Experimental: General Methods

Spectral Data

NMR spectra were recorded with a Bruker WP200 (200MHz, $^1$H), a Bruker WP270, 270 MHz $^1$H, 68.0 MHz $^{13}$C) or with a Bruker AM500 (500 MHz $^1$H, 125.8 MHz $^{13}$C). $^1$H and $^{13}$C chemical shift were based on TMS as an internal standard. IR data was gathered with a Matteson Polaris FT-IR driven by ICON software. High resolution mass spectral data was gathered with Kratos MS-80RFA mass spectrometer with electron impact at 70 eV.

Sealed Tube Reactions

NMR tubes for sealed tube reactions were purchased from Wilmad (504PP-8 medium walled precision).

Chromatography

Analytical tlc was performed with Merck silica gel F254. Preparatory plates were made from a water dispersion of MN-Kieselgel P/UV$_{254}$ silica gel. Column chromatography was performed with Kiesegel 60 silica gel (230-400 mesh). In reference to gas chromatography Column 1: nitrogen carrier gas, Packard Becker 409 gas chromatograph equipped with Alltech, Helilflex, AT-1 (formerly RSL-150), 30 m x 0.25 mm x 0.25 µm film thickness; Column 2: nitrogen carrier gas, Hewlett Packard 5890 equipped with Hp-1 (methyl silicone gum) 10 m x 0.53 mm x 2.65 µm film thickness.
Solvent Purification

Solvents were dried and purified as follows: diethyl ether and tetahydrofuran were distilled from sodium/benzophenone ketyl; toluene was refluxed over and distilled from CaH₂; benzene and methylenechloride were distilled from P₂O₅; acetonitrile was distilled form CaH₂, or P₂O₅ then from K₂CO₃ and stored in a reagent vessel over 4 molecular sieves. Mesitylene was distilled at atmospheric pressure from BaO through a 9 cm vigreux column. Hexane and Pentane (4 L) were stirred 3× with H₂SO₄ until the mineral acid phase no longer yellowed, the hydrocarbon was washed with water, dried over MgSO₄ and distilled from P₂O₅ through 52 cm glass bead column. All other compounds were purchased from Aldrich and purified according to the specific experimental details.
Cinnamyl Vinyl Ether (152):

Bennet has outlined the preparation of compounds like \ref{1.51} and \ref{1.52}. Mercuric acetate (7.6 g, 23.4 mmol) was suspended in 30 mL ethyl vinyl ether in a 50 mL round bottom flask fitted with a reflux condenser. Cinnamyl alcohol (3 mL, 23.4 mmol, Aldrich) was added, and the reaction was refluxed under nitrogen for 20 h. An additional 10 mL ethyl vinyl ether was added along with 80 mL benzene, and heating was continued. After 2 h the reaction was essentially complete as determined by $^1$H NMR; analytical tlc on silica gel, 1:4.5 ether/ hexane, Rf= 0.42. Short path distillation of the product gave a clear colorless liquid, bp 80-90 °C, 0.7 mmHg, (2.29 g, 14.3 mmol \ref{1.51}) 61% yield. The product was contaminated with 20% of the aldehyde \ref{1.52}.

$_{200}$MHz NMR (CDCl$_3$, ppm) $\delta$ 7.4-7.2 (5 H, m) 6.7-6.3 (3 H, m) 4.32 (1 H, dd, J= 2.2, 2.3 Hz) 4.39 (2 H, dd, J= 5.8, 1.3 Hz) 4.07 (1 H, dd, J= 6.8, 2.1 Hz).

3-Phenyl-4-penten-1-al (1.53):

Cinnamyl vinyl ether \ref{1.52} (2.29 g, 14.3 mmol) was taken up in 40 mL mesitylene and refluxed under nitrogen. Complete conversion was realized after 4.5 h as evidenced by tlc assay. Most of the solvent was distilled from the product at reduced pressure and
the residue purified by plug filtration chromatography on silica gel (30x3 cm), hexane then, 10:1 hexane:ether; a pale yellow oil (1.3 g, 8.1 mmol, 57% yield); analytical tlc on silica gel, 1:4.5 ether/hexane, Rf = 0.35; 200 MHz NMR (CDCl₃, ppm) δ 9.72 (1 H, t, J= 2.0 Hz) 7.5-7.2 (5 H, m) 5.99-5.91 (1 H, m) 5.14-5.03 (2 H, m) 3.96 (1 H, q, J= 7.1 Hz) 2.87-2.81 (2 H, m).

3-Phenyl-4-pentenal dimethyl acetal (1.54):
The aldehyde 1.53 (1.09 g, 6.8 mmol) was dissolved in 7 mL 2,2-dimethoxypropane (Aldrich) with a spatula tip of toluene sulfonic acid monohydrate (ca. 0.1 mole%). The reaction flask was fitted with a cold water condenser and the solution was mechanically agitated at 25 ºC for 4 h. The solvent was evaporated. The residue was taken up in ether and washed with ice cold 0.20 N NaOH. The ether phase was dried with MgSO₄/Na₂SO₄/Na₂CO₃ 1:1:1. The residue after filtration and solvent removal was a light yellow oil (1.34 g, 6.5 mmol) 95% yield; 200 MHz NMR (CDCl₃, ppm) δ 7.5-7.2 (5 H, m) 6.05-5.87 (1 H, m) 5.12-5.02 (2 H, m) 4.24 (1 H, t, J= 5.9 Hz) 3.44 (1 H, q, J= 6.5 Hz) 3.30 (3 H, s) 3.28 (3 H, s) 2.05-1.96 (2 H, m).

3-Phenyl-4,5-hexadienal 1,1-dimethyl acetal (1.56): Bravermann's procedure for the preparation of allenes was followed. NaOH (7.85g) was dissolved
in 10 mL H₂O. After the solution cooled to 25 °C, acetal 1.54 (608 mg, 2.95 mmol) and 1 mole % benzyltriethylammonium chloride (Aldrich) was added. Bromoform (300µL, 2 equiv, Aldrich) was added slowly via syringe over 40 min to the briskly agitated reaction mixture cooled with a water bath. Slow addition was necessary to control the exotherm. After addition, the reaction was stirred an additional 5 h, extracted into methylene chloride and the solvent evaporated. The reaction had run to 30% completion by ¹H NMR integration. The above procedure was repeated three times on similar scale to give 95% conversion to dibromocyclopropyl acetal 1.55. Crude 1.55, 988 mg was taken up in 45 mL ether. Methyllithium in ether (12 mL, 1.24 M) was added slowly at -30 °C, and the solution was stirred at -30 °C for 1.5 h, followed by quick cannula transfer at -30 °C into a stirred saturated NaHCO₃ solution (50 mL). The resulting mixture was extracted with 3 X 25 mL ether, and the ether phase dried over MgSO₄/ Na₂CO₃ 1:1. After solvent removal a brown oil remained (408 mg) that consisted of a 95:5 ratio of 1.54: 1.56b; 200 MHz NMR (CDCl₃, ppm) δ 7.5-7.2 (5 H, m) 5.31 (1 H, q, J= 7.0 Hz) 4.83-4.78 (2 H, m) 4.31-4.21 (1 H, m) 3.32 (3 H, s) 3.28 (3 H, s) 2.20-1.80 (2 H, m) 2.05-1.96 (2 H, m).

3-Phenyl-4,5-hexadiene-1-al (1.35b):
This procedure reflects insights gained from 1.35b.
Anderson's work on mild deprotection of aldehydes. The brown oil obtained above was dispersed in 2 mL acetic acid:water, 2:1, and THF was added until an emulsion formed. After 45 min at 55 °C, the mixture was extracted, dried over MgSO\textsubscript{4} and the solvent removed (aspirator). Flash chromatography of the residue gave 96.3 mg of a colorless oil \textit{135b} which contained 5\% \textit{1.53} (19\% yield from \textit{1.53}); analytical tlc on silica gel, 1:4.5 ether/hexane, Rf= 0.30. Short path distillation of the product gave a clear liquid, bp 60-80 °C, 0.02 torr; 200 MHz NMR (CDCl\textsubscript{3}, ppm) \(\delta\) 9.74 (1 H, t, J= 1.7 Hz) 7.5-7.1 (5 H, m) 5.37 (1 H, q, J= 6.6 Hz) 4.89-4.84 (2 H, m) 4.01-3.91 (1 H, m) 3.00-2.66 (2 H, m).

\textbf{Attempted trapping of 1.36b with phenyl vinyl sulfone}

Phenyl vinyl sulfone (14 mg, 0.083 mmol, recrystallized three times from ethanol) was mixed with \textit{1.35b} (17 mg 0.10 mmol). The two compounds were taken up in 1 mL decalin. The headspace above the solution was flushed with N\textsubscript{2} and the reaction refluxed (190 °C). The crude material was analyzed by \textsuperscript{1}H NMR, also the product distribution was analyzed in parts after flash chromatography. The reaction scale above is representative of most other attempts. These are adequately described in the text.

\textbf{Dimethylphenysilyl-2-propyne (1.64):}^{66}

Chlorodimethylphenylsilane (DMPSCl) (8 mL, 50 mmol)
was stirred with 50% excess lithium shavings in 50 mL THF. The wine red silyl anion slowly accumulated over the course of 24 hrs (0.95– 0.85 M). The DMPSLi was determined by titration of the red solution to pale yellow by adding the silyl base to a known amount of menthol in ether at 0 °C. DMPSLi was added dropwise via cannula to an equivalent of propargylchloride at -78 °C in 100 mL THF. The after 14 h at -78 °C the reaction vessel was allowed to warm to 25 °C. Dilution with 150 mL ether, washing with saturated NH₄Cl, drying with MgSO₄ and rotary evaporation left an orange oil. The material was distilled with a shortpath apparatus at 75 °C 0.9 torr to give 4.73 g of the desired product (a clear, colorless oil), 80%.

**Ethyl(E)-3-(4-methoxyphenyl)-2-acetyl-2-propenoate (1.60cE):**

A reflux condenser and a Dean Stark trap was fitted to a 50 mL round bottom flask charged with 4 mL benzene, 5.58 g, 40.9 mmol anisaldehyde, 3.97 g, 34.8 mmol ethyl acetoacetate and 200 µL piperidine. The solution was refluxed for 4 h. The theoretical yield of water appeared in the trap within the first half hour of the reaction. The organic phase was washed with 1N HCl, 5% NaHCO₃, 5% acetic acid (aq) and dried with MgSO₄ after filtration. Rotary evaporation left an red-orange residue consisting mainly of two readily separable geometrical
isomers \textbf{1.60cE} and \textbf{1.60cZ}. The isomers were tentatively assigned on the basis of polarity, but the assignment is not firm; analytical tlc on silica gel: 3:7 EtOAc/hexane, Rf = 0.46. Distillation of the product gave a clear light yellow liquid, bp 170-175 °C, 0.02 mm, 5.49g, 68 % yield, short path forerun containing anisaldehyde and product was discarded and not included in the yield. Molecular ion calcd for C_{14}H_{16}O_4: 248.1047; found m/e = 248.1040, error = 3 ppm; M+1, 249.1089; base peak = 135 amu; IR (CCl₄, cm⁻¹) 1704.0, C=O; 1720.4; 200 MHz NMR (CDCl₃, ppm) δ 7.61 (1 H, s) 6.92-6.85 (2 H, m) 4.29 (2 H, q, J= 7.2 Hz) 3.84 (3 H, s) 2.39 (3 H, s) 1.32 (3 H, t, J= 7.2 Hz). Ethyl (Z)-2-acetyl-3-(4-methoxyphenyl)-2-propenoate (1.60cZ):

Analytical tlc on silica gel: 3:7 EthOAc/hexane, Rf = 0.33. Distillation of the product gave a clear liquid, bp 170-175 °C, 0.02 mm, short path, forerun containing anisaldehyde was discarded. Molecular ion calcd for C_{14}H_{16}O_4: 248.1047; found m/e = 248.1048, error = 0 ppm; M-15, 233.0825, error = 0 ppm; base peak = 248 amu; IR (CCl₄, cm⁻¹) 1695, C=O; 1729, C=O; 1035, C=O; 200 MHz NMR (CDCl₃, ppm) δ 7.51 (1 H, s) 7.45-7.39 (2 H, m) 6.94-6.87 (2 H, m) 4.36 (2
Michael Addition of Dimethylphenylsilyl-2-propyne to Enones

The protocol developed by Hooze for the Michael addition of acetylide to enones \(^{67}\) was adapted to the propargyl silane. The following procedure is typical of all additions in Table VII. DMPS-2-propyne (203 mg, 1.17 mmol) was dissolved in 1.5 mL anhydrous hexane. n-Butyllithium (1.5M/ hexanes) was added dropwise at \(-78^\circ\) C. After addition was complete the mixture was warmed to 0 \(^\circ\) C and recooled to \(-40^\circ\) C. Diethylaluminium chloride (1M in hexanes) was added slowly via syringe. The resulting solution was warmed to room temperature at which time a milky white precipitate appeared. The enone in hexane 500 \(\mu\)L and just enough THF to solubilize the material ca 250 \(\mu\)L was added at 0 \(^\circ\)C. After additions were complete the pot was left to warm to 25 \(^\circ\)C. The organic phase was mixed with water and extracted into ether, washed with 5% NaHCO\(_3\) and brine, separated and dried (MgSO\(_4\)). Yields were calculated after concentration of the organic phase and SiO\(_2\) chromatography. The following compounds were prepared in this way.

1,3-Diphenyl-6-dimethylphenylsilyl-4-hexyn-1-one (1.61a):

(Yield: 40%, scale 40 mg) Analytical tlc on silica gel: 1:9 acetone:hexane, Rf=
0.34. Molecular ion calcd for C_{26}H_{32}O_{2}Si: 382.17529; found m/e= 382.1739, error= 4 ppm; M+1, 383.1810; base peak= 135 amu; IR (CCl₄, cm⁻¹) 1692, C=O; 2225, C=C; 200 MHz NMR (CDCl₃, ppm) δ 7.91 (2 H, d, J= 6.9 Hz) 7.55-7.21 (13 H, m) 4.38 (1 H, ddt, J= 8.4, 5.9, 2.0 Hz) 3.46 (1 H, dd, J= 16.8, 8.4 Hz) 3.22 (1 H, dd, J= 16.8, 5.9 Hz) 1.69 (2 H, d, J= 2.0 Hz) 0.31 (3 H, s) 0.308 (3 H, s).

2,2-Dimethyl-5-(4-methoxyphenyl)-8-dimethylphenylsilyl-6-octyn-2-one (1.61b):

(Yield: 55%, Scale 500 mg)
Analytical tlc on silica gel: 1:3 ether/ cyclohexane, Rf= 0.55.
Molecular ion calcd for C_{25}H_{30}O_{2}Si: 392.21713; found m/e= 392.2131, error= 10 ppm; M-1, 391.2099, error= 1 ppm; base peak= 135 amu; IR (CCl₄, cm⁻¹) 1710, C=O; 200 MHz NMR (CDCl₃, ppm) δ 7.60-7.55 (2 H, m) 7.39-7.32 (3 H, m) 7.28-7.23 (1 H, m) 6.85-6.81 (2 H, m) 4.21-4.14 (1 H, m) 3.78 (3 H, s, J= 1.1, 1.1 Hz) 2.91 (1 H, dd, J= 16.7, 7.4 Hz) 2.72 (1 H, dd, J= 6.7, 16.7 Hz) 1.70 (2 H, d, J= 2.3 Hz) 1.01 (9 H, s) 0.36 (6 H, s).

2,2-Dimethyl-5-(4-methoxyphenyl)-10-dimethylphenylsilyl-6-decen-8-yne-2-one (1.63):
(Yield: 25%) Analytical tlc on silica gel, 1:1 CH₂Cl₂/ cyclo-hexane. Molecular ion calcd for C₂₇H₃₃O₂Si: 418.23279; found m/e= 418.2316, error= 3 ppm; base peak= 135 amu; IR (CCl₄, cm⁻¹) 1710, C=O; 200 MHz NMR (CDCl₃, ppm) δ 7.60-7.55 (2 H, m) 7.39-7.32 (3 H, m) 7.28-7.23 (1 H, m) 6.85-6.81 (2 H, m) 6.59 (1 H, dd, J= 15.6, 1.0 Hz) 5.96 (1 H, dd, J= 15.6, 6.2 Hz) 3.80 (3 H, s) 3.77 (1 H, dddd, J= 17.2, 7.3, 6.9, 6.2 Hz) 2.81 (1 H, dd, J= 17.2, 6.9 Hz) 2.64 (1 H, dd, J= 17.2, 7.3 Hz) 1.73 (2 H, d, J= 2.6 Hz) 1.11 (9 H, s) 0.38 (3 H, s) 0.39 (3 H, s).

Ethyl 2-Acetyl-3-(4-methoxyphenyl)-6-dimethyl-phenylsilyl-4-hexynoate (1.61c): (Yield: 75%, Scale 800mg). The product was isolated as a 58:42 mixture of diastereomers. After removal of solvent (aspirator), the residue was purified by flash chromatography on silica gel (17x2 cm), 1:9 EtOAc/hexane eluent; analytical tlc on silica gel, 3:7 EtOAc/hexane, Rf= 0.50. Molecular ion calcd for C₂₅H₃₀O₄Si: 422.19128; found m/e= 422.1923, error= 2 ppm; M-C₃H₅O₂, 349.1610, error= 4 ppm; base peak= 135 amu; IR (CCl₄, cm⁻¹) 1721, C=O; 1754, C=O; 2223, C C; 200 MHz NMR (CDCl₃, ppm) Most
abundant diastereomer: δ 7.55-7.49 (2 H, m) 7.39-7.32 (3 H, m) 7.22-7.15 (2 H, m) 6.83-6.77 (2 H, m) 4.30 (1 H, dt, J= 11.0, 2.5 Hz) 3.94 (2 H, q, J= 7.0 Hz) 3.8 (3 H, s) 3.73 (1 H, d, J= 11.0 Hz) 2.77 (2 H, d, J= 2.5 Hz) 2.26 (3 H, s) 1.03 (3 H, t, J= 7.0 Hz) 0.34 (6 H, s). Least abundant diastereomer: δ 7.55-7.49 (2 H, m) 7.39-7.32 (3 H, m) 7.22-7.15 (2 H, m) 6.83-6.77 (2 H, m) 4.32 (1 H, dt, J= 11.0, 2.5 Hz) 4.17 (2 H, q, J= 7.0 Hz) 3.8 (3 H, s) 3.86 (1 H, d, J= 11.0 Hz) 2.77 (2 H, d, J= 2.5 Hz) 1.92 (3 H, s) 2.17 (3 H, t, J= 7.0 Hz) 0.36 (6 H, s).

**Allene Formation from the Propargyilsilanes with HCl/Ether.**

Ketones 1.61a-c (10-40) mg were taken up in 300- 500 µL ether in a small stoppered reaction vessel open to an oil bubbler through a hollow needle. HCl gas was introduced in the headspace above the liquid surface at 0 °C for 15 min through another needle at a rate at which the oil bubbler barely indicated a positive pressure. The reaction was allowed to warm to room temperature and the progress of the reaction was monitored by tlc. When the chromatogram indicated complete formation of product, the ether phase was diluted by 3x its volume and quenched into a mixture of ice and saturated NaHCO₃. Extraction into ether, washing with brine, drying with MgSO₄, filtration, concentration and thick layer preparative chromatography gave the products 1.62 depicted in Table VII.
1,3-diphenyl-4,5-hexadiene-1-one (1.62a):  
(Yield: 30%, Scale 20 mg) Analytical tlc on silica gel: 1:13 EtOAc/hexane, Rf= 0.26. Molecular ion calcd for C_{18}H_{16}O: 248.12010; found m/e = 248.1211, error = 4 ppm; M+1, 249.1232; base peak = 105 amu; IR (CCl₄, cm⁻¹) 1956, C=C=C; 1692, C=O; 200 MHz NMR (CDCl₃, ppm) δ 7.95-7.32 (8 H, m) 7.25-7.15 (2 H, m) 5.4 (1 H, q, J = 6.7 Hz) 4.73 (1 H, ddd, J = 10.4, 6.5, 3.6 Hz) 4.79 (1 H, ddd, J = 10.4, 6.7, 3.3 Hz) 4.23-4.10 (1 H, m) 3.54 (1 H, dd, J = 17.2, 8.2 Hz) 3.22 (1 H, dd, J = 17.2, 5.9 Hz). ¹³C NMR (270MHz noise dec., CDCl₃, ppm) δ 207.7, 198.1, 143.1, 137.2, 132.9, 128.5, 128.0, 127.7, 126.7, 94.1, 77.7, 44.6, 39.3.

2,2-Dimethyl-5-(4-methoxyphenyl)-6,7-octadiene-3-one (1.62b): (avg. yield: 30%, avg. scale 20mg) Analytical tlc on silica gel, 1:9 acetone: hexane, Rf= 0.35. Molecular ion calcd for C_{17}H_{22}O₂: 258.16196; found m/e = 258.1615, error = 2 ppm; M+1, 59.1662; IR (CCl₄, cm⁻¹) 1955, C=C=C; 1709, C=O; 2668, C-H; 200 MHz NMR (C₆D₆, ppm) δ 088 (9 H, s) 7.16-7.10 (2 H, m) 6.89-6.74 (2 H, m) 5.39 (1 H, q, J = 6.7 Hz) 4.65 (1 H, ddd, J = 10.3, 6.4, 3.6 Hz) 4.67 (1 H, ddd, J = 10.3, 6.9, 3.6 Hz) 4.25-4.12 (1 H, m) 3.30 (3 H, s) 2.78 (1
Ethyl 2-acetyl-3-(4-methoxyphenyl)-4,5-hexadieneoate (1.62c):

(Yield: 38%, Scale 30mg) The prescribed treatment of 1.62a with HCl in ether gave a 56:44 mixture of diastereomers 1.62c, which were inseparable on SiO₂ gel. After removal of solvent (aspirator), the residue was purified by flash chromatography on silica gel (12x1 cm), 1:9 EtOAc/hexane eluent; analytical tlc on silica gel, 15:85 EtOAc/hexane, Rf= 0.22. Molecular ion calcd for C₁₇H₂₀O₄: 288.13616 found m/e= 288.1354, error= 3 ppm; M+1, 289.1400; base peak= 159 amu; IR (CD₂Cl₂, cm⁻¹) 1972, C=C=C; 1751, C=O; 1719, C=O; 200MHz NMR (CDCl₃, ppm) most abundant diastereomer:  δ 7.18-7.08 (2 H, m) 6.85-6.79 (2 H, m) 5.36 (1 H, q, J= 6.1 Hz) 4.92-4.73 (2 H, m) 4.20 (2 H, t, J= 7.2 Hz) 4.10-4.01 (1 H, m) 3.95 (1 H, d, J= 11.5 Hz) 3.78 (3 H, s) 1.92 (3 H, s) 0.97 (3 H, t, J= 7.2 Hz). Least abundant diastereomer:  δ 7.18-7.08 (2 H, m) 6.85-6.79 (2 H, m) 5.31 (1 H, q, J= 6.2 Hz) 4.92-4.73 (2 H, m) 3.89 (2 H, t, J= 7.2 Hz) 4.20-4.31 (1 H, m) 3.97 (1 H, d, J= 11.0 Hz) 3.78 (3 H, s) 2.31 (3 H, s) 1.28 (3 H, t, J= 7.2 Hz).

Sealed Tube Pyrolysis of Keto Allenes:

A closed end tube (usually an NMR tube) containing the desired solution of the keto allene under study was cooled in a
bath of liquid N\textsubscript{2}. The space above the frozen solvent was evacuated under high vacuum. The pressure was then equalized by closing off the vacuum line and bleeding N\textsubscript{2} into the tube. The sample was thawed slowly to allow the dissolved gasses to escape at a reasonable rate. Freeze-pump-thaw cycles were repeated until there was no visible evolution of dissolved gas in the solution. The open end of the tube was then sealed under vacuum with a natural gas/ oxygen torch. Pyrolysis was done in a iron filings bath contained in a 7x7x13 cm\textsuperscript{3} insulated block of steel heated with a temperature controller.
Bibliography


2. For general reviews on the Claisen rearrangement see:


4. For a review of this concept see Ziegler in ref 1b.


32. 1.35a is a known structure appearing in the vapor phase pyrolysis of 1-Hexen-5-yn-3-ol. The amount of 1.35a isolated was temperature dependent. The authors proposed that 1.35a undergoes an intramolecular ene reaction to 3-cyclopentenecarboxaldehyde. "Vapor Phase Thermolysis of 1-Hexen-5-yn-3-ol. An Acetylenic Oxy-Cope Reaction" Viola, A.; MacMillan, J. H. J. Am. Chem. Soc. 1968, 90, 6141.


43. "Researches on Acetylenic Compounds, Part LXII. The preparation and some Synthetical Applications of Penta-


49. "Variable Transition State Structure in [3,3]Sigmatropic Shifts from -Secondary Deuterium Isotope Effects"


64. See the Lutz review in Ref 1.


66. a) "Photochemical 1,3-Silyl Migration in Allylsilanes Occurring with Inversion of Silyl Configuration" Kira,