acetic acid,[19] 2,2,2-trifluoroethanol,[20] iodomethane,[21] chloroform,[22] and nitromethane[22] were also carried out by previously described procedures. Diphenyl sulfide (Aldrich), *p*-nitrophenyl phenyl sulfide (Aldrich), and silver trifluoromethanesulfonate (Aldrich) were used without further purification.

Methyldiphenylsulfonium Trifluoromethanesulfonate. Methyl iodide (2.03 g, 14.3 mmol) was added to a solution of diphenyl sulfide (2.83 g, 15.2 mmol) and silver trifluoromethanesulfonate (3.67 g, 14.3 mmol) in 15 mL of chloroform. A rapid mildly exothermic reaction occurred, and after filtration through Celite, concentration of the filtrate (rotary evaporator) gave a yellow-green viscous liquid. Addition of pentane and cooling in an ice–salt bath converted the liquid to a pale olive paste. Filtration and rinsing of the paste with ether led to a fine off-white powder: 3.44 g (68.7%); mp 94–97.5 °C; IR (KBr disk) 3090, 3070, 3020, 1475, 1445, 1260, 1170, 1150, 1020, 990, 755, 740, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.68 (s, CH_3, 3 H), 7.50–8.07 (m, C_6H_5, 10 H). Anal. Calcd for $C_{14}H_{13}F_3O_3S_2$: C, 48.00; H, 3.74; S, 18.30. Found: C, 47.90; H, 3.86; S, 18.55. Complete ethanolysis of a tared sample, in a sealed tube at 65 °C for 720 h, led to a titration against a standardized solution of NaOMe in MeOH corresponding to 101.5% of the theoretical value.

Methyl(*p*-nitrophenyl)phenylsulfonium Trifluoromethanesulfonate. Silver trifluoromethanesulfonate (3.67 g, 14.3 mmol) dissolved in 50 mL of nitromethane was added to a mixture of *p*-nitrophenyl phenyl sulfide (3.52 g, 15.2 mmol), methyl iodide (2.03 g, 14.3 mmol), and nitromethane (5 mL). An immediate precipitate of silver iodide was observed. After the mixture was stirred for 1.5 h, acetonitrile (50 mL) was added and stirring was continued for 15 min. Filtration and concentration of the filtrate led to a yellow-green oil that slowly crystallized at 0 °C. Washing with ether led to a colorless powder: 3.33 g (58.9%); mp 131.5–133 °C; IR (KBr disk) 3060, 3020, 2930, 1600, 1520, 1425, 1345, 1285, 1235, 1140, 1025, 760, 735, 680, 670 cm^{-1}; ^1H NMR (CD_3CN) δ 3.67 (s, CH_3, 3 H), 7.22–8.56 (m, aromatic, 9 H). Anal. Calcd for $C_{14}H_{12}NF_3O_5S_2$: C, 42.53; H, 3.06; N, 3.54; S, 16.22. Found: C, 42.61; H, 3.22; N, 3.55; S, 16.06. Complete ethanolysis of a tared sample, in a sealed tube at 65 °C for 670 h, led to a titration against a standardized solution of NaOMe in MeOH corresponding to 101.1% of the theoretical value.

Kinetic Procedures. Each run was carried out by the removal at appropriate time intervals of 5-mL portions from 50 mL of a solution initially ca.6 × 10^{-3} M in reactant. At 50 °C and below, the runs were slow and the interval before determination of the infinity titer was reduced by heating a sample of volume slightly in excess of 5 mL in a sealed ampule at 65 °C. After completion of the solvolysis, the sample was returned to the temperature of the run prior to removal of a 5-mL portion for titration.

For experiments in water, alcohols, and aqueous–organic mixtures, the 5-mL portions were titrated in 25 mL of cooled acetone (ice bath), containing Lacmoid (resorcinol blue) as indicator, against a standardized solution of NaOMe in MeOH. The titration procedures for runs in acetic acid and the calculation of the first-order solvolytic rate coefficients were as previously described.[2]

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Registry No. Methyldiphenylsulfonium trifluoromethanesulfonate, 105229-70-7; methyl(*p*-nitrophenyl)phenylsulfonium trifluoromethanesulfonate, 105229-72-9.

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A Systematic Degradation of Zincophorin: A Stereoselective Synthesis of the C_{17}–C_{25} Fragment

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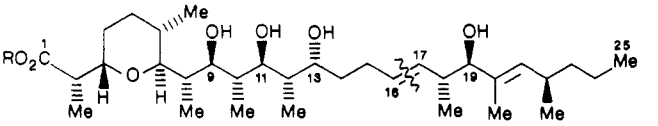
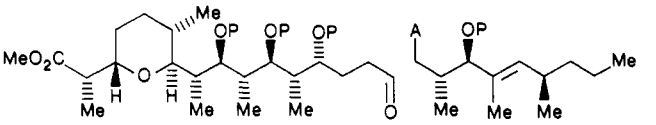
Zincophorin (M144255)(1),[1] recently isolated from a strain of *Streptomyces griseus*., has a remarkable specificity for divalent cations, particularly zinc. It shows good in vitro activity against Gram-positive bacteria. The combination of ionophoric and biological behavior of zincophorin renders it an attractive system for chemical investigation. Access to structurally modified congeners might clarify the roles of various substructural units on binding and on antibiotic properties.



1, R = H (zincophorin)
1a, R = Me



2 3

This goal of synthesizing analogues would be well served by a degradation of zincophorin in a fashion wherein the components of the cleavage can be retrieved. In this paper, we report the attainment of this goal. The method described here has the added feature that the degradation products can be modified and processed with a view toward eventual recombination (cf. systems **2** and **3**: P = protecting groups; A promotes nucleophilic character at C_{17}).

The key reaction is the highly selective osmylation[2] of zincophorin methyl ester (**1a**).[1] Treatment of **1a** with OsO_4 (0.1 equiv)[3] and NMO (3 equiv) in aqueous THF followed by periodate cleavage [$NaIO_4$, 4% AcOH/MeOH/THF (1:1:2)] of the resulting 1,2-diol provided compounds **4** (76%)[4,5] and aldehyde **5** (57%) (Scheme I). Oxidation [10 equiv of Ag_2CO_3/Celite, PhH, Δ][6] of the lactol mixture **4** afforded the stable γ-lactone **6** in 96% yield, *thus accomplishing differentiation between the hydroxyl group at C_{13} from those at C_9 and C_{11}*. Protection of the latter hydroxyl groups as their acetonide [*p*-TsOH, anhydrous $CuSO_4$, acetone] was achieved, leading to compound **7** (96%). Selective reduction of the γ-lactone to the C_{13},C_{16}-diol *in the presence of the methyl ester*[7] proceeded

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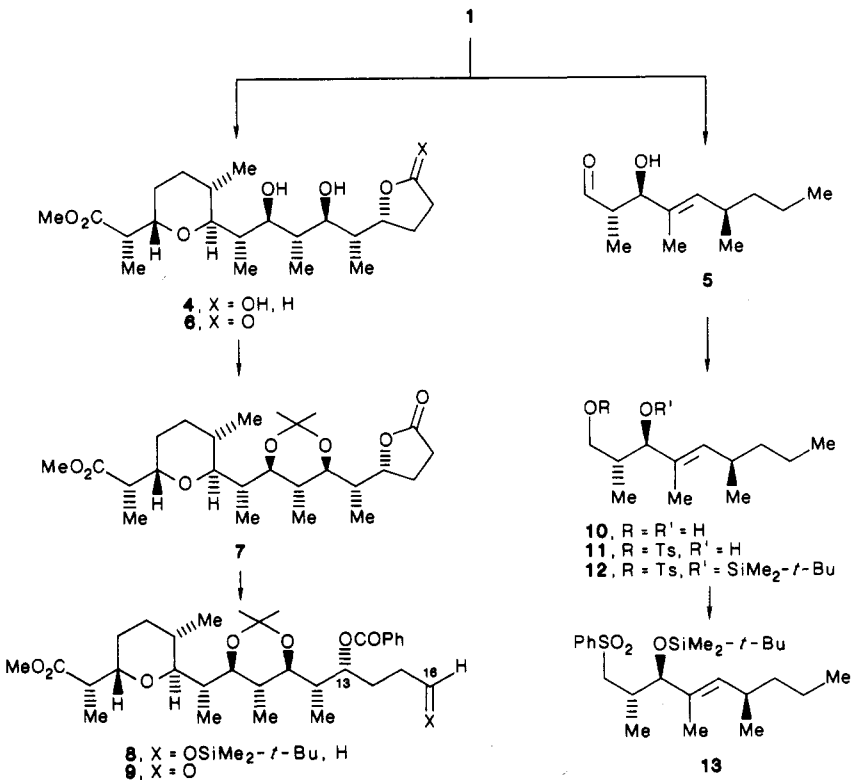
(2) The C_{16}–C_{17} double bond of zincophorin free acid has also been selectively hydrogenated, see ref 1.
(3) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.
(4) Compound **4** exists as a 2:1 mixture of lactols and open chain aldehyde. The intermediate is unstable due to formation of an anhydro sugar upon standing.
(5) All new compounds reported herein gave ^1H NMR, IR, optical rotation, and MS or combustion analytical data consistent with the assigned structure.
(6) Fetizon, M.; Golfier, M. *C. R. Seances Acad. Sci., Ser. C* **1968**, *267*, 900.

0022-3263/86/1951-5032$01.50/0

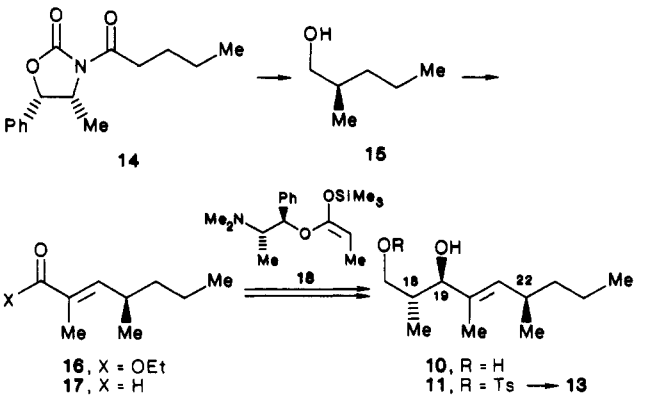
Scheme I



uneventfully [(i) Sia_2BH, THF, −10 °C; (ii) H_2O; (iii) $NaBH_4$, 0 °C]. Selective silylation of the primary alcohol [t-$BuMe_2SiCl$, DMAP, DMF] followed by benzoylation [BzCl, DMAP, pyridine] of the secondary alcohol gave rise to compound **8** in 83% overall yield from **7**. Desilylation [n-Bu_4NF, THF] afforded a primary alcohol, which upon Swern oxidation[8] provided the desired aldehyde **9** in 74% overall yield from **8**. A useful C_1–C_{16} subunit was thus in hand.

As an example of the generic system **3**, we focused on the conversion of compound **5** to the sulfone silyl ether **13**. The unstable aldehyde **5** was converted to diol **10** by reduction with sodium borohydride.[9] Selective tosylation [TsCl, DMAP, pyridine, 45 °C] of the primary alcohol afforded **11** in 76% yield, which upon silylation [t-$BuMe_2SiOTf$, Et_3N, CH_2Cl_2, 0 °C] gave rise to intermediate **12** (mp 88.5–89.5 °C) in 96% yield. Displacement of the primary tosylate [KSPh, DMF] followed by chemoselective oxidation[10] [PhSeSePh, 30% H_2O_2, CH_2Cl_2, 0 °C] afforded the desired sulfone **13** in 91% overall yield from the tosylate.

With a view toward a total synthesis of zincophorin, the synthesis of sulfone **13** was undertaken and accomplished as follows. Valeryloxazolidine **14** was selectively[11] transformed by the methodology of Evans[12] [(1) (i) LDA, THF, −78 °C; (ii) MeI; (2) $LiAlH_4$, Et_2O, 0 °C] to the R-alcohol **15**. Elongation of the chain was accomplished according



to the procedure of Ireland[13] [(i) oxalyl chloride, Me_2SO, CH_2Cl_2, −78 °C; (ii) Et_3N, −78 → 0 °C; (iii) $Ph_3PC(CH_3)CO_2Et$, Δ] to provide enoate **16** in 90% yield. Reduction [DIBAL, CH_2Cl_2, −78 °C], followed by Swern oxidation[8] of the resulting alcohol lead to enal **17**.

The central challenge of the synthesis was the formation of the required C_{18} (R) and C_{19} (R)[14] stereochemistry from substrate **17** in the absence of any likely diastereofacial guidance from the remote stereogenic center at C_{22}. Toward this goal, we employed the method recently described by Gennari.[15] Thus, condensation of enal **17** with silyl ketene acetal **18** under the influence of $TiCl_4$ [CH_2Cl_2, −78 → 0 °C], followed by treatment of the resulting ester with $LiAlH_4$ [Et_2O, 0 °C] provided diol **10**.[16] Monotosylation of this material afforded, after HPLC separation, homogeneous **11**. The infrared and NMR spectra of fully synthetic **11** as well as its optical rotation $[\alpha]_D$ −14.7° (c 3.05,

(7) Brown, H. C.; Bigley, D. B.; Arora, S. K.; Yoon, N. M. *J. Am. Chem. Soc.* **1970**, *92*, 7161.

(8) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.

(9) Diol **10** could not be obtained in homogeneous form at this stage. Its diacetate was amendable to purification. Hydrolysis of the latter afforded pure diol in 64% overall yield from **5**.

(10) Reich, H. J.; Chow, F.; Peaks, S. L. *Synthesis* **1978**, 299.

(11) The methylation afforded an 8:1 mixture which was separated into its components prior to reductive removal of the chiral auxiliary.

(12) (a) Evans, D. A.; Ennis, M. D.; Mathre, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1737. (b) Evans, D. A.; Mathre, D. J.; Scott, W. L. *J. Org. Chem.* **1985**, *50*, 1830.

(13) Ireland, R. E.; Norbeck, D. W. *J. Org. Chem.* **1985**, *50*, 2198.

(14) Zincophorin numbering system.

(15) Gennari, C.; Bernardi, A.; Colombo, L.; Scolastico, C. *J. Am. Chem. Soc.* **1985**, *107*, 5812.

(16) Compound **10** was obtained in 50% yield as an 8:1 mixture of threo/erythro isomers with >20:1 facial selectivity.

$CHCl_3$) and chromatographic properties were identical with those of **11** obtained by degradation. Compound **11** thus obtained was also carried on to the sulfone **13** as described above.

The application of these findings to the total synthesis of zincophorin and to the synthesis of various congeners thereof will be described.

Experimental Section

All reactions were run in flame-dried glassware under dry nitrogen. Solvents were dried by using standard methods. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. Spectral data were recorded on the following instruments: NMR, Bruker WM-250 (250 MHz) or a Bruker WM-500 (500 MHz); IR, Perkin-Elmer 1420; mass spectra, Hewlett-Packard 5985. Preparative column chromatography was carried out with silica gel 60 (E. Merck 9285, 230–400 mesh). Analytical data was obtained from Galbraith Laboratories Inc., Knoxville, TN.

Oxidative Cleavage of Zincophorin Methyl Ester. To a solution of 3.40 g (5.85 mmol) of zincophorin methyl ester (**1a**) and 1.58 g (11.7 mmol) of *N*-methylmorpholine oxide in 35 mL of THF containing 1.7 mL of water was added 1.8 mL (0.585 mmol) of 0.325 M osmium tetraoxide in THF. After 3.5 h, the reaction was treated with Florisil (5 g) and solid sodium bisulfite (5 g). After 12 h, the reaction was filtered through Celite and the solvent removed in vacuo to afford 3.6 g of crude 1,2-diol as a white foam.

The above 1,2 diol was dissolved in 144 mL of 20% aqueous AcOH/MeOH/THF (1:1:2) and treated with 10.0 g (46.8 mmol) of sodium metaperiodate. After 5 min, the reaction was poured into saturated $NaHCO_3$ (75 mL) and water (75 mL) and extracted with Et_2O (4 × 100 mL). The extracts were combined and dried ($MgSO_4$), and the solvent was removed in vacuo. Chromatography of the residue on 120 g of silica gel (elution with 1:1 Et_2O/petroleum ether) afforded 664 mg (57%) of crude aldehyde **5**, which was immediately carried onto the next reaction. Further elution with Et_2O afforded 1.84 g (76%) of lactols **4**, which were used directly in the next reaction.

Preparation of Lactone 6. A mixture of 1.84 g (4.44 mmol) of lactols **4** and 24 g of 48% silver carbonate on Celite in 100 mL of dry benzene was heated at reflux for 1.5 h. The reaction was cooled to room temperature and filtered through a pad of Celite (washing with Et_2O). The solvent was removed in vacuo and the residue directly chromatographed on 70 g of silica gel (elution with 1:1 Et_2O/petroleum ether) to afford 1.74 g (95%) of lactone **6** as a white foam: $[\alpha]_D$ +17.17° (*c* 1.66, $CHCl_3$); IR ($CHCl_3$) 3600–3250, 3000, 2960, 2935, 2875, 1765, 1730, 1460, 1440, 1280, 1220, 1180, 1080, 1015, 975 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.90 (ddd, 1 H, J = 4.6, 6.5, 11.1 Hz), 4.04 (ddd, 1 H, J = 2.4, 5.1, 10.9 Hz), 3.73 (s, 3 H), 3.65 (dd, 1 H, J = 1.0, 10.1 Hz), 3.57 (t, 1 H, J = 5.8 Hz), 3.41 (dd, 1 H, J = 5.0, 7.3 Hz), 3.09 (qd, 1 H, J = 6.9, 10.9 Hz), 2.58–2.50 (m, 2 H), 2.40, (m, 1 H), 2.18–1.55 (m, 7 H), 1.22 (br dq, 1 H, J = 1.4, 7.4 Hz), 1.7 (d, 6 H, J = 6.9 Hz), 1.00 (d, 3 H, J = 7.0 Hz), 0.86 (d, 3 H, J = 6.9 Hz), 0.81 (d, 3 H, J = 6.3 Hz).

Preparation of Acetonide 7. A solution of 1.517 g (3.68 mmol) of 1,3-diol **6** in 42 mL of acetone (predried over K_2CO_3) was treated with 1.17 g (7.36 mmol) of anhydrous cupric sulfate and 70 mg (0.368 mmol) of *p*-toluenesulfonic acid monohydrate. After 4 h, the reaction was quenched by the addition of triethylamine (0.5 mL) and filtered through a plug of Celite (washing with Et_2O). The solvent was removed in vacuo and the residue chromatographed on 70 g of silica gel (elution with 3:7 Et_2O/petroleum ether) to afford 1.598 g (96%) of acetonide **7** as a colorless oil: $[\alpha]_D$ +18.34° (*c* 2.47, $CHCl_3$); IR ($CHCl_3$) 3000, 2980, 2950, 2880, 1770, 1735, 1460, 1280, 1175 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.59 (dt, 1 H, J = 6.5, 9.2 Hz), 3.74 (br dt, 1 H, J = 6.1, 9.1 Hz), 3.68 (s, 3 H), 3.46 (dd, 1 H, J = 3.9, 8.0 Hz), 3.39 (dd, 1 H, J = 3.2 10.2 Hz), 3.37 (dd, 1 H, J = 3.2, 9.9 Hz), 2.65 (dq, 1 H, J = 7.1, 9.1 Hz), 2.56–2.49 (m, 3 H), 1.87 (m, 1 H), 1.79–1.60 (m, 2 H), 1.51 (m, 2 H), 1.42 (m, 1 H), 1.36 (s, 3 H), 1.31 (s, 3 H), 1.10 (d, 3 H, J = 6.9 Hz), 1.07 (d, 3 H, J = 7.0 Hz), 1.03 (d, 3 H, J = 6.8 Hz), 0.96 (d, 3 H, J = 7.1 Hz), 0.81 (d, 3 H, J = 6.4 Hz). Anal. Calcd for $C_{22}H_{38}O_7$: C, 66.01; H, 9.27. Found C, 66.05; H, 9.31.

Preparation of Compound 8. To a solution of 1.598 g (3.535 mmol) of lactone **7** in 8.0 mL of dry THF at −10 °C was added 21.2 mL (10.61 mmol) of cooled (−10 °C) 0.5 M disiamylborane in THF. The bath temperature was allowed to slowly warm to 15–20 °C over a period of 4.5 h. The reaction was then cooled to 0 °C and quenched by the dropwise addition of 2 mL of water. The reaction was then treated with excess sodium borohydride. After 30 min, the reaction was slowly poured into saturated NH_4Cl (40 mL) and extracted with Et_2O (4 × 40 mL). The extracts were combined and dried ($MgSO_4$), and the solvent was removed in vacuo. Chromatography of the residue on 70 g of silica gel (elution with 2:3 Et_2O/petroleum ether → Et_2O) afforded 1.564 g (97%) of diol as a colorless viscous oil: $[\alpha]_D$ +31.50° (*c* 2.74, $CHCl_3$); IR ($CHCl_3$) 3620, 3560–3280, 3000, 2980, 2945, 2880, 1735, 1460, 1385, 1175 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.00 (m, 1 H), 3.74–3.56 (m, 3 H), 3.68 (s, 3 H), 3.51–3.41 (m, 3 H), 3.25–2.90 (br s, 2 H), 2.66 (qd, 1 H, J = 2.4, 7.7 Hz), 1.95–1.40 (m, 11 H), 1.37 (s, 3 H), 1.34 (s, 3 H), 1.08 (d, 3 H, J = 7.0 Hz), 1.04 (d, 3 H, J = 6.8 Hz), 1.01 (d, 3 H, J = 7.1 Hz), 0.98 (d, 3 H, J = 7.1 Hz), 0.74 (d, 3 H, J = 6.5 Hz).

A solution of 1.564 g (3.43 mmol) of diol and 544 mg (4.46 mmol) of 4-(dimethylamino)pyridine in 10 mL of dry DMF was treated with 618 mg (4.12 mmol) of *tert*-butyldimethylsilyl chloride. After 5 h, the reaction was diluted with Et_2O (150 mL) and washed with water (2 × 20 mL) and brine (20 mL). The organic phase was dried ($MgSO_4$) and the solvent removed in vacuo. Chromatography of the residue on 60 g of silica gel (elution with 5:95 Et_2O/petroleum ether) afforded 1.759 g (90%) of silyl ether as a colorless oil: $[\alpha]_D$ +28.53° (*c* 2.25, $CHCl_3$); IR ($CHCl_3$) 3600–3350, 3000, 2960, 2940, 2865, 1735, 1460, 1385, 1255, 1175, 840 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 3.98 (br t, 1 H, J = 5.8 Hz), 3.79–3.59 (m, 4 H), 3.68 (s, 3 H), 3.51–3.39 (m, 3 H), 2.64 (dq, 1 H, J = 7.1, 8.9 Hz), 2.18 (m, 1 H), 1.95–1.38 (m, 11 H), 1.37 (s, 3 H), 1.34 (s, 3 H), 1.08 (d, 3 H, J = 7.4 Hz), 1.05 (d, 3 H, J = 7.4 Hz), 1.00 (d, 3 H, J = 7.1 Hz), 0.98 (d, 3 H, J = 7.1 Hz), 0.89 (s, 9 H), 0.75 (d, 3 H, J = 6.5 Hz), 0.05 (s, 6 H). Anal. Calcd for $C_{31}H_{60}O_7Si$: C, 64.99; H, 10.56. Found C, 64.72; H, 10.42.

A solution of 258 mg (0.453 mmol) of alcohol and 55 mg (0.453 mmol) of 4-(dimethylamino)pyridine in 5 mL of dry pyridine was treated with 626 μL (4.53 mmol) of benzoyl chloride. After 8 h at room temperature, the reaction was poured into saturated $NaHCO_3$ (10 mL) and extracted with Et_2O (3 × 15 mL). The extracts were combined and dried ($MgSO_4$), and the solvent was removed in vacuo. Chromatography of the residue on 30 g of silica gel (elution with 5:95 Et_2O/petroleum ether) afforded 292 mg (96%) of benzoyl ester **8** as an oil: $[\alpha]_D$ +15.58° (*c* 1.72, $CHCl_3$); IR ($CHCl_3$) 3020, 2960, 2935, 2860, 1730, 1715, 1460, 1380, 1280, 1255, 840, 715 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 8.03 (m, 2 H), 7.53 (m, 1 H), 7.40 (m, 2 H), 5.41 (ddd, 1 H, J = 2.1, 5.1, 7.4 Hz), 3.74–3.75 (m, 3 H), 3.67 (s, 3 H), 3.43 (dd, 1 H, J = 2.5, 5.7 Hz), 3.36 (m, 1 H), 3.32 (m, 1 H), 2.58 (qd, 1 H, J = 7.2, 8.8 Hz), 2.20 (m, 1 H), 2.10–1.55 (m, 11 H), 1.24 (s, 3 H), 1.16 (d, 3 H, J = 7.0 Hz), 1.09 (d, 3 H, J = 7.1 Hz), 1.03 (d, 3 H, J = 6.9 Hz), 0.97 (d, 3 H, J = 7.0 Hz), 0.91 (s, 3 H), 0.87 (s, 9 H), 0.76 (d, 3 H, J = 6.4 Hz), 0.040 (s, 3 H), 0.036 (s, 3 H). Anal. Calcd for $C_{38}H_{64}O_8Si$: C, 67.32; H, 9.52. Found C, 66.93; H, 9.51.

Preparation of Aldehyde 9. To a solution of 837 mg (1.24 mmol) of silyl ether **8** in 6 mL of THF was added 2.48 mL (2.48 mmol) of 1 M tetrabutylammonium fluoride in THF. After 1.5 h the reaction was poured into saturated NH_4Cl (20 mL) and extracted with Et_2O (3 × 20 mL). The extracts were combined and dried, ($MgSO_4$) and the solvent was removed in vacuo. Chromatography of the residue on 30 g of silica gel (elution with 2:3 Et_2O/petroleum ether) afforded 626 mg (90%) of alcohol as a viscous colorless oil: $[\alpha]_D$ +16.73° (*c* 2.48, $CHCl_3$); IR ($CHCl_3$) 3620, 3560–3440, 3030, 3000, 2980, 2950, 2880, 1720, 1460, 1380, 1285, 710 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 8.02 (m, 2 H), 7.52 (m, 1 H), 7.40 (m, 2 H), 5.44 (ddd, 1 H, J = 2.0, 4.8, 8.3 Hz), 3.71–3.64 (m, 3 H), 3.66 (s, 3 H), 3.41 (dd, 1 H, J = 2.7, 9.0 Hz), 3.34 (m, 2 H), 2.59 (qd, 1 H, J = 7.1, 8.8 Hz), 2.19 (m, 1 H), 2.07–1.43 (m, 11 H), 1.23 (s, 3 H), 1.17 (d, 3 H, J = 7.1 Hz), 1.08 (d, 3 H, J = 7.1 Hz), 1.01 (d, 3 H, J = 6.9 Hz), 0.96 (d, 3 H, J = 7.0 Hz), 0.91 (s, 3 H), 0.76 (d, 3 H, J = 6.5 Hz).

To a suspension of 183 mg (0.327 mmol) of alcohol, 27 mg (0.327 mmol) of anhydrous sodium acetate, and 285 mg of Celite in 5.6

mL of dry CH_2Cl_2 was added 141 mg (0.654 mmol) of pyridium chlorochromate. After 2 h, the reaction was diluted with Et_2O (10 mL) and filtered through a plug of Florisil (washing with Et_2O). The solvent was removed in vacuo and the residue chromatographed on 10 g of silica gel (elution with 1:4 Et_2O/petroleum ether) to afford 152 mg (82%) of aldehyde **9** as a colorless viscous oil: $[\alpha]_D$ +20.3° (*c* 2.23, $CHCl_3$); IR ($CHCl_3$) 3020, 2990, 2970, 2940, 2880, 2860, 1720, 1455, 1380, 1280, 710 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.78 (t, 1 H, *J* = 1.2 Hz), 8.02 (m, 2 H), 7.53 (m, 1 H), 7.42 (m, 2 H), 5.41 (ddd, 1 H, *J* = 2.2, 3.7, 9.9 Hz), 3.71–3.67 (m, 1 H), 3.67 (s, 3 H), 3.42 (dd, 1 H, *J* = 2.8, 9.0 Hz), 3.34 (m, 2 H), 2.62–2.46 (m, 3 H), 2.19 (m, 1 H), 2.16–2.11 (m, 1 H), 2.05 (m, 1 H), 2.00–1.86 (m, 3 H), 1.79–1.71 (m, 1 H), 1.50 (m, 3 H), 1.23 (s, 3 H), 1.18 (d, 3 H, *J* = 7.1 Hz), 1.08 (d, 3 H, *J* = 7.1 Hz), 1.03 (d, 3 H, *J* = 6.9 Hz), 0.97 (d, 3 H, *J* = 7.0 Hz), 0.91 (s, 3 H), 0.76 (d, 3 H *J* = 6.5 Hz). Anal. Calcd for $C_{32}H_{48}O_8$: C, 68.55; H, 8.63. Found C, 68.51; H, 8.64.

Preparation of Diol 10. A solution of 664 mg (3.35 mmol) of aldehyde **5** in 10 mL of THF containing 1 mL of water at 0 °C was treated with excess sodium borohydride. After 15 min at 0 °C, the reaction was slowly poured into saturated NH_4Cl (10 mL) and extracted with Et_2O (4 × 10 mL). The extracts were combined and dried ($MgSO_4$), and the solvent removed in vacuo. The residue was passed through a plug of silica gel (1 g, elution with Et_2O) to afford 660 mg of diol **10** as an inseparable mixture of compounds.

A solution of the above diol and 1.6 g (13.2 mmol) of 4-(dimethylamino)pyridine in 10 mL of CH_2Cl_2 was treated with 1.25 mL (13.2 mmol) of acetic anhydride. After 19 h at room temperature, the reaction was concentrated in vacuo and the residue directly chromatographed on 5 g of silica gel (elution with 5:95 Et_2O/pentane) to afford 627 mg (67%) of diacetate as a colorless oil: $[\alpha]_D$ +5.07° (*c* 0.73, $CHCl_3$); IR ($CHCl_3$) 3030, 2970, 2935, 2880, 1735 1375, 1250, 1120, 910 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.24 (dd, 1 H, *J* = 1.4, 8.8 Hz), 4.98 (d, 1 H, *J* = 9.4 Hz), 4.02 (AB portion of ABX, 2 H, J_{AB} = 10.9 Hz, J_{AX} = 5.0 Hz, J_{BX} = 4.0 Hz, $\Delta\nu_{AB}$ = 12.62 Hz), 2.35 (m, 1 H), 2.11 (m, 1 H), 2.05 (s, 3 H), 2.02 (s, 3 H), 1.58 (d, 3 H, *J* = 1.4 Hz), 1.28–1.15 (m, 4 H), 0.92 (d, 3 H, *J* = 6.6 Hz), 0.87 (d, 3 H, *J* = 7.0 Hz), 0.85 (m, 3 H).

A mixture of 230 mg (0.809 mmol) of diacetate and 111 mg (0.809 mmol) of anhydrous potassium carbonate in 6 mL of absolute MeOH was stirred at room temperature for 2 h. The reaction was poured into 5% NH_4Cl (10 mL) and extracted with Et_2O (4 × 15 mL). The extracts were combined and dried ($MgSO_4$), and the solvent was removed in vacuo. Chromatography of the residue on 15 g of silica gel (elution with 2:3 Et_2O/petroleum ether) afforded 155 mg (95%) of diol **10** as a colorless oil: $[\alpha]_D$ −43.77° (*c* 2.04, $CHCl_3$); IR ($CHCl_3$) 3610, 3550–3300, 3000, 2960, 2930, 2875, 1455, 1425 1220, 1090, 1030, 1005 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.14 (dd, 1 H, *J* = 1.2, 9.5 Hz), 3.84 (d, 1 H, *J* = 9.2 Hz), 3.68 (AB portion of ABX, 2 H, J_{AB} = 10.8 Hz, J_{AX} = 7.7 Hz, J_{BX} = 4.0 Hz, $\Delta\nu_{AB}$ = 21.5 Hz), 2.75 (br s, 2 H), 2.39 (m, 1 H), 1.92 (m, 1 H), 1.62 (d, 3 H, *J* = 1.2 Hz), 1.31–1.15 (m, 4 H), 0.94 (d, 3 H, *J* = 6.7 Hz), 0.87 (m, 3 H), 0.71 (d, 3 H, *J* = 7.0 Hz).

Preparation of Tosylate 11. A solution of diol **10** (271 mg, 1.36 mmoles) was selectively tosylated using TsCl (534 mg, 2.8 mmol) in pyridine (4 mL) and catalytic DMAP at 60 °C for 30 min. The mixture was concentrated, and the residue was purified by flash chromatography (15% ethyl acetate/hexanes) to afford 365 mg (76%) of the primary tosylate: $[\alpha]_D$ −14.7° (*c* 3.05, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 7.8 (m, 2 H), 7.35 (m, 2 H), 5.22 (br d, 1 H, *J* = 9.5 Hz), 4.16 (m, 2 H), 3.76 (dd, 1 H, *J* = 9.5, 2.7 Hz), 2.48 (s, 3 H), 2.39 (m, 1 H), 1.95 (m, 1 H), 1.58 (s, 3 H), 1.2 (m, 3 H), 0.9 (m, 11 H); IR ($CHCl_3$) 3600, 1220, 970, 900, 700 cm^{-1}; MS (20 eV), *m/z* (relative intensity) 354 (9.1, M^+), 336(5.1). Anal. Calcd for $C_{19}H_{30}O_4S$: C, 64.37; H, 8.53. Found: C, 64.35; H, 8.61.

Preparation of Compound 12. *tert*-Butyldimethylsilyl triflate (263 μL, 1.15 mmol) was added to a solution of alcohol **11** (271 mg, 0.765 mmol) and triethylamine (322 μL, 2.3 mmol) in CH_2Cl_2 (4 mL) at 0 °C. After 1 h, the reaction was quenched by the addition of MeOH (100 μL). The mixture was concentrated in vacuo, and the residue was purified by flash chromatography (10% ether/hexanes) to afford 373 mg of compound **12** as a white solid (96%): mp 88.5–89.5 °C (MeOH/H_2O); $[\alpha]_D$ −10.7° (*c* 7.3, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 7.8 (m, 2 H), 7.32 (m, 2 H), 5.02 (br d, 1 H, *J* = 9.5 Hz), 4.14 (dd, 1 H, *J* = 9.2, 4.0 Hz), 4.0 (dd, 1 H, *J* = 9.2, 6.7 Hz), 3.67 (d, 1 H, *J* = 10.5 Hz), 2.45 (s, 3 H), 2.35 (m, 1 H), 1.9 (m, 1 H), 1.5 (br s, 3 H), 1.2 (m, 2 H), 0.8 (m, 20 H), −0.02 (s, 3 H), −0.05 (s, 3 H); IR ($CHCl_3$) 1465, 1360, 1180, 1065, 970, 840 cm^{-1}; MS (20 eV), *m/z* (relative intensity) 411 (4.1, M^+ −*t*-Bu). Anal. Calcd for $C_{25}H_{44}O_4SSi$: C, 64.06; H, 9.46. Found: C, 63.77; H, 9.71.

Preparation of Sulfone 13. A solution of tosylate **12** (373 mg, 0.8 mmol) in DMF (2 mL) was treated with KSPh (1.6 mL of a freshly prepared 1 M solution in DMF). The solution was heated to 45 °C for 1 h. The mixture was cooled and poured into 0.1 N NaOH (20 mL). The product was extracted with ether (4 × 15 mL). The combined ethereal layers were washed with H_2O (25 mL) and saturated NaCl (25 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude sulfide was dissolved in 15% CH_2Cl_2/Et_2O (4 mL) and treated with diphenyl diselenide (250 mg, 0.8 mmol) and H_2O_2 (0.5 mL of a 30% solution) at 0 °C. After 0.5 h the yellow solution turned colorless, and a white precipitate formed. The mixture was warmed to room temperature, and after 4 h the solution was diluted with CH_2Cl_2 (10 mL) and washed with $NaHCO_3$ (10 mL) and $NaHSO_3$ (10 mL). The solution was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash chromatography (6% ethyl acetate/hexanes) to give 316 mg of sulfone **13** (91%) as a colorless oil: $[\alpha]_D$ −0.53° (*c* 8.8, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 7.9 (m, 2 H), 7.6 (m, 3 H), 5.8 (br d, 1 H, *J* = 9.5 Hz), 3.6 (d, 1 H, *J* = 6.4 Hz), 3.51 (dd, 1 H, *J* = 14.1, 1.3 Hz), 2.75 (dd, 1 H, *J* = 14.1, 10.2 Hz), 2.31 (m, 1 H), 2.11 (m, 1 H), 1.35 (br s, 3 H), 1.2 (m, 2 H), 1.08 (d, 3 H, *J* = 7.0 Hz), 0.85 (m, 17 H), −0.03 (s, 3 H), −0.08 (s, 3 H); IR ($CHCl_3$) 1465, 1310, 1150, 1088, 840 cm^{-1}; MS (20 eV), *m/z* (relative intensity) 423 (1.6, M^+ −Me), 381 (100, M^+ −*t*-Bu). Anal. Calcd for $C_{24}H_{42}O_3SSi$: C, 65.7; H, 9.65. Found: C, 65.67; H, 9.32.

Preparation of Oxazolidinone 14. *n*-Butyl lithium (56.5 mmol as a 2.5 M solution in hexane) was added to a solution of (4*R*,5*S*)-4-methyl-5-phenyl-2-oxazolidinone (10 g, 56.5 mmol) in THF (100 mL) at −78 °C. Immediately, the red solution was treated with valeryl chloride (6.7 mL, 56.5 mmol), and the reaction mixture was warmed to 0 °C for 1 h. The reaction was quenched with NH_4Cl (5 mL) and the mixture was concentrated in vacuo. The residue was diluted with water (50 mL), and the product was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with H_2O (50 mL) and saturated NaCl solution (50 mL) and dried ($MgSO_4$). Concentration under reduced pressure afforded 14.75 g (100%) of **14** as a thick syrup. The product could be recrystallized (hexanes) to give a white solid: mp 45.5–47 °C; $[\alpha]_D$ +43.3° (*c* 4.9, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 7.3 (m, 5 H) 5.65 (d, 1 H, *J* = 7.5 Hz), 4.75 (qn, 1 H, *J* = 7 Hz), 2.9 (m, 2 H), 1.5 (m, 4 H), 0.8 (m, 6 H); IR ($CHCl_3$) 1780, 1700, 1350, 1200, 700 cm^{-1}; MS (20 eV), *m/z* (relative intensity) 261 (5.0, M^+), 233 (2.8), 219 (93.7). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.9; H, 7.3; N, 5.27.

Preparation of (2*R*)-2-Methylpentanol (15). Oxazolidinone **14** (10 g, 38.3 mmol) was added to a solution of LDA (40 mmol, prepared by the addition of 16 mL of 2.5 M *n*-butyllithium to a solution of diisopropylamine (5.63 mL) at 0 °C) at −78 °C. After 30 min, methyl iodide (5 mL, 80 mmol) was added and the solution stirred for 2 h and then warmed to room temperature over 1 h. The reaction was quenched with NH_4Cl (5 mL), and the mixture was concentrated in vacuo. The residue was diluted with water (50 mL), and the product was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with H_2O (50 mL) and saturated NaCl solution (50 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was flash chromatographed (10% ethyl acetate/hexanes) to afford 8.3 g of product as a 8:1 mixture of diastereomers (78%). The desired major product could be purified by preparative HPLC (Waters Prep 500, 7.5% ethyl acetate/hexanes eluant): $[\alpha]_D$ +16.33° (*c* 1.34, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 7.35 (m, 5 H), 5.68 (d, 1 H, *J* = 7.2 Hz), 4.78 (qn, 1 H, *J* = 6.7 Hz), 3.75 (m, 1 H), 1.4 (m, 4 H), 1.2 (d, 3 H, *J* = 6.9 Hz), 0.9 (m, 6 H); IR ($CHCl_3$) 1780, 1700, 1345, 1200, 700 cm^{-1}; MS (20 eV), *m/z* (relative intensity) 275 (66.5, M^+), 246 (63.0), 233 (100); HRMS, $C_{16}H_{21}NO_3$ requires 275.1522, found 275.1522. A solution of oxazolidinone (7 g, 25.5 mmol) in Et_2O (100 mL) was treated with LAH (2 g, 50 mmol) at 0 °C. After 1 h, the reaction was quenched by the sequential addition of H_2O (2 mL), 15% NaOH (2 mL), and H_2O

(6 mL). The mixture was filtered through silica gel, and the filtrate was concentrated in vacuo. The product was purified by bulb-to-bulb distillation under aspirator pressure to afford 2.1 g of alcohol **15** (80%) as a colorless liquid: $[\alpha]_D$ +12.77° (*c* 9.13, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 3.55 (br s, 1 H), 3.35 (m, 2 H), 1.3 (m, 5 H), 0.8 (m, 6 H); IR ($CHCl_3$) 3620, 3450, 2900, 1460, 1030 cm^{-1}.

Preparation of Enoate 16. Me_2SO (3.3 mL, 46.2 mmol) was added dropwise to a solution of oxalyl chloride (1.84 mL, 21.7 mmol) in CH_2Cl_2 (120 mL) at −78 °C. After 5 min, alcohol **15** (1.85 g, 18.1 mmol) was added as a solution in CH_2Cl_2 (5 mL). After 30 min, the mixture was treated with Et_3N (12.7 mL, 90.5 mmol), and the solution was warmed to room temperature. (Carbethoxyethylidene)triphenylphosphorane (8 g, 22 mmol) was added, and the solution was heated to reflux and allowed to concentrate to ~80 mL. After 48 h at reflux, the mixture was concentrated, and the residue was filtered through silica gel (Et_2O eluant). The product was purified by bulb-to-bulb distillation (aspirator pressure) to afford 3.0 g (90%) of pure (*E*)-enoate **16**: $[\alpha]_D$ −27.04° (*c* 7.4, $CHCl_3$); IR ($CHCl_3$) 2900, 1700, 1650, 1450, 1265, 1100 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 6.5 (br d, 1 H, *J* = 10 Hz), 4.2 (q, 2 H, *J* = 7 Hz), 2.5 (m, 1 H), 1.8 (br s, 3 H), 1.3 (m, 5 H), 0.9 (m, 5 H).

Preparation of Enal 17. DIBAL (57 mL of a 1 M solution in hexane, 57 mmol) was added to a solution of enoate **16** (3.0 g, 16.3 mmol) in CH_2Cl_2 (100 mL) at −78 °C. After 1 h the reaction was quenched by the addition of MeOH (1 mL) and saturated NH_4Cl solution (0.5 mL), and the mixture was warmed to room temperature. The mixture was diluted with ether (100 mL) and filtered through silica gel to afford 2.3 g of crude alcohol.

Me_2SO (2.9 mL, 40.5 mmol) was added dropwise to a solution of oxalyl chloride (1.65 mL, 19.4 mmol) in CH_2Cl_2 (100 mL) at −78 °C. After 5 min, the crude alcohol from above (2.3 g, 16.2 mmol) was added as a solution in CH_2Cl_2 (5 mL). After 30 min, the mixture was treated with Et_3N (11.4 mL, 81 mmol), and the solution was warmed to room temperature. The mixture was poured into brine (50 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The organic layers were dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash chromatography (5% ether/hexanes) to give 1.83 g of enal **17** (80%): $[\alpha]_D$ −22.18° (*c* 1.33, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 9.4 (s, 1 H), 6.25 (d, 1 H, *J* = 9.0 Hz), 2.7 (m, 1 H), 1.75 (s, 3 H), 1.35 (m, 4 H), 1.08 (d, 3 H, *J* = 8 Hz), 0.9 (t, 3 H, *J* = 7 Hz); IR ($CHCl_3$) 1685, 1460, 1160 cm^{-1}.

Preparation of Tosylate 11. A solution of aldehyde **17** (381 mg, 2.72 mmol) in CH_2Cl_2 (20 mL) was treated with $TiCl_4$ (598 μL, 5.44 mmol) at −78 °C. After 15 min, silyl ketene acetal **18** (1.25 g, 4.08 mmol) was added dropwise. The solution turned dark red and was warmed to −50 °C for 4 h. The mixture was warmed to 0 °C and quenched with saturated $NaHCO_3$ (10 mL). The product was extracted with CH_2Cl_2 (3 × 30 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was dissolved in THF (20 mL) and treated with LAH (7 mL of a 1 M solution in ether, 7 mmol) at 0 °C. After 1 h, the reaction was quenched by the sequential addition of H_2O (250 μL), 15% NaOH (250 μL), and H_2O (750 μL). The salts were filtered and the filtrate was concentrated. The residue was flash chromatographed (50% ethyl acetate/hexanes) to afford an 8:1 mixture of threo/erythro isomers with > 20:1 face selectivity in 50% overall yield. The mixture of diols (271 mg, 1.36 mmol) was selectively tosylated with TsCl (534 mg, 2.8 mmol) in pyridine (4 mL) and catalytic DMAP at 60 °C for 30 min to obtain (after flash chromatography) 365 mg (76%) of a mixture of primary tosylates **11**. The desired major isomer could be separated by careful column chromatography (15% ethyl acetate/hexanes) or by HPLC: $[\alpha]_D$ −14.7° (*c* 3.05, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 7.8 (m, 2 H), 7.35 (m, 2 H), 5.22 (br d, 1 H, *J* = 9.5 Hz), 4.16 (m, 2 H), 3.76 (dd, 1 H, *J* = 9.5, 2.7 Hz), 2.48 (s, 3 H), 2.39 (m, 1 H), 1.95 (m, 1 H), 1.58 (s, 3 H), 1.2 (m, 3 H), 0.9 (m, 11 H); IR ($CHCl_3$) 3600, 1220, 970, 900, 700 cm^{-1}; MS (20 eV), *m/z* (relative intensity) 354 (9.1, M^+), 336 (5.1). Analysis C, H.

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Communications

Synthesis of Cycloalkenones via the Intramolecular Cyclopropanation of Furanyl Diazo Ketones

Summary: The reaction of α-diazo ketones derived from furanyl and benzofuranyl propionic acids with rhodium(II) acetate leads to cycloalkenones in high yield. Mechanistically, the reaction involves addition of the keto carbene to the furanyl π-bond followed by an electrocyclic ring opening reaction.

Sir: The general importance of cyclohexenones and cyclopentenones has led to the development of various methods for the synthesis of these compounds.[1,2] We report a new route to such systems that is based on the intramolecular cycloaddition reaction of an α-keto carbene.[3] Scheme I summarizes the approach. The key step is the thermal rearrangement of an oxabicyclo[3.1.0]hexene intermediate. Intramolecular cyclization of α-carbonyl carbenes and carbenoids has found widespread application for the preparation of a variety of theoretically and biologically interesting compounds.[4-12] Aside from Scott's elegant synthesis of azulene,[13] however, few other intra-

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