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Novel Conversions of Furandiols and Spiroacetal Enol Ethers into Cyclopentenones: Implications of the Isomerization Mechanism of 2-Furylcarbinols into Cyclopentenones

Biao-Lin Yin,*[a] Yu-Lin Wu,[b] and Jin-Qiang Lai[a]

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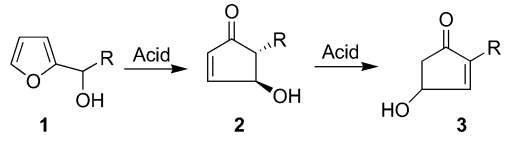
Two acid-catalyzed conversions of furandiols **8** and its dehydration spiroacetalized products **9** into oxabicyclic cyclopentenones **10** in good to excellent yields are reported. To disclose the mechanism of these conversions, the fact that H_2O catalyzes the conversion of **9** into **10** is presented and intermediates **9k** and **20i** have been structurally verified. In addition, two other related conversions of spiroacetal enol ethers **11** and **14** derived from **8** into cyclopentenones are presented, for which an intramolecular aldol reaction is the key step. On the basis of these results, we propose that these conversions occur through an aldol condensation step instead of electrocyclization of the 4π-electron system, which was previously reported.

Introduction

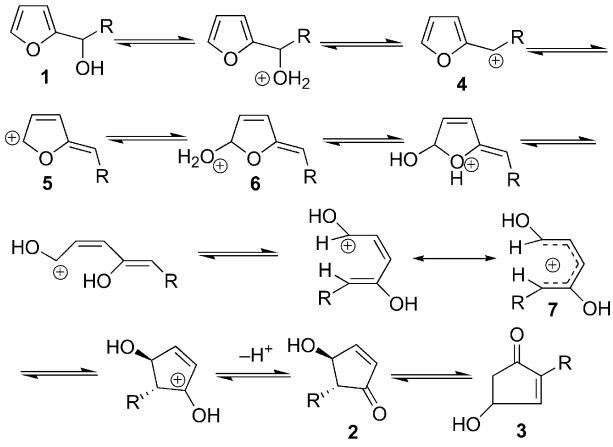
The first acid-catalyzed isomerization reaction of 2-furylcarbinols into cyclopentenones was reported by Piancatelli[1] about 30 years ago, and since then significant research effort has been focused on the reaction mechanism and its applications in the synthesis of numerous biologically active natural products like prostanoids.[2] A brief literature survey reveals that this isomerization involves two steps. In the first step, 2-furylcarbinol **1** forms intermediate **2**, which further rearranges into cyclopentenone **3** (Scheme 1). Usually this isomerization is catalyzed by a protic acid such as formic acid, polyphosphoric acid, and *p*-toluenesulfonic acid or by a Lewis acid such as zinc chloride in an aqueous system.[3] The mechanism of the isomerization of 2-furylcarbinols into cyclopentenones has not yet been fully studied. Piancatelli[1] once proposed that this isomerization underwent a thermal conrotatory electrocyclic reaction of the 4π-electron system (Scheme 2). The key step involves formation of carbocation **5**. A water molecule then attacks the 5-position of the furan ring to form enol ether intermediate **6** (Z isomer). Prototropic shifts and ring opening give intermediate **7**, which cyclizes by a 4π-electron thermal conrotatory electrocyclization. Subsequent isomerization affords **3**. Recently, Lera[4] studied the reaction profile computationally with structurally simple 2-furylcarbinols and predicted its pericyclic nature. However, D'Auria provided evidence that intermediate **2** is an obvious mixture of *trans* and *cis* isomers when the R group is a small alkyl group and proposed an alternative pathway.[5] For this reaction, *cis*-2-alkyl(aryl)-3-hydroxycyclopent-4-en-1-one formed through an alternative conrotatory electrocyclization could be isomerized to the more thermodynamically stable *trans* isomer in acidic media or during purification, complicating the interpretation of the stereochemical outcome. Therefore, mechanistic studies on the isomerization are still needed.



Scheme 1. Isomerization of 2-furylcarbinol into cyclopentenone.

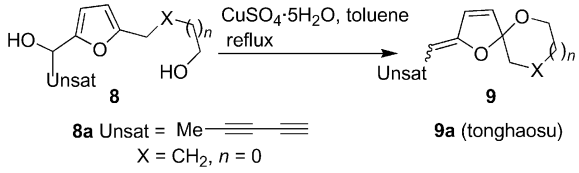
Recently, we developed a concise and general synthetic strategy to tonghaosu and its analogues **9**, characterized by a spiroacetal enol ether subunit, by an acid-catalyzed dehydration–spiroacetalization reaction of corresponding furandiol **8** in an aprotic aromatic solvent such as toluene (Scheme 3).[6] It is worth noting that when the unsaturated part is an aromatic group, the Z isomer is produced exclusively. However, when the unsaturated part is an alkenyl or alkynyl group, the reaction gives rise to a mixture of *Z* and *E* isomers in variable ratios. The conversion of intermediate **8** into tonghaosu analogs seems to involve the formation of an enol ether carbocation like **6** in the acid-catalyzed isomerization of 2-furylcarbinols and a subsequent intramolecular nucleophilic attack of the remaining hydroxy

[a] School of Chemistry and Chemical Engineering, South China University of Technology,
Guangzhou, 510640, China
E-mail: blyin@scut.edu.cn
[b] State Key Laboratory of Bioorganic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science,
Shanghai 20032, China



Scheme 2. Documented mechanism for the isomerization of 2-furylcarbinol.

group on the carbocation. To the best of our knowledge, the conversion of these special 2-furylcarbinols into cyclopentenones in the presence of an acid in an aqueous system has not been reported so far. Meanwhile, this conversion might shed some new light on the mechanism of 2-furylcarbinol isomerization. We herein would like to detail the results.

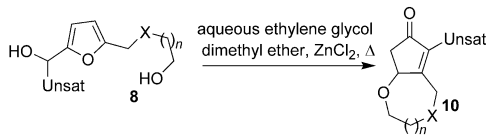


Scheme 3. General strategy to tonghaosu analogues **9**.

Results and Discussion

As can be seen from Table 1, all the 2-furylcarbinols were converted into new compounds with a lower polarity than **8** in good to excellent yields when heated under reflux with a catalytic amount of $ZnCl_2$ in aqueous ethylene glycol dimethyl ether. Spectroscopic data (IR, NMR, MS) showed that the molecular weight of these new compounds is 18 grams less than that of **8** and that they contain a ketone carbonyl group but no olefinic proton, which clearly suggests the formation of oxabicyclic cyclopentenones **10**. The nature of the substituent on the phenyl ring apparently influenced the reaction yield and rate. Electron-donating groups on the phenyl ring led to better yields (**10d** > **10c** > **10b** > **10e** and **10i** > **10h** > **10j**) and shorter reaction times (**10d** < **10c** < **10b** < **10e** and **10i** < **10h** < **10j**). Meanwhile, the side chain at the 5-position of the furan ring also slightly influenced the reaction yield and rate. Relative to substrates bearing a chain length of five carbon atoms or a heteroatom-containing carbon chain, molecules with a chain length of four carbon atoms gave higher yields (**10b** > **10g** and **10h**, **10d** > **10i**, **10e**> **10j**) and had shorter reaction times (**10b** < **10g** and **10h**, **10d** < **10i**, **10e** < **10j**). By using this protocol, a facile synthesis of thiophene-substituted oxabicyclic cyclopentenone **10f** was accomplished in 83% yield from readily accessible **8f** (Table 1, Entry 6). Compound **10f** is also a natural product named chrycorin isolated from the same original plant *Chrysanthemum* as natural product **9f** by Tada and Chiba in 1984.[7] All the spectroscopic data were in accordance with those reported in the literature.

Table 1. Conversion of **8** into **10**.



8b Unsat = Phenyl, X = CH_2, *n* = 0
8c Unsat = *p*-methylphenyl, X = CH_2, *n* = 0
8d Unsat = *p*-methoxyphenyl, X = CH_2, *n* = 0
8e Unsat = *p*-nitrophenyl, X = CH_2, *n* = 0
8f Unsat = thiophene-2-yl, X = CH_2, *n* = 0
8g Unsat = Phenyl, X = CH_2, *n* = 1
8h Unsat = Phenyl, X = O, *n* = 1
8i Unsat = *p*-methoxyphenyl, X = O, *n* = 1
8j Unsat = *p*-nitrophenyl, X = O, *n* = 1
8k Unsat = *trans*-styryl, X = CH_2, *n* = 0

Entry	2-Furylcarbinol	Reaction time [h]	Products (% yield[a])
1	**8b**	5	**10b** (81)
2	**8c**	4	**10c** (85)
3	**8d**	3.5	**10d** (90)
4	**8e**	6	**10e** (75)
5	**8f**	4	**10f** (83)
6	**8g**	6	**10g** (78)
7	**8h**	6	**10h** (75)
8	**8i**	5	**10i** (86)
9	**8j**	8	**10j** (70)
10	**8k**	3	**10k** (84)

[a] Isolated yields.

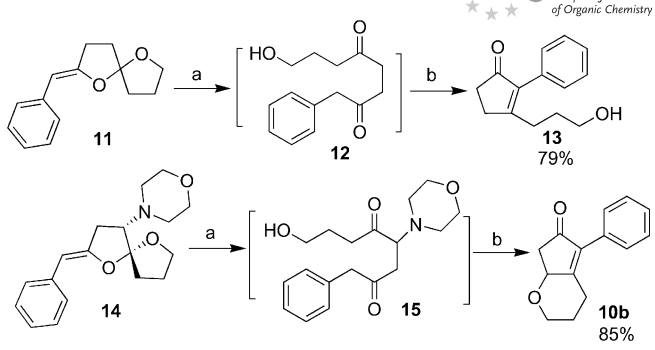
During the course of the reaction, an intermediate was found by TLC as a lower polarity spot than **10**. This intermediate was isolated and its structure was verified by NMR spectroscopic analysis to be **9**, which is the dehydration–spiroacetalized product of **8**. Accordingly, it is reasonable to anticipate that spiroacetal enol ethers **9** could also undergo rearrangement into cyclopentenone **10** under the same reaction conditions. As can be seen from Table 2, compounds **9** indeed underwent isomerization into cyclopentenone **10** in yields comparable to those of **8**. In addition, the reaction time for **9** was shorter. On the basis of the above results, we were interested in the mechanism of the two conversions and envisioned that they might involve the same intermediate. In our previous study we reported a preliminary mechanism of the isomerization of spiroacetal enol ether **9** into cyclopentenone **10** by electrocyclization of a 4π-electron system.[8] However, according to this mechanism, **9** should isomerize into **10** under anhydrous acidic conditions. Surprisingly, after treatment of compound **9b** with either $ZnCl_2$ as Lewis acid or *p*-TosOH as protic acid in refluxing anhydrous solvents such as DME or MeOH, the reaction system was very complicated and compound **10b** was not isolated. Interestingly, the addition of H_2O (1 equiv.) into the anhydrous DME and $ZnCl_2$ system was favorable and compound **10b** was formed in 61% yield. The addition of larger

amounts of H_2O resulted in shorter reaction times and higher yields. In contrast, furandiol **8b**, which produces one equivalent of H_2O in the presence of $ZnCl_2$, can be converted into **10b** in 65% yield in refluxing anhydrous DME. Therefore, we concluded that H_2O catalyzes the isomerization of enol ether **9** into cyclopentenone **10**.

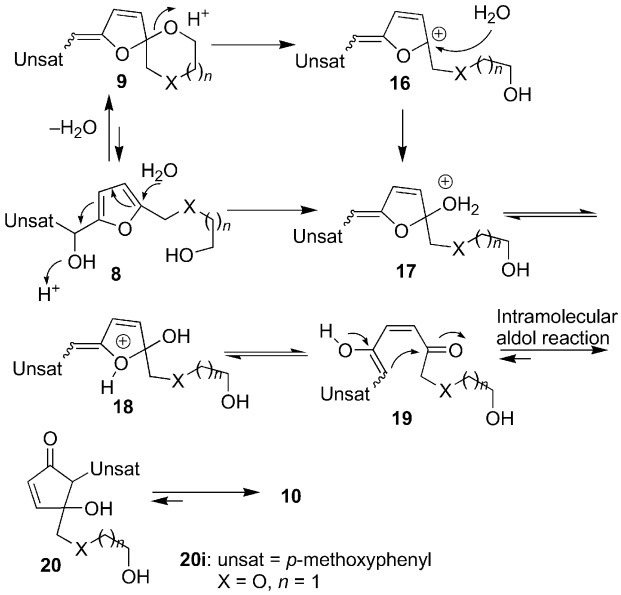
Table 2. Conversion of **9** into **10**.

Entry	Spiroacetal enol ether	Products (% yield)
1	**9b**	**10b** (83)
2	**9c**	**10c** (86)
3	**9d**	**10d** (89)
4	**9e**	**10e** (80)
5	**9f**	**10f** (87)
6	**9g**	**10g** (77)
7	**9h**	**10h** (74)
8	**9i**	**10i** (77)
9	**9j**	**10j** (72)
10	**9k**	**10k** (87)

To obtain further insight into the mechanism of the isomerization of spiroacetal enol ether **9** into cyclopentenone **10**, two other spiroacetal enol ether derivatives **11** and **14** were prepared according to known methods.[6h,9,10] Similarly, treatment of **11** and **14** with aqueous HCl at room temperature followed by base-catalyzed intramolecular aldol reaction afforded cyclopentenone **13** and **10b** in 79 and 85% yield, respectively. As shown by TLC, the more polar spots were very likely to be diketones **12** and **15**, respectively (Scheme 4). Enlightened by these results, we propose a possible mechanism for the conversion of furandiol **8** and spiroacetal enol ether **9** into cyclopentenone **10**, and this mechanism involves an intramolecular aldol reaction as the key step (Scheme 5). Initially, in the presence of acid, a water molecule attacks the 5-position of the furan ring of furandiol **8** to form intermediate **17**. Meanwhile, **8** can also be partially transformed into enol ether **9** after loss of one molecule of H_2O, indicating that **8** can also be converted into **10** under anhydrous conditions. Under the same reaction conditions, ring opening of **9** leads to carbocation **16**, which is then converted into the same intermediate **17** as that of **8**. After prototropic shift and intramolecular aldol reaction steps, **17** is transformed into **20** and then into more stable cyclopentenone **10**. During the conversion of **8k** into **10k**, intermediate **9k** was isolated as a mixture of *cis* and *trans* isomers (2.8:1), indicating that enol ether **17** is probably not always a pure isomer, as reported in the literature, and the configuration of its *exo* double bond depends on the nature of the unsaturated group. This results could be helpful to explain the stereochemical outcome of the isomerization of 2-furylcarbinols. It is worth noting that, fortunately, intermediate **20i**, which is two more polar spots than **8i** on TLC, was isolated successfully as a mixture of *E*/*Z* isomers in a ratio of 1.5:1.[11] Its successful isolation may be possibly due to the more difficult formation of the seven-membered derivative than that of the six-membered derivative.



Scheme 4. Conversions of **11** and **14** into cyclopentenones. Reaction conditions: (a) 2% HCl, THF, r.t.; (b) 5% NaOH in THF, r.t.



Scheme 5. Mechanism for both substrates.

Conclusions

In summary, we have reported the novel conversion of special 2-furylcarbinols **8**, bearing a hydroalkyl side chain at the 5-position of the furan ring, into corresponding oxabicyclic cyclopentenones **10** in good to excellent yields. In contrast, under the same reaction conditions spiroacetal enol ether **9**, the dehydrate product of **8**, can be isomerized into **10** in comparable yields. To investigate the mechanism of the two conversions, the fact that H_2O catalyzes the conversion of **9** into **10** is presented and intermediates **9k** and **20i** have been structurally verified. In addition, two other related conversions of spiroacetal enol ethers **11** and **14** derived from **8** into cyclopentenones are also presented, for which an intramolecular aldol reaction is the key step. On the basis of these results, we proposed that these conversions occur through an aldol condensation step instead of electrocyclization of the 4π-electron system, which was previously reported. This work might be helpful to disclose the presently unclear mechanism of the acid-catalyzed isomerization reaction of 2-furylcarbinols into cyclopentenones. Further study on the asymmetric rearrangement of 2-furyl-

carbinols into chiral cyclopentenones catalyzed by a chiral aldol reaction catalyst is underway in our group, and the results will be disclosed in due course.

Experimental Section

General Remarks: IR spectra were recorded with Perkin–Elmer 983 or Shimadzu IR-440 spectrometers. ^{1}H and ^{13}C NMR spectra were recorded with an AMX-300, DPX-300, Gemini-2000, or INOVA-600 spectrometer with TMS as the internal standard. Mass spectra were recorded with a Mariner (PE, for ESI), HP5973N or HP5989A instrument. HRMS (EI or ESI) spectra were obtained with a Kratos CONCEPT 1H or Bruker APEXIII 7.0 TESLA mass spectrometer. Optical rotations were measured with a Perkin–Elmer 241 MC polarimeter. Elemental analyses were carried out at the Microanalytic Laboratory of Shanghai Institute of Organic Chemistry. Flash column chromatography was performed on silica gel H (10–40 m) with a petroleum ether/ethyl acetate or ethyl acetate/ethanol system as eluent. Compounds **8**,[6b] **9**,[6g] **11**,[6h] **13**,[9] and **14**[10] were prepared according to literature procedures.

Typical Procedure for the Conversion of Furandiol 8 into Cyclopentenone 10: A mixture of furandiol **8** (20 mmol), $ZnCl_2$ (30 mg), and water (20 mL) was heated under reflux until the starting material was fully consumed (monitored by TLC). The reaction mixture was then extracted with diethyl ether. The combined organic layer was washed with brine and dried with Na_2SO_4. Removal of the solvent yielded a crude product, which was purified by flash chromatography to afford cyclopentenone **10**.

5-Phenyl-3,4,7,7a-Tetrahydrocyclopenta[*b*]pyran-6(2*H*)-one (10b): Yield: 346.8 mg (81%), syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (m, 5 H), 4.51 (dd, J = 6.6, 2.6 Hz, 1 H), 4.07 (ddd, J = 11.9, 5.0, 3.0 Hz, 1 H), 3.75 (m, 1 H), 3.04 (ddd, J = 14.6, 4.4, 3.3 Hz, 1 H), 2.85 (dd, J = 18.3, 6.5 Hz, 1 H), 2.52 (dt, J = 14.4, 9.5 Hz, 1 H), 2.47 (dd, J = 18.3, 2.4 Hz, 1 H), 1.83 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.7, 168.8, 138.2, 130.3, 129.1, 128.4, 128.1, 77.4, 67.4, 42.1, 26.9, 26.5 ppm. MS: *m*/*z* (%) = 214 (15) $[M]^+$, 186 (100), 185 (75), 116 (51), 115 (54), 144 (49), 129 (32), 128 (42), 102 (25). IR (film): $\tilde{\nu}$ = 1716, 1630, 1496, 1326, 1090, 699 cm^{-1}. $C_{14}H_{14}O_2$ (214.10): calcd. C 78.48, H 6.59; found C 78.32, H 6.40.

5-(4-Methylphenyl)-3,4,7,7a-tetrahydrocyclopenta[*b*]pyran-6(2*H*)-one (10c): Yield: 387.9 mg (85%), syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (m, 4 H), 4.49 (d, J = 6.3 Hz, 1 H), 4.05 (dd, J = 10.3, 2.2 Hz, 1 H), 3.74 (m, 1 H), 3.06 (br. d, J = 14.8 Hz, 1 H), 2.82 (dd, J = 18.2, 6.4 Hz, 1 H), 2.50 (dd, J = 15.0, 9.8 Hz, 1 H), 2.46 (dd, J = 18.2, 2.4 Hz, 1 H), 2.36 (s, 3 H), 1.82 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.8, 169.2, 150.4, 137.4, 130.6, 120.7, 116.7, 75.6, 67.5, 42.1, 26.8, 26.6, 24.4 ppm. MS: *m*/*z* (%) = 228 (22) $[M]^+$, 200 (28), 185 (100), 171 (49), 141 (23), 128 (30), 129 (29), 115 (40). IR (film): $\tilde{\nu}$ = 1711, 1636, 1514, 1327, 1090 cm^{-1}. $C_{15}H_{16}O_2$ (228.12): calcd. C 78.92, H 7.06; found C 78.78, H 7.34.

5-(4-Methoxyphenyl)-3,4,7,7a-tetrahydrocyclopenta[*b*]pyran-6(2*H*)-one (10d): Yield: 439.4 mg (90%), white solid; m.p. 108–109 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (d, J = 9.9 Hz, 2 H), 6.96 (d, J = 9.8 Hz, 2 H), 4.49 (dd, J = 6.6, 1.8 Hz, 1 H), 4.09 (br. d, J = 12.0 Hz, 1 H), 3.82 (s, 3 H), 3.77 (m, 1 H), 3.09 (br. d, J = 12.2 Hz, 1 H), 2.86 (dd, J = 18.0, 3.0 Hz, 1 H), 2.55 (dt, J = 12.2, 2.4 Hz, 1 H), 2.47 (dd, J = 18.3, 3.0 Hz, 1 H), 1.81 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 167.7, 159.5, 137.7, 130.6, 122.5, 114.2, 75.6, 67.4, 55.3, 42.1, 26.7, 26.5 ppm. MS: *m*/*z* (%) = 244 (100) $[M]^+$, 215 (31), 201 (18), 185 (51), 174 (32). IR (film): $\tilde{\nu}$ = 1702, 1639, 1515, 1326, 1087, 1047, 809 cm^{-1}. $C_{15}H_{16}O_3$ (244.11): calcd. C 73.75, H 6.60; found C 73.56, H 6.68.

5-(4-Nitrophenyl)-3,4,7,7a-tetrahydrocyclopenta[*b*]pyran-6(2*H*)-one (10e): Yield: 388.6 mg (75%), yellow solid; m.p. 156–157 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (d, J = 9.3 Hz, 2 H), 7.51 (d, J = 9.3 Hz, 2 H), 4.54 (dd, J = 6.3, 2.2 Hz, 1 H), 4.09 (br. d, J = 12.2 Hz, 1 H), 3.81 (m, 1 H), 3.05 (br. d, J = 11.8 Hz, 1 H), 2.92 (d, J = 18.3, 6.3 Hz, 1 H), 2.66 (dt, J = 14.8, 10.2 Hz, 1 H), 2.54 (dd, J = 18.6, 2.4 Hz, 1 H), 1.93 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.8, 171.3, 147.6, 137.2, 136.6, 130.2, 123.7, 75.8, 67.5, 42.2, 27.0, 26.9 ppm. MS: *m*/*z* (%) = 259 (74) $[M]^+$, 214 (100), 259 (74), 231 (66), 200 (40), 185 (60), 184 (66), 129 (50), 115 (79). IR (film): $\tilde{\nu}$ = 1714, 1641, 1596, 1510, 1344, 1137, 1089, 852 cm^{-1}. $C_{14}H_{13}NO_4$ (259.08): calcd. C 64.86, H 5.05, N 5.41; found C 64.92, H 5.27, N 5.44.

5-(Thien-2-yl)-3,4,7,7a-tetrahydrocyclopenta[*b*]pyran-6(2*H*)-one (10f): Yield: 365.3 mg (83%), yellow solid; m.p. 70–71 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, J = 3.0 Hz, 1 H), 7.40 (d, J = 5.0 Hz, 1 H), 7.12 (dd, J = 5.0, 3.0 Hz, 1 H), 4.51 (br. d, J = 6.0 Hz, 1 H), 4.11 (br. d, J = 11.0 Hz, 1 H), 3.79 (m, 1 H), 3.46 (br. d, J = 15.0 Hz, 1 H), 2.87 (dd, J = 18.6, 6.0 Hz, 1 H), 2.61 (dt, J = 15.0, 10.0 Hz, 1 H), 2.48 (dd, J = 18.6, 2.7 Hz, 1 H), 1.90 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.3, 166.4, 131.1, 130.9, 127.7, 126.8, 126.4, 75.3, 69.1, 41.6, 26.6, 26.0 ppm. MS: *m*/*z* (%) = 220 (77) $[M]^+$, 192 (100), 191 (64), 178 (32), 150 (36), 135 (36). IR (KBr): $\tilde{\nu}$ = 1710, 1630, 1429 cm^{-1}. $C_{12}H_{12}O_2S$ (220.06): calcd. C 65.43, H 5.49; found C 65.31, H 5.22.

6-Phenyl-2,3,4,5,8,8a-hexahydro-7*H*-cyclopenta[*b*]oxepin-7-one (10g): Yield: 355.9 mg (78%), syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (m, 5 H), 4.77 (m, 1 H), 3.90 (m, 1 H), 3.66 (m, 1 H), 2.94 (dd, J = 18.3, 6.7 Hz, 1 H), 2.77 (m, 1 H), 2.50 (dd, J = 18.3, 3.1 Hz, 1 H), 1.93–1.75 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.1, 167.5, 137.9, 130.4, 129.3, 128.6, 128.2, 75.5, 67.5, 42.4, 27.1, 26.8, 26.5 ppm. MS: *m*/*z* (%) = 228 (100) $[M]^+$, 200 (36), 172 (38), 144 (49), 141 (33), 128 (35), 116 (48), 115 (48). IR (film): $\tilde{\nu}$ = 1689, 1112, 978, 700 cm^{-1}. $C_{15}H_{16}O_2$ (228.12): calcd. C 78.92, H 7.06; found C 79.03, H 7.35.

6-Phenyl-2,3,8,8a-tetrahydrocyclopenta[*e*][1,4]dioxepin-7(5*H*)-one (10h): Yield: 345.1 mg (75%), syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.27 (m, 5 H), 5.04–4.95 (m, 2 H), 4.65 (d, J = 18.7 Hz, 1 H), 4.14 (d, J = 13.0 Hz, 1 H), 3.98 (d, J = 13.0 Hz, 1 H), 3.84 (td, J = 10.7, 2.0 Hz, 1 H), 3.64 (td, J = 10.7, 2.0 Hz, 1 H), 2.99 (dd, J = 16.4, 6.6 Hz, 1 H), 2.54 (dd, J = 18.4, 2.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.6, 167.7, 138.1, 130.5, 129.2, 128.6, 128.2, 78.9, 75.8, 72.6, 71.4, 42.8 ppm. MS: *m*/*z* (%) = 230 (32) $[M]^+$, 115 (90), 172 b (38), 142 (33), 141 (100), 116 (62), 128 (36), 102 (35). IR (film): $\tilde{\nu}$ = 1703, 1442, 1284, 1141, 1005, 780, 767, 702, 556 cm^{-1}. $C_{14}H_{14}O_3$ (230.09): calcd. C 73.03, H 6.13; found C 72.80, H 6.23.

6-(4-Methoxyphenyl)-2,3,8,8a-tetrahydrocyclopenta[*e*][1,4]dioxepin-7(5*H*)-one (10i): Yield: 447.4 mg (86%), syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (dd, J = 6.4, 2.4 Hz, 2 H), 6.94 (dd, J = 6.4, 2.4 Hz, 2 H), 5.02 (d, J = 18.4 Hz, 1 H), 4.93 (d, J = 6.4 Hz, 1 H), 4.65 (d, J = 18.4 Hz, 1 H), 4.13 (d, J = 13.6 Hz, 1 H), 3.97 (d, J = 13.4 Hz, 1 H), 3.87–3.80 (m, 4 H), 3.66 (t, J = 8.4 Hz, 1 H), 2.95 (dd, J = 18.4, 6.8 Hz, 1 H), 2.52 (dd, J = 18.4, 2.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.8, 170.7, 159.6, 137.8, 129.9, 122.5, 113.9, 78.5, 75.8, 72.4, 71.2, 55.2, 42.6 ppm. MS: *m*/*z* (%) = 274 (100) $[M]^+$, 273 (96), 216 (68), 186 (46), 128 (47). IR (film): $\tilde{\nu}$ = 1700, 1501, 1436, 1354, 1241, 1138, 1044 cm^{-1}. $C_{15}H_{16}O_4$ (260.10): calcd. C 69.22, H 6.20; found C 69.34, H 6.07.

6-(4-Nitrophenyl)-2,3,8,8a-tetrahydrocyclopenta[*e*][1,4]dioxepin-7(5*H*)-one (10j): Yield: 385.1 mg (70%), syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, J = 9.0 Hz, 2 H), 7.47 (d, J = 9.0 Hz, 2 H), 4.99 (m, 2 H), 4.64 (d, J = 18.8 Hz, 1 H), 4.16 (br. d, J = 13.2 Hz, 1 H), 4.01 (m, 1 H), 3.86 (m, 1 H), 3.66 (m, 1 H), 3.01 (m, 1 H), 2.56 (dd, J = 18.6, 2.7 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.9, 170.9, 147.8, 137.3, 136.8, 130.3, 123.9, 78.6, 75.9, 72.8, 71.7, 42.7 ppm. MS: *m*/*z* (%) = 275 (32) $[M]^+$, 202 (100), 58 (99), 115 (94), 141 (72), 140 (59), 139 (54), 170 (48), 171 (45). IR (film): $\tilde{\nu}$ = 1716, 1516, 1352, 1133, 852, 703, 557 cm^{-1}. $C_{14}H_{13}NO_5$ (275.08): calcd. C 61.09, H 4.76, N 5.09; found C 60.96, H 4.88, N 5.18.

5-[(*E*)-2-phenylethenyl]-3,4,7,7a-tetrahydrocyclopenta[*b*]pyran-6(2*H*)-one (10k): Yield: 403.4 mg (84%), syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, J = 16.4 Hz, 1 H), 7.47 (d, J = 8.0 Hz, 2 H), 7.34–7.31 (m, 2 H), 7.26–7.23 (m, 1 H), 6.72 (d, J = 16.4 Hz, 1 H), 4.40 (d, J = 5.2 Hz, 1 H), 4.04 (dd, J = 9.6, 2.0 Hz, 1 H), 3.71 (t, J = 8.8 Hz, 1 H), 3.11 (br. d, J = 14.6 Hz, 1 H), 2.76 (dd, J = 18.4, 6.4 Hz, 1 H), 2.39 (dd, J = 18.4, 2.8 Hz, 1 H), 2.36–2.42 (m, 1 H), 1.91–1.84 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.3, 168.2, 137.3, 134.5, 133.1, 128.6, 128.1, 126.6, 116.1, 75.3, 67.2, 42.3, 26.8, 25.9 ppm. MS: *m*/*z* (%) = 240 (54) $[M]^+$, 212 (100), 211 (84), 144 (57), 170 (44), 154 (32), 128 (25). IR (film): $\tilde{\nu}$ = 1708, 1674, 1582, 1348, 1128, 856, 713, 560 cm^{-1}. $C_{16}H_{16}O_2$ (240.12): calcd. C 79.97, H 6.71; found C 79.88, H 6.56.

Typical Procedure for the Conversion of Furandiol 9 into Cyclopentenone 10: To a 100-mL round-bottomed flask was added spiroacetal enol ether **9** (20 mmol), $ZnCl_2$ (30 mg), water (20 mL), and ethylene glycol dimethyl ether (20 mL). The reaction mixture was heated under reflux until the starting material was fully consumed (monitored by TLC). The reaction mixture was then extracted with diethyl ether. The combined organic layer was washed with brine and dried with Na_2SO_4. Removal of the solvent yielded a crude product, which was purified by flash chromatography to afford cyclopentenone **10**.

Procedure for the Conversion of 14 into 10b: To a solution of **14** (301 mg, 1 mmol) in THF (5 mL) was added 2% HCl (3 mL). The reaction mixture was stirred at room temperature for 30 min until the starting material was fully consumed (monitored by TLC). Then, 5% NaOH was added to the mixture until pH 13. The reaction mixture was stirred at room temperature for 4 h and then extracted with diethyl ether. The combined organic layer was washed with brine and dried with Na_2SO_4. Removal of solvents yielded a crude product, which was purified by chromatography to afford **10b** (182 mg, 85%).

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[11] Spectroscopic data for compound **20i**: IR (KBr): $\tilde{\nu}$ = 3415, 2934, 1708, 1610, 1513, 1250, 1179, 1123, 1031, 815 cm^{-1}. H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 5.6 Hz, 0.6 H), 7.56 (d, J = 6.0 Hz, 0.4 H), 7.00 (m, J = 8.8 Hz, 2 H), 6.80 (d, J = 8.8 Hz, 2 H), 6.33 (d, J = 5.6 Hz, 0.4 H), 6.25 (d, J = 6.0 Hz, 0.6 H), 4.54 (dd, J = 20.8, 8.8 Hz, 0.8 H), 3.78–3.56 (m, 10 H), 3.03 (dd, J = 20.8, 8.8 Hz, 1.2 H) ppm. MS (ESI): *m*/*z* = 277 $[M - H]^+$.

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