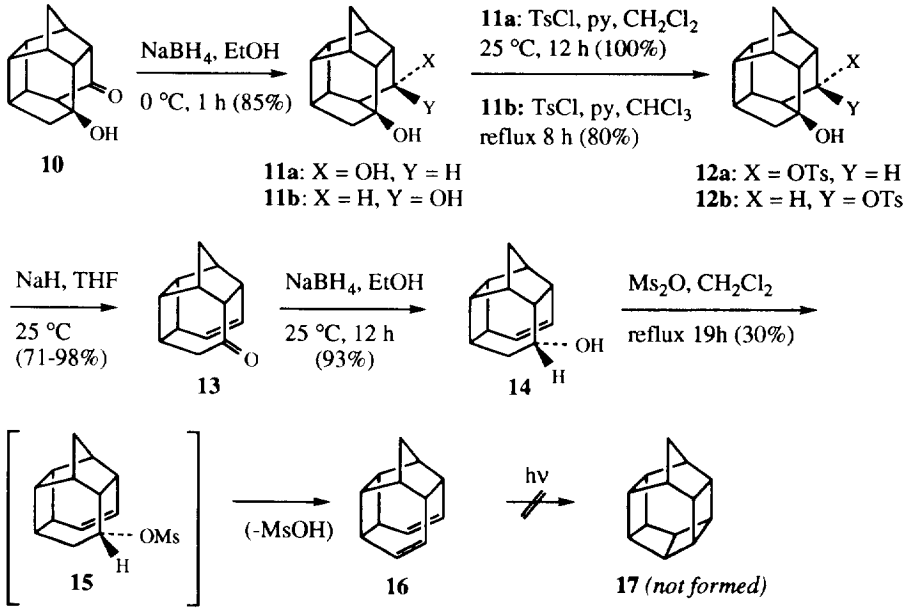
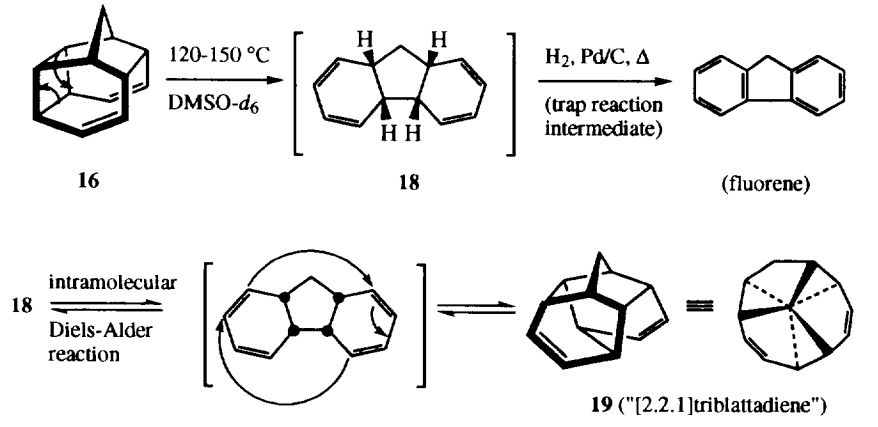
afford a *cis,cisoid,cis* tricyclic tetraene (i. e., a "tetrahydrofluorene"), **18**. Compound **18** is not stable to the reaction conditions; this intermediate undergoes subsequent intramolecular Diels-Alder cycloaddition to afford the ob-served rearrangement product, pentacyclo[7.4.0.0^{2,6}.0^{3,11}.0^{5,10}]trideca-7,12-diene[10] (i.e, "[2.2.1]triblattadiene", **19** (Scheme 3).

Scheme 2



Scheme 3



The intermediacy of **18** was inferred via analysis of the ^{1}H NMR spectrum of partially rearranged **16**.[11] Additional evidence which supports the structure of **18** suggested in Scheme 3 was obtained via a trapping experiment. Thus, when thermal rearrangement of **16** was performed in the presence of 10% palladized charcoal, the bis(dehydrogenation) product, i. e., fluorene, could be isolated. The melting point of an intimate mixture of the material thereby obtained with authentic fluorene was undepressed. Surprisingly,[10] we were unable to trap **18** when thermal rearrangement of **16** was performed in the presence of powerful dienophiles (i. e., maleic anhydride and 1-methyl-1,3,4-triazoline-2,5-dione).

Kinetic Studies.[12] A minimum temperature of *ca.* 120 °C (393 K) is required to initiate thermal rearrangement of **16**, whereas thermal decomposition of the reaction mixture becomes evident at *ca.* 150 °C (423 K). Thus, it became practical for us to perform the kinetic studies only within this relatively narrow temperature range, a situation which necessarily renders our kinetic analysis highly uncertain.

The course of thermal rearrangement of **16** performed at 410 K and at 422.5 K was monitored by using NMR spectral techniques (see the Experimental Section). In order to analyze the NMR data and to extract kinetic information therefrom, we assumed that the rearrangements of **16** to **18** and of **18** to **19** are irreversible processes (rate constants k_1 and k_2, respectively).

Details of the kinetic analysis are given in the Experimental Section. Inspection of least-squares fitted plots of concentration vs. time for thermal rearrangement of **16** reveals a good quality fit of the calculated rate profile to the experimental data obtained at 410 K; however, the corresponding fit in the case of data obtained at 422.5 K is less satisfactory.[13]

Experimental Section

Melting points are uncorrected. High-resolution mass spectra were obtained by personnel at the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, Lincoln, NE 68588. Elemental microanalyses were obtained by personnel at M-H-W Laboratories, Phoenix, AZ and at Galbraith Microanalytical Laboratory, Knoxville, TN. An authentic sample of fluorene purchased from Aldrich Chemical Company was recrystallized from benzene to afford a colorless microcrystalline solid: mp 113 °C.

Sodium Borohydride Promoted Reduction of 10. A solution of **10** (4.50 g, 22.3 mmol) in EtOH (120 mL) was cooled externally to 0 °C. To this cooled solution was added portionwise with stirring $NaBH_4$ (631 mg, 16.7 mmol). After the addition of the reducing agent had been completed, the external cold bath was removed. The reaction mixture was allowed to warm gradually to room temper-ature and then was stirred at ambient temperature for 16 h. The reaction was quenched by addition of solid $NaHCO_3$ (2.35 g, 28.0 mmol), and the resulting mixture was stirred for 1 h and then diluted with water. The resulting aqueous suspension was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. Crude **11a** and **11b** (mixture of isomers, 3.86 g, 85%) was thereby obtained. A portion of this crude product (400 mg) was purified via column chromatography on silica gel by eluting with 20% EtOAc-hexane. The first chromatography fractions afforded a pale yellow, waxy solid (107 mg). This material was recrystallized from CH_2Cl_2-hexane to afford isomerically pure diol **11a** as a colorless microcrystalline solid: mp 270-272 °C; IR (KBr) 3355 (m), 2935 (s), 2860 (w), 1420 (w), 1326 (w), 1263 (w), 1188 (w), 1063 (m), 994 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 1.16 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.40 (*AB*, J_{AB} = 10.2 Hz, 1 H), 1.64 (*AB*, J_{AB} = 11.9 Hz, 1 H), 1.76 (*AB*, J_{AB} = 11.9 Hz, 1 H), 2.01-2.36 (m, 4 H), 2.44 (m, 2 H), 2.59 (m, 2 H), 2.83 (m, 1 H), 3.01 (s, 2 H), 4.03 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 31.78 (d), 32.92 (d), 37.32 (t), 38.21 (d), 40.14 (d), 41.29 (t) , 42.12 (d), 44.12 (d), 51.31 (d), 53.99 (d), 55.26 (d), 76.36 (d), 87.52 (s). Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.30; H, 7.95.

The second chromatography fractions afforded a colorless microcrystalline solid (237 mg) which was recrystallized from $CHCl_3$ to give isomerically pure **11b** as a colorless microcrystalline solid: mp 308-310 °C; IR (KBr) 3288 (s), 3251 (s), 2955 (m), 2865 (m), 1443 (w), 1317 (m), 1159 (w), 1079 (m), 1053 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.17 (t, *J* = 7.0 Hz, 1 H), 1.27 (*AB*, J_{AB} = 9.7 Hz, 1 H), 1.40 (*AB*, J_{AB} = 10.2 Hz, 1 H),

1.56 (m, 3 H), 1.76 (*AB*, J_{AB} = 11.2 Hz, 1 H), 1.97 (m, 1 H), 2.36 (m, 5 H), 2.67 (m, 1 H), 2.81 (m, 1H), 4.50 (t, J = 5.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 31.76 (d), 32.96 (d), 35.64 (d), 37.80 (d), 38.83 (t), 39.02 (d), 40.82 (t), 42.16 (d), 49.08 (d), 51.11 (d), 52.48 (d), 71.70 (d), 84.87 (s). Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.24; H, 7.77.

$NaBH_4$-$CeCl_3$ Promoted Reduction of 10.[7] To a mixture of **10**[3a] (404 mg, 2.0 mmol) and $CeCl_3 \cdot 7H_2O$ (3.7 g, 10 mmol) in MeOH (15 mL) was added $NaBH_4$, (114 mg, 3.0 mmol) portionwise with stirring. After the addition of the reducing agent had been completed, the reaction mixture was stirred at ambient temperature for 3 h. The reaction was quenched by addition of water (15 mL), and the resulting mixture was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were washed sequentially with water (10 mL) and brine (10 mL). The organic layer then was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue (400 mg) was purified via column chromatography on silica gel by eluting with 90% EtOAc-hexane. Two chromatography fractions were thereby obtained. Workup of the first chromatography fraction afforded **11a** (363 mg, 89%); similar workup of the second chromatography fraction gave **11b** (22 mg, 5%).

***exo*-2-Tosyloxypentacyclo[6.5.0.0^{3,7}.0^{4,12}.0^{6,11}]tridecan-8-ol (12a).** To a mixture of **11a** (310 mg, 1.5 mmol) and pyridine (2 mL) in CH_2Cl_2 (8 mL) was added TsCl (300 mg, 1.6 mmol), and the resulting mixture was stirred at room temperature for 12 h. The reaction was quenched by addition of water (10 mL), and the resulting mixture was stirred at room temperature for 2 h. The mixture then was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were washed sequentially with 10% aqueous HCl (2 x 10 mL), 15% aqueous $NaHCO_3$ (20 mL), water (10 mL), and brine (10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. Crude **12a** (540 mg, 100%) was thereby obtained. Repeated recrystallization of this material from EtOAc-hexane afforded pure **12a** as a colorless microcrystalline solid: mp 136-137 °C; IR (KBr) 3500 (s), 1595 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.10-1.20 (m, 2 H), 1.40-1.65 (m, 2 H), 2.10-2.75 (m, 11 H), 5.00 (t, J = 5.5 Hz, 1 H), 7.30 (*AB*, J_{AB} = 10.0 Hz, 2 H), 7.75 (*AB*, J_{AB} = 10.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.07 (q), 31.41 (d), 32.33 (d), 35.97 (d), 37.79 (d), 38.31 (t), 38.77 (d), 40.13 (t), 41.43 (d), 46.57 (d), 49.62 (d), 49.82 (d), 82.53 (d), 83.24 (s), 127.14 (d), 129.35 (d), 133.64 (s), 144.11 (s). Anal. Calcd for $C_{20}H_{22}O_4S$: C, 67.04; H, 6.15. Found: C, 67.04; H, 6.25.

***endo*-2-Tosyloxypentacyclo[6.5.0.0^{3,7}.0^{4,12}.0^{6,11}]tridecan-8-ol (12b).** To a mixture of **11b** (204 mg, 1.0 mmol) and pyridine (2 mL) in $CHCl_3$ (5 mL) was added TsCl (210 mg, 1.1 mmol), and the resulting mixture was refluxed for 8 h. The reaction was quenched by addition of 10% aqueous $NaHCO_3$ (5 mL), and the resulting mixture was stirred at room temperature for 2 h. The mixture then was extracted with $CHCl_3$ (3 x 20 mL). The combined organic extracts were washed sequentially with 10% aqueous HCl (10 mL), water (10 mL), and brine (10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. Crude **11b** (285 mg, 80%) was thereby obtained; repeated recrystallization of this material from EtOAc-hexane afforded pure **11b** as a colorless microcrystalline solid: mp 110-111 °C; IR (KBr) 3510 (m), 2945 (s), 1600 (w), 1349 (s), 1190 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.10-1.40 (m, 2 H), 1.45-1.90 (m, 2 H), 2.00-2.95 (m, 13 H), 4.80 (s, 1 H), 7.30 (*AB*, J_{AB} = 10.0 Hz, 2 H), 7.75 (*AB*, J_{AB} = 10.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.59 (q), 31.41 (t), 32.39 (d), 37.14 (d), 38.18 (d), 41.17 (d), 41.36 (t), 42.08 (d), 45.07 (d), 51.77 (d), 52.48 (d), 52.74 (d), 86.94 (s), 88.70 (d), 127.59 (d), 129.81 (d), 134.12 (s), 144.66 (s). Anal. Calcd for $C_{20}H_{22}O_4S$: C, 67.04; H, 6.15. Found: C, 67.33; H, 6.19.

Pentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]tridec-2-en-6-one (13). Method A. A predried round bottom flask that had been fitted with an argon bubbler was cooled externally to 0 °C (ice-water bath). Into this flask was added under argon NaH (48 mg, 2.0 mmol) and dry THF (3 mL). To this mixture was added via syringe a solution of **12a** (540 mg, 1.5 mmol) in dry THF (10 mL). The cold bath was removed, and the reaction was stirred at room temperature for 16 h. The reaction was quenched by careful, dropwise addition of water (10 mL). The resulting mixture was extracted with EtOAc (4 x 25 mL). The combined organic layers were washed sequentially with water (10 mL) and with brine (15 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. Pure **13** (280 mg, 98%) was thereby obtained as a colorless microcrystalline solid: mp 220-225 °C (dec.); IR (KBr) 1690 (s), 1650 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.40-1.60 (m, 2 H), 1.70-2.10 (m, 2 H), 2.20-2.95 (m, 6 H), 3.00-3.30 (m, 2 H), 5.60-6.00 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 31.60 (d), 32.09 (d), 34.10 (d), 34.88 (d), 38.05 (t), 38.51 (t), 38.82 (d), 39.23 (d), 40.31 (d), 56.38 (d), 127.6 (d), 131.5 (d), 213.6 (s). Anal. Calcd for $C_{13}H_{14}O$: M_r^+ 186.1045. Found (high-resoluton mass spectrometry) M_r^+ 186.1037.

Method B. A predried round bottom flask that had been fitted with an argon bubbler was cooled externally to 0 °C (ice-water bath). Into this flask was added under argon NaH (36 mg, 1.5 mmol) and dry THF (3 mL). To this mixture was added via syringe a solution of **12b** (358 mg, 1.0 mmol) in dry THF (3 mL). The ice-water bath was removed, and the reaction was refluxed for 0.5 h. Workup of the reaction was performed in the same manner as described above for the corresponding reaction of **12a** with NaH. Pure **13** (132 mg, 71%) was thereby obtained.

***endo*-6-Hydroxypentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]tridec-2-ene (14).** A soluion of **13** (186 mg, 1.0 mmol) in EtOH (5 mL) was cooled externally to 0 °C (ice-water bath). To this cooled solution was added with stirring $NaBH_4$, (19 mg, 0.50 mmol). The cold bath was removed, and the reaction was allowed to warm to room temperature. The reaction mixture was stirred at ambient temperature for 12 h. The reaction was then quenched by addition of solid $NaHCO_3$ (210 mg, 2.5 mmol). The resulting mixture was stirred for 1 h, at which time water (1 mL) was added, and stirring was continued for an additional 0.5 h. The mixture was extracted with EtOAc (3 x 25 mL), and the combined organic layers were washed sequentially with water (5 mL) and with brine (10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. Pure **14** (175 mg, 93%) was thereby obtained as a colorless microcrystalline solid: mp 212-215 °C; IR (KBr) 3355 (br, s), 1635 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.10-1.75 (m, 4 H), 1.80-2.20 (m, 3 H), 2.20-2.80 (m, 4 H), 2.80-3.25 (m, 2 H), 3.65-3.90 (m, 1 H), 5.70-6.05 (m, 1 H), 6.30-6.60 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 32.01 (d), 32.41 (t), 33.73 (d), 36.19 (d), 36.30 (d), 36.99 (d), 39.00 (t), 41.25 (d), 41.43 (d), 51.10 (d), 67.91 (d), 131.5 (d), 133.7 (d). Anal. Calcd for $C_{13}H_{16}O$: M_r^+ 188.1201. Found (high-resolution mass spectrometry) M_r^+ 188.1203.

Pentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]trideca-2,6-diene (16). To a solution of **14** (104 mg, 0.55 mmol) and pyridine (1 mL) in $CHCl_3$ (4 mL) under argon atmosphere was added methanesulfonyl anhydride (Ms_2O, 174 mg, 1.0 mmol), and the resulting mixture was refluxed for 3 h. An additional quantity of Ms_2O (174 mg, 1.0 mmol) was added, and the resulting mixture was refluxed for an additional 16 h. The reaction was allowed to cool to room temperature and then was quenched via addition of 10% aqueous $NaHCO_3$ (10mL). The resulting mixture was stirred for 0.5 h. The layers were separated, and the aqueous layer was extracted with $CHCl_3$ (2 x 5 mL). The combined organic extracts were washed sequentially with 10% aqueous HCl (2 x 5 mL), water (5 mL), and brine (5 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 10% EtOAc-hexane. Pure **16** (28 mg, 30%) was thereby obtained as colorless waxy solid: mp 150-152 °C; IR (KBr) 3023 (m) 2929 (s) 2860 (m), 1633 (m), 1451 (w), 1376 (w), 1333 (w), 1238 (w), 806 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.37 (*AB*, J_{AB} = 9.4 Hz, 1 H), 1.48 (*AB*, J_{AB} = 9.4 Hz, 1 H), 2.06 (m, 2 H), 2.59 (m, 2 H), 2.65 (m, 2 H), 3.18 (m, 2 H), 5.69 (m, 2 H), 6.13 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.67 (d), 36.82 (t), 37.56 (d), 39.90 (d), 42.72 (d), 127.97 (d), 131.78 (d). Anal. Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.28 Found: C, 91.60; H, 8.12.

Thermal Rearrangement of 16. A solution of diene **16** (51 mg, 0.3 mmol) in DMSO-d_6 (0.4 mL) was placed in an NMR tube, and the solution was degassed by using a repetitive freeze-evacuate-thaw cycle. After three such cycles, the NMR tube was sealed, placed in a thermostatted oil bath, and heated to 150-155 °C for 14 h. The reaction could be monitored conveniently by ^{1}H and ^{13}C NMR spectral analysis simply by removing the NMR tube from the oil bath at various time intervals during the course of the reaction and then by obtaining NMR spectra at each interval.

In order to characterize the final rearrangement product, the NMR tube was opened, and the reaction mixture was poured into water (3 mL). The resulting aqueous suspension was extracted with hexane (15 x 1 mL) until the cloudy aqueous layer became clear. The combined organic layers were washed with water (4 mL), dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with hexane. The first chromatography fraction afforded pure **18** (14 mg, 32%) as a colorless oil; ^{1}H NMR (DMSO-d_6) δ 1.28 (*AB*, J_{AB} = 5.7 Hz, 1 H), 1.34 (*AB*, J_{AB} = 5.7 Hz, 1 H), 1.55 (t, J = 1.5 Hz, 2 H), 1.76 (t, J = 6.2 Hz, 2 H), 1.87 (m, 2 H), 2.46 (t, J = 6.2 Hz, 2H), 6.09 (m, 2H), 6.37 (m, 2 H); ^{13}C NMR (DMSO-d_6) δ 29.01 (d), 35.65 (t), 45.14 (d), 46.16 (d), 47.61 (d), 128.93 (d), 133.60 (d). These ^{13}C NMR chemical shifts are in close agreement with previously published values for **18**.[10b] Essentially quantitative rearrangement of **16** to **19** could be achieved by heating a degassed solution of **16** in DMSO-d_6 in a sealed NMR tube (as described above) at 145 °C for 40 h.

Characterization of the Reaction Intermediate (18). As the reaction progressed, the transient formation of intermediate **18** could be inferred by the appearance of new peaks in the ^{1}H NMR spectrum of the reaction mixture at δ 5.60-5.88 (m, 8 H) and by the appearance of the following peaks in the corresponding ^{13}C NMR spectrum: ^{13}C NMR (DMSO-d_6) δ 32.60 (t), 49.62 (d), 50.89 (d), 124.3 (d), 130.4 (d), 131.6 (d), 136.4 (d).

Additional evidence for the intermediacy of **18** was obtained by the results of a trapping experiment. Thus, to a solution of **16** (34 mg, 0.23 mmol) in DMSO-d_6 (0.5 mL) was added 10% Pd/C (40 mg), and the resulting mixture was degassed by using repetitive freeze-pump-thaw cycles. The degassed reaction mixture was heated at 140 °C for 14 h. Careful integration of the ^{1}H NMR spectrum of the resulting mixture indicated the presence of fluorene and **19**[10] (ratio 1:2). The reaction mixture was allowed to cool gradually to room temperature, and water (20 mL) was added. The resulting aqueous suspension was extracted with Et_2O (4 x 20 mL), and the combined organic layers were washed with water (10 mL), dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel by eluting with benzene. The first chromatography fraction afforded pure **19** (17 mg, 50%) as a colorless microcrystalline solid: mp 40-41 °C (lit.[10] mp 43 °C). The ^{1}H and ^{13}C NMR spectra of the material thereby obtained were identical with the corresponding spectra as reported previously for **19**.[10b]

The second chromatography fraction afforded fluorene (11 mg, 31%) as a colorless microcrystalline solid: mp 112 °C. The mp of an intimate mixture of this material with a sample of authentic fluorene was undepressed.

Surprisingly,[10] our attempts to trap **18** with added dienophiles were unsuccessful. Thus, to a solution of **16** (24 mg, 0.16 mmol) in DMSO-d_6 (0.5 mL) was added maleic anhydride (19 mg, 0.2 mmol), and the resulting solution was heated at 140 °C for 16 h. Similarly, to a solution of **16** (24 mg, 0.16 mmol) in DMSO-d_6 (0.5 mL) was added 1-methyl-1,3,4-triazoline-2,5-dione (22 mg, 0.2 mmol), and the resulting solution was heated at 140 °C for 16 h. In both cases, careful examination of the ^{1}H NMR spectrum of the crude product thereby obtained revealed only the presence of **19**[10] and unreacted dienophile.

Kinetic studies of the thermolysis of 16. A solution of **16** (10 mg, 0.07 mmol) in DMSO-d_6 (0.5 mL) was placed in a 5 mm NMR tube, and the NMR sample subsequently was degassed by using repetitive freeze-pump-thaw cycles. The NMR tube was then thermostatted in a constant temperature bath whose temperature was maintained by using refluxing solvents (i. e., refluxing xylene, which maintained a bath temperature of 410 K and refluxing DMF, which maintained a bath temperature of 422.5 K). During the course of the reaction, the NMR tube was removed from the bath at fixed time intervals, and the ^{1}H NMR spectrum of the reaction mixture was obtained at each time. The concentrations of the starting material, intermediate, and product (i. e., **[16]**, **[18]**, and **[19]**, respectively) were estimated by careful integration of each NMR spectrum thereby obtained. Plots of concentration *vs* time were obtained; a discussion of the kinetic analyses of these plots is presented below (*vide infra*).

Analysis of the kinetic (^{1}H NMR) data.[12] The integrated rate expressions, with concentrations normalized to $[16]_0 = 1$, are as follows:

$$[16] = \exp(-k_1 t)$$
$$[18] = k_1/(k_2-k_1)[\exp(-k_1 t) - \exp(-k_2 t)]$$
$$[19] = 1 - [18] - [16]$$

A locally written computer program[12] was used to obtain a simultaneous least-squares fit of all of the concentration data to the equations for **[16]**, **[18]**, and **[19]** (*vide supra*) with a single set of k_1 and k_2 at each temperature. This analysis afforded the following rate constants and activation parameters:

For thermal rearrangement of **16** to **18**: $k_1 = 8.6 \times 10^{-5}$ s^{-1} at 410 K, 2.1×10^{-4} s^{-1} at 422.5 K.

For thermal rearrangement of **18** to **19**: $k_2 = 5.8 \times 10^{-5}$ s^{-1} at 410 K, 9.4×10^{-5} s^{-1} at 422.5 K.

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11. A Referee has noted that **18** might result from a competing reaction which does not lie along the reaction coordinate that leads from **16** to **19**. In this event, an alternative stepwise mechanism for the rearrangement of **16** to **19**, which proceeds via a bis(allylic) diradical intermediate, can be envisioned. Whereas the NMR data presented herein are insufficient to distinguish between the concerted and diradical processes, we note that the appearance of the kinetic plots is consistent with our suggestion that consecutive reactions of the type [A] → [I] → product are involved in this rearrangement, particularly with regard to that portion of the concentration profile which corresponds to the formation and disappearance of **18**.

12. We thank Professor Paul Marshall and Mr. Ashutosh Misra, Department of Chemistry, University of North Texas, for having performed the kinetic analysis described herein.

13. A Referee suggested that degenerate thermal [3,3] sigmatropic rearrangement (i. e., Cope rearrangement) of **16** might occur concurrent with thermal rearrangement of **16** to **19**. However, careful examination of relevant ^{1}H and ^{13}C NMR spectra over the temperature range employed in our study (i. e., 410-422.5 K) reveals no evidence of line-broadening, a result which suggests that competing Cope rearrangement of **16** does not occur in this temperature range.

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Intramolecular Hydrogen Atom Abstraction: The β-Oxygen Effect in the Norrish Type II Photoreaction

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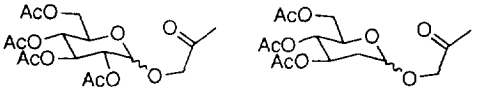
Abstract: *The preparation of phenacyl glycosides of α- and β-tetrabenzylglucopyranose, of α-tetrabenzylmannopyranose, and of 2-hydroxytetrahydropyran is described. Photolysis of each compound through Pyrex results cleanly in lactone formation by the Norrish type II photocleavage. Competition experiments are described which demonstrate that both glucosyl anomers are consumed at the same rate in the course of the photolysis. Similar experiments establish that the phenacyl α-glucoside is marginally more reactive than the corresponding α-mannoside. The tetrahydropyran derivative is cleaved much more rapidly the carbohydrates. This effect is interpreted in terms destabilization of the polarized transition state for hydrogen atom abstraction by the β-oxygen bonds in the carbohydrate series.*

Intramolecular hydrogen atom abstraction in carbohydrates and nucleosides, permitting the preparation of 1-alkoxy-1-glycosyl and of C4' radicals respectively, is an area of considerable current interest.[1] For the case of simple 2-alkoxytetrahydropyran derivatives it has been known for over 10 years that electrophilic radicals, specifically t-butoxy radicals and triplet benzophenone, abstract hydrogen atoms preferentially from the axial site.[2] The microscopic reverse of this process, quenching of 1-alkoxy-1-glycosyl radicals by suitable hydrogen donors, permits the stereoselective synthesis of equatorial glycosides.[1a,b,3] It was of interest to us to establish the effect of β-oxygen bonds, which are known to have a significant impact on radical reactions proceeding through polarized transition states,[4] in hydrogen atom abstraction reactions from the anomeric site of glycopyranosides. We report here on a series of competition experiments designed to probe this question.

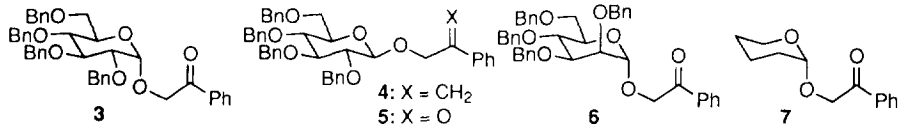
Norrish type II photochemistry of glycosyl ketones leading to aldonolactones has been previously reported by Descotes.[5] Analogous photochemistry of thioglycosyl ketones was described by Vasella as a superior preparation of aldonothiolactones. Binkley has reported the high yield photochemical conversion of the pyruvate ester of 2,3,4,6-tetra-O-acetyl glucopyranose to the aldonolactone lactone.[6] The Descotes study

was particularly interesting in so far it was reported that, for both **1** and **2**, α- and β-anomers had approximately the same reactivity. The comparable reactivity of the α- and β-anomers in a given system was surprising in view of the differing rates of abstraction of axial and equatorial hydrogens from alkoxytetrahydropyrans by electrophilic radicals.[2] Intrigued by these results and their obvious relevance to our ongoing interest in the chemistry of anomeric radicals[1a,3a-d] we decided to carry out a series of competition experiments to probe the effect substitution at C2 on intramolecular hydrogen abstraction in carbohydrates. Ideally, the overall effect of any substitutuent at C2 would be determined by a competition reaction between typical hexopyranose derivatives and a 2-deoxyhexopyranose, whilst any stereoelectronic component could be probed by comparing both α- and β-anomers and the gluco- and manno- series.



1 **2**

Reaction of tetrabenzyl-D-glucopyranose with phenacyl bromide and silver oxide in DMF enabled the isolation, in 35% yield, of phenacyl tetrabenzyl-α-D-glucopyranoside (**3**) as a white crystalline solid. Isolation of a pure sample of the corresponding β-anomer proved more problematic. Eventually, this was achieved by alkylation of tetrabenzyl-D-glucopyranose with sodium hydride and 2-phenylallyl bromide giving **4** in 59% yield, followed by oxidative cleavage to **5** with catalytic OsO_4 and $NaIO_4$ in 97% yield. A sample of phenacyl tetrabenzyl-α-D-mannopyranoside (**6**) was prepared from tetrabenzyl mannopyranose and phenacyl bromide with mediation by silver oxide. Perhaps not too surprisingly, we have not yet succeeded in isolating a satisfactory sample of the β-mannosyl anomer. Phenacyl tetrahydropyranyl ether (**7**) was prepared according to a literature procedure.[7]



3 **4**: X = CH_2 **5**: X = O **6** **7**

Each of the above phenacyl ethers was irradiated using Pyrex-filtered light in a Rayonet photoreactor fitted with 254 nm tubes. The two gluco-anomers (**3**) and (**5**) both gave tetrabenzyl-glucono-1,5-lactone (**8**) as the major product in approximately 60% yield together with two byproducts in a 3:1 ratio, the more significant of which is tentatively assigned as the spirooxetane **9**. No other carbohydrate derived products were formed. The minor byproduct was unstable on silica gel and this has prevented us from isolating a pure sample and elucidating its structure. The proposed structure of the major byproduct (**9**) rests on i) the absense of a carbonyl group according to IR and ^{13}C-NMR spectroscopy; ii) the presence of an OH stretching absorption in the IR spectrum; iii) the absence of an assignable anomeric hydrogen in the ^{1}H-NMR spectrum; iv) a six spin system in the ^{1}H-NMR spectrum attributable to H2-H3-H4-H5-2xH6; v) the doublet nature of H2 ($J_{2,3}$ = 10.2 Hz) indicating gluco-stereochemistry and, again, the absence of an anomeric hydrogen; vi) the abnormally upfield nature of H5 (δ 2.60) and one of the two H6's (δ 2.94) in the ^{1}H-NMR spectrum indicating shielding by the cyclobutylphenyl group; vii) the presence of five discernable AB quartets in the ^{1}H-NMR spectrum in