A New Synthesis of 1,2,4-Benzentriol Congeners

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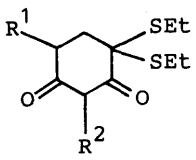
1,2,4-Benzenetriols were synthesized *via* 4,4-bis(ethylthio)-1,3-cyclohexanediones which were prepared by means of two types of Michael–Claisen condensation starting from methyl bis(ethylthio)acetate or 1,1-bis(ethylthio)-2-propanone.

Keywords annelation; aromatic synthesis; 1,2,4-benzenetriol; methyl bis(ethylthio)acetate; 1,1-bis(ethylthio)-2-propanone; C2+C4 annelation; C3+C3 annelation; Michael–Claisen condensation; α,β-unsaturated ester; dibenzofurandiol

Synthesis of aromatic compounds is a major goal of organic synthesis. Construction of benzenoid aromatic systems from aliphatic sources has been achieved extensively *via* annelation reactions.[1] As a part of our studies on synthesis of aromatic compounds from aliphatic ones, a new route to 1,3-benzenediols and its application to pterocarpan synthesis were described in our previous paper. In this paper we describe in detail a new entry to 1,2,4-benzenetriols from aliphatic compounds.[2]

Examples of 1,2,4-oxygen location on aromatic nuclei are found widely in the structures of biologically active compounds and naturally occurring compounds such as oxydopamine, coumestans, pterocarpans, and rotenoids.[3] Conventional synthetic access to 1,2,4-benzenetriols has been performed mostly by successive oxidative and reductive processes[4a-c] or Thiele reaction[4d] starting from appropriately substituted cyclic compounds. There has been no reported approach to the triols *via* annelation using aliphatic sources. Now we wish to present a novel route to 1,2,4-benzenetriols, employing two kinds of Michael–Claisen condensation of α,α-bis(ethylthio) carbonyl compounds with α,β-unsaturated carbonyl compounds.



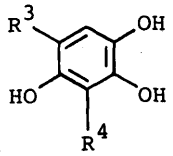
1

a: $R^1=R^2=H$

b: $R^1=Me, R^2=H$

c: $R^1=H, R^2=Me$

d: $R^1=R^2=Me$



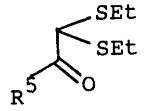
2

a: $R^3=R^4=H$

b: $R^3=Me, R^4=H$

c: $R^3=H, R^4=Me$

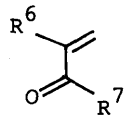
d: $R^3=R^4=Me$



3

a: $R^5=OMe$

b: $R^5=Me$



4

a: $R^6=H, R^7=Me$

b: $R^6=R^7=Me$

c: $R^6=H, R^7=Et$

d: $R^6=Me, R^7=Et$

e: $R^6=H, R^7=OMe$

f: $R^6=Me, R^7=OMe$

Chart 1

Aliphatic six-membered rings (**1**), which were converted to the aromatic rings (**2**) in the next step, were formed by two types of condensation, C2+C4 and C3+C3 annelation. The former condensation, known as Robinson annelation, was performed by employing methyl bis(ethylthio)acetate (**3a**)[5] as the C2 source and several α,β-unsaturated ketones (**4a—d**) as the C4 source. The C3+C3 annelation, regarded as 1,3-Michael–Claisen condensation, was carried out using 1,1-bis(ethylthio)-2-propanone (**3b**)[6] as the C3 source and two α,β-unsaturated esters (**4e** and **4f**) as the other C3 source.

Reaction of **3a** with **4a—d** in the presence of NaH in 1,2-dimethoxyethane (DME) at room temperature gave the 4,4-bis(ethylthio)-1,3-cyclohexanediones (**1a—d**) which were separated from the reaction mixture by taking advantage of their acidic character. Two of them, compounds **1a** and **1b**, were also obtained from the condensation of **3b** and the α,β-unsaturated esters (**4e** and **4f**) in the same way as noted above. These six-membered rings (**1a—d**) are the synthetic precursors of 1,2,4-benzenetriols (**2**).

The produced cyclic compounds (**1a—d**) with the thioketalized cyclohexanetrione structure were converted to the target aromatics by hydrolysis and isomerization as follows. Dethioketalization of the six-membered rings with $HgCl_2$ in $MeOH/H_2O$ gave a crude product, which was heterogeneous on thin-layer chromatography (TLC). The mixture consisted of triol and carbonyl compounds which were considered to be tautomeric. Treatment of the products with refluxing acetic acid or formic acid gave the 1,2,4-benzenetriols (**2a—d**).

The annelation reaction of **3b** was applied to more complicated counterparts, *trans*-hexahydro-3-methylene-2(3*H*)-benzofuranone (**5a**) and *cis*-hexahydro-3-methylene-2(3*H*)-benzofuranone (**6a**) to show the effectiveness of the 1,3-Michael–Claisen condensation. Compounds **5a** and **6a** were prepared from *trans*-hexahydro-2(3*H*)-benzofuranone (**5b**) and *cis*-hexahydro-2(3*H*)-benzofuranone (**6b**), respectively.[7] Reaction of **3b** with **5a** gave an acidic mixture which was subjected to column chromatography to give **7a** (21%) and **7b** (52%). Gradual isomerization of **7b** to **7a** was observed on standing at room temperature. The tautomeric structures of **7a** (the enol form) and **7b** (the keto form) were

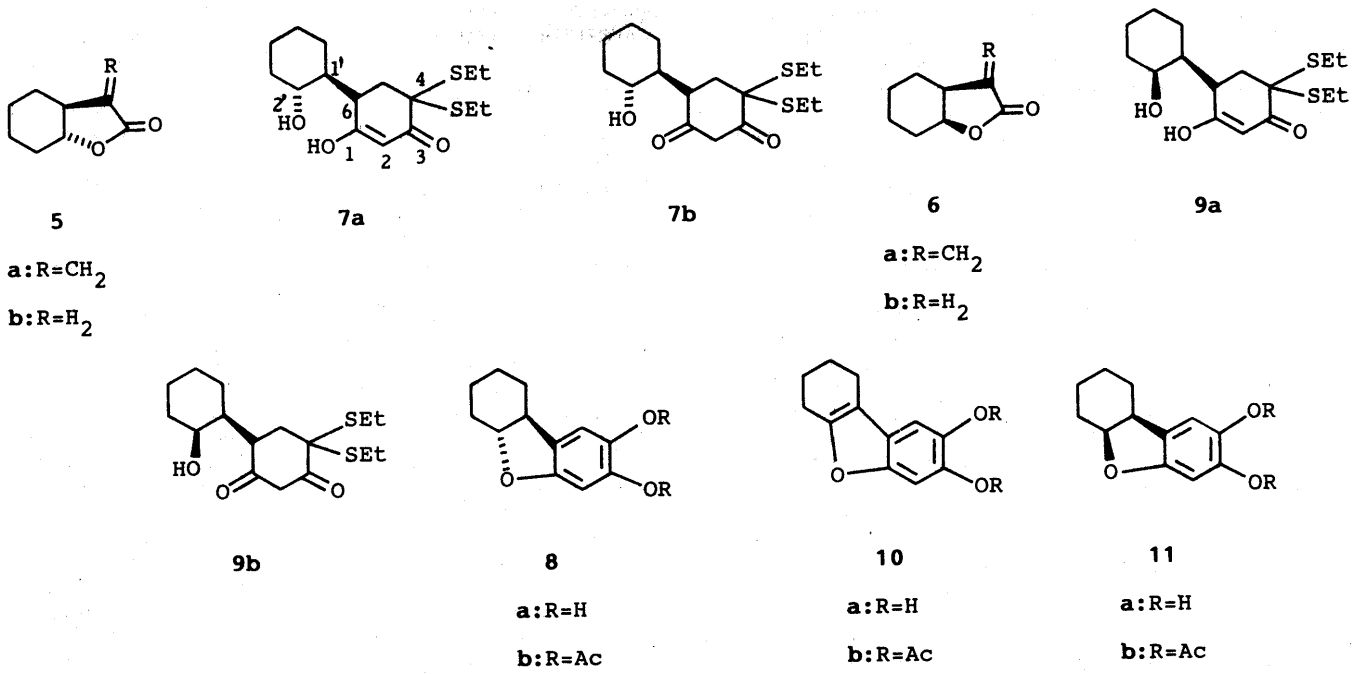


Chart 2

assigned on the following bases: a) gradual isomerization of **7b** to **7a** was observed, b) **7a** shows an infrared (IR) absorption at 1634 cm^{-1} and olefinic proton signals at δ 5.41 (1H, doublet, J = 1.8 Hz, C_2-H) in the proton nuclear magnetic resonance (^{1}H-NMR) spectrum, whereas **7b** shows an IR absorption at 1716 cm^{-1} and methylene proton signals at δ 2.97 and 3.19 (each 1H, doublet, J = 14.5 Hz, C_2-H_2), c) both compounds (**7a** and **7b**) were converted to the dibenzofuran skeleton (**8a**) as mentioned below. Treatment of **7a** with mercuric perchlorate[8] gave an unstable mixture followed by refluxing in acetic acid to give *trans*-5a,6,7,8,9,9a-hexahydro-2,3-dibenzofurandiol (**8a**) in 40% yield from **7a**.[9] The same reaction of **7b** gave **8a** in 39% yield. Similarly the annelation reaction of **3b** with **6a** gave **9a** (38%) and **9b** (41%). Gradual isomerization of **9b** to **9a** was also observed at room temperature. Spectral data of **9a** and **9b** are very similar to those of **7a** and **7b** mentioned above. Conversion of **9a** to *cis*-5a,6,7,8,9,9a-hexahydro-2,3-dibenzofurandiol (**11a**) in the same manner as noted for **7a** was unexpectedly accompanied with production of the dehydrogenated product, 6,7,8,9-tetrahydro-2,3-dibenzofurandiol (**10a**) (41%). Separation of compound **11a** from the reaction mixture was unsuccessful because of its instability on SiO_2. It was purified as the diacetate **11b** (8% from **9a**).[9] The same treatment of **9b** gave **10a** (38%) and **11b** (5%).

In conclusion, 1,2,4-benzenetriol derivatives were obtained from 4,4-bis(ethylthio)-1,3-cyclohexanediones, which were constructed by the annelation reaction of α,α-bis(ethylthio) carbonyl compounds and α,β-unsaturated carbonyl compounds. The present method has been applied successfully to total synthesis of two natural products, maackiain and anhydropisation.[10]

Experimental

Melting points were determined on a Yanaco model MP micro melting point apparatus and are uncorrected. IR spectra were obtained on a Hitachi 285 infrared spectrophotometer or a Hitachi 270-30 infrared spectrometer. ^{1}H-NMR spectra were recorded on a JEOL JNM-PMX 60si spectrometer or a JNM-GX270 FT spectrometer using tetramethylsilane as an internal standard. High-resolution mass spectra (MS) were obtained on a JEOL JMS-DX300 mass spectrometer. All extracts were dried over anhydrous $MgSO_4$. Column chromatography and preparative TLC was performed with Kieselgel 60 (70—230 mesh) and Kieselgel 60 PF_{254} (Merck), respectively.

General Procedure for Annelation Reaction of α,α-Bis(ethylthio) Carbonyl Compound (3a or 3b) A solution of α,α-bis(ethylthio) carbonyl compound (**3a** or **3b**) (0.01 mol) in DME (20 ml) was added to a suspension of NaH (60% in mineral oil, 0.01 mol) in DME (20 ml) with stirring at 0 °C. Stirring was continued for 15 min at room temperature, then a solution of an α,β-unsaturated carbonyl compound (**4a—d**, **4e**, **4f**, **5a**, or **6a**) (0.01 mol) in DME (10 ml) was added to the resultant clear solution at 0 °C. Stirring was continued for 16 h at room temperature. The solvent was evaporated off *in vacuo*, 5% NaOH solution was added to the residue, and the solution was washed with ether. The water layer was acidified with diluted HCl and extracted with CH_2Cl_2. The extract was washed with brine, dried, and then evaporated to give the annelated compound (**1a—d**, **7**, or **9**).

4,4-Bis(ethylthio)-1,3-cyclohexanedione (1a) This compound (**1a**) was obtained from **3a** and methyl vinyl ketone (**4a**) in 56% yield. The reaction using 0.005 mol of NaH (0.5 eq) also gave **1a** in 26.7% yield. mp 104—105 °C (from cyclohexane). IR (Nujol): 1602, 1554 cm^{-1}; ($CHCl_3$): 1734, 1704, 1614 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.20 (6H, t-like, Me × 2), 2.30—2.80 (8H, m), 3.60 (1.5H, s), 5.40 (0.5H, s). *Anal.* Calcd for $C_{10}H_{16}O_2S_2$: C, 51.69; H, 6.98. Found: C, 51.40; H, 7.18. High-resolution MS: Calcd for $C_{10}H_{16}O_2S_2$ (232.0591). Found: m/z 232.0588 (M^+). Compound **1a** was also obtained by the reaction of **3b** with methyl acrylate (**4e**) in 60% yield.

4,4-Bis(ethylthio)-6-methyl-1,3-cyclohexanedione (1b) This compound (**1b**) was obtained from **3a** and 2-methyl-1-buten-3-one (**4b**) in 91% yield. mp 102—103 °C (from cyclohexane). IR (Nujol): 1610, 1544 cm^{-1}; ($CHCl_3$): 1730, 1706 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.19 (3H, d, J = 6 Hz, Me), 1.27 (6H, t, J = 10 Hz, Me × 2), 2.0—3.0 (9H, m), 3.40 (1H, d, J = 17 Hz, C_2-H), 4.05 (1H, d, J = 17 Hz, C_2-H). *Anal.* Calcd for $C_{11}H_{18}O_2S_2$: C, 53.62; H, 7.36. Found: C, 53.54; H, 7.61. High-resolution MS: Calcd for $C_{11}H_{18}O_2S_2$ (246.0748). Found: m/z 246.0753 (M^+). Compound **1b** was also obtained by the reaction of **3b** with methyl methacrylate (**4f**) in 11% yield.

4,4-Bis(ethylthio)-2-methyl-1,3-cyclohexanedione (1c) This compound (**1c**) was obtained from **3a** and ethyl vinyl ketone (**4c**) in 49% yield. mp 91—92 °C (from cyclohexane). IR (Nujol): 1593 cm^{-1}, ($CHCl_3$): 1735, 1704, 1634 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.30 (7H, t and d, Me), 1.75 (2H, s,

Me), 2.2—2.9 (8.5H, m), 4.0 (trace H, m). *Anal.* Calcd for $C_{11}H_{18}O_2S_2$: C, 53.62; H, 7.36. Found: C, 53.41; H, 7.48. High-resolution MS: Calcd for $C_{11}H_{18}O_2S_2$ (246.0748). Found: *m/z* 246.0760 (M^+).

4,4-Bis(ethylthio)-2,6-dimethyl-1,3-cyclohexanedione (1d) This compound (**1d**) was obtained from **3a** and 2-methyl-1-penten-3-one (**4d**) in 46% yield. Oil. IR (Film): 1734, 1704, 1612 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.1—1.8 (12H, m, Me×4), 1.75 (3H, s, Me), 2.0—3.0 (7H, m). High-resolution MS: Calcd for $C_{12}H_{20}O_2S_2$ (260.0905). Found: *m/z*: 260.0909 (M^+).

4,4-Bis(ethylthio)-6-(*trans*-2-hydroxycyclohexyl)-1,3-cyclohexanedione (7a, b) The acidic mixture was obtained from **3b** and **5a**. Separation of **7a** (21%) and **7b** (52%) was effected by column chromatography (2% (v/v) MeOH/CH_2Cl_2). Compound **7b** isomerized to **7a** in 3 d at room temperature. **7a**: mp 119—121 °C (from *n*-hexane). IR (Nujol): 3460, 1634 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.19, 1.26 (each 3H, t, J=7.5 Hz, Me×2), 1.3—1.6 (m), 1.7—2.1 (m), 2.22 (1H, dd, J=11.5, 13.4 Hz, C_5-H), 2.27 (1H, m, $C_{1'}$-H), 2.5—2.9 (m), 3.00 (1H, dddd, J=1.8, 4.9, 11.5, 11.5 Hz, C_6-H), 3.84 (1H, ddd, J=3.8, 11.0, 11.0 Hz, $C_{2'}$-H), 5.41 (1H, d, J=1.8 Hz, C_2-H). **7b**: mp 62—65 °C. IR (Nujol): 3400, 1708, 1584 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.23, 1.25 (each 3H, t, J=7.5 Hz, Me×2), 1.5—2.1 (m), 2.3—2.7 (m), 2.87 (1H, d, J=14.9 Hz, C_2-H), 3.01 (1H, d, J=14.9 Hz, C_2-H), 3.38 (1H, ddd, J=3.6, 10.8, 10.8 Hz, $C_{2'}$-H). High-resolution MS: Calcd for $C_{16}H_{26}O_3S_2$ (330.1323). Found: *m/z* 330.1344 (M^+).

4,4-Bis(ethylthio)-6-(*cis*-2-hydroxycyclohexyl)-1,3-cyclohexanedione (9a, b) An acidic mixture was obtained from **3b** and **6a**. Separation of **9a** (38%) and **9b** (41%) was effected by column chromatography (2% (v/v) MeOH/CH_2Cl_2). Compound **9b** isomerized to **9a** in 3 d at room temperature. **9a**: Oil. IR (Film): 3500, 1642 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.21, 1.26 (each 3H, t, J=7.5 Hz, Me×2), 2.16 (1H, dd, J=11.7, 13.2 Hz, C_5-H), 2.4—2.8 (m), 3.32 (1H, dddd, J=1.8, 4.7, 11.7, 11.7 Hz, C_6-H), 4.62 (1H, ddd, J=6.6, 6.6, 6.6 Hz, $C_{2'}$-H), 5.30 (1H, s, OH), 5.38 (1H, d, J=1.8 Hz, C_2-H). **9b**: mp 116—119 °C. IR (Nujol): 3380, 1716 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.21, 1.26 (each 3H, t, J=7.5 Hz, Me×2), 1.97 (1H, dd, J=12.6, 14.4 Hz, C_5-H), 2.28 (1H, dd, J=5.1, 14.4 Hz, C_5-H), 2.45 (1H, m, C_6-H), 2.5—2.7 (m), 2.74 (1H, d, J=13.9 Hz, C_2-H), 3.14 (1H, d, J=13.9 Hz, C_2-H), 3.37 (1H, s, OH), 4.13 (1H, ddd, J=4.5, 4.5, 4.5 Hz, $C_{2'}$-H). High-resolution MS: Calcd for $C_{16}H_{26}O_3S_2$ (330.1323). Found: *m/z* 330.1347 (M^+).

General Procedure for Dethioketalization of 1 A solution of $HgCl_2$ (2 mmol) in 50% (v/v) MeOH/H_2O (5 ml) was added to a solution of a dithioketal (**1a—d**) (1 mmol) in 50% (v/v) MeOH/H_2O (15 ml) with stirring at room temperature. The stirring was continued for 5 h and the precipitates were filtered off. The filtrate was evaporated *in vacuo*, and the residue was extracted with CH_2Cl_2. The extract was washed with water, dried and then evaporated *in vacuo*. The residue was taken up in acetic acid or 90% formic acid (5 ml), and the solution was refluxed for 1 h, then evaporated *in vacuo*. The residue was subjected to column chromatography with 1—4% (v/v) MeOH/CH_2Cl_2 to give the corresponding aromatic (**2a—d**).

1,2,4-Benzenetriol (2a) This compound (**2a**) was obtained from **1a** in 32% yield. The spectral data and melting point of this compound were identical with those of an authentic sample. mp 139—140 °C (sublimation). IR (Nujol): 3270, 1620 cm^{-1}.

5-Methyl-1,2,4-benzenetriol (2b) This compound (**2b**) was obtained from **1b** in 73% yield. mp 98—99 °C (from benzene), (lit. mp 126—130 °C,[4c] mp 100 °C[11]). ^{1}H-NMR (10% (v/v) $CD_3OD/CDCl_3$) δ: 2.07 (3H, s, Me), 3.93 (3H, s, OH×3), 6.31 (1H, s, C_3-H), 6.53 (1H, s, C_6-H). High-resolution MS: Calcd for $C_7H_8O_3$ (140.0474). Found: *m/z* 140.0478 (M^+). Triacetate: mp 112—114 °C (from EtOH), (lit.[4c] mp 112—114 °C). ^{1}H-NMR ($CDCl_3$) δ: 2.13 (3H, s, Me), 2.23 (6H, s, AcO×2), 2.26 (3H, s, AcO), 6.90 (1H, s, C_3-H), 7.00 (1H, s, C_6-H). High-resolution MS: Calcd for $C_{13}H_{14}O_6$ (266.0790). Found: *m/z* 266.0788 (M^+).

3-Methyl-1,2,4-benzenetriol (2c) This compound (**2c**) was obtained from **1c** in 64% yield. mp 121—122 °C, (lit.[4a] mp 121.5 °C). ^{1}H-NMR (acetone-d_6) δ: 2.07 (3H, s, Me), 6.12 (1H, d, J=8 Hz, C_5-H), 6.40 (1H, d, J=8 Hz, C_6-H), 6.7—7.5 (3H, br, OH×3).

3,5-Dimethyl-1,2,4-benzenetriol (2d) This compound (**2d**) was obtained from **1d** in 75% yield. mp 120—121 °C (from H_2O), (lit.[4b] mp 121—122 °C). ^{1}H-NMR (10% (v/v) $CD_3OD/CDCl_3$) δ: 2.12 (6H, s, Me×2), 4.15 (3H, s, OH×3), 6.40 (1H, s, C_6-H).

***trans*-5a,6,7,8,9,9a-Hexahydro-2,3-dibenzofurandiol (8a)** A solution of $Hg(ClO_4)_2 \cdot 3H_2O$ (900 mg) in tetrahydrofuran (THF) (3 ml) was added to a solution of the dithioketal (**7a**) (330 mg) in THF (3 ml)/$CHCl_3$ (6 ml) with stirring at room temperature. Stirring was continued for 15 min and the precipitates were filtered off. The filtrate was shaken with H_2O, and the water layer was extracted with CH_2Cl_2. The organic extract was washed with water, dried and then evaporated *in vacuo*. The residue was taken up in AcOH (5 ml) and the solution was refluxed for 1 h, then evaporated *in vacuo*. The residue was subjected to column chromatography with 4% (v/v) Et_2O/CH_2Cl_2 to give pale yellow crystals (83 mg, 40%). The same treatment of **7b** gave **8a** in 39% yield. mp 167—170 °C (from benzene). IR (Nujol): 3388, 1640, 1525 cm^{-1}. ^{1}H-NMR (10% (v/v) $CD_3OD/CDCl_3$) δ: 1.2—2.0 (8H, m), 2.68 (1H, br t, C_{9a}-H), 3.76 (1H, ddd, J=3.4, 11.7, 11.7 Hz, C_{5a}-H), 3.87 (2H, br, OH), 6.43 (1H, s, C_4-H), 6.64 (1H, s, C_1-H). High-resolution MS: Calcd for $C_{12}H_{14}O_3$ (206.0943). Found : *m/z* 206.0950 (M^+). Diacetate (**8b**): mp 126—127 °C (from EtOH). IR (Nujol): 1768 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.3—2.3 (8H, m), 2.25 (3H, s, OAc), 2.26 (3H, s, OAc), 2.78 (1H, br t, C_{9a}-H), 3.92 (1H, ddd, J=3.7, 11.7, 12.9 Hz, C_{5a}-H), 6.64 (1H, s, C_4-H), 6.91 (1H, s, C_1-H). High-resolution MS: Calcd for $C_{16}H_{18}O_5$ (290.1155). Found: *m/z* 290.1147 (M^+).

6,7,8,9-Tetrahydro-2,3-dibenzofurandiol (10a), 2,3-Diacetoxy-6,7,8,9-tetrahydrodibenzofuran (10b), and *cis*-2,3-Diacetoxy-5a,6,7,8,9,9a-hexahydrodibenzofuran (11b) A solution of $Hg(ClO_4)_2 \cdot 3H_2O$ (3 g) in THF (12 ml) was added to a solution of the dithioketal (**9a**) (900 mg) in THF (18 ml)–$CHCl_3$ (30 ml) with stirring at room temperature. Stirring was continued for 15 min and the precipitates were filtered off. The filtrate was shaken with H_2O, and the water layer was extracted with CH_2Cl_2. The organic extract was washed with water, dried, and then evaporated *in vacuo*. The residue was taken up in AcOH (15 ml) and the solution was refluxed for 1 h, then evaporated *in vacuo*. The residue was subjected to column chromatography with 4% (v/v) Et_2O/CH_2Cl_2 to give **10a** as pale yellow crystals (230 mg, 41%). The fraction next to **10a** was evaporated to give yellow crystals (180 mg), which were heterogeneous on TLC.[12] These were treated with pyridine (2 ml) and acetic anhydride (1 ml). The reaction mixtrure was allowed to stand for 16 h and then evaporated *in vacuo*. The residue was subjected to preparative TLC (CH_2Cl_2) to afford **10b** (83 mg, 11% from **9a**) and **11b** (65 mg, 8.2% from **9a**) as colorless crystals. The same treatment of **9b** gave **10a** (38%), **10b** (6.3%), and **11b** (4.6%). **10a**: mp 124—125 °C. IR (Nujol): 3360, 1616, 1504 cm^{-1}. ^{1}H-NMR (10% (v/v) $CD_3OD/CDCl_3$) δ: 1.6—2.0 (4H, br, C_7-H_2, C_8-H_2), 2.3—2.8 (4H, br, C_6-H_2, C_9-H_2), 6.76 (1H, s, C_4-H), 6.88 (1H, s, C_1-H). High-resolution MS: Calcd for $C_{12}H_{12}O_3$ (204.0787). Found: *m/z* 204.0806 (M^+). **10b**: mp 112—113 °C (from EtOH). IR (Nujol): 1772 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.6—2.0 (4H, br, C_7-H_2, C_8-H_2), 2.26 (6H, s, OAc×2), 2.4—2.8 (4H, br, C_6-H_2, C_9-H_2), 7.13 (1H, s, C_4-H), 7.19 (1H, s, C_1-H). High-resolution MS: Calcd for $C_{16}H_{16}O_5$ (288.0997). Found: *m/z* 288.1015 (M^+). **11b**: mp 77—78 °C (from EtOH). IR (Nujol): 1768 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.2—2.1 (8H, m), 2.25 (3H, s, OAc), 2.26 (3H, s, OAc), 3.17 (1H, ddd, J=6.9, 6.9, 6.9 Hz, C_{9a}-H), 4.71 (1H, ddd, J=4.9, 4.9, 6.9 Hz, C_{5a}-H), 6.93 (1H, s, C_4-H), 7.27 (1H, s, C_1-H). High-resolution MS: Calcd for $C_{16}H_{18}O_5$ (290.1155). Found: *m/z* 290.1135 (M^+).

***trans*-Hexahydro-3-methylene-2(3*H*)-benzofuranone (5a)** This compound (**5a**) was prepared from *trans*-hexahydro-2(3*H*)-benzofuranone (**5b**)[13,14] by the reported procedure.[7] IR (Nujol): 1774 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.2—2.3 (8H, m), 2.41 (1H, m, C_{3a}-H), 3.72 (1H, ddd, J=3.7, 11.0, 11.0 Hz, C_{7a}-H), 5.39 (1H, d, J=2.9 Hz, C=C-H), 6.06 (1H, d, J=3.3 Hz, C=C-H).

***cis*-Hexahydro-3-methylene-2(3*H*)-benzofuranone (6a)** This compound (**6a**) was prepared from *cis*-hexahydro-2(3*H*)-benzofuranone (**6b**)[13,15] by the reported procedure.[7] IR (film): 1768 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.3—2.0 (8H, m), 3.03 (1H, m, C_{3a}-H), 4.55 (1H, ddd, J=5.1, 5.1, 5.1 Hz, C_{7a}-H), 5.52 (1H, d, J=2.2 Hz, C=C-H), 6.19 (1H, d, J=2.6 Hz, C=C-H).

References and Notes

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