Chromium(II) chloride as a highly selective C(5)-dechlorinating agent for functionalized 2,3,5-trichlorocyclopent-2-en-1-ones

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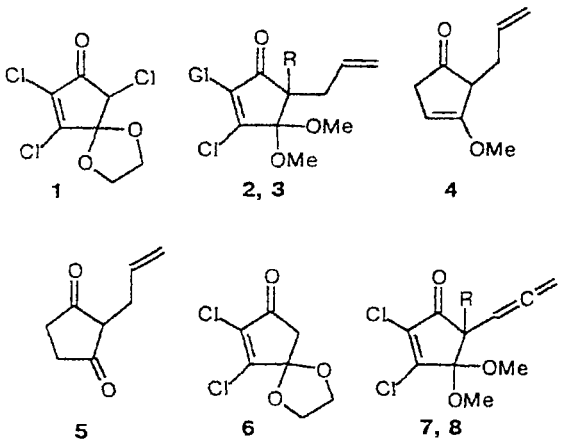
(±)-2,3,5-Trichloro-4,4-ethylenedioxy- and (±)-5-allyl(allenyl)-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-ones undergo regioselective reductive C(5)-dechlorination under the action of $CrCl_2$ to give the corresponding 2,3-dichlorocyclopentenones.

Key words: trichlorocyclopentenones, selective reductive dechlorination; chromium(II) chloride.

In carrying out the synthesis of prostanoids based on 2,3,5-trichloro-4,4-ethylenedioxycyclopent-2-en-1-one (**1**),[1] we faced the problem of its selective reductive mono- and didechlorination with retention of the ring double bond. Because of the commensurable mobility of all three Cl atoms and the high reactivity of the enone double bond, our attempts to carry out selective reductive dechlorination of compounds **1** failed, even with the mildest system (Zn—MeOH). The reactions occurred ambiguously to give several products, unlike behavior of 5-allyl-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-one (**2**), a related compound of ketone **1**, which transformed smoothly into 5-allyl-2,3-dichloro-4,4-dimethoxycyclopent-2-en-1-one (**3**) under the action of Zn—MeOH and into 2-allyl-3-methoxycyclopent-3-en-1-one (**4**) and 2-allylcyclopentane-1,3-dione (**5**) under more drastic conditions (Zn—MeOH—NH_4Cl and Zn—AcOH, respectively).[2] Under conditions of radical dechlorination with Bu_3SnH, compound **2** remains unchanged. 5-Allenyl-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-one (**7**),[4] which is less stable chemically than ketones **1** and **2**, readily resinifies in reactions with the above-mentioned Zn-dechlorinating systems.[5]



R = Cl (**2**, **7**), H (**3**, **8**)

With the aim of carrying out the partial dechlorination of compound **1**, we tested a series of reagents and established that freshly prepared aqueous solutions of $CrCl_2$ allow in H_2O—Me_2CO [6] selective monodechlorination of ketone **1** to give 2,3-dichloro-4,4-ethylenedioxycyclopent-2-en-1-one (**6**) in yields >80%. This reagent also regioselectively reduces trichloride **2** and 5-allenyl-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-one (**7**) to give dichloride **3** and 5-allenyl-2,3-dichloro-4,4-dimethoxycyclopent-2-en-1-one (**8**) in yields of 82 and 71%, respectively.

It is known that $CrCl_2$ in reactions with allyl-, propargyl-, ethynyl-, and alkenylhaloderivatives as well as with alkenyltriflates and allylphosphates in an anhydrous medium readily forms the corresponding organochromium(III) nucleophilic intermediates, which, like Barbier—Grignard reagents, react smoothly *in situ* according to a scheme of 1,2-addition with aldehydes and ketones.[7—12] These transformations occurring under mild conditions are characterized by high chemoselectivity and are widely used in organic synthesis,[13,15] *e.g.*, for the exhaustive reductive dechlorination of α,α-dichloroketones of the cyclopentane series. Judging from the reaction products, in the studied processes of the dechlorination of trichlorocyclopentenones **1**, **2**, and **7**, selective oxidative insertion of $CrCl_2$ at their C(5)—Cl bonds and the formation of C(5)—Cr^{III} intermediates, which rapidly decompose in proton-containing media (H_2O) to give products of reductive dechlorination **3**, **6**, and **8**, also take place. It is remarkable that the most activated and "mobile" chlorine atom at the C(3) atom of compounds **1**, **2**, and **7** remains inert to the action of this reductive agent.

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Experimental

IR spectra were recorded on a UR-20 spectrophotometer (thin layer or suspension in Nujol). NMR spectra were recorded on a Bruker AM-300 spectrometer (^1H at 300 MHz and ^{13}C at 75.47 MHz) with tetramethylsilane as the internal standard. TLC was performed on Silufol plates. Mass spectra were recorded on an MKh-1306 instrument (ionization voltage was 70 eV, ionization chamber temperature was 30—50 °C).

Reductive dechlorination of trichlorocyclopentenones 1, 2, and 7 (general procedure). 20 mL of an aqueous $CrCl_2$ solution prepared according to a procedure described earlier[6] was added gradually with stirring to a solution of trichlorocyclopentenone (2 mmol) in 10 mL of acetone in an argon atmosphere at ~20 °C. The reaction mixture was stirred for 30 min, and acetone was removed on a rotary evaporator. The aqueous phase was extracted with CH_2Cl_2 (3×20 mL) and the combined extracts were washed with a saturated NaCl solution, dried with $MgSO_4$, and concentrated; the residue was chromatographed using SiO_2.

(±)-2,3-Dichloro-4,4-ethylenedioxycyclopent-2-en-1-one (6). Yield 86%, m.p. 129 °C. IR, ν/cm^{-1}: 1480, 1625, 1744. ^1H NMR, δ: 2.80 (s, 2 H, CH_2); 4.0—4.25 (m, 4 H, 2 CH_2O). ^{13}C NMR, δ: 46.57 (C(5)); 66.67 (2 CH_2O); 108.44 (C(4)); 134.70 (C(2)); 158.54 (C(3)); 191.45 (C=O). Found (%): C, 40.10; H, 2.78; Cl, 34.15. $C_7H_6Cl_2O_3$. Calculated (%): C, 40.22; H, 2.89; Cl, 33.92.

(±)-5-Allyl-2,3-dichloro-4,4-dimethoxycyclopent-2-en-1-one (3). Yield 82%. IR, ν/cm^{-1}: 1608, 1640, 1736. ^1H NMR, δ: 2.40—2.55 (m, 2 H, CH_2); 2.79—2.85 (m, 1 H, C(5)H); 3.39 (s, 3 H, OMe); 3.55 (s, 3 H, OMe); 5.05—5.18 (m, 2 H, CH_2=); 5.87—6.03 (m, 1 H, CH=). ^{13}C NMR, δ: 30.75 (CH_2); 51.68 (OMe); 51.86 (OMe); 55.41 (C(5)); 102.69 (C(4)); 117.22 (CH_2=); 134.84 (C(2)); 135.53 (—CH=); 158.32 (C(3)); 194.13 (C=O). MS, m/z: 250 $[M]^+$, 2215 $[M-Cl]^+$, 113 $[M-117]^+$. Found (%): C, 47.96; H, 4.69; Cl, 28.59. $C_{10}H_{12}Cl_2O_3$. Calculated (%): C, 47.81; H, 4.78; Cl, 28.29.

(±)-5-Allenyl-2,3-dichloro-4,4-dimethoxycyclopent-2-en-1-one (8). Yield 71%. IR, ν/cm^{-1}: 870, 1460, 1480, 1612, 1642, 1750, 1980. ^1H NMR, δ: 3.16 (s, 1 H, C(5)H); 3.36 (s, 3 H, OMe); 3.43 (s, 3 H, OMe); 4.75—4.90 (m, 2 H, CH_2=); 5.05—5.15 (m, 1 H, —CH=). ^{13}C NMR, δ: 51.51 (OMe); 51.59 (OMe); 57.20 (C(5)); 76.44 (CH_2=); 83.70 (—CH=); 101.94 (C(4)); 136.15 (C(2)); 158.01 (C(3)); 191.52 (C=O); 210.63 (=C=).

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