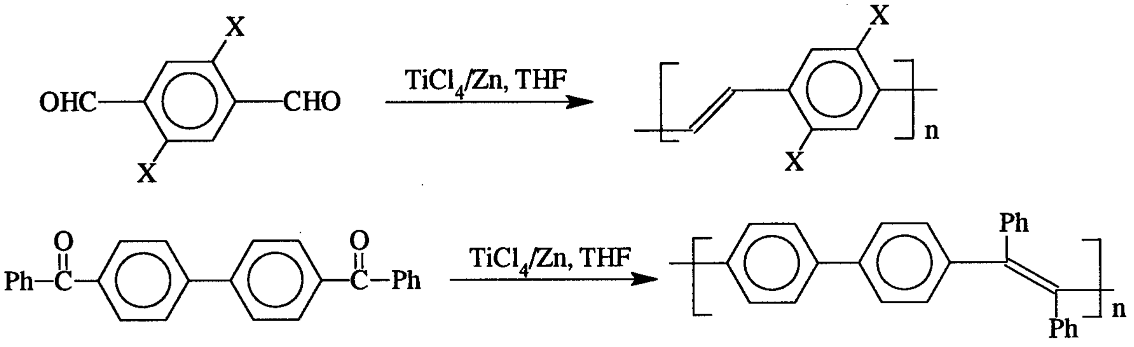
Scheme 33. Preparation of PPV via Wittig reaction

Later, the syntheses of PPV and its derivatives via the Heck reaction[60], and also the McMurry reaction (Scheme 34)[61], were reported by several different groups.

Heck reaction:

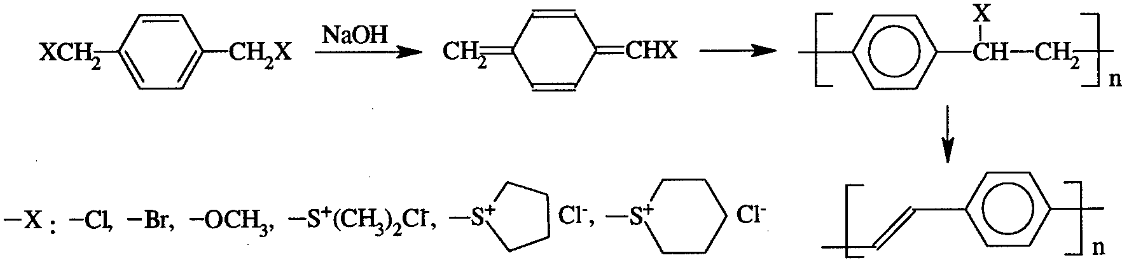


McMurry reaction:



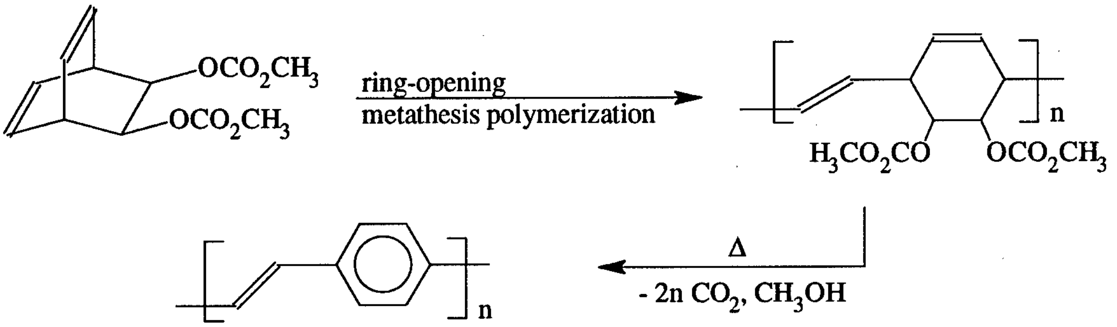
Scheme 34. Syntheses of PPV via Heck and McMurry reactions

Since PPV is not soluble in organic solvents, solution-cast films cannot be made. In order to overcome this problem, the "soluble precursor" synthesis, also named as Wessling reaction [62], was used to prepare PPV and its derivatives. The method is illustrated in Scheme 35. The idea is that a soluble polymeric precursor can be cast into film and then coverted to PPV film by elimination of small molecules.



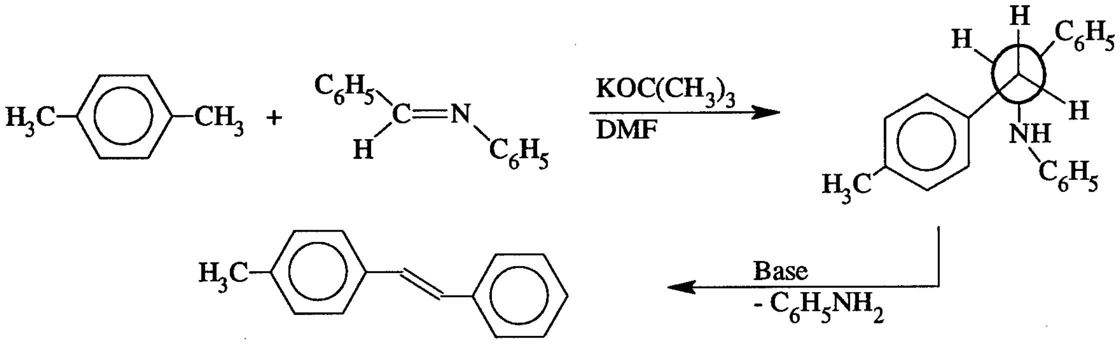
Scheme 35. Synthesis of PPV via Wessling reaction

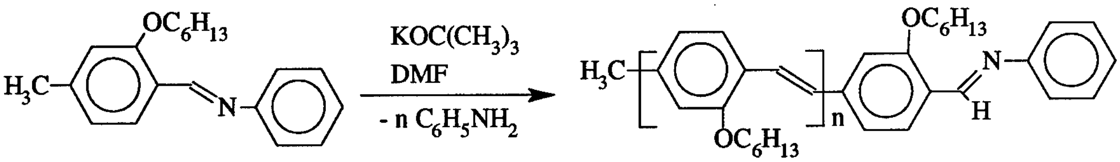
Also, the PPV polymer can be prepared by living, ring-opening metathesis polymerization, as shown in Scheme 36. [63] The advantage of this method is that the precursor polymer thus obtained has narrow molecular weight distributions (PD = 1.2-1.3) and a controlled degree of polymerization. The precursor polymer can then be converted to PPV upon heating.



Scheme 36. Synthesis of PPV through ring-opening metathesis

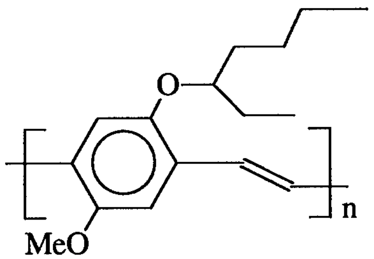
Although precursor routes can provide good films of PPV and its derivatives, there are still saturated carbons in the polymer main chain due to incomplete elimination. Recently, the Siegrist method (Scheme 37) has been used in the direct synthesis of PPV.[64] This method not only gives quantitative yields but also has very high stereoselectivity, which is 1000:1 in favor of the E configuration. Therefore, the resulting PPV derivative has a high content of *trans*-vinylene units, as proved by NMR.





Scheme 37. Siegrist method

The properties of PPV and its derivatives have been extensively studied.[65-68] The current interest in PPV focuses upon its photophysics and opto-electronic applications. Wnek[65] reported that PPV, which was prepared via a Wittig reaction, had a conductivity of 3S/cm after doping with AsF_5. Later, Murase[66] reported that streteched PPV films, which were prepared via Wessling's precursors, show extremely high conductivities of 3000S/cm and 500S/cm after doping with AsF_5 and SO_3, respectively. Also, PPV was the first organic polymer used in the construction of organic-based light-emitting diodes (LEDs). Following the first observation of electroluminescence (EL) of a PPV-based LED[69], a number of PPV derivatives have been studied. It was found that a modified PPV derivative, poly (2-methoxy, 5-(2'-ethylhexoxy)-1,4-phenylene vinylene), abbrivated as MEH-PPV[70], has better solubility in organic solvents and also emits light at longer wavelengths due to the smaller energy gap between HOMO and LUMO produced by the electron donating alkoxy groups.



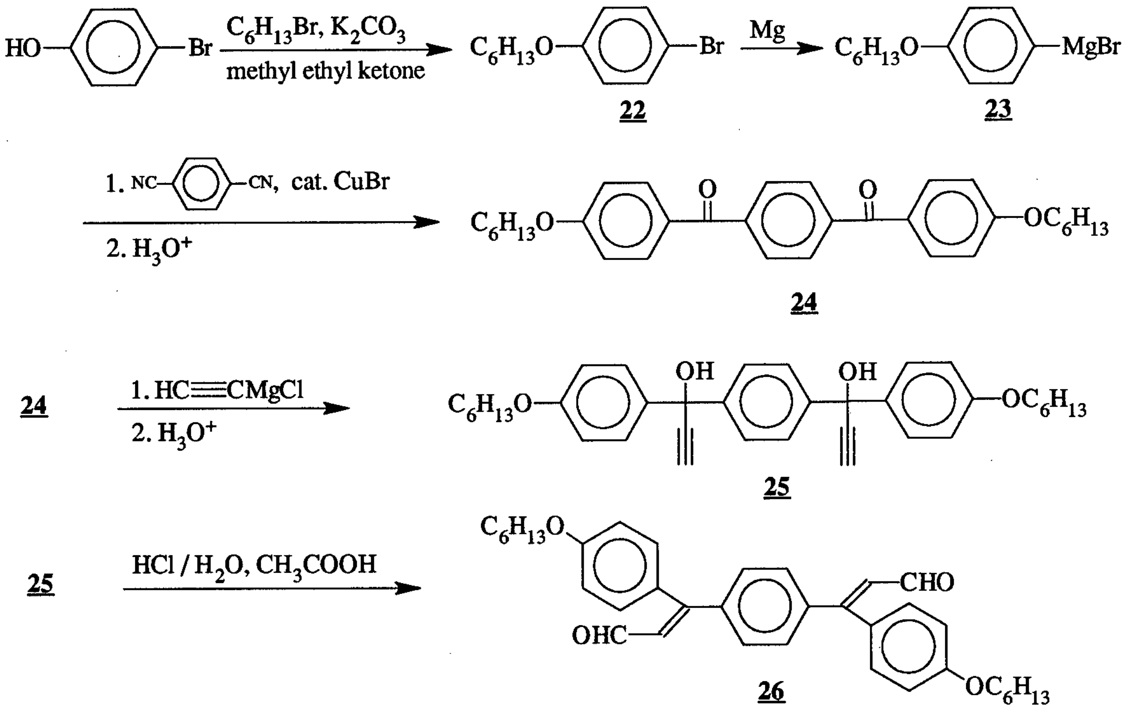
MEH-PPV

Results and Discussions

The objective of this project is to find out if the properties of PPV will be improved by introducing more double bonds into the structure. With more double bonds in the structure, we expected decreased thermal stability to accompany the longer conjugation.

Monomer Preparation

The key monomer used to synthesize PPV-type polymers is aryldivinylene-aldehyde **26**. In order to improve the solubility of the target polymers, alkoxy chains are attached to the phenyl rings. The synthesis is described in Scheme 38.

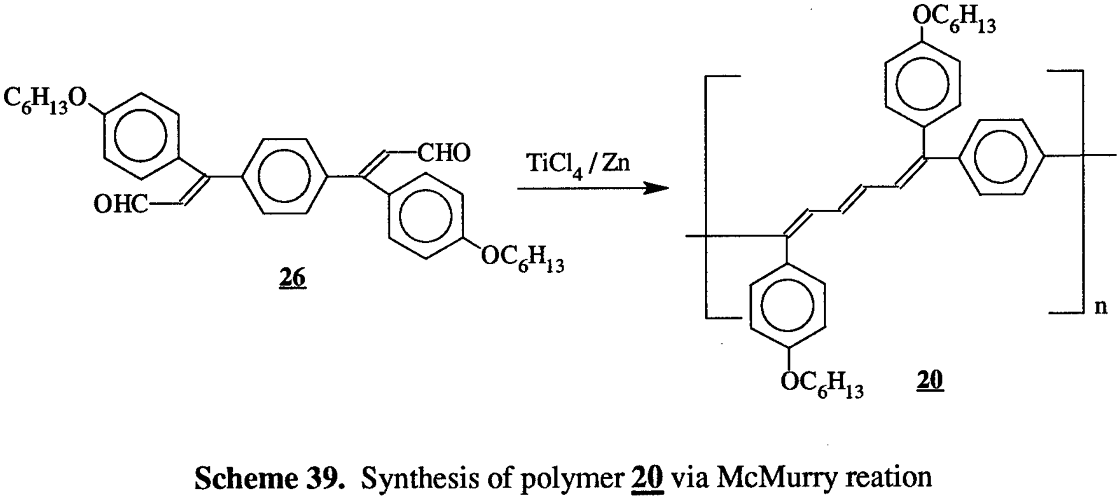


Scheme 38. Synthesis of dialdehyde monomer **26**

p-Bromophenol was reacted with 1-bromohexane and potassium carbonate in methylethyl ketone, giving *p*-hexoxybromobenzene **22** in 96% yield.[76] Compound **22** was easily transformed into a Grignard reagent by reaction with magnesium. Then, the reaction of Grignard reagent **23** and 1,4-dicyanobenzene with catalylic copper (I) bromide, followed by acidic work up, produced 1,4-bis(*p*-hexoxybenzoyl)benzene **24** in 90% total yield.[77] The diketone **24** was treated with ethynyl magnesium chloride to give diacetylenic diol **25**, which isomerized into dialdehyde monomer **26** in 60% yield.[78] Monomer **26** (Figure 8) is a yellow crystalline material which is stable in the air.

Polymerization

Two methods were used to produce the polymers. The first technique is through a McMurry reaction, as shown in Scheme 39. The aldehyde funtional groups were coupled with each other with a low valent titanium reagent to give polymer **20** in 86% yield.[79] Polymer **20** is an orange solid which is very soluble in THF, $CHCl_3$ and CH_2Cl_2.



Scheme 39. Synthesis of polymer **20** via McMurry reation

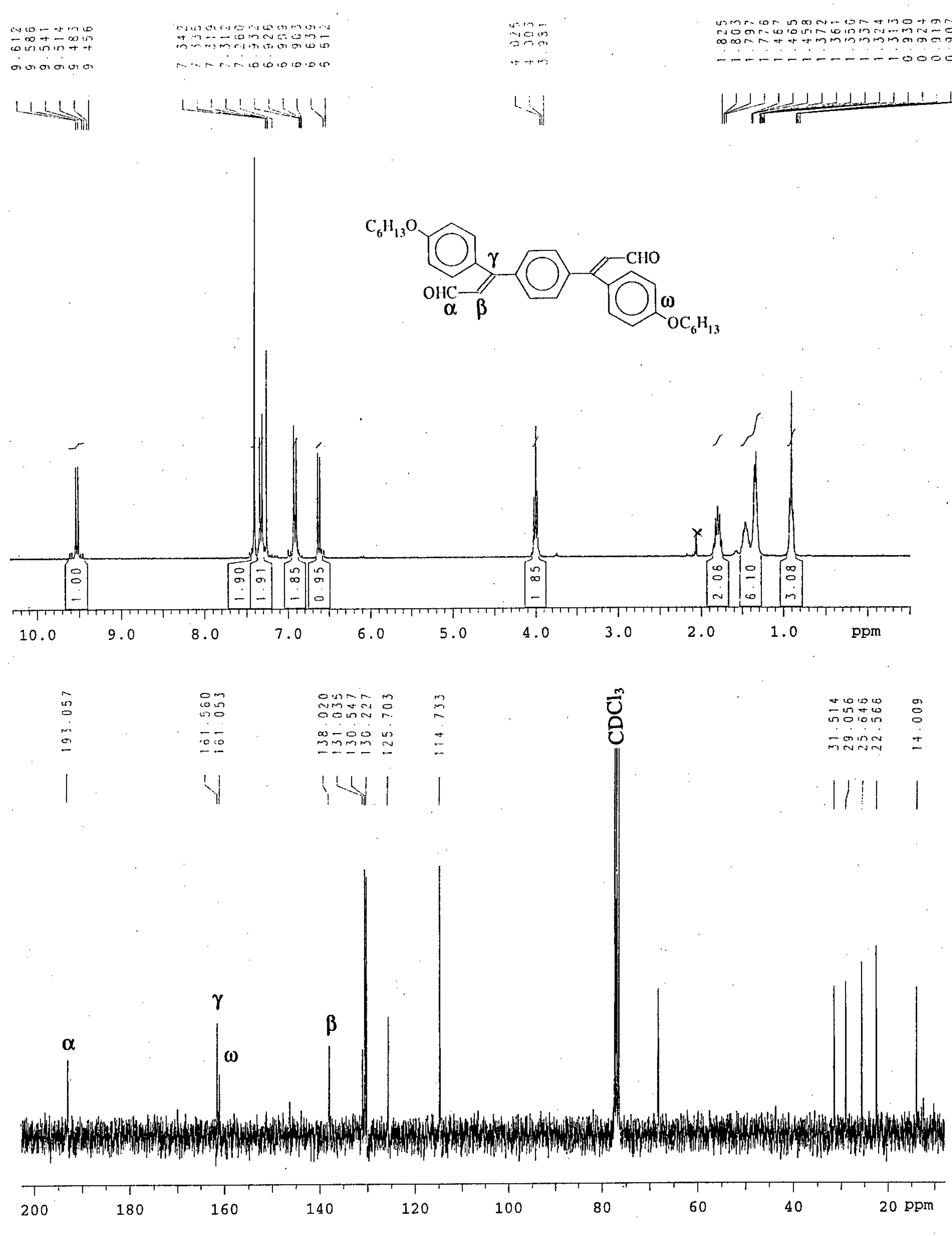
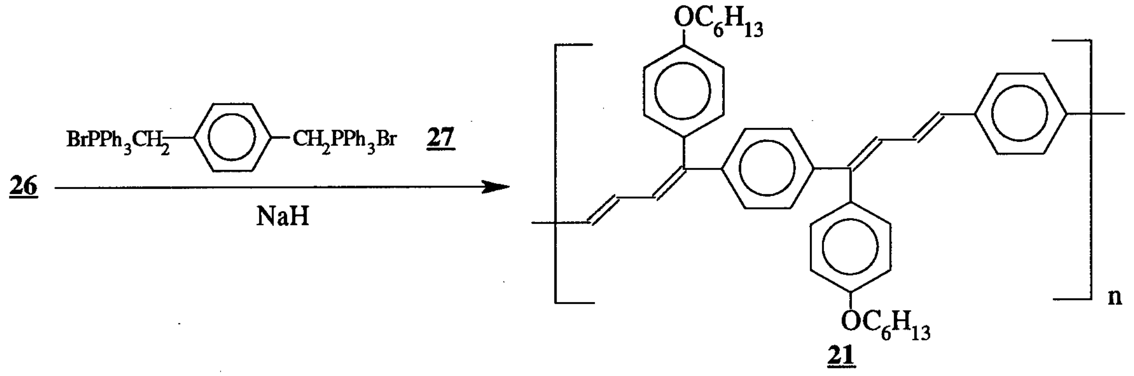


Figure 8. ^1H-NMR and ^{13}C-NMR spectra of monomer 26

Polymer 21 was synthesized by a Wittig reaction in 53% yield (Scheme 40).[80] Dialdehyde monomer 26 reacted with phosphonium salt 27 in THF, by using NaH as a base, producing polymer 21 as an orange solid. The polymer is also very soluble in THF, $CHCl_3$ and CH_2Cl_2.



Scheme 40. Synthesis of polymer 21 via Wittig reaction

Characterization

The polymers were characterized by GPC, ^{1}H-NMR and ^{13}C-NMR. Molecular weight measurements were performed by gel permeation chromatography (GPC) calibrated by polystyrene standard using THF as an eluent. The molecular weight (M_w) of 20 was 4.08×10^3 and that of 21 was 1.23×10^4. The PD (M_w/M_n) are 1.07 and 1.21, respectively. The ^{1}H-NMR spectrum (Figure 9) of polymer 20 shows two groups of protons, one between δ 7.2 and 6.7 for the phenyl and olefinic hydrogens and the other between δ 4.1 and 0.91 for the hexoxy groups. The ^{13}C-NMR spectrum (Figure 9) shows three sp^2 carbons of olefins in the main chain at 135-142 ppm, four peaks at 113, 128, 131, 158 ppm for the phenyl carbons, and six sp^3 hexoxy carbons between 13 and 67 ppm.

The NMR spectra fits the structure of **20** quite well. The ^{1}H-NMR spectrum (Figure 10) of polymer **21** is very similar to that of polymer **20**, having two regions of peaks between 7.4 and 6.8 ppm and between 4.0 and 0.9 ppm, representing the protons of the phenyl & olefin and hexoxy groups, respectively. The only difference between the two spectra is that of polymer **21** has a little hump near 9.6 ppm indicating the remaining aldehyde end groups. The ^{13}C-NMR spectrum (Figure 10) has four sp^{2} carbons at 136-143 ppm for the double bonds on the main chain, one peak at 114 ppm, peaks from 126 to 132 and another peak at 158 ppm for the phenyl carbons, six sp^{3} carbons for the hexoxy groups and two small peaks at 161 and 193 ppm for the vinyl aldehyde end groups.

The thermal stabilities of both polymers were studied by TGA. Both polymers start to lose weight at 400°C. Polymer **20** loses 5% weight at 400°C, but the weight loss increases rapidly in the next 100°C with only 35% weight left at 500°C. The TGA of polymer **21** has the similar pattern by ending the rapid weight loss at 550°C with 48% material left. The thermal behaviors of the polymers were tested by DSC. A DSC thermogram of polymer **20** is shown in Figure 11 where an endothermic peak is observed at ~66°C. Then the polymer starts to give off the heat slowly until an exothermic peak appears at 418°C. For the polymer **21**, the DSC thermogram shows an endothermic peak at 68°C indicating polymer starts to melt. An exothermic reaction starts at 330°C to give a peak at 413°C. This peak is probably due to crosslinking.

UV/Vis absorption spectra of monomer **26** and those of polymer **20** and **21** were measured and given in Figure 12. The λ_{max} of the polymer **20** and **21** are 390 nm and

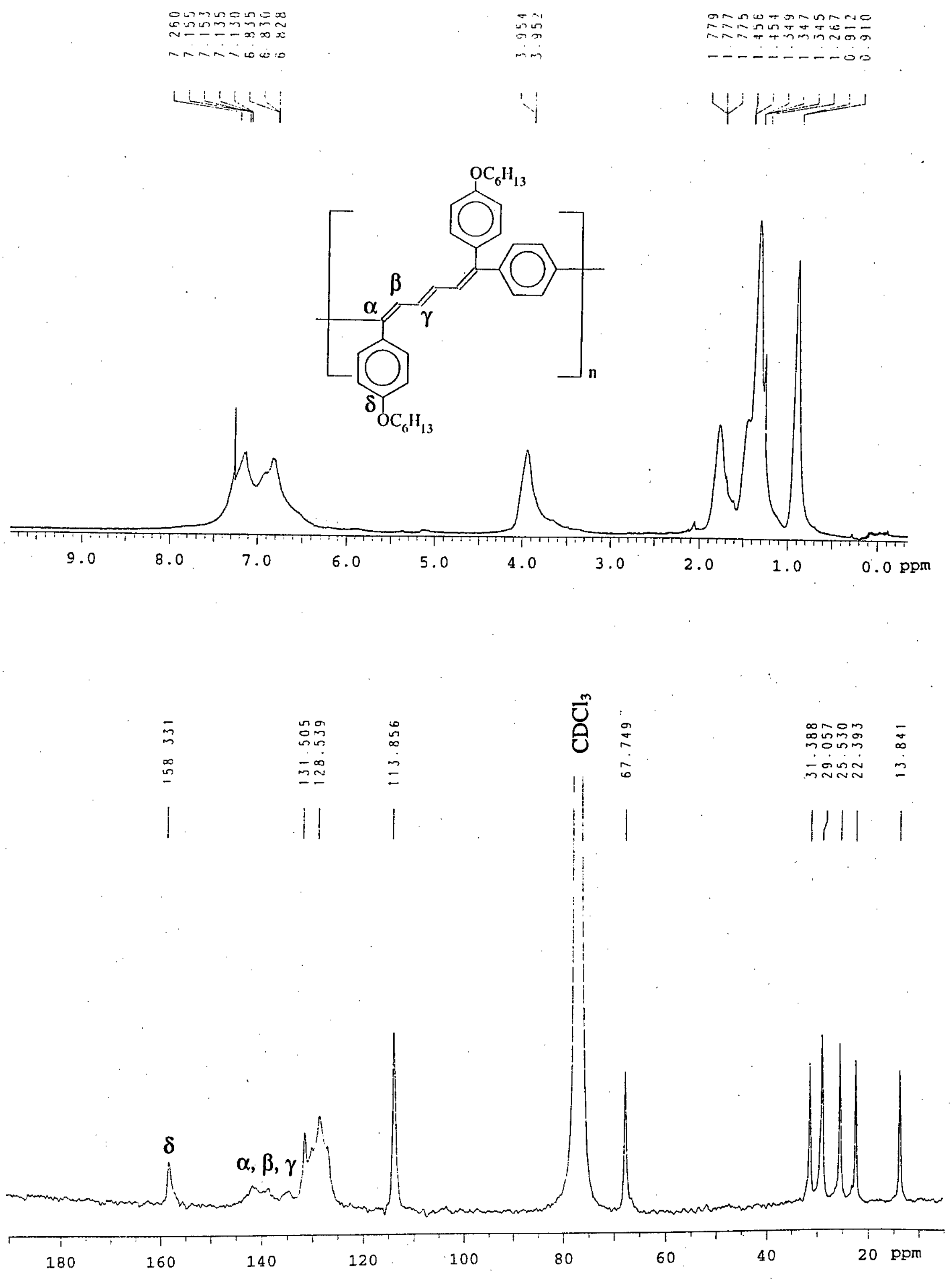


Figure 9. ^{1}H-NMR and ^{13}C-NMR spectra of polymer <u>**20**</u>

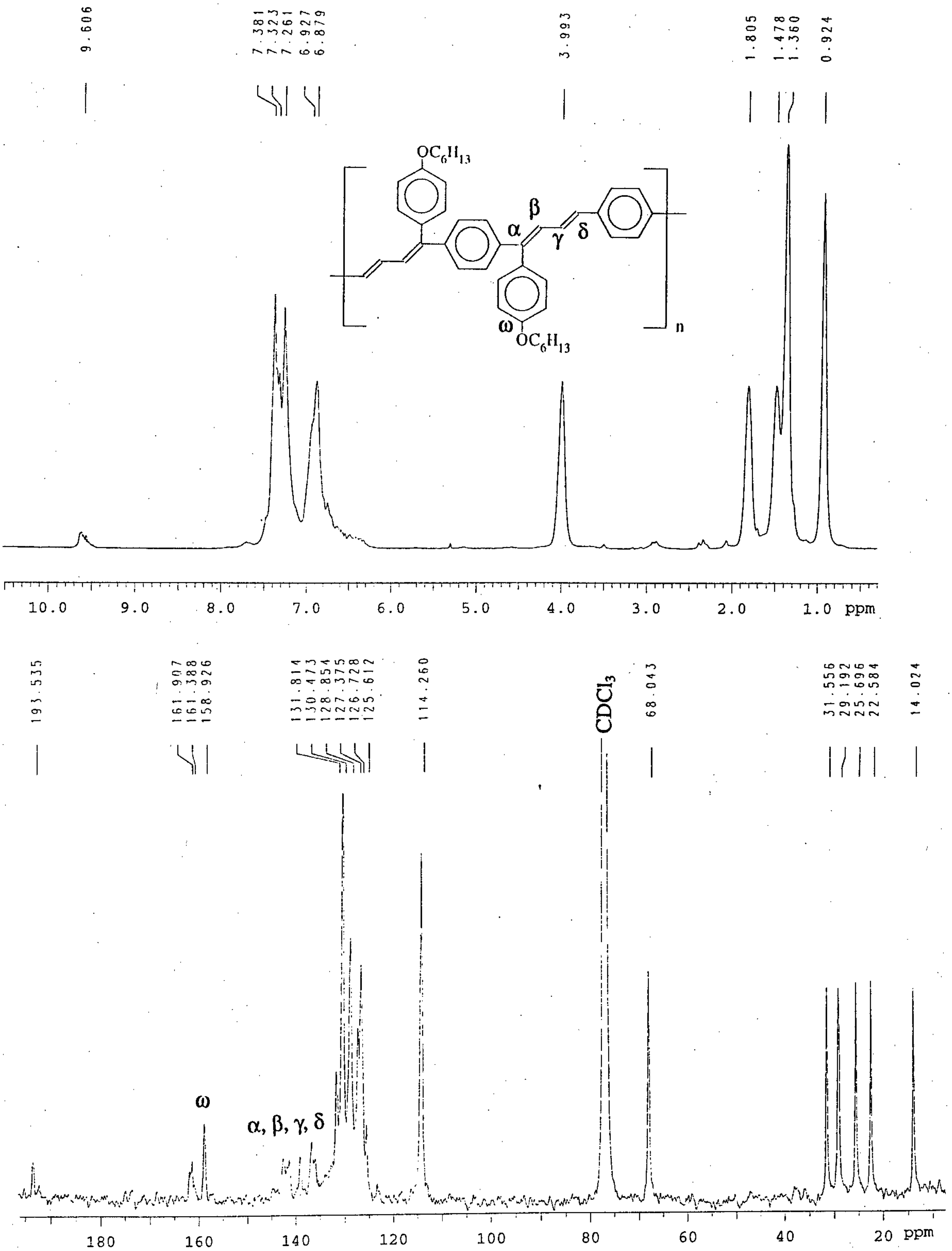


Figure 10. ^{1}H-NMR and ^{13}C-NMR spectra of polymer **21**

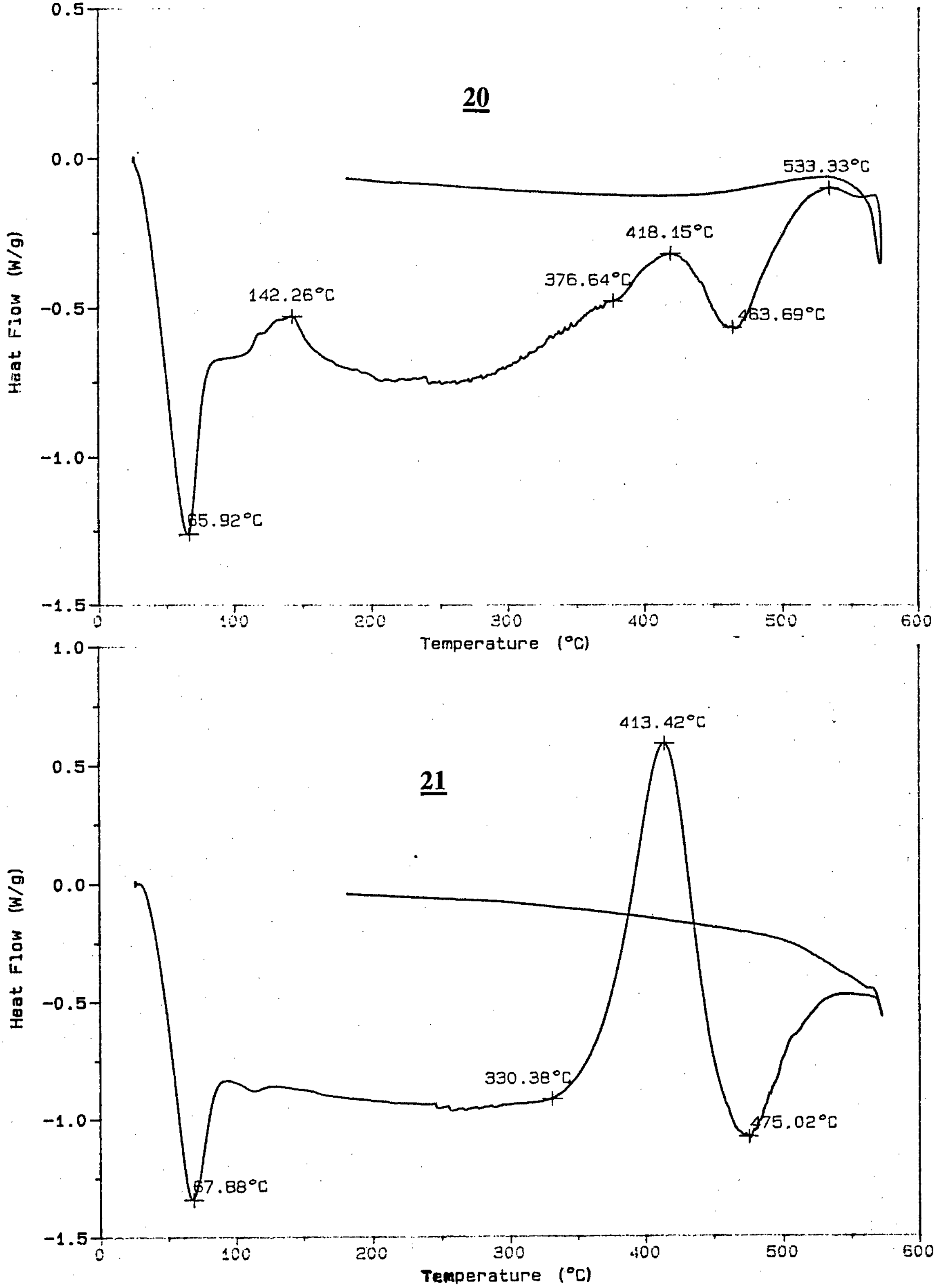


Figure 11. DSC thermograms of polymer **20** and **21**

408 nm respectively. Comparison of the λ_{max} of both polymers with that of PPV [71] (λ_{max} = 459 nm in THF) shows the polymers we made have shorter absorption maxima. At this point, we might conclude that the polymers also have shorter conjugation lengths. The explanation is that the main chains of the polymers are made more flexible by the introduction of more double bonds. The rotations of the single bond in between of the two double bonds twist the strucutures, therefore the phenyl groups on the main chain are not lying on the same plane. Thus, the conjugations are shortened. The UV/Vis absorption of polymer films were also measured. The λ_{max} in the solid state are 6 nm and 10 nm longer than in solution, suggesting that the polymer in the solid state is a little better aligned than in solution.

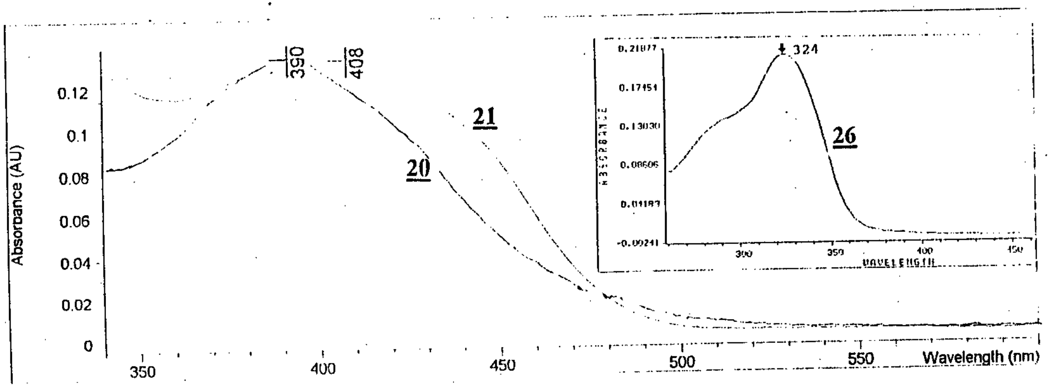


Figure 12. UV/Vis absorptions of monomer **<u>26</u>**, polymer **<u>20</u>** and **<u>21</u>** in THF solution

Both polymers are photoluminescent in solution and solid state. The photoluminescence (PL) spectra of polymers in deoxygenated THF solutions have been obtained (Figure 13). The solutions were excited by the UV/Vis light with excitation wavelength

(λ_{ex}) about 10 nm shorter than the corresponding absorption maximum wavelength (λ_{max}). The resulting emission bands are largely red-shifted compared with their absorption bands. The emission spectra have broader band than the absorption spectra and the tail of the emission band even reaches beyond 750 nm. The emission profiles of both polymers are very similar with only one band for each polymer: λ_e at 514 nm for polymer 20 and λ_e at 538 nm for polymer 21. Both λ_e are little bit shorter than that in the literature, which is around 550 nm.[85]

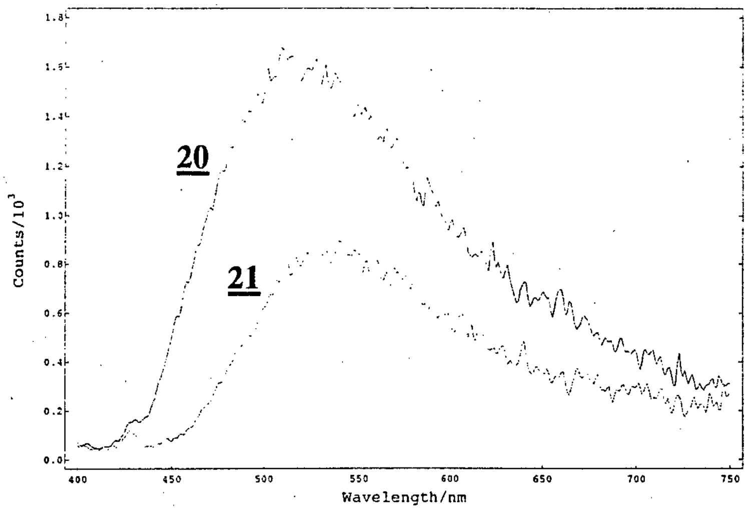


Figure 13. Photoluminescence (PL) spectra of polymer 20 and 21

Conjugated polymers are capable of being doped, through chemical or electro-chemical oxidation or reduction, to states of higher electrical conductivity. The conductivity of polymers were measured by two in-line probes. Both polymers were insulators at its neutral state. After being doped by I_2 vapor under vacuum, they became semiconductive. Polymer **20** has a conductivity of $\sigma = 1\text{-}5 \times 10^{-3}$ S/cm, while polymer **21** has a conductivity of $\sigma = 3\text{-}7 \times 10^{-4}$ S/cm. Those numbers are smaller compared to that of the standard PPV [65,66], indicating poorer conductivities. This could be due to the shorter conjugation, low molecular weight, or poor film-forming ability of the polymers.

Conclusions

Two poly(phenylene vinylene) analogues were synthesized via McMurry reaction and Wittig reaction respectively. Both polymers were characterized by ^{1}H and ^{13}C NMR, GPC, UV/Vis, TGA, DSC.

The thermal stabilities and thermal behaviors of the two polymers were studied. Both of them start to decompose at 400°C. They usually begin to crosslink at about 330°C.

The UV/Vis absorption and photoluminescence spectra were measured. The decreasing of λ_{max} values of UV/Vis absorption of both polymers indicates they have shorter conjugation length than standard PPVs. The photoluminescence spectra show a broad peak at about 520 nm with a long tail reaching beyond 750 nm.

The conductivities were also studied. At undoped states, both polymers are nonconductive. After doped by I_2 vapor in the vacuum, the polymers are semiconductive with conductivities of $1\text{-}5 \times 10^{-3}$ S/cm for polymer **20** and $3\text{-}7 \times 10^{-4}$ S/cm for polymer **21**.

Experimental

^1H and ^{13}C-NMR spectra were acquired on a Varian VXR-300 spectrometer. In order to assure the quantitative features of the ^{13}C-NMR spectra, the relaxation agent chromium (III) acetylacetonate was used in $CDCl_3$ with a relaxation delay of 5 seconds.

The exact masses were obtained from a Kratos MS 50 mass spectrometer with 10,000 resolution. The infrared spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer from neat sample. The UV/Vis spectra were obtained on a Hewlett Packard 8452A diode array UV/Vis spectrometer. Reactions were monitored by Hewlett Packard 5890 series II GC and Hewlett Packard tandem GC-IR-MS (5890A GC-5965A IR-5970 Series MS) parallel connected.

Polymer molecular weights were determined by gel permeation chromatography (GPC) with 6 Microstyragel columns in series of 500 A, 2×10^3 A, 2×10^4 A, $2 \text{ X } 10^5$ A. THF was used as an eluent at a flow rate of 1 mL/min. The system was calibrated by polystyrene standards. GPC analyses were performed on a Perkin-Elmer series 601 LC equipped with Beckman solvent delivery system, a Walter Associate R401 refractive index detector and a Viscotek viscometer. Differential scanning calorimetry (DSC) analyses were performed on a Du Pont 910 Differential Scanning Calorimeter.

THF was distilled over sodium-benzophenone and ether was distilled over CaH_2 right before use. Other reagents were used as received from Aldrich or Fisher Chemical Co. without further purification unless specified otherwise.

***p*-Hexoxybromobenzene <u>22</u>.** A 500 mL oven-dried round bottom flask, equipped with condenser and magnetic stirrer, was charged with *p*-bromophenol (17.3 g, 100 mmol), K_2CO_3 (34.5 g, 250 mmol), 1-bromohexane (16.8 mL, 120 mmol) and methyl ethyl ketone (250 mL). The reaction mixture was refluxed for 80 hours. After filtration, the salts were washed with hot toluene (50 mL). After removal of organic solvents, the excess 1-bromohexane was removed by vacuum distillation. *p*-Hexoxybromobenzene <u>22</u> was obtained as viscous liquid (25.04 g, 96% yield). GC-MS *m/z* 258(13, M+2), 256(14, M), 173(99), 171(100); GC-FTIR ν (cm^{-1}) 2939(s), 2876(m), 1578(w), 1488(vs), 1387(w), 1277(s), 1238(vs), 1169(m), 1073(m), 1007(m), 823(m); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.85(t, J = 6.6 Hz, 3H), 1.20-1.45 (m, 6H), 1.71(p, J = 6.6 Hz, 2H), 3.83(t, J = 6.6 Hz, 2H), 6.68, 6.71, 7.27, 7.30 (AB quartet, J = 9.0 Hz, 4H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 13.20(1C), 21.73(1C), 24.80(1C), 28.27(1C), 30.70(1C), 67.28(1C), 111.64(1C), 115.44(2C), 131.31(2C), 157.31(1C).

1,4-Bis(*p*-hexoxybenzoyl)benzene <u>24</u>. A 250 mL oven-dried round bottom flask, equipped with condenser, addition funnel and magnetic stirrer, was charged with magnesium (2.916 g, 120 mmol). The magnesium was activated by stirring overnight under slow argon flow. After dry THF (70 mL) was charged, 1,2-dibromoethane (0.1 mL) was added to initiate the reaction. *p*-Hexoxybromobenzene <u>22</u> (25.2 g, 100 mmol) in THF (100 mL) was added at a speed to maintain mild reflux. Stirring was continued for another 20 minutes after the addition was finished. To the above Grignard solution <u>23</u>, 1,4-dicyanobenzene (5.89 g, 46 mmol) and copper (I) bromide was added. Refluxing for one hour produced a sticky mixture which was slowly added to 150 mL of 15% cold sulfuric acid in a 1 L beaker with stirring. The black slurry turned to a yellow solid and an additional 70 mL more 15% sulfuric acid was added to break up the precipitate. After refluxing the whole work up mixture for 3.5 hours, the white crystals floating on the solution were filtered and then washed with water three times and ether twice. After vacuum drying in the presence of phosphorous pentaoxide, 1,4-bis(*p*-hexoxybenzoyl) benzene 24 (20.0 g, 90 % yield) was obtained. m.p. 169-170°C; EI-MS *m/z* 487(18, M+1), 486(50, M), 402(14), 318(37), 232(15), 142(35), 127(89), 121(77), 85(100), 67(67), 59(72); FTIR ν (cm^{-1}) 2955(m), 2937(m), 2863(m), 1641(vs), 1602(s), 1578(w), 1506(w), 1309(m), 1286(m), 1251(s), 1155(m), 840(m); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.911(t, J = 6.9 Hz, 6H), 1.25-1.55(m, 12H), 1.82(p, J = 6.9 Hz, 4H), 4.05(t, J = 6.6 Hz, 4H), 6.95, 6.98, 7.83, 7.86 (AB quartet, J = 9.0 Hz, 8H), 7.82(s, 4H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 13.40(2C), 21.90(2C), 25.01(2C), 28.28(2C), 30.86(2C), 67.74(2C), 113.55(4C), 128.65(4C), 131.99(4C), 140.37(2C), 163.54(2C), 194.17(2C).

Diacetylenic diol 25. A 250 mL oven-dried round bottom flask, equipped with condenser, addition funnel and magnetic stirrer, was charged with 1,4-bis(*p*-hexoxybenzoyl)benzene 24 (4.86 g, 10 mmol) and dry THF (20 mL). Ethynyl magnesium chloride (30 mmol, 0.5 M, 60 mL) was added dropwise at -78°C. After addition, the reaction mixture was warmed to room temperature, then refluxed for 10 hours. The reaction solution was poured into a mixture of 50 mL ether and 50 mL 2.0 M HCl acid. The separated organic layer was then washed with water twice and dried over magnesium sulfate. After removal of the solvents, the residue was purified by flash chromatography on a silica gel column eluted with a solution of hexane/ethyl acetate (v:v = 5:1) to give 5.30 g oily **25** in 99% yield. EI-MS *m/z* 538(52, M), 521(11), 448(17), 307(23), 231(67), 223(37), 210(34), 147(100), 121(28), 43(60); FTIR ν (cm^{-1}) 3441(m), 3287(m), 2952(m), 2930(s), 2859(m), 1607(s), 1508(vs), 1300(w), 1246(vs), 1174(s), 987(m), 830(s); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.901(t, J = 6.9 Hz, 6H), 1.18-1.45(m, 12H), 1.76(p, J = 6.9 Hz, 4H), 2.84(s, 2H), 3.93(t, J = 6.6 Hz, 4H), 6.81, 6.84, 7.46, 7.49 (AB quartet, J = 9.0 Hz, 8H), 7.56(s, 4H); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 14.00(2C), 22.57(2C), 25.68(2C), 29.16(2C), 31.54(2C), 68.00(2C), 73.76(2C), 75.27(2C), 86.50(2C), 114.10(4C), 125.87(4C), 127.28(4C), 136.21(2C), 144.09(2C), 158.80(2C).

Dialdehyde monomer 26. A 100 mL round bottom flask, equipped with magnetic stirrer, was charged with acetylenic diol **25** (2.69 g, 5 mmol), acetic acid (50 mL) and THF (25 mL). A mixture of HCl acid (7.5 mL) and water (5 mL) was added dropwise to the solution at room temperature. Stirring was continued for another 3 hours before the reaction mixture was neutralized with 3.0 M NaOH solution. The mixture was then extracted with ether (40 mL) twice. The resulting organic layer was washed with water twice and dried over magnesium sulfate. After removal of the solvents, the crude product was obtained by precipitation from methanol. Recrystalization from $CHCl_3$ and methanol afforded final product as a slightly yellow solid (1.60 g, 60%). m.p. 159-161°C; CI-MS *m/z* 557(21), 556(73, MNH_4^+), 540(17), 539(100, MH^+); FTIR ν (cm^{-1}) 2939(w), 2860(w), 1656(vs), 1602(m), 1585(s), 1567(w), 1509(w), 1256(m), 1235(m), 1179(m), 1131(s), 830(m); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.91(t, J = 6.9 Hz, 6H), 1.31-1.52(m, 12H), 1.80(p, J = 6.9 Hz, 4H), 4.00(t, J = 6.6 Hz, 4H), 6.61, 6.64(d, J = 8.1 Hz), 6.90, 6.93, 7.31, 7.34 (AB quartet, J = 9.0 Hz, 8H), 7.41(s, 4H), 9.51, 9.54(d, J = 8.1 Hz); ^{13}C-NMR (300 MHz, $CDCl_3$) δ 14.00(2C), 22.57(2C), 25.65(2C), 29.06(2C), 31.51(2C), 68.26(2C), 114.73(4C), 125.70(2C), 130.23(4C), 130.55(4C), 131.04(2C), 138.02(2C), 161.05(2C), 161.56(2C), 193.06(2C); UV/Vis λ_{max} = 324 nm (THF).

Polymer 20. Into a 100 mL 3-necked round bottom flask, equipped with a reflux condenser and a magnetic stirrer, was placed zinc powder (0.39 g, 6 mmol) which was washed with 10% HCl, water and acetone sequentially and dried under vacuum right before the use. Under the argon flow, dry THF 20 mL was syringed through the septum and cooled to -10°C. $TiCl_4$ (0.34 mL, 3 mmol) was carefully injected into THF with stirring, resulting in a green-yellow solution. The mixture was refluxed for 1.5 hours causing the color change to dark green with some floating metal particles. The complex was allowed to cool to the room temperature before the dialdehyde monomer **26** (0.2 g, 0.37 mmol) in 20 mL dry THF was transfered into the reductive complex and refluxed for 2 days. After the reaction mixture was cooled to room temperature, 20 mL of 10% K_2CO_3 solution was added and stirring was continued for another hour followed by filtration. Then the filtrate was extracted with ether (10 mL x 3) and dried over magnesium sulfate. After removal of the solvents, the residue was redissolved in CH_2Cl_2 and then precipitated in methanol. Polymer **20** (0.518 g, 86% yield) was obtained as an orange solid after drying under vacuum. FTIR ν (cm^{-1}) 3032(w), 2953(s), 2929(s), 2858(m), 1605(s), 1508(vs), 1469(s), 1245(vs), 830(m); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.91, 1.27, 1.35, 1.45, 1.78, 3.95, 6.82-7.20; ^{13}C-NMR (300 MHz, $CDCl_3$) δ 13.84, 22.39, 25.53, 29.06, 31.29, 67.75, 113.86, 128.54, 131.51, 158.33; GPC $M_n = 3.81 \times 10^3$, $M_w = 4.08 \times 10^3$, PD = 1.07; UV/Vis λ_{max} = 390 nm (THF), 394 nm (film); λ_e = 514 nm (THF); $\sigma = 1\text{-}5 \times 10^{-3}$ S/cm.

***p*-Xylylenebis(triphenylphosphonium bromide) 27.** A 100 mL round bottom flask equipped with a reflux condenser and a magnetic stirrer was charged with α,α'-dibromo-*p*-xylene (2.64 g, 10 mmol) and chloroform (50 mL) under argon flow. Triphenylphosphine (5.25 g, 20 mmol) was added to the stirred solution. After 72 hours of reflux, the mixture was cooled to room temperature and the solvent was removed. The residue was precipitated in hexane from CH_2Cl_2 solution. After drying under vacuum, the desired product (4.74 g, 62% yield) was obtained as a white powder.[81] ^{1}H-NMR (300 MHz, d^4-methanol) δ 4.99(d, J = 14.1 Hz, 4H), 6.89(s, 4H), 7.60-7.71(m, 30H).

Polymer 21. A 100 mL 2-necked round bottom flask equipped with a magnetic bar and condenser was charged with *p*-xylylenebis(triphenylphosphonium bromide) **27** (0.315 g, 0.4 mmol) and dry THF (15 mL). A suspension of NaH (36 mg, 0.9 mmol) and dialdehyde monomer **26** (0.2 g, 0.37 mmol) in THF (20 mL) was added dropwise into this stirred solution. After refluxing for 3 days, the mixture was allowed to cool to the room temperature followed by the addition of 30 mL 3 M NH_4Cl solution. The aqueous layer was extracted with methylene chloride (15 mL x 2). Then the combined organic layer was washed with water (20 mL x 2) and dried over magnesium sulfate. After the removal of the solvents, the precipitation of the residue in methanol from CH_2Cl_2 yield the polymer **21** (0.12 g, 53%). FTIR ν (cm^{-1}) 3027(w), 2950(m), 2928(vs), 2857(m), 1661(s), 1585(vs), 1508(vs), 1246(s), 1178(m), 831(m); ^1H-NMR (300 MHz, $CDCl_3$) δ 0.92, 1.36, 1.48, 1.81, 3.99, 6.85-6.95, 7.26-7.40, 9.61; ^{13}C-NMR (300 MHz, $CDCl_3$) δ 14.03, 22.59, 25.70, 29.19, 31.56, 68.05, 114.26, 125.61, 126.73, 127.37, 128.85, 130.47, 131.80, 158.93, 161.38, 161.88, 193.51; GPC $M_n = 1.02 \times 10^4$, $M_w = 1.23 \times 10^4$, PD = 1.21; UV/Vis λ_{max} = 408 nm (THF), 418 nm (film); λ_e = 538 nm (THF); $\sigma = 3\text{-}7 \times 10^{-4}$ S/cm.

GENERAL CONCLUSIONS

In the first section of this thesis, a series of cumulene-containing compounds were synthesized and characterized. The catalytic, thermal and photochemical reations of the disilane-containing cyclic butatriene produced four isomers, which were characterized by NMR spectroscopy and single crystal X-ray analysis. The mechanisms leading to the isomers were proposed. The reactions of acyclic butatriene and the intermolecular additions of disilane to butatriene did not occur. It is the first study of disilane additions to cumulene.

In the second section of this thesis, two poly(phenylene vinylene) analogues were synthesized via McMurry reaction and Wittig reaction respectively. Both polymers were characterized by ^1H and ^{13}C NMR, GPC, UV/Vis, TGA, DSC. The photoluminescence spectra and conductivities were also measured. The study indicated the both polymers have shorter conjugation length than standard PPVs due to the twisted backbone in the structure.

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