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Hydration of Alkenes and Cycloalkenes in the Presence of Chromium and Copper Complexes

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Abstract—Chromium and copper complexes catalyzed hydration of acyclic and cyclic olefins in the presence of carbon tetrachloride at 110–160°C (4–12 h) with formation of the corresponding alcohols.

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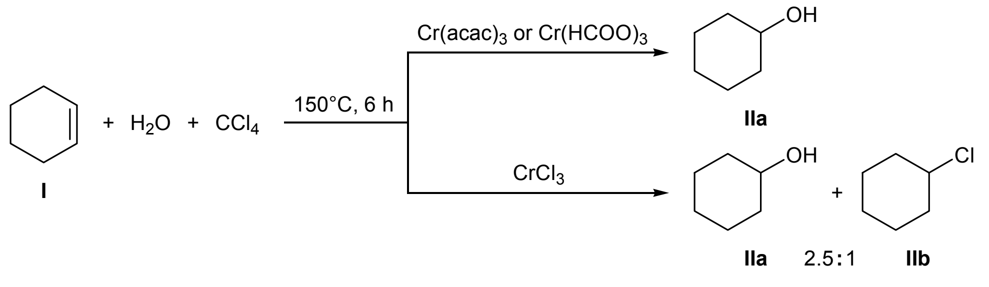
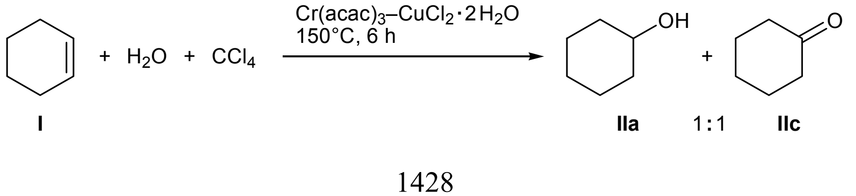
Hydration of olefins occupies a particular place among numerous reactions used in industry and laboratory practice. Acids [1–3], zeolites [4–6], and transition metal complexes [7–9] are used as hydration catalysts. Metal complex catalysts offer a number of advantages over strong acids in the hydration of olefins (low catalyst consumption, no risk of corrosion); however, there are only a few examples of their application in this reaction. The goal of the present work was to find efficient metal complex catalysts ensuring addition of water to olefinic double bond and develop a general catalytic procedure for the preparation of alcohols from accessible olefins.

We previously showed that chromium(III) acetylacetonate in the presence of acetic acid and carbon tetrachloride catalyzes hydration of cyclododecene to cyclododecanol in 67% yield [10]. In this work we used $Cr(acac)_3$, $Cr(HCO_2)_3$, and $CrCl_3$ as catalysts and examined hydration of acyclic, cyclic, and functionally substituted olefins and norbornenes. Preliminary experiments showed that $Cr(acac)_3$ is the best catalyst for the hydration of olefins. A necessary condition for successful addition of water to olefinic double bond under catalysis by chromium complexes is the presence of carbon tetrachloride in the reaction mixture. With a view to elucidate the role of CCl_4, we examined the composition of the system $H_2O–CCl_4–Cr(acac)_3$ after heating for 5 h at 100–160°C. According to the data of mercurimetric titration, the mixture contained hydrogen chloride at a concentration of 5.0–5.7 mg/ml. We previously found by iodometric titration that carbon tetrachloride reacts with water in the presence

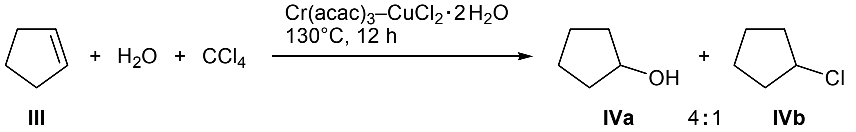
Scheme 1.



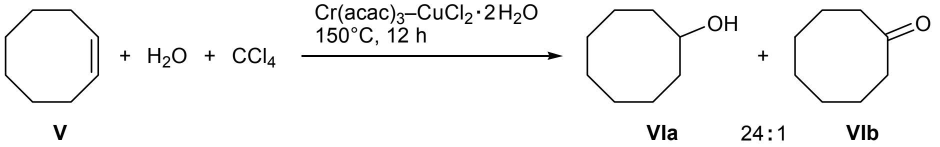
Scheme 2.



Scheme 3.



Scheme 4.



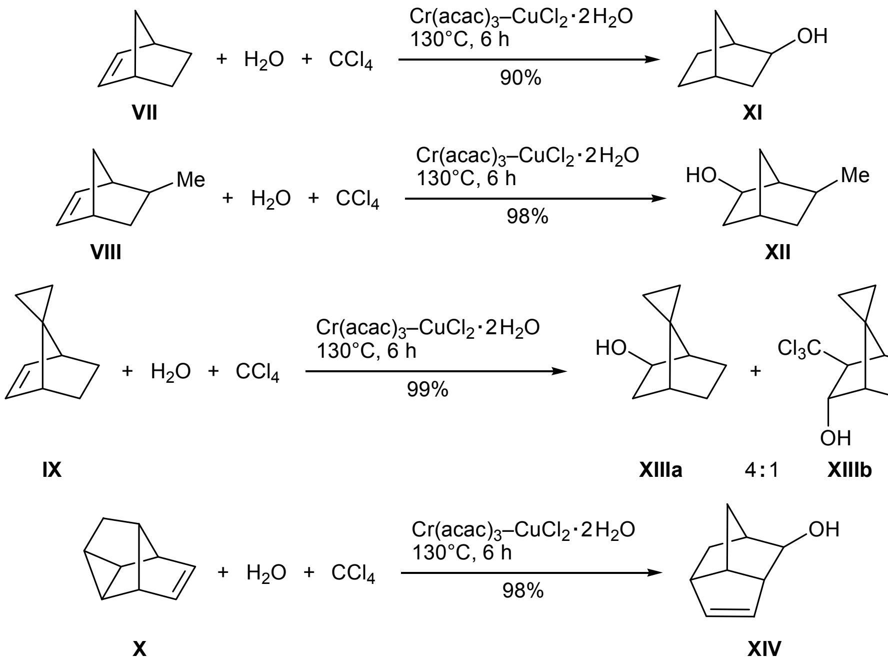
of chromium-, copper-, and ruthenium-containing catalysts to generate 1.2 mg/ml of hypochlorous acid [11]. Taking into account that hypochlorous and hydrochloric acids are fairly reactive compounds, we presumed that they are capable of catalyzing hydration of olefins both taken separately and in combination with chromium and copper complexes.

Using the hydration of cyclohexene (**I**) as model reaction we determined the optimal conditions and reactant ratio [$Cr(acac)_3$–**I**–H_2O–CCl_4 0.01:1:20:1]. The conversion of cyclohexene at 150°C in 6 h was 25%, and the only product was cyclohexanol (**Ia**). Replacement of $Cr(acac)_3$ by $Cr(HCO_2)_3$ or $CrCl_3$ led to reduced conversion of cyclohexene (down to 13 and 19%, respectively). The reaction in the presence of $CrCl_3$ as catalyst gave a mixture of cyclohexanol (**Ia**) and cyclohexyl chloride (**IIb**) (Scheme 1).

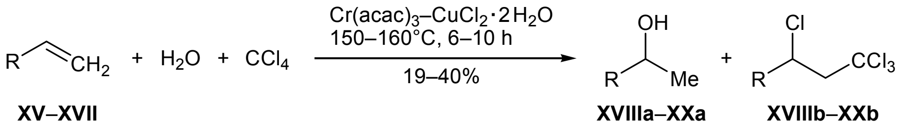
Addition of copper compounds [$CuCl_2\cdot2H_2O$, CuCl, $CuBr_2$, CuBr, $Cu(acac)_2$, $Cu(OAc)_2$] as co-catalysts to $Cr(acac)_3$ improved the conversion of cyclohexene. The catalytic system $Cr(acac)_3$–$CuCl_2\cdot2H_2O$ (1:1) ensured 78% conversion of the substrate, and the products were cyclohexanol (**IIa**) and cyclohexanone (**IIc**) at a ratio of 1:1. Cyclohexanone (**IIc**) is likely to be formed as a result of oxidation of cyclohexanol (**IIa**) with carbon tetrachloride in the presence of $Cr(acac)_3$ [10, 11] (Scheme 2).

The system $Cr(acac)_3$–$CuCl_2\cdot2H_2O$ was used to catalyze the hydration of cyclopentene (**III**). The reaction of **III** with H_2O in CCl_4 at 130°C in 12 h gave a mixture of cyclopentanol (**IVa**) and cyclopentyl chloride (**IVb**) at a ratio of 4:1, the conversion of **III** being complete (Scheme 3). Under analogous conditions, the hydration of cyclooctene (**V**) was charac-

Scheme 5.

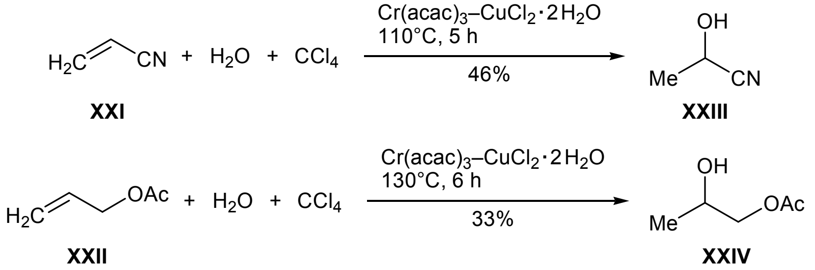


Scheme 6.



XV, **XVIII**, R = C_5H_{11}; **XVI**, **XIX**, R = C_6H_{13}; **XVII**, **XX**, R = C_8H_{17}; **XVIII**, **a** : **b** = 1.2 : 1; **XIX**, **a** : **b** = 1 : 1.5; **XX**, **a** : **b** = 1 : 2.

Scheme 7.



terized by complete conversion, the selectivity with respect to cyclooctanol (**VIa**) being 96% (Scheme 4).

Compounds of the norbornene series, namely bicyclo[2.2.1]hept-2-ene (**VII**), 5-*exo*-methylbicyclo[2.2.1]hept-2-ene (**VIII**), spiro[bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane] (**IX**), and tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (**X**), turned out to be highly reactive under the above hydration conditions (Scheme 5). Unlike other compounds of this series, spiro[bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane] (**IX**) reacted with H_2O and CCl_4 to give a mixture of the corresponding alcohol **XIIIa** and trichloromethyl derivative **XIIIb**. The formation of the latter suggests participation of hypochlorous acid in the process. Compound **X** took up water molecule at the cyclopropane ring to produce tricyclo[6.1.1.0^{3,7}]non-4-ene-2-*exo*-ol (**XIVa**) (Scheme 5).

Terminal olefins [hept-1-ene (**XV**), oct-1-ene (**XVI**), and dec-1-ene (**XVII**)] showed a low reactivity. The major hydration products were 1,1,1,3-tetrachloroalkanes **XVIIIb**–**XXb** resulting from addition of carbon tetrachloride at the double bond (Scheme 6). The hydration of functionally substituted olefins, acrylonitrile (**XXI**) and allyl acetate (**XXII**) was highly selective, but the substrate conversion was fairly moderate (Scheme 7). Raising the temperature or increase of the reaction time induced appreciable polymerization of initial compounds **XXI** and **XXII**, whereas the yield of alcohols **XXIII** and **XXIV** remained almost unchanged.

The progress of the reactions was monitored by GLC, and the product structure was determined by spectral methods and by comparing their properties with those of authentic samples and published data.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 100.62 MHz using $CDCl_3$ as solvent. The mass spectra were obtained on a Shimadzu GCMS-QP2010Plus instrument (SPB-5 capillary column, 30 m×0.25 mm, carrier gas helium, oven temperature programming from 40 to 300°C at a rate of 8 deg/min, injector temperature 280°C, ion source temperature 200°C; electron impact, 70 eV). The elemental compositions were determined on a Carlo Erba 1106 analyzer. The progress of reactions and the purity of products were monitored by GLC using Shimadzu GC-9A and GC-2014 instruments (2-m × 3-mm column packed with 5% of SE-30 on Chromaton N-AW-HMDS; oven temperature programming from 50 to 270°C at a rate of 8 deg/min; carrier gas helium, flow rate 47 ml/min).

Hydration of olefins in the presence of carbon tetrachloride and chromium-containing catalysts (*general procedure*). A 17-ml stainless steel high-pressure micro reactor or a 20-ml glass ampule was charged with 0.01 mmol of $Cr(acac)_3$, $Cr(HCO_2)_3$, $Cr(CO)_6$, or $CrCl_3$, 1 mmol of the corresponding olefin, 1 mmol of carbon tetrachloride, and 20 mmol of water. The reactor was tightly closed (the ampule was sealed) and heated for 6–12 h at 130–160°C under continuous stirring. The reactor (ampule) was then cooled to room temperature and opened, the reaction mixture was filtered through a layer of Al_2O_3 (using hexane–methylene chloride, 1 : 1 by volume, as eluent), unreacted carbon tetrachloride was distilled off, and the residue was distilled under reduced pressure, recrystallized from ethanol, or subjected to column chromatography on silica gel using hexane–methylene chloride (1 : 1 by volume) as eluent.

Hydration of olefins in the presence of carbon tetrachloride and chromium–copper catalyst (*general procedure*). A 17-ml stainless steel high-pressure micro reactor or a 20-ml glass ampule was charged with 0.01 mmol of Cr(acac)$_3$, 0.01 mmol of $CuCl_2 \cdot 2H_2O$, 1 mmol of olefin, 1 mmol of CCl_4, and 20 mmol of water. The reactor was tightly closed (the ampule was sealed) and heated for 6–12 h at 110–160°C under continuous stirring. The products were isolated as described above.

Cyclohexanol (IIa). Yield 39%, bp 49–50°C (5 mm); published data [12]: bp 160–161°C. IR spectrum: ν 3350 cm^{-1} (OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.93 (C^3, C^5), 25.57 (C^4), 35.41 (C^2, C^6), 70.09 (C^1). Found, %: C 71.92; H 12.05. $C_6H_{12}O$. Calculated, %: C 72.35; H 13.87.

Cyclohexyl chloride (IIb). Yield 5%. Mass spectrum, *m*/*z* (I_{rel}, %): 118 (2) $[M]^+$, 29 (9), 39 (25), 40 (7), 41 (48), 42 (7), 53 (9), 54 (30), 55 (41), 56 (9), 67 (100), 68 (7), 69 (5), 81 (7), 82 (70). Found, %: C 60.70; H 9.40; Cl 29.90. $C_6H_{11}Cl$. Calculated, %: C 60.75; H 9.35; Cl 29.90. *M* 118.60.

Cyclohexanone (IIc). Yield 39%, bp 33–35°C (6 mm); published data [12]: bp 155°C. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.07 (C^4), 27.09 (C^3, C^5), 41.99 (C^2, C^6), 210.80 (C^1). Mass spectrum, *m*/*z* (I_{rel}, %): 98 (34) $[M]^+$, 29 (16), 39 (25), 40 (7), 41 (34), 42 (84), 43 (20), 54 (5), 55 (100), 56 (16), 69 (23), 70 (20), 99 (5). Found, %: C 73.45; H 10.30. $C_6H_{10}O$. Calculated, %: C 73.42; H 10.27. *M* 98.14.

Cyclopentanol (IVa). Yield 80%, bp 35–38°C (6 mm); published data [12]: bp 139–140°C. ^{13}C NMR spectrum, δ_C, ppm: 24.72 (C^3, C^4), 36.28 (C^2, C^5), 74.87 (C^1). Mass spectrum, *m*/*z* (I_{rel}, %): 86 (4) $[M]^+$, 40 (4), 41 (16), 42 (8), 43 (24), 44 (31), 45 (5), 55 (6), 57 (100), 58 (19), 59 (3), 67 (13), 68 (13), 69 (4). Found, %: C 69.70; H 11.73. $C_5H_{10}O$. Calculated, %: C 69.72; H 11.70. *M* 86.13.

Cyclopentyl chloride (IVb). Yield 20%, bp 114°C [12]. ^{13}C NMR spectrum, δ_C, ppm: 22.43 (C^3, C^4), 38.61 (C^2, C^5), 60.13 (C^1). Found, %: C 57.40; H 8.63; Cl 33.97. C_5H_9Cl. Calculated, %: C 57.42; H 8.67; Cl 33.90.

Cyclooctanol (VIa). Yield 96%, bp 104–105°C (15 mm); published data [12]: bp 106–108°C (22 mm). IR spectrum, ν, cm^{-1}: 3600, 1150 (OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.48 (C^5), 27.64 (C^4, C^6), 22.95 (C^3, C^7), 34.80 (C^2, C^8), 72.03 (C^1). Mass spectrum, *m*/*z* (I_{rel}, %): 29 (19), 31 (8), 39 (15), 41 (45), 42 (19), 43 (23), 44 (24), 45 (7), 54 (23), 55 (27), 56 (20), 57 (100), 66 (7), 67 (41), 68 (43), 69 (20), 81 (34), 82 (38), 95 (12), 110 (10). Found, %: C 74.63; H 12.44. $C_8H_{16}O$. Calculated, %: C 74.94; H 12.58.

Cyclooctanone (VIb). Yield 4%. Mass spectrum, *m*/*z* (I_{rel}, %): 126 (19) $[M]^+$, 39 (30), 40 (7), 41 (77), 42 (76), 43 (17), 53 (7), 54 (9), 55 (80), 56 (37), 57 (9), 58 (8), 67 (22), 68 (18), 69 (25), 70 (23), 71 (8), 79 (4), 80 (5), 82 (42), 83 (40), 84 (46), 85 (4), 93 (5), 97 (20), 98 (100), 99 (6), 111 (7). Found, %: C 76.05; H 10.95. $C_8H_{14}O$. Calculated, %: C 76.14; H 11.18. *M* 126.20.

Bicyclo[2.2.1]heptan-2-*exo*-ol (IXa). Yield 90%, mp 125–126°C (from EtOH) [12]. ^{13}C NMR spectrum, δ_C, ppm: 24.22 (C^6), 27.96 (C^5), 34.12 (C^7), 35.13 (C^4), 41.80 (C^3), 43.79 (C^1), 74.30 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 112 (2) $[M]^+$, 29 (49), 31 (12), 39 (46), 40 (10), 41 (49), 42 (12), 43 (22), 44 (7), 53 (15), 55 (24), 56 (7), 57 (24), 66 (44), 67 (61), 68 (39), 70 (10), 71 (7), 77 (7), 79 (100), 80 (7), 81 (12), 83 (22), 84 (7), 94 (83), 95 (7), 97 (7), 111 (2), 112 (2). Found, %: C 75.09; H 9.88. $C_7H_{12}O$. Calculated, %: C 74.95; H 10.78. *M* 112.17.

6-*exo*-Methylbicyclo[2.2.1]heptan-2-*exo*-ol (XIIa). Yield 98%, bp 78–80°*C* (5 mm). ^{13}C NMR spectrum, δ_C, ppm: 21.4 (C^8), 30.9 (C^7), 31.30 (C^6), 35.9 (C^4), 37.90 (C^5), 42.90 (C^3), 49.90 (C^1), 74.03 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 126 (2) $[M]^+$, 29 (20), 31 (5), 39 (41), 40 (5), 41 (37), 42 (5), 43 (44), 44 (2), 45 (2), 51 (2), 53 (17), 54 (5), 55 (15), 56 (2), 57 (5), 58 (2), 59 (2), 65 (2), 66 (2), 67 (44), 68 (2), 69 (5), 70 (2), 71 (7), 72 (5), 77 (7), 79 (15), 80 (37), 81 (100), 82 (10), 83 (10), 91 (5), 93 (29), 97 (7), 108 (91), 109 (2), 111 (5). Found, %: C 76.13; H 11.05. $C_8H_{14}O$. Calculated, %: C 76.14; H 11.18. *M* 126.20.

Spiro[bicyclo[2.2.1]heptane-7,1′-cyclopropan]-2-*exo*-ol (XIIIa). Yield 81%, bp 71–73°C (3 mm). ^{13}C NMR spectrum, δ_C, ppm: 10.41 (C^8), 13.99 (C^9), 21.74 (C^6), 31.51 (C^5), 31.87 (C^7), 36.30 (C^3), 46.46 (C^4), 53.36 (C^1), 73.45 (C^2). Found, %: C 78.25; H 9.99. $C_9H_{14}O$. Calculated, %: C 78.21; H 10.21.

3-*exo*-(Trichloromethyl)spiro[bicyclo[2.2.1]-heptane-7,1′-cyclopropan]-2-*endo*-ol (XIIIb). Yield 20%, R_f 0.69 (hexane–CH_2Cl_2). ^{13}C NMR spectrum, δ_C, ppm: 5.17 (C^8), 10.41 (C^9), 22.59 (C^5), 24.64 (C^6), 40.73 (C^7), 50.99 (C^1, C^4), 62.97 (C^3), 73.45 (C^2), 92.87 (C^{10}). Found, %: C 47.48; H 4.95; Cl 41.52.

$C_{10}H_{12}Cl_3O_3$. Calculated, %: C 47.18; H 4.75; Cl 41.78.

Tricyclo[6.1.1.0^{3,7}]non-4-en-2-*exo*-ol (XIV). Yield 98%, mp 107–109°C. ^{13}C NMR spectrum, δ_C, ppm: 34.97 (C^9), 35.10 (C^4), 41.15 (C^3), 49.75 (C^5), 52.52 (C^1), 55.22 (C^8), 77.10 (C^2), 135.06 (C^6), 140.37 (C^7). Mass spectrum, m/z (I_{rel}, %): 136 (62) $[M]^+$, 41 (31), 51 (22), 52 (11), 53 (17), 55 (13), 56 (14), 65 (29), 66 (65), 67 (81), 70 (30), 77 (66), 78 (36), 79 (100), 80 (75), 91 (35), 92 (14), 105 (20), 107 (9), 108 (10), 117 (54), 118 (13). Found, %: C 79.30; H 8.76. $C_9H_{12}O$. Calculated, %: C 79.37; H 8.88. M 136.19.

Heptan-2-ol (XVIIIa). Yield 20%, bp 25–27°C (1 mm); published data [13]: bp 80°C (30 mm). ^{13}C NMR spectrum, δ_C, ppm: 13.99 (C^7), 22.94 (C^6), 23.30 (C^1), 25.92 (C^4), 32.35 (C^5), 39.48 (C^3), 67.22 (C^2). Mass spectrum, m/z (I_{rel}, %): 40 (15), 41 (23), 42 (9), 43 (34), 44 (10), 45 (100), 55 (24), 56 (10), 57 (14), 58 (10), 59 (11), 69 (10), 70 (8), 83 (8), 98 (7), 101 (4). Found, %: C 72.39; H 13.85. $C_7H_{16}O$. Calculated, %: C 72.35; H 13.87.

1,1,1,3-Tetrachlorooctane (XVIIIb). Yield 16%, bp 107–109°C (10 mm) [11]. ^{13}C NMR spectrum, δ_C, ppm: 97.09 (C^1), 55.32 (C^2), 62.41 (C^3), 39.07 (C^4), 31.09 (C^5), 25.69 (C^6), 22.49 (C^7), 13.96 (C^8). Found, %: C 38.09; H 5.55; Cl 56.36. $C_8H_{14}Cl_4$. Calculated, %: C 38.12; H 5.60; Cl 56.28.

Octan-2-ol (XIXa). Yield 17%, bp 36–38°C (1 mm); published data [13]: bp 92–93°C (30 mm). ^{13}C NMR spectrum, δ_C, ppm: 13.99 (C^8), 22.87 (C^7), 23.45 (C^1), 25.90 (C^4), 29.70 (C^5), 32.20 (C^6), 39.60 (C^3), 67.28 (C^2). Mass spectrum, m/z (I_{rel}, %): 29 (7), 31 (2), 39 (9), 41 (17), 42 (6), 43 (14), 44 (5), 45 (100), 46 (3), 55 (20), 56 (8), 57 (4), 58 (2), 69 (7), 70 (6), 83 (3), 84 (5), 96 (2), 97 (6), 110 (2), 112 (2), 115 (2). Found, %: C 73.73; H 13.90. $C_8H_{18}O$. Calculated, %: C 73.78; H 13.93.

1,1,1,3-Tetrachlorononane (XIXb). Yield 19%, bp 106–107°C (9 mm) [11]. ^{13}C NMR spectrum, δ_C, ppm: 14.06 (C^9), 22.55 (C^8), 25.97 (C^7), 28.58 (C^6), 31.64 (C^5), 39.10 (C^4), 57.66 (C^3), 62.41 (C^2), 97.12 (C^1). Found, %: C 40.55; H 6.09; Cl 53.36. $C_9H_{16}Cl_4$. Calculated, %: C 40.63; H 6.06; Cl 53.31.

Decan-2-ol (XXa). Yield 6%. Mass spectrum, m/z (I_{rel}, %): 29 (17), 31 (2), 39 (7), 41 (21), 43 (20), 44 (6), 45 (100), 46 (2), 55 (13), 56 (9), 57 (11), 69 (15), 70 (7), 71 (5), 83 (8), 84 (4), 85 (4), 97 (3), 98 (3), 111 (2), 112 (4), 140 (2), 143 (2). Found, %: C 75.90; H 14.00. $C_{10}H_{22}O$. Calculated, %: C 75.88; H 14.01.

1,1,1,3-Tetrachloroundecane (XXb). Yield 13%, bp 93–95°C (1 mm) [11]. ^{13}C NMR spectrum, δ_C, ppm: 14.03 (C^{11}), 22.61 (C^{10}), 23.87 (C^8), 25.97 (C^9), 27.71 (C^7), 28.31 (C^6), 32.20 (C^5), 35.64 (C^4), 58.89 (C^3), 63.60 (C^2), 94.02 (C^1). Found, %: C 44.85; H 6.96; Cl 48.19. $C_{11}H_{20}Cl_4$. Calculated, %: C 44.92; H 6.85; Cl 48.23.

2-Hydroxypropanenitrile (XXIII). Yield 46%, bp 44–46°C (1 mm). ^{13}C NMR spectrum, δ_C, ppm: 121.19 (C^1), 56.89 (C^2), 20.99 (C^3). Found, %: C 50.72; H 19.67; N 22.50. C_3H_5NO. Calculated, %: C 50.69; H 19.71; N 22.51.

2-Hydroxypropyl acetate (XXIV). Yield 33%. ^{13}C NMR spectrum, δ_C, ppm: 18.04 (C^3), 18.92 (**C**H_3CO), 65.02 (C^1), 65.17 (C^2), 170.03 (C=O). Found, %: C 50.79; H 8.50. $C_5H_{10}O_3$. Calculated, %: C 50.84; H 8.53.

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