Unusual removal of the ethylene ketal protection from 2,3-dichloro-4,4-ethylenedioxycyclopent-2-en-1-one under alkaline conditions. Simple synthesis of naturally occurring cyclopentenedione analogs

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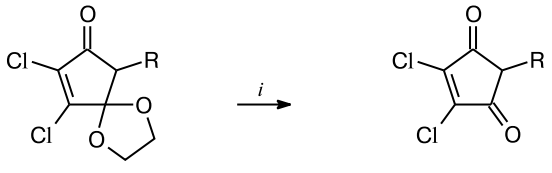
A reaction of 2,3-dichloro-4,4-ethylenedioxycyclopent-2-en-1-one with MeONa in MeOH to furnish 2-chloro-3-hydroxycyclopent-2-en-1,4-dione has been studied. The latter under the action of CH_2N_2 has been converted to the corresponding enol ether. This methodology has been used for the synthesis of 4-chloro-5-methoxy-2-cinnamylidenecyclopent-4-en-1,3-diones and related compounds starting from the parent dichlorocyclopentenone.

Key words: 2,3-dichloro-4,4-ethylenedioxycyclopent-2-en-1-one, ketals, aldol reaction, organochlorine compounds.

Cyclic ketone acetals, in particular 1,3-dioxolanes, are inert in water and alcohol solutions of strong alkalis[1] and can be hydrolyzed upon the action of mineral[2,3] and organic acids,[4,5] $Py(HF)_x$,[6] Lewis acids[1,2,7] (Al, Ti, B, Pd compounds, *etc.*), SiO_2,[8] Me_3SiI,[9] $LiBF_4$,[10] dimethyldioxirane,[11] *etc*.

We encountered the problem with hydrolysis of dioxolane protecting group[12,13] during the search for mild and convenient methods for the transformation of chlorine-containing 4,4-ethylenedioxycyclopentenones **1** and **2** into corresponding cyclopentenediones **3** and **4** (Scheme 1). Testing some of the procedures mentioned above for these purposes was unsuccessful. It turned out that hydrolysis of the ethylene ketal protecting group of compounds **1** and **2** is successful only under extreme conditions under the action of 98% aq. H_2SO_4, as it was shown earlier[14] for ketal **2**.

Scheme 1

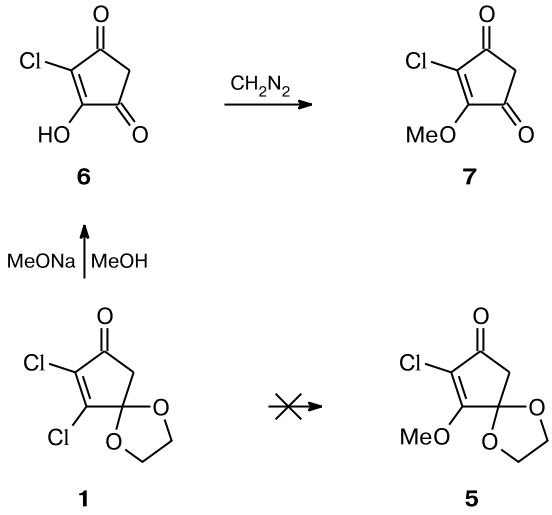


1, 2 **3, 4**

R = H (**1**, **3**), Cl (**2**, **4**)
i. 98% aq. H_2SO_4, 0 °C, 1 h.

We observed an interesting example of nontrivial removal of the dioxolane protecting group during the reaction of dichlorocyclopentenone **1** with MeONa in MeOH (Scheme 2). Initially, we planed to obtain vinylog ether **5** by the Ad_NE substitution of the Cl atom at C(3) of dichlorocyclopentenone **1** for the methoxide anion. Rather, this reaction afforded a new compound, *viz.*, the enolized cyclopentanetrione derivative **6**, in almost quantitative yield. The latter was converted into the enol ether **7** upon treatment with CH_2N_2.

Scheme 2



6 **7**

1 **5**

Unlike for compound **1**, the reaction of trichlorocyclopentenone **2** with MeONa took several directions and was accompanied by formation of a mixture of products and, therefore, we did not study it. As it can be seen, the formal result of the reaction of ketal **1** with MeONa is

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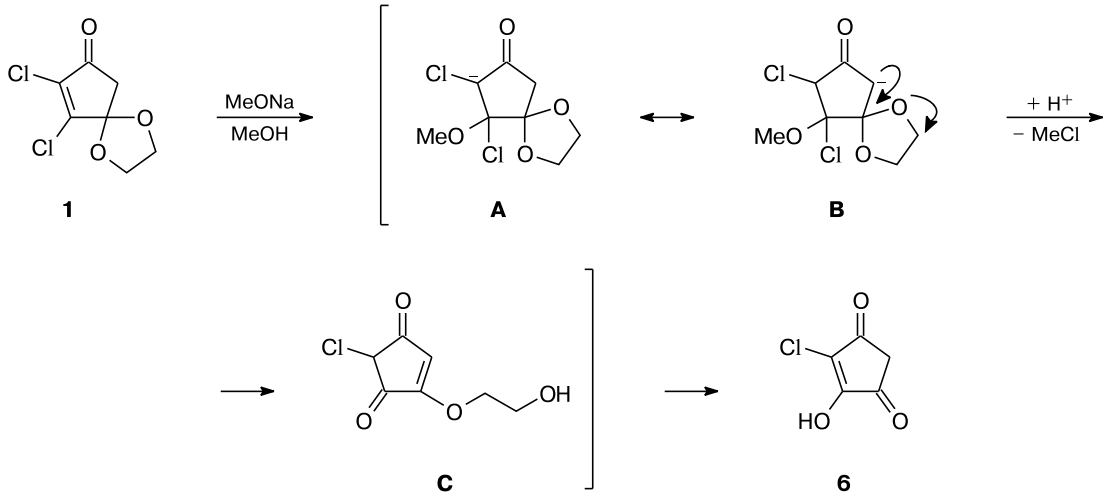
Scheme 3



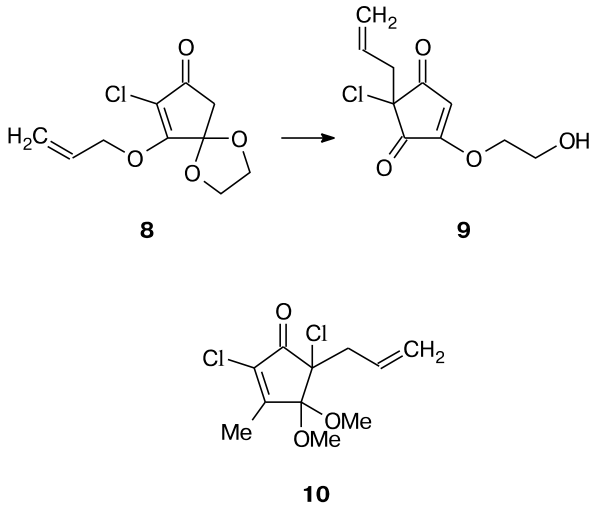
a "double hydrolysis" of expected compound **5** in the dioxolane and enol ether parts. We will discuss a possible version of this interesting transformation below (Scheme 3). It is obvious that the initial attack of the MeO anion on the activated enone system **1** generates carbanion **A**, which by trivial removal of the Cl atom at C(3) should have led to the product of Ad_NE substitution **5**.[15] However, the reaction takes another way. The initial carbanion **A** is converted into the isomeric carbanion **B**, which after the dioxolane ring opening and removal of the MeCl (or *vice versa*) gives enedione **C**. Aqueous treatment of the reaction mixture (without acidification) quickly leads to trione **6**.

A facile dioxolane ring opening[16] during the thermal Claisen rearrangement of allyl vinyl ether **8** into dione **9** should be noted as a precedent close to the cycle of transformations under discussion (Scheme 4). We also found an unusual example of elimination of MeOCl from compound **10** with generation of the corresponding cyclopentadienone derivative in Ref. 17. Unlike suggested intermediate **C**, diketone **9** has been isolated in the individual state, it is hydrolytically stable enough, it can stand aqueous treatment and chromatography on SiO_2. As it can be seen from the structures **9** and **C**, the latter has a labile H atom at C(2) and, as cyclopentane triketones,[18] should possess strong acidic properties. It is likely that even upon aqueous treatment of the reaction mixture, some sort of acidification of the medium and hydrolysis of the enol ether **C** take place. In point of fact, the trione **6**, partially existing in the reaction medium, after addition of water initiates fast hydrolysis of the intermediate **C** ("self-catalysis").

Further, we used the "C(3)-enol formation—C(4)-deketalization" version developed for ketal **1** in the construction of the 2-cinnamylidenecyclopentenedione structures **11** and **12** (Scheme 5).

The condensation of ketone **1** lithium enolate with cinnamaldehyde and cinnamoyl chloride proceeds smoothly

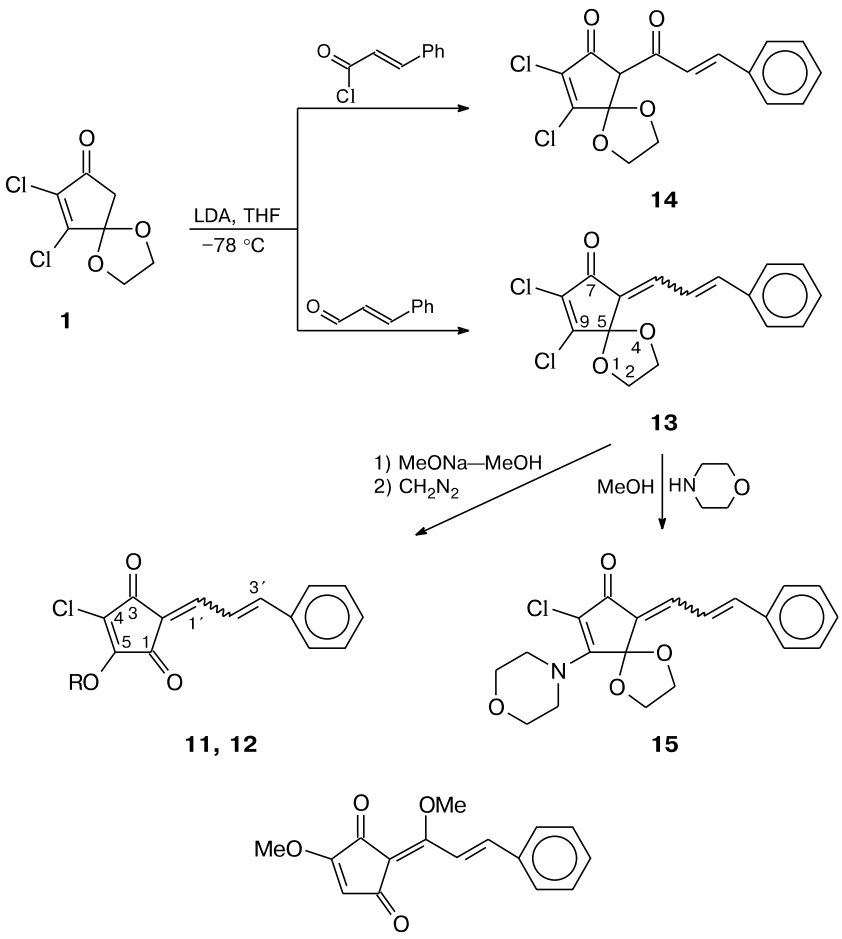
Scheme 4



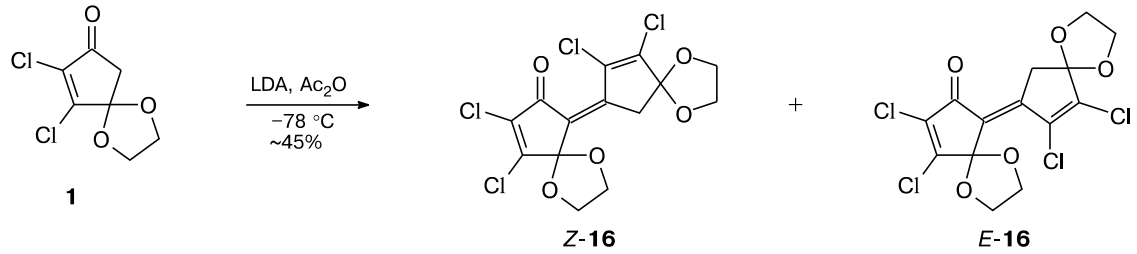
to form the crotonization **13** (as a mixture of *Z*/*E*-isomers in the ratio ~6 : 5) and substitution **14** products. Compound **13** upon treatment with MeONa and subsequent methylation of the enol **11** obtained by the action of CH_2N_2 was converted into enol ether **12**. Compound **12** can be synthesized by similar for **1** crotonization of the vinyl ether **7**, however, this reaction is accompanied by intensive resinification. The higher reactivity of the dichloro-substituted double bond as compared to the side bonds in compound **13** is confirmed by the chemoselective formation of the vinylog amide **15** in the reaction with morpholine.

Unexpected result was observed when acetic anhydride was used in the condensation with dichloroketone **1**. The product of aldol condensation of two ketone molecules **1**, *viz.*, a dimeric compound **16** as a mixture of *Z*,*E*-isomers

Scheme 5



Scheme 6



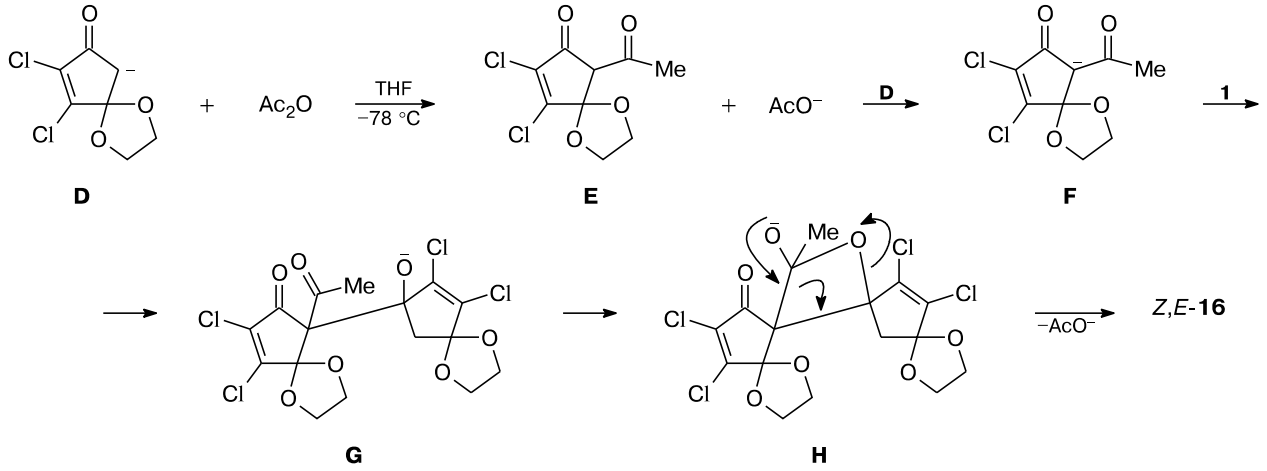
(Scheme 6) separable by column chromatography on SiO_2, was isolated in this case.

Note that the dimer **16** is not formed in the conversion **1** → **16** without addition of Ac_2O, as well as to the model condensations of equimolar amounts of ketone **1** and its Li enolate. Here, the role of Ac_2O promoting the self-condensation of compound **1** is obvious. Apparently, the process can be presented as Scheme 7.

In the initial step, the addition of Ac_2O to a solution of Li enolate **D** leads to the strong CH acid in form of β-diketone **E**, which is rapidly metallated with unreacted enolate **D** to produce anion **F** capable to react with the liberated ketone **1**. The ketol **G** generated at this step affords the *E*,*Z*-isomeric mixture **16** by the mechanism of 1,3-diketone cleavage through the cyclic oxetane **H** and removal AcO^- (see Scheme 7).

The compounds **11**—**15** obtained are considered by us as close analogs of naturally occurring antifungal cyclopentenediones coruscanones A and B,[18] calitrone,[19] stigmachamone,[20] methyllucidone,[21] *etc*.

Scheme 7



Experimental

IR spectra were recorded on a Specord M-80 and Shimadzu IR Prestige-21 spectrophotometers for neat samples or in Nujol. NMR spectra were recorded on a Bruker AM-300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75.47 MHz) for solutions in $CDCl_3$ using Me_4Si as the internal standard. Mass spectra were recorded on a Thermo Finnigan MAT 95XP (the temperature of the ionizing chamber was 200 °C, the temperature of the sample injection was 5—270 °C, the temperature was raised at the rate of 22 °C min^{-1}) and Shimadzu LCMS-2010 instruments (chemical ionization under atmospheric pressure). The reaction course was monitored by TLC on Silufol and Sorbphil plates with visualization of compounds by charring or in the alkaline solution of potassium permanganate. The products synthesized were isolated by column chromatography on silica gel (30—60 g of adsorbent per 1 g of compound), freshly distilled solvents were used as the eluents.

2-Chloro-3-hydroxycyclopent-2-en-1,4-dione (6). A solution of compound **1** (0.5 g, 2.39 mmol) in THF (2 mL) was added to a stirred solution of MeONa (3 mL) obtained from Na (0.11 g, 4.78 mmol) and MeOH (3 mL). The reaction mixture was stirred for 1 h, then acidified with concentrated HCl to pH 2. The solvents were evaporated, the mixture was diluted with brine (5 mL) and extracted with EtOAc (3×5 mL). The combined organic extracts were dried with $MgSO_4$, the solvent was evaporated to obtain compound **6** in quantitative yield (0.35 g) as white crystals, m.p. 96—98 °C. IR, ν/cm^{-1}: 721, 769, 901, 935, 975, 1034, 1080, 1126, 1259, 1355, 1377, 1458, 1612, 1647, 1685, 1751, 2852, 2922, 2953, 3392. ^{1}H NMR, δ: 3.10 (s, 2 H, CH_2); 5.30 (br.s, 1 H, OH). ^{13}C NMR, δ: 41.14 (C(5)), 125.03 (C(2)), 165.19 (C(3)), 189.14, 192.18 (C(1), C(4)).

2-Chloro-3-methoxycyclopent-2-en-1,4-dione (7). An ethereal solution of CH_2N_2 was added to a stirred solution of compound **6** (0.35 g, 2.39 mmol) in diethyl ether (10 mL) until evolution of the gas stopped. The reaction mixture was stirred for 30 min, dried with $MgSO_4$, the solvent was evaporated to obtain compound **7** in quantitative yield (0.38 g) as beige crystals, m.p. 110—112 °C. Found (%): C, 45.35; H, 3.53; Cl, 21.39. $C_6H_5ClO_3$. Calculated (%): C, 44.88; H, 3.14; Cl, 22.08. IR, ν/cm^{-1}: 613, 669, 690, 798, 869, 904, 927, 949, 968, 983, 1037, 1064, 1082, 1128, 1184, 1203, 1259, 1303, 1330, 1375, 1454, 1612, 1712, 1749, 2856, 2920, 2959, 3373. ^{1}H NMR, δ: 3.76 (s, 2 H, CH_2); 5.02 (s, 3 H, OMe). ^{13}C NMR, δ: 42.03 (C(5)), 59.69 (OMe), 128.90 (C(2)), 164.46 (C(3)), 188.50, 191.47 (C(1), C(4)).

(6*E*,*Z*)-8,9-Dichloro-6-(3-phenylprop-2(*E*)-enylidene)-1,4-dioxaspiro[4.4]non-8-en-7-one (13). A solution of BuLi in hexane (0.86 *M*, 3.4 mL, 2.87 mmol) was added dropwise under argon to a solution of Pr^i_2NH (0.41 mL, 2.87 mmol) in anhydrous THF (10 mL) cooled to −10 °C. The reaction mixture was stirred for 15 min followed by a dropwise addition of a solution of compound **1** (0.5 g, 2.39 mmol) in THF (3 mL). After 15 min, the reaction mixture was cooled to −78 °C followed by a dropwise addition of a solution of cinnamaldehyde (0.3 mL, 2.39 mmol) in THF (6 mL), the mixture was stirred for 1 h at −78 °C and for 2 h at ~20 °C, then, a saturated solution of NH_4Cl, (2—3 mL) was added and the stirring was continued for 10 min, then, THF was evaporated, and the residue extracted with $CHCl_3$. The combined organic layers were washed with brine, dried with $MgSO_4$, and concentrated. The residue was recrystallized from Et_2O to obtain compound **13** (0.60 g, 77%) as a mixture of isomers in the ratio ~6 : 5 (determined from the correlation of integral intensities of the signals for the protons at C(3′) atom).[22] White powder, m.p. 120—122 °C. IR, ν/cm^{-1}: 690, 825, 908, 951, 983, 1004, 1126, 1161, 1186, 1450, 1460, 1571, 1599, 1614, 1632, 1701, 1720, 3024, 3057, 3143, 3174. *Major isomer.* ^{1}H NMR, δ: 4.30—4.63 (m, 4 H, OCH_2CH_2O); 7.07 (m, 1 H, H(1′)); 7.26 (d, 1 H, H(3′), J = 10.3 Hz); 7.38, 7.46 (both m, 3 H each, H(2′), Ph). ^{13}C NMR, δ: 66.92 (C(2), C(3)), 108.05 (C(5)), 121.63 (C(1′)), 127.77, 128.85, 129.86, 135.55 (Ph), 129.92 (C(8)), 134.97 (C(3′)), 136.41 (C(6)), 145.37 (C(2′)), 155.77 (C(9)), 182.54 (C(7)). *Minor isomer.* ^{1}H NMR, δ: 4.30—4.63 (m, 4 H, OCH_2CH_2O); 7.05 (d, 1 H, H(1′), J = 10.5 Hz); 7.27 (d, 1 H, H(3′), J = 10.3 Hz); 7.38, 7.46 (both m, 3 H each, H(2′), Ph). ^{13}C NMR, δ: 66.99 (C(2), C(3)), 107.68 (C(5)), 123.27 (C(1′)), 127.52, 128.73, 129.65, 135.66 (Ph), 130.15 (C(8)), 136.41 (C(6)), 137.79 (C(3′)), 145.26 (C(2′)), 154.18 (C(9)), 182.77 (C(7)).

(6*E*,*Z*)-8,9-Dichloro-6-(1-oxo-3-phenylprop-2(*E*)-enyl)-1,4-dioxaspiro[4.4]non-8-en-7-one (14) was obtained similarly to **13** from compound **1** (0.3 g, 1.43 mmol) and cinnamoyl chloride

(0.24 g, 1.43 mmol). The yield was 0.1 g (~21%). Bright yellow crystals, m.p. 180—182 °C. IR, ν/cm^{-1}: 690, 791, 824, 953, 991, 1024, 1092, 1143, 1188, 1205, 1271, 1450, 1462, 1595, 1604, 1638, 1665, 1736, 3024, 3059, 3138, 3179. ^{1}H NMR, δ: 2.89 (s, 1 H, H(6)); 4.12, 4.28 (both m, 2 H each, OCH_2CH_2O); 6.45 (d, 1 H, H(2′), J = 16.1 Hz); 7.39 (m, 3 H, Ph); 7.54 (d, 2 H, Ph, J = 6.2 Hz); 7.78 (d, 1 H, H(3′), J = 16.1 Hz). ^{13}C NMR, δ: 46.84 (C(6)), 66.83 (OCH_2CH_2O), 108.74 (C(5), 117.29 (C(2′)), 128.96 (C(8)), 128.73, 129.34, 130.70, 134.10 (Ph), 146.99 (C(3′)), 158.80 (C(9)), 171.71 (C(1′)), 191.61 (C(7)).

4-Chloro-5-hydroxy-2(*Z*,*E*)-(3-phenylprop-2(*E*)-en-1-ylidene)cyclopent-4-en-1,3-dione (11) was obtained similarly to **6** from compound **13** (0.1 g, 0.31 mmol) and Na (0.014 g, 0.61 mmol) in MeOH (3 mL) as a mixture of *E*/*Z*-isomers (in the ratio ~6 : 5 determined from the correlation of integral intensities of the signals for the protons at C(2′) atom). The yield was 0.08 g (~98%). Pale yellow crystals, m.p. 98—99 °C. IR, ν/cm^{-1}: 721, 758, 783, 839, 983, 993, 1060, 1143, 1168, 1211, 1259, 1271, 1363, 1377, 1458, 1647, 1688, 1695, 2950, 3196. *Major isomer*. ^{1}H NMR, δ: 7.24 (d, 1 H, H(1′), J = 11.79 Hz); 7.43 (m, 2 H, Ph); 7.65 (m, 4 H, H(3′), Ph); 8.19 (dd, H(2′), ^3J = 15.72 Hz, ^2J = 11.79 Hz). ^{13}C NMR, δ: 124.14 (C(2′)), 125.81 (C(2)), 129.63, 130.62, 131.94, 137.37 (Ph), 136.41 (C(4)), 139.22 (C(3′), 150.22 (C(1′)), 165.68 (C(5)), 185.00 (C(1)), 187.54 (C(3)). *Minor isomer*. ^{1}H NMR, δ: 7.27 (d, 1 H, H(1′), J = 11.78 Hz); 7.43 (m, 4 H, Ph); 7.65 (m, 2 H, H(3′), Ph), 8.07 (dd, H(2′), ^3J = 15.71 Hz, ^2J = 11.78 Hz). ^{13}C NMR, δ: 124.26 (C(2′)), 125.81 (C(2)), 129.63, 130.62, 131.94, 137.37 (Ph), 136.41 (C(4)), 139.22 (C(3′), 150.33 (C(1′)), 165.68 (C(5)), 185.00 (C(1)), 187.54 (C(3)).

4-Chloro-5-methoxy-2(*Z*,*E*)-(3-phenylpropen-2(*E*)-ylidene)-cyclopent-4-en-1,3-dione (12) was obtained similarly to **7** by methylation of compound **11** (0.08 g, 0.309 mmol) as a mixture of *Z*/*E*-isomers. The yield was 0.08 g (~94%). Bright yellow crystals, m.p. 229—231 °C. MS, *m*/*z*: 275 $[MH]^+$, 259 $[M - Me]^+$. IR, ν/cm^{-1}: 759, 837, 929, 1039, 1088, 1126, 1223, 1267, 1290, 1327, 1373, 1448, 1601, 1684, 1702, 1750, 2853, 2922, 2953, 3022, 3063, 3391. *Major isomer*. ^{1}H NMR, δ: 4.39 (s, 3 H, OMe); 7.19 (m, 2 H, H(1′), H(3′)); 7.35 (m, 3 H, Ph); 7.56 (m, 2 H, Ph), 8.10 (dd, H(2′), J = 15.0 Hz, J = 11.7 Hz). ^{13}C NMR, δ: 60.21 (OMe), 122.98 (C(2′)), 127.28 (C(2)), 128.36, 128.93, 130.61, 135.37 (Ph), 133.40 (C(4)), 139.53 (C(3′)), 149.62 (C(1′)), 163.40 (C(5)), 183.76 (C(1)), 184.63 (C(3)). *Minor isomer*. ^{1}H NMR, δ: 4.41 (s, 3 H, OMe); 7.19 (m, 2 H, H(1′), H(3′)); 7.35 (m, 3 H, Ph); 7.56 (m, 2 H, Ph); 8.02 (dd, H(2′), J = 15.7 Hz, J = 11.9 Hz). ^{13}C NMR, δ: 60.21 (OMe), 122.68 (C(2′), 123.30 (C(2)), 128.36, 128.93, 130.61, 135.37 (Ph), 133.40 (C(4)), 139.74 (C(3′)), 149.90 (C(1′)), 163.10 (C(5)), 183.76 (C(1)), 184.14 (C(3)).

8-Chloro-9-morpholino-6(*E*,*Z*)-(3-phenyl-2(*E*)-propen-1-ylidene)-1,4-dioxaspiro[4.4]non-8-en-7-one (15). A solution of morpholine (0.13 mL, 1.49 mmol) in MeOH (5 mL) was added dropwise to a stirred solution of compound **13** (0.16 g, 0.49 mmol) in MeOH (5 mL). The reaction mixture was stirred for 3 h at ~20 °C until complete conversion of the starting compound (TLC monitoring). Methanol was evaporated, the residue was diluted with cold H_2O (10 mL) and extracted with $CHCl_3$ (4×20 mL). The combined extracts were washed with brine, dried with $MgSO_4$, the solvent was evaporated. The residue was purified by column chromatography on silica gel (EtOAc—light petroleum, 1 : 4) to obtain compound **15** (0.12 g, ~65%) as clear pale yellow crystals, m.p. 144—146 °C. MS, *m*/*z*: 376, 374 $[MH]^+$. *Major isomer*. ^{1}H NMR, δ: 3.25 (t, 4 H, CH_2N, J = 4.5 Hz, J = 4.7 Hz); 3.66 (t, 4 H, CH_2O, J = 4.6 Hz, J = 4.8 Hz); 4.36 (s, 4 H, OCH_2CH_2O); 6.71 (d, 1 H, H(1′), J = 15.9 Hz); 6.91 (d, 1 H, H(3′), J = 11.5 Hz); 7.25—7.38 (m, 4 H, H(2′), *o*-Ph, *p*-Ph); 7.45 (d, 2 H, *m*-Ph, J = 7.3 Hz). ^{13}C NMR, δ: 48.49 (CH_2N), 64.88 (CH_2O), 66.34 (OCH_2CH_2O), 109.52 (C(5), 109.93 (C(8)), 123.99 (C(2′)), 127.12, 128.47, 128.70, 136.35 (Ph), 129.39 (C(3′)), 133.38 (C(6)), 140.49 (C(1′)), 156.20 (C(9)), 182.57 (C(7)). *Minor isomer*. ^{1}H NMR, δ: 3.25 (t, 4 H, CH_2N, J = 4.5 Hz, J = 4.7 Hz); 3.66 (t, 4 H, CH_2O, J = 4.6 Hz, J = 4.8 Hz); 4.36 (s, 4 H, OCH_2CH_2O); 6.34 (d, 1 H, H(1′), J = 11.3 Hz); 6.84 (d, 1 H, H(3′), J = 11.7 Hz); 7.25—7.38 (m, 4 H, H(2′), *o*-Ph, *p*-Ph); 7.45 (d, 2 H, *m*-Ph, J = 7.3 Hz). ^{13}C NMR, δ: 48.72 (CH_2N), 65.89 (CH_2O), 66.34 (OCH_2CH_2O), 110.28 (C(5)), 110.80 (C(8)), 121.86 (C(2′)), 128.91 (C(3′)), 126.93, 128.47, 128.70, 136.12 (Ph), 133.50 (C(6)), 142.07 (C(1′)), 158.63 (C(9)), 183.09 (C(7)).

(6*E*,*Z*)-8,8′,9,9′-Tetrachloro-6,7′-bi(1,4-dioxaspiro[4.4]-nonane)-6(7′),8,8′-trien-7-ones (16). A solution of BuLi in hexane (2.3 *M*, 1.14 mL, 2.63 mmol) was added dropwise under argon to a solution of Pr^i_2NH (0.37 mL, 2.63 mmol) in anhydrous THF (10 mL) cooled to −10 °C. The reaction mixture was stirred at this temperature for 15 min followed by a dropwise addition of a solution of compound **1** (0.5 g, 2.39 mmol) in THF (3 mL). After 15 min, the reaction mixture was cooled to −78 °C and a solution of acetic anhydride (0.22 mL, 2.39 mmol) in THF (6 mL) was added dropwise to it. The reaction mixture was stirred for 1 h at −78 °C and 2 h at ~20 °C, diluted with saturated aq. NH_4Cl, (2—3 mL), and stirred for 10 min, THF was evaporated, the residue was extracted with $CHCl_3$. The combined organic layers were washed with brine, dried with $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (EtOAc—light petroleum, 1 : 4) to obtain compound **16** (0.12 g, ~45%) as colorless needle-like crystals, m.p. 228—230 °C. Found (%): C, 42.44; H, 2.33; Cl, 35.05. $C_{14}H_{10}Cl_4O_5$. Calculated (%): C, 42.03; H, 2.52; Cl, 35.45. IR, ν/cm^{-1}: 565, 856, 950, 989, 1035, 1058, 1170, 1201, 1460, 1616, 1635, 1718, 2953. MS, *m*/*z*: 399, 401, 403 $[MH]^+$. (*Z*)-*Isomer*. ^{1}H NMR, δ: 3.57 (s, 2 H, CH_2); 4.10, 4.23 (both m, 2 H each, OCH_2CH_2O); 4.46, 4.54 (both m, 2 H each, OCH_2CH_2O). ^{13}C NMR, δ: 41.21 (CH_2), 66.34, 66.61 (OCH_2CH_2O), 109.00 (C(5)), 110.64 (C(5′)), 127.83, 132.66 (C(8′), C(9′)), 137.39 (C(8)), 145.14 (C(6)), 149.42 (C(7′)), 154.21 (C(9)), 178.96 (C=O). (*E*)-*Isomer*. ^{1}H NMR, δ: 3.09 (s, 2 H, CH_2); 4.07, 4.25 (both m, 2 H each, OCH_2CH_2O); 4.32, 4.51 (both t, 2 H each, OCH_2CH_2O, J = 7.10 Hz). ^{13}C NMR, δ: 41.31 (CH_2), 66.44, 67.02 (OCH_2CH_2O), 109.10 (C(5)), 110.75 (C(5′)), 124.94, 132.76 (C(8′), C(9′)), 137.52 (C(8)), 145.22, 149.51 (C(6), C(7′)), 154.28 (C(9)), 179.03 (C=O).

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