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An efficient approach to either enantiomer of *trans*-cyclohex-2-ene-1,4-diol

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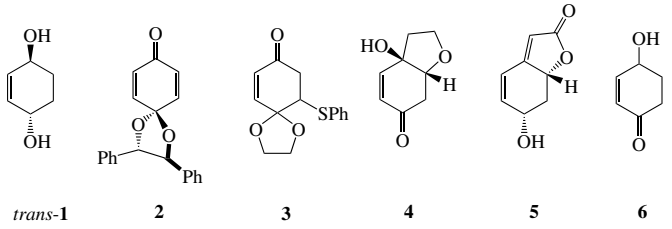
Abstract—(1*S*,4*S*)-Cyclohex-2-ene-1,4-diol has been synthesised starting from a chiral *p*-benzoquinone equivalent. The sequence can be equally applied to the preparation of the (1*R*,4*R*)-enantiomer of the target diol.

1. Introduction

There are a large number of natural compounds possessing a polysubstituted cyclohexane unit as a fundamental structural part. Among them, polyoxygenated derivatives such as conduritols,[1] conduramines,[2] inositols,[3] gabosines[4] and several epoxides[5] are particularly attractive targets because of their diverse biological activities and the synthetic challenge of binding oxygen atoms to a carbocycle in a regio- and stereocontrolled fashion. In 1984 Bäckvall et al. reported the stereoselective synthesis of both diastereomers of cyclohex-2-ene-1,4-diol, *cis*- and (±)-*trans*-**1** (Fig. 1), through a palladium-catalysed 1,4-diacetoxylation of 1,3-cyclohexadiene.[6] Nowadays, the racemate of *trans*-**1** is commercially available, but only one procedure has been reported to obtain nonracemic *trans*-**1**, by a chloroperoxidase-catalysed oxidation of cyclohexa-1,3-diene using *tert*-butylhydroperoxide as the terminal oxidant.[7] This procedure furnished (+)-*trans*-**1** in 34% yield and 70% ee. Comparison with the major oxidation product along with mechanistic considerations led the authors to assign the (1*R*,4*R*) configuration to the dextrorotatory enantiomer of *trans*-**1**. On the other hand, a lipase-based protocol developed for desymmetrisation of the diacetate of *cis*-**1** gave access to an alternative chiral equivalent of *trans*-**1**, which has been used as an intermediate for the synthesis of petasins[8] and cyclohexane prostanoids.[9]

In previous work, we had prepared a series of chiral derivatives of *p*-benzoquinone, such as **2**[10,11] and **3**,[11,12] and explored their utility as synthetic precursors of more complex target cyclohexanes.[13–15] As a result of these studies, we developed the first syntheses of (+)-rengyolone, **4**, and (+)- and (−)-menisdaurilide, **5**,[16] along with new synthetic approaches to (*R*)- and (*S*)-4-hydroxy-2-cyclohexenone, **6**.[17] In connection with our previous work, we herein report the synthesis of *trans*-**1**, starting from **3**, a masked *p*-benzoquinone in which one of each



trans-**1** **2** **3** **4** **5** **6**

Figure 1.

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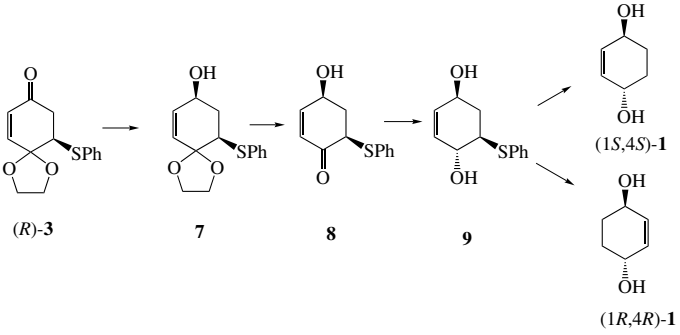


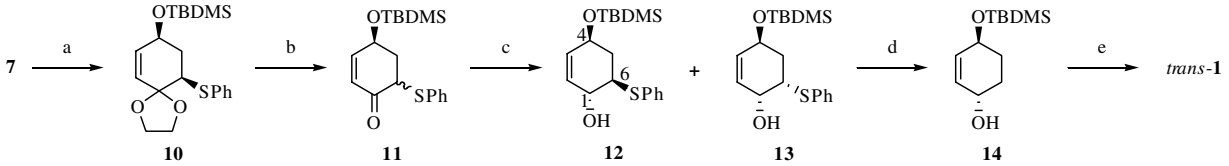
Scheme 1.

pair of equivalent functional groups has been differentiated.

2. Results and discussion

The racemate of compound **3** is easily available on multi-gram scale with its resolution being effectively performed by liquid chromatography on cellulose triacetate.[11,12] The reduction of **3** with $NaBH_4$ exclusively gives the *cis*-alcohol **7**, which when hydrolysed furnishes the hydroxyketone **8** in excellent overall yield[16] (Scheme 1). We initially envisaged the conversion of **8** into *trans*-**1** by consecutive reduction of the ketone and thioether functions. According to this plan, the overall transformation starting from (*R*)-**3** would provide the (1*S*,4*S*)-enantiomer of **1**. Alternatively, the double bond of diol **9** could be hydrogenated and a new double bond generated by oxidation–pyrolysis of the sulfur moiety, affording the opposite antipode (1*R*,4*R*)-**1**. To test the effectiveness of the approach, we first undertook the synthesis starting from racemic **8**.

In practice, all attempts to perform the reduction of ketone **8** with a variety of hydrides and conditions gave poor stereoselectivity. Moreover, decomposition of the formed diols was frequently observed before complete conversion of the substrate. Protection of the hydroxyl group of **8** prior to the reduction of the ketone proved equally ineffective, leading consistently to complex mixtures of unidentified products. This problem could be overcome by protecting the alcohol in **7** before the ketal hydrolysis. Treatment of **7** with different silyl chlorides in basic media caused decomposition, but the reaction with *tert*-butyldimethylsilylimidazole (TBDMS-Im) in dichloromethane at room temperature for several days gave the expected silyl ether **10** (Scheme 2) in 83% yield. Various standard procedures for the hydrolysis of the dioxolane were also unsuccessful with ketone **11** finally being obtained in 75% yield by treatment of **10** with montmorillonite K-10 in dichloromethane.[16,18] Due to the configurational instability of the α-carbonyl stereogenic centre, the initially formed isomer *cis*-**11** slowly became contaminated with its *trans* diastereomer. In the ^1H NMR spectrum of *cis*-**11**, the proton at the epimerisable centre displayed a signal at δ 3.79 with coupling constants of 13.2 and 4.4 Hz in agreement with a pseudoaxial orientation, while for *trans*-**11** the corresponding signal at δ 3.97 showed two similar vicinal coupling constants of around 4.5 Hz and a long distance coupling of 1.0 Hz, in agreement with its pseudoequatorial location. The use of a mixture of epimers in the next step was not detrimental for the synthesis. The reduction of **11** with DIBAL-H in THF at −78 °C furnished a mixture of diols **12** and **13**, in which the former isomer was strongly predominant. NOE experiments demonstrated that **12** and **13** were epimers at C-6, but both presented the desired *trans* relationship between the hydroxy and silyloxy groups. Thus, presaturation of the signal of H-4 (δ 4.38 for **12** and δ 4.34 for **13**) caused enhancement of the signal of H-6 for compound **12** (δ 2.97) but not for **13** (δ 3.79), while irradiation of the H-1 signal (δ 4.10 for **12** and δ 4.13 for **13**) produced enhancement of the signal corresponding to H-6 only for isomer **13**. Occasionally, trace amounts of the all-*cis* isomer of **12** and **13** were also detected. Desulfuration of **12** and **13** was accomplished by treatment with $SnBu_3H$ in refluxing toluene in the presence of 2,2′-azobisisobutyronitrile (AIBN). We were unable to let this reaction go to completion, but the conditions could be adjusted to obtain the desulfuration product **14** in a fair yield (67%, 86% over converted substrate) along



Scheme 2. Reagents and conditions: (a) TBDMS-Im, CH_2Cl_2, rt, 5 days, 83%; (b) montmorillonite K-10, CH_2Cl_2, rt, 18 h, 75%; (c) DIBAL-H, THF, −78 °C, 2.5 h, 72%; (d) $SnBu_3H$, AIBN, toluene, Δ, 5 h, 86%; (e) Bu_4NF, THF, rt, 20 h, 78%.

with the unreacted starting material, which could be easily recovered. The overall sequence from **3** to **14** was 38%. Compound **14** is a monoprotected derivative of the target diol *trans*-**1** and would formally result from differentiation of the two initially equivalent alcohols, making it especially attractive for synthetic purposes. Finally, treatment of **14** with tetrabutylammonium fluoride in THF produced *trans*-**1** in 78% yield.

When the complete sequence was repeated starting from (8*S*,10*R*)-**7**, readily available by $NaBH_4$ reduction of (*R*)-**3**,[17] the diol (1*S*,4*S*)-**1**, $[\alpha]_D^{20} = -112$ (*c* 0.25, $CHCl_3$), was obtained. Analysis by CHPLC showed an ee of 95%.

3. Conclusion

In summary, starting with the *p*-benzoquinone equivalent **3**, a procedure has been set up for the synthesis of *trans*-cyclohex-2-ene-1,4-diol, *trans*-**1**, suitable for the preparation of either enantiomer of the diol. Application of the sequence to (*R*)-**3** furnished the levorotatory antipode (1*S*,4*S*)-**1**, confirming the (1*R*,4*R*)-configuration tentatively assigned to the main enantiomer of *trans*-**1** obtained by a chloroperoxidase-catalysed oxidation of cyclohexa-1,3-diene.[7] Taking into account that any antipode of **3** can be re-equilibrated to the racemate by a base catalysed process involving elimination/conjugate addition of thiophenol, racemic **3** can be converted into either enantiomer of *trans*-**1**.

4. Experimental

4.1. General

Reaction mixtures were stirred magnetically. The organic extracts were dried over anhydrous magnesium sulfate. Reaction solutions were concentrated using a rotary evaporator at 5–10 Torr. Flash chromatography was performed using Merck silica gel (230–400 mesh). Infrared spectra were recorded on an IR-FT Perkin Elmer 2000 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Brucker AC-250-WB or AM-400-WB instruments at 250 or 400 MHz and 62.5 or 100 MHz, respectively, in $CDCl_3$ solutions. Tetramethylsilane or $CHCl_3$ were used as internal standards for ^1H and ^{13}C NMR spectra. Mass spectra were performed on a Hewlett–Packard 5989A at 70 eV or on a Brucker Esi-it instruments; only peaks with higher intensity than 20% are reported, unless they belong to molecular ions or to significant fragments. Enantiomeric excesses (ee's) were determined by CHPLC analyses using a Daicel Chiracel OD column (4.6×250 mm).

4.2. (8*S*,10*R*)-10-Phenylthio-1,4-dioxaspiro[4.5]dec-6-en-8-ol, (8*S*,10*R*)-7

Compound (8*S*,10*R*)-**7**, $[\alpha]_D^{20} = -15$ (*c* 0.95, $CHCl_3$), ee 100% (CHPLC, hexane/2-propanol, 95:5), was prepared from (*R*)-**3** in 85% yield following the procedure previously described for the racemate.[17]

4.3. *cis*-8-(*tert*-Butyldimethylsilyloxy)-10-phenylthio-1,4-dioxaspiro[4.5]dec-6-ene, 10

To a stirred solution of **7** (2.00 g, 7.56 mmol) in CH_2Cl_2 (60 mL) at 0 °C under nitrogen, TBDMS-Im (2.35 mL, 12.10 mmol) was slowly added (5 min), the cooling bath removed and the mixture stirred at room temperature for 5 days. Water (5 mL) was then added and the mixture slightly acidified with 4% HCl. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3×30 mL). The combined organic extracts were washed, dried and concentrated under vacuum. Purification of the oily residue (2.82 g) by flash chromatography (diethyl ether/hexane, 1:5) furnished compound **10** (2.38 g, 6.29 mmol, 83%) as a white solid: mp 35–37 °C; IR (KBr) 3069, 2955, 2884, 1584, 1472, 1386, 1248, 1154, 1086 cm^{-1}; ^1H NMR (250 MHz) δ 7.46 (m, 2H), 7.22 (m, 3H), 5.76 (dt, $J = 10.2$, 1.9 Hz, 1H), 5.57 (dd, $J = 10.2$, 2.0 Hz, 1H), 4.25 (m, 1H), 4.10 (m, 4H), 3.40 (dd, $J = 14.0$, 3.2 Hz, 1H), 2.28 (dddd, $J = 12.5$, 5.7, 3.2, 1.8 Hz, 1H), 2.05 (ddd, $J = 14.0$, 12.5, 9.8 Hz, 1H), 0.83 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (62.5 MHz) δ 136.1, 135.6, 130.9, 128.8, 127.7, 126.5, 106.1, 68.0, 66.4, 66.1, 52.7, 39.7, 25.7, 18.0, −4.5, −4.7; MS *m*/*z* 378 (M^+, 0.1), 269 (7), 242 (100), 75 (63), 73 (52). Anal. Calcd for $C_{20}H_{30}O_3SSi$: C, 63.45; H, 7.99; S, 8.47. Found: C, 63.42; H, 7.99; S, 8.14.

The same procedure starting from (8*S*,10*R*)-**7** gave (8*S*,10*R*)-**10**, $[\alpha]_D^{20} = -56$ (*c* 0.85, $CHCl_3$), ee 100% (CHPLC, hexane/2-propanol, 90:10).

4.4. 4-(*tert*-Butyldimethylsilyloxy)-6-phenylthiocyclohex-2-enone, 11

A mixture of **10** (914 mg, 2.41 mmol) and montmorillonite K-10 (3.2 g) in CH_2Cl_2 (28 mL) was stirred at room temperature for 18 h. The mixture was filtered and the solvent removed under vacuum. Flash chromatography of the crude material (759 mg) using diethyl ether/hexane (1:10) as eluent afforded *cis*-**11** (601 mg, 1.80 mmol, 75%) as oil: IR (neat) 3059, 2954, 2929, 2857, 1685, 1472, 1253, 1097 cm^{-1}; ^1H NMR (250 MHz) δ 7.42 (m, 2H), 7.27 (m, 3H), 6.76 (dt, $J = 10.2$, 1.9 Hz, 1H), 5.98 (dd, $J = 10.2$, 2.0 Hz, 1H), 4.52 (ddt, $J = 9.6$, 4.7, 2.0 Hz, 1H), 3.79 (dd, $J = 13.2$, 4.4 Hz, 1H), 2.42 (dddd, $J = 12.9$, 4.7, 4.4, 1.7 Hz, 1H), 2.06 (ddd, $J = 13.2$, 12.9, 9.6 Hz, 1H), 0.84 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (62.5 MHz) δ 194.5, 153.7, 132.9, 128.9, 127.7, 67.6, 52.3, 40.4, 25.7, 18.0, −4.6, −4.8; MS *m*/*z* 334 (M^+, 0.2), 225 (20), 224 (22), 168 (35), 167 (100), 75 (31), 73 (36). Anal. Calcd for $C_{18}H_{26}O_2SSi$: C, 64.62; H, 7.83; S, 9.58. Found: C, 64.66; H, 7.73; S, 9.13.

Compound *cis*-**11** epimerises slowly to its isomer *trans*-**11**: ^1H NMR (250 MHz) δ 7.42 (m, 2H), 7.29 (m, 3H), 6.76 (ddd, $J = 10.2$, 2.7, 1.2 Hz, 1H), 5.91 (ddd, $J = 10.2$, 1.8, 1.0 Hz, 1H), 4.73 (dddd, $J = 10.0$, 3.2, 2.7,

1.8 Hz, 1H), 3.97 (td, $J = 4.5$, 1.0 Hz, 1H), 2.35 (complex, 2H), 0.88 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (62.5 MHz) δ 193.8, 152.1, 133.4, 127.8, 126.9, 64.5, 50.7, 38.7, 25.7, 18.0, −4.6, −4.8.

The same procedure starting from (8*S*,10*R*)-**10** gave a mixture of (4*S*,6*R*)-**11** and (4*S*,6*S*)-**11**.

4.5. Reduction of 11: (1*RS*,4*SR*,6*RS*)-, 12, and (1*RS*,4*SR*,6*SR*)-4-(*tert*-butyldimethylsilyloxy)-6-phenylthiocyclohex-2-enol, 13

To a stirred solution of **11** (1.54 g, 4.6 mmol) in anhydrous THF (62 mL) at −78 °C under nitrogen, a solution of DIBAL-H in THF (1 M, 18.4 mL, 18.4 mmol) was added. After stirring the mixture at −78 °C for 2.5 h, MeOH (62 mL) was added and stirring was continued for 1 h, while warming to room temperature. The mixture was then filtered through Celite® and the solvent removed under vacuum. The oily residue (1.12 g, 3.34 mmol, 72%) was identified as a mixture of **12** and **13**, which was used in the next step without further purification. For characterisation purposes, an analytical sample of the major isomer **12** was isolated by repeated flash chromatography: IR (neat) 3401, 3033, 2954, 2856, 1472, 1253, 1087 cm^{-1}; ^{1}H NMR (250 MHz) δ 7.45 (m, 2H), 7.31 (m, 3H), 5.71 (dt, $J = 10.2$, 1.7 Hz, 1H), 5.62 (dq, $J = 10.2$, 1.8 Hz, 1H), 4.38 (m, 1H), 4.10 (m, 1H), 2.97 (ddd, $J = 13.6$, 9.1, 2.9 Hz, 1H), 2.68 (broad, 1H), 2.28 (dddd, $J = 12.7$, 5.5, 2.9, 1.8 Hz, 1H), 1.67 (ddd, $J = 13.6$, 12.7, 9.0 Hz, 1H), 0.85 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (62.5 MHz) δ 134.3, 133.4, 129.5, 128.1, 70.0, 68.2, 51.6, 39.4, 25.8, 18.1, −4.6, −4.7; MS m/z 279 ([M−^{t}Bu]$^+$, 16), 209 (65), 151 (45), 95 (20), 75 (100), 73 (41). Anal. Calcd for $C_{18}H_{28}O_2SSi$: C, 64.23; H, 8.39; S, 9.51. Found: C, 64.35; H, 8.57; S, 9.13.

Compound **13** (data extracted from an enriched sample): ^{1}H NMR (250 MHz) δ 7.43 (m, 2H), 7.25 (m, 3H), 5.79 (complex, 2H), 4.34 (m, 1H), 4.13 (m, 1H), 3.79 (dt, $J = 11.2$, 3.2 Hz, 1H), 2.47 (d, $J = 5.2$ Hz, 1H), 2.15 (ddd, $J = 13.4$, 11.2, 4.5 Hz, 1H), 1.88 (dt, $J = 13.4$, 3.5 Hz, 1H), 0.87 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (62.5 MHz) δ 133.9, 132.3, 129.7, 129.1, 127.1, 64.9, 64.3, 48.3, 33.9, 25.8, 18.1, −4.6, −4.7.

Occasionally, trace amounts of the (1*RS*,4*RS*,6*SR*)-isomer of **12** and **13** were also detected (data extracted from an enriched sample): ^{1}H NMR (400 MHz) δ 7.44 (m, 2H), 7.33 (m, 3H), 5.85 (ddd, $J = 10.0$, 4.7, 1.7 Hz, 1H), 5.78 (dt, $J = 10.0$, 0.9 Hz, 1H), 4.27 (m, 1H), 3.95 (m, 1H), 3.28 (dt, $J = 13.5$, 3.0 Hz, 1H), 2.62 (d, $J = 9.4$ Hz, 1H), 2.00 (m, 1H), 1.87 (ddd, $J = 13.5$, 12.0, 10.0 Hz, 1H), 0.87 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (62.5 MHz) δ 136.2, 132.1, 129.3, 127.5, 127.1, 68.4, 63.1, 49.1, 32.8, 25.8, 18.1, −4.5, −4.7.

The same procedure starting from a mixture of (4*S*,6*R*)-**11** and (4*S*,6*S*)-**11** gave a mixture of (1*R*,4*S*,6*R*)-**12** and (1*R*,4*S*,6*S*)-**13**.

4.6. *trans*-4-(*tert*-Butyldimethylsilyloxy)cyclohex-2-enol, 14

To a stirred solution of a mixture of **12** and **13** (200 mg, 0.59 mmol) and AIBN (1.0 mg, 0.006 mmol) in anhydrous toluene (6 mL) under nitrogen at the reflux temperature, $SnBu_3H$ (1.46 mL, 5.94 mmol) was added dropwise. A solution of AIBN (300 mg, 1.83 mmol) in anhydrous toluene (12 mL) was added to the reaction mixture in 0.25 mL portions every 5 min and, after the last addition, heating was prolonged 1 h further. The solvent was evaporated under vacuum and purification of the residue (200 mg) by flash chromatography (hexane/ethyl acetate, 12:1) yielded the starting materials **12** and **13** (45 mg, 0.13 mmol, 22% recovered) and **14** (91 mg, 0.40 mmol, 67%, 86% over unrecovered substrate): colourless oil; IR (neat) 3338, 3029, 2952, 2929, 2857, 1472, 1388, 1257, 1084 cm^{-1}; ^{1}H NMR (250 MHz) δ 5.71 (m, 2H), 4.24 (m, 2H), 2.10 (m, 1H), 1.87 (m, 1H), 1.52 (m, 1H), 1.44 (m, 1H), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (62.5 MHz) δ 133.8, 131.7, 67.0, 66.6, 30.9, 30.4, 25.8, 18.7, −4.5, −4.6; MS m/z 251 ([M+Na]$^+$, 100). Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 63.09; H, 10.65.

The same procedure applied to a mixture of (1*R*,4*S*,6*R*)-**12** and (1*R*,4*S*,6*S*)-**13** furnished (1*S*,4*S*)-**14**, $[\alpha]_D^{20} = -95$ (*c* 0.95, $CHCl_3$), ee 94% (CHPLC, hexane/2-propanol, 99:1).

4.7. *trans*-Cyclohex-2-ene-1,4-diol, *trans*-1

To a solution of **14** (54 mg, 0.24 mmol) in THF (0.5 mL) was added Bu_4NF in THF (1 M, 0.5 mL, 0.5 mmol) and the mixture stirred at room temperature for 20 h. Removal of the solvent under vacuum furnished a residue (95 mg), which purification by flash chromatography ($CHCl_3$/MeOH, 30:1) gave *trans*-**1**[6] (21 mg, 0.18 mmol, 78%).

The same procedure applied to (1*S*,4*S*)-**14** gave (1*S*,4*S*)-**1**, $[\alpha]_D^{20} = -112$ (*c* 0.25, $CHCl_3$), ee 95%; lit.[7] $[\alpha]_D^{20} = +144.7$ (*c* 0.25, $CHCl_3$), ee 94% (CHPLC, hexane/2-propanol, 98:2), for (1*R*,4*R*)-**1**.

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