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Direct Synthesis of 2,3,5-Trichloro-4,4-dimethoxy- and 2,5-Dichloro-3,4,4-trimethoxycyclopent-2-en-1-ones from Hexachlorocyclopentadiene and Some Aspects of Their Reactivity

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Abstract—2,3,5-Trichloro-4,4-dimethoxy- and 2,5-dichloro-3,4,4-trimethoxycyclopent-2-en-1-ones were synthesized directly by treatment of hexachlorocyclopentadiene with methanol in the presence of potassium hydroxide at room temperature or on heating and subsequent acidification of the reaction mixture. Reactions of 2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-one with some reducing agents and nucleophiles were studied.

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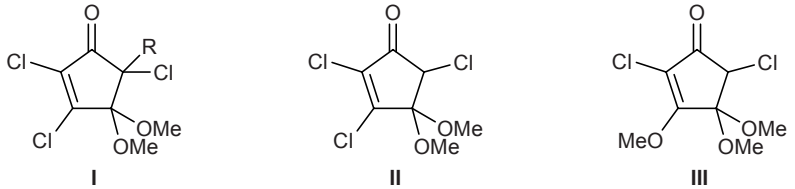
Highly functionalized cyclopentane building blocks possess a broad synthetic potential and are promising for subsequent versatile transformations; they are quite valuable initial compounds for the synthesis of cyclopentane derivatives. Such compounds are oxygenated chlorocyclopentenones **I** which were obtained by us previously from hexachlorocyclopentadiene [1]. They attract interest as key intermediate products in the synthesis of chlorine-containing natural compounds (such as chlorovulones [2], punaglandins, cryptosporiopsin [3], etc.), design of heterocycles and new bioactive cyclopentanoids, etc. In continuation of our studies in this line, the present article reports on a practical procedure for the preparation of the simplest chlorocyclopentenone building block **II** and new cyclopentanetrione derivative, 2,5-dichloro-3,4,4-trimethoxycyclopent-2-en-1-one (**III**), using low-expensive technical chemicals (KOH, MeOH, H_2SO_4) and some reactions of trichlorocyclopentenone **II**.

In the synthesis of cyclopentenone **II**, a mixture of hexachlorocyclopentadiene and potassium hydroxide at a ratio of 1:(7–10) in methanol was stirred for 10 h at 55°C, cooled to 0°C, acidified with 50% sulfuric acid, and stirred for 8 h at 60°C. After appropriate treatment of the reaction mixture, chlorocyclopentenone **II** was isolated by vacuum distillation in more than 70% yield (Scheme 1). This one-step procedure is simpler and more practical than the known methods [5–7]. By carrying out analogous reaction under more severe conditions (70–80°C), the reactant ratio and concentrations remaining the same, we obtained previously unknown trimethoxycyclopentenone **III**.

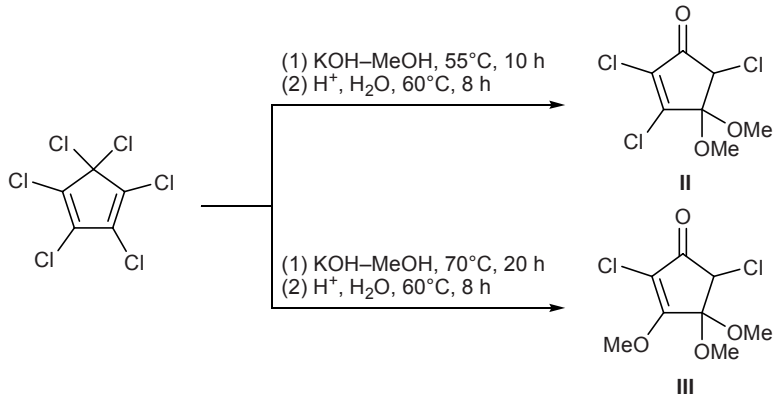
Compound **II** was brought into several transformations typical of trichlorocyclopentenones **I** (Scheme 2) [1]. Trichlorocyclopentenone **II** was readily reduced with sodium tetrahydridoborate to produce stereochemically pure cyclopentenol **IV** in a high yield. The *cis* orientation of the hydroxy group and chlorine atom



I **II** **III**

R = aryl, furyl, allenyl, benzyl, etc.

Scheme 1.



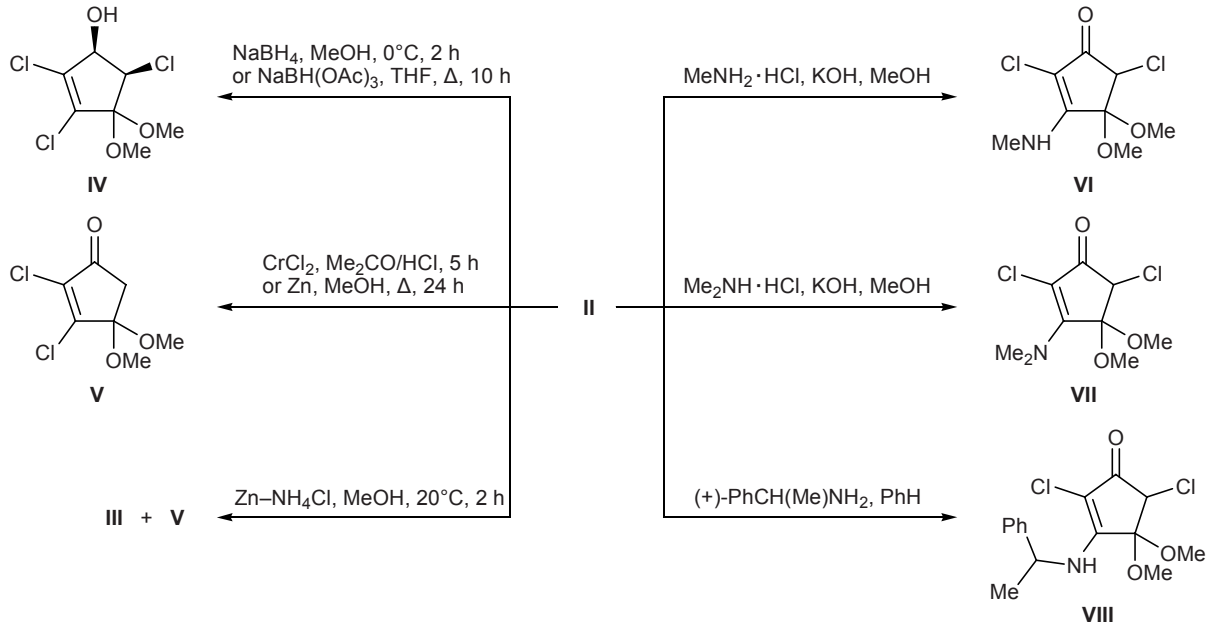
in the 5-position followed from the coupling constant $J_{1,5}$ equal to 5.0 Hz in ^{1}H NMR spectrum [8]. The same product was obtained by reduction of **II** with $NaBH(OAc)_3$, but in this case the reaction required more severe conditions (boiling tetrahydrofuran).

Chemoselective hydrodechlorination of trichloroketone **II** with formation of expected dichlorocyclopentenone **V** was effected by the action of $CrCl_2$ [9]. Analogous reactions with zinc in methanol in the absence and in the presence of ammonium chloride were less effective. In the first case, the conversion of **II** did not exceed 70%, and in the second, compound **III** was formed as by-product (Scheme 2).

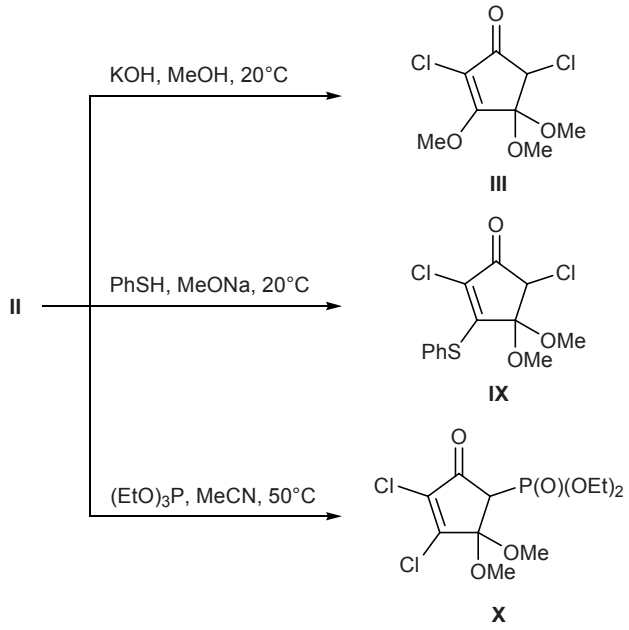
Reactions of trichlorocyclopentenone **II** with nitrogen-centered nucleophiles, such as methylamine, dimethylamine, and (+)-1-phenylethanamine, followed the nucleophilic addition–elimination pattern, leading to the corresponding aminocyclopentenones **VI–VIII**. With a view to extend the series of nucleophiles, we examined reactions of **II** with oxygen, sulfur, and phosphorus reagents (Scheme 3). Strong nucleophiles, such as sodium benzenethiolate and sodium methoxide reacted with trichlorocyclopentenone **II** to give products of replacement of the chlorine atom at C^3 (addition–elimination pattern), sulfide **IX** and trimethoxycyclopentenone **III**, respectively. In the reaction with a neutral nucleophile, triethyl phosphite, the process followed the Arbuzov reaction scheme with formation of phosphonate **X** as result of replacement of the 5-chlorine atom.

We also performed deketalization of trichlorocyclopentenone **II** and cyclopentenol **IV**. Compound **II** did not change under standard acid hydrolysis conditions. We succeeded in obtaining symmetric diketone **XI**

Scheme 2.



Scheme 3.



only after prolonged keeping of **II** in concentrated sulfuric acid [10] (Scheme 4). By contrast, chlorocyclopentenol **IV** was readily hydrolyzed in aqueous–organic medium in the presence of a mineral acid (Scheme 4). The reaction was accompanied by *cis–trans* isomerization; the major product was *trans* isomer **XII** ($J_{4,5}$ = 2.5 Hz), while the fraction of *cis* isomer **XIII** did not exceed 10% (according to the ^{1}H NMR data).

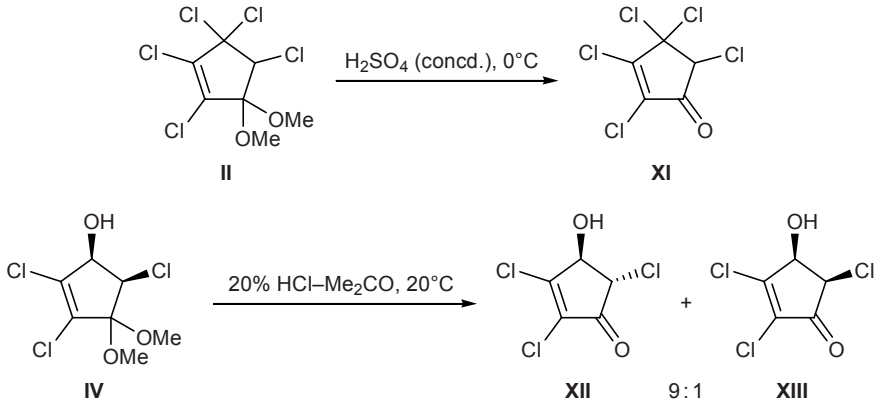
Thus we have developed a preparatively convenient one-pot procedure for the transformation of hexachlorocyclopentadiene into functionalized chloromethoxycyclopentenones **II** and **III** that are attractive from the synthetic viewpoint. Their synthetic potential has been demonstrated by various reactions of 2,3,5-trichloro-4,4-dimetoxycyclopent-2-en-1-one (**II**).

EXPERIMENTAL

The IR spectra were recorded on UR-20 and Specord M-80 instruments from samples prepared as films (neat) or dispersed in mineral oil. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer at 300.13 and 75.47 MHz, respectively, using $CDCl_3$ as solvent and reference (δ 7.27 ppm, δ_C 77.00 ppm). The mass spectra (electron impact, 20 or 70 eV) were obtained on an MKh-1306 instrument, ion source temperature 75–100°C. The progress of reactions was monitored by TLC on Silufol plates using hexane–ethyl acetate as eluent; spots were detected by treatment with an alkaline solution of potassium permanganate [11].

2,3,5-Trichloro-4,4-dimethoxycyclopent-2-en-1-one (II). A mixture of 27.3 g (0.1 mol) of hexachlorocyclopentadiene and 56.0 g (1.0 mol) of potassium hydroxide in 250 ml of methanol was stirred for 24 h at room temperature. The mixture was then cooled to 0°C, 50% sulfuric acid was slowly added under stirring to pH 1, the mixture was stirred for 10 h at 50°C, and the precipitate (NaCl) was filtered off. The filtrate was concentrated under reduced pressure and extracted with ethyl acetate (3×50 ml). The combined extracts were washed with a 10% aqueous solution of sodium hydrogen carbonate and a saturated solution of sodium chloride, dried over $MgSO_4$, and concentrated, and the residue was distilled under reduced pressure, a fraction boiling at 100–103°C (0.2 mm) being collected. Yield 18.4 g (75%), colorless oily substance, which crystallized on storage to form colorless crystals with mp 52–54°C, R_f 0.42 (petroleum ether–ethyl acetate, 9:1). IR spectrum, ν, cm^{-1}: 1050, 1596, 1636, 1752. ^{1}H NMR spectrum, δ, ppm: 3.53 s (3H, OCH_3), 3.51 s (3H, OCH_3), 4.64 s (1H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 52.03 (OCH_3), 52.07 (OCH_3), 62.19 (C^5), 100.49 (C^4),

Scheme 4.



133.77 (C^2), 157.65 (C^3), 186.17 (C^1). Mass spectrum, *m*/*z* (I_{rel}, %): 249 (7.5), 247 (22.3), 245 (27.3) $[M]^+$, 218 (31.4), 216 (93.6), 214 (100) $[M - OCH_3]^+$, 212 (19.8), 210 (30.9) $[M - Cl]^+$, 190 (4.9), 188 (14.0), 186 (15.5) $[M - CH_3O - CO]^+$, 136 (6.1), 134 (13.8), 112 (2.5), 110 (9.7), 108 (13.3), 97 (31.9), 89 (7.4), 87 (22.8), 69 (11.9), 59 (17.7) $[OCOCH_3]^+$, 55 (11.1), 41 (8.0), 38 (5.5), 36 (14.8) $[HCl]^+$, 28 (23.9). Found, %: C 34.10; H 2.82; Cl 43.46. $C_7H_7Cl_3O_3$. Calculated, %: C 34.25; H 2.87; Cl 43.33.

2,5-Dichloro-3,4,4-trimethoxycyclopent-2-en-1-one (III). *a*. Following an analogous procedure, a mixture of 3.0 g (0.01 mol) of hexachlorocyclopentadiene and 4.2 g (0.08 mol) of potassium hydroxide in 10 ml of methanol was heated for 10 h at 70–80°C. After standard treatment, the residue was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (8:2) as eluent to isolate 2.40 g (80%) of compound **III** as a yellow oily substance, R_f 0.31 (petroleum ether–ethyl acetate, 9:1, double elution).

b. A solution of 6.72 g (12.0 mmol) of potassium hydroxide in 50 ml of methanol was added under stirring to a solution of 1.0 g (4.0 mmol) of trichlorocyclopentenone **II** in 30 ml of methanol, and the mixture was stirred at room temperature until the initial compound disappeared completely (2 h, TLC). The solvent was distilled off under reduced pressure, a saturated solution of sodium chloride was added to the residue, and the mixture was neutralized with 10% hydrochloric acid to pH 7 and extracted with ethyl acetate (3×10 ml). The combined extracts were washed with a saturated solution of NaCl, dried over $MgSO_4$, and concentrated, and the residue was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (8:2) as eluent. Yield 0.78 g (88 %). IR spectrum, ν, cm^{-1}: 1080, 1610, 1740. ^1H NMR spectrum, δ, ppm: 3.46 s (3H, OCH_3), 3.50 s (3H, OCH_3), 4.42 s (3H, OCH_3), 4.48 s (1H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 51.70 and 52.02 (OCH_3), 57.79 (OCH_3), 60.44 (C^5), 100.13 (C^4), 108.14 (C^2), 171.94 (C^3), 187.05 (C^1). Found, %: C 39.83; H 4.06; Cl 29.30. $C_8H_{10}Cl_2O_4$. Calculated, %: C 39.86; H 4.18; Cl 29.41.

1*r*,5*c*-2,3,5-Trichloro-4,4-dimethoxycyclopent-2-en-1-ol (IV). *a*. A solution of 0.2 g (0.8 mmol) of trichlorocyclopentenone **II** in 10 ml of methanol was cooled to 0°C, 0.11 g (2.4 mmol) of sodium tetrahydridoborate was added, the mixture was stirred for 0.5 h at 0°C and for 1.5 h at room temperature, and 10 ml of acetone was added under continuous stirring. The solvent was distilled off under reduced pressure, a saturated solution of sodium chloride was added to the residue, and the mixture was extracted with ethyl acetate (3×10 ml). The combined extracts were washed with a saturated solution of sodium chloride, dried over $MgSO_4$, and concentrated, and the residue was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (7:3) as eluent. Yield 0.19 g (95%), colorless crystals, mp 82–84°C, R_f 0.57 (petroleum ether–ethyl acetate, 7:3, double elution). IR spectrum, ν, cm^{-1}: 1090, 1640, 3400. ^1H NMR spectrum, δ, ppm: 2.56 d (1H, OH, J = 10.5 Hz), 3.46 s (3H, OCH_3), 3.47 s (3H, OCH_3), 4.50 d (1H, 5-H, J = 5.0 Hz), 4.65 d.d (1H, 1-H, J = 10.5, 5.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 50.81 and 51.89 (OCH_3), 65.33 (C^5), 73.13 (C^1), 103.97 (C^4), 130.86 (C^3), 136.09 (C^2). Found, %: C 33.83; H 3.54; Cl 42.86. $C_7H_9Cl_3O_3$. $C_7H_9Cl_3O_3$. Calculated, %: C 33.97; H 3.67; Cl 42.97.

b. A solution of 0.1 g (0.4 mmol) of trichlorocyclopentenone **II** in 3 ml of anhydrous THF was cooled to 0°C, 0.75 g (2 mmol) of $NaBH(OAc)_3$ was added under argon, and the mixture was stirred for 5 h at room temperature. The mixture was diluted with 5 ml of acetone and treated as described above in *a* to isolate 0.08 g (80%) of compound **IV**.

2,3-Dichloro-4,4-dimethoxycyclopent-2-en-1-one (V). *a*. An aqueous solution of $CrCl_2$ [9], 30 ml, was added to a solution of 6.0 g (24.1 mmol) of trichlorocyclopentenone **II** in 60 ml of acetone under stirring at 20°C in a stream of argon. The mixture was stirred for 3 h (TLC), the precipitate was filtered off, the filtrate was concentrated under reduced pressure, a saturated solution of sodium chloride was added to the residue, and the mixture was extracted with ethyl acetate (3× 30 ml). The combined extracts were washed with a 10% aqueous solution of sodium hydrogen carbonate to pH 7 and a saturated solution of sodium chloride, dried over $MgSO_4$, and concentrated. The product was isolated by column chromatography on silica gel using petroleum ether–ethyl acetate (9:1) as eluent. Yield 5.0 g (96%), yellow oily substance, R_f 0.33 (petroleum ether–ethyl acetate, 9:1, double elution). IR spectrum, ν, cm^{-1}: 1080, 1600, 1740. ^1H NMR spectrum, δ, ppm: 2.81 s (2H, 5-H), 3.65 s (6H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 45.29 (C^5), 51.26 and 51.28 (OCH_3), 102.22 (C^4), 134.99 (C^2), 158.57 (C^3), 191.30 (C^1). Found, %: C 39.76; H 3.96; Cl 33.46. $C_7H_8Cl_2O_3$. Calculated, %: C 39.84; H 3.82; Cl 33.60.

b. Trichlorocyclopentenone **II**, 0.1 g (4.1 mmol), was dissolved in 5 ml of methanol, 0.92 g (16.4 mmol)

of zinc dust and 0.05 g of ammonium chloride were added under stirring, and the mixture was stirred for 1 h on heating under reflux. The precipitate was filtered off, the solvent was distilled off from the filtrate under reduced pressure, a saturated solution of sodium chloride was added to the residue, and the mixture was extracted with ethyl acetate (3×5 ml). After standard treatment, column chromatography on silica gel using petroleum ether–ethyl acetate (9:1) as eluent gave 0.04 g (45%) of dichlorocyclopentenone **V**.

2,5-Dichloro-4,4-dimethoxy-3-methylaminocyclopent-2-en-1-one (VI). Trichlorocyclopentenone **II**, 0.2 g (0.8 mmol), was dissolved in 5 ml of methanol, 0.27 g (4 mmol) of methylamine hydrochloride and 0.22 g (4 mmol) of potassium hydroxide were added at 20°C, and the mixture was stirred for 2 h at room temperature. The solvent was distilled off under reduced pressure, the residue was treated with 5 ml of a saturated solution of sodium chloride, and the mixture was extracted with ethyl acetate (3×10 ml). The combined extracts were washed with 10% hydrochloric acid to pH 7 and with a saturated solution of sodium chloride, dried over $MgSO_4$, and concentrated, and the product was isolated by column chromatography on silica gel using petroleum ether–ethyl acetate (1:1) as eluent. Yield 0.13 g (66%), colorless crystals, mp 95–96°C, R_f 0.4 (petroleum ether–ethyl acetate, 1:1). IR spectrum, ν, cm^{-1}: 1080, 1360, 1600, 1705, 3320. ^1H NMR spectrum, δ, ppm: 1.65 s (3H, NCH_3), 3.35 s (3H, OCH_3), 3.45 s (3H, OCH_3), 4.59 s (1H, 5-H), 7.10 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 30.09 (NCH_3), 51.49 and 52.88 (OCH_3), 60.51 (C^5), 96.47 (C^2), 100.23 (C^4), 160.61 (C^3), 183.72 (C^1). Found, %: C 40.14; H 4.54; Cl 29.67; N 5.74. $C_8H_{11}Cl_2NO_3$. Calculated, %: C 40.02; H 4.62; Cl 29.5; N 5.83.

2,5-Dichloro-3-dimethylamino-4,4-dimethoxycyclopent-2-en-1-one (VII). Trichlorocyclopentenone **II**, 0.2 g (0.8 mmol), was dissolved in 5 ml of methanol, 0.13 g (1.6 mmol) of dimethylamine hydrochloride and 0.1 g (1.6 mmol) of potassium hydroxide were added under stirring at 20°C, and the mixture was stirred for 2 h at room temperature. The solvent was distilled off under reduced pressure, the residue was treated with 5 ml of a saturated solution of sodium chloride, and the mixture was extracted with ethyl acetate (3×10 ml). The combined extracts were washed with 10% hydrochloric acid to pH 7 and with a saturated solution of sodium chloride, dried over $MgSO_4$, and concentrated, and the product was isolated by column chromatography on silica gel using petroleum ether–ethyl acetate (1:1) as eluent. Yield 0.16 g (76%), yellow crystals, mp 89–90°C, R_f 0.4 (petroleum ether–ethyl acetate, 1:1). IR spectrum, ν, cm^{-1}: 1080, 1360, 1400, 1600, 1705. ^1H NMR spectrum, δ, ppm: 3.27 s (3H, OCH_3), 3.37 br.s (6H, NMe_2), 3.52 s (3H, OCH_3), 4.59 s (1H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 41.74 (NMe_2), 51.49 and 52.88 (OCH_3), 60.72 (C^5), 102.57 (C^2), 103.29 (C^4), 159.68 (C^3), 183.84 (C^1). Found, %: C 42.65; H 5.02; Cl 27.78; N 5.38. $C_9H_{13}Cl_2NO_3$. Calculated, %: C 42.54; H 5.16; Cl 27.90; N 5.51.

2,5-Dichloro-4,4-dimethoxy-3-(1-phenylethylamino)cyclopent-2-en-1-one (VIII). (+)-1-Phenylethanamine, 0.13 ml (1.6 mmol), was added at 20°C under stirring in a stream of argon to a solution of 0.2 g (0.8 mmol) of trichlorocyclopentenone **II** in 3 ml of anhydrous benzene, and the mixture was stirred for 1.5 h. The solvent was distilled off under reduced pressure, the residue was treated with a saturated solution of sodium chloride, and the mixture was extracted with ethyl acetate (3×10 ml). The combined extracts were washed with a saturated solution of sodium chloride, dried over $MgSO_4$, and concentrated, and the product was isolated by column chromatography on silica gel using petroleum ether–ethyl acetate (1:1) as eluent. Yield 0.15 g (55%), orange oily substance, R_f 0.63 (petroleum ether–ethyl acetate, 1:1). IR spectrum, ν, cm^{-1}: 1000, 1080, 1580, 1620, 1710, 3300. ^1H NMR spectrum, δ, ppm: 1.65 d (3H, CH_3, J = 6.7 Hz), 3.42 s and 3.48 s (3H each, OCH_3), 4.42 s (1H, 5-H), 5.60 q (1H, NCH, J = 6.7 Hz), 5.75 m (1H, NH), 7.30–7.40 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 23.22 (CH_3); 51.83 and 52.59 (OCH_3); 59.90 (NCH); 60.16 (C^5); 98.10 (C^2); 100.75 (C^4); 125.66, 127.71, and 128.77 (C_{arom}); 142.01 (C^2); 142.2 (C^i); 158.82 (C^3); 185.45 (C^1). Found, %: C 54.63; H 5.23; Cl 21.64; N 4.16. $C_{15}H_{17}Cl_2NO_3$. Calculated, %: C 54.56; H 5.19; Cl 21.47; N 4.24.

2,5-Dichloro-4,4-dimethoxy-3-phenylsulfanylcyclopent-2-en-1-one (IX). Benzenethiol, 0.12 ml (1.1 mmol), was added dropwise under stirring to a solution of 0.06 g (1 mmol) of sodium methoxide in 3 ml of anhydrous methanol, the mixture was kept for 20 min, and the resulting solution of sodium benzenethiolate was added to a solution of 0.5 g (2.0 mmol) of trichlorocyclopentenone **II** in 10 ml of anhydrous methanol. When the reaction was complete (3 h; TLC, petroleum ether–ethyl acetate, 8:2), the mixture was treated with a saturated solution of sodium chloride, the solvent was distilled off under reduced pressure, and the product was extracted into ethyl acetate (3×10 ml). The combined extracts were washed with a sat-

urated solution of sodium chloride, dried over $MgSO_4$, and concentrated, and the residue was recrystallized from petroleum ether (bp 40–70°C). Yield 0.65 g (90%). Colorless crystals, mp 80–82°C, R_f 0.34 (petroleum ether–ethyl acetate, 8:2). IR spectrum, ν, cm^{-1}: 1060, 1550, 1590, 1730. ^1H NMR spectrum, δ, ppm: 3.49 s (3H, OCH_3), 3.50 s (3H, OCH_3), 4.52 s (1H, 5-H), 7.40 m (3H, H_{arom}), 7.55 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 51.70 and 52.15 (OCH_3); 61.43 (C^5); 103.65 (C^4); 126.44, 128.96, 130.00, and 134.65 (C_{arom}); 129.48 (C^2); 162.93 (C^3); 187.05 (C^1). Found, %: C 48.80; H 3.92; Cl 22.35; S 10.18. $C_{13}H_{12}Cl_2O_3S$. Calculated, %: C 48.92; H 3.79; Cl 22.21; S 10.05.

Diethyl (3,4-dichloro-5,5-dimethoxy-2-oxocyclopent-3-en-1-yl)phosphonate (X). Triethyl phosphite, 0.33 ml (1.6 mmol), was added under stirring to a solution of 0.2 g (0.8 mmol) of trichlorocyclopentenone **II** in 3 ml of anhydrous acetonitrile, and the mixture was stirred for 5 h at 50°C. The solvent was distilled off under reduced pressure, the residue was treated with a saturated solution of sodium chloride, and the product was extracted into ethyl acetate (3×10 ml). The combined extracts were washed with a saturated solution of sodium chloride, dried over $MgSO_4$, and concentrated, and the residue was subjected to column chromatography on silica gel using chloroform–methanol (50:1 to 30:1) as eluent to isolate 0.07 g (30%) of phosphonate **X** as a yellow oily substance, R_f 0.34 (petroleum ether–ethyl acetate, 1:1). IR spectrum, ν, cm^{-1}: 1031, 1269, 1638. ^1H NMR spectrum, δ, ppm: 1.38 t (6H, CH_3, J = 4.5 Hz), 3.42 s (6H, OCH_3), 4.25 q (4H, OCH_2, J = 7 Hz), 5.79 s (1H, 5-H). Found, %: C 38.24; H 4.83; Cl 20.35; P 9.05. $C_{11}H_{17}Cl_2O_6P$. Calculated, %: C 38.06; H 4.94; Cl 20.43; P 8.92.

2,4,5-Trichlorocyclopent-4-ene-1,3-dione (XI). A mixture of 0.1 g (0.4 mmol) of trichlorocyclopentenone **II** and 3 ml of concentrated sulfuric acid was kept for 1 h at 0°C. The product was extracted into chloroform (3×5 ml), the combined extracts were neutralized with a saturated solution of sodium hydrogen carbonate, washed with a saturated solution of sodium chloride, dried over $MgSO_4$, and concentrated, and the residue was subjected to column chromatography on silica gel using chloroform–methanol (9:1) as eluent. Yield 0.08 g (90%), brown oily substance, R_f 0.73 (chloroform–methanol, 9:1). IR spectrum, ν, cm^{-1}: 1458, 1605, 1720, 1740. ^1H NMR spectrum: δ 4.76 ppm, s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 62.58 (C^2), 151.17 (C^4, C^5), 183.78 (C^1, C^3). Found, %: C 30.24; H 0.59; Cl 53.41. $C_5HCl_3O_2$. Calculated, %: C 30.11; H 0.51; Cl 53.33.

2,3,5β-Trichloro-4α-hydroxycyclopent-2-en-1-one (XII) and 2,3,5α-trichloro-4α-hydroxycyclopent-2-en-1-one (XIII). Trichlorocyclopentenol **IV**, 1.0 g (0.8 mmol), was dissolved in 30 ml of acetone, and 15% hydrochloric acid was added dropwise under stirring until pH 1. The mixture was stirred at room temperature until the initial compound disappeared completely (3 h; TLC, petroleum ether–ethyl acetate, 7:3) and neutralized with a 10% aqueous solution of sodium hydrogen carbonate to pH 7. The solvent was distilled off under reduced pressure, the residue was treated with a saturated solution of sodium chloride, and the mixture was extracted with ethyl acetate (3× 15 ml). The combined extracts were washed with a saturated solution of sodium chloride, dried over $MgSO_4$, and concentrated, and the residue was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (8:2) as eluent to isolate 0.7 g (90%) of a mixture of stereoisomers **XII** and **XIII** at a ratio of 9:1.

2,3,5β-Trichloro-4α-hydroxycyclopent-2-en-1-one (XII). Yellow oily substance, R_f 0.42 (petroleum ether–ethyl acetate, 8:2, double elution). IR spectrum, ν, cm^{-1}: 1089, 1636, 1747, 3440. ^{1} NMR spectrum, δ, ppm: 3.58 d (1H, OH, J = 5.3 Hz), 4.43 d (1H, 5-H, J = 2.5 Hz), 4.95 d.d (1H, 4-H, J = 2.5, 5.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 60.92 (C^5), 78.51 (C^4), 132.78 (C^2), 161.71 (C^3), 188.20 (C^1). Found, %: C 29.98; H 1.39; Cl 52.67. $C_5H_3Cl_3O_2$. Calculated, %: C 29.81; H 1.50; Cl 52.80.

2,3,5α-Trichloro-4α-hydroxycyclopent-2-en-1-one (XIII). Yellow oily substance, R_f 0.31 (petroleum ether–ethyl acetate, 8:2, double elution). IR spectrum, ν, cm^{-1}: 1090, 1616, 1738, 3430. ^1H NMR spectrum, δ, ppm: 4.72 d (1H, 5-H, J = 5.8 Hz), 5.00 d (1H, 4-H, J = 5.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 57.66 (C^5), 70.33 (C^4), 129.88 (C^2), 158.78 (C^3), 183.72 (C^1).

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