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Novel manganese(III) oxidation chemistry: X-ray crystal structures of (1α,2α,4β)-1,2-diacetoxy-4-(4-methoxyphenyl)-6-methoxy-1,2,3,4-tetrahydronaphthalene (compound A) and (1α,2α,4β)-1,2-diacetoxy-4-(2-methoxyphenyl)-8-methoxy-1,2,3,4-tetrahydronaphthalene (compound B)

John R. Peterson,*[1] **Terrence P. Everson,**[2] **and Robin D. Rogers***[2]

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Compound **A** is (1α,2α,4β)-1,2-diacetoxy-4-(4-methoxyphenyl)-6-methoxy-1,2,3,4-tetrahydronaphthalene, $C_{22}H_{24}O_6$, M_r = 384.43, monoclinic, $P2_1/n$, with a = 11.074(3), b = 10.353(4), c = 17.616(4) Å, β = 94.96(2)°, V = 2012.1 Å^3, D_{calc} = 1.27 g cm^{-3} and μ = 0.55 cm^{-1} for Z = 4. Least-squares refinement of 1371 observed [$F_o \geq 5\,\sigma\,(F_o)$] reflections led to the final agreement index of R = 0.052. A twofold disorder was observed for the 1-acetoxy group whereas the 2-acetoxy group was ordered. Compound **B**, (1α,2α,4β)-1,2-diacetoxy-4-(2-methoxyphenyl)-8-methoxy-1,2,3,4-tetrahydronaphthalene, $C_{22}H_{24}O_6$, M_r = 384.43, crystallizes in the monoclinic space group, $P2_1/c$, with a = 16.209(2), b = 10.076(1), c = 13.357(4) Å, β = 111.41(2)°, V = 2030.9 Å^3, D_{calc} = 1.26 g cm^{-3} and μ = 0.54 cm^{-1} for Z = 4. A final agreement index of R = 0.045 was realized by least-squares refinement of 1486 observed [$F_o \geq 5\,\sigma\,(F_o)$] reflections. Intermolecular interactions in the cell lattices of compounds **A** and **B** are noted. The title compounds **A** and **B** were prepared by manganese(III) acetate oxidative dimerization of two molecules of 4-methoxystyrene and 2-methoxystyrene, respectively.

Introduction

The single-electron-transfer oxidation (SETO) of electron-rich alkenes by manganese(III) acetate was previously reported to provide 1,2-diacetates, 1,2-hydroxyacetates, and their oxidation products (Fristad *et al.*, 1986). Products of these structural types result from solvolysis of an alkene radical-cation intermediate by acetic acid. We recently reported a novel oxidative dimerization of 2,4,5-trimethoxystyrene to a 1-aryl-1,2-dihydronaphthalene in an acetic acid solution of manganese(III) acetate (Peterson *et al.*, 1989). Mechanistically, this transformation is also felt to proceed via SETO of the styrene, with slow or rapidly reversible solvolysis of the radical-cation intermediate. We have since begun to examine several additional methoxy-substituted styrenes to explore fully the synthetic utility and mechanistic aspects of this process. Herein we describe the X-ray crystal structures and the closest contacts between neighboring molecules in the crystal lattices for title compounds **A** and **B**. **A** and **B** are structurally related, oxidative-dimerization products of 4-methoxystyrene and 2-methoxystyrene, respectively.

Experimental

The X-ray structural data were collected on an Enraf-Nonius CAD-4 diffractometer. Nmr spectra were accumulated at 200 MHz for proton and at 50 MHz for

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[1] Department of Pharmacognosy, School of Pharmacy, The University of Mississippi, University, Mississippi 38677.
[2] Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115.

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carbon on an IBM WP-200 instrument. Chemical shifts are reported as parts per million downfield relative to tetramethylsilane in chloroform-*d*. Infrared spectra were obtained on a Sargent-Welch 3-200 spectrophotometer. Elemental analyses were performed by Ms. Paulanne Rider of the Northern Illinois University Chemical Instrumentation Laboratory with a Perkin Elmer Model 240 analyzer.

Preparation

The title compounds **A** and **B** were prepared by reaction of a 70°C glacial acetic acid (28 ml) solution of potassium acetate (549 mg, 5.59 mmol) and 4-methoxystyrene (750 mg, 5.59 mmol) or 2-methoxystyrene, respectively, with manganese(III) acetate dihydrate (3.0 g, 2.0 mol equivalents of oxidant). Each reaction was monitored for complete reduction of Mn(III) to Mn(II) with starch-potassium iodide test paper. The workup consisted of dilution with water, extraction with chloroform and water washes of the combined extracts. Medium pressure liquid chromatography of the crude red concentrate from each workup on a silica gel column (Merck) eluting with 12% ethyl acetate in hexane afforded compound **A** in 42% yield and compound **B** in 11% yield, each as a mixture of isomers. Crystals suitable for X-ray structural analysis of pure compound **A** (mp 148°C) and compound **B** (mp 154°C) were obtained by crystallization of each isomeric mixture from methanol/chloroform.

Table 1. Final fractional coordinates for compound **A**, $C_{22}H_{24}O_6$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B(eqv)[a]
O(1)	0.8906(3)	0.2068(4)	0.4275(2)	3.56
O(2)	0.9274(9)	0.1150(8)	0.5424(4)	5.24
O(2)′[b]	0.910(1)	0.082(2)	0.5391(6)	10.14
O(3)	0.6653(3)	0.1568(3)	0.4775(2)	2.85
O(4)	0.6476(5)	−0.0521(5)	0.5059(2)	4.94
O(5)	0.9648(4)	0.0753(4)	0.0944(2)	3.51
O(6)	0.2583(4)	−0.1187(4)	0.1523(2)	3.87
C(1)	0.8205(5)	0.0961(6)	0.3948(3)	2.53
C(2)	0.6870(5)	0.1219(5)	0.4001(3)	2.37
C(3)	0.6441(5)	0.2334(5)	0.3490(3)	2.56
C(4)	0.6531(4)	0.1982(5)	0.2653(3)	2.21
C(5)	0.7768(4)	0.1417(5)	0.2534(3)	2.08
C(6)	0.8127(5)	0.1399(5)	0.1794(3)	2.46
C(7)	0.9221(5)	0.0822(5)	0.1653(3)	2.39
C(8)	0.9968(5)	0.0291(5)	0.2243(3)	2.52
C(9)	0.9605(5)	0.0321(5)	0.2971(3)	2.24
C(10)	0.8511(5)	0.0884(5)	0.3129(3)	2.10
C(11)	0.9393(6)	0.197(1)	0.5009(4)	5.20
C(12)	1.002(1)	0.336(1)	0.5181(6)	5.49
C(12)′	1.040(2)	0.268(2)	0.523(1)	6.76
C(13)	0.6492(6)	0.0585(7)	0.5254(3)	3.18
C(14)	0.6365(6)	0.1060(7)	0.6036(3)	4.23
C(15)	0.8877(6)	0.1184(7)	0.0312(3)	4.97
C(16)	0.5505(4)	0.1084(5)	0.2352(3)	2.00
C(17)	0.4376(5)	0.1583(6)	0.2137(3)	3.02
C(18)	0.3423(5)	0.0803(6)	0.1861(3)	3.33
C(19)	0.3589(5)	−0.0516(6)	0.1806(3)	2.73
C(20)	0.4700(5)	−0.1034(6)	0.2022(3)	2.64
C(21)	0.5648(5)	−0.0239(5)	0.2284(3)	2.46
C(22)	0.2701(6)	−0.2518(6)	0.1442(4)	4.10

[a] $B(eqv) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\,\beta_{12} + ac(\cos\beta)\,\beta_{13} + bc(\cos\alpha)\,\beta_{23}]$.

[b] Primed atoms are disordered—see Experimental section.

Elemental and spectral data

Compound **A**. Found C, 68.85; H, 6.49. $C_{22}H_{24}O_6$ requires C, 68.74; H, 6.29%. Ir (KBr) 3000, 2950,

Table 2. Final fractional coordinates for compound **B**, $C_{22}H_{24}O_6$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B(eqv)[a]
O(1)	0.1628(2)	−0.2369(3)	0.1181(2)	2.54
O(2)	0.1228(3)	−0.4277(3)	0.1750(3)	5.25
O(3)	0.3084(2)	−0.3036(3)	0.2959(2)	2.95
O(4)	0.2695(3)	−0.3462(4)	0.4373(3)	5.18
O(5)	−0.0012(2)	−0.1226(3)	0.1475(2)	3.15
O(6)	0.4726(2)	0.1291(3)	0.3329(2)	3.04
C(1)	0.1744(3)	−0.1704(4)	0.2193(3)	2.14
C(2)	0.2726(3)	−0.1704(4)	0.2882(3)	2.15
C(3)	0.3236(3)	−0.0823(4)	0.2395(3)	2.24
C(4)	0.2960(2)	0.0625(4)	0.2476(3)	2.05
C(5)	0.1962(3)	0.0770(4)	0.2050(3)	2.14
C(6)	0.1598(3)	0.2040(4)	0.1791(3)	2.50
C(7)	0.0694(3)	0.2221(5)	0.1425(4)	3.06
C(8)	0.0130(3)	0.1152(5)	0.1308(4)	3.08
C(9)	0.0484(3)	−0.0105(4)	0.1556(3)	2.50
C(10)	0.1398(3)	−0.0310(4)	0.1930(3)	1.94
C(11)	0.1384(3)	−0.3654(5)	0.1075(4)	3.17
C(12)	0.1373(4)	−0.4192(5)	0.0030(4)	4.31
C(13)	0.3014(3)	−0.3817(5)	0.3748(5)	3.27
C(14)	0.3394(4)	−0.5157(5)	0.3703(6)	5.58
C(15)	−0.0948(3)	−0.1080(5)	0.1097(4)	3.82
C(16)	0.3388(3)	0.1149(4)	0.3616(3)	2.03
C(17)	0.4300(3)	0.1467(4)	0.4030(4)	2.43
C(18)	0.4697(3)	0.1917(4)	0.5077(4)	2.85
C(19)	0.4211(3)	0.2073(5)	0.5730(4)	3.44
C(20)	0.3320(3)	0.1788(4)	0.5331(4)	3.30
C(21)	0.2919(3)	0.1328(4)	0.4293(3)	2.50
C(22)	0.5651(3)	0.1570(6)	0.3716(5)	4.35

[a] $B(eqv) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\,\beta_{12} + ac(\cos\beta)\,\beta_{13} + bc(\cos\alpha)\,\beta_{23}]$.

Table 3. Bond distances (Å) and angles (deg) for compound **A**, $C_{22}H_{24}O_6$

Atoms	Distance	Atoms	Distance
O(1)—C(1)	1.473(7)	O(1)—C(11)	1.361(7)
O(2)—C(11)	1.14(1)	O(2)′—C(11)	1.42(2)
O(3)—C(2)	1.450(6)	O(3)—C(13)	1.344(7)
O(4)—C(13)	1.195(8)	O(5)—C(7)	1.374(6)
O(5)—C(15)	1.416(7)	O(6)—C(19)	1.369(7)
O(6)—C(22)	1.393(8)	C(1)—C(2)	1.514(7)
C(1)—C(10)	1.512(7)	C(2)—C(3)	1.515(7)
C(3)—C(4)	1.531(7)	C(4)—C(5)	1.521(7)
C(4)—C(16)	1.527(7)	C(5)—C(6)	1.396(7)
C(5)—C(10)	1.390(7)	C(6)—C(7)	1.392(8)
C(7)—C(8)	1.385(7)	C(8)—C(9)	1.378(7)
C(9)—C(10)	1.393(7)	C(11)—C(12)	1.62(2)
C(11)—C(12)′	1.37(2)	C(13)—C(14)	1.480(8)
C(16)—C(17)	1.375(7)	C(16)—C(21)	1.385(7)
C(17)—C(18)	1.383(8)	C(18)—C(19)	1.382(9)
C(19)—C(20)	1.366(8)	C(20)—C(21)	1.382(7)

Atoms	Angle	Atoms	Angle
C(1)—O(1)—C(11)	117.8(5)	C(2)—O(3)—C(13)	116.3(4)
C(7)—O(5)—C(15)	117.8(4)	C(19)—O(6)—C(22)	117.3(5)
O(1)—C(1)—C(2)	108.9(4)	O(1)—C(1)—C(10)	105.0(4)
C(2)—C(1)—C(10)	111.6(4)	O(3)—C(2)—C(1)	110.1(4)
O(3)—C(2)—C(3)	107.4(4)	C(1)—C(2)—C(3)	110.8(4)
C(2)—C(3)—C(4)	110.4(4)	C(3)—C(4)—C(5)	111.0(4)
C(3)—C(4)—C(16)	111.7(4)	C(5)—C(4)—C(16)	111.7(4)
C(4)—C(5)—C(6)	117.8(4)	C(4)—C(5)—C(10)	122.1(5)
C(6)—C(5)—C(10)	120.1(5)	C(5)—C(6)—C(7)	119.7(4)
O(5)—C(7)—C(6)	123.9(4)	O(5)—C(7)—C(8)	115.5(5)
C(6)—C(7)—C(8)	120.6(5)	C(7)—C(8)—C(9)	119.1(5)
C(8)—C(9)—C(10)	121.6(5)	C(1)—C(10)—C(5)	122.1(5)
C(1)—C(10)—C(9)	118.9(4)	C(5)—C(10)—C(9)	118.9(5)
O(1)—C(11)—O(2)	127.4(8)	O(1)—C(11)—O(2)′	115.0(8)
O(1)—C(11)—C(12)	104.1(7)	O(2)—C(11)—C(12)	128.2(8)
O(1)—C(11)—C(12)′	119(1)	O(2)′—C(11)—C(12)′	122(1)
O(3)—C(13)—O(4)	122.9(5)	O(3)—C(13)—C(14)	111.2(6)
O(4)—C(13)—C(14)	125.9(6)	C(4)—C(16)—C(17)	119.8(5)
C(4)—C(16)—C(21)	123.0(4)	C(17)—C(16)—C(21)	117.1(5)
C(16)—C(17)—C(18)	121.7(5)	C(17)—C(18)—C(19)	120.0(5)
O(6)—C(19)—C(18)	114.7(5)	O(6)—C(19)—C(20)	125.9(6)
C(18)—C(19)—C(20)	119.4(5)	C(19)—C(20)—C(21)	119.9(5)
C(16)—C(21)—C(20)	121.9(5)		

2930, 2830, 1730, 1605, 1580, 1495, 1460, 1440, 1360, 1300, 1250, 1170, 1030, 970, 830, 750 cm^{-1}. ^{1}H nmr δ 7.30 (d, J = 8.54 Hz, 1 H), 7.10 (d, J = 8.69 Hz, 2 H), 6.86 (d, J = 8.69 Hz, 2 H), 6.79 (dd, J = 8.54, 2.51 Hz, 1 H), 6.41 (d, J = 2.51 Hz, 1 H), 5.99 (d, J = 4.16 Hz, 1 H), 5.3-5.2 (m, 1 H), 4.2-4.05 (m, 1 H), 3.80 (s, 3 H), 3.65 (s, 3 H), 2.4-2.0 (m, 2 H), 2.11 (s, 3 H), 2.04 (s, 3 H). ^{13}C nmr, 170.14, 169.96, 159.60, 158.29, 141.71, 136.89, 131.33, 129.61, 114.20, 114.01, 112.90, 69.77, 69.48, 55.15, 55.04, 40.86, 33.15, 21.17, 20.98 ppm.

Compound ***B***. Found C, 68.66; H, 6.33. $C_{22}H_{24}O_6$ requires C, 68.74; H, 6.29%. Ir (KBr) 3060, 3010, 2950, 2940, 2840, 1740, 1600, 1585, 1485, 1460, 1435, 1365, 1330, 1320, 1290, 1260, 1240, 1110, 1045, 1025, 980, 940, 910, 800, 750 cm^{-1}. ^{1}H nmr δ 7.3-7.1 (m, 2 H), 6.89 (d, J = 7.51 Hz, 1 H), 6.85-6.65 (m, 2 H), 6.65-6.55 (m, 2 H), 6.40 (dd, J = 7.51, 1.46 Hz, 1 H), 5.11 (dt, J = 13.03, 3.50 Hz, 1 H), 4.84 (brd, J = 6.06 Hz, 1 H), 3.90 (s, 3 H), 3.83 (s, 3 H), 2.65-2.45 (m, 1 H), 2.06 (s, 3 H), 1.95 (s, 3 H), 2.0-1.8 (m, 1 H). ^{13}C nmr 170.27, 170.12, 158.27, 156.66, 140.47, 133.59, 130.07, 129.73, 127.65, 123.18, 122.47, 120.39, 110.27, 108.22, 67.97, 63.81, 55.60, 55.39, 38.07, 28.57, 21.06.

Crystal data, structure determination, and refinement

Compound A. A transparent single crystal of $C_{22}H_{24}O_6$ with dimensions 0.10 × 0.15 × 0.28 mm was mounted on a pin and transferred to the goniometer. The space group was determined to be the centric $P2_1/n$ from the systematic absences. Cell constants were obtained from the setting angles of 25 reflections ($\theta > 14°$). Unit-cell dimensions were a = 11.074(3), b = 10.353(4), c = 17.616(4) Å, β = 94.96(2)°, V = 2012.1 Å^3, Z = 4, D_{calc} = 1.27 g cm^{-3}, and μ = 0.55 cm^{-1}. 3930 reflections were measured, of which 1371 were considered observed [$F_o \geq 5\,\sigma\,(F_o)$] and included in the refinement. The intensities were corrected for Lorentz-polarization effects. Data were collected utilizing $MoK\alpha$ (λ = 0.71073 Å) radiation out of $2\theta \leq 50°$ (h 0 to 12, k 0 to 11, l −19 to 19). The structure was solved using the MULTAN80 (Main *et al.*, 1980) direct methods program. A least-squares refinement with isotropic thermal parameters led to R = 0.096. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with **B** fixed at 5.5 Å^2. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C—H = 0.95 Å, B = 5.5 Å^2). Disorder of one of the acetate groups was resolved. O(2) and C(12) have two orientations each, O(2) and C(12) with 60% occupancy and O(2)′ and C(12)′ with 40% occupancy. These atoms were refined in alternate least-squares cycles. Scattering factors and anomalous-dispersion corrections were from the *International Tables for X-Ray Crystallography* (1974). The structure was refined with SHELX76 (Sheldrick, 1976), $\Sigma\, w\,(|F_o| - |F_c|)^2$ minimized, weights = $[\sigma(F_o)^2 + 0.0002\,F_o^2]^{-1}$, 286 parameters varied, final R = 0.052, R_w = 0.053, S = 0.96, Δ/σ in final least-squares refinement cycle < 0.01, $\Delta\rho$ < 0.3 e-Å^{-3} in final difference map. The final values of the positional parameters of the nonhydrogen atoms for compound **A** are given in Table 1.

Compound B. A transparent crystal of $C_{22}H_{24}O_6$ with dimensions 0.08 × 0.15 × 0.20 mm was mounted on a pin and placed on the diffractometer. The systematic absences indicated the space group to be the centric $P2_1/c$. Cell constants were obtained from the setting angles of 25 reflections ($\theta > 18°$). Unit-cell dimensions were a = 16.209(2), b = 10.076(1), c = 13.357(4) Å, β = 111.41(2)°, V = 2030.9 Å^3, Z = 4, D_{calc} = 1.26 g cm^{-3}, and μ = 0.54 cm^{-1}. A total of 3533 reflections were measured; 1486 were considered observed [$F_o \geq 5\sigma(F_o)$] reflections and included in the refinement. Index range: h −18 to 18, k 0 to 11, l 0 to 15 for $2\theta \leq 48°$. The structure was determined and refined in the same manner as described for compound **A**, with the exception that disorder of the acetate group was not observed in compound **B**. $\Sigma\, w\,(|F_o| - |F_c|)^2$ was minimized and 265 parameters were varied in the final refinement cycle.

Table 4. Torsion angles (deg) for compound **A**, $C_{22}H_{24}O_6$

Atoms	Angle
C(9)—C(10)—C(1)—O(1)	79.1
C(9)—C(10)—C(1)—C(2)	−163.1
C(9)—C(10)—C(1)—H(1)C1	−43.6
C(10)—C(1)—C(2)—O(3)	−167.5
C(10)—C(1)—C(2)—C(3)	−48.7
C(10)—C(1)—C(2)—H(1)C2	71.5
O(1)—C(1)—C(2)—O(3)	−52.0
O(1)—C(1)—C(2)—C(3)	66.8
O(1)—C(1)—C(2)—H(1)C2	−173.0
H(1)C1—C(1)—C(2)—O(3)	70.9
H(1)C1—C(1)—C(2)—C(3)	−170.4
H(1)C1—C(1)—C(2)—H(1)C2	−50.2
C(1)—C(2)—C(3)—C(4)	65.0
C(1)—C(2)—C(3)—H(1)C3	−174.6
C(1)—C(2)—C(3)—H(2)C3	−54.9
O(3)—C(2)—C(3)—C(4)	−174.7
O(3)—C(2)—C(3)—H(1)C3	−54.2
O(3)—C(2)—C(3)—H(2)C3	65.4
H(1)C2—C(2)—C(3)—C(4)	−53.6
H(1)C2—C(2)—C(3)—H(1)C3	66.8
H(1)C2—C(2)—C(3)—H(2)C3	−173.6
C(2)—C(3)—C(4)—C(5)	−48.8
C(2)—C(3)—C(4)—C(16)	76.6
C(2)—C(3)—C(4)—H(1)C4	−166.5
H(1)C3—C(3)—C(4)—C(5)	−169.2
H(1)C3—C(3)—C(4)—C(16)	−43.8
H(1)C3—C(3)—C(4)—H(1)C4	73.1
H(2)C3—C(3)—C(4)—C(5)	71.0
H(2)C3—C(3)—C(4)—C(16)	−163.6
H(2)C3—C(3)—C(4)—H(1)C4	−46.7
C(6)—C(5)—C(4)—C(3)	−161.6
C(6)—C(5)—C(4)—C(16)	73.0
C(6)—C(5)—C(4)—H(1)C4	−44.3

Table 5. Bond distances (Å) and angles (deg) for compound **B**, $C_{22}H_{24}O_6$

Atoms	Distance	Atoms	Distance
O(1)—C(1)	1.458(5)	O(1)—C(11)	1.346(5)
O(2)—C(11)	1.199(6)	O(3)—C(2)	1.451(4)
O(3)—C(13)	1.352(6)	O(4)—C(13)	1.187(6)
O(5)—C(9)	1.367(5)	O(5)—C(15)	1.421(5)
O(6)—C(17)	1.363(5)	O(6)—C(22)	1.424(5)
C(1)—C(2)	1.520(5)	C(1)—C(10)	1.505(5)
C(2)—C(3)	1.512(5)	C(3)—C(4)	1.541(5)
C(4)—C(5)	1.513(5)	C(4)—C(16)	1.520(5)
C(5)—C(6)	1.398(5)	C(5)—C(10)	1.392(5)
C(6)—C(7)	1.377(5)	C(7)—C(8)	1.384(6)
C(8)—C(9)	1.380(6)	C(9)—C(10)	1.396(5)
C(11)—C(12)	1.492(7)	C(13)—C(14)	1.494(7)
C(16)—C(17)	1.412(5)	C(16)—C(21)	1.390(6)
C(17)—C(18)	1.385(6)	C(18)—C(19)	1.381(6)
C(19)—C(20)	1.375(6)	C(20)—C(21)	1.379(6)

Atoms	Angle	Atoms	Angle
C(1)—O(1)—C(11)	118.2(4)	C(2)—O(3)—C(13)	116.7(4)
C(9)—O(5)—C(15)	117.5(4)	C(17)—O(6)—C(22)	117.1(4)
O(1)—C(1)—C(2)	108.2(3)	O(1)—C(1)—C(10)	107.5(3)
C(2)—C(1)—C(10)	111.1(3)	O(3)—C(2)—C(1)	110.3(3)
O(3)—C(2)—C(3)	107.8(3)	C(1)—C(2)—C(3)	110.8(3)
C(2)—C(3)—C(4)	107.9(3)	C(3)—C(4)—C(5)	111.3(3)
C(3)—C(4)—C(16)	111.1(3)	C(5)—C(4)—C(16)	112.2(3)
C(4)—C(5)—C(6)	118.5(4)	C(4)—C(5)—C(10)	122.3(4)
C(6)—C(5)—C(10)	119.2(4)	C(5)—C(6)—C(7)	120.4(4)
C(6)—C(7)—C(8)	120.7(4)	C(7)—C(8)—C(9)	119.2(4)
O(5)—C(9)—C(8)	124.0(4)	O(5)—C(9)—C(10)	115.0(4)
C(8)—C(9)—C(10)	121.0(4)	C(1)—C(10)—C(5)	122.0(4)
C(1)—C(10)—C(9)	118.5(4)	C(5)—C(10)—C(9)	119.5(4)
O(1)—C(11)—O(2)	124.1(5)	O(1)—C(11)—C(12)	110.5(5)
O(2)—C(11)—C(12)	125.4(5)	O(3)—C(13)—O(4)	123.7(5)
O(3)—C(13)—C(14)	110.0(6)	O(4)—C(13)—C(14)	126.4(6)
C(4)—C(16)—C(17)	120.1(4)	C(4)—C(16)—C(21)	122.6(4)
C(17)—C(16)—C(21)	117.3(4)	O(6)—C(17)—C(16)	115.0(4)
O(6)—C(17)—C(18)	124.8(4)	C(16)—C(17)—C(18)	120.2(4)
C(17)—C(18)—C(19)	120.8(4)	C(18)—C(19)—C(20)	119.5(5)
C(19)—C(20)—C(21)	120.1(5)	C(16)—C(21)—C(20)	121.9(4)

Weights = $[\sigma(F_o)^2 + 0.00011\,F_o^2]^{-1}$, final $R = 0.045$, $R_w = 0.045$, $S = 0.72$. Δ/σ in final least-squares refinement cycle < 0.01, $\Delta\sigma < 0.2\text{e-Å}^{-3}$ in final difference map. The final fractional coordinates of the nonhydrogen atoms for compound **B** are listed in Table 2.

Results and discussion

The derived bond distances and angles for compound **A** are provided in Table 3, torsion angles of **A** in Table 4, and the corresponding data for compound **B** in Tables 5 and 6. ORTEP drawings (Johnson, 1976) of title compounds **A** and **B** are shown in Figs. 1 and 2, respectively. Cell packing diagrams are illustrated in Figs. 3 and 4.

The *cis* relationship of the two acetoxy groups and the *trans* disposition of the 4-aryl ring with respect to these groups is apparent for both compounds upon examination of the ORTEP diagrams. Consistent with this finding are the O(1)—C(1)—C(2)—O(3) torsion angles of −52.0° and −51.5° for compounds **A** and **B**, respectively. The corresponding H(1)C(1)—C(1)—C(2) —H(1)C(2) torsion angles are −50.2° and −49.7°.

Table 6. Torsion angles (deg) for compound **B**, $C_{22}H_{24}O_6$

Atoms	Angle
C9—C(10)—C(1)—O(1)	78.4
C(9)—C(10)—C(1)—C(2)	−163.3
C(9)—C(10)—C(1)—H(1)Cl	−42.9
C(10)—C(1)—C(2)—O(3)	−169.4
C(10)—C(1)—C(2)—C(3)	−50.0
C(10)—C(1)—C(2)—H(1)C2	70.4
O(1)—C(1)—C(2)—O(3)	−51.5
O(1)—C(1)—C(2)—C(3)	67.9
O(1)—C(1)—C(2)—H(1)C2	−171.8
H(1)C1—C(1)—C(2)—O(3)	70.6
H(1)Cl—C(1)—C(2)—C(3)	−170.0
H(1)Cl—C(1)—C(2)—H(1)C2	−49.7
C(1)—C(2)—C(3)—C(4)	67.9
C(1)—C(2)—C(3)—H(1)C3	−171.8
C(1)—C(2)—C(3)—H(2)C3	−51.5
O(3)—C(2)—C(3)—C(4)	−171.2
O(3)—C(2)—C(3)—H(1)C3	−51.0
O(3)—C(2)—C(3)—H(2)C3	69.3
H(1)C2—C(2)—C(3)—C(4)	−50.9
H(1)C2—C(2)—C(3)—H(1)C3	69.3
H(1)C2—C(2)—C(3)—H(2)C3	−170.4
C(2)—C(3)—C(4)—C(5)	−49.9
C(2)—C(3)—C(4)—C(16)	75.9
C(2)—C(3)—C(4)—H(1)C4	−167.4
H(1)C3—C(3)—C(4)—C(5)	−170.1
H(1)C3—C(3)—C(4)—C(16)	−44.3
H(1)C3—C(3)—C(4)—H(1)C4	72.4
H(2)C3—C(3)—C(4)—C(5)	69.3
H(2)C3—C(3)—C(4)—C(16)	−164.9
H(2)C3—C(3)—C(4)—H(1)C4	−48.2
C(6)—C(5)—C(4)—C(3)	−162.9
C(6)—C(5)—C(4)—C(16)	71.9
C(6)—C(5)—C(4)—H(1)C4	−45.4

Bond distances and angles are normal for both compounds. The tetrahydronaphthalene ring atoms C(5) through C(10) describe a plane to within 0.006 Å for compound **A** and to within 0.003 Å for **B**. Atoms C(1) and C(4) deviate from this plane by −0.087 and 0.079 Å, respectively, in compound **A** and by −0.002 and −0.037 Å, respectively, in compound **B**. The tetrahydronaphthalene system puckers about ring atoms C(2) and C(3) in both compounds to relieve steric eclipsing interactions between vicinal ring substituents. Atoms C(2) and C(3) lie 0.330 and −0.368 Å, respectively, out of the C(5) through C(10) plane of compound **A**, while the analogous deviations in compound **B** are −0.411 and 0.387 Å. The pendant aryl ring atoms C(16) through C(21) also define unique planes in both compounds. Atoms C(16) through C(21) are within 0.007 Å of planarity in **A** and within 0.006 Å of planarity in **B**. The pendant aryl ring plane intersects the previously described tetrahydronaphthalene plane at an angle of 96.4° in compound **A** and at 80.9° in **B**. The significant reduction in the latter angle is likely the result of increased steric congestion of 2-methoxy substitution on the pendant aryl ring of **B**.

An analysis of the closest intermolecular contact distances reveals that van der Waals forces are likely to be the dominant stabilizing forces in the crystal lattices of the title compounds. Several interactions were noted to occur between neighboring molecules of compound **A** and the most prominent of these are tabulated with their symmetry relationships in Table 7. In contrast, fewer significant crystal lattice interactions were found in compound **B**. The shortest contact distances between neighboring molecules of **B** are listed in Table 8 along with their symmetry relationships.

The oxidative dimerization of two molecules of 4-methoxystyrene or 2-methoxystyrene to title compounds **A** and **B**, respectively, sheds important insight on the synthetic utility and mechanistic aspects of this process. First, the employment of extremely electron-rich substrates such as 2,4,5-trimethoxystyrene is not mandated, although somewhat lower yields of naphthalene type products should be expected at the expense of "classical" 1,2-diacetate and 1,2-hydroxyacetate formation. Indeed, compounds **A** and **B** are felt to be the subsequent diacetoxylation product (Fristad *et al.*, 1986) of the initially formed, oxidative-dimerization product, a 1-aryl-1,2-dihydronaphthalene (Peterson *et al.*, 1989). Second, the radical-cation intermediate derived from even the less electron-rich styrenes must have a sufficient lifetime in glacial acetic acid to encounter a second styrene molecule. Third, the formation of only the 4-aryl isomer, rather than a 3-aryl counterpart, substantiates dimerization in only a β,β'-fashion. The production of such a dimeric radical-cationic intermediate would disperse the charge deficiency over both benzylic sites. Finally, ring closure by radical addition to the aromatic nucleus (Mohan *et al.*, 1987) seems plausible at this time as the conventional ring activating and directing effects of a methoxy group (March, 1985) would not be expected to facilitate direct carbocationic cyclization for either of these substrates. Further investigations of this unusual oxidation process are now in progress in our laboratories.

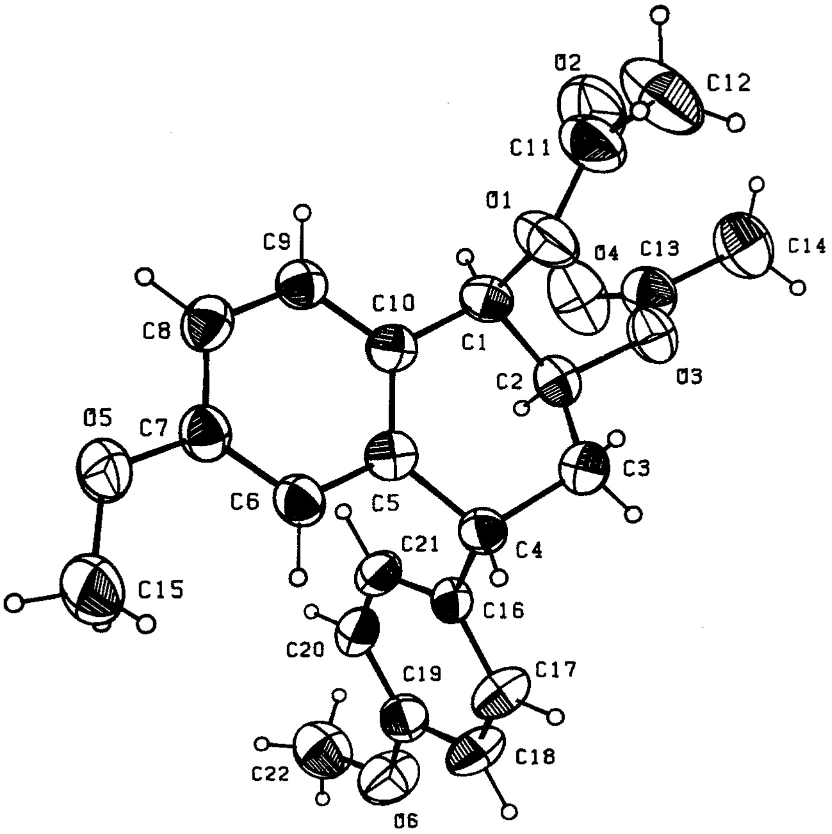

Fig. 1. Thermal-ellipsoid plot of title compound **A** showing the atom-numbering scheme. The hydrogen atom radii are arbitrarily reduced.

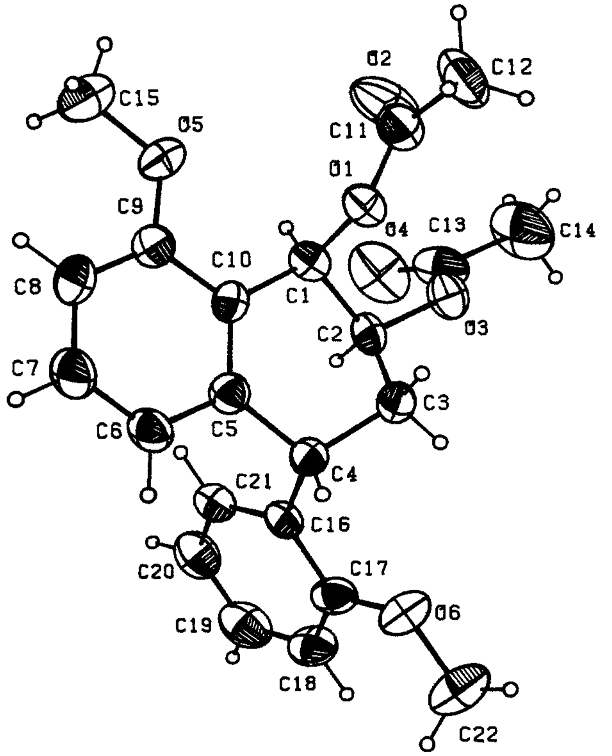

Fig. 2. Thermal-ellipsoid plot of title compound **B** utilizing the same atom-numbering scheme as for compound **A**. The hydrogen atom radii are arbitrarily reduced.

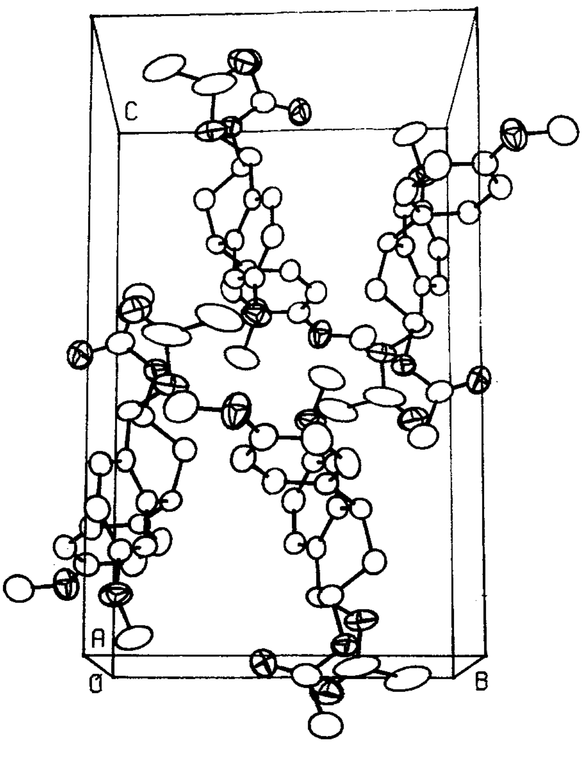

Fig. 3. Cell packing diagram for title compound **A**.

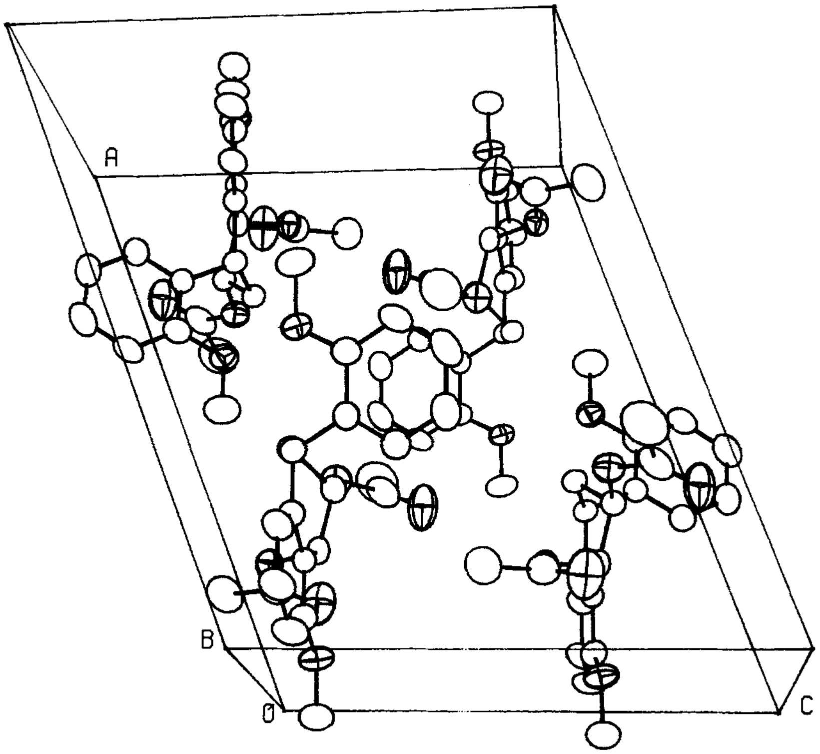

Fig. 4. Cell packing for title compound **B**.

Table 7. Intermolecular contact distances (Å) for compound **A**, $C_{22}H_{24}O_6$

Atoms	Distance	Atoms	Distance
O(2)—C(9)[a]	3.353(9)	O(2)—H(1)C(9)[a]	2.45
O(2)′—C(9)[a]	3.33(1)	O(2)′—H(1)C(9)[a]	2.41
O(2)—O(2)[a]	3.30(2)	O(2)—O(2)′[a]	3.15(2)
O(2)′—O(2)′[a]	3.04(3)	H(1)C(1)—H(2)C(12)′[a]	2.53
C(17)—H(3)C(12)′[b]	2.79	H(1)C(6)—H(1)C(12)[b]	2.52
H(1)C(6)—H(3)C(12)′[b]	2.78	H(1)C(18)—H(3)C(14)[b]	2.70
H(3)C(15)—H(1)C(12)′[b]	2.78		
C(15)—O(4)[c]	3.489(9)	H(2)C(15)—O(4)[c]	2.59
H(1)C(12)′—H(3)C(22)[c]	2.63	H(2)C(12)′—H(3)C(22)[c]	2.53
H(1)C(17)—H(1)C(8)[c]	2.78		
H(1)C(8)—O(6)[d]	2.67		
O(5)—H(1)C(15)[e]	2.68		
O(4)—H(1)C(22)[f]	2.72		

[a] Atom related to that in Table 1 by $2 - x, -y, 1 - z$.

[b] $x - 1/2, 1/2 - y, z - 1/2$.

[c] $3/2 - x, 1/2 + y, 1/2 - z$.

[d] $1 + x, y, z$.

[e] $2 - x, -y, -z$.

[f] $1/2 + x, -1/2 - y, 1/2 + z$.

Table 8. Intermolecular contact distances (Å) for compound **B**, $C_{22}H_{24}O_6$

Atoms	Distance	Atoms	Distance
H(1)C(22)—O(3)[a]	2.74	C(22)—O(3)[a]	3.566(7)
H(3)C(22)—H(2)C(3)[a]	2.65		
O(2)—H(3)C(12)[b]	2.65	H(1)C(12)—H(1)C(21)[b]	2.64
O(6)—H(1)C(19)[c]	2.75	H(1)C(4)—H(1)C(20)[c]	2.52
H(1)C(6)—H(1)C(20)[c]	2.57		
H(1)C(21)—H(2)C(12)[d]	2.35	H(1)C(1)—H(3)C(12)[d]	2.76
H(3)C(14)—H(1)C(6)[e]	2.68		
H(1)C(3)—H(1)C(18)[f]	2.65		

[a] Atom related to that in Table 2 by $1-x$, $1/2 + y$, $1/2 - z$.
[b] $-x$, $y - 1/2$, $1/2 - z$.
[c] x, $1/2 - y$, $z - 1/2$.
[d] x, $-1/2 - y$, $1/2 + z$
[e] x, $y - 1$, z.
[f] $1 - x$, $-y$, $1 - z$.

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