

SHORT
COMMUNICATIONS

Racemic *cis,cis*-2,3,5-Trichloro-2-cyclopentene-1,4-diol

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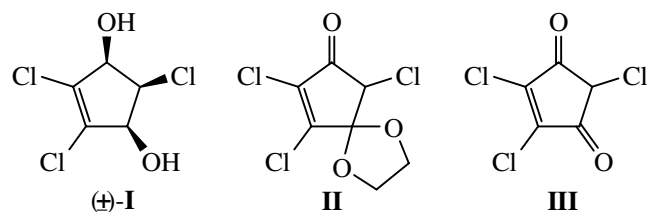
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Cyclopentene blocks functionalized with various substituents possess obvious synthetic interest for they are extensively used in approaches to prostaglandins [1, 2], carbonucleosides [3, 4], cyclopentene antibiotics [5, 6], as binding components in building up heterocyclic structures [7, 8], etc.

In extension of studies on application of trichlorocyclopentenones, readily available from hexachlorocyclopentadiene [9], we report here on a new synthesis of *cis,cis*-trichlorocyclopentendiol (**I**), where the “orthogonality” of the carbon atoms functionalization combined with the *meso*-topology of the structure ensure also the opportunity to effectively apply enzymatic and chemical chiralization methods.



Compound **I** was prepared from the formerly described cyclopentenone ethylene ketal **II** [10]. The latter by a stringent acid hydrolysis (98% H_2SO_4 , 0°C , 1 h) was first converted into the known trichlorocyclopentenedione (**III**) [11] in a quantitative yield, and then the reduction of compound **III** with sodium borohydride under standard conditions (2 equiv of NaBH_4 , EtOH, 0°C , 1 h) provided the target diol **I** (yield 40%). The reduction of diketone **III** is highly stereospecific, for the bulky Cl atom at C^5 atom efficiently blocks the approach of anion BH_4^- from the rear side thus ensuring a stereoselective formation of diol **I** possessing *cis,cis*-structure.

In the ^1H NMR spectrum of diol **I** doublet signals appear from protons attached to C^1 , C^4 , and C^5 in a ratio 2:1 (J 5.5 Hz) characteristic of close in structure cyclopentene *cis*-chlorohydrins [9].

2,3,5-Trichloro-2-cyclopentene-1,4-diol (I). To a stirred suspension of 0.07 g (1.80 mmol) of NaBH_4 in 5 ml of ethanol at 0°C was added 0.2 g (1.0 mmol) of compound **III** in 3 ml of ethanol, the reaction mixture was stirred at this temperature till disappearance of the initial diketone (TLC monitoring, ~1 h). Then the reaction mixture was quenched by adding saturated solution of NH_4Cl , and ethanol was evaporated. The residue was extracted with CHCl_3 (4×5 ml), the combined organic solutions were washed with a saturated NaCl solution (2×10 ml), dried with MgSO_4 , filtered off, and evaporated. The residue was purified by column chromatography on silica gel (eluent CH_3COOEt –petroleum ether, 1:2). Yield 0.08 g (~40%). IR spectrum, ν , cm^{-1} : 735, 835, 1105, 1160, 1280, 1635, 3230–3390. ^1H NMR spectrum, δ , ppm: 3.20 br.s (2H, OH), 4.64 d (2H, C^1H , C^4H , J 5.5 Hz), 4.80 t (1H, CHCl , J 5.5 Hz). ^{13}C NMR spectrum, δ , ppm: 62.48 (C^5), 74.01 (C^1 , C^4), 134.0 (C^2 , C^3). Found, %: C 30.12; H 2.83; Cl 53.25. $\text{C}_5\text{H}_5\text{Cl}_3\text{O}_2$. Calculated, %: C 29.59; H 2.48; Cl 53.08.

2,3,5-Trichloro-2-cyclopentene-1,4-dione (III). In a reaction flask containing 1 ml of concn. H_2SO_4 cooled to 0°C was added at stirring by small portions 0.2 g (0.82 mmol) of compound **II**. The reaction mixture was stirred for ~1 h, diluted with 20 ml of CHCl_3 , the organic layer was separated, the acid layer was extracted with CHCl_3 (2×10 ml). The combined organic solutions were washed with a saturated NaCl solution (2×10 ml), dried with MgSO_4 , filtered, and evaporated. The residue was recrystallized from a mixture CH_3COOEt –petroleum ether, 1:10. Yield 0.16 g (~98%), colorless crystals, mp

66.5–68°C (67–68°C [11]). IR spectrum, ν , cm^{-1} : 730, 835, 1175, 1220, 1570, 1700, 1740, 1780. ^1H NMR spectrum, δ , ppm: 4.78 s (1H, CHCl). ^{13}C NMR spectrum, δ , ppm: 52.03 (C^5), 150.92 (C^2 , C^3), 183.55 (C^1 , C^4). Found, %: C 30.20; H 0.70; Cl 53.25. $\text{C}_5\text{HCl}_3\text{O}_2$. Calculated, %: C 30.11; H 0.51; Cl 53.33.

IR spectra were recorded on spectrophotometers UR-20 and Specord-80 from thin films or mulls in mineral oil. ^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM-300 at operating frequencies 300.13 and 75.47 MHz respectively, internal reference TMS.

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