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Telomerization of *Z,Z*-Cyclooctadiene with Halomethanes Catalyzed by Chromium, Copper, and Molybdenum Compounds in the Presence of Water

R. I. Khusnutdinov, N. A. Shchadneva, T. M. Oshnyakova, and U. M. Dzhemilev

Institute of Petroleum Chemistry and Catalysis, Russian Academy of Sciences, Ufa, Russia

e-mail: ink@anrb.ru

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Abstract—The telomerization of *1Z,5Z*-cyclooctadiene with halogenated methanes (CCl_4, $CBrCl_3$, $CHCl_3$, CH_2Cl_2) mediated by chromium, copper, and molybdenum complexes has been investigated. It has been shown that the use of water as a nucleophilic additive promotes the formation of 1,4- and 1,5-epoxycyclooctanes and *anti*-8-(trichloromethyl)bicyclo[3.2.1]octan-*exo*-2-ol.

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It is known that complexes of Group VI–VIII transition metals are effective catalysts for the radical telomerization of unsaturated compounds with halogenated methanes and a particular case of it: the addition of CH_nX_{4-n} (X = Cl, Br, or I; n = 0–2) halomethanes to the double bond [1].

An important feature and advantage of metal catalysts is the possibility of enhancing the activity and selectivity of their action by introducing nucleophilic coinitiators into their structure, since their variety is wide and includes both "neutral" ligands (PPh_3, nitriles, tertiary amines, DMF, HMPA) and compounds with a labile hydrogen atom (alcohols, primary and secondary amines) [1].

We have previously reported that effective catalysts for the telomerization of olefins and dienes with CCl_4 are Mo and Cr complexes activated by water, which acts as a nucleophilic coinitiator [2, 3]. The activating effect of water is due to its participation in the generation of hypochlorous acid (HOCl), which is prone to radical decomposition according to the following scheme:

$$H_2O + CCl_4 \xrightarrow[-CHCl_3]{[catalist]} HOCl$$

In this work, we studied the interaction of *1Z,5Z*-cyclooctadiene (1,5-COD) with halomethanes mediated by metal catalysts in the presence of water as the nucleophilic coinitiator. The interest in 1,5-COD is due to the fact that it has been found to undergo a variety of unusual transformations in the reactions with CCl_4 and water in the presence of catalytic systems based on Cr, Mo, and Cu compounds and coordination complexes. As in the previous studies, the reaction of water with CCl_4 in the presence of chromium ($Cr(acac)_3$, $Cr(CO)_6$, $Cr(HCO_2)_3$) or molybdenum ($Mo(CO)_6$) complexes yields hypochlorous acid, as was confirmed by iodometric titration (0.05–0.3 mg/ml) and UV spectroscopy (229–236 nm) [4, 5].

EXPERIMENTAL

The reactions of 1,5-COD with halomethanes (CCl_4, $CBrCl_3$, $CHCl_3$, CH_2Cl_2) were conducted in the presence of reagent-grade transition metal complexes: $Cr(acac)_3$, $Cr(CO)_6$, $Cr(HCO_2)_3$, $Mo(CO)_6$, and $CuCl_2 \cdot 2H_2O$, which were used after recrystallization and vacuum drying. 1,5-Cyclooctadiene was dried over calcined zeolite 3A and distilled before use. The halomethanes, pyridine, and acetonitrile were purified and dehydrated according to standard procedures [6].

The reaction products were analyzed by GLC, ^1H and ^{13}C NMR, and GC–MS techniques. The chromatographic analysis of the products was performed on a Chrom-5 instrument (column length, 1.2 m or 2 m × 3 mm; stationary phase, SE-30 silicone (5%) on Chromaton N-AW-HMDS; carrier gas, helium; programmed temperature rise from 50 to 280°C at a rate of 8°C/min) using an internal standard (octane, octanol-1, 1,1,1,3-tetrachlorononane). ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400Q instrument operating at 100.62 and 400.13 MHz, respectively, in $CDCl_3$; chemical shifts (δ) are given in ppm. Mass spectra were taken on a Finnigan MAT 112 S GC–MS instrument in the electron ionization mode at an ionization energy of 70 eV and an ion source temperature of 22°C. The elemental composition of the products was determined with a Karlo Erba Model 1106 analyzer. The R_f values for compounds (**3**), (**4**), and (**8**) were determined on Silufol 200 × 200 UV 256 TLC plates.

General Procedure for Addition of Halomethanes to 1Z,5Z-Cyclooctadiene

A stainless steel microautoclave (V = 17 ml) or a glass ampoule (V = 10 ml) was charged with 0.1 mmol of $Cr(acac)_3$ ($Cr(HCO_2)_3$, $Cr(CO)_6$, or $Mo(CO)_6$), 10 mmol of 1,5-COD, 10 mmol of CCl_4 ($CBrCl_3$, $CHCl_3$, CH_2Cl_2), and 200 mmol of water. The autoclave was tightly closed (ampoule, sealed) and the reaction mixture was heated at 140–150°C for 6 h with continuous stirring. The autoclave (ampoule) was cooled and unsealed. To separate the catalyst, the reaction mixture was filtered through an alumina (Brockmann II, neutral) bed in a glass column (50 × 10 mm) with a tapered end plugged with a cotton ball to prevent the adsorbent from loss and eluted with a 1 : 1 hexane–ether blend; the solvent was distilled off; and the residue was distilled in a vacuum.

Heating $CHCl_3$ or CH_2Cl_2 with *1Z,5Z*-cyclooctadiene over the catalysts in the presence or absence of water at 150–160°C for 6 h with continuous stirring did not lead to significant transformations of the reactants, which were recovered unchanged from the reaction mixture.

The reaction of CCl_4 with *1Z,5Z*-cyclooctadiene in the presence of $CuCl_2 \cdot 2H_2O$ and experiments with admixed ligands were carried out in a similar fashion.

General Procedure for Addition of Halomethanes to 1Z,5Z-Cyclooctadiene in the Presence of Nitrogen Compounds

A stainless steel microautoclave (V = 17 ml) or a glass ampoule (V = 10 ml) was charged with 0.1 mmol of $Cr(acac)_3$ ($Cr(HCO_2)_3$, $Cr(CO)_6$ or $Mo(CO)_6$), 10 mmol of 1,5-COD, 10 mmol of CCl_4 ($CBrCl_3$, $CHCl_3$, CH_2Cl_2), 200 mmol of water, and 10 mmol of a nitrogen compound; the autoclave was tightly closed (ampoule, sealed); and the reaction mixture was heated at 140–150°C for 6 h with continuous stirring. The reaction mixture was treated as described above, using a 1 : 1 hexane–dichloromethane blend as an eluent. The solvent was distilled off, and the residue was distilled in a vacuum or chromatographed on a silica gel column with diethyl ether eluting.

anti-8-(Trichloromethyl)-exo-2-chlorobicyclo[3.2.1]octane Hydrolysis Procedure

A stainless steel microautoclave (V = 17 ml) was charged with 0.1 mmol of $Cr(acac)_3$, 0.1 mmol of $CuCl_2 \cdot 2H_2O$ 10 mmol of *anti*-8-(trichloromethyl)-*exo*-2-chlorobicyclo[3.2.1]octane, 10 mmol of CCl_4, and 200 mmol of water, and the mixture was heated at 150°C for 6 h with continuous stirring. After completion of the reaction, the autoclave was cooled and unsealed, the reaction mixture was filtered through an alumina layer (eluent, hexane : ether = 1 : 1), the solvent was distilled off, and the residue was distilled in a vacuum.

The isomeric compounds 9-oxobicyclo[4.2.1]nonane (**3**) and 9-oxobicyclo[3.3.1]nonane (**4**) were isolated by column chromatography. The mixture of **3** and **4** was eluted with diethyl ether on a 200 × 10 mm column, packed with silica gel (40/100 μm) to have a bed height of 100 mm. Compounds **9**, **10**, **11**, and **13** were isolated in pure form by fractionating vacuum distillation.

The isolated products had the following characteristics.

2-(Trichloromethyl)-*endo*-6-chloro-*cis*-bicyclo[3.3.0]octane (2). Yield 75%. Bp 94–95°C/133 Pa. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.70–2.30 (m, 8H, $4CH_2$), 2.70–2.90 (m, 3H, 2CH, $CHCCl_3$), 4.14 (s, 1H, CHCl). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 45.62 (C^1), 65.40 (C^2), 32.13 (C^3), 31.24 (C^4), 55.97 (C^5), 69.05 (C^6), 34.90 (C^7), 30.07 (C^8), 103.53 (C^9). Mass spectru, m/z (I, rel. %): M^+ (absent), 225 (5)/224 (2), 200 (8), 198 (10), 191 (14), 189 (20), 163 (8), 153 (30), 149 (57), 145 (25), 143 (83), 127 (8), 117 (24), 107 (100), 91 (20), 81 (43), 79 (85), 67 (22), 65 (13), 53 (11), 51 (11), 41 (13). Found, %: C 41.52, H 4.64, Cl 53.84. Calculated for $C_9H_{12}Cl_4$, %: C 41.25, H 4.62, Cl 54.13. Published data: Bp 70°C/13.30 Pa [7].

9-Oxobicyclo[4.2.1]nonane (3). Yield 30%. R_f (diethyl ether) 0.71. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.25–1.38 (m, 2H, CH_2), 1.46–1.56 (m, 2H, CH_2), 1.38–1.57 (s, 8H, $4CH_2$), 4.30–4.45 (m, 2H, CH–O–CH). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 77.52 (C^1, C^4), 31.34 (C^2, C^3), 35.92 (C^5, C^8), 24.24 (C^6, C^7)). Found, %: C 76.10, H 11.20. Calculated for $C_8H_{14}O$, %: C 76.14, H 11.18, O 12.68. Published data: ^{1}H NMR (δ, ppm): 1.30–2.10 (m, 12H, CH_2), 4.50 (m, 2H, CH–O–CH) [8].

9-Oxobicyclo[3.3.1]nonane (4). Yield 20%. R_f (diethyl ether) 0.42. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.38–1.56 (m, 4H, $2CH_2$), 1.48–1.66 (m, 8H, $4CH_2$) 3.80–3.95 (m, 2H, CH–O–CH). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 66.90 (C^1, C^5), 29.51 (C^2, C^4, C^6, C^8), 19.01 (C^3, C^7). Found, %: C 76.16, H 11.17. $C_8H_{14}O$. Calculated for, %: C 76.14; H 11.18; O 12.68.

Published data: ^{13}C NMR ($CDCl_3$, δ, ppm): 66.5 (C^1, C^5), 29.3 (C^2, C^4, C^6, C^8), 18.8 (C^3, C^7) [9].

Mixture of 1,3-cyclooctadiene (5) and bicyclo[3.3.0]octene (6). Yield 30%. Ratio (**5**) : (**6**) = 1 : 1. Bp 20–30°C/1600 Pa. ^{13}C NMR spectrum ($CDCl_3$, δ, ppm) for **5**: 125.94 (C^1, C^4), 129.32 (C^2, C^3), 23.15 (C^5, C^8), 28.46 (C^6, C^7); for **6**: 40.60 (C^1), 134.44 (C^2), 131.13 (C^3), 40.09 (C^4), 40.99 (C^5), 35.65 (C^6), 25.18 (C^7), 32.28 (C^8). Found, %: C 88.80, H 11.17. Calculated for $C_{16}H_{24}$, %: C 88.82, H 11.18. Published data: Bps 140–146 (**5**) and 130–133°C (**6**) [10].

5-Chlorocyclooctene-1 (7). Yield 10%. Bp 30–32°C/133 Pa. ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 129.34 (C^1), 129.57 (C^2), 25.32 (C^3), 38.77 (C^4), 62.52 (C^5), 36.62 (C^6), 24.13 (C^7), 26.05 (C^8). Found, %: C

66.40, H 04.09, Cl 24.56. Calculated for $C_8H_{13}Cl$, %: C 66.43, H 9.06, Cl 24.51.

4-Cyclooctene-1-ol (8). Yield 3%. R_f(diethyl ether) 0.42. ^{13C} NMR spectrum ($CDCl_3$, δ, ppm): 72.45 (C^1), 37.04 (C^2), 22.77 (C^3), 129.29 (C^4), 130.02 (C^5), 25.57 (C^6), 24.62 (C^7), 36.22 (C^8). Found, %: C 76.15, H 11.15. Calculated for $C_8H_{14}O$, %: C 76.14, H 11.18, O 12.68. Published data: ^{13}C NMR ($CDCl_3$, δ, ppm): 72.26 (72.26 (C^1), 37.17 (C^2), 22.58 (C^3), 129.15 (C^4), 129.89 (C^5), 25.42 (C^6), 24.70 (C^7), 36.07 (C^8)) [11].

***anti*-8-(Trichloromethyl)-*exo*-2-chlorobicyclo[3.2.1]octane (9).** Yield 34%. Bp 95–97°C/133 Pa. ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 50.00(C^1); 56.05(C^2); 32.13(C^3); 28.04(C^4, C^7); 35.07(C^5); 31.03 (C^6); 65.73(C^8); 103.54(C^9). Mass spectrum, *m/z* (*I*, rel. %): M^+ (absent), 225 (2)/224 (2), 197 (10), 191 (15), 189 (17), 155 (66), 153 (24), 149 (41), 145 (27), 143 (78), 129 (17), 117 (17), 115 (44), 111 (15), 109 (28), 108 (10), 107 (100) 92 (44), 81 (73), 80 (20), 79 (98), 78 (10), 77 (34), 75 (20), 67 (39), 66 (12), 65 (24), 54 (24), 53 (22), 51 (22), 41 (41). Found, %: C 41.28, H 4.50, Cl 54.22. Calculated for $C_9H_{12}Cl_4$, %: C 41.25, H 4.62, Cl 54.13.

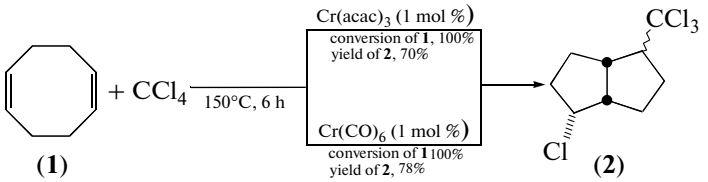
***anti*-8-(Trichloromethyl)bicyclo[3.2.1]octan-*exo*-2-ol (10).** Yield 34%. Bp 97–100°C/133 Pa. ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 46.13(C^1, C^5), 70.02(C^2), 30.86(C^3), 28.04(C^4), 29.21(C^6); 27.75(C^7), 64.95(C^8), 103.54(C^9). Mass spectrum (EI, 70 eV), *m/z* (*I*, rel. %): $[M]^+$ (absent), 198 (15), 191 (17), 189 (24), 153 (32) 151 (41), 149 (61), 145 (24), 143 (71), 142 (15), 117 (17), 115 (17), 111 (20), 109 (20), 107 (76), 91 (22), 85 (20), 81 (100), 80 (27), 79 (78), 78 (7), 77 (24), 75 (12), 67 (39), 65 (20), 57 (24), 55 (27), 54 (29), 53 (20), 51 (22), 44 (22), 43 (20), 42 (10), 41 (51), 39 (49). Found, %: C 44.35, H 5.40, Cl 43.50. Calculated for $C_9H_{12}Cl_3O$, %: C 44.38, H 5.38, Cl 43.67; O 6.57.

***endo*-2-Bromo-6-(trichloromethyl)-*cis*-bicyclo[3.3.0]octane (11).** Yield 59%. Bp 103–105°C/133 Pa. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.19–2.22 (m, 8H, $4CH_2$), 2.23–2.29 (m, 1H, $CHCCl_3$), 2.30–2.45 (m, 2H, 2CH), 4.21 (s, 1H, CHBr). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 45.72 (C^1), 69.09 (C^2), 32.06 (C^3), 31.86 (C^4), 56.67 (C^5), 56.79 (C^6), 35.86 (C^7), 31.56 (C^8), 103.51 (C^9). Mass spectrum, *m/z* (*I*, rel. %): M^+ 306 (15), 191 (18), 189 (22), 155 (25), 153 (74), 127 (20), 125 (35) 117 (100), 109 (23), 91 (31), 81 (12), 79 (50), 67 (36), 41 (32). Found, %: C 35.30, H 4.01, Br 26.02, Cl 34.67. Calculated for $C_9H_{12}BrCl_3$, %: C 35.27, H 3.95, Br 26.07, Cl 34.71.

***trans*-5-Bromo-6-(trichloromethyl)cyclooct-1-ene (13).** Yield 19%. Bp 100–103°C/133 Pa. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm.) 1.20–2.27 (m, 4H, $2CH_2$), 2.75–2.85 (m, 2H, CH_2), 2.85–2.95 (m, 2H, 2CH), 2.98–3.20 (m, 1H, $CHCCl_3$), 5.08 (s, 1H, CHBr), 5.60–5.70 (m, 1H, HC=C), 5.89–5.96 (m, 1H, HC=C). ^{13}C NMR spectrum ($CDCl_3$, δ, ppm): 131.43 (C^1), 129.98 (C^2), 23.24 (C^3), 37.59 (C^4), 55.43 (C^5), 58.06 (C^6), 30.28 (C^7), 22.65 (C^8), 104.84 (C^9). Mass spectrum, *m/z* (*I*, rel.%): M^+ (absent), 191 (25), 189 (37), 155 (36), 153 (100), 127 (23), 125 (27), 117 (82), 109 (32), 91 (31), 81 (31), 79 (42), 67 (25), 41 (19). Found, %: C 35.25, H 3.97, Br 26.09, Cl 34.69. Calculated for $C_9H_{12}BrCl_3$, %: C 35.27, H 3.95, Br 26.07, Cl 34.71.

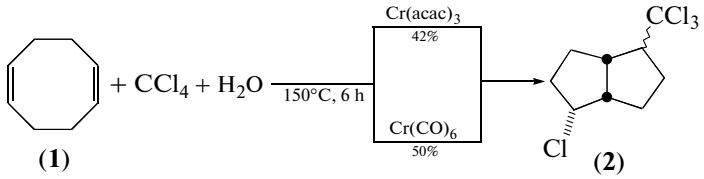
RESULTS AND DISCUSSION

We studied the interaction of *polyhalogenated methanes* ((CCl_4, $CBrCl_3$, $CHCl_3$, CH_2Cl_2) with *1Z,5Z*-cyclooctadiene mediated by chromium ($Cr(acac)_3$, $Cr(HCO_2)_3$, $Cr(CO)_6$) and molybdenum ($Mo(CO)_6$) catalysts in the absence or presence of water. Thus, the heating of 1,5-COD CCl_4 in the presence of Cr-containing catalysts ($Cr(acac)_3$, $Cr(CO)_6$) at 150°C for 6 h gives 2-(trichloromethyl)-*endo*-6-chloro-*cis*-bicyclo[3.3.0]octane (**2**) with a yield of 70–78%, while the rest of the diene is converted into a polymer.

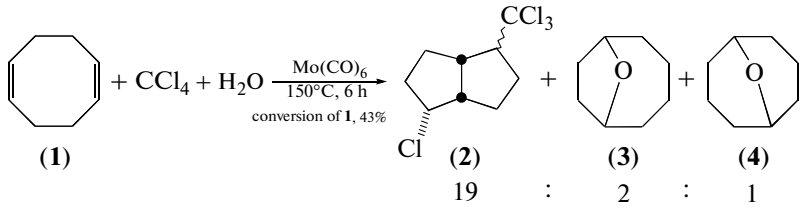


The structure of compound **2** was established on the basis of ^{1}H NMR spectra and their comparison with published data [7, 12]. In particular, the presence of the singlet signal in the ^{1}H NMR spectrum at 4.14 ppm suggests that the hydrogen atom at C^6 is in the *exo*-position relative to the hydrogen atom at the carbon junction atom (C^5); i.e., the compound has the structure of 2-(trichloromethyl)-*endo*-6-chloro-*cis*-bicyclo[3.3.0]octane (**2**).

When water is added ([$Cr(acac)_3$] : [1,5-COD] : [CCl_4] : [H_2O] = 1 : 100 : 100 : 2000) the yield of **2** decreases to 42–50%, but higher oligomers are not produced in this case.

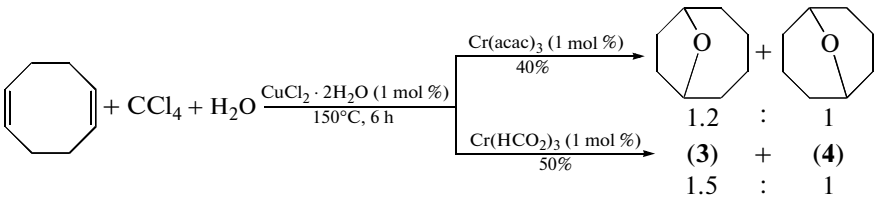


If the reaction is carried out in the presence of $Mo(CO)_6$ under the same conditions, the yield of **2** is 37%, but the selectivity decreases because of the formation of 9-oxobicyclo[4.2.1]nonane (**3**) and 9-oxobicyclo[3.3.1]nonane (**4**).

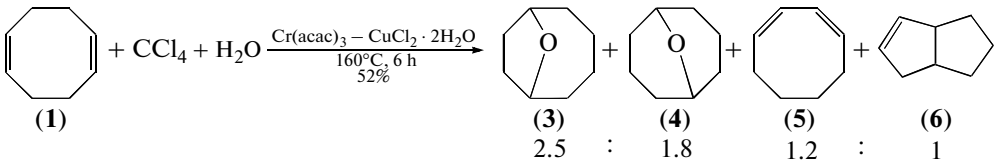


Based on the results of a set of experiments, preferred catalyst and reactant concentrations were determined as [catalyst] : [1,5-COD] : $[CCl_4]$: $[H_2O]$ = 1 : 100 : 100 : 2000. Although a large excess of water reduces the yield of 2-(trichloromethyl)-*endo*-6-chloro-*cis*-bicyclo[3.3.0]octane (**2**), the reaction selectivity for **2** nevertheless can reach 100% on the Cr-containing catalysts or 86% in the presence of $Mo(CO)_6$.

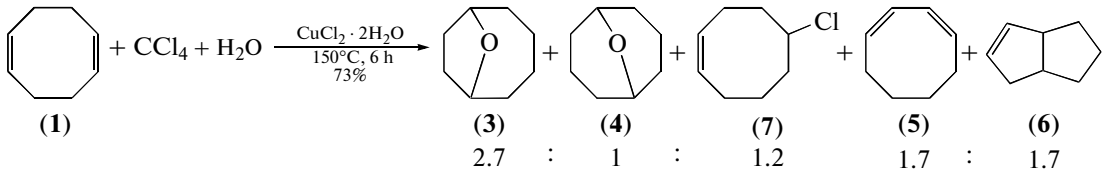
It was found that the admixture of copper(II) chloride ($CuCl_2 \cdot 2H_2O$) as a cocatalyst to $Cr(acac)_3$ promotes the change of the reaction route toward the formation of 9-oxobicyclo[4.2.1]nonane (**3**) and 9-oxobicyclo [3.3.1]nonane (**4**) with a total yield of 40%. When $Cr(acac)_3$ is replaced by $Cr(HCO_2)_3$ in the catalyst system, the yield of **3** and **4** increases to 50%.



As the temperature is elevated to 160°C, the side reaction of *1Z,5Z*-cyclooctadiene isomerization to 1,3-cyclooctadiene (**5**) and bicyclo[3.3.0]oct-2-ene (**6**) is observed.

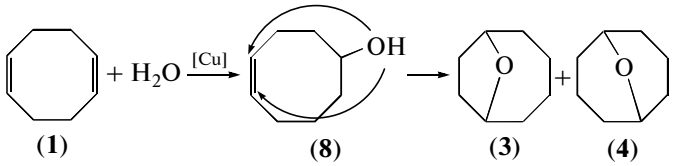


The $CuCl_2 \cdot 2H_2O$-catalyzed reaction of 1,5-COD with H_2O in the presence of CCl_4 also results in **3** and **4**, but the product composition is further complicated by the formation of 5-chlorocyclooctene-1 (**7**):



Regarding the mechanism of formation of 9-oxobicyclo[4.2.1]nonane (**3**) and 9-oxobicyclo[3.3.1]nonane (**4**), the process apparently begins from the hydration of 1,5-COD yielding 4-cyclooctene-1-ol (**8**). The hydra-

tion of 1,5-COD is facilitated by HCl generated from CCl_4 and water by the action of chromium and copper complexes (formation of HCl with a concentration of 13–15 mg/ml was confirmed by titration). At the final stage, the intramolecular addition of the OH group to the double bond takes place [13]:



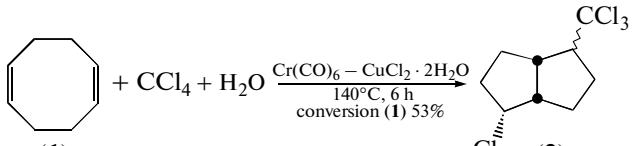
(1) **(8)** **(3)** **(4)**

The structure of 9-oxobicyclo[4.2.1]nonane (**3**) and 9-oxobicyclo[3.3.1]nonane (**4**) was established on the basis of ^{13}C NMR spectra and published data [8, 9]. For example, a compound that exhibits a signal with the chemical shift at 66.90 ppm (CH–O–CH) was assumed to have the 9-oxobicyclo[3.3.1]nonane structure **4**.

The use of nitrogen compounds (NCs) (triethylamine, acetonitrile, DMF) as a nucleophilic agent and cosolvent ([water] : [NC] ratio = 20 : 1) under the reaction conditions of 150°C and 6 h gives 2-(trichloromethyl)-*endo*-6-chloro-*cis*-bicyclo[3.3.0]octane (**2**) with a yield of 75%. In addition, the reaction temperature in the case of nitrogen compounds can be lowered to 140°C (table).

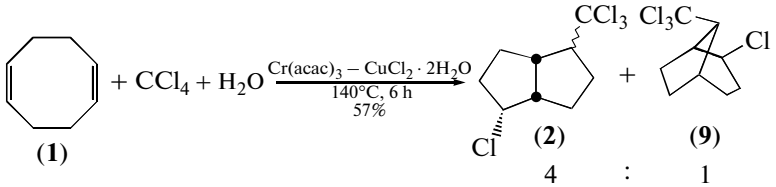
As is seen from the table, the addition of acetonitrile leads to either complete (in the case of $Cr(acac)_3$–$CuCl_2 \cdot 2H_2O$) or partial (in the case of $Mo(CO)_6$) catalyst deactivation; thus, compound **2** is not produced (run 6) or forms with a yield of 20% (run 7).

The reaction of 1,5-COD with CCl_4 in water at 140°C for 6 h over the $Cr(CO)_6$–$CuCl_2 \cdot 2H_2O$ or $Mo(CO)_6$–$CuCl_2 \cdot 2H_2O$ system also leads to the formation of **2**, but its yield does not exceed 50%. The reaction of 1,5-COD with CCl_4 in water in the presence of the $Cr(CO)_6$– $CuCl_2 \cdot 2H_2O$ catalyst system has a 93% selectivity for **2** at a 1,5-COD conversion of 53%. Similarly, a portion of the diene (~7%) converts into the polymer, and the remainder is recovered unchanged from the reaction.



(1) **(2)**
conversion 93%
total yield 49%

The reaction of 1,5-COD with CCl_4 mediated by the $Cr(acac)_3$–$CuCl_2 \cdot 2H_2O$ catalyst system in water proceeds in an interesting manner. In this case, a mixture of 2-(trichloromethyl)-*endo*-6-chloro-*cis*-bicyclo[3.3.0]octane (**2**) and *anti*-8-(trichloromethyl)-*exo*-2-chlorobicyclo[3.2.1]octane (**9**) is produced with a **2 : 9** ratio of 4 : 1 and a total yield of 57%:



(1) **(2)** **(9)**
4 : 1

Such a reaction yielding bicyclo[3.2.1]octane derivatives is exemplified by 1,5-COD chlorination on the $SbCl_5$ catalyst in CCl_4 as described in [14]. Uemura et al. [14] have suggested that the bicyclo[3.2.1]octane derivatives are produced as a result of isomerization of the dichloro derivatives of bicyclo[3.3.0]octane on $SbCl_5$, which is a strong Lewis acid. Most likely, the formation of **9** is also due to the isomerization of 2-(trichloromethyl)-*endo*-6-chloro-*cis*-bicyclo[3.3.0]octane (**2**), and the catalyst is hydrogen chloride (in concentration of 13–14 mg/ml), which, along with the $Cr(acac)_3$–$CuCl_2 \cdot 2H_2O$ catalyst system, initiates this transformation.

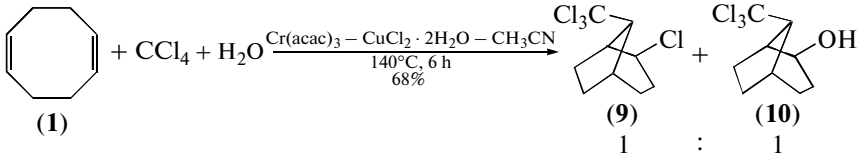
The introduction of acetonitrile as an activating ligand into the $Cr(acac)_3$–$CuCl_2 \cdot 2H_2O$ catalytic sys-

Yield of 2-(trichloromethyl)-*endo*-6-chloro-*cis*-bicyclo[3.3.0]octane (2) depending on the nature of nitrogen compound

Run no.	Catalyst system	NC	Reaction conditions	Product yield, %
1	$Cr(acac)_3$–$CuCl_2 \cdot 2H_2O$	Triethylamine	150°C, 6 h	75
2	"	"	140°C, 6 h	55
3	$Cr(HCO_2)_3$–$CuCl_2 \cdot 2H_2O$	"	140°C, 6 h	56
6	$Cr(acac)_3$–$CuCl_2 \cdot 2H_2O$	Acetonitrile	150°C, 6 h	0
7	$Mo(CO)_6$	"	150°C, 6 h	20
8	$Cr(acac)_3$–$CuCl_2 \cdot 2H_2O$	DMF	140°C, 6 h	18

The catalyst to reactants ratio is[Cr] or [Mo]: [$CuCl_2 \cdot 2H_2O$] : [1,5-COD] : [CCl_4] : [H_2O] : [NC] = 1 : 1 : 100 : 100 : 2000 : 100.

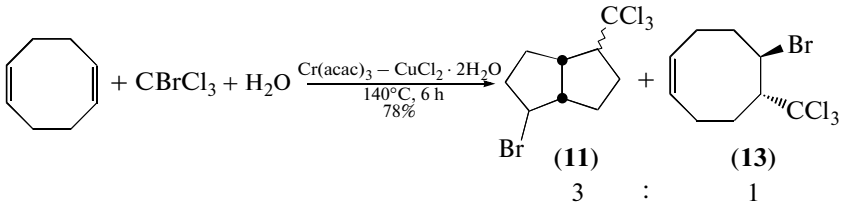
tem ([$Cr(acac)_3$] : [$CuCl_2 \cdot 2H_2O$] : [CH_3CN] = 1 : 1 : 10) has two important consequences: the complete absence of compounds with the bicyclo[3.3.0]octane structure from the reaction products and the formation, along with *anti*-8-(trichloromethyl)-*exo*-2-chlorobicyclo[3.2.1]octane (**9**), of *anti*-8-(trichloromethyl)bicyclo[3.2.1]octan-*exo*-2-ol (**10**), which is formally a hydrolysis product of **9**:



Earlier, it was suggested that alcohol **10** can form by partial hydrolysis of adduct **9** [3]. However, we failed to hydrolyze **9** under the given reaction conditions. Therefore, it is reasonable to assume that alcohol **10** results from the simultaneous interaction of 1,5-COD with CCl_4 and water or HOCl in the presence of $Cr(acac)_3$–$CuCl_2 \cdot 2H_2O$–CH_3CN.

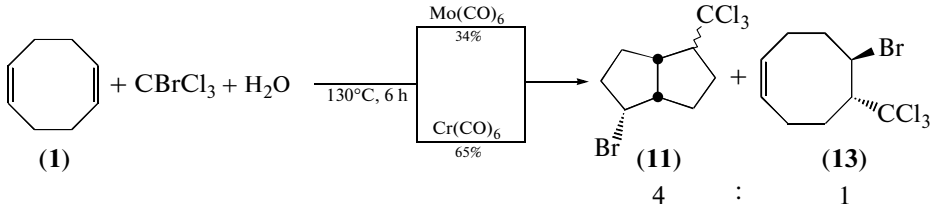
The structure of telomers **9** and **10** was established on the basis of ^{13}C NMR data. Thus, the spectrum of *anti*-8-(trichloromethyl)-*exo*-2-chlorobicyclo[3.2.1]octane (**9**) displays signals at 56.05 and 103.54 ppm characteristic of the –CHCl and –CCl_3 groups, respectively, and the spectrum of *anti*-8-(trichloromethyl)bicyclo[3.2.1]octan-*exo*-2-ol (**10**) contains signals at 70.02 and 103.54 ppm, characteristic of the –CHOH and –CCl_3 groups, respectively. The configuration of **9** and **10** was determined on the basis of the chemical shifts of carbon atoms and their matching with those of authentic samples [15].

According to published data [16–18], the reaction of 1,5-COD with $CBrCl_3$ under conditions of radical initiation with benzoyl peroxide leads to a mixture of 2-bromo-6-(trichloromethyl)bicyclo[3.3.0]octane (**11**) and 2-(bromodichloromethyl)-6-chlorobicyclo[3.3.0]octane (**12**). The outcome of the $Cr(acac)_3$–$CuCl_2 \cdot 2H_2O$-catalyzed reaction of 1,5-COD with $CBrCl_3$ in the presence of water at 140°C for 6 h turned different. In this case, a mixture of *endo*-2-bromo-6-(trichloromethyl)-*cis*-bicyclo[3.3.0]octane (**11**) and *trans*-5-bromo-6-(trichloromethyl)-cyclooctene 1 (**13**) in a 3 : 1 ratio was produced with a yield of 78%:



The use of $Cr(CO)_6$ or $Mo(CO)_6$ in an analogous reaction leads to the formation of *endo*-2-bromo-6-(trichloromethyl)-*cis*-bicyclo[3.3.0]octane (**11**) and*trans*-5-bromo-6-(trichloromethyl)cyclooctene-1-

ene (**13**), and the reaction temperature is lowered to 130°C in this case. A further increase in the temperature leads to polymerization of *1Z,5Z*-cyclooctadiene:



The yields of the compounds were determined by isolating the desired products and by GLC (internal standard 1,1,1,3-tetrachlorononane). The structure of telomers **11** and **12** was established on the basis of ^{13}C NMR data and by matching with authentic compounds prepared according to the published procedures [7, 19]. For example, the spectrum of 2-bromo-6-(trichloromethyl)bicyclo[3.3.0]octane (**11**) exhibits signals at 56.79 ppm (CHBr) and 103.51 ppm (CCl_3), and that of *trans*-5-bromo-6-(trichloromethyl) cyclooct-1-ene (**13**) displays signals at 55.43 ppm (CHBr) and 104.84 ppm (CCl_3) together with the signals at 131.42 (C^1) and 129.98 ppm (C^2) characteristic of carbon atoms at the double bond.

Neither chloroform nor methylene chloride reacts with 1,5-COD under these conditions.

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REFERENCES

1. R. Kh. Freidlina, F. K. Velichko, S. S. Zlotskii, et al., in *Radikal'naya telomerizatsiya* (Khimiya, Moscow, 1988) [in Russian].
2. R. I. Khusnutdinov, N. A. Shchadneva, A. R. Baiguzina, et al., Neftekhimiya **44**, 380 (2004) [Pet. Chem. **44**, 350 (2004)].
3. R. I. Khusnutdinov, N. A. Shchadneva, T. M. Oshnyakova, and U. M. Dzhemilev, Neftekhimiya **49**, 349 (2009) [Pet. Chem. **49**, 331 (2009)].
4. I. Kh. Bikbulatov, F. Kh. Valitov, A. G. Gromova, et al., Zh. Prikl. Khim. (St. Petersburg) **58**, 2499 (1985).
5. B. P. Nikol'skii, V. G. Krunchak, T. V. L'vova, et al., Dokl. Akad. Nauk SSSR **191**, 1324 (1970).
6. H. Becker, W. Berger, H. Domschke, et al., *Organikum* (VEB Deutscher Verlag die Wissenschaften, Berlin, 1976), vol. 2.
7. Y. Shvo and R. Green, J. Organomet. Chem. **675**, 77 (2003).
8. N. I. Kapustina, A. Yu. Popkov, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2538 (1988).
9. R. J. Waseman and H. O. Krabbenhoft, J. Org. Chem. **42**, 2240 (1977).
10. P. R. Stapp and R. F. Kleinschmidt, J. Org. Chem. **30**, 3006 (1965).
11. K. G. Penman, W. Kiching, and A. P. Wells, J. Chem. Soc., Perkin Trans. 1, 721 (1991).
12. A. S. Dneprovskii, A. N. Kasatochkin, V. P. Boyarskii, et al., Zh. Org. Khim. **42**, 1142 (2006).
13. A. C. Cope and P. E. Peterson, J. Am. Chem. Soc. **81**, 1643 (1959).
14. S. Uemura, A. Onoe, and M. Okano, Bull. Chem. Soc. Jpn. **50**, 1078 (1977).
15. J. K. Whitesell and M. A. Minton, *Stereocemical Analysis of Alicyclic Compounds by C-13 NMR Spectroscopy* (Chapman and Hall, London, 1987).
16. R. Dowbenko, US Patent No. 3305346 (1967).
17. R. Dowbenko, US Patent No. 3422155 (1969).
18. R. Dowbenko, US Patent No. 3585244 (1971).
19. A. S. Dneprovskii, A. A. Ermoshkin, A. N. Kasatochkin, and V. P. Boyarskii, Zh. Org. Khim. **39**, 994 (2003).