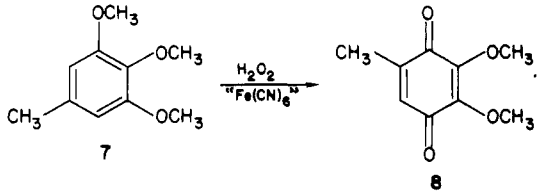
Scheme IV



to scarcely participate in the present oxidation by the results of runs 1 and 2 in Table I[6] and by those in the oxidation of 1,3,5-trimethoxybenzene (vide infra). Anyhow, the first step (phenol formation) does not likely make a difference in product distribution (2:3) between the hexacyanoferrate system and other iron systems. The reaction paths from intermediary phenols **4** and **5** might be affected by the species of iron used since Fe(III) also acts as an oxidant.

Iron-catalyzed oxidation of 1,3,5-trimethoxybenzene (**6**) with H_2O_2 gave simply quinone **3** as shown in Table II, where the superiority of hexacyanoferrate over the other iron catalysts was further clearly demonstrated. The oxidation of **6** to **3** proceeded effectively not only in acetic acid but also in acetonitrile and in acetone, in which participation of peracid was not possible (Scheme III).

The hexacyanoferrate-catalyzed oxidation with H_2O_2 could be applied to the conversion of 3,4,5-trimethoxytoluene (**7**) to 2,3-dimethoxy-5-methyl-*p*-benzoquinone (**8**) in a moderate yield (Scheme IV). Last, it is worth pointing out that benzene itself was oxidized to phenol with H_2O_2 by the use of potassium hexacyanoferrate as a catalyst.[7]

Experimental Section

Infrared (IR) spectra were recorded on a Jasco Model A-202 spectrometer. Mass spectra were recorded at 70 eV on a Hitachi RMU-6M mass spectrometer. A Varian XL-100 spectrometer was used to obtain ^1H nuclear magnetic resonance (NMR) spectra. 3,4,5-Trimethoxytoluene (**7**) was prepared by the published procedure.[8] All other reagents were commercial products of the highest purity obtainable.

The experiments summarized in Table I were performed according to the following general procedures.

Oxidation of 1,2,3-Trimethoxybenzene (1). Aqueous hydrogen peroxide (30%, 1.3 g, 11 mmol) was added to a solution of 1,2,3-trimethoxybenzene (**1**, 840 mg, 5 mmol) and Fe(II) or Fe(III) salt (50–800 mg) in acetic acid (5 mL). The solution was stirred at room temperature until hydrogen peroxide was consumed (KI test). The reaction mixture was diluted with CH_2Cl_2 and was successively washed with water, saturated aqueous solution of $NaHCO_3$, and brine. The organic layer was separated and was dried over $MgSO_4$. After removal of the solvent, the residue was rinsed with methanol to separate crystalline 2,6-dimethoxy-*p*-benzoquinone (**3**). The methanol solution was concentrated, and the residue was chromatographed on silica gel (Wako C-200). Elution with hexane–CH_2Cl_2 (1:1) afforded unreacted 1,2,3-trimethoxybenzene (**1**) and then 2,3-dimethoxy-*p*-benzoquinone (**2**).

2,3-Dimethoxy-*p*-benzoquinone (**2**): red needles (from hexane); mp 66–67 °C (lit.[9] 66–67 °C); NMR ($CDCl_3$) δ 4.00 (s, 6 H), 6.57 (s, 2 H); IR (KBr) 1680, 1670, 1635, 1590, 1305, 1210, 1080 cm^{-1}; mass spectrum, *m/e*, (relative intensity) 168 (M^+, 73), 153 (31), 123 (100), 82 (44), 69 (72).

2,6-Dimethoxy-*p*-benzoquinone (**3**): yellow needles (from acetic acid); mp 240–242 °C (lit.[10] 240–242 °C); NMR ($CDCl_3$) δ 3.80 (s, 6 H), 5.82 (s, 2 H); IR (KBr) 1700, 1640, 1590, 1325, 1260, 1220, 1100 cm^{-1}; mass spectrum, *m/e* (relative intensity) 168 (M^+, 50), 138 (18), 125 (13), 97 (12), 80 (35), 69 (100).

Oxidation of 1,3,5-Trimethoxybenzene (6). To a solution of potassium hexacyanoferrate (100 mg) in water (500 mg) was added a solution of 1,3,5-trimethoxybenzene (840 mg, 5 mmol) in acetone (5 g) and hydrogen peroxide (30% aqueous solution, 15 mmol) successively. After being stirred for 15 h at room temperature, the solution was diluted with CH_2Cl_2, washed with water, and dried over $MgSO_4$. The solution was concentrated, and the residue was rinsed with methanol to separate yellow crystalline 2,6-dimethoxy-*p*-benzoquinone (**3**) (660 mg, 79% yield).

The other experiments (runs 1–5) in Table II were carried out similarly to above experiment (run 6).

Oxidation of 3,4,5-Trimethoxytoluene (7). A solution of 3,4,5-trimethoxytoluene (**7**, 377 mg, 2.07 mmol) in acetonitrile (2 g) and hydrogen peroxide (30% aqueous solution, 480 mg, 4.24 mmol) were added to a solution of potasium hexacyanoferrate(III) (20 mg) in water (200 mg). After being stirred for 42 h at room temperature, the reaction mixture was diluted with CH_2Cl_2, washed with water, and then dried over $MgSO_4$. The CH_2Cl_2 solution was concentrated, and the residue was chromatographed on silica gel (Wako C-200). Elution with CH_2Cl_2 gave unreacted **7** (170 mg) and 2,3-dimethoxy-5-methyl-*p*-benzoquinone (**8**, 89 mg).

2,3-Dimethoxy-5-methyl-*p*-benzoquinone (**8**): red needles (from hexane); mp 58–59 °C (lit.[8] 59 °C); NMR ($CDCl_3$) δ 2.05 (d, J = 1.5 Hz, 3 H), 4.02 (s, 3 H), 4.04 (s, 3 H), 6.46 (q, J = 1.5 Hz, 1 H); IR (KBr) 1680, 1660, 1640, 1605, 1285, 1240, 1130 cm^{-1}; mass spectrum, *m/e*, (relative intensity) 182 (M^+, 59), 167 (33), 137 (100), 83 (79), 69 (36), 68 (44).

Registry No. 1, 634-36-6; **2**, 3117-02-0; **3**, 530-55-2; **4**, 19676-64-3; **6**, 621-23-8; **7**, 6443-69-2; **8**, 605-94-7; H_2SO_4, 7664-93-9; $Fe_2(SO_4)_3$, 10028-22-5; $FeSO_4$, 7720-78-7; $Fe(acac)_3$, 14024-18-1; $Fe(NO_3)_3$, 10421-48-4; $Fe(OAc)_2$, 3094-87-9; $Fe(phen)_3Cl_2$, 14978-15-5; $Fe(phen)_2(CN)_2$, 14768-11-7; Fe(III)EDTA, 15275-07-7; $K_4Fe(CN)_6$, 13943-58-3; $K_3Fe(CN)_6$, 13746-66-2; benzene, 71-43-2; phenol, 108-95-2.

(6) Peracetic acid or perbenzoic acid has been reported to oxidize arene **1** to afford quinone **3** in a poor yield: (a) Friess, S. U.; Soloway, A. H.; Morse, B. K.; Ingersoll, W. C. *J. Am. Chem. Soc.* **1952**, *74*, 1305. (b) Davidge, H.; Davies, A. G.; Kenyon, J.; Mason, R. F. *J. Chem. Soc.* **1958**, 4569. However, reexamination of oxidation of **1** with a peracid gave different result from the previous works. When **1** was treated with an equimolar amount of *m*-chloroperbenzoic acid in CH_2Cl_2 at room temperature for 3 h, no quinone **3** but 2,3,4-trimethoxyphenol (**4**) was obtained in a 26% yield (selectivity 50%). On the other hand, quinone **3** was more stable than its isomer **2** under the oxidation conditions. These facts suggest that arene **1** is attacked more easily at 4-position (leading to **4**) than at 5-position (leading to **5**) by electrophilic oxidant such as peracid and OH radical.

(7) The reaction was carried out in two-phase system (benzene/H_2O–H_2O_2–$K_3Fe(CN)_6$), and the reaction mixture was qualitatively analyzed.

(8) Sugihara, H.; Watanabe, H.; Kawamatsu, Y.; Morimoto, H. *Justus Liebigs Ann. Chem.* **1972**, *763*, 109.

(9) Baker, W.; Smith, H. A. *J. Chem. Soc.*, **1931**, 2542.

(10) Baker, W. *J. Chem. Soc.* **1941**, 662.

Contrasting Directed-Aldol Reactivity of a Pair of Epimeric Trimethylsilyl Enol Ethers

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As a general reaction type, directed aldol condensations constitute a most useful group of processes that have many obvious applications in organic synthesis.[1,2] The variant involving trimethylsilyl enol ethers and acetals or ketals under the influence of titanium tetrachloride holds particular advantage because of its high regio- and chemoselectivity and its operation under mild conditions (−78 °C).

(1) Mukaiyama, T. *Org. React. (N.Y.)* **1982**, *28*, 203.

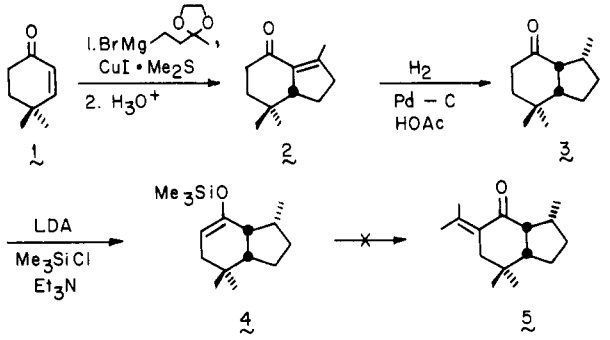
(2) Heathcock, C. H. In "Asymmetric Synthesis, Volume 3, Part B", Morrison, J. D., Ed.; Academic Press: New York, 1984; Chapter 2.

0022-3263/85/1950-1768$01.50/0

Chelation to Ti(IV) by the reaction partners appears to provide an important driving force to carbon–carbon bond formation.

In connection with a projected sesquiterpene synthesis, a need arose to prepare the bicyclic α,η-unsaturated ketone **5** and consideration was given to introduction of the isopropylidene group by means of the aforementioned methodology. However, trimethylsily enol ether **4** failed to react with 2,2-dimethoxypropane, apparently because of the steric influence of the secondary methyl group. Inasmuch as there does not appear to be a recorded analysis of the effect of steric influences on the directed aldol reaction and because further application of this process required an understanding of such steric control, we have investigated the comparative reactivity of **4** and its C-9 epimer.

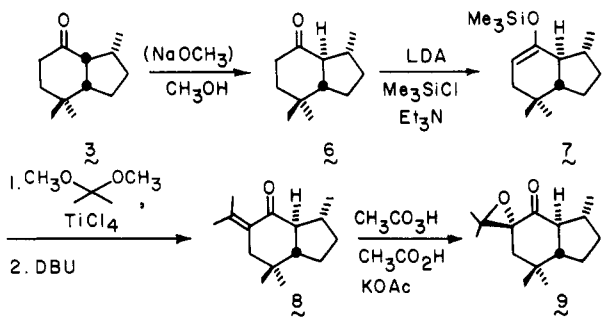
Conversion of the readily available 4,4-dimethylcyclohex-2-enone (**1**)[3] to **2** was readily accomplished by conjugate additon of [3,3-(ethylenedioxy)butyl]magnesium bromide[4] and acid hydrolysis. Saturation of the double



bond in **2** by catalytic hydrogenation over palladium on charcoal in acetic acid cleanly set two additonal stereocenters. That **3** was a single isomer was evident from the 12 lines observed in its ^{13}C NMR spectrum. The secondary methyl group was assigned the α-configuration on the basis of the expection that delivery of hydrogen should occur from the less hindered β face. The large coupling constant (J = 7.5 Hz) for the triplet due to the proton α to the carbonyl (δ 2.68) was considered confirmatory for this assignment.[5]

Trapping of the kinetic enolate[6] of **3** with chlorotrimethylsilane led to **4** and set the stage for the Lewis acid mediated aldol condensation. However, all attempts to effect reaction of **4** with 2,2-dimethoxypropane led to no observable reaction (except the inevitable hydrolysis on workup). Inspection of Dreiding models reveals that cis fusion of the bicyclo[4.3.0]nonanone ring system as in **4** forces the α-oriented secondary methyl group into exceptionally close proximity to the ether oxygen. Might the resultant crowding impede formation of the chelated β-methoxy ketone intermediate and thereby curtail reaction?

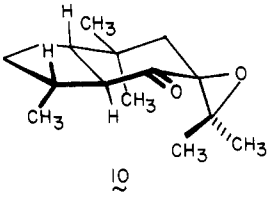
To probe this question, **3** was exposed to a catalytic quantity of sodium methoxide in methanol. Efficient conversion to **6** resulted within 8 h at room temperature. In this epimer, the methyl doublet is considerably shielded (δ 1.00) relative to that in **3** (δ 1.25); this observation conforms to its spatial displacement from an original coplanar relationship with the carbonyl group.[7] Following



conversion to **7**, aldol condensation with 2,2-dimethoxypropane and $TiCl_4$ proceeded uneventfully. Direct treatment of the β-methoxy enone with diazabicycloundecene and 3-Å molecular sieves[8] gave rise to **8** in 58% yield following purification.

Since the secondary methyl group in **7** finds itself projected into a plane virtually parallel to the pπ orbitals of the double bond, it cannot provide meaningful steric encumbrance as in **4**. Although it is not clear whether the inertness of **4** is due to a kinetic or thermodynamic factor, intramolecular congestion about the seat of Ti···O complexation appears most plausibly responsible. In this connection, results from those two diastereomers having β secondary methyl groups would be informative.

The conformational rigidity of **8** lends itself to stereocontrolled addition to its isopropylidene double bond. The clean conversion to epoxide **9** upon reaction with peracetic acid in acetic acid exemplifies this chemistry. Designation of the oxirane stereochemistry as the end result of α attack is based on the downfield migration of both tertiary cyclohexane-bound methyls in **9** (δ 1.15, 1.10) relative to their position in **8** (δ 1.00, 0.95). The absorption of the secondary methyl substituent (δ 1.10) is unaffected by this chemical event. Projection of the epoxide oxygen as in **10** uniquely serves to insulate the transannular axial methyl group from strong shielding influences.[9]



10

Experimental Section

5,6,7,7a-Tetrahydro-3,7,7-trimethylinden-4(2*H*)-one (2). A solution of 2-(2-bromoethyl)-2-methyl-1,3-dioxolane (33.8 g, 180 mmol) and 1,2-dibromoethane (5 mL) in tetrahydrofuran (14 mL) was added over 6 h to magnesium turnings (13.0 g, 540 mmol) in tetrahydrofuran (250 mL). In a separate flask, copper iodide (4.40 g, 23 mmol) in dimethyl sulfide (20 mL) was cooled to −78 °C and the Grignard solution was transferred by canula to this mixture. 4,4-Dimethylcyclohexenone (7.50 g, 60.0 mmol) in tetrahydrofuran (12 mL) was added over 8 h at −78 °C. The reaction mixture was maintained at −78 °C for 4 h and at room temperature for 4 h. At this point, ammonium chloride solution was added, the mixture was filtered, and the filtrate was extracted with ether. The ether layer was washed with sodium bicarbonate solution and brine, dried, and evaporated. The residue was dissolved in a mixture of tetrahydrofuran (600 mL), water (60 mL), and concentrated hydrochloric acid (12 mL) and then stirred for 40 h. This mixture was neutralized with solid potassium

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(9) Paquette, L. A.; Fristad, W. F.; Schuman, C. A.; Beno, M. A.; Christoph, G. G. *J. Am. Chem. Soc.* **1979**, *101*, 4645.

carbonate, evaporated, and extracted with ether. The ether solution was washed with sodium bicarbonate solution and brine, dried, and evaporated. Purification by HPLC (elution with petroleum ether/ethyl acetate, 30:1) gave **2** (6.33 g, 60%); IR (neat, cm^{-1}) 2940, 1678, 1618; ^1H NMR (90 MHz, $CDCl_3$) δ 2.8 (m, 1 H), 2.5–2.2 (m, 4 H), 2.1 (m, 3 H), 2.0–1.3 (m, 4 H), 0.97 (s, 3 H), 0.82 (s, 3 H); MS, m/z calcd (M^+) 178.1358, obsd 178.1362.

(3*R,3a*R**,7a*S**)-Tetrahydro-3,7,7-trimethyl-4(3a*H*)-indanone (3).** Ketone **2** (2.69 g, 15.1 mmol) and 10% palladium on carbon (300 mg) in acetic acid (50 mL) was shaken under an atmosphere of hydrogen (50 psi) for 12 h. The solution was filtered and added to a mixture of ether and water. The biphasic mixture was neutralized with solid potassium carbonate. The aqueous layer was extracted with ether and the combined ether phases were washed sodium bicarbonate solution and brine prior to drying and solvent evaporation. There was obtained 2.61 g (96%) of **3**: IR (neat, cm^{-1}) 2940, 2865, 1710, 1460, 1365, 900, 710; ^1H NMR (90 MHz, $CDCl_3$) δ 2.68 (t, J = 7.5 Hz, 1 H), 2.5–1.4 (series of m, 10 H), 1.25 (d, J = 6 Hz, 3 H), 1.24 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR ($CDCl_3$) ppm 215.13, 54.50, 53.83, 38.72, 37.93, 34.78, 31.13, 29.74, 28.64, 27.79, 25.85, 16.32; MS, m/z calcd (M^+) 180.1514, obsd 180.1519.

Trimethylsilyl Enol Ether 4. A tetrahydrofuran solution (10 mL) of **3** (100 mg, 0.56 mmol) was added during 1 h to lithium diisopropylamide (0.73 mmol) in the same solvent (10 mL) at −78 °C. An 0.6-mL aliquot of a centrifuged solution containing no precipitate (triethylamine hydrochloride) was drawn off by syringe from a mixture of chlorotrimethylsilane (1.68 mL), triethylamine (2 mL), and tetrahydrofuran (4 mL) and added to the cold (−78 °C) enolate anion solution. The reaction mixture was allowed to warm to room temperature and poured into a mixture of petroleum ether (60 mL) and ice-cold saturated sodium bicarbonate solution (60 mL). The organic phase obtained after thorough shaking was dried and evaporated to give 130 mg (93%) of **4** as a colorless oil: IR (neat, cm^{-1}) 2960, 2280, 1650, 1460, 1250, 1180; ^1H NMR (90 MHz, $CDCl_3$) δ 4.60 (d, J = 5 Hz, 1 H), 3.4 (m, 1 H), 2.4–1.0 (series of m, 8 H), 0.99 (d, J = 6.5 Hz, 3 H), 0.88 (s, 3 H), 0.80 (s, 3 H), 0.11 (s, 9 H); MS, m/z calcd (M^+) 252.1909, obsd 252.1915.

(3*R,3a*S**,7a*S*)-Tetrahydro-3,7,7-trimethyl-4(3a*H*)-indanone (6).** Ketone **3** (4.83 g, 27 mmol) was stirred with sodium methoxide in methanol (from 1.0 g of sodium metal in 100 mL of methanol) for 8 h. The mixture was evaporated to one-half its volume, poured into ammonium chloride solution, and extracted with ether. The combined ether layers were washed with sodium bicarbonate solution and brine, dried, and evaporated to give 4.19 g (85%) of **6**: IR (neat, cm^{-1}) 2940, 2060, 1710; ^1H NMR (90 MHz, $CDCl_3$) δ 2.5–1.4 (series of m, 11 H), 1.02 (s, 3 H), 0.92 (d, J = 4 Hz, 3 H), 0.90 (s, 3 H); MS, m/z calcd (M^+) 180.1514, obsd 180.1519.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.98; H, 11.24.

Trimethylsilyl Enol Ether 7. Ketone **6** (1.0 g, 5.56 mmol) in tetrahydrofuran (10 mL) was added to a cold (−78 °C) solution of lithium diisopropylamide (7.23 mmol) in tetrahydrofuran (30 mL) over 1 h. This solution was treated with a portion (5.6 mL) of a mixture of trimethylsilyl chloride (3.4 mL), triethylamine (4 mL), and tetrahydrofuran (8 mL). This mixture was spun in a centrifuge tube to settle the white precipitate formed and the supernatant that was added to the enolate solution was free of any precipitate. The reaction mixture was stirred at ambient temperature for 1 h and poured into petroleum ether. The petroleum ether solution was washed with sodium bicarbonate solution and brine, dried, and evaporated to give **7** (1.43 g, 100%): IR (neat, cm^{-1}) 2940, 2860, 1640, 1245, 1195, 895, 830; ^1H NMR (90 MHz, CCl_4/CH_2Cl_2) δ 4.3 (m, 1 H), 3.4 (m, 1 H), 2.1–1.1 (series of m, 8 H), 1.0 (d, J = 2 Hz, 3 H), 0.85 (s, 3 H), 0.75 (s, 3 H), 0.10 (s, 9 H); MS, m/z calcd (M^+) 252.1909, obsd 252.1915.

(3*R,3a*S**,7a*S**)-Tetrahydro-5-isopropylidene-3,7,7-trimethyl-4(3a*H*)-indanone (8).** A solution of **7** (1.43 g, 5.56 mmol) in dichloromethane (10 mL) was added to a cold (−78 °C) solution of 2,2-dimethoxypropane (0.75 mL, 6.5 mmol) and titanium(IV) chloride (2.75 mL, 5.56 mmol) in dichloromethane (50 mL). The reaction mixture was allowed to warm to room temperature during 5 h and then treated carefully with water at −78 °C. The mixture was poured into water and extracted with ether. The combined ether phases were washed with water and brine, dried, and evaporated. The residue was admixed with diazabicycloundecene (1.52 g, 10 mmol) and molecular sieves (3-Å, 1.25 g) in dichloromethane (25 mL) and was heated at the reflux temperature for 8 h. This mixture was filtered, poured into 10% hydrochloric acid, and extracted with ether. The combined ether solutions were washed with sodium bicarbonate solution and brine, dried, and evaporated. Purification by HPLC (elution with petroleum ether/ethyl acetate, 40:1) gave **8** (700 mg, 58%); IR (CCl_4, cm^{-1}) 2940, 2860, 1685, 1625, 1450, 1360; ^1H NMR (90 MHz, $CDCl_3$) δ 2.6–2.0 (m, 4 H), 1.9 (s, 3 H), 1.75 (s, 3 H), 1.6–1.2 (m, 5 H), 1.10 (d, J = 6 Hz, 3 H), 1.00 (s, 3 H), 0.95 (s, 3 H); MS, m/z calcd (M^+) 220.1827, obsd 220.1833.

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.46, H, 10.98.

(3*R,3a*S**,7a*S**)-Tetrahydro-3,3′,3′,7,7-pentamethylspiro[indan-5(4*H*),2′-oxiran]-4-one (9).** Ketone **8** (260 mg, 1.18 mmol) in acetic acid (5 mL) previously saturated with potassium acetate was cooled to 15 °C. To this solution was added 38% peracetic acid (222 mg, 1.18 mmol). The reaction mixture was warmed to room temperature, stirred for 24 h, poured into ether and water, neutralized with solid potassium carbonate, and extracted with ether. The ether layer was washed with sodium bicarbonate solution and brine, dried, and evaporated to give **9** as colorless crystals (210 mg, 75%): mp 91.0–91.5 °C (from petroleum ether); IR (CCl_4, cm^{-1}) 2940, 2860, 1725, 1455, 1380, 1370, 1235; ^1H NMR (90 MHz, $CDCl_3$) δ 2.5–1.5 (series of m, 9 H), 1.45 (s, 3 H), 1.25 (s, 3 H), 1.15 (s, 3 H), 1.10 (d, J = 6 Hz, 3 H), 1.10 (s, 3 H); ^{13}C NMR ($CDCl_3$) ppm 206.52, 70.15, 63.48, 60.20, 57.35, 46.36, 33.56, 31.80, 31.37, 29.25, 24.64, 20.39, 19.66; MS, m/z calcd (M^+) 236.1776, obsd 236.1784.

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.07; H, 10.21.

Acknowledgment. This research was supported by the National Institutes of Health (Grant GM-28468).

Registry No. **1**, 1073-13-8; **2**, 91763-57-4; **3**, 96041-18-8; **4**, 96041-19-9; **6**, 96041-20-2; **7**, 96041-21-3; **8**, 96041-22-4; **9**, 96041-23-5; 2-(2-bromoethyl)-2-methyl-1,3-dioxolane, 37865-96-6.

Structural Effects on Intramolecular Furan Cycloadditions

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The intramolecular Diels–Alder reaction has been a valuable tool for the construction of polycyclic ring systems.[1] The versatility of furan as the diene in this process has been demonstrated by elaboration of its cycloadducts into aromatic systems,[2] oxabicyclo[2.2.1.]heptane systems,[3] and cis-2,5-disubstituted tetrahydrofuran products.[4] We are interested in utilizing these cycloadducts for the preparation of highly substituted tetrahydrofuran natural product systems such as **1**.[5] In this work we demonstrate

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