A similar experiment was carried out with (*R*)-(−)-octan-2-ol [182 mg, 1.40 mmol, Fluka; $[\alpha]_D$ −10.9° (EtOH, *c* 1.10)] and a solution of DIS (2 mmol) in CH_2Cl_2 (3 mL). This reaction was completed within 2 h at 27 °C, affording, after the usual workup, (*S*)-(+)-2-iodooctane (315 mg, 93%), $[\alpha]_D$ +34.0° (ethanol, *c* 1.52) (approximately 57% optical purity).

The above experiment with (*R*)-(−)-octan-2-ol and DIS was repeated as described (2 h at 27 °C). After completion, the reaction mixture was stirred at 17 °C for 3 days. The usual workup afforded (*S*)-(+)-2-iodooctane (315 mg, 93%), $[\alpha]_D$ +30.8° (ethanol, *c* 1.98) (approximately 51% optical purity).

B. With TMSI. A similar experiment was carried out with (*S*)-(+)-octan-2-ol (182 mg, 1.40 mmol) with TMSI (4 mmol) instead of DIS. The reaction was completed within 3 days at 17 °C, affording (*R*)-(−)-2-iodooctane (283 mg, 85%),[28b] $[\alpha]_D$ −49.4° (ethanol, *c* 1.44) (approximately 82% optical purity).

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Registry No. $PhSiH_3$, 694-53-1; $PhSiH_2I$, 18139-86-1; SiH_3I, 13598-42-0; SiH_2I_2, 13760-02-6; *t*-BuOH, 75-65-0; $PhCH_2OH$, 100-51-6; EtOH, 64-17-5; *sec*-BuOH, 78-92-2; *i*-PrOH, 67-63-0; $PhCH_2OCH_2Ph$, 103-50-4; *t*-BuOMe, 1634-04-4; $(i\text{-Pr})_2O$, 108-20-3; *sec*-BuOMe, 6795-87-5; *i*-PrOMe, 598-53-8; *i*-PrOBu-*n*, 1860-27-1; *n*-BuOMe, 628-28-4; $(Et)_2O$, 60-29-7; $(n\text{-Bu})_2O$, 142-96-1; $(n\text{-Hex})_2O$, 112-58-3; PhOMe, 100-66-3; PhOEt, 103-73-1; $PhCH_2I$, 620-05-3; *t*-BuI, 558-17-8; MeOH, 67-56-1; MeI, 74-88-4; $I(CH_2)_4OH$, 3210-08-0; $I(CH_2)_4I$, 628-21-7; *i*-PrI, 75-30-9; *sec*-BuI, 513-48-4; *n*-BuI, 542-69-8; *n*-BuOH, 71-36-3; EtI, 75-03-6; *n*-HexI, 638-45-9; β-naphthylOMe, 93-04-9; ethyl acetate, 141-78-6; butane-1,3-diol, 107-88-0; 3-iodobutan-1-ol, 6089-13-0; 5α,3β-cholestanol, 80-97-7; 3α-iodocholestane, 29108-97-2; 3β-iodocholestane, 82863-87-4; (*R*)-octan-2-ol, 5978-70-1; (*S*)-octan-2-ol, 6169-06-8; (*R*)-2-iodooctane, 29117-48-4; (*S*)-2-iodooctane, 1809-04-7; β-naphthyl alcohol, 135-19-3; phenol, 108-95-2; TMSI, 16029-98-4; THF, 109-99-9.

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Oxidation of Vicinal Diols to α-Dicarbonyl Compounds by Trifluoroacetic Anhydride "Activated" Dimethyl Sulfoxide

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Trifluoroacetic anhydride "activated" dimethyl sulfoxide is an effective oxidant for the conversion of vicinal diols into the corresponding α-dicarbonyl compounds or products derived therefrom. Unlike the Swern oxidant, the title reagent system gives good yields of products derived from halogenated substrates. The method has permitted syntheses of previously inaccessible compounds including tropolones, a σ-homo-*o*-benzoquinone, and a "hyperreactive" α-keto aldehyde.

In connection with the development of a new route to tropolones, we observed[2] that the trifluoroacetic anhydride (TFAA)/dimethyl sulfoxide/triethylamine (Et_3N) reagent system[3] efficiently (≥73% yield) converts various 7-halobicyclo[4.1.0]heptane-2,3- and -3,4-diols into the corresponding α-diketones. In contrast, the use[2] of other oxidizing agents, many of which have been previously employed for converting vicinal diols into α-hydroxy ketones[4,5] or α-diketones,[6-9] led to decomposition of the bicyclic diols [with $(Ph_3P)_3RuCl_2$, benzalacetone, tetrahydrofuran (THF), 195 °C, 10 h[8]], low yields (≤25%) of the desired products (oxalyl chloride, dimethyl sulfoxide, Et_3N[9]), or no reaction (*N*-chlorosuccinimide, dimethyl sulfide, Et_3N;[4] acetic anhydride, dimethyl sulfoxide;[6] pyridine, SO_3, dimethyl sulfoxide;[5,7] dicyclohexylcarbodiimide, dimethyl sulfoxide, H^+ [10]).[11] Other workers have noted[13,16] the inability of the last group of reagents to oxidize certain vicinal diols. In view of these results, and because no systematic assessment has been made of the ability of the TFAA "activated" dimethyl sulfoxide oxidant[17] to effect the synthetically valuable vicinal diol to α-dicarbonyl conversion,[18] a more extensive investigation of this reagent

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(11) Other oxidizing systems[12-15] have also been employed for the preparation of α-hydroxy ketones or α-diketones from vicinal diols. However, all of these employ reagents incompatible with the functionality present in our substrates and were, therefore, not investigated. Thus, both the bis(tributyltin) oxide/Br_2[12,13] and dimethyl sulfoxide/Cl_2/Et_3N[14] procedures are likely to effect undesired halogenation of unsaturated centers. The ability of Ag(I) ions to promote cleavage of halogenated cyclopropanes deterred us from using Ag_2CO_3 on Celite[15] as an oxidant.
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(17) To our knowledge, only one example of the use of TFAA/dimethyl sulfoxide/Et_3N for the oxidation of a vicinal diol has been reported.[16]

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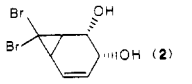
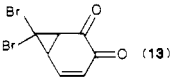
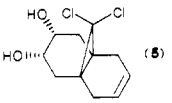
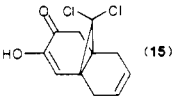
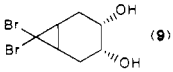
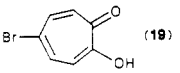
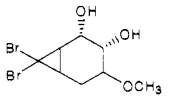
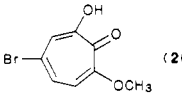
Table I. Oxidation of Vicinal Diols by Trifluoroacetic Anhydride "Activated" Dimethyl Sulfoxide

entry	diol	oxidation product(s)[a]	yield, %[b]
1	1,2-dodecanediol (**1**)	2-hydroxy-2-dodecenal (**12**)	79
2	 (**2**)	 (**13**)	68 (25)[f]
3	*trans*-1,2-cyclohexanediol (**3**)	2-hydroxy-2-cyclohexen-1-one (**14**)	79
4	*cis*-1,2-cyclohexanediol (**4**)	2-hydroxy-2-cyclohexen-1-one (**14**)	82
5	 (**5**)	 (**15**)	54 (0)[f]
6	*cis*-1,2-cyclooctanediol (**6**)	1,2-cyclooctanedione (**16**)	95[c] (91)[f]
7	*erythro*-2,3-octanediol (**7**)	2,3-octanedione (**17**)	87
8	*meso*-1,2-diphenyl-1,2-ethanediol (**8**)	benzil (**18**)	98 (97)[f]
9	 (**9**)	 (**19**)	76 (25)[f]
10	 (**10**)	 (**20**)	85
11	5α-cholestane-2α,3α-diol (**11**)	2-hydroxy-5α-cholest-1-en-3-one (**21**) and 3-hydroxy-5α-cholest-3-en-2-one (**22**)	84[d] 71[e]

[a] The tautomeric preference in compound **20** has not been determined. All other oxidation products are depicted in the tautomeric form, which predominated in deuteriochloroform solution at 18 °C as established by NMR analysis. [b] Of isolated and pure products unless otherwise stated. [c] This material contains some 4-(diethylamino)-1,1,1-trifluorobut-3-en-2-one. [d] Yield after preparative TLC isolation. [e] Yield after recrystallization of preparative TLC material. [f] Yield of product obtained by using oxalyl chloride "activated" dimethyl sulfoxide as the oxidant.

system seemed warranted. The results of such a study, which we now report, suggest that this oxidizing system is particularly well suited to the present purpose and allows the preparation of hitherto inaccessible α-dicarbonyl and related compounds.

The tabulated data demonstrate that the title reagent system smoothly converts both open-chain and cyclic[19] vicinal diols into the corresponding α-dicarbonyl compounds or products derived therefrom. Noteworthy results include the formation of the "hyperreactive"[9] α-keto aldehyde (isolated as its monoenolic tautomer **12**) from diol **1** (Table I, entry 1) and the oxidation of compound **2** to the σ-homo-*o*-benzoquinone **13** (entry 2). Product **13** is only the third example[20] of this rare class of compound. The tropolones **19** and **20** (entries 9 and 10) are formed as a result of in situ ring expansion of the initially produced bicyclic diketones.[2] Since several recent reports[21] have stressed the useful biological activity of tropolones containing three or more contiguously oxygenated ring carbons, the synthesis of compound **20** is especially interesting. The oxidation procedure appears insensitive to the geometry of the hydroxyl groups in the starting diol since analogous treatment of the *trans*- and *cis*-diols **3** and **4** (entries 3 and 4) gave reaction product **14** in similar yields.

In some instances, small quantities (≤8%) of 4-(diethylamino)-1,1,1-trifluorobut-3-en-2-one[22] were observed in the crude oxidation mixtures. This material, which was easily separated from the desired α-dicarbonyl compounds by chromatography, probably arises by a single electron transfer initiated reaction of TFAA with Et_3N.[23] In a control experiment, treatment of the preformed dimethyl sulfoxide/TFAA complex (maintained at −60 °C in CH_2Cl_2, no diol present) with Et_3N afforded a 33% yield of the acylated enamine. Presumably, complex formation between TFAA and dimethyl sulfoxide is reversible and, in the absence of an alcohol oxidation pathway, reaction between the anhydride and the amine becomes a significant process.

Interestingly, entries 2, 5 and 9 (Table I) show that the oxalyl chloride "activated" dimethyl sulfoxide system (Swern oxidation)[3,9] is a much less effective oxidant, at least when the substrate contains a halogen atom. Why this is so remains unclear.

In conclusion, the TFAA "activated" dimethyl sulfoxide reagent system provides an especially useful method for the oxidation of vicinal diols to α-dicarbonyl compounds. The procedure requires mild reaction conditions, gives high yields of product, is relatively general, and uses readily available reagents.

Experimental Section

General Procedures. ^1H NMR spectra were recorded on a Varian T60 or JEOL FX-90Q spectrometer and ^{13}C NMR spectra on a JEOL FX-60 or FX-90Q instrument. Deuteriochloroform was used as solvent unless otherwise stated. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane (δ 0.0 ppm) as an internal standard. Data are reported as follows: chemical shift (multiplicity, coupling constants, integrated intensity). Infrared spectra (IR) were recorded on a Shimadzu IR-27G spectrometer. Electron-impact mass spectra (MS) and high-resolution mass spectra (HRMS) were measured

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(20) The parent σ-homo-*o*-benzoquinone is known; see: Engelhardt, M.; Luttke, W. *Chem. Ber.* **1977**, *110*, 3759. Sugihara, Y.; Yamoto, A.; Murata, I. *Tetrahedron Lett.* **1981**, *22*, 3257. One functionalized derivative has been synthesized; see: Vol'eva, V. B.; Prokof'eva, T. I.; Novikova, I. A.; Belostotskaya, I. S.; Ershov, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1632; *Chem. Abstr.* **1984**, *101*, 230384.

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(22) Platoshkin, A. M.; Cheburkov, Yu. A.; Knunyants, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, 112–119; *Chem. Abstr.* **1969**, *70*, 114541.

(23) Schreiber, S. L. *Tetrahedron Lett.* **1980**, *21*, 1027.

on Varian MAT CH7 and AEI-MS3074 mass spectrometers, respectively. Ultraviolet spectra (UV) were determined on a Varian DMS-100 instrument. Melting points were observed on a Reichert-Kofler block and are uncorrected. Microanalyses were performed by Professor A. D. Campbell and associates at the University of Otago, Dunedin, New Zealand, or by the Australian Microanalytical Service, Melbourne, Australia. Analytical thin-layer chromatography (TLC) was conducted on aluminum-backed 2-mm-thick silica gel 60 F_{254} plates supplied by Merck. Chromatograms were visualized with iodine vapor, anisaldehyde-/H_2SO_4/EtOH (2:5:93, v/v/v) spray reagent, or under a 254-nm UV lamp. Preparative TLC was conducted on 20 × 20 cm glass plates loaded with Merck Kieselgel 60 GF_{254} (34 g/plate) or Reidel de Haën aluminum oxide DGF (400 mesh ASTM, 38 g/plate) using the solvent system indicated. All extraction, recrystallization, and chromatographic solvents were distilled prior to use. Dimethyl sulfoxide was distilled from CaH_2 under reduced pressure. THF and diethyl ether (Et_2O) were distilled from benzophenone ketyl before use. Et_3N was distilled from KOH pellets and dichloromethane (CH_2Cl_2) from CaH_2. Aldrich Gold Label TFAA and Fluka oxalyl chloride were used as obtained. All reactions requiring anhydrous conditions were run under an argon atmosphere in oven-dried glassware.

Diols 1,[24] 4,[29] 6,[25] 7,[26] 9,[2] and 11[27] were perpared from the corresponding olefins by using either the literature procedure or the dihydroxylation method of Ray and Matteson.[28] Diols 3[29] and 8[30] were prepared from cyclohexene and benzil, respectively, by using the cited procedures. All compounds had spectroscopic and physical properties in accord with those reported in the literature. Compounds **2**, **5**, and **10** were synthesized by the methods detailed below.

(1α,2α,3α,6α)-7,7-Dibromobicyclo[4.1.0]hept-4-ene-2,3-diol (2). A 1.0 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol (20 mL) was added over a period of 4 h to a chilled (ice) solution of (1α,6α)-8,8-dimethyl-7,9-dioxabicyclo[4.3.0]nona-2,4-diene[31] (1.25 g, 8.22 mmol) in *tert*-butyl alcohol (5 mL) containing bromoform (3.32 g, 13.15 mmol). The resulting mixture was stirred at ca. 5 °C for 1 h and then at ambient temperatures overnight before being poured into hexane (25 mL) and quenched with water (25 mL). The two phases were separated, and the aqueous phase was extracted with hexane (25 mL). The combined organic phases were washed with water (3 × 30 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give an oil. Preparative TLC (silica gel, CH_2Cl_2) afforded two bands, A (R_f 0.6) and B (R_f 0.5). Extraction (CH_2Cl_2) of band A afforded a solid, which on recrystallization (methanol) gave (3aα,5aβ,6aβ,6bα)-6,6-dibromo-2,2-dimethyl-3a,6,6a,6b-tetrahydro-5a*H*-cyclopropa[*e*]-1,3-benzodioxole (**23**)[32] (780 mg, 29%) as white crystalline masses: mp 80.5–82 °C; ^{1}H NMR δ 5.90 (m, 2 H), 4.65 (br d, J = 7 Hz, 1 H), 4.40 (d of m, J = 7 Hz, 1 H), 2.35 (m, 2 H), 1.40 (s, 6 H); ^{13}C NMR δ 128.0, 123.1, 109.4, 70.3, 69.3, 32.8, 29.9, 28.2, 27.6, 25.8; IR (KBr) 2975, 1370, 1244, 1210, 1160, 1040, 1025, 880, 860, 765, 700 cm^{-1}; MS, m/e 265 (4), 267 (9), 269 (3) [[M – H_3C· – CH_2CO]$^+$], 43 (100) [[CH_3CO]$^+$]. Anal. Calcd for $C_{10}H_{12}Br_2O_2$: C, 37.07; H, 3.73; Br, 49.32. Found: C, 37.20; H, 3.92; Br, 49.48. Extraction (CH_2Cl_2/Et_2O) of band B afforded phenol (120 mg, 13%) identical by ^{1}H NMR, IR, and TLC with an authentic sample. Acidification and then extraction (CH_2Cl_2) of the aqueous phase obtained in the workup procedure detailed above gave additional phenol (270 mg, 29%).

A solution of compound **23** (160 mg, 0.49 mmol) in THF (5 mL) was treated with 3 M aqueous HCl (2.9 mL), and the resulting mixture was allowed to stand at ambient temperatures for 55 h before being poured into water (30 mL) and extracted with Et_2O (3 × 5 mL) and then CH_2Cl_2 (3 × 25 mL). The combined organic phases were washed with water (50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a pale yellow oil (100 mg), which solidified on standing. ^{1}H NMR, ^{13}C NMR, and TLC analyses of this material showed it to be a ca. 9:1 mixture of the required diol **2** and precursor **23**. (This mixture was used in the subsequent oxidation step.) Recrystallization (C_6H_6) of the solid mixture afforded spectroscopically pure **2** as off-white crystalline masses: mp 83–85 °C; ^{1}H NMR δ 5.95 (m, 2 H), 4.0 (m, 2 H), 2.80 (br s, 2 H, O*H*), 2.40 (dd, J = 6.5 and 2.5 Hz, 1 H), 2.10 (dd, J = 6.5 and 3.5 Hz); ^{13}C NMR δ 131.6, 127.0, 66.7, 64.3, 35.2, 33.7, 29.6; IR (KBr) 3375, 1630 cm^{-1}; MS, m/e 264 (2), 266 (9), 268 (3) [[M – H_2O]$^{+\cdot}$], 77 (100).

(2α,3α,4aβ,8aβ)-9,9-Dichloro-1,2,3,4,5,8-hexahydro-4a,8a-methanonaphthalene-2,3-diol (5). A mixture of (4aα,8aα)-9,9-dichloro-1,4,5,8-tetrahydro-4a,8a-methanonaphthalene[33] (1.20 g, 5.58 mmol), *tert*-butyl alcohol (23 mL), water (6.8 mL), pyridine (1.0 mL), and trimethylamine *N*-oxide dihydrate (1.38 g) was treated in one portion with osmium tetraoxide in *tert*-butyl alcohol (0.46 mL of a 2.5 wt % solution, Aldrich), and the resulting solution was heated at reflux under an argon atmosphere for 48 h. The dark brown solution thus obtained was cooled, treated with sodium metabisulfite (20 mL of a 20 wt % aqueous solution), and then filtered and concentrated. The residue was partitioned between Et_2O (50 mL) and water (50 mL), and the resulting phases were separated. Extraction of the aqueous phase with Et_2O (2 × 30 mL) and drying ($MgSO_4$) of the combined organic phases followed by filtration and concentration afforded a light brown solid. Recrystallization (CH_2Cl_2) of this material afforded diol **5** (0.95 g, 68%) as white needles: mp 117.5–118.5 °C; ^{1}H NMR δ 5.50 (m, 2 H), 3.75 (m, 2 H), 2.50–1.50 (complex m, 10 H); ^{13}C NMR (C_5D_5N) δ 76.8, 68.4, 36.9, 32.0, 27.2 [the signal due to the vinylic carbons is obscured by the solvent resonances but is observed in $CDCl_3$ at δ 122.85]; IR (KBr) 3500, 3425, 3380, 2900 cm^{-1}; MS, m/e 230 (21), 232 (12.5), 234 (1) [[M – H_2O]$^{+\cdot}$], 91 (100) [[C_7H_7]$^+$]. Anal. Calcd for $C_{11}H_{14}Cl_2O_2$: C, 53.03; H, 5.66; Cl, 28.46. Found: C, 53.05; H, 5.78; Cl, 28.28.

(1α,2α,3α,4β,6α)-7,7-Dibromo-4-methoxybicyclo[4.1.0]heptane-2,3-diol (10).[32] 7,7-Dibromobicyclo[4.1.0]hept-3-ene[34] (6.0 g, 23.8 mmol) was added to a stirred suspension of freshly recrystallized *N*-bromosuccinimide (4.26 g, 24 mmol) in dried methanol (12 mL). Following the slow addition of ca. 0.5 mL of 98% H_2SO_4, the reaction mixture was allowed to stir at ambient temperatures for 48 h. The resulting deep yellow solution was poured into water (100 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a yellow oil. Trituration (methanol) of this material gave a white crystalline solid, recrystallization (methanol) of which afforded **(1α,3α,4β,6α)-3,7,7-tribromo-4-methoxybicyclo[4.1.0]heptane (24)**[32] (5.0 g, 58%) as white plates: mp 70.5–72 °C; ^{1}H NMR δ 4.05 (q with further coupling, J = 8 Hz, 1 H), 3.40 (s, 3 H), 3.25 (m, 1 H), 2.65 (complex m, 3 H), 1.95 (complex m, 2 H), 1.34 (complex m, 1 H); ^{13}C NMR δ 79.3, 57.5, 50.6, 37.3, 33.3, 28.8, 27.0, 26.9; IR (KBr) 2870, 1430, 1127, 1098, 1040, 825, 746, 723, 622 cm^{-1}; MS, m/e 328 (<1), 330 (2), 332 (2), 334 (<1) [[M – CH_3OH]$^{+\cdot}$], 281 (4), 283 (7), 285 (4) [[M – Br·]$^+$], 249 (27), 251 (53), 253 (27) [[M – CH_3OH – Br·]$^+$], 71 (100). Anal. Calcd for $C_8H_{11}Br_3O$: C, 26.48; H, 3.06; Br, 66.06. Found: C, 26.53; H, 3.25; Br, 66.22. Flash chromatography (silica gel, CH_2Cl_2) of the concentrated mother liquors from the trituration and recrystallization procedures afforded additional **24** (1.33 g, 15%; R_f, CH_2Cl_2, 0.8) as well as **(1α,3β,4α,6α)-4,7,7-tribromobicyclo[4.1.0]heptan-3-ol**[32] (1.02 g, 12% after recrystallization from hexane; R_f, CH_2Cl_2, 0.45) obtained as white crystalline masses: mp 70–71 °C; ^{1}H NMR δ 4.11 (ddd, J = 11, 11, and 7 Hz, 1 H), 3.65 (dddd, J = 11, 11, 6 and 1.8 Hz, 1 H), 2.93–2.22 (complex m, 4 H) 2.22–1.25 (complex m, 3 H); ^{13}C NMR δ 70.4, 56.6, 36.8,

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33.2, 29.4 (two peaks superimposed), 27.4; IR (KBr) 3440, 2973, 1429, 1371, 1115, 1082, 1065, 829, 729 cm^{-1}; MS, *m/e* 249 (51), 251 (100), 253 (48) [[M – Br· – H_2O]$^+$]. Anal. Calcd for $C_7H_9Br_3O$: C, 24.10; H, 2.60; Br, 68.71. Found: C, 23.90; H, 2.40; Br, 68.40.

A solution of compound **24** (3.0 g, 8.27 mmol) in anhydrous dimethyl sulfoxide (8 mL) was treated in one portion with 1,5-diazabicyclo[4.3.0]non-5-ene (1.50 g, 12.1 mmol), and the resulting mixture was heated at 130 °C for 3.0 h. After cooling to room temperature, the dark red solution was poured into aqueous 2 M HCl (100 mL) and extracted with hexane (3 × 30 mL). The combined organic phases were washed with water (3 × 100 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a light yellow oil. Kugelrohr distillation [120 °C (0.8 mmHg)] afforded **(1α,4β,6α)-7,7-dibromo-4-methoxybicyclo[4.1.0]hept-2-ene (25)** (1.59 g, 68%) as a clear colorless oil: ^1H NMR δ 6.05 (d, *J* = 10 Hz, 1 H), 5.60 (dm, *J* = 10 Hz, 1 H), 3.85 (m, 1 H), 3.35 (s, 3 H), 2.90–1.05 (complex m, 4 H); ^{13}C NMR δ 135.8, 123.5, 73.3, 55.8, 41.5, 28.9, 27.9, 27.3; IR (KBr) 2950, 2845, 1380, 1188, 1108, 978, 757, 703 cm^{-1}; MS, *m/e* 201 (8), 203 (7) [M – Br·]$^+$], 169 (37), 171 (37) [[M – Br· – CH_3OH]$^+$], 121 (100). Anal. Calcd for $C_8H_{10}Br_2O$: C, 34.08; H, 3.57; Br, 56.68. Found: C, 34.38; H, 3.76; Br, 57.08.

A solution of alkene **25** (1.59 g, 5.64 mmol), *tert*-butyl alcohol (25 mL), water (6.8 mL), pyridine (1.0 mL), and trimethyamine *N*-oxide dihydrate (1.4 g) was treated in one portion with osmium tetraoxide in *tert*-butyl alcohol (0.46 mL of a 2.5 wt % solution, Aldrich), and the resulting mixture was heated at reflux under an argon atmosphere for 14 h. The dark brown solution thus obtained was cooled and then worked up, in the same manner as described for the preparation of diol **5**, to give a dark brown oil (1.35 g). Flash chromatography (silica gel, Et_2O) afforded diol **10** (1.10 g, 62%, R_f 0.55) as a light yellow oil, which crystallized on standing. Recrystallization (C_6H_6) afforded spectroscopically pure **10** as off-white crystalline masses: mp 117–119 °C; ^1H NMR δ 4.30 (d, *J* = 4 Hz, 1 H), 3.45 (s, 3 H), 3.95–1.00 (complex m, 8 H); ^{13}C NMR δ 75.55, 70.9, 67.0, 56.9, 34.6, 32.8, 27.1, 25.7; IR (KBr) 3400, 2920, 1090, 1030, 725 cm^{-1}; MS, *m/e* 282 (<1) 284 (<1) 286 (<1) [[M – CH_3OH]$^{+\cdot}$], 96 (100).

A sample of diol **10** was converted into the corresponding acetonide (acetone, 1 drop 60% aqueous perchloric acid, 3 h, ca. 20 °C), mp 82.5–83.5 °C (as white needles from methanol). Anal. Calcd for $C_{11}H_{16}Br_2O_3$: C, 37.11; H, 4.53; Br, 44.88. Found: C, 37.16; H, 4.65; Br, 45.01.

Generalized Procedure for the Oxidation of Diols 1–11 Using Trifluoroacetic Anhydride "Activated" Dimethyl Sulfoxide. A magnetically stirred solution of dimethyl sulfoxide (300 μL, 4.23 mmol) in CH_2Cl_2 (18 mL) maintained under an argon atmosphere at ca. –60 °C (dry ice or liquid nitrogen/$CHCl_3$ bath) was treated in a dropwise fashion with TFAA (540 μL, 3.82 mmol). The resulting clear colorless solution was stirred at –60 °C for 10 min, and then the appropriate diol (1.33 mmol) dissolved in a minimum volume of CH_2Cl_2 or CH_2Cl_2/dimethyl sulfoxide[35] was added in a dropwise fashion. The clear colorless solution thus obtained was stirred at –60 °C for 1.5 h. After the dropwise addition of Et_3N (1.23 mL, 8.82 mmol), the light yellow reaction mixture was stirred for a further 1.5 h at –60 °C, warmed to ca. 5 °C, poured into aqueous 2 M HCl (50 mL), and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic extracts were washed with water (1 × 50 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure to give the crude oxidation product.

2-Hydroxy-2-dodecenal (12).[36] Preparative TLC (silica gel, CH_2Cl_2) of the crude reaction mixture obtained from oxidation of diol **1** afforded a single major chromophoric band, R_f 0.5, which was extracted (CH_2Cl_2) to give compound **12** as a wax: ^1H NMR (CCl_4) δ 9.05 (s, 1 H), 5.90 (br s, 1 H), 5.35 (t, *J* = 7.5 Hz, 1 H), 2.32 (m, 2 H), 1.14 (br s, 16 H), 0.85 (m, 3 H); ^{13}C NMR δ 187.9, 150.1, 127.9, 31.9, 29.5 (two signals superimposed), 29.4 (two signals superimposed), 28.5, 25.6, 22.7, 14.1; IR (neat) 3450, 2945, 2860, 1680, 1660 cm^{-1}; MS, *m/e* 198 (2.5), [[M]$^{+\cdot}$], 169 (41) [[M – ·CHO]$^+$], 43 (100); UV (MeOH) 240 (log ε = 3.6) nm.

7,7-Dibromobicyclo[4.1.0]hept-4-ene-2,3-dione (13). Preparative TLC (silica gel, CH_2Cl_2) of the crude reaction mixture obtained from oxidation of diol **2** afforded a single major chromophoric (and yellow) band (R_f 0.5). Extraction (CH_2Cl_2) of this band afforded a yellow oil, which crystallized on standing. Recrystallization (CCl_4) afforded **13** as yellow masses: mp 119–120.5 °C; ^1H NMR [$(CD_3)_2CO$] δ 7.40 (dt, *J* = 10.5 and 4 Hz, 1 H), 6.40 (d, *J* = 10 Hz, 1 H), 3.35 (d, *J* = 4 Hz, 2 H); ^1H NMR ($CDCl_3$) δ 7.32 (ddd, *J* = 10, 6, and 2 Hz, 1 H), 6.60 (d, *J* = 10 Hz, 1 H), 3.42–2.95 (complex m, 2 H); ^{13}C NMR δ 183.5, 177.1, 145.5, 133.7, 42.8, 36.6, 31.7; IR (KBr) 1710, 1670 cm^{-1}; MS, *m/e* 279 (14), 281 (26), 283 (12) [[M + H]$^+$], 63 (100); HRMS calcd *m/e* for [M + H]$^+$ 278.8656, obsd 278.8650; UV (C_2H_5OH) 207 (log ε = 3.66), 252 (3.81) nm. Anal. Calcd for $C_7H_4Br_2O_2$: C, 30.04; H, 1.44; Br, 57.09. Found: C, 30.26; H, 1.47; Br 57.35.

2-Hydroxy-2-cyclohexen-1-one (14).[37] Kugelrohr distillation [70–72 °C (8 mmHg)] of the crude reaction mixture obtained from oxidation of either diol **3** or **4** gave hydroxy enone **14** as a white crystalline solid: mp 36–39°C (lit.[37] mp 38–40 °C). ^1H NMR δ 6.50 (br s, 1 H), 6.10 (t, *J* = 4 Hz, 1 H), 2.90–1.30 (complex m, 6 H); ^{13}C NMR δ 195.7, 147.0, 118.7, 36.5, 23.9, 23.2; IR (melt) 3425, 2950, 1665 cm^{-1}; MS, *m/e* 112 (75) [[M]$^{+\cdot}$], 55 (100).

(4aα,8aα)-9,9-Dichloro-3-hydroxy-5,8-dihydro-4a,8a-methanonaphthalene-2(1*H*)-one (15). Recrystallization (hexane/THF) of the crude solid obtained by oxidation of diol **5** afforded **15** as white crystalline needles: mp 152–155 °C; ^1H NMR δ 6.10 (br s, 1 H), 6.00 (s, 1 H), 5.55 (m, 2 H), 3.25 (d, *J* = 19 Hz, 1 H), 2.65 (d, *J* = 19 Hz, 1 H), 2.71–1.85 (complex m, 4 H); ^{13}C NMR δ 185.5, 143.9, 119.6, 119.4, 114.5, 40.0, 29.4, 27.6, 26.9, 26.4 [the signal due to C-9 is obscured by the solvent resonances but is observed in C_5D_5N solution at δ 76.5]; IR (KBr) 3400, 1655 cm^{-1}; MS, *m/e* 244 (10), 246 (6), 248 (1) [[M]$^{+\cdot}$], 209 (15), 211 (5) [M – Cl·]$^+$], 202 (24), 204 (17), 206 (2) [[M – CH_2CO]$^{+\cdot}$], 166 (100), 168 (41). Anal. Calcd for $C_{11}H_{10}Cl_2O_2$: C, 53.90; H, 4.11; Cl, 28.93. Found: C, 54.02; H, 4.30; Cl, 29.09. Compound **15** is unstable, both in solution and in the crystalline state, and slowly decomposes on standing at room temperature.

1,2-Cyclooctanedione (16).[38] Kugelrohr distillation [130 °C (3 mmHg)] of the crude reaction mixture obtained from oxidation of diol **6** afforded **16** as a light yellow oil, which was contaminated with small amounts (ca. 8%) of 4-(diethylamino)-1,1,1-trifluorobut-3-en-2-one: ^1H NMR δ 2.55 (m, 4 H), 1.65 (br s, 8 H); ^{13}C NMR δ 209.95, 40.0, 26.4, 21.3; IR (neat), 1700 cm^{-1}; MS, *m/e* 140 (26%) [[M]$^{+\cdot}$], 55 (100). A sample of diketone **16** was converted into the quinoxaline derivative (acetic acid, *o*-diaminobenzene, reflux, 45 min) mp 122.5–123.5 °C (lit.[39] mp 120.2–120.7 °C).

2,3-Octanedione (17).[40] Preparative TLC (silica gel, pentane/CH_2Cl_2 1:1) of the crude reaction mixture obtained from oxidation of diol **7** afforded a single major chromophoric band (R_f 0.5), which on extraction (CH_2Cl_2) gave diketone **17** as a bright yellow oil: ^1H NMR δ 2.65 (t, *J* = 7 Hz, 2 H), 2.28 (s, 3 H), 1.80–0.60 (complex m, 9 H); IR (neat) 2975, 2950, 1710 cm^{-1}; MS, *m/e* 142 (<1) [[M]$^{+\cdot}$], 99 (25) [M – CH_3CO]$^+$], 71 (36) [[CH_3COCO]$^+$], 43 (100) [CH_3CO]$^+$].

Benzil (18).[37] Preparative TLC (silica gel, CH_2Cl_2) of the crude mixture obtained by oxidation of diol **8** afforded a single major and chromophoric band, (R_f 0.9), which on extraction (CH_2Cl_2) gave benzil, mp 95–96 °C (lit.[37] mp 95 °C), identical in all respects with an authentic sample.

5-Bromo-2-hydroxycyclohepta-2,4,6-trien-1-one (19). Recrystallization ($CHCl_3$/hexane) of the crude solid obtained by oxidation of diol **9** afforded **19** as pale yellow prisms: mp 192–193 °C (sealed tube) (lit.[41] mp 189–190 °C); ^1H NMR δ 7.90 (br s, 1

(35) The reaction mixture should remain clear at all times. Any problems associated with attempting to oxidize insoluble substrates under the prescribed conditions can be overcome by using dimethyl sulfoxide as a cosolvent. We have found that dimethyl sulfoxide can constitute up to one-fifth of the total reaction volume without there being any adverse effect on product yield.

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H), 7.40 (d, J = 12 Hz, 2 H), 7.10 (d, J = 12 Hz, 2 H); ^{13}C NMR δ 171.2, 140.4, 123.1, 122.9; IR (KBr) 3210, 1610, 1605, 1550, 1480, 1450, 1410, 1340, 1250, 1200 cm^{-1}; MS, m/e 200 (83), 202 (82) [[M]$^{\cdot+}$], 172 (79), 174 (75) [[M – CO]$^{\cdot+}$]; UV ($CHCl_3$) 247 (log ϵ = 4.2), 318 (infl), 328 (4.0), 366 (3.7), 385 (3.6) nm.

4-Bromo-2-hydroxy-7-methoxycyclohepta-2,4,6-trien-1-one (20). The crude reaction mixture obtained from oxidation of diol **10** was allowed to stir at ambient temperatures for 2 h before being worked up as described in the generalized procedure. Recrystallization (hexane/THF) of the crude solid thus obtained afforded tropolone **20** as yellow needles: mp 139–141 °C; ^{1}H NMR δ 7.65 (d, J = 1.8 Hz, 1 H), 7.40 (dd J = 11 and 1.8 Hz, 1 H), 6.85 (d, J = 11 Hz, 1 H), 3.95 (br s, 4 H, OCH_3 and OH); ^{13}C NMR δ 170.6, 159.9, 159.0, 128.8, 124.9, 121.9, 116.9, 56.6; IR (KBr) 3245, 1580, 1550, 1460, 1340, 1240, 1195 cm^{-1}; MS, m/e 230 (65), 232 (62) [M]$^{\cdot+}$], 187 (40), 189 (39) [M – [$CH_3\dot{C}O$]$^+$], 51 (100) [C_4H_3]$^+$]; HRMS calcd m/e for [M]$^{\cdot+}$ 229.9579, obsd 229.9559; UV ($CHCl_3$) 255 (log ϵ = 4.83), 320 (infl), 332 (4.15), 372 (4.21), 382 (4.22). Anal. Calcd for $C_8H_7BrO_3$: C, 41.59; H, 3.05; Br, 35.48. Found: C, 41.84; H, 3.20; Br, 34.60.

2-Hydroxy-5α-cholest-1-en-3-one (21) and 3-Hydroxy-5α-cholest-3-en-2-one (22).[42] Preparative TLC (silica gel, CH_2Cl_2/Et_2O, 95:5) of the crude reaction mixture obtained from oxidation of diol **11** afforded a major chromophoric band (R_f 0.5), which on extraction (CH_2Cl_2/Et_2O) gave a white crystalline solid. ^{13}C and ^{1}H NMR analyses of this solid show it to consist of a ca. 2:1 mixture of **21** and **22**. The low-field region in the ^{13}C NMR spectrum of this mixture was particularly diagnostic displaying two sets of three signals (δ 195.9, 146.2, 121.1; 195.6, 145.8, 127.2) due to the sp^2 hybridized carbons of each isomer. Recrystallization (CH_3CO_2H) afforded a ca. 9:1 mixture of **21** and **22** as off-white needles: mp 126–128 °C. ^{1}H NMR δ 5.70 (m, 2 H, OH and vinylic H), 2.60–0.80 (complex m, 36 H), 0.80 (s, 3 H), 0.65 (s, 3 H); ^{13}C NMR (signals due to major isomer) δ 195.9, 146.2, 126.2, 56.2, 53.0, 50.3, 45.5, 42.7, 42.1, 39.7, 39.5, 36.2, 35.7, 34.6, 31.8, 28.2, 28.0, 27.2, 24.1, 23.9, 22.8, 22.6, 21.2, 18.7, 12.8, 12.1 (one peak obscured); IR (KBr) 3425, 1662 cm^{-1}; MS, m/e 400 (43) [[M]$^{\cdot+}$], 43 (100); UV (hexane) 269 (log ϵ = 3.45) nm.

Generalized Procedure for the Oxidation of Diols 2, 5, 6, 8, and 9 Using Oxalyl Chloride "Activated" Dimethyl Sulfoxide. Dimethyl sulfoxide (108 μL, 2.54 mmol) was added to a stirred solution of oxalyl chloride (67 μL, 0.78 mmol) in CH_2Cl_2 (7 mL) maintained at ca. –60 °C (dry ice or liquid nitrogen/$CHCl_3$ bath). After 10 min, a solution of the appropriate diol (0.31 mmol) in CH_2Cl_2/dimethyl sulfoxide (1 mL of a 1:1 mixture) was added to the reaction mixture. After 15 min, the reaction mixture was treated with Et_3N (0.44 mL, 3.14 mmol) and allowed to warm to ca. 5 °C and then poured into aqueous 2 M HCl (25 mL) and extracted with CH_2Cl_2 (2 × 15 mL). The combined organic extracts were washed with water (1 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the crude oxidation mixture.

Diones **13**, **16** and **18** were purified by the methods detailed under the TFAA/dimethyl sulfoxide oxidation procedure and proved identical in all respects with the materials obtained previously. The tabulated yields for compounds **15** and **19** were estimated by TLC and/or ^{1}H NMR analysis of the crude oxidation mixture.

Reaction of Trifluoroacetic Anhydride with Triethylamine in the Presence of Dimethyl Sulfoxide. Formation of 4-(Dimethylamino)-1,1,1-trifluorobut-3-en-2-one.[32] TFAA (0.23 mL, 1.63 mmol) was added in a dropwise fashion to a stirred solution of dimethyl sulfoxide (0.5 mL, 0.7 mmol) in CH_2Cl_2 (8 mL) maintained at ca. –60 °C under an argon atmosphere. After 10 min at this temperature, the resulting solution was treated with Et_3N (0.3 mL, 2.15 mmol), and stirring was continued at –60 °C for 1.5 h before the cooling bath was removed. When the reaction mixture had warmed to ca. 5 °C, it was quenched with aqueous 2 M HCl (20 mL) and extracted with CH_2Cl_2 (20 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a colorless oil. Preparative TLC (alumina, CH_2Cl_2) of this material afforded a single major chromophoric band (R_f 0.55), which on extraction gave the title enamine (45 mg, 33%) as a colorless oil: ^{1}H NMR δ 7.75 (d, J = 12 Hz, 1 H), 5.25 (d, J = 12 Hz, 1 H), 3.40 (q, J = 7 Hz, 2 H), 3.25 (q, J = 7 Hz, 2 H), 1.25 (t, J = 7 Hz, 3 H), 1.20 (t, J = 7 Hz, 3 H); ^{13}C NMR δ 177.6 (q, $J_{19F-13C}$ = 26.5 Hz), 154.8, 117.8 (q, $J_{19F-13C}$ = 218 Hz), 87.8, 51.2, 43.4, 14.6, 11.5; MS, m/e 195 (10) [[M]$^{\cdot+}$], 126 (100) [[M – ·CF_3]$^+$]; UV (CH_3OH) 311 (log ϵ = 4.33) nm.

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Registry No. **1**, 1119-87-5; **2**, 102064-72-2; **3**, 1460-57-7; **4**, 1792-81-0; **5**, 110045-36-8; **6**, 27607-33-6; **7**, 37163-97-6; **8**, 579-43-1; **9**, 102064-70-0; **10**, 110045-37-9; **10** (acetonide), 110045-45-9; **11**, 20312-09-8; **12**, 110045-38-0; **13**, 110045-39-1; **14**, 10316-66-2; **15**, 110045-40-4; **16**, 3008-37-5; **16** (quinoxaline derivative), 27430-86-0; **17**, 585-25-1; **18**, 134-81-6; **19**, 3172-00-7; **20**, 110076-79-4; **21**, 571-14-2; **22**, 571-13-1; **23**, 110045-41-5; **24**, 110045-42-6; **25**, 110045-44-8; (1α,6α)-8,8-dimethyl-7,9-dioxabicyclo[4.3.3]nona-2,4-diene, 80409-75-2; phenol, 108-95-2; (4aα,8aα)-9,9-dichloro-1,4,5,8-tetrahydro-4a,8a-methanonaphthalene, 39623-22-8; (1α,3β,4α,6α)-4,7,7-tribromobicyclo[4.1.0]heptan-3-ol, 6802-78-4; (1α,3β,4α,6α)-4,7,7-tribromobicyclo[4.1.0]heptan-3-ol, 110045-43-7; triethylamine, 121-44-8; 4-(diethylamino)-1,1,1-trifluorobut-3-en-2-one, 21045-62-5; dimethyl sulfoxide, 67-68-5; trifluoroacetic anhydride, 407-25-0; *o*-diaminobenzene, 95-54-5.

(42) Lack, R. E.; Ridley, A. B. *J. Chem Soc. C* **1968**, 3017.

Selective Oxidation of Alcohol Function in Allylic Alcohols to α,β-Unsaturated Carbonyl Compounds Catalyzed by Zirconocene Complexes

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Bis(η^5-cyclopentadienyl)zirconium(IV) complexes, Cp_2ZrH_2 (1) and $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ (4), in the presence of an appropriate hydrogen acceptor such as benzaldehyde or cyclohexanone catalyze the Oppenauer-type oxidation of allylic alcohols to α,β-unsaturated carbonyl compounds. For instance, primary allylic terpenoid alcohols, geraniol and nerol, were oxidized to α- and β-citrals, which are essential compounds in the perfumery industry, in substantial yields without any treatment. Similarly, secondary allylic alcohols such as 3-hexen-2-ol and 2-cyclohexen-1-ol were also oxidized with ease to give 3-hexen-2-one and 2-cyclohexen-1-one in 93% and 89% yields, respectively. But the present OPP-type oxidation by zirconocene complexes is ineffective for propargylic alcohols.

The conversion of allylic alcohols to the corresponding α,β-unsaturated aldehydes or ketones plays an important role in synthetic organic chemistry. Although a variety of methods have been developed for this purpose, most of

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