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# Thermal Reactions of a 2-Aryl-1-Vinylcyclobutanol

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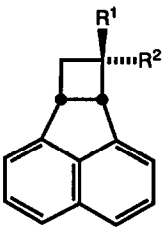
*Abstract Thermolysis reactions of the exo (distal) and endo (proximal) isomers of 7-vinyl-6b,7,8,8a-tetrahydrocyclobut[a]acenaphthylen-7-ol (**1a** and **1b**) have been studied, both in refluxing xylene and in a packed pyrolysis column These epimers were prepared from the corresponding cyclobutanone (**3**) An oxy-Cope rearrangement of **1b** was not observed under any conditions Both epimers gave the same thermolysis products, a fused cyclohexanone derivative **15** (a formal [1,3] shift product) and vinyl ketone **16** (a retro-ene product) At temperatures above 250 °C some acenaphthylene was also obtained The anionic oxy-Cope variant gave only **15** A common diradical intermediate is proposed for the thermal reactions*

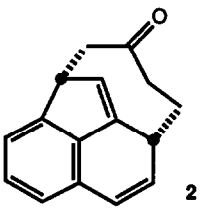
Thermal [3,3] sigmatropic (Cope) rearrangements of cis-1,2-dialkenylcyclobutanes provide a useful route to 1,5-cyclooctadienes [1,2] The corresponding trans isomers cannot undergo an equivalent pericyclic reaction, but react by a combination of a formal [1,3] sigmatropic shift to 4-alkenyl-1-cyclohexenes, and epimerization to the cis isomer [2,3] A short-lived bisallylic diradical is a plausible intermediate in the reactions of the trans isomer; and relief of four-membered ring strain facilitates the reactions of both isomers

The oxy-Cope modification, employing cis-1,2-dialkenylcyclobutanols, leads to a range of 4-cyclooctenones, generated by tautomerization of the initially formed cyclooctadienols [4,6] These reactions are accelerated substantially by formation of the substrate oxyanion,[5] and have provided an elegant approach to the synthesis of natural products incorporating eight-membered carbocyclic rings [7] Rearrangements of trans- (or distal) 1,2-dialkenylcyclobutanols are more varied, proceeding in some cases to 4-alkenylcyclohexanones by a [1,3] shift,[4,8] in other instances to ring-opened dienones by a retro-ene (or β-hydroxyolefin cleavage) reaction,[4a,6,9] and even to cyclooctenones by a formal [3,3] sigmatropic process [6]

Based on these facts and principles, we began a study of thermolysis reactions of the exo (distal) and endo (proximal) isomers of 7-vinyl-6b,7,8,8a-tetrahydrocyclobut[a]acenaphthylen-7-ol (**1a** and **1b**) Molecular mechanics examination of the vinyl rotamers of **1b** (the proximal isomer) led us to conclude that an oxy-Cope rearrangement was plausible [10] Such a rearrangement would lead to the novel bridged acenaphthene **2**, following ketonization of the initially formed enol The unusual conformational interconversions and transannular reactions we anticipated for **2** provided additional incentive for our study The distal isomer **1a** should not undergo an oxy-Cope rearrangement unless it experiences prior epimerization to **1b**



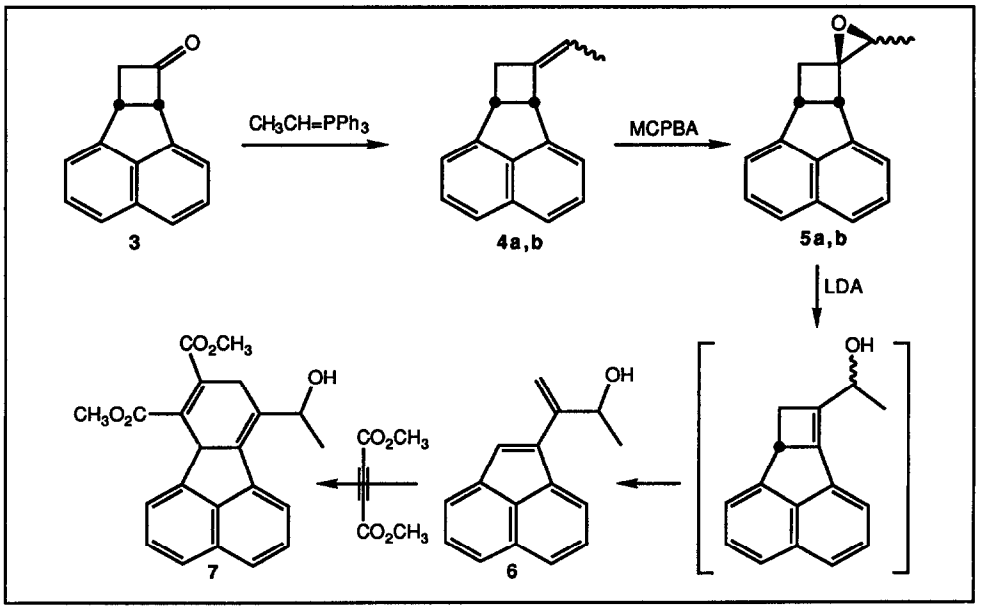

**1a** $R^1$ = $CH{=}CH_2$, $R^2$ = OH
**1a** $R^1$ = OH, $R^2$ = $CH{=}CH_2$
**3** $R^1$, $R^2$ = O




**2**

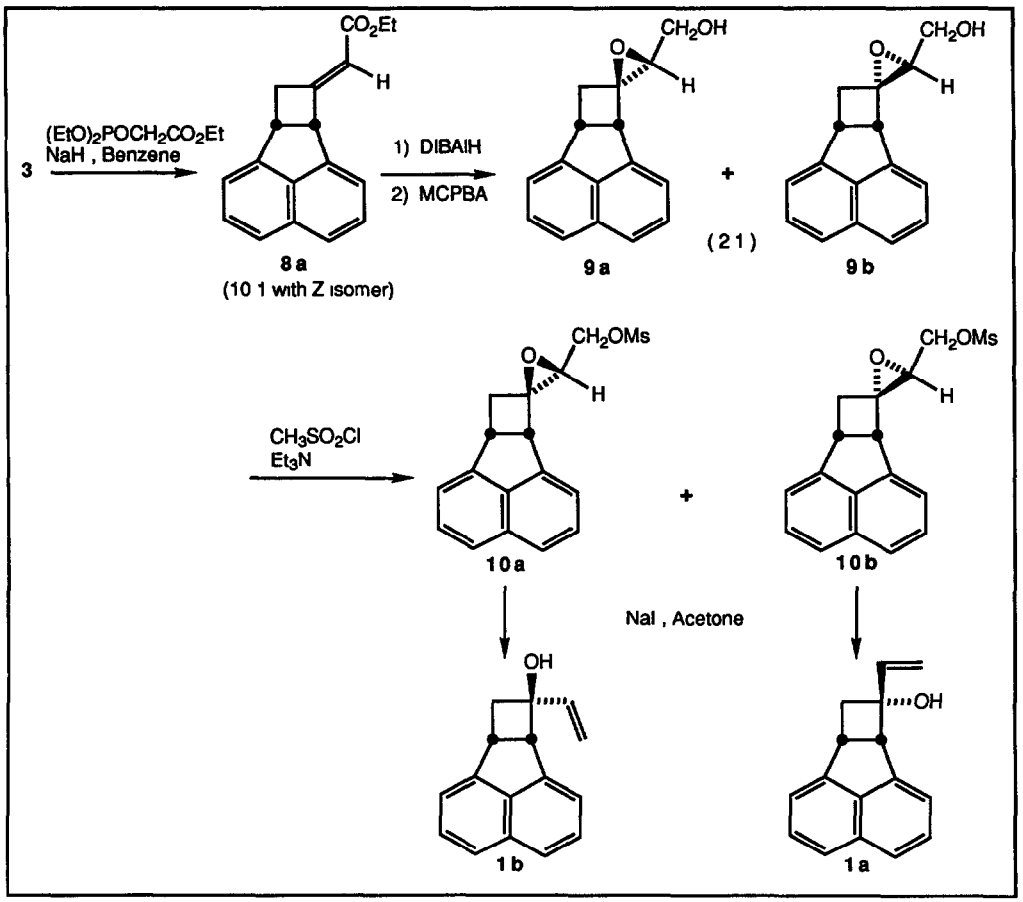
Synthesis of **1a** and **1b**, and other compounds used in this project, proceeded from 6b,7,8,8a-tetrahydrocyclobut[a]acenaphthylen-7-one, **3**,[12b] prepared from acenaphthylene in two steps [12a] The cis-fused four-membered ring in **3** causes the structure to fold in such a way that the convex (exo) side of the carbonyl groups is less hindered than its concave (endo) face Addition of organometallic reagents occurs predominantly from the convex side Thus, reaction of **3** with vinyl magnesium bromide gave **1a**, but no detectable **1b**

Our efforts to prepare epimer **1b** were based on the expectation that an exocyclic double bond, derived from ketone **3**, would be epoxidized predominantly from the convex face. Regioselective E2 opening of such an epoxide would then yield the desired endo-vinyl epimer. Thus, ethylidenetriphenylphosphorane reacted with **3** to give a modest yield of the ethylidene derivative **4**, as a 1·1 mixture of stereoisomers Epoxidation of this mixture yielded the expected exo-epoxides **5**, together with a trace of endo isomers (> 10 1) Attempts to effect elimination of **5** to generate **1b** failed, although we had successfully achieved an equivalent conversion in an earlier study [13] Treatment of epoxide **5a** or **b** with LDA gave the unstable diene **6**, apparently by an initial E2 elimination involving the benzylic hydrogen atom in **5**, followed by electrocyclic opening of the resulting cyclobutene (Scheme 1) A Diels-Alder reaction of **6** with dimethyl acetylenedicarboxylate gave adduct **7**, which served to confirm this assignment




**Scheme 1**

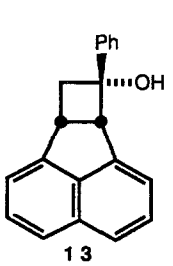
By establishing regiocontrol in the elimination step, we were able to correct the problem encountered in our first approach to **1b**. Thus, triethyl phosphonoacetate reacted with **3** in the expected fashion[14] to give a 10 1 mixture of unsaturated esters **8a** and **8b**. The assignment of **8a** as the E-isomer was founded on lanthanide shift measurements and NOE experiments. Reduction of **8a** with diisobutyl aluminum hydride, followed by epoxidation of the allylic alcohol product gave a 2:1 mixture of exo and endo epoxides **9a** and **9b** (Scheme 2) These alcohols were converted to their mesylate derivatives (**10a,b**), separated by chromatography, and finally each was treated with excess sodium iodide in refluxing acetone As expected, **10a** gave **1b** and **10b** gave **1a**




**Scheme 2**

The eliminative opening of **10** by iodide ion proceeds via an initial $S_n2$ reaction, the intermediate epoxy iodide is actually isolated as a minor product of the reaction An alternative procedure, in which an epoxy mesylate is treated with sodium naphthalide[15], did not yield any **1** from **10** Other compounds used in this study were the acetate derivatives of **1a** and **1b** (**11a,b**), the t-butyldimethylsilyl (TBDMS) derivative of **1a** (**12a**), the exo-phenylcyclobutanol **13** and the exo-cyclopropylcyclobutanol **14**.

Thermolysis studies were conducted in two ways The first involved reflux of a 0 01 to 0.02 M solution of the substrate in o-xylene (bp ca. 165 °C) for periods of 24 to 48 h These reactions were conducted under argon in peroxide-free solvents The second procedure used an electrically- heated pyrex pyrolysis column packed with pyrex beads, to which a solution of the substrate in THF was introduced dropwise, as a stream of argon swept volatile products into a cooled receiver The material balance was better in the former procedure, but even then it seldom exceeded 70% at >95% conversion of the starting material



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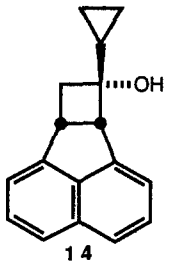

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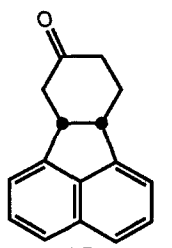

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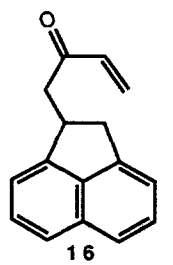

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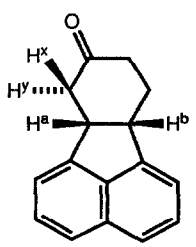
The results of thermolysis experiments in refluxing xylene are easily summarized, inasmuch as only the vinyl alcohols **1a** and **1b**, and the TBDMS derivative **12a**, undergo any reaction Both **1a** and **1b** were transformed completely in the course of heating for 48h, each yielding an identical 3 2 mixture of cyclohexanone **15** and vinyl ketone **16** in 70% yield after chromatographic separation No interconversion of these epimers was observed at shorter reaction times The acetate derivatives **11a,b** were recovered unchanged under the same conditions, but the TBDMS derivative **12a** reacted to give **15** as the only isolable product (ca 70%) The expected silyl enol ether precursor of this product was not detected, even at short reaction times, and using non-acidic workup conditions Cyclohexanone **15** was also the only product obtained when **1a** or **1b** was treated under anionic oxy-Cope reaction conditions (KH in THF/HMPA at 0° C)

The assignment of structure **15**, expected on mechanistic grounds, to the major thermolysis product was not trivial The location of the carbonyl function on the six-membered ring, and the ring fusion configuration required independent support Base-catalyzed deuterium exchange of **15** ($D_2O$/ DMF/ $Et_3N$, 24h reflux) gave the tetra-deuterated analog, **17**, identified by mass spectrometry and $^1$HNMR This not only established the presence of a methylene group on each side of the carbonyl function, but also exposed the coupling pattern of the β-methylene group ($CH^mH^n$)with the vicinal bridgehead proton ($H^b$) We were able to analyze the $^1$HNMR spectra of **15**, **17** and the bis-thioacetal **18** to provide an unambiguous ring fusion assignment The coupling constants $J_{ax}$, $J_{ay}$, $J_{bm}$, $J_{bn}$ were particularly informative (see Table 1, Experimental Section)



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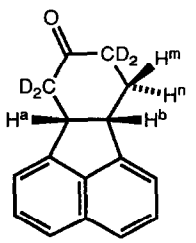

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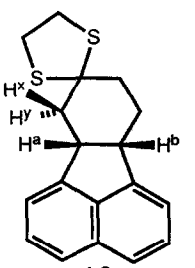

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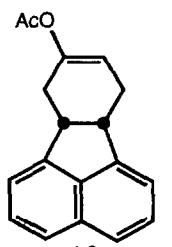

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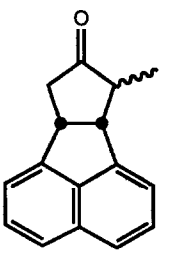
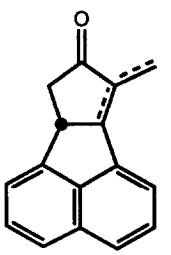
Thermolysis reactions conducted in refluxing solution are complicated by the possibility that labile products may undergo subsequent transformations For example, a retro-ene reaction of **2** could generate vinyl ketone **16** Consequently, we explored a rapid-flow pyrolysis procedure in which short-lived products might be preserved by condensation in a cooled receiver When the pyrolysis column was held at 300 °C, both **1a** and **1b** were converted in 20 to 45% yield to mixtures of cyclohexanone **15**, vinyl ketone **16** and acenaphthylene in roughly a 2 1 1 ratio. The formation of acenaphthylene is very temperature dependent, since at 245 °C none is formed - the products consisting only of **15** and **16** These products are stable under the pyrolysis conditions, save for **16** which suffers some polymerization Although acetate derivatives **11a,b** failed to react in refluxing xylene, flow pyrolysis at 250 °C gave a moderate yield (>40%) of enol acetate **19**, the product of a formal [1,3] sigmatropic shift Acid-catalyzed hydrolysis of **19** produced the expected **15**

Palladium-catalysis has been effective for some [3,3]-sigmatropic rearrangements[16], including the oxy-Cope variant, and the relatively mild conditions under which these reactions proceed augured well for the isolation of sensitive products In the event, treatment of **1a** or **1b** with bis (acetonitrile) palladium dichloride in THF gave a mixture of cyclopentanone and cyclopentenone products we believe to be **20** and **21** This mode of reaction was previously observed by Clark and Thiensathit[17] for a simpler vinyl cyclobutanol derivative The product mixture proved difficult to separate, and the components were therefore not well characterized



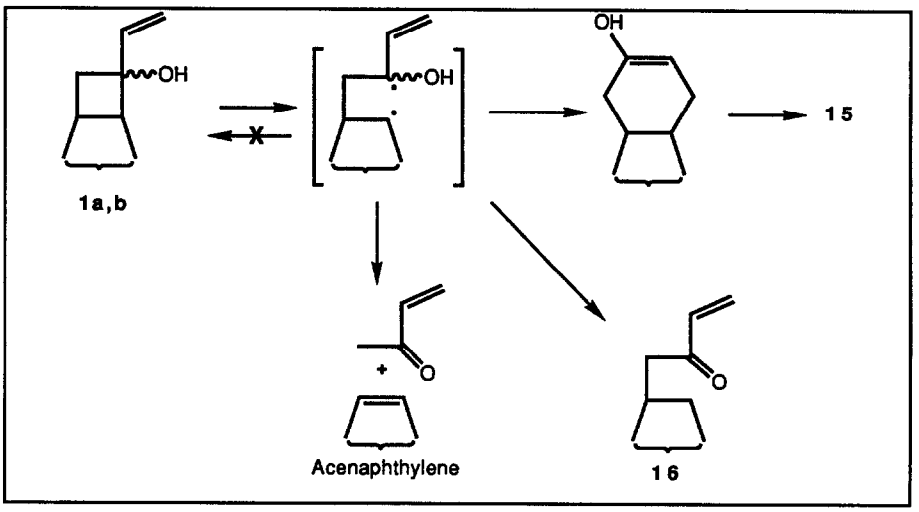

**20 a,b**




**21 a,b**

## Discussion

Our efforts to induce **1b** or derivatives thereof to undergo an oxy-Cope [3,3] sigmatropic rearrangement have been unsuccessful The initially formed trans, trans-cyclooctadienol tautomer has a considerably greater strain energy than **1b** Consequently, other lower-energy transformations dominate the reactions The nature of these suggests a common diradical intermediate, formed by homolysis of the 6b 7 bond (Scheme 3) Since the starting cyclobutanol is not epimerized, this homolysis is unlikely to be reversible Instead, allylic bonding generates a six-membered ring precursor to **15**, hydrogen transfer (essentially a retro-Norrish type II process) gives vinyl ketone **16**, and a second homolysis (8 8a) leads to acenaphthylene Efforts to intercept the 1,4-diradical intermediate proposed here, for example by reaction with excess tributyltin hydride, were unsuccessful




**Scheme 3**

The combination of hydroxyl, naphthyl and vinyl substituents on the 6b 7 bond, together with ring strain makes the homolysis of this bond more facile than normal All these factors contribute to the exceptional reactivity of compounds **1a** and **1b**, as is demonstrated by the failure of the acetate derivatives and the phenyl and cyclopropyl analogs (**13** and **14**) to give similar or derived homolysis products. The lack of reaction by the phenyl analog is particularly surprising, and from MMX calculations[10] we believe it reflects the predominance of a stereoelectronically unfavorable conformer about the phenyl cyclobutane bond.

## EXPERIMENTAL

In general, all reactions were conducted under a dry argon or nitrogen atmosphere, using solvents distilled from appropriate drying agents Melting points were measured on either a Thomas-Hoover capillary melting point apparatus or a Reichert hot stage microscope Infrared (IR) spectra were recorded with a Nicolet IR/42 spectrometer Mass spectra (MS) were obtained with a Finnigan 4000 GC/MS spectrometer NMR spectra, both $^{1}H$ and $^{13}C$, of deuteriochloroform solutions were measured using either a Brucker WM 250 or a Varian VXR 300 spectrometer, and are calibrated in parts per million ($\delta$) from tetramethylsilane (TMS) as an internal standard High-resolution mass spectra (HRMS) were measured by the Michigan State University, Department of Biochemistry, Mass Spectroscopy Facility, East Lansing, MI, microanalyses were performed by Jerri James in the analytical services laboratory of the Michigan Biotechnology Institute, East Lansing, MI Flow Thermolysis was conducted using a glass column (35 cm long, 20 mm in diameter) packed with glass beads and equipped with a 125 mL addition funnel The column was heated by resistance windings on an external ceramic jacket, and the temperature was monitored by a thermocouple placed between the jacket and the column The bottom of the column was attached to a 250 mL flask, cooled to -78° C and partially filled with tetrahydrofuran An argon stream carried volatile materials through the column into the collection flask

**Cyclobutanone (3)** Acenaphthylene (7.00 g, 46 0 mmol) was reacted with dichloroketene, generated *in situ* by ultrasonic enhanced dechlorination of trichloroacetylchloride (17.0 mL, 152 3 mmol) by zinc dust (10 10 g, 154 5 mmol) suspended in ether (200 mL). The resulting crude brown oil was used without further purification in the next step A small amount of this material was chromatographed (2·1 hexane to ether), followed by crystallization from hexane to give the dichlorocyclobutanone adduct as off-white crystals, mp 115 °C (lit[12a] 115-116 °C), $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 5 51 (d, J = 7 3 Hz, 1H), 4 91 (d, J = 7 3 Hz, 1H) ppm, $^{13}$C NMR (62.5 MHz, $CDCl_3$) δ 191 5, 139 3, 138 5, 136 2, 131 8, 128 4, 128 1, 125 3, 124 8, 124 3, 121 1, 87 0, 67 1, 57 9 ppm, IR($CH_2Cl_2$) 1807 cm$^{-1}$, MS (EI) m/z (rel int ) 262 (3), 199 (100), 163 (31), 152 (29) Dechlorination of the crude adduct was effected by zinc dust in cold methanol, saturated with ammonium chloride Chromatography of this product (silica gel, 2 1 hexane ether) yielded cyclobutanone **3** (6 69 g, 84% from acenaphthylene), which was crystallized from hexanes to give needles, mp 78-80 °C (lit[12b] 80-81 °C), $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7.2 (m, 6H), 5 18 (m, 1H), 4 25 (m, 1H), 3 61 (ddd, J = 18 3, 9 5, 3 7 Hz, 1H), 2 83 (ddd, J = 18 3, 4 4, 3 7 Hz) ppm, $^{13}$C NMR (75 MHz, $CDCl_3$) δ 205 31, 146 23, 139 13, 137 91, 131 91, 128 53, 128 25, 124 09, 123 80, 120 60, 120 15, 71 94, 52 61, 34 63ppm, IR ($CH_2Cl_2$) 1780 cm$^{-1}$, MS (EI) m/z (rel int ) 194 (7), 165 (28), 154 (100)

**Ethylidene cyclobutane (4)** A suspension of ethylidenetriphenylphosphorane in toluene (17 2 mmol) was reacted with cyclobutanone **3** at reflux The crude product was chromatographed (silica gel, hexanes) to yield ethylidene cyclobutane **4** (a yellow oil, 0 20 g, 37%) as a 1 1 mixture ($^1$H NMR) of inseparable stereoisomers $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 12H), 5 42 (m, 1H), 5 20 (m, 1H), 4 88 (m, 1H), 4 74 (m, 1H), 4 19 (m, 2H), 3 26 (m, 2H), 2 45 (m, 2H), 1 76 (m, 3H), 1 41 (m, 3H) ppm, $^{13}$C NMR (75 MHz, $CDCl_3$) δ 148 78, 147 12, 146 10, 141 06, 139 93, 139 91, 132 17, 132 08, 128 15, 128 00, 127 95, 123 39, 122 83, 122 79, 122 72, 122 68, 122 63, 119 97, 119 11, 119 04, 119 00, 118 73, 118.69, 118 52, 53 48, 52 34, 40 32, 40 20, 36 95, 34 95, 13 94, 13 28 ppm, MS (EI) m/z (rel int ) 206(6), 191(5), 152(6), 40 (100) HRMS, M$^+$ calcd for $C_{14}H_{10}O$, 194 0732, found, 194 0721

**Spiro ethylidene oxide (5)** Epoxidation of **4** (124 3 mg, 0 60 mmol) was effected by meta-chloroperbenzoic acid (129 0 mg, 0 75 mmol) in methylene chloride Spiro oxides **5** were obtained (yellow oil 133 6 mg, 99%) as a 10 10 1 1 mixture ($^1$H NMR) of stereoisomers $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 Hz (m, 6H), 4 55 (d, J = 6 5 Hz, 1H), 4 40 (d, J = 6 5 Hz, 1H), 4 1 (overlapping m, 1H), 2 8 (overlapping m, 2H), 2 2 (overlapping m, 1H), 1 38 (d, J = 5 5 Hz, 3H), 1 21 (d, J = 5 5, 3H), 1 15 (d, J = 5 5 Hz, 3H), 0 77 (d, J = 5 5 Hz, 3H) ppm, MS (EI) m/z (rel int ) 222 (8), 207 (2), 193 (1), 178 (17), 165 (100), 152 (64)

**Diene (6)** Reaction of epoxide isomers **5** (50 2 mg, 0 23 mmol) with LDA (0 23 mmol) in ether (3 00 mL) was complete in 30 min at 0 °C Chromatography of the crude product (silica gel, methylene chloride) yielded diene **6** as a pale yellow oil (41 7 mg, 83%) $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 3 (m , 6H), 7 08 (s, 1H), 5 69 (s, 1H), 5 61 (s, 1H), 4 92 (q, J = 8 3 Hz, 1H), 1 85 (br s, 1H), 1 49 (d, J = 8 3 Hz, 3H) ppm, $^{13}$C NMR (62 5 MHz, $CDCl_3$) δ 147 8, 140 8, 139 0, 129 0, 128 2, 127 8, 127 5, 127 0, 125 3, 124 4, 123 8, 112 7, 69 7, 23 0 ppm, MS (EI) m/z (rel int ) 222 (4), 178 (9), 152 (72), 84 (75), 43 (100)

**Diels-Alder cycloadduct (7)** Dimethylacetylene dicarboxylate (0 02 mL, 0 16 mmol) reacted slowly with diene **6** (15 0 mg, 0 07 mmol) Chromatography of the crude product (silica gel, 4 1 hexane ether) gave Diels-Alder cycloadduct **7** (17 3 mg, 70%) $^1$H NMR (250 MHz, $CDCl_3$) δ 7.8-7 3 (m, 6H), 5 58 (q, J = 8 3 Hz, 1H), 4 08 (dd, J = 7 9, 5 0 Hz, 1H), 3 92 (s, 3H), 3 63 (s, 3H), 3 32 (dd, J = 17 5, 5 0 Hz, 1H), 2 72 (dd,

J=17 5, 7 9 Hz, 1H), 2 30 (br s, 1H), 1 44 (d, J = 8.3 Hz, 3H) ppm, MS (EI) m/z (rel int ) 364 (3), 362 (2), 332 (8), 315 (6), 304 (26), 287 (12), 273 (23), 261 (30), 229 (93), 217 (41), 202 (100)

**Vinyl ester (8)** Reaction of cyclobutanone **3** (7 30 g, 37.6 mmol) with triethylphosphonoacetate ylide (50 4 mmol) gave, after initial chromatography (silica gel, 2 1 hexane.ether), vinyl esters **8** as an oil (72%) as a 10.1 mixture ($^1$H NMR) of stereoisomers Further chromatography permitted isolation of each isomer, both as oils Major isomer (**8a**). $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 5.83 (dd, J = 4 6, 2 8 Hz, 1H), 4 74 (br s, 1H), 4 16 (m, 1H), 4 00 (q, J = 7 0 Hz, 2H), 3 65 (dddd, J = 18 9, 9 2, 2 8, 1 2 Hz, 1H), 2 91 (ddd, J = 18 9, 4 6, 4 0 Hz, 1H), 1 12 (t, J = 7 0 Hz, 3H) ppm, $^{13}$C NMR (62 5 MHz, $CDCl_3$) δ 166 3, 166 2, 147 4, 144 1, 139 7, 132 0, 128 2 (overlapping), 123 6, 123 1, 119 4, 119 3, 115 1, 59 7, 54 3, 41 6, 39 7, 14 2 ppm, IR ($CH_2Cl_2$) 1709, 1265 cm$^{-1}$, MS (EI) m/z (rel int ) 264 (39), 249 (2), 235 (16), 218 (24), 205 (6), 189 (57), 179 (24), 165 (19), 152 (100) Anal calcd for $C_{18}H_{16}O_2$, C, 81 78, H, 6 11 Found C, 81 98, H, 6 14 Minor isomer (**8b**) HRMS, $M^+$ calcd for $C_{18}H_{16}O_2$, 264 1150, found, 264 1138

**Epoxy alcohol (9)** Reduction of the major vinyl ester isomer **8a** (3 00 g, 11 4 mmol) in ether (25 0 mL) was effected by DIBAH. Chromatography of the crude product (silica gel, 2 1 hexane ether) yielded unreacted vinyl ester **8a** (0 97 g, 32%) together with the corresponding allylic alcohol (1 54 g, 61%), which was crystallized from hexane as needles, mp 75-76° C, $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 5 41 (m, 1H), 4 62 (br s, 1H), 4 05 (m, 1H), 3 67 (t, J = 5 5 Hz, 2H), 3 17 (ddt, J = 16 5, 9 5, 1 4 Hz, 1H), 2 37 (ddt, J = 16 5, 5 8, 3 1 Hz, 1H), 1 82 (br s, 1H) ppm, $^{13}$C NMR (62 5 MHz, $CDCl_3$) δ 148 1, 144 9, 139 7, 131 9, 128 1, 128 0, 123 0, 122 9, 122 5, 119 5, 119 1, 118 9, 59 2, 53 4, 40 5, 35 2 ppm, IR ($CH_2Cl_2$) 3605, 3055, 2927, 2876, 1603 cm$^{-1}$, MS (EI) m/z (rel int ) 222 (18), 203 (50), 191 (26), 178 (33), 165 (20), 152 (100) HRMS, $M^+$ calcd for $C_{16}H_{14}O_2$, 238 0094, found, 238 1007 This allylic alcohol (876 mg, 3 94 mmol) was epoxidized by MCPBA (880 mg, 5 11 mmol) in methylene chloride (20 0 mL) Spiro epoxy alcohol **9** (940 mg, 99%) was obtained as a 2 1 mixture ($^1$H NMR) of stereoisomers Chromatography (silica gel, 2 1 ether hexane) yielded both isomers as off-white solids Major isomer (**9a**) $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 4 47 (br d, J = 7 0 Hz, 1H), 4 21 (m, 1H), 3 40 (br d, J = 12 8 Hz, 1H), 3 10 (m, 1H), 2 95 (m, 2H), 2 24 (ddd, J = 14 0, 4 0, 1 5 Hz, 1H), 2 10 (br s, 1H) ppm, $^{13}$C NMR (62 5 MHz, $CDCl_3$) δ 147 1, 143 2, 143 1, 131 8, 128 1, 128 0, 123 5, 123 3, 119 7, 119 6, 67 7, 61 2, 58 6, 54 1, 37 7, 34 3 ppm, IR ($CH_2Cl_2$) 3601, 3055, 2938, 1605, 1493 cm$^{-1}$, MS (EI) m/z (rel int ) 238(10), 219(3), 207(8), 191(5), 178(27), 165(85), 152(100), Minor isomer (**9b**) $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 4 50 (d, J = 5 8 Hz, 1H), 3 98 (dt, J = 8 8, 5 8 Hz, 1H), 3 75 (dd, J = 12 2, 3 5 Hz, 1H), 3 49 (dd, J = 12 2, 5 2 Hz, 1H), 3 25 (dd, J = 5 2, 3 5 Hz, 1H), 2 97 (ddd, J = 14 0, 9 0, 1 5 Hz, 1H), 2 13 (dd, J = 14 0, 4 9 Hz, 1H), 2 37 (br s, 1H) ppm, $^{13}$C NMR (62 5 MHz, $CDCl_3$) δ 148 3, 141 7, 140 0, 132 1, 128 0, 127 9, 123 4, 123 1, 121 4, 118 6, 64 1, 61 6, 61 2, 53 1, 37 7, 35 5 ppm, IR ($CH_2Cl_2$) 3698, 3601, 3057, 2940, 1604 cm$^{-1}$, MS (EI) m/z (rel int ) 238(23), 219(7), 207(27), 178(33), 165(93), 152(100)

**Epoxy mesylate (10)** was prepared from the 2 1 mixture of epoxy alcohols **9a,b** (2 21 mmol) by reaction with methanesulfonyl chloride (2 58 mmol) and triethylamine (3 23 mmol) in methylene chloride (10 0 mL) The epoxy mesylates **10** (689 mg, 98%) were obtained as a 2 1 mixture ($^1$H NMR) of stereoisomers Chromatography yielded both isomers as unstable oils which were used immediately in subsequent steps

**Exo-Vinylcyclobutanol (1a).** Cyclobutanone **3** (840 mg, 4 32 mmol) reacted smoothly with vinyl magnesium bromide (70 9 mmol) in tetrahydrofuran (55 0 mL) at 0 °C Chromatography of the crude product

(silica gel, methylene chloride) gave exo-vinylcyclobutanol **1a** (629 mg, 67 %), which was crystallized (hexane) as needles, mp 82-83 °C, $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 6 37 (d, J = 17.7, 10 4 Hz, 1H), 5 47 (d, J =17 7 Hz, 1H), 5 23 (d, 10 4 Hz, 1H), 4.41 (br d, J = 6 1 Hz, 1H), 3.84 (dt, J = 8.5, 6 1 Hz, 1H), 2 97 (ddd, J = 12 8, 8 5, 2 4 Hz, 1H), 1.96 (br s, 1H), 1 88 (dd, 12 8, 6 1 Hz, 1H) ppm, $^{13}$C NMR (62 5 MHz, $CDCl_3$) δ 149 6, 143 0, 141 4, 140 6, 132 1, 127 9, 127 7, 123 7, 122.5, 122 2, 118 4, 111 3, 73 2, 57 4, 43 5, 34 9 ppm, IR ($CH_2Cl_2$) 3572, 3053, 1604, 1363, 1221, 1009 cm$^{-1}$, MS (EI) m/z (rel int ) 222 (6), 167 (15) 152 (100) Anal calcd for $C_{16}H_{14}O$, C, 86 45, H, 6 35 Found C, 86 42, H, 6 33

Thermolysis A solution of **1a** (0 296 g, 1 33 mmol) in o-xylene (20 0 mL) was refluxed 48h, and the residue chromatographed (silica gel, 2 1 hexane ether) to yield cyclohexanone **15** (46%) and vinyl ketone **16** (25%)

**Endo-Vinylcyclobutanol (1b)** The major epoxy mesylate isomer **10a** (36 0 mg, 0 99 mmol) in acetone containing sodium iodide (13 34 mmol) was refluxed 72h Chromatography of the crude product (silica gel, 2 1 hexane ether) gave epoxy iodide (45 0 mg, 13%), starting epoxy mesylate **10a** (38 0 mg, 11%), and endo-vinylcyclobutanol **1b** (89 2 mg, 41%) mp 87-88 °C, $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 5 43 (dd, J = 17 4, 10 7 Hz, 1H), 4 92 (dd, J = 17 4, 1 2 Hz, 1H), 4 72 (dd, J = 10 7, 1 2 Hz, 1H), 4 20 (m, 2H), 2 63 (ddd, J = 12 7, 9 2, 2 7 Hz, 1H), 2 42 (br s, 1H), 2 09 (dd, J = 12 7, 5 2 Hz, 1H) ppm, $^{13}$C NMR (62 5 MHz, $CDCl_3$) δ 148 7, 143 0, 141 5, 140 2, 131 9, 127 9, 127 8, 123 2, 122 8, 121 4, 118 9, 112 3, 78 3, 58 6, 41 7, 37 1 ppm, IR ($CH_2Cl_2$) 3685, 3056, 1605, 1179 cm$^{-1}$, MS (EI) m/z (rel int ) 222 (3), 205 (1), 193 (17), 178 (7), 165 (36), 152 (53), 55 (100)

Thermolysis. A solution of **1b** (44 2 mg, 0 20 mmol) in o-xylene (15 0 mL) was refluxed 48h, and the residue was chromatographed (silica gel, 2 1 hexane ether) to yield cyclohexanone **15** (18 9 mg, 43%) and vinyl ketone **16** (12 0 mg, 27%), a colorless oil $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 6 37 (dd, J = 17 7, 10 2 Hz, 1H), 6 17 (d, J = 17 7 Hz, 1H), 5 80 (d, J =10 2 Hz, 1H), 4 15 (m, 1H), 3 69 (dd, J = 17 4, 8 1 Hz, 1H), 3 13 (dd, J= 17 4, 5 2 Hz, 1H), 2 89 (m, 2H) ppm, $^{13}$C NMR (250 MHz, $CDCl_3$) δ 199 6, 144 0, 138 4, 136 8, 128 5, 128 0, 127 8, 123 1, 122 4, 119 4, 118 9, 114 7, 46 7, 38 4, 38 3 ppm

**Exo-Vinylcyclobutyl acetate (11a)** Reaction of exo-alcohol **1a** (84 0 mg, 11 3 mmol) in benzene (2 00 mL) with acetic anhydride (7 00 mL, 74 0 mmol) was promoted by triethylamine (0 15 mL, 1 08 mmol) and DMAP Chromatography of the crude product (silica gel, 2 1 ether hexane) gave **11a** (89 3 mg, 89%) as a yellow oil $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 6 40 (dd, J = 17 4, 10 7 Hz, 1H), 5 38 (d, J = 17 4 Hz, 1H), 5 25 (d, J = 10 7 Hz, 1H), 4 53 (dd, J = 5 5, 2 4 Hz, 1H), 3 77 (m, 1H), 2 89 (ddd, J = 12 8, 8 4, 3 1 Hz, 1H), 2 04 (dd, J = 12 8, 7 3 Hz, 1H), 1 74 (s, 3H) ppm, $^{13}$C NMR (250 MHz, $CDCl_3$) δ 169 9, 148 8, 142 2, 140 8, 132 3, 127 9, 127 7, 123 7, 122 9, 122 8, 118 2, 113 6, 79 5, 55 8, 41 7, 37 3, 21 2 ppm, IR ($CH_2Cl_2$) 1738, 1368, 1252, 1223, 824, 789 cm$^{-1}$, MS (EI) m/z (rel int ) 264 (2), 222 (4), 193 (3), 178 (1), 165 (18), 152 (100) Anal calcd for $C_{18}H_{16}O_2$, C, 81 78, H, 6 11 Found C, 81 74, H, 5 86

Thermolysis A solution of **11a** (0 023 g, 0 09 mmol) in o-xylene (15 0 mL) was refluxed 48h, and the residue was chromatographed (silica gel, 2 1 hexane ether) to yield only recovered starting material

**Endo-Vinylcyclobutyl acetate (11b)** was prepared from endo-vinylcyclobutanol **1b** (11 8 mg, 0 05 mmol) as above Chromatography (silica gel, 2 1 ether hexane) gave **11b** (12 0 mg, 87%) $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 5 52 (dd, J = 17 4, 11 0 Hz, 1H), 4 64 (d, J = 11 0 Hz, 1H), 4 57 (d, J = 17 4 Hz, 1H), 4 49 (d, J = 7 0, 1H), 4 11 (m, 1H), 2 96 (ddd, J = 13 7, 10 1, 1 8 Hz, 1H), 2 29 (ddd, J = 13 7, 4 6, 1 2 Hz, 1H), 2 10 (s, 3H) ppm HRMS, $M^+$ calcd for $C_{18}H_{16}O_2$, 264 1150, found, 264 1142

Thermolysis: A solution of acetate **11b** (0 012 g, 0 05 mmol) in o-xylene (15 0 mL) was refluxed 48h, and the residue was chromatographed (silica gel, 2·1 hexane:ether) to yield only recovered starting material.

**Exo-Vinyl t-butyldimethylsilyl ether (12a)** was prepared by reaction of **1a** (0 254 g, 1.142 mmol) in DMF (50 0 mL) with t-butyldimethylsilyl chloride (11 28 mmol) and imidizole. Chromatography gave **12a** (0 197 g, 51%) as an oil: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.8-7.2 (m, 6H), 6 36 (dd, J = 17.4, 10 8 Hz, 1H), 5 45 (d, J = 17 4 Hz, 1H), 5 20 (d, J = 10 8 Hz, 1H), 4 28 (d, J = 2 7 Hz, 1H), 3.77 (dt, J = 8 4, 6 0 Hz, 1H), 2 96 (ddd, J = 12.3, 8.4, 2 7 Hz, 1H), 2.00 (dd, J = 12.3, 6 0 Hz, 1H), 0.64 (s, 9H), -0.12 (s, 3H), -0 57 (s, 3H) ppm, $^{13}$C NMR (75 MHz, $CDCl_3$) δ 149.85, 145 38, 143.19, 140.90, 132.10, 127.67, 127 41, 123 24, 122 90, 122 61, 117.76, 110 70, 58 34, 42.44, 35 83, 25.56, 17.90, -2 93, -3.69 ppm, IR($CH_2Cl_2$) 2957, 2930, 1256, 1250, 1127 cm$^{-1}$ HRMS, M$^+$ calcd for $C_{22}H_{28}OSi$, 336.1909, found, 336.1925

Thermolysis: A solution of **12a** (0 187 mmol) in o-xylene (10 0 mL) was refluxed for 48h Chromatography of the product yielded cyclohexanone **21** (18.9 mg, 45%) and recovered starting material (9 7 mg, 15%)

**Exo-Phenylcyclobutanol (13)** was prepared from cyclobutanone **3** (80 1 mg, 0 41 mmol) in tetrahydrofuran (50 0 mL) by reaction with 1 8M phenyllithium (0 50 mL, 0 90 mmol) in 7:3 hexane ether Chromatography (silica gel, 3 1 hexane ether) yielded **13** (85.1 mg, 76%) $^1$H NMR (300 MHz, $CDCl_3$) δ 7 8-7 2 (m, 11H), 4 63 (d, J = 6 6 Hz, 1H), 4 00 (dt, J = 9 3, 6.0 Hz, 1H), 3 27 (ddd, J = 13 2, 9 3, 1 8 Hz, 1H), 2.14 (s, 1H), 2.13 (dd, J = 13 2, 6.0 Hz, 1H) ppm, $^{13}$C NMR (75 MHz, $CDCl_3$) δ 149 75, 146 93, 141 50, 140 85, 132 39, 128 50, 128.30, 127 98, 127.06, 124 63, 124.14, 122 90, 122.35, 118.89, 74 95, 59.57, 45 49, 36.00 ppm, IR($CH_2Cl_2$) 3568, 3052, 2974, 2932, 1603 1495, 1449 cm$^{-1}$ Anal calcd. for $C_{20}H_{16}O$, C, 88 20, H, 5 93 Found· C, 88 05, H, 5.80

Thermolysis: A solution of phenylcyclobutanol **13** (29 2 mg, 0 107 mmol) in o-xylene (10 0 mL) was refluxed for 48h, and the residue was chromatographed (silica gel, 2:1 hexane.ether) to yield recovered starting material

**Exo-Cyclopropylcyclobutanol (14)** was prepared by reaction of cyclobutanone **3** (50 0 mg, 0 25 mmol) in tetrahydrofuran (50 0 mL) with cyclopropyl magnesium bromide ( 0 50 mmol) Chromatography (silica gel, 2 1 hexane.ether) yielded **14** (48 0 mg, 79%) mp 74-75 °C, $^1$H NMR (300 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 4 23 (dd, J = 6 6, 0 9 Hz, 1H), 3 69 (dt, J = 9 0, 6.0 Hz, 1H), 2,62 (ddd, J = 12 6, 5 7, 2 1 Hz, 1H), 1 72 (s, 1H), 1 66 (dd, J = 12 6, 6 0 Hz, 1H), 1 40 (m, 1H), 0.5 to 0 7 (m, 4H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) δ 150 11, 142.00, 140 73, 132 33, 128 10, 127 89, 123 77, 122 67, 122 02, 118 55, 73 74, 56 49, 41 82 35 70, 20 11, 1.06, 0 74 ppm, IR($CH_2Cl_2$) 3574, 3053, 2978, 1605, 1221, 1107, 1020 cm$^{-1}$, MS(EI) m/z (rel int ) 236(24), 167(23), 152(100) HRMS, M$^+$ calcd for $C_{17}H_{16}O$, 236 1202, found, 236 1199 Anal calcd for $C_{17}H_{16}O$, C, 86 40, H, 6 83. Found C, 86 26; H, 6 41

Thermolysis A solution of cyclopropylcyclobutanol **14** (111 1 mg, 0.470 mmol) in o-xylene (20.0 mL) was refluxed for 48h Chromatography yielded recovered starting material (88%)

**Preparation of Cyclohexanone 15 from 1a** To a cooled (-15° C) solution of potassium hydride (1 67 g, 40 0 mmol) in tetrahydrofuran (10 0 mL) was added hexamethylphosphoramide (8.00 mL, 46.00 mmol) and exovinylcyclobutanol **1a** (197 mg, 0 89 mmol) This solution was stirred 1h at -15° C, 1h at 0° C, and 30 min at 25° C After quenching with cold 1 1 mixture of aqueous acetic acid pentane, the reaction mixture was extracted with pentane Chromatography (silica gel, methylene chloride) yielded cyclohexanone **15** (111 mg, 56%), which was crystallized from hexane to give colorless needles, mp 113° C, $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 4 04 (m, 1H), 3 91 (m, 1H), 2 91 (dd, J = 15 6, 6 4 Hz, 1H), 2 66 (dd, J = 15 6, 7 0 Hz,

1H), 2 5-2.3 (m, 1H), 2 3-2.1 (m, 1H), 2.1-1.9 (m, 2H) ppm, $^{13}C$ NMR (62 5 MHZ, $CDCl_3$) δ 212 1, 131 3, 128.2, 123 2, 123 1, 119 1, 119.0, 43 0, 41 8, 40.9, 36.9, 26 5 ppm; IR ($CH_2Cl_2$) 3055, 1715, 1605, $cm^{-1}$, MS (EI) m/z (rel. int.) 222 (40), 193 (3), 179 (18), 165 (100), 152 (20) Anal. calcd for $C_{16}H_{14}O$, C, 86 45; H, 6 35 Found· C, 86.75; H, 6 25.

The configuration of **15** was assigned on the strength of $^1H$ NMR coupling constants The protons labeled in an earlier structure display the couplings listed in the following table. Two boat conformers of roughly equal energy constitute the cis isomer, but one of these is strongly favored in thioacetal **18**

**Table 1**

**Vicinal Coupling Constants for Derivatives of 15**

| Coupling Constant | Observed for 15 | Calculated for cis (boat conformers) | Calculated for trans (chair conformer) | Observed for thioacetal 18 | Calculated for thioacetal 18 |
|---|---|---|---|---|---|
| $J_{ax}$ | 64Hz | 43Hz | 27Hz | 60Hz | 46Hz |
| $J_{ay}$ | 7 0 | 7 4 | 12 4 | 10 7 | 11 8 |
| $J_{bm}$ | 5 6 | 4 4 | 2 4 | | |
| $J_{bn}$ | 7 0 | 7 3 | 12 4 | | |

**Tetradeuteriocyclohexane 17** was prepared from cyclohexanone **15** (12 6 mg, 0 06 mmol) in DMF (1 00 mL) by heating with triethylamine (0 05 mL, 0 36 mmol) and deuterium oxide (0 10 mL, 5 53 mmol) Chromatography (silica gel, 2 1 hexane ether) gave tetradeuteriocyclohexanone **17** (11 0 mg, 86%): $^1H$ NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 4 07 (m, 1H), 3 96 (m, 1H), 2 42 (dd, J = 14 1, 5 6 Hz, 1H), 2 03 (dd, J = 14 1, 7 0 Hz, 1H) ppm, MS (EI) m/z (rel int ) 226(92), 181(31), 165(100), 152(32)

**Thioketal 18** was prepared by reaction of cyclohexanone **15** (4 50 mmol) with ethanedithiol (17 2 mmol) and boron trifluoride etherate (4 07 mmol) in methylene chloride Chromatography (silica gel, 1 1 hexane ether) yielded **18** (94%) as a yellow oil $^1H$ NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 3 68 (m, 1H), 3 53 (m, 1H), 3 15 (m, 4H), 2 39 (ddd, J = 13 6, 6 0, 0 9 Hz, 1H), 2 15 (m, 2H), 1 95 (m, 2H), 1 71 (dd, J = 13 6, 10 7 Hz, 1H) ppm, MS (EI) m/z (rel int ) 298 (25), 281 (3), 269 (5), 237 (7), 205 (100), 165 (77), 152 (56)

**Enol acetate 19** Pyrolysis of a solution of exo-vinylcyclobutyl acetate **11a** (77 0 mg, 0 292 mmol) in tetrahydrofuran (250° C), followed by chromatography (silica gel, 2 1 hexane ether) of the product, yielded recovered starting material (10 0 mg, 13%) and enol acetate **19** (31 2 mg, 41%)· $^1H$ NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 6 45 (t, J = 6 6 Hz, 1H), 4 01 (q, J = 7 2 Hz, 1H), 3 83 (q, J = 5 9, 1H), 2 78 (m, 2H), 2 30 (m, 2H), 2 01 (s, 3H) ppm, MS(EI) m/z (rel int ) 264(8), 222(7), 193(2), 178(2), 164(14), 152(100)

**Palladium catalyzed reactions** A solution of endo-vinylcyclobutanol **1b** (20 3 mg, 0 09 mmol) in tetrahydrofuran (3 00 mL) was treated with bis(acetonitrile) palladium dichloride (2 6 mg, 0 01 mmol) The reaction mixture was stirred 24h , filtered through a Celite pad, and the residue chromatographed (silica gel, 1 1 hexane ether) to give a mixture of **20 a,b** and **21 a,b** (12 3 mg, 61%) as a 14 4 1 1 mixture ($^1H$ NMR) Like treatment of exo-vinylcyclobutanol **1a** gave a similar mixture (22 3 1 7) Repeated chromatography allowed for isolation of Exo-methylcyclopentanone **20a**, and for tentative assignment of other products **(21a)**· $^1H$ NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 6 16 (d, J = 1 Hz, 1H), 5 78 (d, J = 1 Hz, 1H), 4.88 (m, 1H), 4 30 (m, 1H), 3 13 (dd, J = 19 2, 9 6 Hz, 1H), 2 67 (dd, J = 19 2, 4 4 Hz, 1H) ppm, **(21b)** $^1H$ NMR (250 MHz, $CDCl_3$) δ 7 8-7 2 (m, 6H), 4 71 (m, 1H), 3 21 (dd, J = 18 0, 7 6 Hz, 1H), 2 71 (dd, J = 18 0, 5 8 Hz,

1H), 2.08 (d, J = 2.4 Hz, 3H) ppm; **(20a)**: $^1$H NMR (250 MHz, $CDCl_3$) δ 7 8-7.2 (m, 6H), 4.17 (m, 1H), 3.68 (t, J = 8.4 Hz, 1H), 2.86 (dd, J = 18.8, 10 5 Hz, 1H), 2 56 (ddd, J = 18.8, 5.5, 1 8 Hz, 1H), 2 06 (m, 1H), 1 25 (d, J = 7 3 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, CDCl3) δ 219.39, 147.69, 147 64, 137.53, 131 80, 128 34, 128.19, 123 41, 123.35, 119 64, 118 92, 52.85, 50.03, 42 36, 42.08, 14.26 ppm, **(20b)** $^1$H NMR (250 MHz, CDCl3) d 7.8-7.2 (m, 6H), 4.6 (m, 1H), 1 10 (d, J = 7.3 Hz, 3H) ppm.

**Tributyltinhydride trapping experiments.** In a representative procedure, a solution of **12a** (20.3 mg, 0 060 mmol) and tributyltin hydride (0 10 mL, 0.371 mmol) in o-xylene (10.0 mL) was refluxed for 1h. The residue was chromatographed (silica gel, 2 1 hexane ether) to yield acenaphthylene (1 1 mg, 12%), recovered starting material (2.0 mg, 10%) and cyclohexanone **15** (6 7 mg, 50%)

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10 (a) MM calculations were run either on an IBM AT computer or a modified Macintosh SE-30, using programs distributed by Serena Software, Box 3076, Bloomington, IN 47402 These programs were adapted from the original MM programs of N L Allinger by J J Gajewski and K E Gilbert
(b) Although naphthalene is aromatic, the 1,2-double bond in 1-vinylnaphthalene is sufficiently localized to permit Diels-Alder cycloaddition reactions with reactive dienophiles such as maleic anhydride[11]

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