ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 5, pp. 764–766. © Pleiades Publishing, Ltd., 2008.
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**SHORT COMMUNICATIONS**

# Features of 2,3,5-Trichloro-4-hydroxy-2-cyclopenten-1-one Reduction with Sodium Borohydride

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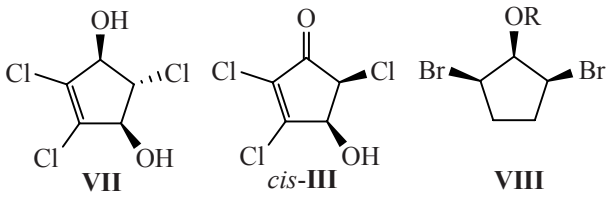
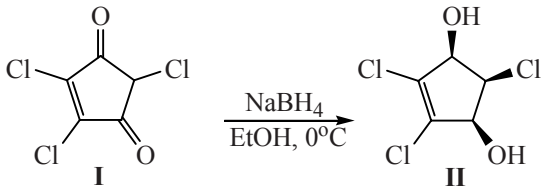
Received September 1, 2007

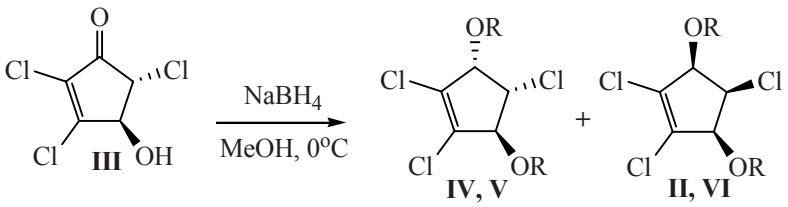
**DOI:** 10.1134/S1070428008050242

Formerly [1] a borohydride reduction of cyclopentendione (**I**) was described and spectral characteristics of the formed *cis,cis*-cyclopentenediol (**II**) were reported.

The study of analogous reaction of the related cyclopentene *trans*-chlorohydrin **III** [2] revealed a number of interesting facts. For instance, whereas the borohydride reduction of highly reactive cyclopentenedione **I** proceeded stereoselectively to give *cis,cis*-diol **II**, the reaction with hydroxycyclopentenone **III** yielded a mixture of isomeric diols **IV** and **II** in a ratio 1:2 (as was estimated from the integral intensities of signals of protons $H^1$, $H^4$, and $H^5$ in the $^1H$ NMR spectrum of the mixture of diacetates **V** and **VI** obtained by acetylation of the corresponding mixture of diols). In the studied reduction of *trans*-chlorohydrin **III** the unexpected fact was the formation of *cis,cis*-diol **II** instead of the expected *trans,trans*-diol **VII**. The reasonable cause of it is the assumed ready isomerization of initial *trans*-chlorohydrin **III** into *cis*-chlorohydrin under alkaline conditions of the borohydride reduction. Note that the characteristic indication for assignment of vicinal *cis*- and *trans*-disubstitution in cyclopentenes (and cyclopentanes) is the value of coupling constants of protons at these substituents; therewith the larger coupling constants (from 5–6 Hz and more till 9 Hz in norbornanes) correspond to the *cis*-disubstitution , and




R = H (**II, IV**), Ac (**V, VI**).

the lesser values (2–4 Hz) are observed in the *trans*-substituted compounds [3]. For instance, whereas in *trans*-isomer **III** $J_{4,5}$ is 2.4 Hz, in *cis*-isomer **III** $J_{4,5}$ is 5.8 Hz [2]. Likewise according to [4] in saturated cyclopentane **VIII** the *cis,cis*-orientation of the substituents is indicated by the presence of a triplet signal of proton H$^1$, $J$ 4.9 Hz.

The $^{13}$C NMR spectrum of symmetric diol **II** contains only 3 signals: 53.03 (C$^5$), 74.17 (C$^1$, C$^4$), and 133.12 (C$^2$, C$^3$) ppm, whereas in the spectrum of *cis,trans*-diol **IV** due to its unsymmetrical structure appear the signals from all five carbon atoms of the cyclopenteneone.

The estimation of the coupling constants of *cis,trans*-diol **VII** was performed using well-resolved spectra of diacetates **V** and **VI**. Thus the $^1$H NMR spectrum of symmetric diacetate **VI** contained a triplet from proton H$^5$ at 4.73 ppm, $J$ 6.0 Hz, and a doublet of doublets from protons H$^1$ and H$^4$ at 5.68 ppm, $J$ 6.0 and 0.7 Hz (coupling constant 0.7 Hz corresponded to W-coupling of protons H$^1$ and H$^4$). The $^1$H NMR spectrum of *cis,trans*-diacetate **V** contained a doublet of doublets signal from H$^5$ at 4.37 ppm, $J_{4,5}$ 4.3 and $J_{1,5}$ 6.0 Hz; signals from protons H$^1$ and H$^4$, same as in the spectrum of compound **VI**, appeared as a doublet of doublets at 5.78 and 5.88 ppm, $J_{1,4}$ 1.7, $J_{4,5}$ 4.3 and $J_{1,4}$ 1.7, $J_{1,5}$ 6.0 Hz respectively. Thus in *cis,trans*-diacetate **V** contrary to expectations also is observed the spin-spin coupling of W-type between H$^1$ and H$^4$ ($J_{1,4}$ 1.7 Hz).

Hence the borohydride reduction of ketoalcohol **III** in contrast to highly reactive cyclopentenedione **I** occurred less selectively and resulted in the formation of a stereoisomeric mixture of *cis*,*cis*- and *cis*,*trans*-trichlorocyclopentenediols.

**Reduction of chlorohydrin III with $NaBH_4$ in MeOH.** To a solution of 0.2 g (0.8 mmol) of trichlorohydroxycyclopentenone **III** in 10 ml of methanol was added at 0°C 0.11 g (2.4 mmol) of $NaBH_4$, and the reaction mixture was stirred for 0.5 h at 0°C and 1.5 h at room temperature. Then while stirring to the reaction mixture 10 ml of acetone was added. The solvent was distilled off in a vacuum, to the residue a saturated solution of NaCl was added, and the product was extracted into EtOAc (3 × 10 ml). The combined extracts were washed with saturated solution of NaCl, dried with $MgSO_4$, and concentrated. The reaction products were isolated by column chromatography on $SiO_2$ (eluent petroleum ether–ethyl acetate, 7:3).

**1β,4β-Dihydroxy-2,3,5β-trichloro-2-cyclopentene (II).** Yield 46%. Colorless crystals, mp 101–103°C, $R_f$ 0.38 (petroleum ether–ethyl acetate, 7:3, double elution). IR spectrum, ν, cm$^{-1}$: 1090, 1640, 3400. $^1$H NMR spectrum, δ, ppm: 4.64 d (1H, H$^1$, C$^4$H, $J$ 5.54 Hz), 4.81 t (1H, H$^5$, $J$ 5.60 Hz). $^{13}$C NMR spectrum, δ, ppm: 61.48 (C$^5$), 74.09 (C$^1$, C$^4$), 133.06 (C$^2$, C$^3$). Found, %: C 29.91; H 2.34; Cl 52.95. $C_5H_5Cl_3O_2$. Calculated, %: C 29.52; H 2.48; Cl 52.28.

**1α,4β-Dihydroxy-2,3,5α-trichloro-2-cyclopentene (IV).** Yield 19%. Colorless oily substance, $R_f$ 0.52 (petroleum ether–ethyl acetate, 7:3, double elution). $^{13}$C NMR spectrum, δ, ppm: 64.16 (C$^5$), 73.56 (C$^1$), 79.88 (C$^4$), 131.04 (C$^2$), 134.22 (C$^3$).

**Acetylation of a mixture of isomeric diols II and IV.** To a solution of 0.1 g (0.50 mmol) of the mixture of trichlorocyclopentenediols **IV** and **II** in 0.24 ml (3 mmol) of pyridine was added at 0°C 0.14 ml (1.5 mmol) of $Ac_2O$, and the reaction mixture was left overnight. The solvent was distilled off in a vacuum, to the residue a saturated solution of NaCl was added, and the product was extracted into EtOAc (3 × 10 ml). The combined extracts were washed with saturated solution of NaCl, dried with $MgSO_4$, and concentrated. The reaction products were isolated by column chromatography on $SiO_2$ (eluent petroleum ether–ethyl acetate**,** 95:5). We obtained 0.08 g (58%) of a mixture of diacetates **V** and **VI** as yellow oily substance, $R_f$ 0.59 (petroleum ether–ethyl acetate, 9:1, double elution).

**1α,4β-Diacetoxy-2,3,5α-trichloro-2-cyclopentene (V)**. IR spectrum, ν, cm$^{-1}$: 1090, 1748. $^1$H NMR spectrum, δ, ppm: 2.09 s (3H, $CH_3$), 2.10 s (3H, $CH_3$), 4.37 d.d. (1H, H$^5$, $J$ 4.3 and 6.0 Hz), 5.78 d.d (1H, H$^1$, $J$ 1.7 and 6.0 Hz), 5.88 d.d (1H, H$^4$, $J$ 1.7 and 4.3 Hz). $^{13}$C NMR spectrum, δ, ppm: 20.42 and 20.52 (2$CH_3$), 58.44 (C$^5$), 74.16 (C$^1$), 80.74 (C$^4$), 130.52 (C$^2$), 132.60 (C$^3$), 169.46 and 169.80 (2CO). Found, %: C 37.51; H 3.04; Cl 36.95. $C_9H_9Cl_3O_4$. Calculated, %: C 37.60; H 3.16; Cl 36.99.

**1β,4β-Diacetoxy-2,3,5β-trichloro-2-cyclopentene (VI).** $^1$H NMR spectrum, δ, ppm: 2.11 s (6H, $CH_3$), 4.73 t (1H, H$^5$, $J$ 6.0 Hz), 5.68 d.d (2H, H$^1$, H$^4$, $J$ 0.7 and 6.0 Hz). $^{13}$C NMR spectrum, δ, ppm: 20.42 (2$CH_3$), 56.23 (C$^5$), 73.91 (C$^1$, C$^4$), 131.76 (C$^2$, C$^3$), 169.63 (2CO).

IR spectra were recorded on spectrophotometers UR-20 and Specord M-80 (from films or mulls in mineral oil). $^{1}H$ and $^{13}C$ NMR spectra were registered on a spectrometer Bruker AM-300 (operating frequencies 300.13 and 75.47 MHz respectively) in $CDCl_3$ using the solvent signals as internal references (7.27, 77.00 ppm). Mass spectra were measured on MKh-1306 instrument, ionizing electrons energy 20 and 70 eV, ionization chamber temperature 75–100°C.

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