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[6] All new compounds gave satisfactory spectral data and analytical values. Selected ^{1}H NMR (400 MHz, TMS) data are as follows: **1a** ($CDCl_3$, 24 °C): $\delta = 7.47$ (br d, $J = 7.8$ Hz, 4H), 7.40 (dd, $J = 7.8$, 1.5 Hz, 2H), 7.21 – 7.32 (m, 6H), 7.12 (m, 4H), 6.97 (br dd, $J = 7$, 7 Hz, 2H), 6.87 – 6.94 (m, 4H), 6.61 (br d, $J = 7.8$ Hz, 2H); **2a**-$(BF_4)_2$ (CD_3CN, 20 °C): $\delta = 8.48$ (ddd, $J = 6.8$, 6.8, 1.5 Hz, 4H), 8.31 (br d, $J = 8.3$ Hz, 4H), 7.75 (ddd, $J = 6.8$, 6.8, 1.5 Hz, 2H), 7.73 (dd, $J = 8.3$, 1.5 Hz, 4H), 7.58 (ddd, $J = 6.8$, 6.8, 1.0 Hz, 4H), 7.47 (ddd, $J = 7.8$, 7.8, 1.0 Hz, 2H), 7.37 (dd, $J = 7.8$, 1.8 Hz, 2H), 7.32 (br d, $J = 7.8$ Hz, 2H).

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[8] Comparisons of the coefficients obtained by linear combination of atomic orbitals (LCAO) in singly occupied molecular orbitals (SOMO) between xanthyl and thioxanthyl indicate that the considerable spin exists on S in thioxanthyl whereas much larger spin density is expected at C9 in xanthyl (K. Okada, T. Imakura, M. Oda, A. Kajiwara, M. Kamachi, M. Yamaguchi, *J. Am. Chem. Soc.* **1997**, *119*, 5740). This fact may be related to the reason for the different number of electrons involved in E_1^{red} of $\mathbf{2}^{2+}$. One possible explanation might be the rapid equilibrium of $\mathbf{2a}^{\bullet\bullet}$ with some closed-shell species, which facilitates the disproportionation of $\mathbf{2a}^{+\bullet}$ to make the E_2^{red} wave ambiguous. Such a process is less likely in $\mathbf{2b}^{\bullet\bullet}$, in which the spin density is delocalized over thioxanthyl moieties.

[9] When the dication salt **2a**-$(BF_4)_2$ was reduced by SmI_2 in THF followed by quenching with air, peroxide **1a** was obtained in 85% yield. This result indicates that (**2**-O_2)$^{\bullet\bullet}$ is also generated by 2e reduction of $\mathbf{2a}^{2+}$ followed by C–O bond making (EEC process).

[10] Crystal structure analyses: **1a**: $C_{38}H_{24}O_5$, $M_r = 560.60$, monoclinic, $P2_1/c$, $a = 10.211(3)$, $b = 16.311(5)$, $c = 16.931(3)$ Å, $\beta = 103.88(2)°$, $V = 2737(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.360$ g cm^{-1}, $Rw = 0.069$. **1b**·0.5 AcOEt (–100 °C): $C_{40}H_{28}O_4S_2$, $M_r = 636.78$, monoclinic, $C2/c$, $a = 31.597(1)$, $b = 10.2379(3)$, $c = 22.9976(7)$ Å, $\beta = 123.615(1)°$, $V = 6195.3(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.365$ g cm^{-1}, $Rw = 0.055$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-136844 and -136845. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] The O–O bond length in 1,4-diphenyl-2,3-dioxabicyclo[2.2.1]heptane is 1.501(2) Å (D. J. Coughlin, R. S. Brown, R. G. Salomon, *J. Am. Chem. Soc.* **1979**, *101*, 1533) and that in tetrabenzopentacene endoperoxide is 1.496(5) Å (A. Izuoka, T. Murase, M. Tsukada, Y. Ito, T. Sugawara, A. Uchida, N. Sato, H. Inokuchi, *Tetrahedron Lett.* **1997**, *38*, 245). Long O–O distances are more common for small ring peroxides, such as dioxiranes (1.503(5) Å for dimesityldioxirane: W. Sander, K. Schroeder, S. Muthusamy, A. Kirschfeld, W. Kappert, R. Boese, E. Kraka, C. Sosa, D. Cremer, *J. Am. Chem. Soc.* **1997**, *119*, 7265) or dioxetanes (1.500 and 1.55 Å in 1,6-diphenyl-2,5,7,8-tetraoxobicyclo[4.2.0]octane derivatives: W. Adam, E. Schmidt, E.-M. Peters, K. Peters, H. G. von Schnering, *Angew. Chem.* **1983**, *95*, 566; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 546). The last one is surprisingly long for an O–O bond although the error in the determination was not given.

[12] When the similar oxidation was conducted under the presence of tetraphenylcyclopentadienone (10 equiv) no detectable amount of *cis*-dibenzoylstilbene was formed, which suggests that the major reaction path does not produce $^1O_2$.

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[14] Reductive oxygenation would also occur by the combination of $\mathbf{2}^{2+}$ with $O_2^{-\bullet}$, which is generated by 1e reduction of O_2. This process seems, however, less likely when it is considered that O_2 is a weaker electron acceptor ($E^{red} < -0.8$ V versus SCE in CH_2Cl_2) than $\mathbf{2}^{2+}$.

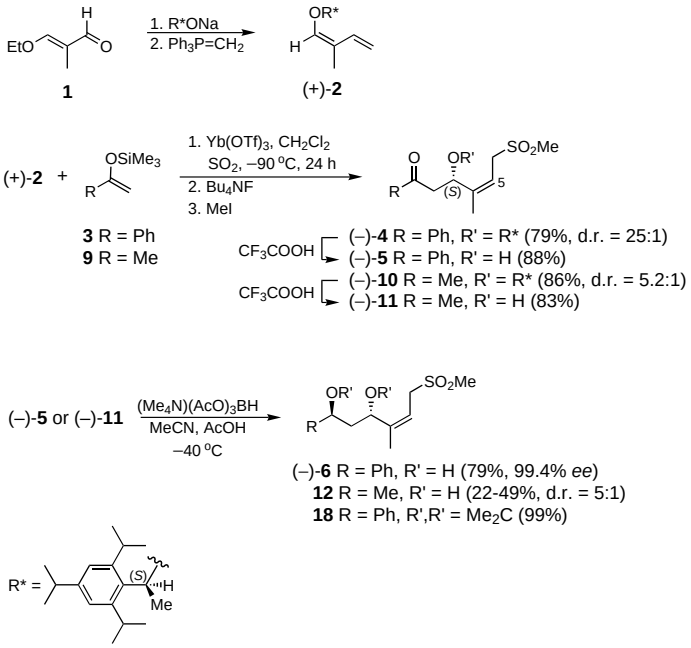
A New Asymmetric Carbon – Carbon Bond Forming Reaction: Four-Component Stereoselective Synthesis of (*Z*)-4,6-Dihydroxy-3-methylalk-2-enyl Methyl Sulfones**

Vera Narkevitch, Kurt Schenk, and Pierre Vogel*

Dedicated to Professor Horst Prinzbach on the occasion of his 68th birthday

In the presence of a Lewis acid, 1-alkoxy- or 1-silyloxy-1,3-dienes can be combined with enoxysilanes and sulfur dioxide to generate (*Z*)-6-oxo-4-oxyalk-2-ene sulfinates, which react with methyl iodide (S-alkylation) to afford the corresponding methyl sulfones.[1, 2] We report here an asymmetric version of this new carbon – carbon bond forming reaction that can be used to construct polyketide fragments stereoselectively.

Enantiomerically pure (>99% *ee*) diene (+)-**2** was obtained by reaction of **1** with sodium (–)-(*S*)-1-(2,4,6-triisopropylphenyl)ethoxide[3] followed by Wittig methylenation (Scheme 1).[4] In the presence of Yb(OTf)$_3$ (Tf = F_3CSO_2) and



Scheme 1. Asymmetric synthesis of 4,6-*anti*-(*Z*)-4,6-dihydroxy-3-methylalk-2-enyl methyl sulfones; see text for details.

an excess of SO_2, (+)-**2** reacted with enoxysilane **3** to give a trimethylsilyl sulfinate, which was desilylated with Bu_4NF and treated with MeI to afford a 25:1 mixture of sulfone (–)-**4** and its diastereomer (79% yield, recovery of 20% of (+)-**2**).[5]

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[**] This work was supported by the Swiss National Science Foundation.

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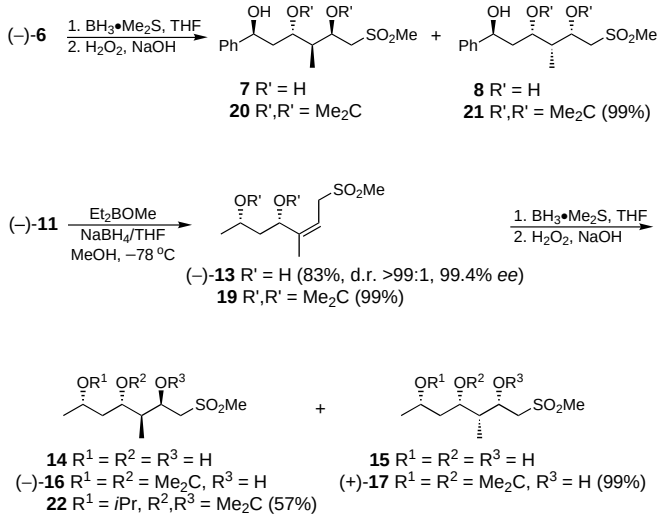
Pure (−)-**4** was obtained by flash chromatography on silica gel. Trifluoroacetolysis[6] of (−)-**4** gave (−)-**5** (88% yield), which was reduced with $(Me_4N)(AcO)_3BH$ in MeCN/AcOH (−40 °C, 15 h)[7] to produce *anti*-diol (−)-**6** (79% yield). Hydroboration of (−)-**6** with $BH_3 \cdot Me_2S$ (THF, −8 °C, 24 h) provided a 3.9:1 mixture of triols **7** and **8** (91% yield, Scheme 2).



Scheme 2. Synthesis of polyketides; see text for details.

Under similar conditions, (+)-**2** and SO_2 reacted with enoxysilane **9** to give a 5.2:1 mixture of (−)-**10** and its diastereomer (86% yield). Pure (−)-**10** was obtained by flash chromatography on silica gel. Trifluoroacetolysis of (−)-**10** gave aldol (−)-**11**, which was reduced with $(Me_4N)(AcO)_3BH$ in MeCN/AcOH[7] to form **12** as the major *anti*-diol (Scheme 1). Alternatively, reduction of (−)-**11** with $Et_2BOMe/NaBH_4$[8] afforded *syn*-diol (−)-**13** (83% yield, Scheme 2), the hydroboration of which with $BH_3 \cdot Me_2S$ in THF (0 °C, 24 h) led to a 2.2:1 mixture of triols **14** and **15** (83%). Their acetonides **16** and **17**, obtained under standard conditions ($(Me_2O)_2CMe_2$/acetone/pyridinium *p*-toluenesulfonate (PPTS)), could be separated by flash chromatography. The modest diastereoselectivities for the hydroborations of (−)-**6** and (−)-**13** might be due to competing effects arising from $A^{1,2}$ and $A^{1,3}$ allylic strain.[9]

The structures of (−)-**4** and (−)-**10** were established by single-crystal X-ray radiocrystallography.[10] The enantiomeric purity (99.4% *ee*) of diols (−)-**6** and (−)-**13** was determined from the ^{17}F NMR spectra (^{13}C satellite for C–F coupling) of their Mosher diesters[11] derived from (*S*)-α-methoxy-α-phenylacetyl chloride. The *anti* and *syn* relative configurations of (−)-**6** and (−)-**13**, respectively, were confirmed by the ^{13}C NMR spectra of their acetonides **18** ($\delta = 25.0$, 24.7; Me_2C) and **19** ($\delta = 30.2$, 19.6; Me_2C),[12] obtained upon treatment with $(MeO)_2CMe_2$ and PPTS. Under similar conditions, triols **7** and **8** were converted selectively into acetonides **20** and **21**; their ^{13}C NMR and 2D NOESY ^1H NMR spectra of the latter proved the structures of the former. Treatment of **16** and **17** with acid ($AcOH/H_2O$) provided pure triols **14** and **15**. Hydroboration of **19** provided **16** as the major alcohol. Further treatment of **16** with $BH_3 \cdot THF$ led to a diol that gave acetonide **22** on treatment with $(MeO)_2CMe_2$/acetone/PPTS ($\delta = 23.7$, 24.9; Me), establishing the relative configurations of **14** and **15**.

An asymmetric version of our four component reaction (1-alkoxy-1,3-diene + SO_2 + enoxysilane + alkyl iodide) has been realized. Exploration of its versatility and its application to the synthesis of polyketides and analogues, as well as studies of its mechanism,[13] are underway in our laboratory.[14]

Experimental Section

(−)-**4**: A mixture of (+)-**2** (192 mg, 0.6 mmol), **3** (0.6 mL, 3 mmol), and $Yb(OTf)_3$ (298 mg, 0.48 mmol) in anhydrous CH_2Cl_2 (6 mL) was degassed on the vacuum line. SO_2, purified by flowing through a column of basic alumina (Merck, activity Is, 1.28 g, 20 mmol), was added at −196 °C. The mixture was stirred at −90 °C for 24 h, and SO_2 was pumped away at −90 °C and then at −65 °C. 1M Bu_4NF in THF (6 mL, 6 mmol) and MeI (1.2 mL, 20 mmol) were added under an argon atmosphere, and the mixture stirred at 0 °C for 1 h and then at 20 °C for 15 h. After addition of H_2O (30 mL), the mixture was extracted with CH_2Cl_2 (5 × 20 mL). The combined organic extracts were dried over $MgSO_4$. Solvent evaporation and flash chromatography on silica gel (CH_2Cl_2/Et_2O 24/1; R_f ((−)-**4**) = 0.35) afforded (−)-**4** (244 mg, 79%) and (+)-**2** (36 mg, 20%); colorless crystals were obtained by recrystallization from MeOH, m.p. 116–118 °C (MeOH). $[\alpha]_D^{25} = -0.7$ ($c = 1.0$, $CHCl_3$); UV (MeCN): λ_{max} (ε) = 241 (5700), 205 nm (12500); IR (KBr): $\tilde{\nu} = 3055$, 2965, 1685, 1420, 1305, 1265, 895, 745, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.86$–7.41 (m, 5H), 7.06–6.98 (m, 2H), 5.55 (ddq, ^3J(H-5,H-6) = 9.4, ^3J(H-5,H′-6) = 4.7, ^4J(H-5,Me-C(4)) = 1.3 Hz, H-5), 5.01 (q, ^3J(H-1′,H-2′) = 6.7 Hz, H-1′), 4.70 (dd, ^3J(H-3,H-2) = 8.8, ^3J(H-3,H′-2) = 4.0 Hz, H-3), 4.03 (dd, ^2J(H,H) = 15.2, ^3J(H-6,H-5) = 9.4 Hz, H-6), 3.93 (sept, CH*i*Pr), 3.47 (dd, ^2J(H,H) = 17.3, ^3J(H-2,H-3) = 8.8 Hz, H-2), 3.25 (dd, ^2J(H,H) = 15.2, ^3J(H-6,H-5) = 4.7 Hz, H′-6), 3.19 (dd, ^2J(H,H) = 17.3, ^3J(H-2,H-3) = 4.0 Hz, H′-2), 3.12, 2.85 (2 sept, 2 CH*i*Pr), 2.78 (s, $MeSO_2$), 1.88 (d, ^4J(Me-C(4),H-5) = 1.3 Hz, Me-C(4)), 1.54 (d, ^3J(H-1′,H-2′) = 6.7 Hz, $H_3C(2')$), 1.40–1.13 (m, 2 Me_2C), 1.26 (d, ^3J(Me,CH) = 6.9 Hz, *i*Pr); elemental analysis calcd for $C_{32}H_{48}O_5S$ ((−)-**4** · MeOH): C 70.55, H 8.88, S 5.88; found: C 70.86, H 8.60, S 5.99.

(−)-**5**. A mixture of (−)-**4** (149 mg, 0.29 mmol), CH_2Cl_2 (4.5 mL), and CF_3COOH (0.3 mL) was stirred at 20 °C for 40 min. A saturated aqueous solution of $NaHCO_3$ (30 mL) was added, and the mixture extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over $MgSO_4$. Solvent evaporation and flash chromatography on silica gel (CH_2Cl_2/EtOAc) afforded (−)-**5** (72 mg, 88%) as a yellow oil after removal of solvent. $[\alpha]_D^{25} = -52$ ($c = 1.0$, $CHCl_3$).

Received: November 25, 1999 [Z14313]

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[14] Preliminary experiments have shown that (*E*)-1-alkoxybutadienes and (*E*,*E*)-1-alkoxy-2-methylpenta-1,3-dienes can be combined with enoxysilanes **3**, **9**, and others, and with carbon electrophiles different from MeI.

Metamorphic Channels in Periodic Mesoporous Methylenesilica**

Tewodros Asefa, Mark J. MacLachlan, Hiltrud Grondey, Neil Coombs, and Geoffrey A. Ozin*

Since the discovery of mesoporous silica, MCM-41, in 1992,[1, 2] the synthesis of mesoporous inorganic materials using supramolecular organic templates continues to draw a great deal of attention due to the potential application of these materials in catalysis,[3] nanoelectronics,[4] separation science,[5] and environmental remediation.[6] The composition of mesoporous materials span a variety of inorganic compounds, including a range of oxides,[7, 8] Pt metal,[9] phosphates,[10] CdS,[11] and M/Ge_4S_{10},[12] but, until very recently,[13–16] none have included organic moieties as a structural component of the framework.

A vast number of organic, inorganic, organometallic, and polymeric species have been included inside the periodic hexagonal channels of MCM-41.[17] In particular, many species have been anchored or grafted to the channel wall of the silica by synthesis or postsynthesis treatment with $RSi(OR')_3$ compounds.[17, 18] These organic groups, which protrude into the channels, have potential for many useful transformations, catalysis, separations, and other interesting chemistry.

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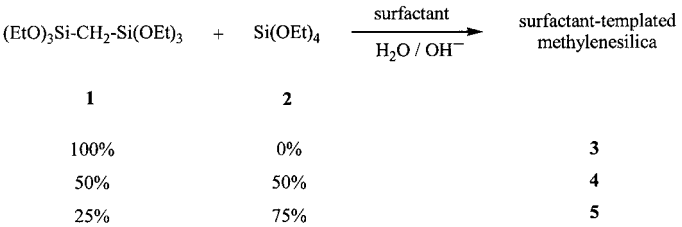
[**] This work was supported by the NSERC of Canada. M.J.M. is grateful to NSERC for postgraduate (1995–1999) and postdoctoral fellowships (1999–2001). G.A.O. thanks the Killam Foundation for the award of an Isaac Walton Killam research fellowship (1995–1997).

We and others have recently reported an interesting class of materials possessing organic groups fused "within" the mesoporous frameworks.[13–16] These novel organic–inorganic hybrid materials, denoted periodic mesoporous organosilicas (PMOs), are prepared through the surfactant-templated condensation of bifunctional organosiloxane precursors, $(R'O)_3SiRSi(OR')_3$.[19] This new approach extends the realm of mesoporous materials to "chemistry of the channel walls" rather than limiting it to "chemistry of the void space". In contrast to mesoporous materials that have terminally bonded organic groups dangling into the channels, PMOs offer a unique opportunity to affect the chemistry of the framework through organic transformations. The physical and chemical properties of these materials may be modified with suitable choice of organic and organometallic groups (R) inside the channel wall of the PMO. Examples of PMOs containing ethane, ethene, acetylene, ferrocene, thiophene, and benzene inside the framework have been reported.[13–16] Here we report the discovery of thermally robust periodic mesoporous methylenesilica and demonstrate a unique thermal transformation in which bridging methylene groups "inside the channel walls" convert into terminally bound methyl groups residing "within the channel spaces".

Methylene-bridged PMOs are also an interesting class of materials from the point of view of fundamental theory and applications. As the simplest organic group, methylene is a useful moiety to study for sophisticated ab initio calculations.[20, 21] Methylene is also useful for the preparation of silicon carbides and oxycarbides.[22, 23] Since methylene is isoelectronic with oxygen, periodic mesoporous methylenesilica is a useful analogue for structural, mechanical, and electronic comparison with the widely studied periodic mesoporous silica. Moreover, periodic mesoporous methylenesilica may be useful as a precursor for additional chemical modifications.

To prepare hexagonal mesoporous methylenesilica, we used a procedure similar to that of other PMOs.[13, 14] With a surfactant as the template, samples were synthesized with different proportions of methylene groups (Scheme 1). For this, a mixture of two precursors was used: bis(triethoxysilyl)methane (**1**), containing the bridging methylene groups, and tetraethoxysilane (**2**). The cationic cetyltrimethylammonium surfactant template was then removed from the samples by solvent extraction with methanol/hydrochloric acid.

The mesoporous methylenesilica materials were investigated by powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM) before and after solvent extrac-



1	**2**	
100%	0%	**3**
50%	50%	**4**
25%	75%	**5**

Scheme 1. Synthesis of the hexagonal mesoporous methylenesilica. The ratio of **1** and **2** corresponds to the molar contribution of Si from each reagent (i.e., **5** was prepared from BTM **1** and TEOS **2** in a molar ratio of 1:6; see the Experimental Section).

  0044-8249/00/11210-1878 $ 17.50+.50/0 *Angew. Chem.* **2000**, *112*, Nr. 10