Tetrahedron Vol. 49, No. 36, pp. 8159-8168, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Acid-Catalyzed Reactions of a Strained Ring Nazarov Substrate

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(*Received in USA* 2 *March* 1993; *accepted* 22 *April* 1993)

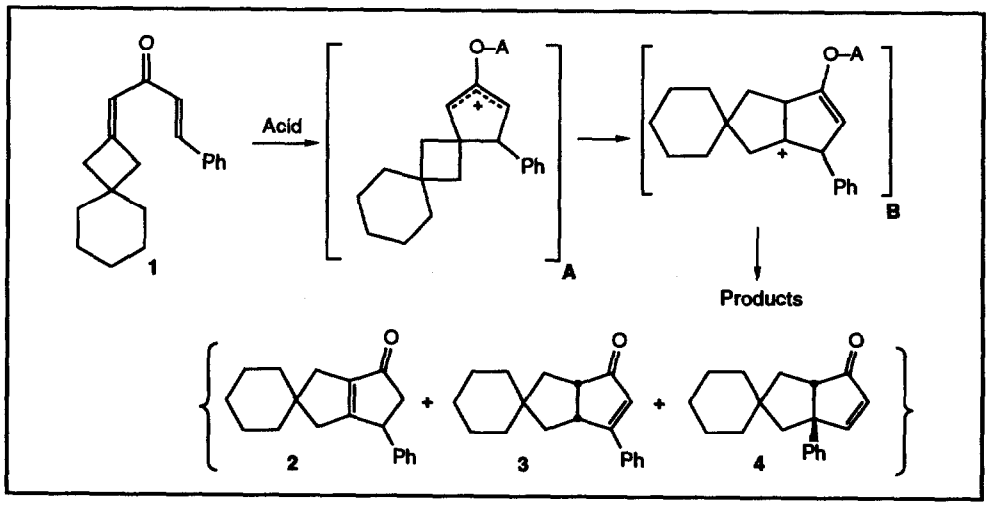
Abstract: The synthesis and acid-catalyzed rearrangements of cross-conjugated cyclobutylidene ketone **1** are described. With strong Bronsted acids it gave a mixture of 5,7-dimethyltetralin **10** and 2-cyclohexenyl-1-methyl-3-phenylbenzene **11**, the former by an initial retroaldol reaction and the latter by a series of tautomerizations and electrocyclic reactions following cation induced four-membered ring cleavage. Iodotrimethylsilane converted **1** to **11** in excellent yield. Tin (IV) chloride converted **1** to a kinetically controlled mixture of Nazarov rearrangement products **2**, **3** and **4**. This mixture was stable under the reaction conditions, but treatment with toluene sulfonic acid converted **2** completely to **3**. Even under more severe conditions, however, **4** could not be induced to isomerize.

This paper is dedicated to Professor Sir Derek H. R. Barton on the happy occasion of his seventy-fifth birthday.

During the 1940's and 50's, studies by I. N. Nazarov and coworkers[1] established the foundation for a general synthesis of 2-cyclopentenones by acid-induced cyclization of allyl vinyl ketones, divinyl ketones and dienynes. This procedure is now referred to as the Nazarov reaction, and an excellent review of its scope and mechanism has been published.[2]

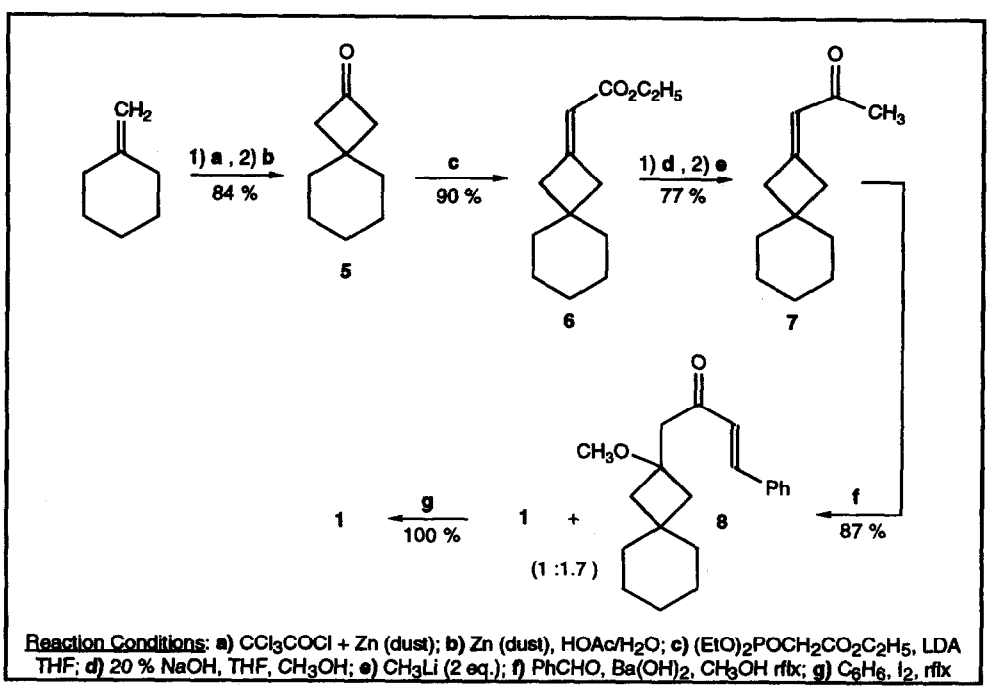
In this paper we report our study of a Nazarov substrate, **1**, designed to generate a bicyclo [3.3.0] octane product by subsequent ring enlargement of a spirocyclobutane intermediate (Scheme 1). For most Nazarov reactions, the initially formed cyclopentenyl cation (for example **A**) normally leads directly to cyclopentenone products, and only a few cases of intervening rearrangement have been reported.[3] However, the four-membered ring strain in **A** should provide a driving force for a ring expansion rearrangement, as the elegant work of Fitjer has demonstrated.[4] We were interested, therefore, in ascertaining the sequence of rearrangements that would follow formation of **A** from **1**. Assuming that **A** is initially transformed to **B**, we anticipated subsequent conversion to isomers **2**, **3** or **4**, the latter by a 1,2-phenyl shift in **B** followed by proton loss. A sequence of rearrangements of this kind might provide a novel route to triquinane derivatives starting from bis-cyclobutylidene ketone intermediates.

The choice of substrate **1** for this study was made for ease of synthesis. However, an unfortunate consequence of this selection was that the *gem.*-dialkyl substitution at the homoallylic position of the cyclobutylidene moiety served to divert the reaction from the desired Nazarov course. The synthesis outlined



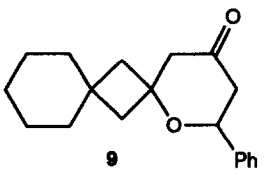
Scheme 1

in Scheme 2 is straightforward; but we note that the aldol condensation of **7** with benzaldehyde is very sensitive to reaction conditions, and even a change in solvent from methanol to ethanol significantly lowered the yield of **1**. The methanol addition coproduct **8** was readily converted to **1** by refluxing in benzene containing a trace of iodine.



Scheme 2

A common acidic system for effecting the Nazarov reaction is a mixture of 85% phosphoric acid and 88% formic acid.[5] Compound **1** was not soluble in this mixture at room temperature, but on adding THF, the resulting homogeneous solution gave the spiro ether **9** together with recovered starting material. If **1** was heated in this acid mixture (70 °C for 3 hr) a 2:11 mixture of 5,7-dimethyltetralin,[6] **10**, and 2-cyclohexenyl-1-methyl-3-phenylbenzene, **11**, was obtained in fair yield. At 90 °C the relative amounts of **10** and **11** changed to 6:1 (75% isolated yield).



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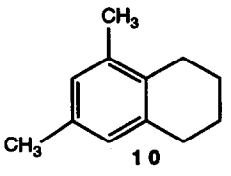

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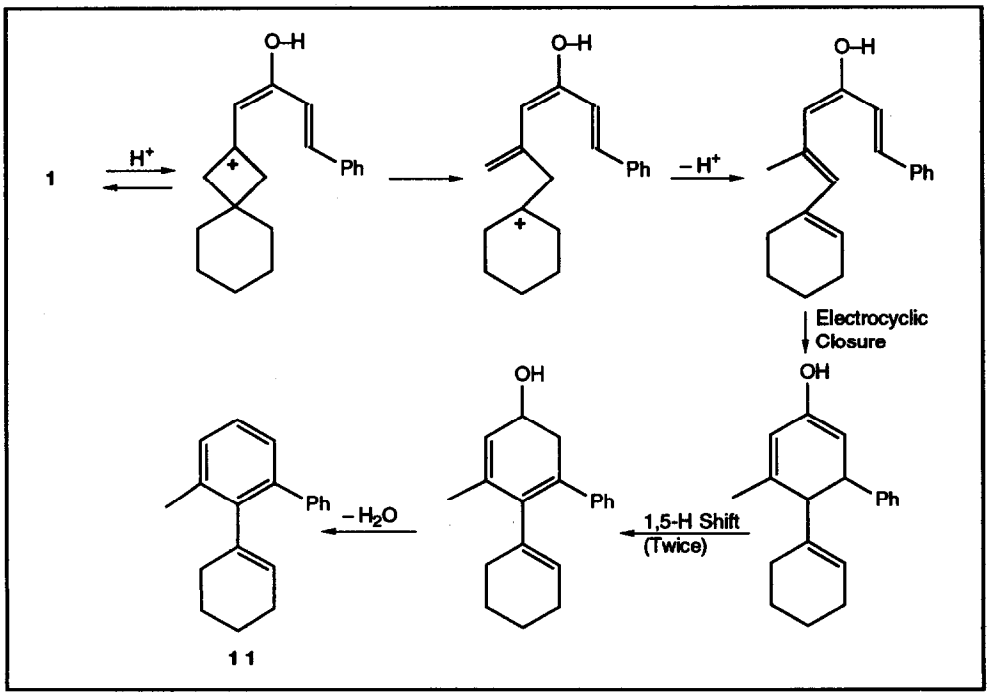
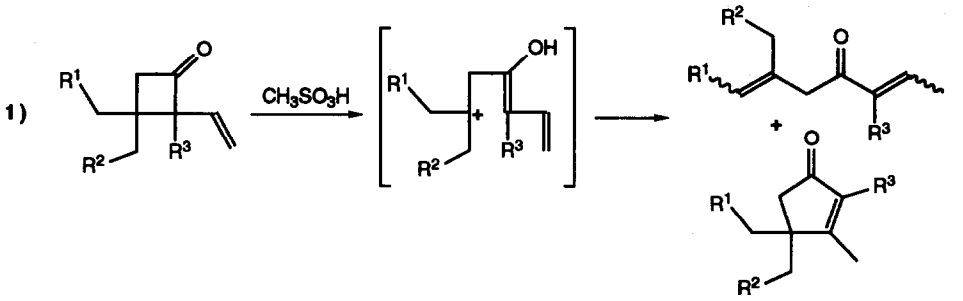
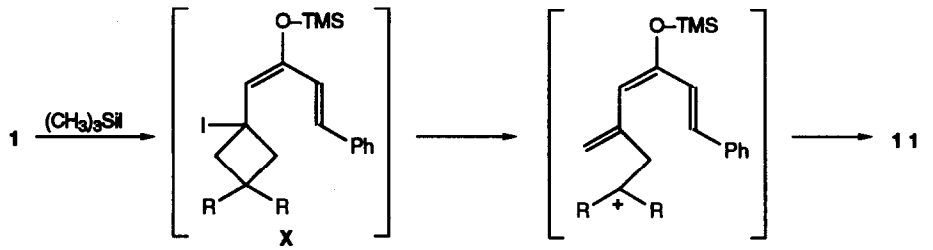
We attribute this unexpected result to *gem.*-dialkylation on the four-membered ring, which facilitates cleavage of the conjugate acid of **1** to a homoallylic cation intermediate,[7] as shown in Scheme 3 for product **11**. A similar substitution effect may be operating in acid-catalyzed reactions of 2-vinyl-2, 3, 3-trialkylcyclobutanones,[8] as shown in equation 1. Formation of tetralin **10** may be rationalized in a similar way, assuming a prior retro-aldol fragmentation. Indeed, when **7** was treated with acid under equivalent conditions, an excellent yield of **10** was obtained.



Scheme 3

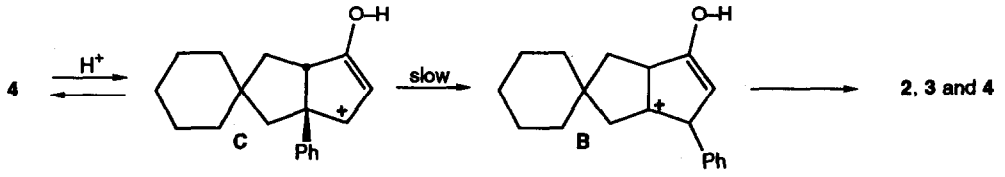


During our examination of other catalytic systems, we were intrigued to find that iodotrimethylsilane (TMSCl and NaI in DMF)[9] converted **1** to **11** in high yield (95 %). We assume that an adduct such as **X** serves to initiate a series of tautomerizations and hydrogen shifts similar to those described in Scheme 3.



Finally, treatment of **1** with one equivalent of tin (IV) chloride[10] in refluxing chloroform gave a mixture of the anticipated Nazarov products **2**, **3** and **4** in roughly 70 % combined yield. Other Lewis acids such as boron trifluoride gave complex mixtures of products; thus the tin (IV) chloride procedure is clearly superior. The proportion of **2**, **3** and **4** in the product mixture varied slightly with the substrate to catalyst ratio, but in general was nearly equimolar. Each of these isomers was isolated by repetitive flash chromatography, **2** and **4** as colorless oils, **3** as a crystalline solid. Structural assignment of each was made from characteristic spectroscopic data, as noted in the Experimental Section. In this respect it is interesting to note that UV absorption spectroscopy nicely distinguishes these isomers, the $\pi \rightarrow \pi^*$ λ_{max} being 241 nm for **2**, 289 nm for **3** and 217 nm for **4**.

Treatment of each isomer in turn under the reaction conditions gave essentially no conversion to the other two (<3 %). This suggests that the product mixture obtained from the tin (IV) chloride-induced Nazarov reaction reflects the relative rates at which **B** (Scheme 1) is converted to **2**, **3** and **4** , i.e. kinetic product control. When each of the isomers, **2**, **3** and **4** was treated with p-toluenesulfonic acid in refluxing chloroform, we found that **2** was converted to **3** within 24 h; whereas, **3** and **4** resisted isomerization by similar treatment over a 48 h period. Since the interconversion of **2** and **3** occurs *via* their common β,γ-unsaturated isomer, it is not surprising that it is facile under these conditions. Furthermore, we expect the fully conjugated isomer **3** to predominate at equilibrium. The failure of **4** to isomerize is interesting, and we suggest this reflects a high barrier for the conversion of the oxyallyl conjugate acid cation **C** to the isolated cation **B**, a key species in these reactions (Scheme 1). Clearly, if **B** were generated, an equilibrium pathway would exist, and isomer **3** would presumably be the favored component.



Although our selection of **1** as a substrate for this study introduced unnecessary complications associated with the *gem* - disubstituted four-membered ring, the tin (IV) chloride procedure demonstrates that subsequent ring enlargement rearrangements may be effectively coupled to Nazarov ring closure to give fused cyclopentane ring systems. The stage is now set for sequential rearrangements leading to triquinane products.

Acknowledgments: The NMR data were obtained on instrumentation purchased in part with funds from NIH grant #1-S10-RR04750, NSF grant #CHE-88-00770 and NSF grant #92-13241. The TRIO-1 GC/MS mass spectrometer was purchased with funds provided by NIH grant #S10-RR-06506.

EXPERIMENTAL

In general, all reactions were conducted under a dry argon or nitrogen atmosphere, using solvents distilled from appropriate drying agents. For example, diethyl ether and tetrahydrofuran were freshly distilled under nitrogen from sodium/benzophenone ketyl. Thin layer chromatography (TLC) analyses were performed using Merck Aluminum-backed F_{254} Silica Gel plates. Ultraviolet light or a 5% sulfuric acid methanol solution with subsequent heating served for visualization. Flash chromatography was performed using Merck Silica Gel 60 (230~400 mesh, ASTM, column diameter 10~50 mm), according to the method of Still et al.[11] Gas liquid chromatography was performed on a Hewlett Packard 5880A gas chromatograph. Melting points were measured on either a Thomas-Hoover capillary melting point apparatus or a Reichert hot stage microscope. ^{1}H NMR spectra were obtained using Gemini 300 (300 MHz), Varian VXR 300 (300 MHz) or Varian VXR 500 (500 MHz) spectrometers. Chemical shifts for proton resonances are reported in parts per million (δ) down field from tetramethylsilane (δ = 0 ppm) or relative to residual chloroform (δ = 7.24 ppm) as internal standards. Signal patterns are indicated as s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet). Coupling constants (J) are given in Hertz. ^{13}C NMR spectra were measured at 75 MHz, using the 300 MHz spectrometers noted above. Chemical shifts for carbon resonances are reported in parts per million (δ) down field from tetramethylsilane (δ = 0 ppm) or the deuterated chloroform triplet signal (δ = 77.0 ppm). Infrared (IR) spectra were obtained on a Nicolet PC/IR Fourier Transform spectrometer, equipped with a Nicolet IR/42 optical bench, using sodium chloride salt plates. Ultraviolet spectra were recorded on a Shimadzu UV 160 spectrometer. Mass spectra (MS) were obtained on a Finnigan 4000 GC/MS mass spectrometer equipped with an Incos 4021 data system or a TRIO-1 GC/MS mass spectrometer, both operating at an ionization energy of 70 ev. High-resolution mass spectra (HRMS) were measured on a JEOL HX 100 spectrometer at the Michigan State University, Department of Biochemistry, Mass Spectroscopy Facility, East Lansing, MI. Microanalyses were performed by Spang Microanalytical Laboratory, Star Rt. 1, Box 142, Eagle Harbor, MI 49951.

Spiro[3.5]nonan-2-one (5). To a 250 mL three-neck round bottomed flask fitted with a rubber septum, an addition funnel and a reflux condenser was added 2.00 g (20.8 mmol) methylenecyclohexane, 1.80 g (27.5 mmol) Zn dust and 100 mL of diethyl ether. To this suspension, agitated by an ultrasonic bath (Branson 2200) and maintained at 20 °C, was added dropwise 3.0 mL (4.89 g, 26.9 mmol) of trichloroacetic chloride in 50 mL of diethyl ether. This mixture was sonicated for three hours, the solids were removed by filtration through a Celite pad and the ether solution was washed with ammonium chloride solution, saturated sodium bicarbonate and brine. Evaporation of the dried (sodium sulfate) solution gave a pale yellow liquid, which proved to be 1,1-dichlorospiro[3,5]nonan-2-one, 4.08 g (95.0% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.03 (s, 2H), 1.88~1.62 (m, 7H), 1.38~1.22 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 93.2, 52.0, 46.1, 33.6, 25.0, 23.4 ppm; IR (NaCl) 2936, 2859, 1809, 1452, 990, 750 cm^{-1}; MS (EI) m/z (relative intensity) 210 (0.03), 208 (0.12), 206 (M, 0.19), 171 (5), 164 (34), 93 (29), 81 (73), 68 (100), 55 (35).

A stirred mixture of 3.00 g (14.5 mmol) 1,1-dichlorospiro[3,5]nonan-2-one, 2.70 g (41.3 mmol) Zn dust, 60 mL of water and 40 mL of acetic acid was reacted overnight at room temperature. Solids were removed by filtration through a Celite pad, followed by hexane washes. The hexane extract was washed with 2N aqueous sodium hydroxide and brine, and then dried (sodium sulfate). Evaporation of the solvent gave a pale yellow liquid, which proved to be ketone **5**, 1.78 g (88.9 % yield). This material was used without further purification in the next step, but a small amount was purified by flash chromatography using a 24 :1 mixture of hexane and diethyl ether to give a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.70 (s, 4H), 1.63~1.61 (m, 4H), 1.54~1.41 (bs, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.7, 57.1, 37.5, 30.5, 25.6, 24.0 ppm; IR (NaCl) 2934, 2853, 1782 cm^{-1}; MS (EI) m/z (relative intensity) 138 (M, 3), 110 (9), 96 (23), 81 (100), 67 (70), 55 (54).

Ethyl spiro[3.5]-2-nonanylideneacetate (6). A solution of LDA was prepared by reacting a cold (-78 °C) solution of 2.5 mL (1.81 g, 17.8 mmol) of diisopropylamine and 20 mL of tetrahydrofuran with 6.0 mL 2.5 M (15.0 mmol) of butyllithium in a 7 : 3 mixture of hexane and diethyl ether (added dropwise over 10 min.). To this was added a solution of 3.40 g (15.2 mmol) triethyl phosphonoacetate in THF, followed 10 min. later by a solution of 2.00 g (14.5 mmol) ketone **5** in 5 mL of tetrahydrofuran (temperature maintained at - 78 °C throughout). The cooling bath was removed and the resulting mixture was stirred at room temperature for 2h and then poured into water. This mixture was concentrated to a yellow slurry, hexane and brine were added and the hexane extract was washed with brine and dried. Evaporation of solvent gave ester **6** as a pale yellow liquid, 2.75 g (91.2% yield). A small sample was further purified by flash chromatography using a 9 : 1 mixture of hexane and diethyl ether to give a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68~5.64 (m, 1H), 4.14 (q, J = 7.2 Hz, 2H), 2.79 (s, 2H), 2.48 (s, 2H), 1.50 (m, 4H), 1.47~1.34 (m, 6H), 1.27 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 163.5, 114.2, 59.5, 44.6, 43.3, 37.7, 36.9, 25.8, 23.3, 14.4 ppm; IR (NaCl) 3050, 2934, 2926, 2853, 1716, 1678, 1199, 1186 cm^{-1}; MS (EI) m/z (relative intensity) 208 (M, 85), 179 (32), 163 (59), 135 (100), 119 (53), 105 (51), 91 (63), 81 (77), 67 (43), 53 (33). High resolution MS, Calc., 208.1463 for formula $C_{13}H_{20}O_2$; Found, 208.1499.

1-Spiro[3.5]-2'-nonanylidene-2-propanone (7). Ester **6**, 2.00 g (9.6 mmol), 50 mL of 20% sodium hydroxide, 20 mL of methanol and 5 mL of tetrahydrofuran were mixed (argon atmosphere). After refluxing

for two h, this mixture was cooled to room temperature, 40 mL of water was added and most of the methanol was evaporated. The residue was neutralized by 2 N hydrochloric acid and extracted with diethyl ether. The ethereal extracts were washed with brine, dried and evaporated. The colorless residue was then crystalized from absolute ethanol and dried (vac.) to give 1.47 (84.9% yield) of spiro[3,5]-2-nonanylideneacetic acid, as cubic crystals, mp 102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.5 (s, 1H), 5.68 (m, 1H), 2.82 (s, 2H) 2.52 (s, 2H), 1.55~1.48 (m, 4H), 1.48~1.34 (m, 6H) ppm; ^{13}C NMR (75 MHz, CDCl3) δ 172.8, 168.3, 114.2, 45.1, 43.7, 37.7, 36.9, 25.8, 23.3 ppm; IR (NaCl) 3350~2400, 2926, 2849, 2631, 2550, 1688, 1655, 1449, 1433, 1408, 1292, 1259, 1240, 959, 938, 868, 845 cm^{-1}; MS (EI) m/z (relative intensity) 180 (M, 40), 162 (22), 135 (100), 121 (45), 98 (40), 81 (100), 67 (32), 55 (22).

A solution of 1.00 g (5.5 mmol) spiro[3,5]-2-nonanylideneacetic acid in 60 mL of diethyl ether was cooled to 0 °C while 8.1 mL 1.4 M (11.3 mmol) of methyllithium in diethyl ether was added dropwise with stirring (10 min.). The resulting milk-white suspension slowly turned pale yellow, and following a 2h reaction period was neutralized by 1 N hydrochloric acid and extracted with diethyl ether. The ethereal extract was washed with brine, dried and evaporated to give a yellow liquid. Purification by flash chromatography using a 9 : 1 mixture of hexane and diethyl ether gave methyl ketone **7**, as a colorless liquid, 0.90 g (91.0% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 (m, 1H), 2.72 (s, 2H), 2.43 (s, 2H), 2.08 (s, 3H), 1.42 (d, J = 5.7 Hz, 4H), 1.40~1.25 (bs, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8, 162.2, 124.0, 45.0, 43.5, 37.5, 36.8, 29.9, 25.5, 23.0 ppm; IR (NaCl) 2924, 2852, 1697, 1671, 1637, 1449, 1360, 1254, 1198, 1184 cm^{-1}; MS (EI) m/z (relative intensity) 179 (2), 178 (M, 6), 163 (13), 149 (13), 135 (100), 121 (25), 105 (23), 96 (45), 81 (66), 66 (70), 55 (63). High resolution MS, Calc., 178.1358 for formula $C_{12}H_{18}O$; Found, 178.1340.

Aldol Condensation of (7). A 2.00 g (11.22 mmol) sample of methyl ketone **7**, was mixed with 1.20 g (11.32 mmol) freshly distilled benzaldehyde, 90 mL of methanol containing 4 drops of water and 0.82 g (4.79 mmol) barium hydroxide. This mixture was refluxed for two hours, 150 mL of water was added and most of the methanol was removed by evaporation. The concentrate was mixed with ether, filtered, washed with saturated ammonium chloride and brine, then dried. Evaporation of the solvent gave 2.84 g of a mixture of **1** (31.8% yield based on ^{1}H NMR integration) and **8** (56.5% yield based on ^{1}H NMR integration).

2-(2'-Oxo-(E)-4'-phenyl-3'-butenylidene) spiro[3.5]nonane (1). mp 44 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 16.1 Hz, 1H), 7.51 (m, 2H), 7.36 (m, 3H), 6.79 (d, J = 16.1 Hz, 1H), 6.34 (m, 1H), 2.89 (m, 2H), 2.54 (m, 2H), 1.57~1.48 (m, 4H), 1.47~1.26 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.3, 164.3, 141.9, 135.0, 130.1, 128.8, 128.2, 127.1, 121.6, 45.6, 44.0, 37.6, 37.5, 25.7, 23.2 ppm; IR (NaCl) 3060, 3025, 2922, 2851, 1676, 1638, 1598, 1449, 1202, 694 cm^{-1}; UV (95% ethanol) λ_{max} 308 nm, ε_{max} $2.3x10^4$, 227 nm, ε_{max} $6.8x10^3$; MS (EI) m/z (relative intensity) 266 (M, 5), 223 (9), 184 (17), 167 (11), 153 (8), 141 (10), 131 (88), 115 (20), 103 (70), 91 (63), 77 (100), 67 (48), 55 (69). Elemental analysis, Calc. for formula $C_{19}H_{22}O$: C, 85.66%; H, 8.33%; Found, C, 85.69%; H, 8.47%.

2-Methoxyl-2-(2'-oxo-(E)-4'-phenyl-3'-butenyl) spiro[3,5]nonane (8). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 16.2 Hz, 1H), 7.54~7.50 (m, 2H), 7.35~7.32 (m, 3H), 6.79 (d, J = 16.2 Hz, 1H), 3.18 (s, 3H), 2.89 (s, 2H), 1.94 (AB, q, J = 12.9 Hz, $\Delta\nu_{AB}$ = 19.3 Hz, 4H), 1.49~1.30 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.0, 142.2, 134.5, 130.2, 128.7, 128.2, 126.4, 74.8, 49.7, 49.3, 42.3, 39.2, 38.9, 31.6, 25.6, 23.0, 22.5 ppm; IR (NaCl) 3090, 3060, 3030, 2924, 2851, 1682, 1640, 1607, 1576, 1440, 1332, 1201, 1148, 1064,

978, 743, 693 cm^{-1}; MS (EI) m/z (relative intensity) 298 (M, 2) 266 (5), 238 (2), 202 (22), 174 (100), 128 (12), 103 (100), 91 (16), 77 (90), 67 (28), 55 (28).

Conversion of (8) to (1). A solution of 0.95 g (3.34 mmol) compound **8** in 150 mL of benzene containing a catalytic amount of iodine and 0.5 g 4Å molecular sieve was refluxed for three hours. The reaction mixture was filtered, washed with 20% sodium bisulfite and brine, then dried. Solvent evaporation gave 0.84 g (99% yield) of dienone **1**.

Reaction of (1) with phosphoric acid A solution of 0.300 g (1.13 mmol) dienone **1**, 15 mL of 85% phosphoric acid, 7.5 mL of 88% formic acid and 7.5 mL of tetrahydrofuran was stirred at room temperature for two hours. Benzene and water were added to the dark red mixture, and the benzene extracts were washed with sat. sodium bicarbonate solution and brine. Evaporation of the dried extract solution gave 0.296 g of a pale yellow liquid, 0.099 g (31% yield). Purification by flash chromatography gave: **Dispiro[cyclohexane-1,1'-cyclobutane -3',2"-6"-phenyldihydro-2"*H*-pyran-4"(3"*H*)-one] (9).** ^1H NMR (300 MHz, $CDCl_3$) δ 7.38~7.29 (m, 5H), 4.68 (t, J = 7.5 Hz, 1H), 2.60 (AB, q, J = 13.8 Hz, $\Delta\nu_{AB}$ = 37.4 Hz, 2H), 2.52 (d, J = 7.5 Hz, 2H), 2.06 (AB, q, J = 12.6 Hz, $\Delta\nu_{AB}$ = 70.6 Hz, 2H), 1.86 (s, 2H), 1.49~1.33 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.5, 140.9, 128.5, 127.8, 125.7, 75.5, 73.0, 53.9, 49.1, 45.7, 42.0, 40.1, 38.4, 31.1, 25.6, 22.9, 22.6 ppm; IR (NaCl) 3090, 3070, 3050, 2924, 2851, 1720, 1450, 1282, 1251, 1056, 989, 742, 698 cm^{-1}; MS (EI) m/z (relative intensity) 284 (M, 1), 266 (1), 131 (100), 104 (82), 94 (13), 81 (17), 67 (19), 56 (20), 41 (12). High resolution MS, Calc., 284.1776 for formula $C_{19}H_{24}O_2$; Found, 284.1723.

Reaction of (1) with phosphoric acid at 90 °C. A 0.490 g (1.84 mmol) sample of dienone **1** was mixed with 5 mL each of 85% phosphoric acid and 88% formic acid, then heated at 90 °C with stirring for three hours. The dark blue mixture was diluted with 20 mL of water and heated an additional hour. Benzene and water were then added to the cooled reddish brown mixture. The benzene extracts were washed with sat. sodium bicarbonate and brine, then dried. Solvent evaporation gave 0.38 g of a mixture consisting of 0.188 g (64% yield) of 5,7-dimethyltetralin **10**[6] and 0.046 g (10% yield) of 2-cyclohexenyl-1-methyl-3-phenylbenzene **11**. Pure samples of these products were obtained by flash chromatography.

5,7-dimethyltetralin (10). ^1H NMR (300 MHz, $CDCl_3$) δ 6.82 (m, 1H), 6.77 (m, 1H), 2.74 (t, J = 6.3 Hz, 2H), 2.59 (t, J = 6.3 Hz, 2H), 2.26 (s, 3H), 2.18 (s, 3H), 1.89~1.71 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9, 136.5, 134.4, 132.4, 127.9, 127.4, 30.0, 26.3, 23.5, 23.0, 20.8, 19.4 ppm; IR (NaCl) 3004, 2928, 2859, 2838, 1614, 1580, 1481, 1451, 1437, 847, 823, 700 cm^{-1}; MS (EI) m/z (relative intensity) 161 (5), 160 (M, 47), 145 (100), 132 (32), 117 (22), 105 (8), 91 (11), 77 (7), 65 (5).

2-Cyclohexenyl-1-methyl-3-phenylbenzene (11). ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (m, 1H), 7.60 (m, 1H), 7.48~7.32 (m, 5H), 7.07~6.96 (m, 2H), 2.92~2.82 (m, 4H), 2.42 (s, 3H), 2.00~1.81 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 137.4, 136.5, 134.8, 131.8, 129.9, 129.5, 128.7, 127.4, 126.7, 126.5, 123.8, 30.1, 26.5, 23.5, 22.8, 21.0 ppm; IR (NaCl) 3010, 3058, 3025, 3007, 2928, 2856, 2838, 1601, 1576, 1495, 1466, 1448, 1439, 1074, 1028, 960, 862, 752, 692 cm^{-1}; MS (EI) m/z (relative intensity) 250 (2), 249 (16), 248 (M, 100), 233 (67), 220 (25), 205 (50), 191 (16), 170 (18), 155 (35), 141 (22), 128 (34), 115 (33), 108 (27), 91 (46), 89 (17), 77 (16), 65 (7), 55 (1). High resolution MS, Calc., 248.1565 for formula $C_{19}H_{20}$; Found, 248.1563.

Conversion of (7) to (10). A 0.100 g (0.56 mmol) sample of methyl ketone **7** was added to a mixture of 4 mL each of 85% phosphoric acid and 88% formic acid. This mixture was stirred at 85~90 °C for three hours, benzene and water were added to the dark red solution, and the benzene extracts were washed with sat. sodium bicarbonate and brine, then dried. Solvent evaporation gave 0.86 g (96% yield) of compound **10**.

Reaction of (1) with iodotrimethylsilane. A solution of 0.100 g (0.376 mmol) dienone **1** and 0.563 g (3.76 mmol) sodium iodide in 2 mL of dimethyl formamide was treated with 0.48 mL (0.41 g, 3.77 mmol) of trimethylsilyl chloride were added. This mixture was then stirred at 60 °C for 10 minutes, then raised to 110-120 °C for five hours. The cooled mixture was diluted with water and diethyl ether and the ethereal extract was washed with 20% sodium bisulfite and brine, then dried. Solvent evaporation gave 0.88 g (95% yield) of compound **11**.

Reaction of (1) with tin(IV) chloride. A solution of 0.50 g (1.9 mmol) dienone **1** in 100 mL of dry chloroform was treated with 1.9 mL of 1 M (1.9 mmol) tin (IV) chloride in methylene chloride. This solution was refluxed for twenty-four hours, poured into water, filtered and diluted with methylene chloride. The methylene chloride extract was washed with saturated sodium bicarbonate and water, then dried. The solvent was removed giving a mixture of **2**, **3** and **4** in 20.8%, 16.2% and 34.0% GC yields. GC yields were determined using phenanthrene as a standard. Isomer **2** and isomer **3** were isolated by successive flash chromatography using a 35% diethyl ether/hexane mixture. Isomer **4** was isolated by flash chromatography, using a 8% diethyl ether/hexane mixture. Isolated yields of mixtures of these isomers over several repetitions of this procedure averaged 70%.

Spiro[cyclohexane-1,5'-3'-phenyl-3',4',5',6'-tetrahydropentalen-1'(2'*H*)-one] (2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.21 (m, 3H), 7.12-7.08 (m, 2H), 3.96-3.90 (m, 1H), 3.18 (dd, J = 18.5, 6.6 Hz, 1H), 2.62 (dd, J = 18.5, 2.2 Hz, 1H), 2.40-2.15 (m, 4H), 1.60-1.30 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.7, 186.1, 147.2, 141.1, 128.9, 126.1, 50.4, 48.9, 44.1, 43.5, 38.8, 38.5, 37.5, 25.7, 23.1, 22.9 ppm; IR (NaCl) 3050, 2922, 2849, 1699, 1642, 1453, 1223, 762 cm^{-1}; UV (95% ethanol) λ_{max} 241 nm, ε_{max} $7.7x10^3$; MS (EI) m/z (relative intensity) 267 (21), 266 (M, 100), 238 (33), 209 (27), 186 (52), 171 (41), 141 (64), 115 (39), 91 (75), 77 (53). High resolution MS, Calc., 266.1671 for formula $C_{19}H_{22}O$; Found, 266.1632.

Spiro[cyclohexane-1,5'-3'-phenyl-4',5',6',6'a-tetrahydropentalen-1'(3'a*H*)-one] (3). mp 119 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68~7.58 (m, 2H), 7.55~7.40 (m, 3H), 7.31 (s, 1H), 3.80~3.78 (q, m, 1H), 3.12~3.03 (m, 1H), 2.12~1.95 (m, 2H), 1.52~1.15 (m, 12H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.0, 177.1, 133.5, 131.0, 128.8, 127.7, 125.0, 51.1, 47.3, 46.0, 42.7, 38.8, 38.3, 36.3, 26.2, 23.6, 23.0 ppm; IR (NaCl) 3050, 2924, 2853, 1693, 1593, 1570, 1449, 1186, 768 cm^{-1}; UV (95% ethanol) λ_{max} 289 nm, ε_{max} $1.3x10^4$, 220 nm, ε_{max} $6.2x10^3$; MS (EI) m/z (relative intensity) 267 (9), 266 (M, 39), 170 (100), 158 (98), 141 (37), 115 (29), 91 (32), 77 (31). High resolution MS, Calc., 266.1671 for formula $C_{19}H_{22}O$; Found, 266.1646.

Spiro[cyclohexane-1,5'-3'a-phenyl-4',5',6',6'a-tetrahydropentalen-1'(3'a*H*)-one] (4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, J = 5.5 Hz, 1H), 7.35~7.18 (m, 5H), 6.00 (d, J = 5.5 Hz, 1H), 3.00 (dd, J = 8.9 Hz, J = 5.5 Hz, 1H), 2.11 (AB, q, J = 13.7 Hz, $\Delta\nu_{AB}$ = 25.7 Hz, 2H), 1.98 (m, 2H), 1.47~1.29 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.5, 171.6, 145.3, 129.9, 128.7, 126.6, 125.9, 61.0, 58.0, 47.8, 46.4, 39.7, 37.3, 26.0, 23.7, 23.0 ppm; IR (NaCl) 3050, 3015, 2926, 2855, 1711, 1495, 1450, 761, 700 cm^{-1}; UV (95%

ethanol) λ_{max} 217 nm, ε_{max} 7.1x10^3; MS(EI) m/z (realative intensity) 267 (6), 266 (M, 32), 238 (7), 224 (23), 170 (100), 158 (51), 141 (35), 128 (37), 115 (31), 91 (350), 77 (28), 67 (35), 55 (31). High resolution MS, Calc., 266.1671 for formula $C_{19}H_{22}O$; Found, 266.1680.

Acid Catalyzed Isomerisms of (2), (3) and (4). Isomers **2**, **3** and **4** were each refluxed in chloroform solution with an equivalent of p-toluenesulfonic acid monohydrate. GC identification and yields were determined using phenanthrene as an internal standard. Isomer **2** was completely converted to **3** and a trace of **4** within 24 h; however isomers **3** and **4** remained unchanged, save for a little decomposition, over a 48 h period.

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