Studies directed toward the synthesis of pentalenic acid
by Mark James Schulz

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University

Abstract:
The design of efficient, stereocontrolled pathways for the preparation of natural products holds promise as ground for developing and testing new synthetic strategies. The intramolecular photochemical [2+2] cycloaddition reaction is a highly useful reaction in organic synthesis. The process allows the formation of two carbon-carbon bonds and the possibility of four stereocenters.

This method was utilized in the synthesis of the tricyclic core of the natural product, pentalenic acid. Subsequent fragmentation/cyclization of the formed cyclobutane ring can be accomplished through the use of an oxovanadium reagent to establish the 5-5-5 ring system of pentalenic acid.

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MONTANA STATE UNIVERSITY
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APPROVAL

of a thesis submitted by

Mark J. Schulz

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Thomas S. Livinghouse — (Signature) — 4/23/01 (Date)

Approved for the Department of Chemistry & Biochemistry

Paul A. Grieco — (Signature) — 4/23/01 (Date)

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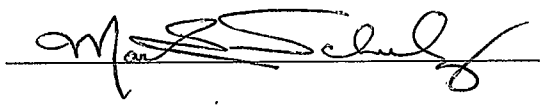
Signature 

Date 4-23-01

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ABSTRACT

The design of efficient, stereocontrolled pathways for the preparation of natural products holds promise as ground for developing and testing new synthetic strategies. The intramolecular photochemical [2+2] cycloaddition reaction is a highly useful reaction in organic synthesis. The process allows the formation of two carbon-carbon bonds and the possibility of four stereocenters.

This method was utilized in the synthesis of the tricyclic core of the natural product, pentalenic acid. Subsequent fragmentation/cyclization of the formed cyclobutane ring can be accomplished through the use of an oxovanadium reagent to establish the 5-5-5 ring system of pentalenic acid.

Stereoselectivity in the photochemical [2+2] cycloaddition was poor. The stereoselectivity may be improved by increasing the steric interaction during cyclobutane ring formation. Greater stereocontrol is needed in order for the synthesis of pentalenic acid to be successful.

CHAPTER 1

INTRODUCTION

Terpenoids are a diverse group of natural products with a stunning array of polycyclic frameworks. Nature has bestowed these natural products with an unusual assemblage of rings and functionalities. Within the terpene family exists an interesting subgroup known as polyquinanes, which are composed of fused five-membered rings. Polyquinane natural products have been discovered in marine, plant, and microbial sources. They have been known to contain up to four fused five-membered rings, which display four characteristic carbocyclic skeleta (Figure 1).

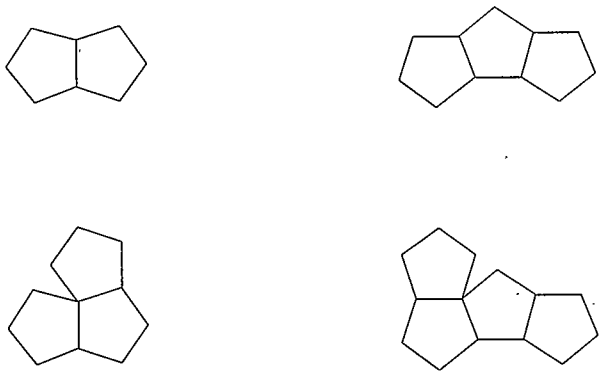


Figure 1. Characteristic Polyquinane Skeleta

Many polyquinane natural products have been shown to exhibit significant biological activities, which range from antibiotic properties to antitumor activity. As a consequence of this biological activity, polyquinanes have attracted rigorous attention from the scientific community. They have been used as prime subjects for synthetic and biosynthetic studies. In addition to the potential for drug discovery, interest in polyquinanes has resulted from their structural diversity. Which is primarily due to the structurally alluring assembly of five-membered rings, displaying a variety of functionality. As with many classes of natural products, polyquinanes hold promise as ground for developing and testing new synthetic strategies. In fact, polyquinanes have provided the impetus for the development of synthetic strategies for cyclopentannulations. The literature is rich with methods directed toward polyquinane synthesis.[1-5] Throughout the last twenty years, polyquinane synthesis has been an intriguing area of natural product synthesis and interest in them still remains.

Polyquinanes, which contain three fused five-membered rings, are known as triquinanes. The first natural product containing a triquinane nucleus, retigeranic acid was isolated twenty-nine years ago by Shibata (Figure 2).[6] Since then, numerous triquinanes have been isolated from natural sources. Triquinanes are classified as either linear or angular (nonlinear), based on the topology of the ring fusion.

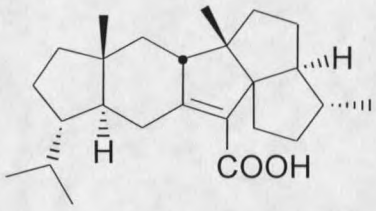
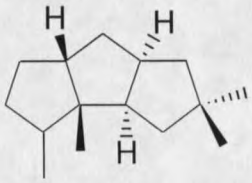
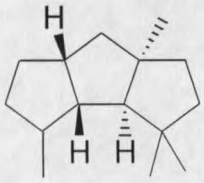


Figure 2. Retigeranic Acid

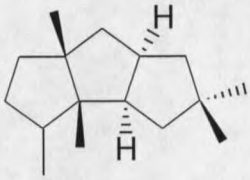
Linear triquinanes favor the *cis,anti,cis*-ring fusion, which is overwhelmingly preferred (thermodynamically). Among the linear triquinanes, only four different skeletal types exist (Figure 3). These skeletal types only differ



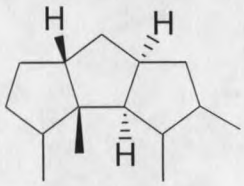
Hirsutane



Capnellane



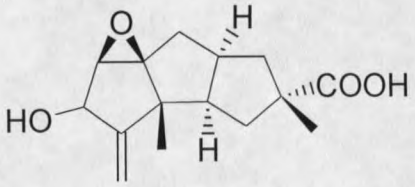
Ceratopicane



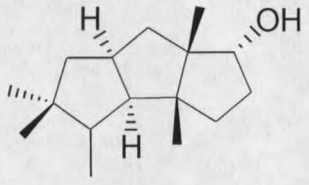
Pleurotellane

Figure 3. Linear Triquinane Skeletal Types

in the location of the four carbon substituents and quaternary carbon centers. The difficult task in linear triquinane synthesis has been the rapid formation of five-membered rings. Numerous synthetic strategies for cyclopentannulation have been developed, which allow for the stereochemical control of the ring junction (*cis,anti,cis*-stereochemistry). The linear triquinane Hirsutic acid-C was isolated from Basidomycete *Stereum hirsutum* (Figure 4).[7] It was the first triquinane natural product to be isolated and characterized through spectroscopy and x-ray crystallography.[8] Ceratopicanol is the only member of the ceratopicane skeletal type, isolated from the fungus *Ceratoystis piceae* in 1988 (Figure 4).[9] The two quaternary bridgehead carbons and five stereocenters make ceratopicanol quite a structurally intriguing molecule.



Hirsutic acid-C



Ceratopicanol

Figure 4. Linear Triquinanes

Among the natural products bearing an angular triquinane skeleton, only four different skeletal types are known (Figure 5). Classification within the

angular triquinane family is based on the arrangement of the four carbon substituents on the tricyclo[6.3.0.0]undecane core. Difficulty encountered in the synthesis of angular triquinanes is primarily due to installation of methyl groups and quaternary carbon centers as well as stereocontrol of the remote secondary methyl group.

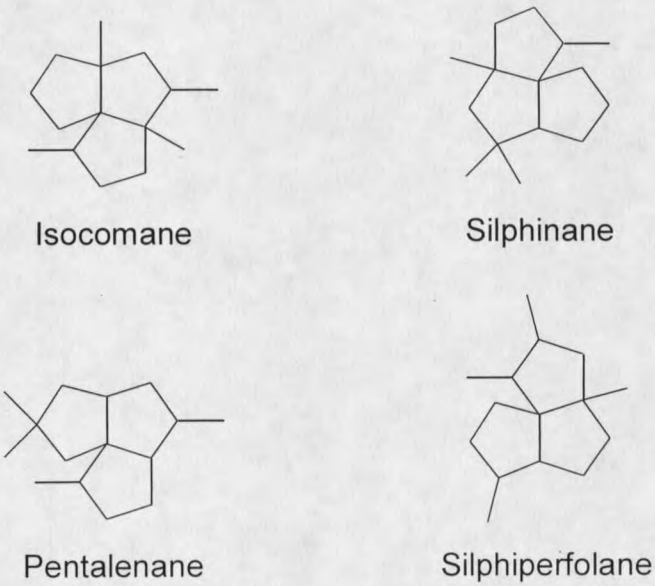
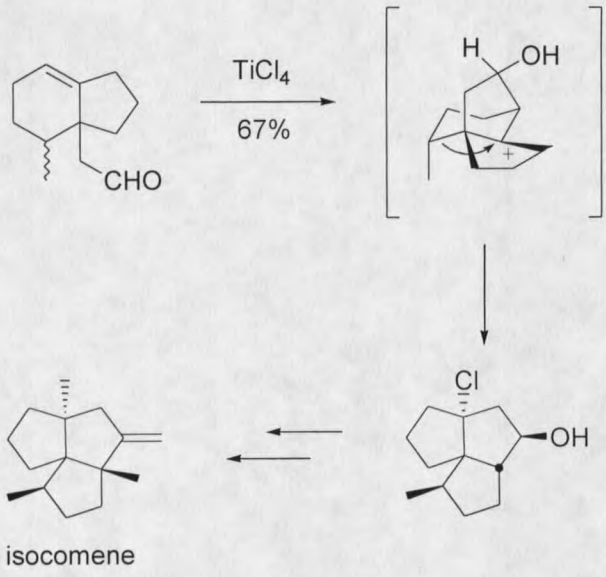


Figure 5. Angular Triquinane Skeletal Types

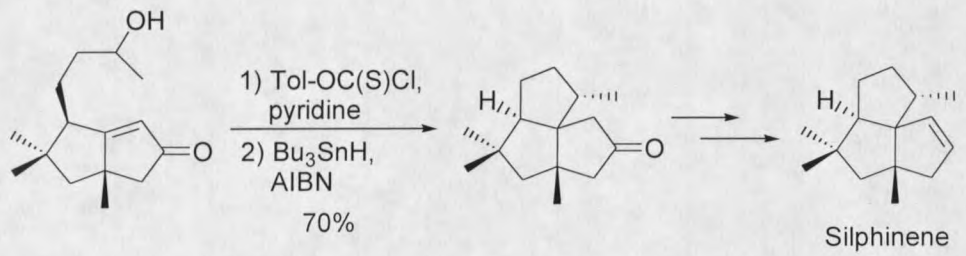
Isocomanes have been isolated from *Isocoma wrightii* and display three contiguous quaternary centers, which contain two angular methyl groups. Isocomene was the first angular triquinane to be isolated and characterized.[10] Several syntheses have followed its discovery. Kennedy and co-workers[11] have

employed a $TiCl_4$-promoted Prins reaction and subsequent carbonium ion-mediated ring contraction for installation of the tricyclic core (Scheme 1). Further elaboration completed the synthesis of isocomene.



Scheme 1

The angular triquinane silphinene, of the silphinane family, was isolated from the plant *Silphuim perfoliatum* by Bohhlmamn and co-workers.[12] In the past, its synthesis has aroused significant interest. Nagarajan and Rao[13] utilized an intramolecular radical cyclization as a key step in the synthesis of silphinene (Scheme 2).



Scheme 2

Pentalenic acid **1**, pentalenene **2**, and pentalenic acid glucuron **3** were isolated together with pentalenolactone from the fermentation broth of *Streptomyces* sp. in 1978 (Figure 6).[14] The angular triquinanes **1**, **2**, and **3** are biosynthetically related to the antibiotic, pentalenolactone, which has displayed antibiotic activity against fungi and bacteria.[15] Intensive efforts have been directed toward the synthesis of these compounds and several synthetic approaches have appeared in the literature.[1,3]

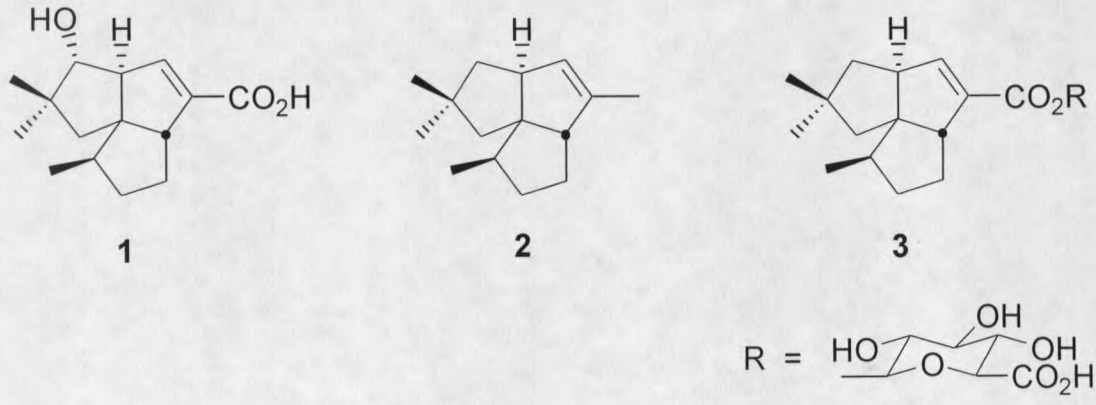
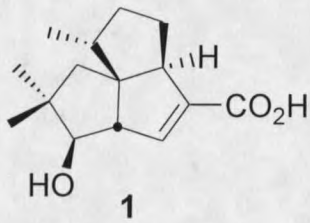


Figure 6. Pentalenane Family

CHAPTER 2

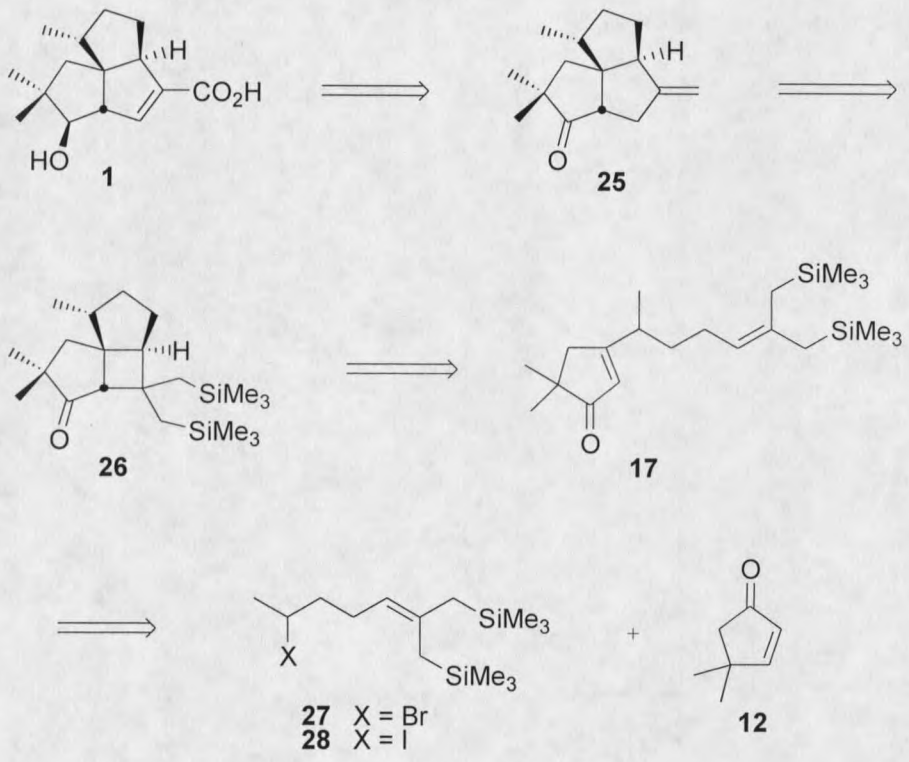
BACKGROUND



1

Interest in pentalenic acid **1** has resulted from its demonstrated role in the biosynthesis of the antibiotic, pentalenolactone.[16] Additional interest in pentalenic acid **1** has resulted from the fact that it is a somewhat structurally intriguing molecule. Pentalenic acid **1** displays a tricyclo[6.3.0.0]undecane skeleton with five stereocenters. The skeletal framework contains a quaternary carbon center as part of four contiguous stereocenters.

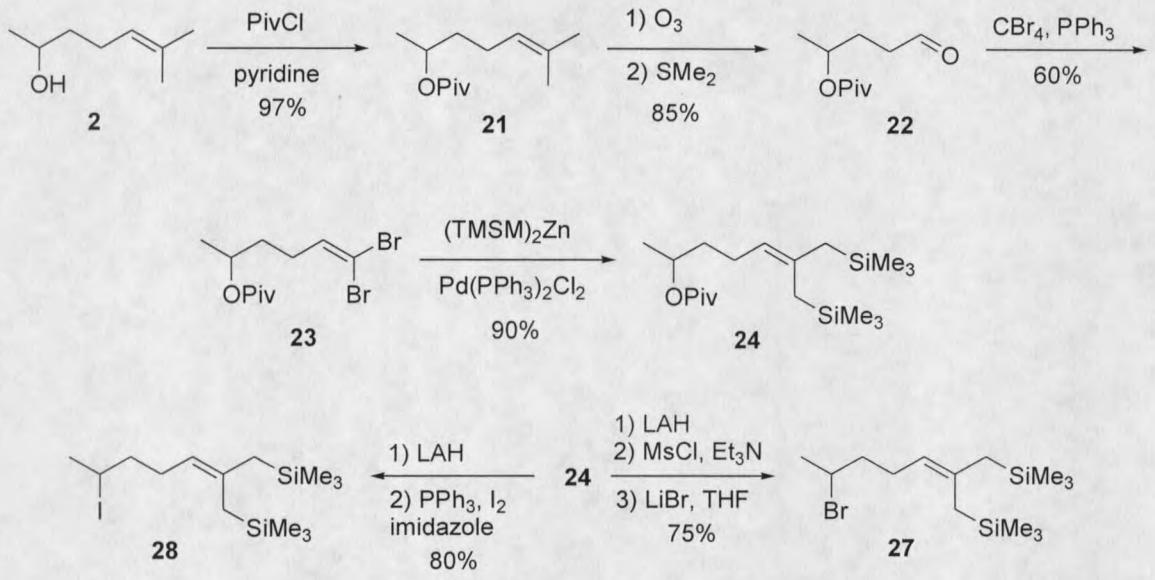
Initial retrosynthetic analysis of the target revealed that pentalenic acid **1** could be obtained through an oxovanadium catalyzed fragmentation/cyclization sequence from the tricyclic cyclobutane **26** (Scheme 3). Utilization of a [2+2] photocycloaddition of photosubstrate **17** should secure the desired tricyclic cyclobutane **26**. The synthesis of the photocyclization precursor **17** could then be achieved by coupling of the halides **27** or **28** with 4,4-dimethyl-cyclopent-2-enone **12**.



Scheme 3

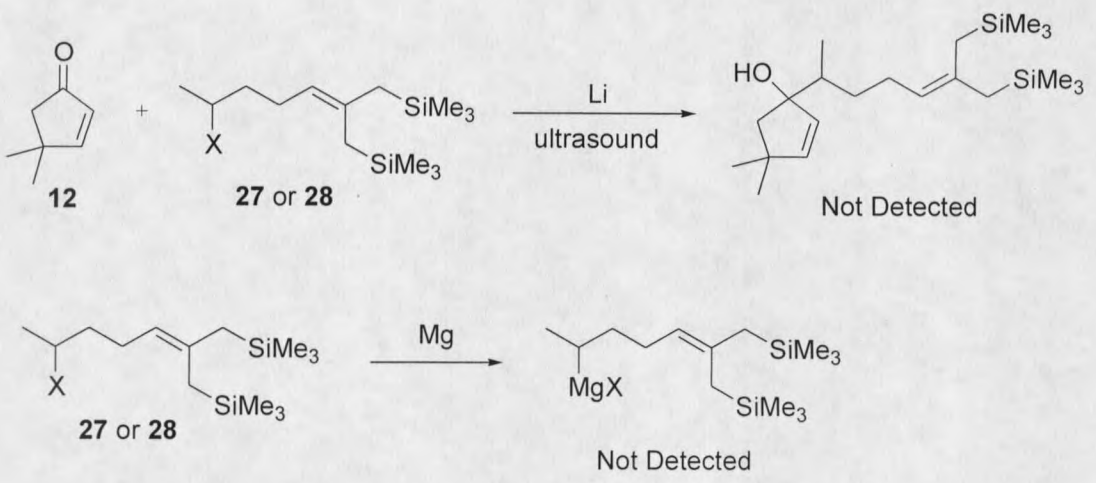
The preparation of halides **27** and **28** were accomplished in seven and six steps, respectively (Scheme 4). Alcohol **2** was prepared by sodium borohydride reduction of 6-methyl-5-hepten-2-one. Subsequent protection of the alcohol **2** was accomplished as the pivalate ester **21**. Ozonolysis of **21,** followed by treatment with dimethyl sulfide afforded the aldehyde **22**. Exposure of **22** to carbon tetrabromide and triphenyl phosphine furnished the dibromo olefin **23**.

Palladium catalyzed cross coupling of **23** with $(TMSM)_2Zn$ secured the allyl bis(silane) **24**. The halides **27** and **28** were then obtained by deprotection and subsequent halogenation of **24**.



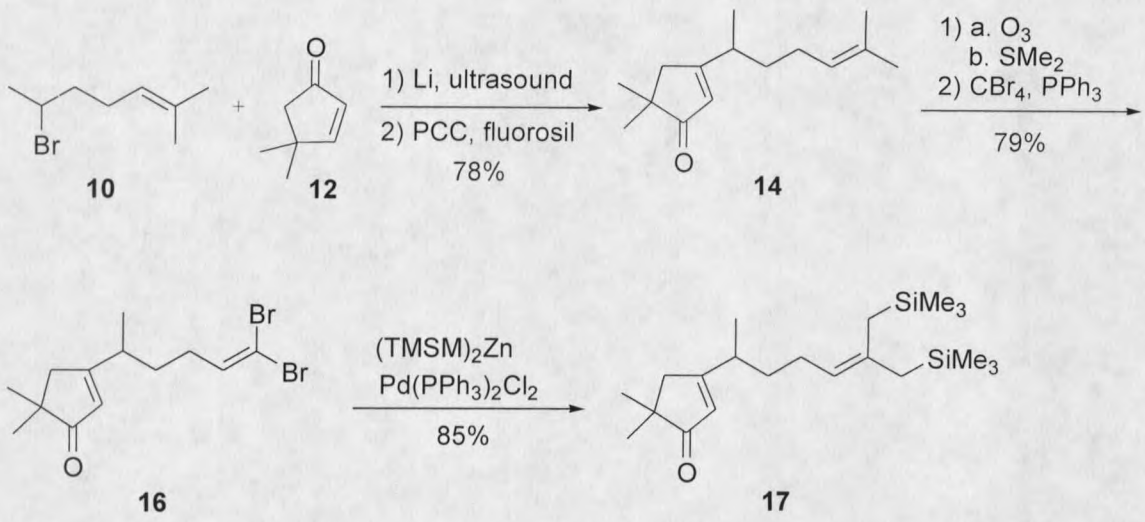
Scheme 4

Several attempts to couple enone **12** with **27** or **28**, via 1,2-addition, were unsuccessful (Scheme 5). It was realized that the allyl bis(silane) functionality would not tolerate the ultrasonic irradiation conditions. Ultrasonic irradiation[17] of a mixture of enone **12**, bromide **27**, and lithium in diethyl ether resulted in destruction of starting materials. Efforts to prepare the corresponding Grignard reagents from **27** or **28** were also unsuccessful, yielding desilylated material.



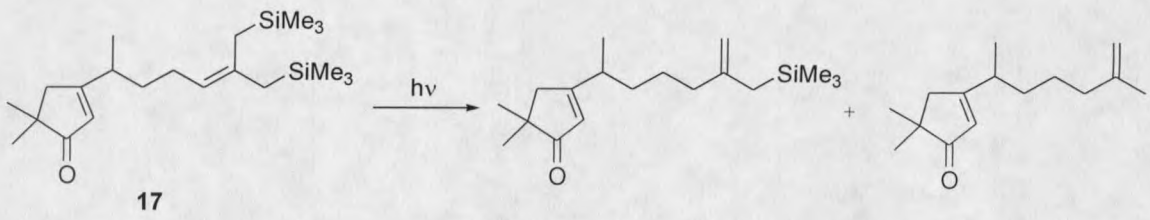
Scheme 5

Alternatively, another synthetic route was envisaged for the construction of the photocyclization precursor **17** (Scheme 6). Coupling of the bromide **10** with enone **12** followed by oxidative rearrangement by the action of pyridinium chlorochromate and florisil furnished the transposed enone **14**.[18] Exposure of the aldehyde **15** obtained from ozonolysis of **14** to carbon tetrabromide and triphenyl phosphine provided the dibromo olefin **16**. Final coupling of **16** with $(TMSM)_2Zn$, utilizing the procedures developed by Kercher and Livinghouse[19] yielded the photocyclization precursor **17**.



Scheme 6

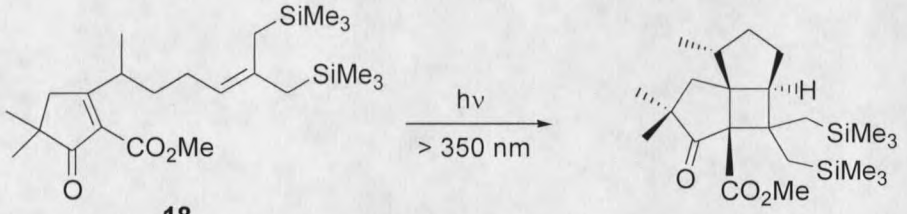
Photocyclization precursor **17** was irradiated in degassed benzene, methylene chloride, acetonitrile, and hexane (Scheme 7). Unfortunately, the desired [2+2] photocycloaddition was not successful, leading to either no reaction or desilylation of the starting material. Furthermore, efforts to induce the [2+2] photocycloaddition by the inclusion of CuOTf were undertaken. In order to increase the reactivity of the alkenes, CuOTf was added to solutions of **17** in benzene or methylene chloride, which resulted in desilylation of **17**.



17

Scheme 7

It has been shown that the presence of a α-ester on cyclopentenones sufficiently activates the enone toward [2+2] photocycloaddition.[20] The introduction of ester functionality, as in **18**, should facilitate photocyclization to yield **19** (Scheme 8). Therefore, preparation of the α-substituted enone **18** should commence in order to facilitate progress towards the synthesis of (±) pentalenic acid **1**.



18 **19**

Scheme 8

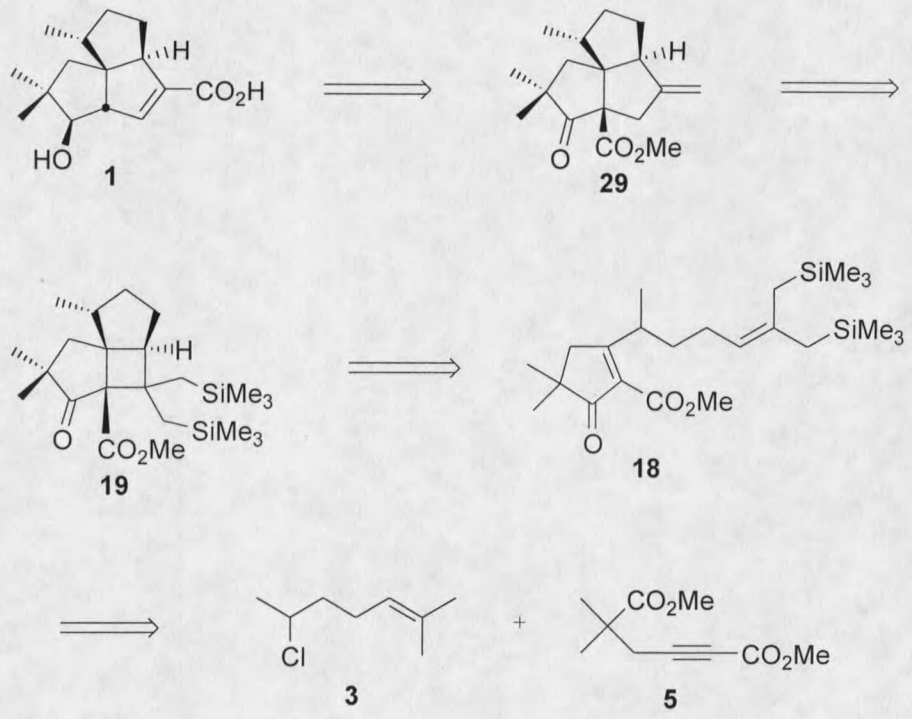
CHAPTER 3

RESULTS AND DISCUSSION

Attempted Synthesis of (±) Pentalenic Acid

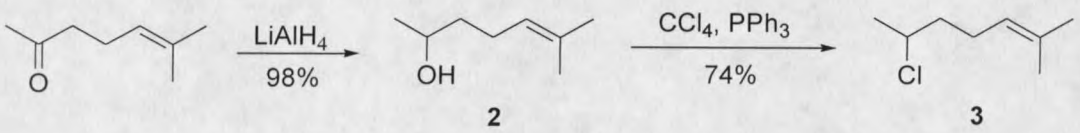
Research described herein is directed toward the synthesis of pentalenic acid **1**. Several research groups have previously synthesized pentalenic acid **1**.[18,21,22] In contrast, the present attempted synthesis features a 2-propylidene-1,3-bis(silane) [2+2] photocycloaddition to provide a tricyclic cyclobutane **19**. Successive fragmentation/cyclization can then be accomplished through the use of an oxovanadium reagent to establish the core 5-5-5 ring system of pentalenic acid **1**.

It was envisaged that pentalenic acid **1** could be prepared from the tricyclic intermediate **29** (Scheme 9). Elaboration of the exocyclic alkene, decarbonylation of the methyl ester, and reduction of the ketone function should provide **1**. The tricyclic intermediate **29** can be obtained by a (TFEO)$VOCl_2$ catalyzed fragmentation/cyclization sequence of the tricyclic cyclobutane **19**. A [2+2] photocycloaddition of diene **18** can be utilized to provide **19**. Preparation of the photocyclization precursor **18** is possible by conjugate addition-cycloacylation of fragments **3** and **5**.



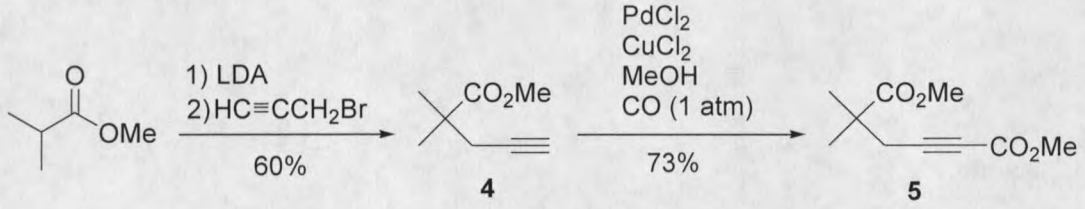
Scheme 9

Synthesis of the chloride **3** was accomplished in a straightforward manner (Scheme 10). Alcohol **2** was prepared by lithium aluminum hydride reduction of 6-methyl-5-hepten-one. Halogenation of the alcohol **2** was accomplished by treatment with carbon tetrachloride and triphenyl phosphine to provide the chloride **3**.



Scheme 10

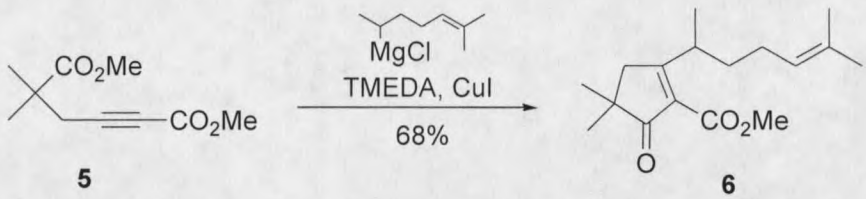
Acetylenic diester **5** was prepared in two steps from the commercially available methyl isobutyrate (Scheme 11). Treatment of the lithium enolate of methyl isobutyrate with propargyl bromide furnished the acetylenic ester **4**. Oxidative carbonylation of **4** by the method of Tsuji[23] yielded the acetylenic diester **5** in 66% overall yield.



Scheme 11

Treatment of the acetylenic diester **5** with the Grignard reagent prepared from chloride **3** in the presence of TMEDA and Cu(I) iodide resulted in the production of diene **6** (Scheme 12). This particular reaction was developed by Crimmins and co-workers[22] with a reported yield of 48%. It was discovered in our laboratory that preparation of the Grignard reagent was critical for the

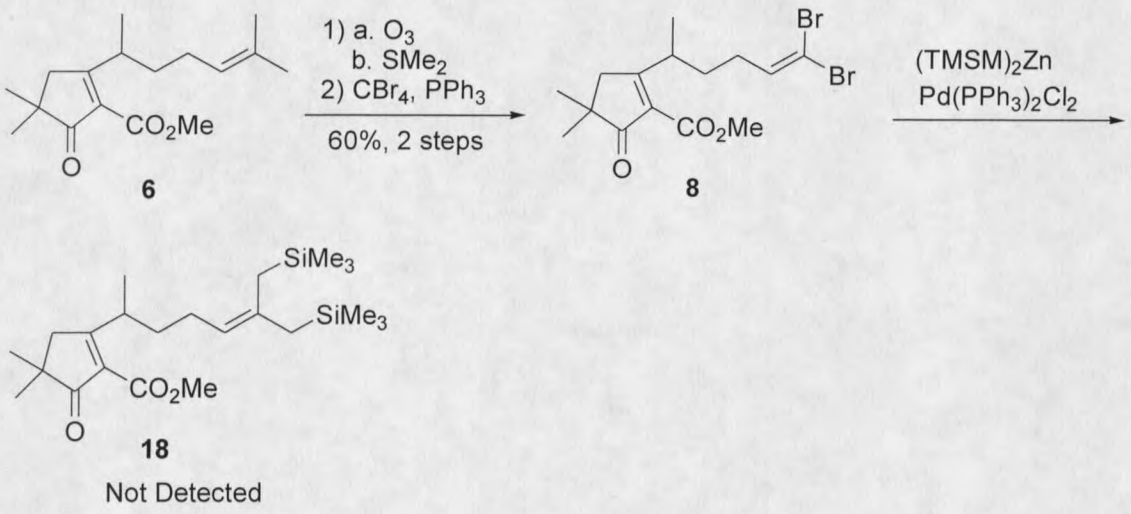
success of the conjugate addition-cycloacylation reaction. The Grignard reagent must be allowed to stand for at least 24 h, at room temp, whereupon MgX_2 precipitates. Addition of the supernatant to a mixture of Cu(I) iodide and TMEDA, followed by addition of the acetylenic diester **5** consistently resulted in ~ 20% increase in yield.



5 **6**

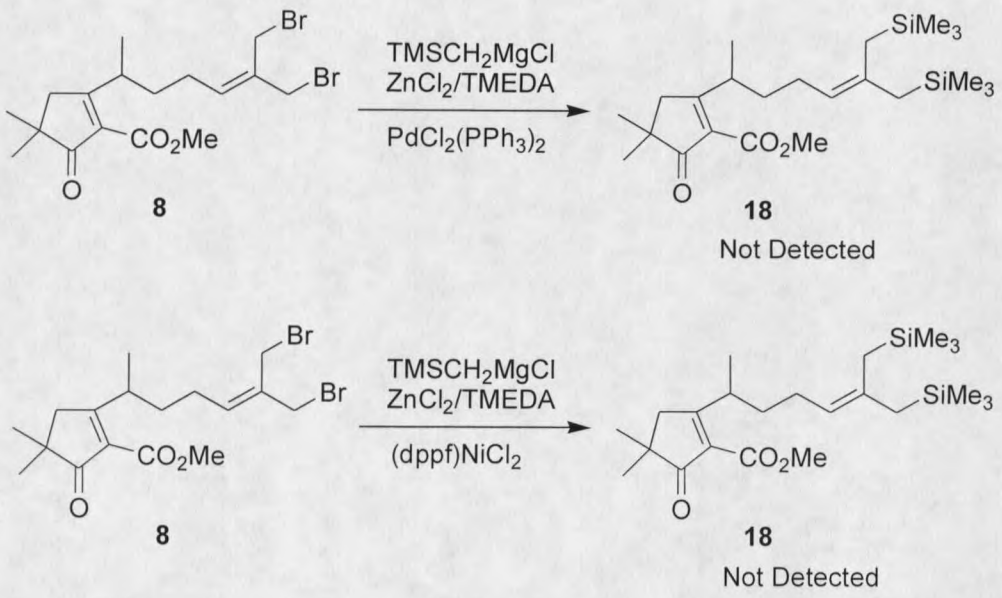
Scheme 12

Ozonolysis of diene **6**, followed by reductive workup with dimethyl sulfide afforded the aldehyde **7** (Scheme 13). Exposure of the aldehyde **7** to carbon tetrabromide and triphenyl phosphine provided the dibromo olefin **8**. The coupling of **8** with $(TMSM)_2Zn$ proved troublesome. Utilization of the procedures developed by Kercher and Livinghouse[19] for the installation of the allyl bis(silane) moiety were unsuccessful.



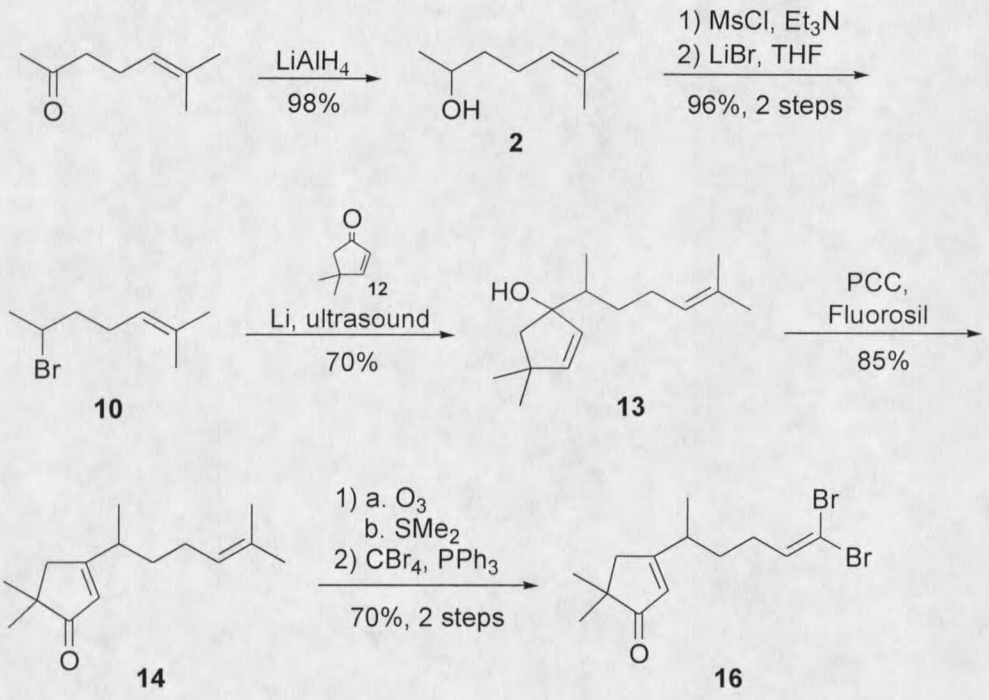
Scheme 13

Confronted with the inability to prepare the photocyclization precursor **18**, we decided to investigate the reaction reagents (Scheme 14). Initially, it was believed that the $ZnCl_2$/THF solution might be responsible. The use of $ZnCl_2$/TMEDA complex, however, did not facilitate the reaction. The cross coupling was then attempted with a Ni catalyst. Utilization of (dppf)$NiCl_2$ as catalyst failed to yield the desired product **18**. Therefore, it was decided to attempt to install the allyl bis(silane) functionality in the absence of the α-ester.



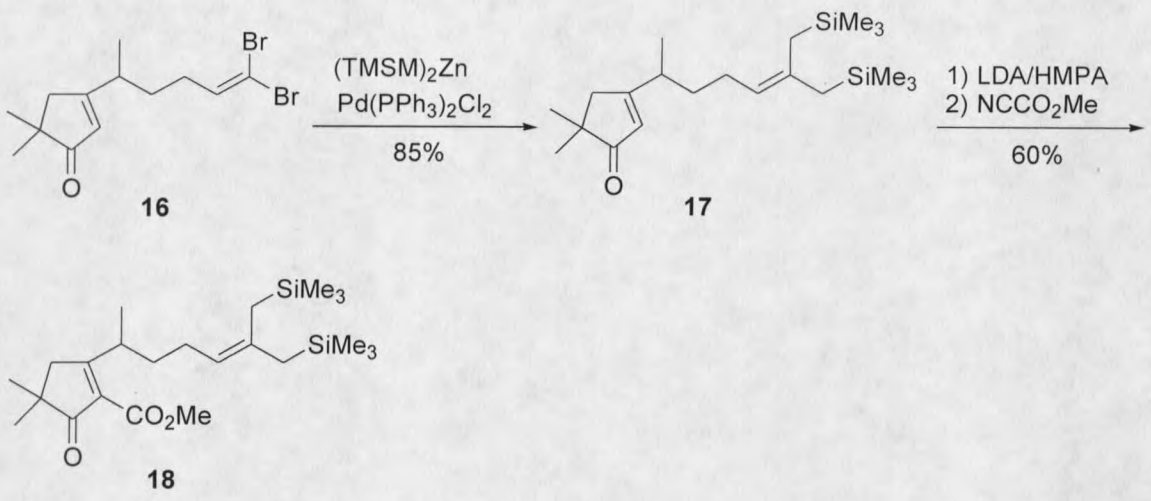
Scheme 14

An alternative synthetic route was realized for the construction of the photocyclization precursor **18**. The synthesis begins with lithium aluminum hydride reduction of 6-methyl-5-hepten-2-one to furnish the alcohol **2** (Scheme 15). Bromide **10** was easily prepared through mesylation and halogentation of **2**. Ultrasound assisted 1,2-addition[17] of **10** with enone **12** in the presence of lithium wire provided the desired allylic alcohol **13**. Oxidative rearrangement of **13** by pryidinium chlorochromate in the presence of florisil yielded the transposed enone **14**.[18] Treatment of the aldehyde **15**, obtained from ozonolysis of **14**, with carbon tetrabromide and triphenyl phosphine produced the dibromo olefin **16**.



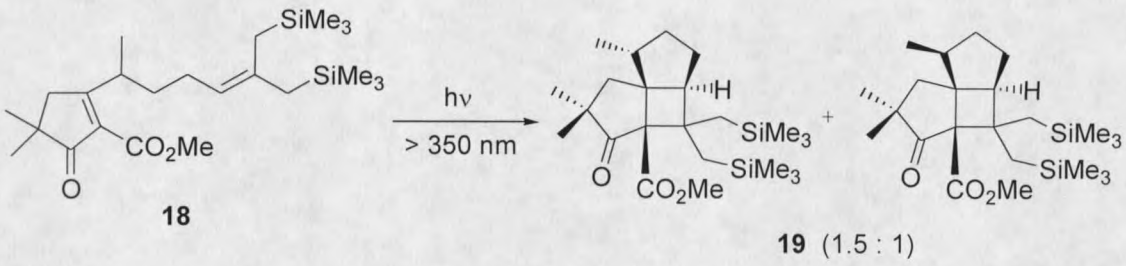
Scheme 15

Although the desired photocyclization precursor **18** was not obtained by previous methods (Scheme 13), the construction of **18** smoothly took place when the allyl bis(silane) was installed prior to the α-ester function. Thus, palladium catalyzed cross coupling of **16** with $(TMSM)_2Zn$ secured the allyl bis(silane) **17** in 85% yield (Scheme 16). The photocyclization precursor **18** was then obtained by acylation of the lithium enolate of **17** with methyl cyanoformate.[24]



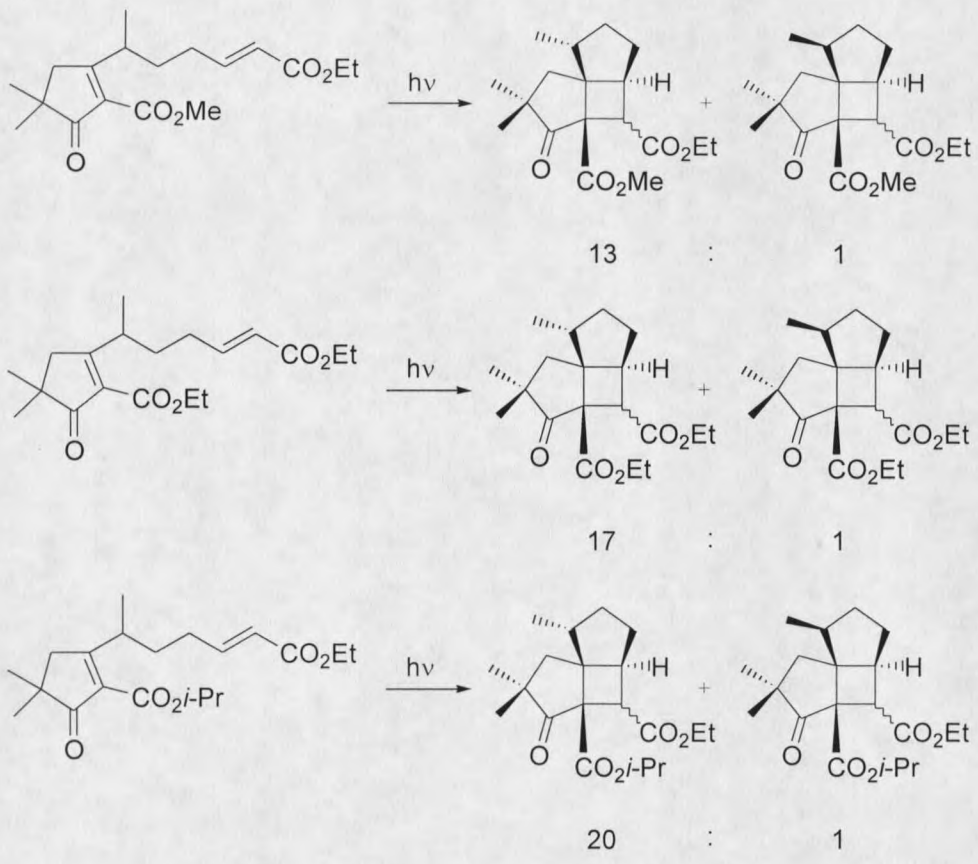
Scheme 16

Since the photocyclization precursor **18** was in hand, the stage was set for the key [2+2] photocycloaddition reaction. Irradiation of **18** in hexane through a uranium glass filter (λ > 350 nm) produced the photoadduct **19** as a 1.5:1 mixture (Scheme 17). The photoadduct **19** has not been fully characterized. ^{1}H NMR spectra have been difficult to interpret, due to the inseparable mixture of diastereomers. However, high resolution mass spectra and analytical thin layer chromatography suggest formation of the desired tricyclic cyclobutane **19**.



Scheme 17

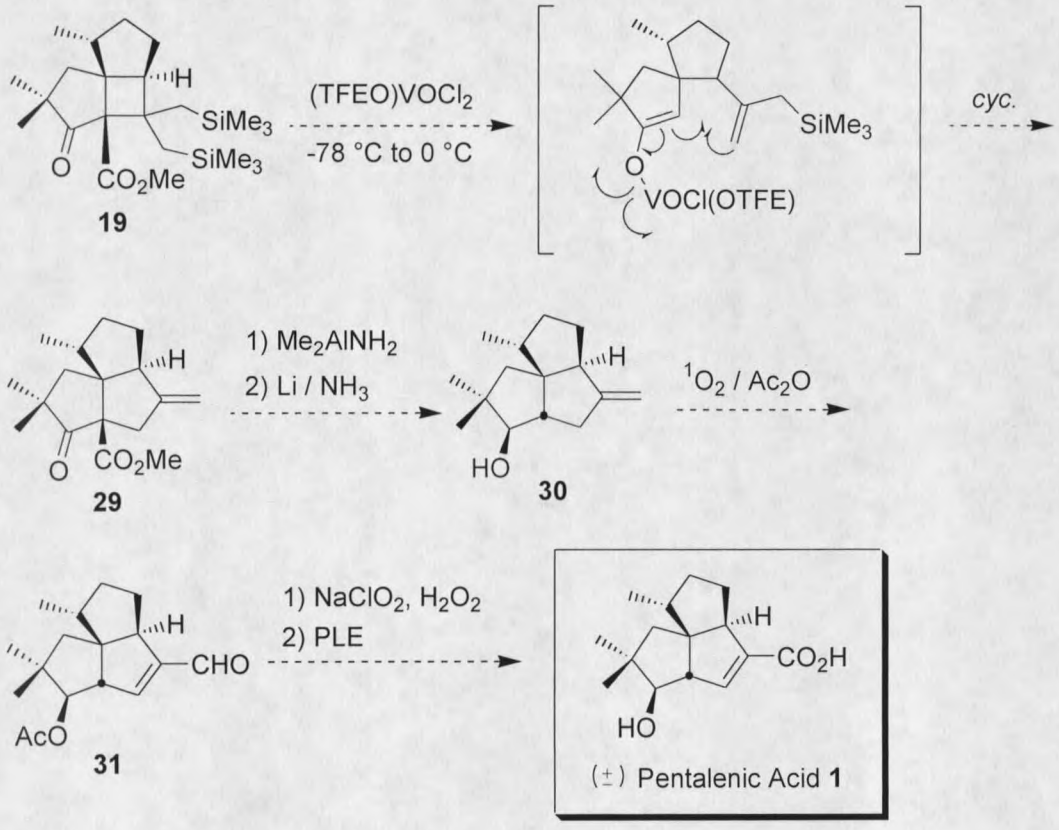
The stereoselectivity in the photocycloaddition is believed to result from a steric interaction between the secondary methyl and the α-ester during cyclobutane ring formation. Crimmins and co-workers[22] have presented evidence in a similar system to support this hypothesis. The stereoselectivity in the photocycloaddition can be improved by increasing the size of the α-ester (Scheme 18). Replacement of the methyl ester with an ethyl ester increases selectivity to 17:1, installation of an isopropyl ester increases selectivity even further to 20:1.



Scheme 18

The results from the photocycloaddition are discouraging, we had hoped for much greater stereoselectivity. If it is possible to increase the stereo-selectivity, as previously stated, then synthetic studies toward pentalenic acid **1** should progress. The completion of the synthesis is proposed as outlined (Scheme 19). Reaction of the tricyclic cyclobutane **19** with (TFEO)$VOCl_2$ should proceed through the proposed intermediate by mono-desilylation and fragmentation of the cyclobutane ring, upon coordination to the oxovanadium

species. Subsequent cyclization by a radical cascade followed by desilylation provides **29**, the tricyclic core of pentalenic acid **1**. Treatment of **29** with dimethyl aluminum amine and then Li/NH_3 reduction allows for the removal of the ester and reduction of the ketone functionality. Oxidation of **30** with singlet oxygen and exposure of **31** to sodium chlorite and hydrogen peroxide followed by deprotection should yield **1**.



Scheme 19

CHAPTER 4

SUMMARY

The formation of the tricyclic core of the natural product, pentalenic acid has been achieved by utilization of an intramolecular [2+2] photocycloaddition. Investigations into the stereoselectivity of the process should prove useful in the progress toward pentalenic acid. The discovery of conditions needed to optimize the conjugate addition-cycloacylation reaction resulted in the production of highly functionalized cyclopentenones in good yield. Further studies into the mechanism of the reaction may allow even greater increases in yield. It was realized that the palladium catalyzed cross coupling of β-ketoesters with $(TMSM)_2Zn$ proved unsuccessful. However, removal of the ester function allowed the coupling to proceed smoothly. It is hoped that the aforementioned contributions are useful for future synthetic studies directed toward the synthesis of pentalenic acid.

CHAPTER 5

EXPERIMENTAL

General Methods

^{1}H NMR and ^{13}C NMR spectra were performed with a Bruker AL-300 or 250 MHz spectrometer. ^{1}H NMR chemical shifts are reported as δ values in ppm relative to the residual proton signal of $CDCl_3$ (δ 7.27). ^{13}C NMR chemical shifts are reported as δ values in ppm relative to the residual proton signal of $CDCl_3$ (δ 77.23). ^{1}H NMR peaks refer to multiplicities which are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), app d (apparent doublet), app t (apparent triplet), and app q (apparent quartet. Infrared spectra were recorded with a Perkin Elmer 1800 FTIR.

Gas chromatography was performed on a Varian Model 3700 Gas Chromatograph equipped with an Alltec Econocap SE 54 column (15 m, 0.54 mm id) and flame ionization detector. Low resolution mass spectra were recorded on a Hewlett Packard 5890A Gas Chromatograph equipped with a Hewlett Packard 5970 Mass Selective Detector. Analytical thin layer chromatography (TLC) was performed on silica gel POLYGRAM® SIL G/UV_{254} plates supplied by Alltec. Visualization of TLC plates were effected by either: 1) ultraviolet illumination (254 nm), 2) $KMnO_4$ oxidation, or 3) anisaldehyde

derivitization. $KMnO_4$ indicator (TLC) was prepared with Na_2CO_3 (12.5 g), $KMnO_4$ (2.5 g), and H_2O (500 mL). Anisaldehyde indicator (TLC) was prepared with *p*-anisaldehyde (5 mL), ethanol (95 mL), acetic acid (3.5 mL), and H_2SO_4 (0.5 mL). Column chromatography was performed using Scientific Adsorbents Inc. silica gel (32-63 μm particle size, 60 Å pore size). Solvent systems used for elution are reported in % volume/volume.

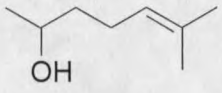
Solvents used for reactions were distilled immediately prior to use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Diisopropylamine, hexamethylphosphoramide (HMPA), hexane, tetramethylethylenediamine (TMEDA), dichloromethane, triethylamine, and dimethylformamide (DMF) were distilled under nitrogen or argon from calcium hydride. Methanol was distilled from $Mg(OCH_3)_2$ under argon. Carbontetrachloride (CCl_4) was distilled under argon from phosphorous pentoxide (P_2O_5).

The molarities of organolithium reagents were determined by direct titration using *N*-pivaloyl-o-toulidine. The molarities of organomagnesium (Grignard) reagents were determined by titration of a standard solution of 2-butanol in toluene using 1,10-phenanthroline as an indicator.

All reactions were carried out in oven-dried vessels under argon or nitrogen, unless otherwise indicated. Reaction mixtures were magnetically stirred. Temperatures reported are bath temperatures. Solvent concentrations were performed under reduced pressure with a Büchi (RE-111) rotary

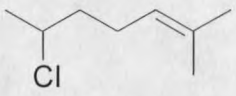
evaporator.

6-Methyl-hept-5-en-2-ol (**2**)



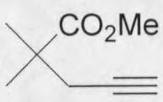
To a 250 mL round-bottomed flask containing Et_2O (94 mL) was added $LiAlH_4$ (2.90 g, 75.0 mmol) at 0 °C. A solution of 6-methyl-5-hepten-2-one (10.0 g, 79.0 mmol) in Et_2O (5 mL) was added dropwise, via an addition funnel, and the mixture was stirred for 1 h at 0 °C under argon. The mixture was then successively treated with 4 mL H_2O, 4 mL NaOH, and 4 mL H_2O. The resulting solution was filtered over a pad of celite and the filtrate was concentrated in vacuo to afford the alcohol **2** as a clear liquid (9.85 g, 97 %): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.14 (app t, 1 H, J = 5.9 Hz), 3.78 (br, 1 H), 2.05 (m, 2 H), 1.68 (s, 3 H), 1.60 (s, 3 H), 1.46 (m, 2 H), 1.15 (d, 3 H, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 132.3 (C), 124.3 (CH), 68.2 (CH), 39.4 (CH_2), 25.9 (CH_2), 24.7 (CH_3), 23.7 (CH_3), 17.9 (CH_3); FTIR (neat) 3354, 2967, 2925, 2728, 1672, 1450, 1376, 1128, 1073 cm^{-1}; LRMS *m/z* 128 (M^+); R_f 0.15 (10% ethyl acetate/hexanes).

6-Chloro-2-methyl-hept-2-ene (**3**)



To a 250 mL round-bottomed flask containing the alcohol **2** (13.69 g, 0.107 mol) in CCl_4 (138 mL, 1.43 mol) was added Ph_3P (34.10 g, 0.130 mol). The mixture was heated to reflux and held for 24 h. The reaction mixture was cooled to 0 °C, filtered over a pad of silica gel, and concentrated in vacuo. The residue was purified by column chromatography (0-5% ethyl acetate/hexanes) to furnish the chloride **3** as a clear liquid (10.10 g, 75%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.09 (m, 1 H), 4.03 (m, 1 H), 2.15 (q, 2 H, J = 7.2 Hz), 1.74 (m, 2 H), 1.70 (s, 3 H), 1.64 (s, 3 H), 1.51 (d, 3 H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 132.9 (C), 123.2 (CH), 58.5 (CH), 40.6 (CH_2), 25.9 (CH_2), 25.6 (CH_3), 25.4 (CH_3), 17.9 (CH_3); R_f 0.69 (10% ethyl acetate/hexanes).

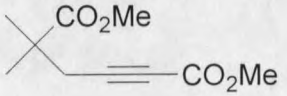
2,2-Dimethyl-pent-4-ynoic acid methyl ester (**4**)[25]



To a 3-necked round-bottomed flask containing diisopropylamine (30.2

mL, 0.216 mol) in THF (200 mL) at 0 °C was added *n*-BuLi (145 mL of a 1.49 M solution, 0.216 mol), dropwise. The solution was stirred for 15 min and cooled to -78 °C. A solution of methyl isobutyrate in THF (20 mL) was added, dropwise. The solution was stirred for 1 h at -78 °C, and then a solution of propargyl bromide in HMPA (37 mL) was added, dropwise. After stirring for 1 h at -78 °C, the mixture was quenched with saturated aq. NH_4Cl and warmed to room temperature. The solvent was removed in vacuo and the resulting residue was dissolved in Et_2O. The ethereal layer was washed with H_2O (4X), dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude residue was distilled at reduced pressure (12 torr, bp 48-50 °C) to furnish the acetylenic ester **4** as a clear liquid (16.46 g, 60%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.64 (s, 3 H), 2.38 (d, 2 H, J = 2.6 Hz), 1.96 (t, 1 H, J = 2.6 Hz), 1.22 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 177.1 (C), 81.0 (C), 70.6 (CH), 52.1 (CH_3), 42.1 (C), 29.6 (CH_2), 24.5 (($CH_3)_2$); R_f 0.57 (20% ethyl acetate/hexanes).

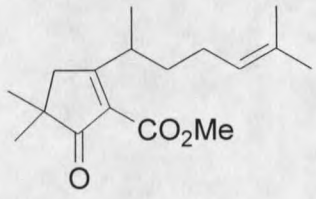
5,5-Dimethyl-hex-2-ynedioic acid dimethyl ester (**5**)[23]



To a 1 L round-bottomed flask was added NaOAc (13.45 g, 0.164 mol),

$CuCl_2$ (22.12 g, 0.164 mol), and $PdCl_2$ (122 mg, 0.69 mmol). The reaction vessel was degassed (carbon monoxide) and methanol (345 mL) was added. To the mixture was added the acetylenic ester **4** (11.48 g, 0.082 mol). The mixture was stirred at room temperature, under an atmosphere of carbon monoxide, for 6 h. The solvent was removed in vacuo and the residue was dissolved in Et_2O. The ethereal layer was washed with H_2O, 50% aq. NH_4OH, and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude residue was purified by bulb-to-bulb distillation (0.5 torr, bp 81-82 °C) to provide the acetylenic diester **5** as a clear liquid (11.89 g, 73%): ^1H NMR ($CDCl_3$, 300 MHz) δ 3.72 (s, 3 H), 3.67 (s, 3 H), 2.57 (s, 2 H), 1.26 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.5 (C), 154.0 (C), 86.2 (C), 74.9 (C), 52.7 (CH_3), 52.3 (CH_3), 42.1 (C), 29.7 (CH_2), 24.8 (CH_3); R_f 0.38 (20% ethyl acetate/hexanes).

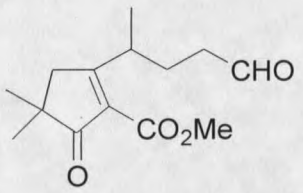
2-(1,5-Dimethyl-hex-4-enyl)-4,4-dimethyl-5-oxo-cyclopent-1-enecarboxylic acid methyl ester (**6**)



The Grignard reagent (allowed to stand for 24 h; MgX_2 ppt.) prepared from

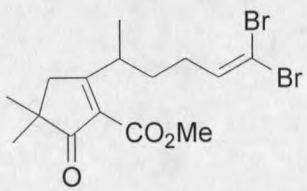
chloride **3** (1.00 g, 6.82 mmol), magnesium turnings (340 mg, 13.98 mmol), and THF (10 mL) was added to a mixture of CuI (884 mg, 4.64 mmol) and TMEDA (792 mg, 6.82 mmol) in THF (30 mL) at -78 °C. After the mixture was stirred for 1 h at -78 °C, the acetylenic diester **5** (919 mg, 4.64 mmol) in THF (2 ml) was added slowly. The mixture was stirred at -78 °C for 1 h and allowed to warm to room temperature, overnight. The mixture was poured into 10% HCl and diluted with Et_2O. The ethereal layer was washed with saturated aq. $NaHCO_3$ (3X) and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude residue was purified by column chromatography (5-10% ethyl acetate/hexanes) to afford **6** as a clear liquid (876 mg, 68%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.05 (t, 1 H, *J* = 7.2 Hz), 4.94 (m, 1 H), 3.69 (s, 3 H), 2.59 (s, 2H), 2.01 (q, 2H, *J* = 7.4 Hz), 1.7-1.5 (m, 2 H), 1.66 (s, 3 H), 1.58 (s, 3 H), 1.30 (s, 6 H), 1.24 (d, 3 H, *J* = 6.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.5 (C), 153.3 (C), 132.4 (C), 123.2 (CH), 85.2 (C), 75.5 (C), 72.7 (C), 52.2 (CH_3), 42.1 (CH), 35.8 (CH_2), 29.6 (CH_2), 25.7 (CH_2), 24.7 (C), 24.0 (CH_3), 19.9 (CH_3), 17.6 (CH_3); LRMS *m/z* 279 (M^+); R_f 0.33 (10% ethyl acetate/hexanes).

4,4-Dimethyl-2-(1-methyl-4-oxo-butyl)-5-oxo-cyclopent-1-enecarboxylic acid methyl ester (**7**)



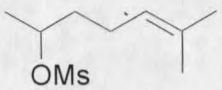
A solution of the **6** (1.88 g, 6.75 mmol) in CH_2Cl_2 (34 mL) was cooled to -78 °C and bubbled with ozone for 15 min. The reaction vessel was purged with argon and then dimethyl sulfide (1.1 mL, 14.8 mmol) was added. After stirring at -78 °C for 15 min, the mixture was allowed to warm to room temperature and stirred overnight. The mixture was washed with H_2O (2X) and the organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo to afford the crude aldehyde **7** as a yellow liquid.

2-(5,5-Dibromo-1-methyl-pent-4-enyl)-4,4-dimethyl-5-oxo-cyclopent-1-enecarboxylic acid methyl ester (**8**)



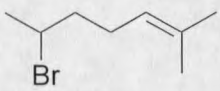
To a 100 mL round bottom flask was added CBr_4 (4.47 g, 13.5 mmol) and CH_2Cl_2 (21 mL). The solution was cooled to 0 °C and PPh_3 (7.07 g, 27.0 mmol) in CH_2Cl_2 (14 mL) was added, dropwise. The aldehyde **7** (1.70 g, 6.75 mmol) was added to the mixture. The reaction mixture was stirred at 0 °C for 0.5 h, under argon. The solvent was removed in vacuo and the residue was triturated with Et_2O, followed by filtration over a pad of silica gel. The filtrate was concentrated and the crude residue was purified by column chromatography (5-10% ethyl acetate/hexanes) to furnish the dibromo olefin **8** as a pale yellow liquid (1.65 g, 60%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.38 (t, 1 H, J = 7.3 Hz), 4.93 (m, 1 H), 3.69 (s, 3 H), 2.59 (s, 2 H), 2.14 (q, 2 H, J = 7.5 Hz), 1.8-1.6 (m, 2 H), 1.29 (s, 6 H), 1.26 (d, 3 H, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.4 (C), 153.1 (C), 137.2 (C), 89.7 (CH), 85.7 (C), 75.2 (C), 71.9 (C), 52.2 (CH_3), 42.0 (CH), 33.5 (CH_2), 29.5 (CH_2), 29.0 (CH_2), 24.7 (CH_3), 19.7 (CH_3); FTIR (neat) 2977, 2950, 2875, 2320, 2237, 1733, 1709, 1625, 1470, 1434, 1387, 1316, 1255, 1200, 1136, 1069, 845 cm^{-1}; LRMS *m/z* 393 $(M\text{-}CH_3)^+$; R_f 0.18 (10% ethyl acetate/hexanes).

1,5-Dimethyl-hex-4-enyl methane sulfonate (**9**)



To a solution of the alcohol **2** (9.78 g, 0.076 mol) and triethylamine (15.9 mL, 0.114 mol) in CH_2Cl_2 was added mesyl chloride (6.50 mL, 0.084 mol), dropwise, over 15 min. The mixture was stirred at 0 °C for 1 h, under argon. The reaction mixture was washed with ice-water (2X), cold 10% HCl (2X), saturated aq. $NaHCO_3$, and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo to afford the crude mesylate **9** as a pale yellow liquid (15.70 g, 99%).

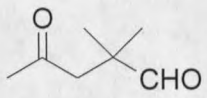
6-Bromo-2-methyl-hept-2-ene (**10**)



To a solution of the mesylate **9** (15.46 g, 0.075 mol) in THF (375 mL) was added lithium bromide (9.76 g, 0.112 mol). The mixture was heated to reflux and held overnight. The reaction mixture was washed with H_2O and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by column chromatography (0-5% ethyl acetate/hexanes) to provide the bromide **10** as a clear liquid (12.98 g, 91%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.04 (m, 1 H), 4.10 (m, 1 H), 2.16 (q, 2 H, J = 7.3 Hz), 1.91-1.75 (m, 2 H), 1.69 (d, 3 H, J = 6.5 Hz), 1.67 (s, 3 H), 1.62 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz)

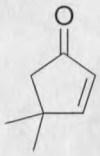
δ 133.0 (C), 123.0 (CH), 51.6 (CH), 41.4 (CH_2), 26.7 (CH_2), 26.6 (CH_3), 25.9 (CH_3), 18.0 (CH_3); R_f 0.67 (10% ethyl acetate/hexanes).

2,2-Dimethyl-4-oxo-pentanal (**11**)[26]



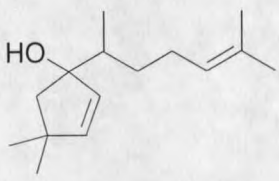
A mixture of CuCl (1.00 g, 10.0 mmol) and $PdCl_2$ (360 mg, 2.0 mmol) in 9% H_2O/DMF (11 mL) was stirred at room temperature for 2 h with O_2 bubbling through the suspension. To the mixture was added 2,2-dimethyl-4-pentenal, the suspension was stirred at room temperature for 40 h with continued bubbling of O_2. The reaction mixture was poured into H_2O and the aqueous phase was extracted with Et_2O (4X). The aqueous phase was then acidified (6M HCl) and extracted with Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to furnish the crude keto-aldehyde **11** (800 mg, 63%): ^1H NMR ($CDCl_3$, 300 MHz) δ 9.54 (s, 1 H), 2.71 (s, 2 H), 2.12 (s, 3 H), 1.11 (s, 6 H).

4,4-Dimethyl-cyclopent-2-enone (**12**)[26]



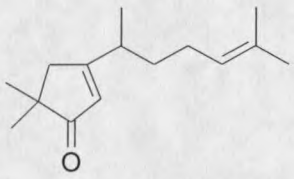
A solution of 5% KOH (24 mL), Et_2O (48 mL), and THF (24 mL) was cooled to 0 °C. The keto-aldehyde **11** (7.24 g, 56.5 mmol) was added and the mixture was heated to reflux and held for 48 h. After cooling to room temperature, NaCl was added and the layers were separated. The aqueous layer was extracted with Et_2O (2X) and the combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude residue was purified by reduced pressure distillation (19 torr, bp 59-60 °C) to afford the cyclopentenone **12** as a clear liquid (4.00 g, 65%): ^1H NMR ($CDCl_3$, 300 MHz) δ 7.45 (d, 1 H, J = 5.5 Hz), 6.00 (d, 1 H, J = 5.5 Hz), 2.25 (s, 2 H), 1.24 (s, 6 H); Rf 0.29 (20% ethyl acetate/hexanes).

1-(1,5-Dimethyl-hex-4-enyl)-4,4-dimethyl-cyclopent-2-enol (**13**)



To a round bottom flask containing lithium wire (24 mg, 4.76 mmol) and Et_2O (2.5 mL) was added a small portion of a mixture of bromide **10** (287 mg, 1.50 mmol) and cyclopentenone **12** (150 mg, 1.36 mmol) in Et_2O (2.5 mL). Ultrasonic irradiation (50 Hz) was initiated and continued throughout the addition, over 30 min. After the addition was complete, the irradiation was continued for 1.5 h. The mixture was cooled to 0 °C and quenched with saturated aq. NH_4Cl. The organic layer was diluted with Et_2O and washed successively with 10% HCl and brine. The ethereal layer was then dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by column chromatography (5-10% ethyl acetate/hexanes) to furnish the allylic alcohol **13** as a clear liquid (211 mg, 70%): ^1H NMR ($CDCl_3$, 300 MHz) δ 5.68 (d, 1H, *J* = 5.5 Hz), 5.55 (m, 1H, *J* = 5.5 Hz), 5.12 (app q, 1H, *J* = 7.0 Hz), 2.11 (br, 2H), 1.93 (m, 1H), 1.85 and 1.80 (s, 0.5 H each), 1.69 (s, 3H), 1.64 (m, 2H), 1.62 (s, 3H), 1.39 (s, 1H), 1.18 (s, 3H), 1.07 (s, 3H), 0.97 and 0.88 (d, 1.5 H each, *J* = 6.8 Hz each); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.8 and 144.7 (C), 132.9 (CH), 131.6 (C), 124.9 (CH), 89.9 and 89.8 (C), 49.9 and 49.5 (CH_2), 44.5 (CH), 41.6 (CH_2), 32.6 and 31.6 (C), 31.0 and 29.2 (CH_3), 26.5 (CH_2), 25.9 (CH_3), 17.9 (CH_3), 15.1 and 14.3 (CH_3); FTIR (neat) 3442, 3034, 2955, 2863, 2728, 1673, 1618, 1461, 1376, 1360, 1140, 1020, 983 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{26}O$ $(M-H_2O)^+$ 204.1878, found 204.1874; R_f 0.33 (20% ethyl acetate/hexanes).

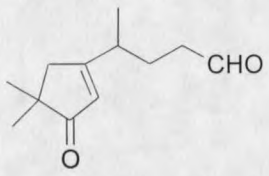
3-(1,5-Dimethyl-hex-4-enyl)-5,5-dimethyl-cyclopent-2-enone (**14**)



To a 25 mL round bottom flask was added pyridinium chlorochromate (582 mg, 2.70 mmol) and florisil (600 mg). The allylic alcohol **13** (300 mg, 1.35 mmol) in CH_2Cl_2 (5 mL) was added and the mixture was stirred at room temperature for 1 h, under argon. The reaction mixture was treated with Et_2O and filtered through a pad of celite. The filtrate was washed with 10% aq. KOH and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by column chromatography (5-10% ethyl acetate/hexanes) to provide the transposed enone **14** as a colorless liquid (250 mg, 85%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.86 (s, 1H), 5.08 (t, 1H, J = 7.0 Hz), 2.56 (m, 1H), 2.45 (s, 2H), 1.96 (q, 2H, J = 7.4 Hz), 1.69 (s, 3H), 1.58 (s, 3H), 1.48 (m, 2H), 1.14 (d, 3H, J = 6.9 Hz), 1.11 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 214.6 (C), 184.2 (C), 132.3 (C), 126.3 (CH), 123.8 (CH), 45.8 (C), 44.0 (CH), 37.0 (CH_2), 35.2 (CH_2), 25.9 (CH_3), 25.8 (CH_2), 25.4 (CH_3), 25.2 (CH_3), 19.0 (CH_3), 17.9 (CH_3); FTIR (neat) 2963, 2925, 2866, 2729, 1706, 1612, 1457, 1432, 1378, 1359, 1269, 1224, 1129, 870 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{24}O$ (M^+) 220.1827, found 220.1835;

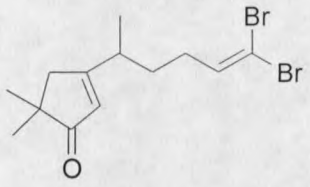
R_f 0.36 (10% ethyl acetate/hexanes).

4-(4,4-Dimethyl-3-oxo-cyclopent-1-enyl)-pentanal (**15**)



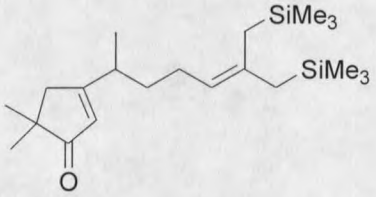
A solution of the transposed enone **14** (1.00 g, 4.54 mmol) in CH_2Cl_2 (30 mL) was cooled to -78 °C and bubbled with ozone for 3 min. The reaction vessel was purged with argon and then dimethyl sulfide (73 μL, 0.99 mmol) was added. After stirring at -78 °C for 15 min, the mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was diluted with CH_2Cl_2 and washed with H_2O (2X). The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo to afford the crude aldehyde **15** as a yellow liquid.

3-(5,5-Dibromo-1-methyl-pent-4-enyl)-5,5-dimethyl-cyclopent-2-enone (**16**)



To a 100 mL round bottom flask was added CBr_4 (3.00 g, 9.06 mmol) and CH_2Cl_2 (14mL). The solution was cooled to 0 °C and PPh_3 (4.75 g, 18.12 mmol) in CH_2Cl_2 (9 mL) was added, dropwise. The aldehyde **15** (880 mg, 4.54 mmol) was added to the mixture. The reaction mixture was stirred at 0 °C for 0.5 h, under argon. The solvent was removed in vacuo and the residue was triturated with Et_2O, followed by filtration over a pad of silica gel. The filtrate was concentrated and the crude residue was purified by column chromatography (5-10% ethyl acetate/hexanes) to furnish the dibromo olefin **16** as a pale yellow liquid (951 mg, 68%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.38 (t, 1 H, J = 7.3 Hz), 5.89 (s, 1 H), 2.56 (app q, 1 H, J = 6.8 Hz), 2.45 (s, 2 H), 2.10 (q, 2 H, J = 7.6 Hz), 1.5-1.7 (m, 2 H), 1.18 (d, 3 H, J = 6.9 Hz), 1.11 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 214.3 (C), 182.6 (C), 137.7 (CH), 126.6 (CH), 89.8 (C), 45.7 (C), 44.0 (CH), 36.8 (CH_2), 32.9 (CH_2), 30.9 (CH_2), 25.4 (CH_3), 25.2 (CH_3), 19.0 (CH_3); FTIR (neat) 2961, 2926, 2865, 1704, 1612, 1458, 1430, 1378, 1270, 1224, 1130, 871, 805 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{18}Br_2O$ $(M\text{-}CH_3)^+$ 332.9490, found 332.9507; R_f 0.15 (10% ethyl acetate/hexanes).

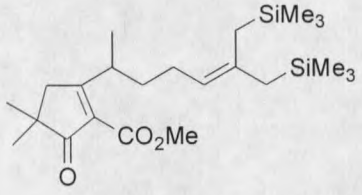
5,5-Dimethyl-3-(1-methyl-6-trimethylsilanyl-5-trimethylsilanylmethyl-hex-4-enyl)-cyclopent-2-enone (**17**)



To a 50 mL round bottom flask was added $ZnCl_2$/TMEDA complex (539 mg, 2.14 mmol) and THF (11 mL). The solution was cooled to 0 °C and $TMSCH_2MgCl$ (2.7 mL of a 1.6 M solution, 4.29 mmol) was added dropwise, followed by stirring at 0 °C for 15 min. $PdCl_2(PPh_3)_2$ (70 mg, 0.10 mmol) was added and the reaction mixture was allowed to warm to room temperature. The dibromo olefin **16** (500 mg, 1.43 mmol) was added, dropwise, and stirring at room temperature was continued overnight. The reaction was quenched with saturated aq. NH_4Cl, poured into a separatory funnel, and the layers separated. The aqueous layer was extracted with Et_2O (3X) and the combined organic layers were washed with brine (2X), dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude residue was purified by column chromatography (5-10% ethyl acetate/hexanes) to furnish the allyl bis(silane) **17** as a clear liquid (438 mg, 84%): ^1H NMR ($CDCl_3$, 300 MHz) δ 5.82 (s, 1 H), 4.72 (t, 1 H, J = 6.9 Hz), 2.53 (app q, 1 H, J = 6.8 Hz), 2.41 (s, 2 H), 1.85 (q, 2 H, J = 7.4 Hz), 1.50 (m, 2 H), 1.39 (s, 2 H), 1.36 (s, 2 H), 1.11 (d, 3 H, J = 6.9 Hz), 1.08 (s, 6 H), - 0.02 (s, 18

H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 214.5 (C), 184.3 (C), 135.3 (C), 126.2 (CH), 118.7 (CH), 45.9 (C), 43.9 (CH), 36.9 (CH_2), 35.8 (CH_2), 29.6 (CH_2), 26.4 (CH_2), 25.3 (CH_3), 25.2 (CH_3), 24.0 (CH_2), 19.0 (CH_3), - 0.50 (($CH_3)_3$), - 0.95 (($CH_3)_3$).

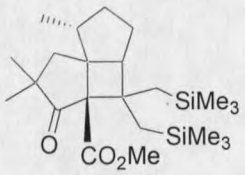
4,4-Dimethyl-2-(1-methyl-6-trimethylsilanyl-5-trimethylsilanylmethyl-hex-4-enyl)-5-oxo-cyclopent-1-enecarboxylic acid methyl ester (**18**)



n-BuLi (600 μL of a 1.70 M solution, 1.02 mmol) was added to a solution of diisopropylamine (134 μL, 1.02 mmol) in THF (2 mL) at -20 °C. After stirring for 20 min, the solution was cooled to -78 °C and the allyl bis(silane) **17** (310 mg, 0.85 mmol) in THF (0.85 mL) was added, the mixture was warmed to 0 °C and held for 1 h. The temperature was lowered to -78 °C, HMPA (148 μL, 0.85 mmol) in THF (0.85 mL) and methyl cyanoformate (81 μL, 1.02 mmol) were added. After stirring at -78 °C for 1.5 h, the mixture was quenched with saturated aq. NH_4Cl and concentrated in vacuo. The residue was dissolved in Et_2O, washed with H_2O, dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude material was purified by column chromatography (5-10% ethyl acetate/hexanes) to furnish

the photocyclization precursor **18** as a clear liquid (213 mg, 60%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.75 (t, 1H, J = 6.9 Hz), 3.84 (s, 3H), 3.49 (app q, 1H, J = 7.1 Hz), 2.50 (s, 2H), 1.85 (m, 2H), 1.48 (m, 2H), 1.41 (s, 2H), 1.38 (s, 2H), 1.16 (d, 3H, J = 6.9 Hz), 1.14 (s, 6H), 0.00 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 208.5 (C), 188.6 (C), 164.4 (C), 135.4 (C), 129.8 (CH), 118.5 (C), 52.0 (CH_3), 43.8 (C), 42.7 (CH_2), 35.9 (CH), 35.5 (CH_2), 29.6 (CH_2), 27.0 (CH_2), 25.5 (CH_3), 25.2 (CH_3), 24.0 (CH_2), 18.9 (CH_3), - 0.46 ((CH_3)$_3$), - 0.92 ((CH_3)$_3$); FTIR (neat) 2975, 2932, 2876, 2323, 2237, 1736, 1709, 1470, 1449, 1379, 1317, 1255, 1200, 1135, 1063, 986, 916, 856 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{42}O_3Si_2$ (M^+) 422.2672, found 422.2655; R_f 0.22 (10% ethyl acetate/hexanes).

2,2,7-Trimethyl-3-oxo-4,4-bis-trimethylsilanylmethyl-hexahydro-cyclobuta[1,2:1,4]dicyclopentene-3a-carboxylic acid methyl ester (**18**)



To a Pyrex toroid cell equipped with a reflux condenser and a water-cooled quartz immersion well was added a solution of the photocyclization precursor **18** (275 mg, 0.65 mmol) in hexane (30 mL). A uranium glass filter

sleeve and a 450-W Hanovia medium pressure mercury vapor lamp were placed in the immersion well. The solution was irradiated for 24 h, under a positive pressure of nitrogen. The solvent was removed in vacuo and the resulting residue was purified by column chromatography (0-2% ethyl acetate/hexanes) to provide the photoadduct **19** as a 1.5:1 mixture of inseparable diastereomers (155 mg, 56%). HRMS (PCI/NH_3) calcd for $C_{23}H_{42}O_3Si_2$ $(M+H)^+$ 423.2751, found 423.2765; FTIR (neat) 2953, 2868, 1740, 1650, 1605, 1143, 1415, 1343, 1248, 1209, 1166, 1068, 1026, 838 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.69 (s, 3H), 3.67 (s, 3H), 1.26 (s, 3H), 1.25 (s, 3H), 1.21 (s, 6H), 0.84 (d, 3H, J = 4 Hz), 0.81 (d, 3H, J = 4 Hz), 0.04 (s, 9H), 0.02 (s, 9H), -0.01 (s, 9H), -0.02 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.0, 181.1, 138.3, 136.8, 127.4, 126.2, 104.5, 104.4, 66.1, 55.9, 55.6, 55.1, 51.2, 51.0, 49.6, 45.6, 42.5, 42.2, 42.1, 31.7, 31.5, 31.0, 30.0, 28.0, 27.0, 26.4, 26.3, 23.2, 22.9, 17.0, 15.2, 0.3, 0.1, 0.00; R_f 0.71 (10% ethyl acetate/hexanes).

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