ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 3, pp. 397–401. © Pleiades Publishing, Ltd., 2008.
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Specificity of the Reaction of 2,3-Dichloro-4,4-dimethoxy-5-(2-methylfuran-3-yl)cyclopent-2-en-1-one with Amines

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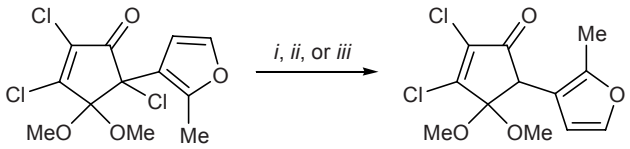
Received March 30, 2007

Abstract—2,3-Dichloro-4,4-dimethoxy-5-(2-methylfuran-3-yl)cyclopent-2-en-1-one reacted with diethyl- and dipropylamines to give products of Ad_NE replacement of the chlorine atom at the vinylic C^3 atom and substitutive opening of the furan ring with simultaneous deprotection of the dimethyl acetal moiety in the 2,3-dichlorocyclopentenone fragment.

DOI: 10.1134/S1070428008030147

While attempting to generate anionoid intermediates from the furan fragment of trichlorocyclopentenone **I** [1] by the action of lithium diisopropylamide (tetrahydrofuran, –78°C) we revealed smooth selective reductive dechlorination at the C^5–Cl bond with formation of dichlorocyclopentenone **II** (Scheme 1). The same compound was obtained later by treatment of trichlorocyclopentenone **I** with $CrCl_2$ [2], as well as by the action of zinc in methanol in the presence of ammonium chloride (in a poor yield).

Scheme 1.



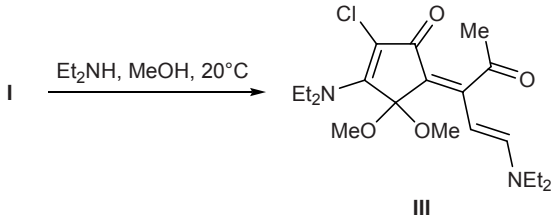
I **II**

i: $(i\text{-Pr})_2NLi$, THF, –78°C (yield 60%); *ii*: $CrCl_2$, Me_2CO (68%); *iii*: Zn, NH_4Cl, MeOH (20%).

We previously described reactions of trichlorocyclopentenone **I** with secondary amines, such as diethylamine, morpholine, pyrrolidine, dipropylamine, etc. These reactions afforded unusual products of substitutive opening of the furan ring. For example, compound **III** was formed in the reaction of **I** with diethylamine [3] (Scheme 2).

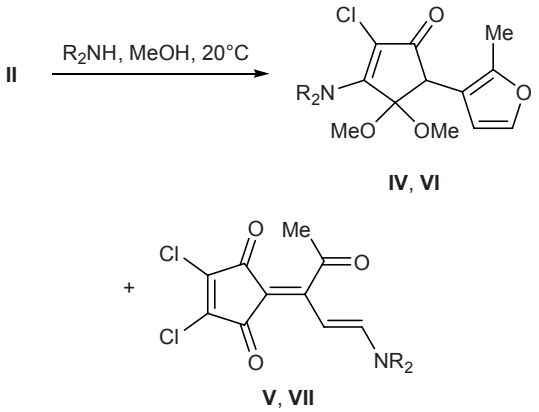
Dichloride **II** obtained from trichlorocyclopentenone **I** was also brought into reactions with amines. However, the behavior of **II** in the reaction with diethylamine differed from the behavior of trichloro derivative **I**. We isolated two main products at a ratio of ~2:1. On the basis of spectral data, they were assigned structures **IV** and **V** (minor product). Likewise, the reaction of **II** with dipropylamine gave a mixture of compounds **VI** and **VII** (Scheme 3).

Scheme 2.



III

Scheme 3.



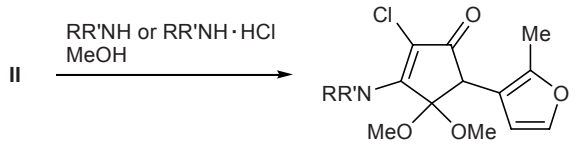
IV, **VI**

V, **VII**

IV, **V**, R = Et; **VI**, **VII**, R = Pr.

On the other hand, no cross-conjugated triketones like **V** and **VII** were formed in the reactions of dichlorocyclopentenone **II** with morpholine, pyrrolidine, and dimethylamine. In these cases, we isolated in good yields the expected Ad_NE replacement products [4] at the C^3–Cl bond, i.e., cyclic vinylogous amides **VIII**, **IX**, and **XII** that are structurally related to compounds **IV** and **VI**. Furthermore, unlike trichlorocyclopentenone **I**, dichloro ketone **II** reacted fairly smoothly with primary amines. Its reactions with benzylamine, α-methylbenzylamine, and methylamine led to the formation of products **X**, **XI**, and **XIII** as a result of replacement of the chlorine atom on C^3 (Scheme 4).

Scheme 4.

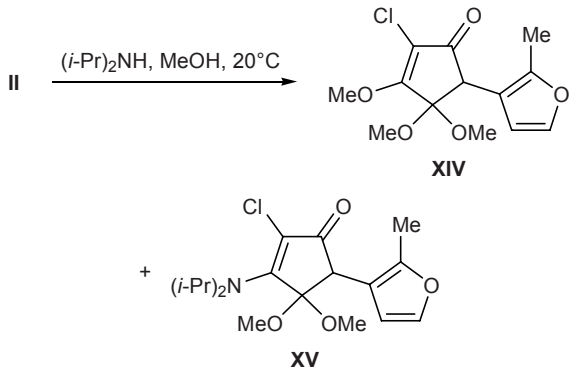


VIII–XIII

VIII, RR′N = morpholino; **IX**, RR′ = $(CH_2)_4$; **X**, R = H, R′ = $PhCH_2$; **XI**, R = H, R′ = PhCH(Me); **XII**, R = R′ = Me; **XIII**, R = H, R′ = Me.

Unexpectedly, the major product formed in the reaction of **II** with diisopropylamine in methanol was trimethoxy derivative **XIV** which was isolated as a mixture with expected 3-substituted ketone **XV** at a ratio of ~3:1 (according to the ^{1}H NMR data). Presumably, the reaction of less active dichloro derivative **II** with methanol to give compound **XIV** competes with the reaction with sterically loaded diisopropylamine (Scheme 5).

Scheme 5.



Among the examined reactions of dichloro ketone **II** with diethyl- and dipropylamines, the formation of cyclopentene triketones **V** and **VII** attracts undoubted interest. Presumably, the reaction direction leading to triketones **V** and **VII** is determined by the following factors: first, diethyl- and dipropylamines can be regarded as somewhat stronger and less sterically hindered nucleophiles than the other amines involved; second, structural specificity of compound **II** related to the absence of chlorine on C^5 (unlike trichloro ketone **I**) makes it capable of undergoing enolization during the process.

EXPERIMENTAL

The IR spectra were recorded on Specord M-80 and UR-20 spectrophotometers from samples prepared as thin films (neat) or dispersed in Nujol. The NMR spectra were measured on a Bruker AM-300 instrument at 300 MHz for ^{1}H and 75.47 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on Shimadzu LCMS-2010 and Thermo Finnigan MAT 95XP spectrometers; ion source temperature 200°C, batch inlet probe temperature 5–270°C, temperature ramp 22 deg/min. Thin-layer chromatography was performed on Silufol and Sorbfil plates; spots were detected by treatment with iodine vapor or by spraying with a solution of *p*-methoxybenzaldehyde and sulfuric acid in ethanol and subsequent heating at 120–150°C. The products were isolated by column chromatography on silica gel L (200–280 μm, Russia) using 30–60 g of the sorbent per gram of substrate; freshly distilled solvents were used as eluents. Liquid amines were purified by drying over powdered potassium hydroxide, followed by distillation.

2,3-Dichloro-4,4-dimethoxy-5-(2-methylfuran-3-yl)cyclopent-2-en-1-one (II). Compound **I**, 0.28 g (0.86 mmol), was dissolved in 10 ml of acetone, 20 ml of a freshly prepared solution of $CrCl_2$ was added under stirring, and the mixture was stirred for ~1 h at room temperature. Acetone was evaporated, the aqueous phase was extracted with chloroform (3×10 ml), the extracts were combined, washed with a solution of sodium chloride, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography on silica gel using ethyl acetate–petroleum ether (1:9) as eluent. Yield 0.14 g (68%), colorless crystals, mp 96–98°C. ^{1}H NMR spectrum, δ, ppm: 2.24 s (3H, CH_3), 3.35 s (3H) and 3.43 s (3H, OCH_3), 3.88 s (1H, 5-H), 6.15 d (1H, 4′-H, J = 1.9 Hz), 7.26 d (1H, 5′-H, J = 1.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.94 (CH_3), 51.38 and 51.51 (OCH_3), 54.74 (C^5), 102.49 (C^4), 111.53 (C^2), 111.35 ($C^{4'}$), 134.81 ($C^{3'}$), 140.34 ($C^{5'}$), 150.49 ($C^{2'}$), 158.49 (C^3), 192.14 (C=O). Found, %:

C 50.03; H 4.50; Cl 23.96. $C_{12}H_{12}Cl_2O_4$. Calculated, %: C 49.51; H 4.15; Cl 24.36.

Reaction of compound II with diethylamine. A solution of 0.3 ml (2.28 mmol) of diethylamine in 5 ml of methanol was added dropwise under stirring to a solution of 0.22 g (0.76 mmol) of compound **II** in 5 ml of methanol. The mixture was stirred for 3 h at room temperature until the initial compound disappeared according to the TLC data. The solvent was evaporated, 10 ml of cold water was added to the residue, and the mixture was extracted with chloroform (4×20 ml). The extracts were combined, washed with a saturated aqueous solution of sodium chloride, dried over $MgSO_4$, and evaporated. The residue was subjected to column chromatography on silica gel (ethyl acetate–petroleum ether, 1:4) to isolate 0.09 g (~36%) of compound **IV** and 0.040 g (18%) of **V**.

2-Chloro-3-diethylamino-4,4-dimethoxy-5-(2-methylfuran-3-yl)cyclopent-2-en-1-one (IV). Light yellow crystals, mp 78–80°C. IR spectrum, ν, cm^{-1}: 642, 781, 858, 935, 981, 1069, 1098, 1140, 1271, 1449, 1578, 1682. ^{1}H NMR spectrum, δ, ppm: 1.26 t (6H, CH_3, J = 7.0 Hz), 2.27 s (3H, CH_3), 3.00 s and 3.31 s (3H each, OCH_3), 3.65 m (2H) and 3.89 q.d (2H, NCH_2, ^2J = 14.0, ^3J = 7.1 Hz), 3.68 s (1H, 5-H), 6.11 d (1H, 4′-H, J = 1.9 Hz), 7.21 d (1H, 5′-H, J = 1.9 Hz). Mass spectrum: m/z 327 $[M]^+$.

(5*Z*)-2,3-Dichloro-5-[(1*E*)-diethylamino-4-oxopent-1-en-3-ylidene]cyclopent-2-ene-1,4-dione (V). Brown needles liquefying on exposure to air at room temperature. IR spectrum, ν, cm^{-1}: 993, 1078, 1136, 1194, 1254, 1439, 1506, 1612, 1661, 1707. ^{1}H NMR spectrum, δ, ppm: 1.26 t (3H, CH_3, J = 7.0 Hz) and 1.29 t (3H, CH_3, J = 7.2 Hz), 2.45 s (3H, $COCH_3$), 3.39 q (2H, J = 7.2 Hz) and 3.45 q (2H, NCH_2, J = 7.1 Hz), 6.87 d (1H, 4′-H, J = 13.2 Hz), 7.05 d (1H, 5′-H, J = 13.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.76 and 14.33 (CH_3), 29.11 (CH_3), 43.64 and 52.02 (CH_2N), 94.39 ($C^{2'}$), 102.16 (C^5), 143.49 (C^2), 144.49 (C^3), 155.51 ($C^{1'}$), 159.32 ($C^{3'}$), 182.54 and 183.64 (C^1, C^4), 204.09 ($C^{4'}$). Mass spectrum, m/z (I_{rel}, %): 315, 317, 319 (75) $[M]^+$; 274, 272 (50) $[M - CH_3CO]^+$; 244, 246 (100) $[M - NEt_2]^+$; $[M - CH_3CO - NEt_2]^+$ 201, 203.

Compounds **VI**–**VIII**, **XI**, **XIV**, and **XV** were synthesized in a similar way.

Compounds **VI** and **VII** were obtained from 0.14 g (0.48 mmol) of dichlorocyclopentenone **II** and 0.26 ml (1.92 mmol) of dipropylamine.

2-Chloro-3-dipropylamino-4,4-dimethoxy-5-(2-methylfuran-3-yl)cyclopent-2-en-1-one (VI). Yield 0.08 g (~48%), oily substance. ^{1}H NMR spectrum, δ, ppm: 0.93 t (6H, CH_3, J = 7.4 Hz), 1.67 m (4H, CH_2, J = 7.4 Hz), 2.28 s (3H, CH_3), 3.01 s and 3.32 s (3H each, OCH_3), 3.46 m and 3.89 m (2H each, NCH_2), 3.68 s (1H, 5-H), 6.13 d (1H, 4′-H, J = 1.8 Hz), 7.23 d (1H, 5′-H, J = 1.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 10.87 and 11.86 (CH_3), 22.35 and 29.63 (CH_2), 47.72 (C^5), 50.58 and 51.44 (OCH_3), 59.35 (CH_2N), 103.19 (C^4), 106.34 (C^2), 111.23 ($C^{4'}$), 113.59 ($C^{3'}$), 140.05 ($C^{5'}$), 149.64 ($C^{2'}$), 160.18 (C^3), 190.63 (C^1).

(5*Z*)-2,3-Dichloro-5-[(1*E*)-dipropylamino-4-oxopent-1-en-3-ylidene]cyclopent-2-ene-1,4-dione (VII). Yield 0.04 g (24%), oily substance. ^{1}H NMR spectrum, δ, ppm: 0.91 m (6H, CH_3), 1.62 m (4H, CH_2), 2.47 s (3H, $COCH_3$), 3.16 s (6H, OCH_3), 3.45 m and 3.82 m (2H each, NCH_2), 6.87 d (1H, 4′-H, J = 13.3 Hz), 7.05 d (1H, 5′-H, J = 13.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.32 (CH_3), 19.99 and 22.13 (CH_2), 31.63 (CH_3), 58.56 (CH_2N), 94.47 ($C^{2'}$), 106.34 (C^5), 137.48 (C^2, C^3), 151.69 ($C^{1'}$), 159.26 ($C^{3'}$), 179.83 and 179.90 (C^1, C^4), 204.09 ($C^{4'}$). Found: $[M]^+$ 355.1552. $C_{18}H_{23}ClNO_4$. Calculated: M 355.1540.

2-Chloro-4,4-dimethoxy-5-(2-methylfuran-3-yl)-3-morpholinocyclopent-2-en-1-one (VIII) was obtained from 0.1 g (0.34 mmol) of compound **VII** and 0.12 ml (1.36 mmol) of morpholine. Yield 0.08 g (68%), white powder, mp 112–114°C. ^{1}H NMR spectrum, δ, ppm: 2.26 s (3H, CH_3), 3.0 s and 3.35 s (3H each, OCH_3), 3.69 s (1H, 5-H), 3.79 m (4H, NCH_2), 3.97 m (4H, OCH_2), 6.12 d (1H, 4′-H, J = 1.8 Hz), 7.22 d (1H, 5′-H, J = 1.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.84 (CH_3), 47.79 (C^5), 48.93 (CH_2N), 50.96 and 51.73 (OCH_3), 67.19 (CH_2O), 104.01 (C^4), 106.31 (C^2), 111.08 ($C^{4'}$), 113.02 ($C^{3'}$), 140.23 ($C^{5'}$), 149.85 ($C^{2'}$), 159.64 (C^3), 190.86 (C^1). Found, %: C 55.90; H 6.20; Cl 9.89; N 3.86. $C_{16}H_{20}ClNO_5$. Calculated, %: C 56.23; H 5.90; Cl 10.37; N 4.10.

2-Chloro-4,4-dimethoxy-5-(2-methylfuran-3-yl)-3-(pyrrolidin-1-yl)cyclopent-2-en-1-one (IX) was obtained from 0.14 g (0.48 mmol) of compound **II** and 0.16 ml (1.91 mmol) of pyrrolidine. Yield 0.14 g (89%), light yellow powder, mp 92–94°C. IR spectrum, ν, cm^{-1}: 723, 870, 1126, 1231, 1279, 1375, 1395, 1582, 1690. ^{1}H NMR spectrum, δ, ppm: 1.91 (4H, CH_2), 2.27 s (3H, CH_3), 3.00 s and 3.32 s (3H each, OCH_3), 3.71 s (1H, 5-H), 3.83 m (2H) and 4.09 m (2H, NCH_2), 6.14 d (1H, 4′-H, J = 1.6 Hz), 7.22 d (1H, 5′-H, J = 1.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.82 (CH_3), 25.04 (CH_2), 47.76 (C^5), 50.0 (CH_2N), 50.74 and 51.38 (OCH_3), 103.40 (C^4), 105.65 (C^2), 111.27

($C^{4'}$), 113.54 ($C^{3'}$), 140.11 ($C^{5'}$), 149.73 ($C^{2'}$), 159.30 (C^{3}), 190.86 (C^{1}). Found, %: C 58.60; H 6.35; Cl 10.42; N 4.12. $C_{16}H_{20}ClNO_4$. Calculated, %: C 58.99; H 6.19; Cl 10.88; N 4.30.

3-Benzylamino-2-chloro-4,4-dimethoxy-5-(2-methylfuran-3-yl)cyclopent-2-en-1-one (X) was obtained from 0.1 g (0.34 mmol) of compound **II** and 0.15 ml (1.36 mmol) of benzylamine. Yield 0.08 g (64%), yellow–brown powder, mp 130–132°C. IR spectrum, ν, cm^{-1}: 700, 743, 843, 951, 1273, 1294, 1377, 1454, 1533, 1593, 1695, 3048, 3273. ^{1}H NMR spectrum, δ, ppm: 2.27 s (3H, CH_3), 3.11 s and 3.30 br.s (3H each, OCH_3), 3.67 s (1H, 5-H), 4.33 m and 4.96 m (2H each, NCH_2), 6.09 d (1H, 4′-H, J = 1.6 Hz), 7.22–7.44 m (6H, 5′-H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 11.80 (CH_3); 44.38 (CH_2); 51.26 (C^5); 50.76 (OCH_3); 103.40 (C^4); 110.88 ($C^{3'}$); 113.02 ($C^{4'}$); 127.14 (C^2); 127.20, 127.66, 128.13, 137.34 (C_6H_5); 149.93 ($C^{2'}$); 140.00 ($C^{5'}$); 138.87 (C^3); 176.86 (C^1). Found, %: C 62.76; H 5.60; Cl 9.32; N 3.58. $C_{19}H_{20}ClNO_4$. Calculated, %: C 63.07; H 5.57; Cl 9.80; N 3.87.

2-Chloro-4,4-dimethoxy-5-(2-methylfuran-3-yl)-3-(2-phenylethylamino)cyclopent-2-en-1-one (XI) was obtained as a mixture of diastereoisomers from 0.12 g (0.41 mmol) of compound **II** and 0.2 ml (1.64 mmol) of α-methylbenzylamine. Yield 0.12 g (77%), brown powder, mp 196–199°C. IR spectrum, ν, cm^{-1}: 700, 1072, 1122, 1377, 1458, 1570, 1587, 1629, 3327. Mass spectrum, m/z (I_{rel}, %): 375, 377, 379 (80) $[M]^+$; 340 $[M - Cl]^+$; 270; 268, 266 (30) $[M - PhCHCH_3]^+$; 105 (100) $[PhCHCH_3]^+$; 77 [Ph]. ^{1}H NMR spectrum, δ, ppm: major isomer: 1.68 m (3H, CH_3), 2.28 s (3H, CH_3), 3.13 s and 3.36 s (3H each, OCH_3), 3.64 s (1H, 5-H), 4.79 q.d (1H, CH, ^3J = 6.7, ^2J = 13.6 Hz), 5.66 br.s (1H, NH), 6.13 s (1H, 4′-H), 7.16–7.39 m (6H, 5′-H, C_6H_5); minor isomer: 1.38 d (3H, CH_3, J = 6.8 Hz), 2.27 s (3H, CH_3), 3.19 s and 3.31 s (3H each, OCH_3), 3.66 s (1H, 5-H), 4.91 m (1H, CH), 5.66 br.s (1H, NH), 5.98 br.s (1H, 4′-H), 7.16–7.39 m (6H, 5′-H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: major isomer: 11.87 (CH_3); 22.61 (CH_3); 49.97 (C^5); 50.75 (OCH_3); 51.18 (CH); 103.0 (C^4); 110.97 ($C^{3'}$); 113.11 ($C^{4'}$); 125.73, 128.50, 128.92, 142.48 (C_6H_5); 139.96 ($C^{5'}$); 144.38 (C^2); 149.89 ($C^{2'}$); 156.83 (C^3); 189.06 (C^1); minor isomer: 11.77 (CH_3); 23.60 (CH_3); 49.97 (C^5); 51.79 (OCH_3); 52.36 (CH); 103.0 (C^4); 110.57 ($C^{3'}$); 113.0 ($C^{4'}$); 125.88, 126.94, 127.82, 142.83 (C_6H_5); 139.96 ($C^{5'}$); 144.38 (C^2); 149.76 ($C^{2'}$); 156.83 (C^3); 189.06 (C^1).

2-Chloro-3-dimethylamino-4,4-dimethoxy-5-(2-methylfuran-3-yl)cyclopent-2-en-1-one (XII). Dimethylamine hydrochloride, 0.23 g (2.75 mmol), was added to a suspension of 0.16 g (2.75 mmol) of potassium hydroxide in 5 ml of methanol, the mixture was stirred for 15 min, a solution of 0.2 g (0.68 mmol) of furylcyclopentenone **II** in 3 ml of methanol was added dropwise, and the mixture was stirred at room temperature until the initial compound disappeared according to the TLC data (ethyl acetate–petroleum ether, 1:4). The mixture was then treated as described above in the synthesis of compound **IV**, and the residue was subjected to column chromatography on silica gel using ethyl acetate–petroleum ether (1:5) as eluent to isolate 0.16 g (76%) of compound **XII**. White needles, mp 90–92°C. ^{1}H NMR spectrum, δ, ppm: 2.28 s (3H, CH_3), 3.03 s and 3.34 s (3H each, OCH_3), 3.38 s (6H, NCH_3), 3.71 s (1H, 5-H), 6.15 d (1H, 4′-H, J = 1.9 Hz), 7.25 d (1H, 5′-H, J = 1.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.78 (CH_3), 41.65 (NCH_3), 47.72 (C^5), 50.82 and 51.45 (OCH_3), 103.81 (C^4), 105.99 (C^2), 109.41 ($C^{4'}$), 113.22 ($C^{3'}$), 140.08 ($C^{5'}$), 149.73 ($C^{2'}$), 161.22 (C^3), 190.69 (C^1). Found, %: C 55.73; H 6.35; Cl 11.39; N 4.48. $C_{14}H_{18}ClNO_4$. Calculated, %: C 56.10; H 6.05; Cl 11.83; N 4.67.

2-Chloro-4,4-dimethoxy-3-methylamino-5-(2-methylfuran-3-yl)cyclopent-2-en-1-one (XIII) was obtained in a similar way from 0.1 g (0.34 mmol) of compound **II** and 0.095 g (1.21 mmol) of methylamine hydrochloride. Yield 0.04 g (36%), yellow–brown crystals, mp 147–149°C. IR spectrum, ν, cm^{-1}: 358, 897, 1130, 1155, 1182, 1271, 1377, 1419, 1458, 1533, 1606, 1695, 3294. ^{1}H NMR spectrum, δ, ppm: 2.28 s (3H, CH_3), 3.03 s and 3.34 s (3H each, OCH_3), 3.38 s (6H, NCH_3), 3.71 s (1H, 5-H), 6.15 d (1H, 4′-H, J = 1.9 Hz), 7.25 d (1H, 5′-H, J = 1.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.78 (CH_3), 41.65 (NCH_3), 47.72 (C^5), 50.82 and 51.45 (OCH_3), 103.81 (C^4), 105.99 (C^2), 109.41 ($C^{4'}$), 113.22 ($C^{3'}$), 140.08 ($C^{5'}$), 149.73 ($C^{2'}$), 161.22 (C^3), 190.69 (C^1). Mass spectrum, m/z (I_{rel}, %): 286, 288 (70) $[M + H]^+$; 254, 256 (100) $[M + H - CH_3OH]^+$; 220 (20) $[M + H - CH_3OH - HCl]^+$.

Compounds **XIV** and **XV** were isolated as a mixture at a ratio of ~4:1 from 0.14 g (0.48 mmol) of cyclopentenone **II** and 0.5 ml (1.92 mmol) of diisopropylamine. Overall yield 0.1 g (~ 69%).

2-Chloro-3,4,4-trimethoxy-5-(2-methylfuran-3-yl)cyclopent-2-en-1-one (XIV). ^{1}H NMR spectrum, δ, ppm: 2.28 s (3H, CH_3); 3.27 s, 3.39 s, and 4.45 s (3H each, OCH_3); 3.74 s (1H, 5-H); 6.15 d (1H, 4′-H, J =

1.8 Hz); 7.25 d (1H, 5′-H, J = 1.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.93 (CH_3); 51.32 (C^5); 51.32, 52.13, and 60.18 (OCH_3); 102.24 (C^4); 108.91 (C^2); 111.43 ($C^{4'}$); 112.52 ($C^{3'}$); 140.08 ($C^{5'}$); 150.22 ($C^{2'}$); 173.56 (C^3); 193.32 (C^1).

2-Chloro-3-diisopropylamino-4,4-dimethoxy-5-(2-methylfuran-3-yl)cyclopent-2-en-1-one (XV). ^{1}H NMR spectrum, δ, ppm: 1.34 d (3H, CH_3, J = 6.4 Hz), 2.29 s (3H, CH_3), 3.16 s and 3.31 s (3H each, OCH_3), 3.43 m and 3.63 m (1H each, CH), 3.67 s (1H, 5-H), 6.34 d (1H, 4′-H, J = 1.8 Hz), 7.22 d (1H, 5′-H, J = 1.96 Hz).

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