20 in 15 mL of distilled methanol was ozonized at −78 °C. After removal of the excess ozone, the solution was stood for 10 h at room temperature. The solvent was removed in vacuo, and the residue was purified on silica gel with chloroform/acetone/ethanol (100/10/2) as an eluent.

4-Benzoylcatechol (6f): mp 205–207 °C (from ethanol); IR (KBr) 3300, 1730, 1620, 1590, 1580, 1560, 1520 cm^{-1}; ^1H NMR (CD_3OD) δ 4.9 (br s, D_2O exchangeable, 2 H), 6.87 (d, J = 8.3 Hz, 1 H), 7.2–7.8 (m, 7 H); ^{13}C NMR (CD_3OD) δ 15.5 (d), 117.9 (d), 125.4 (d), 128.9 (d), 130.0 (s), 130.3 (d), 132.6 (d), 139.4 (s), 146.0 (s), 151.7 (s), 197.6 (s). Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.88; H, 4.70. Found: C, 72.81; H, 4.71.

Cis–Trans Mixture of 2,3-Dimethyl-3-methoxy-1,4-benzodioxan-2-ol (26): mp 125–127 °C (from *n*-hexane); IR (KBr) 3400, 1580, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (s, 6 H), 3.20 (s, 1 H), 3.24 (s, 2 H), 6.88 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 17.3 (q), 22.1 (q), 49.3 (q), 96.1 (s), 98.6 (s), 117.2 (d), 117.5 (d), 121.7 (d), 122.5 (d), 139.8 (s), 141.1 (s); MS, m/e 210. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.93; H, 6.72.

Registry No. **5a**, 255-37-8; **5a** (2,3-dihydro deriv), 493-09-4; **5b**, 110306-99-5; **5b** (2,3-dihydro deriv), 93591-46-9; **5c**, 67470-96-6; **5c** (2,3-dihydro deriv), 57744-68-0; **5d**, 110307-00-1; **5d** (2,3-dihydro deriv), 110851-10-0; **5e**, 67470-95-5; **5e** (2,3-dihydro deriv), 16498-20-7; **5f**, 110851-11-1; **5f** (2,3-dihydro deriv), 93637-87-7; **6a**, 120-80-9; **6b**, 98-29-3; **6c**, 2138-22-9; **6d**, 1020-31-1; **6e**, 3316-09-4; **6f**, 10425-11-3; **7a**, 583-63-1; **7b**, 1129-21-1; **7c**, 31222-02-3; **7d**, 3383-21-9; **8**, 29619-33-8; **9a**, 110851-16-6; **9b**, 110851-17-7; **9c**, 110851-18-8; **9d**, 110851-19-9; **9e**, 110851-20-2; **9f**, 110851-21-3; **10a**, 91201-66-0; **17a**, 110851-12-2; **18**, 36122-03-9; **20**, 79792-92-0; **21**, 110851-22-4; **22**, 635-67-6; **23**, 2848-25-1; **24**, 110851-23-5; *cis*-**26**, 110851-23-5; *trans*-**26**, 110851-15-5; $Br(CH_2)_2Br$, 106-93-4; H_3C-$COCHClCH_3$, 4091-39-8; 2,3-dimethyl-1,4-benzodioxan-2-ol, 110851-13-3.

Notes

P_2O_5/DMSO/Triethylamine (PDT): A Convenient Procedure for Oxidation of Alcohols to Ketones and Aldehydes

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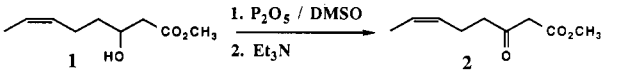
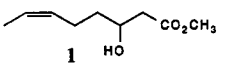
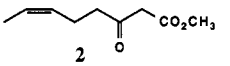
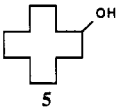
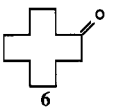
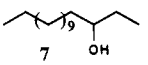
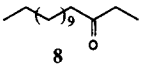
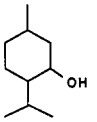
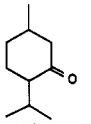
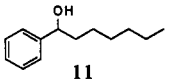
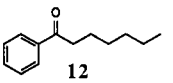
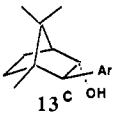
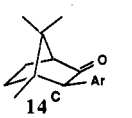
We recently faced the problem of oxidizing alcohol **1** (Table I) to the corresponding ketone **2** on a large scale. Swern oxidation of **1**[1] gave chlorinated products, indicating that oxidation procedures involving positive halogen[2] would be unacceptable. Chromic acid oxidation gave **2** only in low yield, accompanied by polar byproducts. While PCC oxidation[3] proceeded in reasonable yield, separation of the product from the chromium-containing residue was cumbersome.

Pursuing Moffatt oxidation,[4] we found references in the carbohydrate literature to the use of P_2O_5[5] to activate DMSO. Ketone formation, however, required long reaction times. By analogy to the Swern procedure, it seemed reasonable that triethylamine[6,7] might accelerate transformation of the initial (uncharacterized) adduct to the ketone. In fact, addition of P_2O_5 (1.8 equiv) to a solution of alcohol **1** (1.0 equiv) and DMSO (2.0 equiv) in CH_2Cl_2 at room temprature leads to immediate disappearance of starting material, with formation of a suspension. On addition of triethylamine (3.5 equiv), the suspension dissolves, and ketone **2** is liberated.



This appears (Table I) to be a general method for oxidation of alcohols to ketones and aldehydes. It is advan-

Table I. Oxidation of Alcohols by PDT[a]

starting alcohol	product	yield[b] %
 1	 2	85
$CH_3(CH_2)_{15}OH$ 3	$CH_3(CH_2)_{14}CH{=}O$ 4	83
 5	 6	86
 7	 8	81
 9	 10	82
 11	 12	83
 13[c]	 14[c]	90[d]

Ar = 1-naphthyl

[a] Phosphorus pentoxide/dimethyl sulfoxide; triethylamine. [b] Yields are for pure, isolated material. [c] Reference 8. [d] In this case, the reaction proceeded to only about 50% conversion.

(1) Muncusco, A. J.; Huang, S. L.; Swern, D. J. *J. Org. Chem.* **1978**, *43*, 2480.
(2) Stevens, R. V.; Chapman, K. T.; Weller, H. N. *J. Org. Chem.* **1980**, *45*, 2030.
(3) Covey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, *16*, 2647.
(4) (a) Pfitzner, K. E.; Moffatt, J. G. *J. Am. Chem. Soc.* **1963**, *85*, 3027. (b) Moffatt, J. G. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 242.
(5) (a) Onodera, K.; Hirano, S.; Kashimura, N. *J. Am. Chem. Soc.* **1965**, *87*, 4651. (b) Georges, M.; Fraser-Reid, B. *J. Org. Chem.* **1985**, *50*, 5754.
(6) Triethylamine has been used in conjunction with P_2O_5 and DMSO, but not to effect alcohol oxidation: Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.
(7) Alternative bases (K_2CO_3, pyridine) gave reversion to the starting alcohol, with little if any oxidation.

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tageous in that it requires neither cryogenic temperatures nor heavy metals.

Experimental Section[8-10]

Oxidation of 1 to 2 (Large Scale). A flame-dried, two-necked, 500-mL round-bottomed flask equipped with an N_2 inlet, dropping funnel, and mechanical stirrer was charged with alcohol 1 (64.5 g, 375 mmol) in CH_2Cl_2 (0.2 M in starting alcohol). The flask was immersed in an ice–water bath. Dimethyl sulfoxide (58.5 g, 750 mmol, 2 equiv) and phosphorus pentoxide (95.85 g, 675 mmol, 1.8 equiv) were added sequentially. The reaction mixture was allowed to stir and warm to room temperature until disappearance of starting material by TLC (30 min). The flask was immersed again in the ice–water bath; then triethylamine (132.6 g, 1322 mmol, 3.5 eq) was added dropwise over 10 min. Stirring was continued for 30 min. The reaction was quenched with 10% aqueous HCl and extracted with CH_2Cl_2. The organic extracts were washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was distilled bulb-to-bulb (bp_{10} 140–150 °C) to give 54 g (85%) of **2** as a colorless oil, TLC R_f (20% EtOAc/hexane) 0.54. ^1H NMR δ: 1.62 (d, 6.6 Hz, 3 H); 2.3 (q, 7.4 Hz, 2 H); 2.6 (t, 7.3 Hz, 2 H); 3.5 (s, 2 H); 3.7 (s, 3 H); 5.3–5.5 (m, 2 H). ^{13}C NMR δ: 12.6, q; 20.9, t; 42.6, t; 48.9, t; 52.2, q; 125.4, d; 128.0, d; 167.5, s; 202.2, s. IR cm^{-1}: 3020, 1745, 1715, 1655, 1540, 1450, 1325, 1270, 1050. MS m/z (relative intensity): 170 (43); 154 (33); 123 (25); 101 (100).

Oxidation of 3 to 4 (Small Scale). A flame-dried, one-necked, 25-mL round-bottomed flask equipped with an N_2 inlet was charged with alcohol **3** (1.0 g, 4.1 mmol) in CH_2Cl_2 (0.2 M in starting alcohol). The flask was immersed in an ice–water bath. Dimethyl sulfoxide (643 mg, 8.25 mmol, 2 equiv) and phosphorus pentoxide (1.17 g, 8.25 mmol, 2.0 equiv) were added sequentially. The reaction mixture was allowed to stir and warm to room temperature until disappearance of starting material by TLC (30 min). The flask was immersed again in the ice–water bath; then triethylamine (2.02 mL, 14.4 mmol, 3.5 equiv) was added dropwise over 1 min. Stirring was continued for 30 min. The reaction was quenched with 10% aqueous HCl and extracted with CH_2Cl_2. The organic extracts were washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed[11] on 50 g of TLC mesh silica gel to give 4 (826 mg, 83% yield) as a white solid, TLC R_f (20% EtOAc/hexane) 0.67. ^1H NMR δ: 0.9 (t, 5.3 Hz, 3 H); 1.0–1.6 (m, 26 H); 2.4 (t, 7.1 Hz, 2 H); 9.7 (s, 1 H). ^{13}C NMR δ: 14.0, q; 22.0, t; 22.6, t; 29.1, t; 29.3, t; 29.4, t; 29.5, t (×2); 29.6, t (×5); 31.9, t; 43.9, t; 202.7, d. IR cm^{-1}: 2976, 2853, 2715, 1730, 1466, 1350.

Preparation of 3-Pentadecanone (8). This same small-scale procedure was used to oxidize 130 mg of alcohol **7**, yielding, after chromatography, ketone **8** (105 mg, 81% yield), TLC R_f (20% EtOAc/hexane) 0.68. ^1H NMR δ: 0.9 (t, 5.8 Hz, 3 H); 1.05 (t, 7.3 Hz, 3 H); 1.3 (m, 18 H); 1.6 (m, 2 H); 2.4 (m, 4 H). ^{13}C NMR δ: 7.9, q; 14.1, q; 22.7, t; 24.0, t; 29.4, t (×2); 29.5, t (×2); 29.9, t (×3); 31.9, t; 35.9, t; 42.5, t; 212, s. IR cm^{-1}: 2955, 2855, 1719, 1450, 1102. MS m/z (relative intensity): 198 (43); 141 (10); 85 (31).

Preparation of 1-Phenylheptan-1-one (12). This same small-scale procedure was used to oxidize 939 mg of alcohol **11**, yielding, after chromatography, ketone **12** (768 mg, 83% yield), TLC R_f (20% EtOAc/hexane) 0.61. ^1H NMR δ: 0.9 (t, 6.4 Hz, 3 H); 1.3–1.4 (m, 8 H); 2.9 (t, 7.1 Hz, 2 H); 7.5 (m, 3 H); 7.9 (d, 8.2 Hz, 2 H). ^{13}C NMR δ: 14.0, q; 22.5, t; 24.4, t; 29.0, t; 31.7, t; 38.6, t; 128.0, d (×2); 128.5, d (×2); 132.8, d; 137.2, s; 200.5, s. IR cm^{-1}: 3062, 2970, 2850, 1694, 1581, 1223, 974.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

(8) For the preparation of **13** and **14**, see: Taber, D. F.; Raman, K.; Gaul, M. D. *J. Org. Chem.* **1987**, *52*, 28.

(9) For general experimental procedures, see ref 8, above.

(10) The authenticity of products **6** and **10** was established by direct comparison (^1H NMR, TLC) with the commercially available ketones.

(11) Taber, D. F. *J. Org. Chem.* **1982**, *47*, 1351.

Registry No. 1, 110874-82-3; 2, 110874-83-4; 3, 36653-82-4; 4, 629-80-1; 5, 1724-39-6; 6, 830-13-7; 7, 53346-71-7; 8, 18787-66-1; 9, 1490-04-6; 10, 10458-14-7; 11, 614-54-0; 12, 1671-75-6; 13, 86852-75-7; 14, 111001-29-7; DMSO, 67-68-5; Et_3N, 121-44-8; P_2O_5, 1314-56-3.

Simple Entries to 1*H*-Cyclooctapyrazoles. A New 8,5-Heterocyclic System

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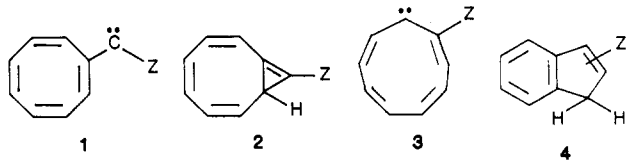
An interest of this laboratory is the electrophilic behavior of 1,3,5,7-cyclooctatetraen-1-ylmethylenes (**1**) and the rearrangements of **1** to bicyclo[6.1.0]nona-2,4,6,8-tetraenes (**2**), cyclononatetraenylidenes (**3**), and then indenes (**4**). As part of this study we now describe the preparations



1 2 3 4

(eq 1) and the pyrolytic decompositions (eq 2) of sodium salts (**7a–c**) of *p*-tosylhydrazones (**6a–c**) of 1,3,5,7-cyclooctatetraene-1-carboxaldehyde (**5a**), 1,3,5,7-cyclooctatetraen-1-yl methyl ketone (**5b**) and 1,3,5,7-cyclooctatetraen-1-yl phenyl ketone (**5c**).[1] Sodium *p*-tosylhydrazonates **7a–c** are obtained readily (eq 1) by reactions of *p*-tosylhydrazine with **5a–c**, respectively, and then displacement of hydrogen from **6a–c** with sodium hydride.

Vacuum thermolyses of **7a–c** (eq 2) are presently reported because elimination of sodium *p*-toluenesulfinate, retention of nitrogen, heterocyclization, and prototropic isomerization occur efficiently (76–99%) at 280–340 °C (0.1–0.3 Torr) to give 1*H*-cyclooctapyrazoles **11a–c**, members of a new system of 8,5-heterocycles. At the temperatures necessary for effective decomposition of **7a–c** (eq 2), it cannot be concluded whether **8a–c** or/and **9a–c** are the reaction intermediates leading to **10a–c**.[2] Cyclooctapyrazoles **11a–c** are acidic crystalline solids whose gross structures are derived from their elemental analyses, their IR, ^1H NMR, UV, and mass spectra, and their origins. The products are assigned dominantly as tautomers **11a–c** in equilibrium with **12a–c**.[3] The choices as **11a–c** are

(1) (a) Decomposition of salts of sulfonylhydrazones of aldehydes and ketones in aprotic environments to give diazo compounds and/or their products is a widely used method for effecting carbenic reaction processes. (b) Bamford, W. R.; Stevens, T. C. *J. Chem. Soc.* **1952**, 4735–4740. (c) Powell, J. W.; Whiting, M. C. *Tetrahedron* **1959**, *7*, 305–310. (d) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512–5513. (e) Kaufman, G. M.; Smith, J. A.; Van der Stouw, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1965**, *87*, 935–936.

(2) (a) Intramolecular processes leading to pyrazoles have been reported which are similar to those proposed in equation 2.[2b-e] (b) Closs, G. L.; Böll, W. A. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 399. (c) Closs, G. L.; Böll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3904–3905. (d) Bartlett, R. K.; Stevens, T. S. *J. Chem. Soc. C* **1967**, 1964–1968. (e) Bailey, R. J.; Shechter, H. *J. Am. Chem. Soc.* **1974**, *96*, 8116–8117.

(3) (a) Annular tautomerism in pyrazoles is discussed by: Katritsky, A. R.; Lagowski, J. M. In *Advances in Heterocyclic Chemistry*; Katritsky, A. R., Boulton, A. J., Eds.; Academic: New York, 1963; Vol. 2, pp 27–81. Katritsky, A. R.; Lagowski, J. M. In *Comprehensive Heterocyclic Chemistry*; Katritsky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 5(4A), pp 1–38. (b) The proposition is advanced that, since the NH moiety is closer to the cycloocta system and more conjugating in a 1*H*- than in a 2*H*-cyclooctapyrazole, there will be greater 10-π electron cyclooctatetraenoid delocalization in **11a–c** than in a comparable **12a–c**.[5]

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