

SHORT  
COMMUNICATIONSAddition of Water and Carbon Tetrachloride to Cyclododecene  
in the Presence of Chromium Catalysts

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Synthetic transformations of cyclododecene (**I**) have been studied in sufficient detail [1]. This compound has become accessible due to development of large-scale manufacture of cyclododeca-1,5,9-triene by trimerization of butadiene over titanium- and nickel-containing catalysts. An important product of transformations of cyclododecene (**I**) is cyclododecanol (**II**) which is used as starting material for the synthesis of dodecanedioic acid, dodecane-1,12-diol, and  $\omega$ -dodecalactam [1, 2]. The latter are widely used in the manufacture of polyesters, polyamides, Nylon-12, and high-quality plasticizers [1, 2]. Several methods for the synthesis of cyclododecanol (**II**) from cyclododecene (**I**) are known, in particular those based on epoxidation followed by catalytic reduction with hydrogen [3] and on treatment with three-fold excess of 96%  $\text{H}_2\text{SO}_4$  with subsequent hydrolysis [4].

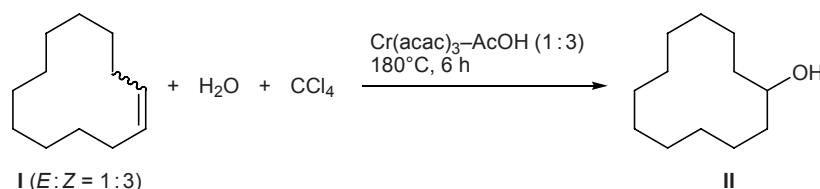
The present communication reports on the direct hydration of cyclododecene (**I**, a mixture of *E* and *Z* isomers at a ratio of 3:1) with water in carbon tetrachloride in the presence of the catalytic system  $\text{Cr}(\text{acac})_3$ -AcOH (1:3). The reaction takes 6 h at 180°C and gives cyclododecanol (**II**) in an overall yield of 67% (Scheme 1). The conversion of olefin **I** is ~72%. Apart from alcohol **II**, 1-chloro-2-trichloro-

methylcyclododecane (**III**) is formed as a result of addition of carbon tetrachloride at the double bond of cyclododecene (**I**); the yield of compound **III** does not exceed 5%.

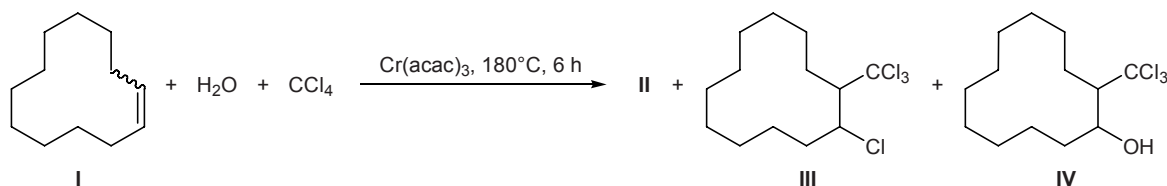
The use of mineral acids ( $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , HCl) as promoter instead of acetic acid did not improve the reaction outcome. On the other hand, we found that copper compounds such as CuCl and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , act as promoters with respect to  $\text{Cr}(\text{acac})_3$ , but the yield of cyclododecanol (**II**) did not exceed 35% in the presence of catalysts containing these copper salts. Chromium(III) formate  $\text{Cr}(\text{HCO}_2)_3$  and hexacarbonylchromium(0)  $\text{Cr}(\text{CO})_6$  also showed a catalytic activity comparable with that of  $\text{Cr}(\text{acac})_3$ .

On the basis of the results of a series of experiments we determined the optimal conditions and reactant concentrations: temperature 180°C, reaction time 6 h, concentration ratio  $[\text{Cr}(\text{acac})_3]$ - $[\text{AcOH}]$ - $[\text{I}]$ - $[\text{CCl}_4]$ - $[\text{H}_2\text{O}]$  1:3:100:100:2000. The conversion of cyclododecene (**I**) initially increases, reaches its maximum value (72%) in 6 h, and then decreases, indicating that the process is reversible. This was confirmed experimentally: under the above conditions cyclododecanol (**II**) underwent dehydration with formation of cyclododecene (**I**) as a 3:2 mixture of *E* and *Z* isomers

Scheme 1.



Scheme 2.



(yield ~75%). Apart from compound **I**, the reaction mixture contained chlorocyclododecane and cyclododecanone.

According to published data, dehydration of cyclododecanol (**II**) catalyzed by *p*-toluenesulfonic acid occurs at 250–270°C [5]. Lowering of the reaction temperature to 180°C in the system CCl<sub>4</sub>–H<sub>2</sub>O–Cr(acac)<sub>3</sub>–AcOH is likely to result from the effect of the catalyst. It should be noted that the formation of cyclododecene (**I**) as a mixture of *E* and *Z* isomers was not surprising. An analogous pattern is observed in the synthesis of cyclododecene (**I**) by different methods, specifically by dehydrochlorination of chlorocyclododecane [6] and by dehydration of cyclododecanol (**II**) in the presence of *p*-toluenesulfonic acid [5]. Therefore, the use of pure *E* and *Z* isomers as initial compounds seems to be unreasonable.

Unlike selective dehydration of cyclododecene (**I**) in the presence of chromium-containing catalyst promoted by acetic acid, the main pathway in the reaction catalyzed by Cr(acac)<sub>3</sub> without promoter is addition of carbon tetrachloride at the double bond of olefin **I**. In this case, the process is accompanied by partial hydrolysis of the adduct, 1-chloro-2-trichloromethylcyclododecane (**III**), to give 2-trichloromethylcyclododecan-1-ol (**IV**) (Scheme 2). The conversion of cyclododecene (**I**) reaches 62%, and the yields of **II**, **III**, and **IV** are 12, 28, and 20%, respectively. When the reaction was carried out using a large excess of water to ensure complete hydrolysis of **III**, the conversion of olefin **I** decreased to 15%, while the product composition remained almost unchanged. Other chromium compounds, such as Cr(CO)<sub>6</sub> and Cr(HCO<sub>2</sub>)<sub>3</sub>, also catalyzed the process, but their catalytic activity was lower than that of Cr(acac)<sub>3</sub>.

The reactions were carried out in 20-ml glass ampules or in a 17-ml stainless-steel high-pressure micro reactor. The reactor (or ampule) was charged with 0.1 mmol of Cr(acac)<sub>3</sub> (in the synthesis of cyclododecanol, 0.3 mmol of acetic acid was also added), 10 mmol of cyclododecene (**I**), 10 mmol of carbon

tetrachloride, and 200 mmol of water. The reactor was hermetically closed (the ampule was sealed) and heated for 6 h at 180°C under stirring. It was then cooled to room temperature and opened, and the mixture was extracted with methylene chloride (3 × 5 ml). The extracts were combined, the solvent was distilled off, and the residue was subjected to column chromatography on aluminum oxide of Brockmann activity grade II using methylene chloride–hexane (1:1 by volume) as eluent.

**Cyclododecanol (II).** Yield 67%, mp 79–80°C (from MeOH); published data [5]: mp 77.6–78.5°C (from petroleum ether). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 64.66 (C<sup>1</sup>), 33.96 (C<sup>2</sup>, C<sup>12</sup>), 27.48 (C<sup>3</sup>, C<sup>11</sup>), 28.42 (C<sup>4</sup>, C<sup>10</sup>), 29.95 (C<sup>5</sup>, C<sup>6</sup>, C<sup>7</sup>, C<sup>8</sup>, C<sup>9</sup>). Found, %: C 77.98; H 13.09. C<sub>12</sub>H<sub>24</sub>O. Calculated, %: C 78.19; H 13.12.

**1-Chloro-2-(trichloromethyl)cyclododecane (III).** Yield 28% (isolated by column chromatography). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 58.89 (C<sup>1</sup>), 59.29 (C<sup>2</sup>), 32.68 (C<sup>3</sup>), 26.01 (C<sup>4</sup>), 32.13 (C<sup>5</sup>), 26.27 (C<sup>6</sup>, C<sup>7</sup>, C<sup>8</sup>, C<sup>9</sup>, C<sup>10</sup>), 26.98 (C<sup>11</sup>), 40.17 (C<sup>12</sup>), 91.58 (C<sup>13</sup>). Found, %: C 48.57; H 6.88; Cl 44.55. C<sub>13</sub>H<sub>22</sub>Cl<sub>4</sub>. Calculated, %: C 48.77; H 6.93; Cl 44.30.

**2-Trichloromethylcyclododecan-1-ol (IV).** Yield 20% (isolated by column chromatography). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 77.97 (C<sup>1</sup>), 59.28 (C<sup>2</sup>), 32.13 (C<sup>3</sup>), 24.83 (C<sup>4</sup>), 31.61 (C<sup>5</sup>), 26.98 (C<sup>6</sup>, C<sup>7</sup>, C<sup>8</sup>, C<sup>9</sup>, C<sup>10</sup>), 26.01 (C<sup>11</sup>), 34.76 (C<sup>12</sup>), 91.58 (C<sup>13</sup>). Found, %: C 51.69; H 7.62; Cl 35.28. C<sub>13</sub>H<sub>23</sub>Cl<sub>3</sub>O. Calculated, %: C 51.75; H 7.68; Cl 35.26.

The products were analyzed by gas–liquid chromatography using Tsvet-102 and Chrom-5 instruments; flame ionization detector, 1.2-m × 3-mm column packed with 5% of SE-30 on Chromaton N-AW-HMDS (0.125–0.160 mm), carrier gas helium (50 ml/min), oven temperature programming from 50 to 220°C. The <sup>13</sup>C NMR spectra were recorded on a Jeol FX-90Q spectrometer at 22.5 MHz; the chemical shifts were measured relative to tetramethylsilane.

The elemental compositions were determined on a Carlo Erba 1106 analyzer.

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