quenched with the addition of 5 mL of 5% aqueous $Na_2S_2O_3$. The resulting mixture was then extracted with diethyl ether (50 mL). The organic layer was washed with 5% aqueous $Na_2S_2O_3$ (20 mL) and brine (50 mL) and dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue thus obtained was purified by flash column chromatography on silica gel with hexanes as the eluent. Recrystallization from petroleum ether afforded an analytical sample.

1,4-Dimethylphenanthrene (2). 1,4-Dimethylphenanthrene (2) was prepared as a white solid from either **34** or **37**. Yields: 173 mg (84%) from **34** and 161 mg (78%) from **37**. Recrystallization from petroleum ether gave colorless needles: mp 50–51 °C (lit.[5b] mp 49.5–50.5 °C); R_f 0.70 (hexanes); ^{1}H NMR (300 MHz) δ 2.74 (s, 3 H, 1-CH_3), 3.12 (s, 3 H, 4-CH_3), 7.35 and 7.39 (AB q, 2 H, J_{AB} = 7.3 Hz, 9- and 10-Hs), 7.58-7.62 (m, 2 H, 6- and 7-Hs), 7.76 (d, 1 H, J = 9.1 Hz, 2-H), 7.92 (dd, 1 H, J = 2.7, 9.4 Hz, 8-H), 7.96 (d, 1 H, J = 9.1 Hz, 3-H), 8.89 (dd, 1 H, J = 2.3, 9.4 Hz, 5-H); ^{13}C NMR (75.3 MHz) δ 20.25 (q), 27.30 (q), 123.38 (d), 125.24 (d), 125.62 (d), 126.79 (d), 127.27 (d), 127.67 (d), 128.43 (d), 130.32 (s), 130.62 (d), 131.89 (s), 132.17 (s), 132.69 (s), 133.10 (s), 133.27 (s); IR (KBr) 1452, 1431, 819 (s), 747 (s), 711 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{14}$: C, 93.15; H, 6.85. Found: C, 93.02; H, 6.80.

2,4-Dimethylphenanthrene (3). Purification by column chromatography gave **3** (167 mg, 81%) as a white solid. Recrystallization from petroleum ether gave white flakes: mp 108–109.5 °C (lit.[5d] mp 111 °C); R_f 0.76 (hexanes); ^{1}H NMR (300 MHz) δ 2.52 (s, 3 H, 2-CH_3), 3.12 (s, 3 H, 4-CH_3), 7.34 (s, 1 H, 3-H), 7.53–7.70 (m, 5 H, 1-, 6-, 7-, 9-, and 10-Hs), 7.89 (dd, 1 H, J = 1.8, 7.7 Hz, 8-H), 8.87 (dd, 1 H, J = 1.5, 8.0 Hz, 5-H); ^{13}C NMR (75.3 MHz) δ 20.99 (q), 27.16 (q), 125.30 (d), 125.48 (d), 127.07 (d), 127.11 (d), 127.16 (d), 127.31 (s), 127.74 (d), 128.65 (d), 131.75 (s), 132.97 (d), 133.21 (s), 134.00 (s), 135.30 (s), 135.38 (s); IR (KBr) 1452, 1432, 865, 856, 813 (s), 748 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{14}$: C, 93.15; H, 6.85. Found: C, 93.07; H, 6.72.

3,4-Dimethylphenanthrene (4). Purification by column chromatography provided **4** (182 mg, 88%) as a glassy resin, which gradually solidified upon standing in the refrigerator. Recrystallization from petroleum ether gave white flakes: mp 38–39 °C (lit.[7b] mp 53–54 °C); R_f 0.75 (hexanes); ^{1}H NMR (300 MHz) δ 2.56 (s, 3 H, 3-CH_3), 2.95 (s, 3 H, 4-CH_3), 7.45 (d, 1 H, J = 7.0 Hz, 2-H), 7.52–7.59 (m, 2 H, 6- and 7-Hs), 7.62 (s, 2 H, 9- and 10-Hs), 7.64 (d, 1 H, J = 7.0 Hz, 1-H), 7.87 (dd, 1 H, J = 1.8, 9.1 Hz, 8-H), 8.71 (dd, 1 H, J = 1.6, 9.4 Hz, 5-H); ^{13}C NMR (75.3 MHz) δ 21.58 (q), 21.65 (q), 124.73 (d), 125.65 (d), 126.06 (d), 126.14 (d), 127.53 (d), 128.24 (d), 128.32 (d), 128.66 (s), 128.76 (d), 131.15 (s), 132.04 (s), 133.26 (s), 133.90 (s), 136.41 (s); IR (KBr) 1449, 1441, 839 (s), 797, 745 (s), 716 cm^{-1}. Anal. Calcd for $C_{16}H_{14}$: C, 93.15; H, 6.85. Found: C, 93.20; H, 6.79.

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Synthesis of New Chiral Auxiliaries Derived from L-Threitol

Jean-Louis Gras,* Hélène Pellissier, and Robert Nouguier

Lasco, U.A. CNRS No. 109, Université d'Aix-Marseille 3, Faculté des Sciences St.-Jérome, 13397-Marseille Cedex 13, France

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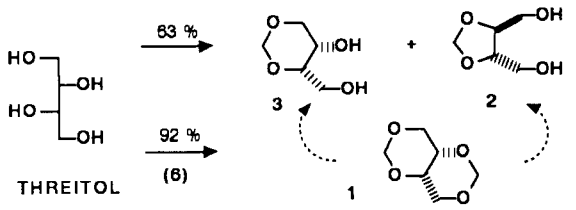
Several new chiral auxiliaries are derived from L-threitol by cleavage reactions of the methylene acetal of threitol diformal **1**. Total acetolysis (Ac_2O/H_2SO_4) leads to an acyclic tetraacetate that is converted to 1,4-diol **2** by treatment with $ZnBr_2$. A limited acetolysis procedure ($AcOH/(CF_3CO)_2O$) leads either to 1,3-diol **3** or, upon chemical manipulations, to each of its corresponding monoprotected monohydroxy derivatives.

Tartaric acid is a widely used source of reagents and chelating ligands to induce chirality in stereoselective chemical reactions.[1] We have studied the preparation of new chiral auxiliaries from L-threitol, a little examined commercially available reduced form of tartaric acid[2] that would bear a stable methylene acetal ring and the chemically active hydroxy group. A search of the literature revealed that little attention has been paid to these substrates,[3] most of the studies on butanetetrol being related to the stereoisomeric erythritol.[4] Due to its optical activity, threitol would have greater utility in synthesis, provided that protection of the hydroxy groups could be introduced both selectively and practically.

Scheme I



Direct methylenation of threitol using aqueous formaldehyde and hydrochloric acid led to a mixture of various products and optimization of this reaction seems of little hope. A much simpler result was achieved when (±)-threitol was submitted to acid-catalyzed transacetalization with dimethoxymethane.[5]

According to experimental conditions either a mixture of two diols in a moderate yield or the pure 1,3:2,4-di-*O*-methylene-L-threitol (**1**) in preparative yield can be obtained[6] (Scheme I).

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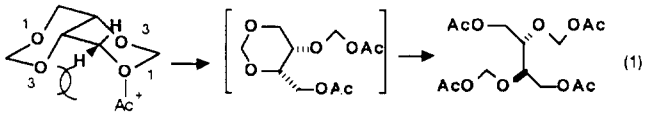
0022-3263/89/1954-5675$01.50/0

We now report on the chemical derivatizations of chiral (*S,S*)-threitol diformal **1** that efficiently lead to various selectively protected auxiliaries bearing one or two hydroxy functions.

The kinetically controlled cleavage of one of the two dioxane rings under various acidic conditions failed to afford pure diol **3**, diformal **1** being transformed more or less quickly to threitol.

When diformal **1** was submitted to formolysis (a simple and mild method to regenerate sensitive aldehydes from their acetals[7]) by refluxing it with a large excess of formic acid during 2 to 24 h, a mixture of unisolated monocyclic diformates and monoformates along with 10 to 20% of residual **1** was obtained.[8] Upon saponification, the mixture led to a 72% yield of diols **3** and **2** in a ratio ranging from 1:3 to 1:2 depending on reaction time of the first step. The reaction proceeds through the successful acid-catalyzed opening of one of the two formal rings and, during the chemical transformations of the intermediates, **3** isomerizes into **2** by acetal migration, a well-established phenomenon under acidic conditions.[9]

Formolysis having failed to produce diols **2** or **3** selectively, we looked for alternative methods of ring cleavage. Under appropriate conditions, acetals may be converted to mixtures of esters and mixed acetal esters. Methylene bridges between primary and secondary alcohols of sugars are especially prone to acetolysis.[10] The standard conditions ($Ac_2O/AcOH/H_2SO_4$) were modified to induce limited acetolysis. When **1** was treated with a 3-fold excess of acetic anhydride at 0 °C in the presence of a catalytic amount of sulfuric acid, the reaction reached completion after 30 min with both rings having been cleaved. The resulting product, (*S,S*)-1,4-di-*O*-acetyl-2,3-bis-*O*-(acetoxymethyl)threitol (**4**) (86% yield after recrystallization), indicates that only one of the oxygen linkages of each methylene acetal grouping is ruptured and that the resulting potential hydroxymethyl groups undergo acetylation. The high regioselectivity observed is a consequence of the most favored conformation of the unsubstituted *cis*-tetraoxadecalin **1**, with the oxygens "inside". In this conformation, acylium ion attack on the ring at the 3-oxygen atom axial with respect to the acetal ring is difficult, due to steric hinderance by an equatorial β-hydrogen atom. This hinderance is similar to the well-known 1,3-diaxial interaction in cyclohexane conformational analysis (eq 1).



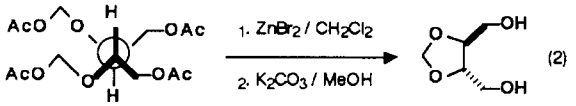
(1)

Under the experimental conditions used, the second ring is attacked at nearly the same rate and once more regioselectively cleaved, the rupture also being confined by the stereochemical environment to the primary hydroxy linkage. Attempts to isolate the intermediate product or any derivative thereof at lower temperature gave mixed results. In all experiments tetraacetate **4** starts to form long before diformal **1** is totally consumed.

Fortunately, the relatively uninteresting compound **4** can be conveniently transformed to a single chiral material.

Isolation of 1,4-di-*O*-acetylthreitol was not possible through selective deacetylation of the acetoxymethyl groups, but we succeeded in combining together those two groups on the basis of previous results. Thus, upon treatment with zinc bromide in refluxing methylene chloride, the intramolecular mechanism observed during formolysis became major and tetraacetate **4** underwent a remarkable ring closure to afford, after saponification, pure (*S,S*)-2,3-bis(hydroxymethyl)dioxolane (**2**) in nearly quantitative yield.

The conformation of **4** that most minimizes interactions between all the acetyl functions brings the two acetoxymethyl groups into proximity, favoring the cyclization process toward the dioxolane ring (eq 2).



(2)

With a preparative sequence for the formation of diol **2** in hand, we focused our attention on a modified acetolysis procedure that would enable diol **3** to be obtained cleanly. Trifluoroacetic anhydride in equimolecular amount with acetic acid provided the mixed anhydride (the acyl trifluoroacetate), which in the presence of trifluoroacetic acid, the other product of the interaction is a source of acylium ions. This reagent is selective in effecting ring fission of substituted cyclic acetals,[11] with a high degree of specificity.

When (*S,S*)-threitol diformal **1** was treated with a 2-fold excess of an equimolecular mixture of acetic acid and trifluoroacetic anhydride for 2 h at 21 °C, only one of the two rings of the diacetal cleaved in the expected manner to give *S,S* acetyl (trifluoroacetoxy)methyl compound **6**, with the other dioxane ring intact. Prolonged exposure of the derivative to the AcOH/TFAA solution resulted in some scission of the second ring. After careful neutralization of the acids by the addition of dry potassium carbonate followed by filtration and evaporation of the solvent, the residue was saponified by potassium carbonate in methanol. Direct chromatography of the filtered reaction mixture afforded a 92% yield of diol (*S,S*)-**3** that was contaminated with diol **2** if the neutralization of the acids was not moderated by an ice bath or was incomplete.

Beside the fact that only one of the two rings of the diacetal is cleaved and, further, entirely in the one direction, treatment with trifluoroacetic anhydride offers an important advantage in that the unstable trifluoroacetoxy group in the product can be selectively removed without detriment to the acetyl group.

Hence, the reaction mixture from acetolysis containing **6** was partially neutralized by the addition of dry sodium bicarbonate at 0 °C and hydrolyzed with aqueous $NaHCO_3$ to give **7** in 99% yield, an L-threitol derivative O-acetylated in the primary position and with a free hydroxy group in the secondary position. During all these operations the second dioxane ring was not affected, the diacetate of diol **3**, the isomeric monoacetate **8**, and diol **2** being the only side products we isolated. The diacetate may arise from further attack by the unsymmetric anhydride ($Ac^{+-}OCOCF_3$) during acetolysis, but a slight excess of TFAA impedes this process. The possibility that a significant

(6) Key starting material **1** is obtained in 92% yield from L-(−)-threitol after optimization of the procedure described in ref 5.

(7) Gorgues, A. *C.R. Acad. Sci. Paris* **1967**, *265*, 1130.

(8) 100% conversion of diformal **1** results in more double ring-opening and in a lower yield of diols.

(9) Hibbert, T. H.; Carter, N. M. *J. Am. Chem. Soc.* **1928**, *50*, 3120.

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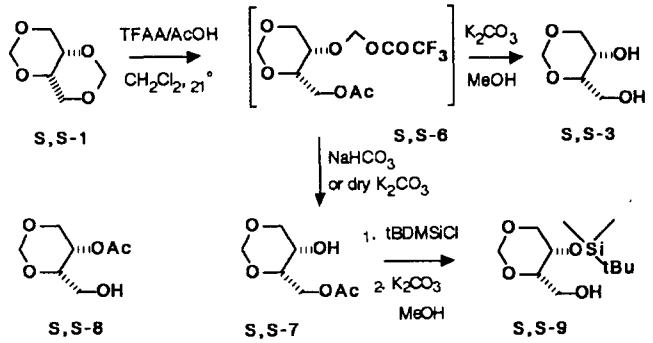
Scheme II



amount of ring scission occurred with involvement of the 3-oxygen atoms (with respect to the dioxane ring) to give the 2-*O*-acetyl-4-*O*-[(trifluoroacetoxy)methyl]threitol derivative leading to **8** is remote. Rather, the acyl group that is prone to migrate under both acidic or basic conditions may switch from the 4 to the 2 position during treatments of the reaction mixture. Effecting the neutralization and hydrolysis processes by $NaHCO_3$ at 0 °C was sufficient to avoid the acyl migration and limit the hydrolysis to the (trifluoroacetoxy)methyl residue.

Attempts to achieve total acyl migration failed, but the 4-hydroxy can be liberated while the 2-hydroxy is protected by subsequent chemical manipulation. Monoalcohol **7** was thus condensed with *tert*-butyldimethylsilyl chloride and the resulting acetyl silyl ether was saponified by K_2CO_3/MeOH to afford in 77% yield the threitol derivative (*S,S*)-**9** bearing a primary hydroxy function.

This sequential treatment of **1** thus allows the preferential protection of one hydroxy group at a time within diol **3**, whether primary or secondary (Scheme II).

Finally, the work described herein illustrates an approach to the systematic synthesis of new protected or functionalized threitol derivatives, by employing two modified cleavage reactions of the methylene acetal bond in threitol diformal **1**. This versatile intermediate allows the concomittant regioselective modification of 1,3-, 2,3-, 1,2,3- or 1,3,4-hydroxy groups in threitol and, although we report only on the L series, the chirality can obviously be reversed. Applications of these chiral auxiliaries in asymmetric synthesis are currently underway.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 298 infrared spectrophotometer. The ^1H NMR spectra were recorded on an EM 360 Varian instrument, and the ^{13}C NMR spectra on a XL 200 Varian instrument, in $CDCl_3$ with TMS as internal reference. Rotations were measured on a Perkin-Elmer 141 polarimeter with a Hg lamp.

(2*S*,3*S*)-1,4-Di-*O*-acetyl-2,3-bis-*O*-(acetoxymethyl)threitol (4). Sulfuric acid (100 μL) was added to an ice-cooled solution of threitol diformal **1** (10 mmol, 1.46 g) in freshly distilled acetic anhydride (30 mmol, 2.83 mL) under argon. After 30 min of stirring at 0 °C, the solution was neutralized by the addition of solid NaOAc and then stirred at room temperature for 30 min. Filtration with the aid of CH_2Cl_2 and concentration afforded 3.50 g (100%) of crystalline material, which was used as such in the next step. Recrystallization from CH_2Cl_2/Et_2O afforded 0.90 g of pure tetraacetate **4** (86%): mp 54 °C; $[\alpha]^{21}_{546}$ +13.85° (*c* 0.1, $CHCl_3$). IR (neat): 1725 cm^{-1}. ^1H NMR: δ 5.32 (s, 4 H), 4.15 (m, 6 H), 2.12 (s, 12 H). ^{13}C NMR: δ 170.4 and 170.3 (C=O), 88.65, 77.1 (CH), 63.2, 20.9 and 20.7 (CH_3). Anal. Calcd for $C_{14}H_{22}O_{10}$: C, 48.00; H, 6.33. Found: C, 48.02; H, 6.27.

(2*S*,3*S*)-2,3-*O*-Methylenethreitol (2). A solution of crude tetraacetate **4** (10 mmol, 3.50 g) in dry CH_2Cl_2 (30 mL) was refluxed for 5 h in the presence of $ZnBr_2$ (30 mmol, 6.75 g). After cooling to room temperature, the mixture was hydrolyzed with a saturated $NaHCO_3$ solution, stirred for 15 min, and extracted with CH_2Cl_2, to afford 2.18 g of diacetate. Chromatographic purification over silica gel (elution with CH_2Cl_2/Et_2O mixtures) gave 2.11 g (97%). IR (neat): 1740 cm^{-1}. ^1H NMR: δ 5.05 (s, 2 H), 4.10 (m, 6 H), 2.10 (s, 6 H). ^{13}C NMR: δ 170.5 (C=O), 95.4, 75.7 (CH), 63.5, 20.7 (Me).

The crude diacetate (10 mmol, 2.18 g) was saponified at room temperature by K_2CO_3 (0.70 g) in methanol (20 mL) for 30 min. After filtration and distillation of the solvent, the crude material was chromatographed over silica gel (elution with 5 to 10% MeOH/CH_2Cl_2 mixtures) to afford 1.29 g of pure diol **2** (96%); $[\alpha]^{20}_{546}$ −30.0° (*c* 0.1, MeOH). IR (neat): 3380, 1110, 1090, 1030 cm^{-1}. ^1H NMR: δ 4.30 (s, 2 H), 3.10 (m, 6 H), 2.6 (s, OH). ^{13}C NMR: δ 95.9, 79.6 (CH), 62.7. Anal. as the diacetate. Calcd for $C_9H_{14}O_6$: C, 53.39; H, 5.93. Found: C, 53.27; H, 5.90.

(2*S*,3*S*)-1,3-*O*-Methylenethreitol (3). Glacial acetic acid (20 mmol, 1.14 mL) was added to an ice-cooled solution of threitol diformal **1** (10 mmol, 1.46 g) and trifluoroacetic anhydride (20 mmol, 2.824 g). The solution was stirred for 2 h at room temperature under argon and then cooled with an ice bath before careful addition of K_2CO_3 (50 mmol, 6.90 g). The resulting mixture was stirred at room temperature for 1.5 h, filtered, and concentrated. The residue was treated with K_2CO_3 (20 mmol, 2.76 g) in methanol (10 mL), until no more acetate was present on TLC. Direct chromatography over silica gel (elution with 10 to 20% MeOH/CH_2Cl_2 mixtures) afforded 1.30 g of diol **3** (97%), slightly contaminated by traces of diformal **1** and diol **2**. Diol **3** had the following properties: $[\alpha]^{20}_{546}$ +22.9° (*c* 0.033, $CHCl_3$). IR ($CDCl_3$): 3580, 3450, 1095, 1064, 1025, 900 cm^{-1}. ^1H NMR: δ 4.90 (d, 1 H, *J* = 6 Hz), 4.60 (d, 1 H, *J* = 6 Hz), 3.65 (m, 8 H), 4.0 (s, OH). ^{13}C NMR: 93.8, 79.0 (CHC), 72.1, 65.1 (CHO), 62.4 (CH_2OH). Anal. as the diacetate. Calcd for $C_9H_{14}O_6$: C, 49.54; H, 6.42. Found: C, 49.55; H, 6.39.

(2*S*,3*S*)-4-*O*-Acetyl-1,3-*O*-methylenethreitol (7). Diformal **1** (20 mmol, 2.92 g) was subjected to acetolysis as previously described, but after cooling, the mixture was carefully neutralized either by the addition of K_2CO_3 (50 mmol, 6.90 g), stirring at room temperature for 14 h and filtration, or by the addition of solid $NaHCO_3$ (60 mmol, 5.04 g) and stirring for 1 h at 0 °C, followed by the addition of a saturated solution of $NaHCO_3$ (30 mL) and stirring for 2 h at 0 °C. After extraction with CH_2Cl_2, drying, and concentration, the residue was chromatographed over silica gel (elution with 4 to 10% MeOH/CH_2Cl_2 mixtures) to afford 3.50 g of alcohol **7** (99%): $[\alpha]^{20}_{546}$ +2.29° (*c* 0.088, $CHCl_3$). IR (neat): 3470, 1740, 1080, 1040 cm^{-1}. ^1H NMR: δ 5.09 (d, 1 H, *J* = 7 Hz), 4.68 (d, 1 H, *J* = 7 Hz), 3.7 to 4.35 (m, 6 H), 3.44 (s, 1 H), 1.96 (s, 3 H). ^{13}C NMR: δ 93.9, 77.0 (CH), 72.0, 64.6 (CH), 64.0, 20.8 (Me). Anal. Calcd for $C_7H_{12}O_5$: C, 47.72; H, 6.81. Found: C, 47.68; H, 6.78.

(2*S*,3*S*)-2-*O*-(*tert*-Butyldimethylsilyl)-1,3-*O*-methylenethreitol (9). Crude alcohol **7** (4.50 mmol) was treated with TBDMSCl (6.75 mL) and imidazole (13.5 mmol) in DMF (2.7 mL) for 18 h at 21 °C. After simple hydrolysis, extraction with CH_2Cl_2, and standard treatment, the crude silyl ether was saponified with K_2CO_3 (0.7 g) in MeOH (9 mL) for 2 h at 21 °C. After filtration, the solution was chromatographed over silica gel (elution with 4 to 10% MeOH/CH_2Cl_2 mixtures) to afford 0.88 g of primary alcohol **9** (79% from **1**): $[\alpha]^{22}_{546}$ +20.6° (*c* 0.07, $CHCl_3$). IR (neat): 3420, 1258, 1125, 1088, 1040, 840 cm^{-1}. ^1H NMR: δ 5.18 (d, 1 H, *J* = 8 Hz), 4.80 (d, 1 H, *J* = 8 Hz), 3.6 to 4.05 (m, 6 H), 2.2 (s, 1 H), 0.95 (s, 9 H), 0.12 (s, 6 H). ^{13}C NMR: δ 93.0, 79.1 (CH), 71.6, 65.8 (CH), 62.8, 25.7 (Me), 18.1 (C), −4.5 and −4.9 (Me). Anal. Calcd for $C_{11}H_{24}O_4Si$: C, 53.44; H, 9.71. Found: C, 53.41; H, 9.63.

Registry No. (*S,S*)-**1**, 122674-82-2; (*S,S*)-**2**, 122674-83-3; (*S,S*)-**2** (diacetate), 122623-41-0; (*S,S*)-**3**, 122674-84-4; (*S,S*)-**4**, 122623-40-9; (*S,S*)-**7**, 122623-42-1; (*S,S*)-**9**, 122623-44-3; (*S,S*)-**9** (acetate), 122623-43-2.