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Chlorination of Hydrocarbons with CCl_4 Catalyzed by Complexes of Mn, Mo, V, Fe

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Abstract—Catalytic chlorination of alkanes, cycloalkanes, and adamantane utilizing tetrachloromethane as the source of chlorine and applying catalysts containing manganese, molybdenum, vanadium, and iron activated with nitrile ligands, alcohols, and water was fulfilled. The optimum ratios of catalysts and reagents and the best reaction conditions were found for selective synthesis of chlorine-substituted hydrocarbons derivatives.

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Hydrocarbons chlorination with the use of tetrachloromethane as the chlorine source is interesting as one of the promising methods of an appropriate processing and utilization of CCl_4 and is important for manufacturing practically valuable chlorinated hydrocarbons.

The application of halomethanes (CCl_4, CBr_4, CHI_3) in the halogenation of hydrocarbons in the presence of catalysts has been known for a long time. The adamantane chlorination with tetrachloromethane in the presence of anhydrous $AlCl_3$ was described in [1]. Analogous reactions are catalyzed by Lewis acids like $SbCl_5$ and $FeCl_3$ [2]. Recently it was suggested to perform the alkanes halogenation with CX_4 (X = Cl, Br, I) using phase transfer catalysts [3], complexes of Rh [4], Pd [5], Pt [6], Cu [7, 8], and Mn [9, 10]. In the mentioned publications the catalytic chlorination with the use of CCl_4 was investigated by examples of a limited number of hydrocarbons (hexane, cyclohexane, adamantane) [1–10]. The catalytic bromination of hydrocarbons with CBr_4 was carried out in the presence of copper and nickel compounds [11].

Since the development of unconventional and environmentally friendly processes of manufacturing organochlorine compounds avoiding the use of gaseous chlorine is urgent and promising and the problem of CCl_4 utilization is also topical we have prepared metal complex catalysts based on compounds of Mn, Mo, V, and Fe providing the possibility of alkanes and cycloalkanes chlorination using tetrachloromethane as the halogen source.

In the presence of manganese compounds [$MnSO_4$, $MnCl_2$, MnO_2, $Mn(C_{17}H_{35}CO_2)_2$, $Mn(OAc)_2$, $Mn(acac)_3$] unbranched alkanes undergo the chlorination with CCl_4, and the conversion of the initial hydrocarbon decreases with the growing length of its chain. The chlorination of unbranced alkanes occurs under severe conditions (200°C) not only at the methylene but also at the methyl groups affording practically valuable 1-chloroalkanes **Ia–IVa** in up to ~30% yield. The most active catalysts formed from $Mn(OAc)_2$ and $Mn(acac)_3$ at adding to them 2–4 mol% of CH_3CN. The alkane conversion, yields of products, and isomers distribution is strongly affected by the duration of the reaction. The optimum conditions for obtaining monochlorinated alkanes are heating at 200°C in the course of 8–10 h. The conversion of the initial alkane reached 70%. On increasing the reaction time to 20 h the alkane conversion may reach 84%, but the selectivity decreases due to the formation of a complex mixture of di-, tri-, and polychlorinated alkanes.

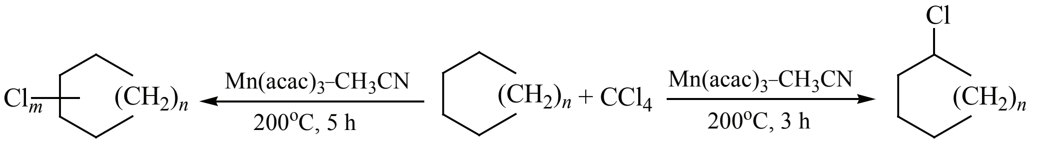
The yields of 1-chloroalkanes **Ia–IVa** and 2-chloroal-

$$RCH_2CH_3 + CCl_4 \xrightarrow[200^{o}C,\ 8\ h]{Mn(acac)_3\text{–}CH_3CN} \underset{\textbf{Ia–IVa}}{RCH_2CH_2Cl} + \underset{\textbf{Ib–IVb}}{RCHClCH_3}$$

R = C_4H_9 (**Ia, Ib**), C_8H_{17} (**IIa, IIb**), $C_{10}H_{21}$ (**IIIa, IIIb**), $C_{16}H_{33}$ (**IVa, IVb**).

kanes **Ib–IVb** depending on the alkane structure and the reaction conditions are compiled in Table 1.

In the presence of the catalyst $Mn(acac)_3–CH_3CN$ cyclic hydrocarbons, cyclopentane, cyclohexane, and cyclooctane, actively undergo chlorination. At the incomplete conversion of the initial cycloalkane (80–90%) they can be selectively converted into the monochloro derivatives at 200°C within 3 h. At longer heating (200°C, 5 h) a complete conversion of hydrocarbons was obtained with the formation of a mixture of mono-, di-, tri-, and tetrachloro derivatives with a random distribution of the chlorine atoms in the ring (Table 2).



$n = 1, 2, 4$; $m = 2–4$.

In continuation of the search for new catalytic systems for alkanes chlorination using CCl_4 as chlorine source we found that molybdenum compounds were efficient catalysts of this reaction, and their activity grew in the series $MoO_3 < MoCl_5 \leq MoO_2(C_5H_7O_2)_2 < Mo(CO)_6$.

At heating the alkane mixture with CCl_4 at 140–160°C in the presence of molybdenum hexacarbonyl (the most active catalyst) the hydrocarbon chlorination is the main reaction direction, and the conversion of the initial hydrocarbon, like in the case of Mn-containing catalysts, depends on its structure and chain length. The unbranched alkanes undergo chlorination both at the methylene and methyl groups affording 1-chloro-alkanes with the selectivity up to ~40% (at low conversions, with

Table 1. Chlorination of aliphatic hydrocarbons at the use of CCl_4 under the action of catalytic system $Mn(acac)_3$– CH_3CN[a]

Alkane	Catalyst	Reaction time, h	Conversion of alkane, %	Yield, %		
				1-chloroalkane	2-chloroalkane	Polychloroalkanes
Hexane	$MnCl_2$	10	30	12	88	0
Hexane	$MnCl_2$	20	53	10	62	28
Hexane	$Mn(OAc)_2$	10	45	25	75	0
Hexane	$Mn(OAc)_2$	20	69	18	51	31
Hexane	$Mn(acac)_3$	10	64	32	67	1
Hexane	$Mn(acac)_3$	16	71	19	37	44
Hexane	$Mn(acac)_3$	20	84	20	31	49
Hexane[b]	$Mn(acac)_3$	10	46	20	80	0
Hexane[c]	$Mn(acac)_3$	10	70	24	76	0
Hexane	$Mn(acac)_3$	8	58	31	69	0
Decane	$Mn(acac)_3$	8	48	30	70	0
Decane	$Mn(acac)_3$	20	57	14	65	21
Dodecane	$Mn(acac)_3$	8	43	29	71	0
Dodecane	$Mn(acac)_3$	20	54	12	62	26
Octadecane	$Mn(acac)_3$	8	40	28	72	0
Octadecane	$Mn(acac)_3$	20	49	10	61	29

[a] The ratio catalyst–CH_3CN–alkane–CCl_4 1 : 4 : 100 : 300, 200°C.
[b] $Mn(acac)_3$–CH_3CN–alkane–CCl_4 1 : 4 : 100 : 100, 200°C.
[c] $Mn(acac)_3$–CH_3CN–alkane–CCl_4 1 : 4 : 100 : 500, 200°C.

Table 2. Chlorination of cycloalkanes with CCl_4 under the action of catalytic system $Mn(acac)_3$–CH_3CN[a]

Cycloalkane	Reaction time, h	Conversion of cycloalkane, %	Yield, %	
			monochlorocycloalkanes	polychlorocycloalkanes
Cyclopentane[b]	2.5	65	100	0
Cyclopentane[b]	3	79	95	5
Cyclopentane	3	91	92	8
Cyclopentane[c]	3	89	90	10
Cyclopentane	5	100	82	18
Cyclohexane	2	71	99	1
Cyclohexane	3	93	96	4
Cyclohexane	5	100	88	12
Cyclooctane	2	76	97	3
Cyclooctane	2	87	87	13
Cyclooctane	5	100	72	28

[a] The ratio $Mn(acac)_3$–CH_3CN–cycloalkane–CCl_4 1 : 4 : 100 : 300, 200°C.

[b] $Mn(acac)_3$–CH_3CN–cycloalkane–CCl_4 1 : 4 : 100 : 100, 200°C.

[c] $Mn(acac)_3$–CH_3CN–cycloalkane–CCl_4 1 : 4 : 100 : 500, 200°C.

selectivity up to до 20%). The conversion of alkanes, the yield of chlorinated derivatives, and the isomers distribution depend on the duration of the reaction. At the increase of the reaction time to 12 h the alkane conversion may attain ~100%, but the selectivity is reduced due to the formation of a complex mixture of tri- and tetrachloro-substituted alkanes.

As a result of a targeted search for promoters, which contained first of all organophosphorus and nitrogen-containing organic ligands, we found that the activity and selectivity of the action of the molybdenum-based catalysts might be enhances by adding to them alcohols (MeOH or EtOH). An important consequence of the use of alcohols as promoters of the molybdenum-based catalysts was the decrease in the reaction temperature to 130–150°C.

In order to reveal the reason of the feasible influence of alcohol additives on the catalytic chlorination of alkanes with CCl_4 we investigated the composition of the reaction mixture, where by the iodometric titration active chlorine was detected [the concentration of the active chlorine 5 min after the start of the reaction (150°C) was 1.5–2 mg/mL, and after 20 min, 3.5 mg/mL] showing that the alcohols were oxidized with CCl_4 to alkyl hypochlorites. The detection of alkyl hypochlorites in the reaction mixture allows an assumption on their probable involvement into the process of alkane chlorination due to the readiness of the generation from ROCl of radicals $RO^\bullet$ and $Cl^\bullet$.

The main laws of the chlorination with the use of halomethanes in the presence of molybdenum complexes we explore by an example of hexane. The optimum molar ratios of the catalyst components and reagents were determined and the feasible conditions for the preparation of 1- and 2-chlorohexanes were found (130–160°C, 3–6 h).

The increase in the concentration of CCl_4 (hexane–CCl_4 1 : 3 × 5) resulted in the growing of the overall yield of chloroalkanes **Ia, Ib** to 77%. The longer reaction time (>12 h) is unwanted both for hexane and the higher alkane (decane, dodecane), since the 1- and 2-chloroalkanes suffer dehalogenation. Besides, the composition of products gets more complex because of the formation of 3-chloroalkanes **Ic–IIIc**.

The yields of 1-, 2-, and 3-chloroalkanes depending on the alkane structure and the reaction conditions are compiled in Table 3.

At the use of ethanol as the alcohol component besides 2-chlorohexane (**Ib**) acetaldehyde diethyl-acetal was found in the products. At the increased concentration of C_2H_5OH (hexane–ethanol, 1 : 4 × 8) the yield of the acetal reached 88% due to the effect of HCl formed at the alcohol oxidation with CCl_4 into ethyl hypochlorite decomposed with the liberation of HCl and acetic aldehyde. The hexane conversion grew simultaneously.

$$\mathrm{RCH_2CH_2CH_3 + CCl_4 + CH_3OH \xrightarrow[140\text{–}160^\circ C,\ 3\text{–}6\ h]{Mo(CO)_6} \underset{\textbf{Ia–IIIa}}{RCH_2CH_2CH_2Cl} + \underset{\textbf{Ib–IIIb}}{RCH_2CHClCH_3} + \underset{\textbf{Ic–IIIc}}{RCHClCH_2CH_3}}$$

R = C_3H_7 (**Ia–Ic**), C_7H_{15} (**IIa–IIc**), C_9H_{19} (**IIIa–IIIc**).

The results of hexane chlorination under the catalysis with $Mo(CO)_6$ using ethanol as promoter are presented in Table 4.

The action of catalyst $Mo(CO)_6$ in the presence of CH_3OH led to the efficient chlorination with CCl_4 of cyclic hydrocarbons, in particular, cyclopentane, cyclohexane, cyclooctane, and cyclododecane, which at incomplete conversion of the initial cycloalkane (60–80%) were selectively converted into monochloro derivatives **Va, VIa** (170°C, 3 h). At the longer heating (170°C, 6 h) the conversion of cycloalkanes was virtually complete, but a complex mixture formed of mono-, di-, tri-, and tetrachloro derivatives with a fairly random distribution of the chlorine atoms in the ring (Table 5).

Table 3. Chlorination aliphatic hydrocarbon using CCl_4 in the presence of $Mo(CO)_6$ and MeOH

Alkane	Molar ratio $Mo(CO)_6$–alkane–CCl_4–CH_3OH	Reaction conditions	Conversion of alkane, %	Composition of reaction products, %		
				1-chloroalkanes (**Ia–IIIa**)	2-chloroalkanes (**Ib–IIIb**)	3-chloroalkanes (**Ic–IIIc**)
Hexane	1 : 200 : 600 : 2400	130°C, 3 h	15	2	98	–
Hexane	1 : 200 : 600 : 2400	140°C, 3 h	22	2	98	–
Hexane	1 : 200 : 600 : 2400	150°C, 3 h	30	3	97	–
Hexane	1 : 200 : 600 : 2400	150°C, 6 h	77	20	78[a]	–
Hexane	1 : 200 : 600 : 2400	160°C, 3 h	34	13	87	–
Hexane	1 : 200 : 600 : 2400	160°C, 4 h	69	22	78	–
Hexane	1 : 200 : 600 : 0	150°C, 3 h	–	–	–	–
Hexane	1 : 100 : 100 : 100	150°C, 6 h	44	3	97	–
Hexane	1 : 100 : 200 : 100	150°C, 6 h	39	4	95	–
Hexane	1 : 100 : 200 : 100	150°C, 6 h	81	5	96	–
Decene	1 : 200 : 800 : 1200	140°C, 12 h	25	31	69	
Decane	1 : 200 : 800 : 1200	140°C, 6 h	32	8	46	46
Decane	1 : 200 : 800 : 0	140°C, 3h	–	–	–	-
Decane	1 : 200 : 800 : 0	140°C, 6 h	–	–	–	
Decane	1 : 100 : 100 : 100	150°C, 6 h	17	–	35	65
Decane	1 : 100 : 200 : 100	150°C, 6 h	24	1	36	63
Decane	1 : 100 : 200 : 200	150°C, 6 h	40	3	15	20
Dodecane	1 : 200 : 800 : 200	140°C, 3 h	3	2	61	37
Dodecane	1 : 200 : 800 : 200	140°C, 6 h	5	3	62	35
Dodecane	1 : 200 : 1600 : 2400	140°C, 3 h	19	1	59	40
Dodecane	1 : 100 : 100 : 100	150°C, 6 h	45	1	49	50
Dodecane	1 : 100 : 200 : 100	150°C , 6 h	30	2	41	57
Dodecane	1 : 100 : 200 : 200	150°C, 6 h	44	1	47	52
Dodecane	1 : 200 : 800 : 0	140°C, 3 h	–	–	–	

[a] The reaction mixture contained hexachloroethane (~2%).

Table 4. Hexane chlorination with CCl_4 in the presence of $Mo(CO)_6$ and C_2H_5OH

Molar ratio hexane–CCl_4–C_2H_5OH– $Mo(CO)_6$	Reaction conditions	Hexane conversion	Yield, %	
			Ib	**Ic**
200 : 200 : 200 : 1	130°C, 6 h	28	89	11
200 : 200 : 200 : 1	130°C, 17 h	42	86	14
200 : 200 : 400 : 1	130°C, 6 h	26	88	12
200 : 400 : 1600 : 1	160°C, 3 h	28	69	28
100 : 200 : 800 : 1	160°C, 3 h	23	77	33
200 : 200 : 0 : 1	130°C , 6 h	8	100	–
100 : 300 : 1200 : 1	150°C, 12 h	28	72	28
100 : 300 : 1200 : 1	130°C, 3 h	25	80	20
100 : 300 : 1200 : 1	140°C, 3 h	39	88	12
200 : 600 : 2400 : 1	160°C, 3 h	61	78	22
200 : 600 : 2400 : 1	160°C, 4 h	66	81	19
200 : 600 : 2400 : 1	150°C, 3 h	32	81	19
200 : 200 : 400 : 1	130°C, 6 h	31	80	20
200 : 200 : 1200 : 1	130°C, 3 h	28	77	23
200 : 200 : 1200 : 1	130°C , 6 h	19	78	22

Table 5. Cycloalkaneoв chlorination with CCl_4 in the presence of $Mo(CO)_6$ and CH_3OH[a]

Cycloalkane	Reaction conditions	Conversion of cycloalkane, %	Composition of reaction products, %	
			monochlorocycloalkanes	polychlorocycloalkanes
Cyclopentane	170°C, 6 h	87	58	42
Cyclohexane	130°C, 3 h	42	~ 100	–
Cyclohexane	140°C, 3 h	60	97	3
Cyclohexane	150°C, 3 h	64	90	10
Cyclohexane	160°C, 3 h	69	79	21
Cyclohexane	170°C, 3 h	75	81	19
Cyclohexane	170°C, 1 h	53	93	7
Cyclohexane	170°C, 6 h	97	68	33
Cyclohexane	180°C, 2 h	81	90	10
Cyclooctane	170°C, 1 h	49	94	6
Cyclooctane	170°C, 6 h	95	65	35
Cyclooctane	180°C, 2 h	89	81	19
Cyclododecane	170°C, 1 h	30	97	3
Cyclododecane	170°C, 6 h	82	42	58
Cyclododecane	180°C, 2 h	90	65	35

[a] The ratio $Mo(CO)_6$– cycloalkane– CCl_4– CH_3OH 1 : 100 : 400 : 800.

$$C_2H_5OH + CCl_4 \xrightarrow[-CHCl_3]{[Mo]} C_2H_5OCl \xrightarrow[-HCl]{} CH_3CHO$$

$$CH_3CHO + 2C_2H_5OH \xrightarrow{HCl} CH_3CH(OC_2H_5)_2$$

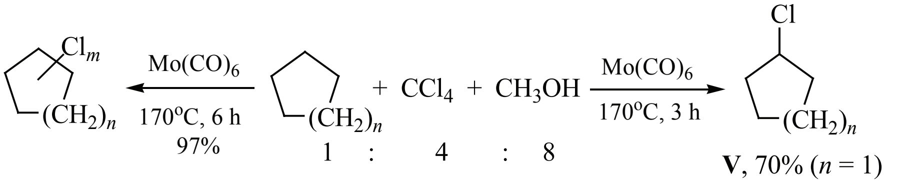
$m = 1–4$, $n = 1, 2$.

The addition to the reaction mixture of catalytic quantities of water caused an unexpected result: At 170°C within 1 h monochlorocyclopentane (**V**) and monochlorocyclohexane (**VI**) were obtained in nearly quantitative yields. Cyclododecane under similar conditions at 30% conversion formed monochlorocyclododecane (**VIII**). The increased duration of the reaction (165°C, 6 h) led to the formation of exclusively polychlorinated products at the total conversion of the initial cycloalkane.

The water concentration is crucial. Thus, at the addition of a stoichiometric amount of water with respect to the hydrocarbon the cycloalkane chlorination did not proceed even at the prolonged heating (170°C, 20 h).

In order to understand the feasible effect of water on the course of the chlorination we examined the composition of the reaction mixture [$Mo(CO)_6$–CCl_4–H_2O, 1 : 100 : 4] incubated at 170°C for 1 h. The iodometric titration showed the presence in the reaction mxture of active chlorine, and chloroform was found by GLC. Therefore. presumably a reaction $CCl_4 + H_2O \rightarrow HOCl + CHCl_3$ occurred.

The hypochloric acid is known to decompose easily giving radicals $HO^•$ and $Cl^•$. Apparently the formation of HOCl is the reason of the increased yield of compounds **V, VI** in the presence of water.

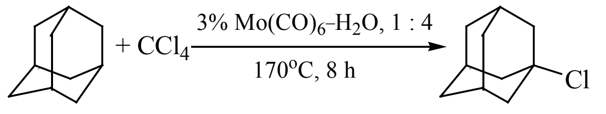


V, 70% ($n = 1$)
VI, 68% ($n = 2$)

We explored the preparative opportunities of the catalytic chlorination with CCl_4 cycloalkanes of more complex structure, in particular, of adamantane, whose chlorinated derivatives were widely used in preparation of pharmaceuticals, diagnosticums, polymers possessing thermal and chemical resistance [12].

We formerly demonstrated the possibility of catalytic chlorinationя of adamantane and its derivatives using CCl_4 as chlorine source in the presence of Mn-, V-, and Mo-containing catalysts promoted with alcohols and nitrile ligands [13].

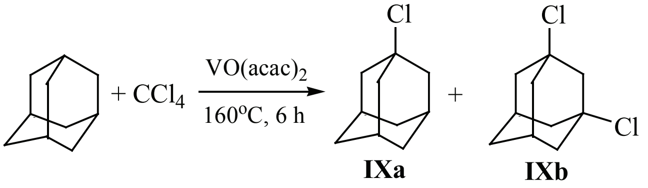
In the adamantane chlorination the promoting effect of water was observed at the use of Mo- and V-containing catalysts. The system $Mo(CO)_6$–H_2O, 1 : 4, catalyzed the selective chlorination of adamantane in the node position. At 170°C in 8 h and adamantane conversion of ~48% a single product was obtained, 1-chloroadamantane (**IXa**).



IXa

At the use of water in a stoichiometric amount with respect to adamantane the reaction proceeds under milder conditions (150°C), but notwithstanding the high conversion of adamantane (92%) the selectivity of the chlorination sharply fell due to the formation of mono- and polychlorinated (1,3-dichloro-, 1,3,5-trichloro-, 1,3,5,7-tetrachloro-) and oxygen-containing adamantanes (adamantan-1-ol, adamantane-1,3-diol, adamantan-2-one).

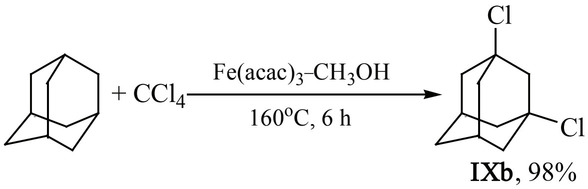
The best results were obtained at the adamantane chlorination n the presence of the vanadium-containing catalyst. At the addition to $VO(acac)_2$ of a stoichiometric amount of water 1-chloroadamantane (**IXa**) is formed selectively in 60% yield. At the 5–7-fold excess of CCl_4 and water the complete conversion of adamantane was attained, and the yield of chloroadamantane (**IXa**) grew to 90%.



According to Kovacic et al. [2], one of the first catalysts of adamantane chlorination with CCl_4 was $FeCl_3$. We attempted to find whether alcohols and water would work as promoters in the reaction under study with respect to the iron compounds and complexes.

The promoting effect of water with respect to $Fe(acac)_3$ and $Fe(C_5H_5)_2$ proved to be insignificant. In the presence of the catalytic system $Fe(C_5H_5)_2$–H_2O, 12 : 10, the conversion of adamantane did not exceed 7%, a and the only reaction product was 1-chloroadamantane (**IXa**).

Better results were obtained at promoting the iron-containing catalysts with alcohols, methanol and ethanol, which considerably affect the yield as well as the selectivity of the reaction. In the presence of the catalytic system $Fe(acac)_3$–CH_3OH, 1 : 30, at 160°C (6 h) the single product of adamantane reaction with CCl_4 was 1,3-dichloroadamantane (**IXb**).



$Fe(acac)_3$–AdH–CCl_4–CH_3OH, 0.03 : 1 : 2 : 1.
[Fe] = $Fe(acac)_3$–C_2H_5OH, $Fe(C_5H_5)_2$–C_2H_5OH;
Fe–AdH–CCl_4–ROH, 0.035 : 1 : 2 : 1.

The replacement of methanol by ethanol resulted in the selective formation of 1-chloroadamantane (**IXa**), whose yield in the presence of the catalytic system $Fe(acac)_3$–C_2H_5OH was 79%, and at the use of the ferrocene-containing catalyst, 93%.

The experiments of adamantane chlorination using CCl_4 were carried out in sealed ampules or in a pressure microreactor of stainless steel at 160–170°C over 1–6 h. By means of GLC and GC-MS we found in the reaction mixture chloroform (the main reaction product) and dichloromethane, indicating that the chlorination occurred by replacing the hydrogen atom in adamantine molecule predominantly in the node position.

Thus, compound and complexes of Mn, Mo, V, and Fe promoted with alcohols and water catalyze the chlorination of alkanes, cycloalkanes, and adamantine with CCl_4 used as chlorine source.

The structure of compounds synthesized was established by spectral methods, and by their comparison with authentic samples and published data.

EXPERIMENTAL

^{13}C NMR spectra were registered on a spectrometer Bruker Avance-400 (operating frequency 100.62 MHz) in $CDCl_3$. Mass spectra were measured on an instrument Shimadzu GCMS-QP2010Plus (capillary column SPB-5 30 m × 0.25 mm, carrier gas helium, ramp from 40 to 300°C at a heating rate 8 deg/min, vaporizer temperature 280°C, ion source temperature 200°C, ionizing energy 70 eV). Elemental composition of the samples was determined on an analyzer Carlo Erba 1106.

The reaction progress was monitored and the purity of compounds obtained was checked by GLC on an instrument Shimadzu GC-9A, GC-2014 [column 2 m × 3 mm, stationary phase silicone SE-30 (5%) on the carrier Chromaton N-AW-HMDS, ramp from 50 to 270°C at a heating rate 8 deg/min, carrier gas helium (47 mL/min)].

General procedure of chlorination of alkanes and cycloalkanes. (a) Into a pressure microreactor of stainless steel of 17 mL capacity or into a glass ampule of 20 mL capacity (the results of parallel runs materially coincide) was charged 1 mmol of $Mn(acac)_3$, 4 mmol of acetonitrile, 100 mmol of alkane or cycloalkane, and 300 mmol of CCl_4. The reactor was pressure-tight closed (the ampule was sealed), and the reaction mixture was heated at 200°C for 1–8 h. On the completion of the reaction the reactor (ampule) was cooled to room temperature, opened, the reaction mixture was filtered through a bed of Al_2O_3. The unreacted CCl_4 was distilled off, the residue was distilled in a vacuum or crystallized from ethanol.

(b) Into a pressure microreactor of stainless steel of 17 mL capacity or into a glass ampule of 20 mL capacity was charged 0.3 mmol of $Mo(CO)_6$, 10 mmol of alkane (or cycloalkane), 40 mmol of CCl_4, 40–80 mmol of ethanol (methanol), the reactor was pressure-tight closed (the ampule was sealed), and the reaction mixture was heated at 130–180°C for 3–14 h.

1-Chlorohexane (Ia). Yield 24%, bp 134°C (bp 133–134°C [14]). Mass spectrum, *m/z* (I_{rel}, %) : 29 (60), 32 (5), 39 (35), 41 (97), 42 (58), 43 (86), 53 (5), 54 (6), 55 (96), 56 (59), 57 (12), 69 (22), 90 (6), 90 (100), 92 (5), 93 (31). Found, % : C 59.68; H 10.82; Cl 29.50. $C_6H_{13}Cl$. Calculated % : C 59.74; H 10.86; Cl 29.40. *M* 120.60.

2-Chlorohexane (Ib). Yield 77%, bp 133.5–134°C (bp 133–134°C [14]). ^{13}C NMR spectrum, δ, ppm: 15.17 (C^6), 22.23 (C^5), 27.77 (C^1), 28.62 (C^4), 38.81 (C^3), 59.22 (C^2), Mass spectrum, *m/z* (I_{rel}, %) : 29 (49), 38 (5), 39 (30), 40 (12), 41(91), 42 (79), 43 (82), 53 (5), 54 (10), 55 (75), 56 (100), 57 (22), 58 (7), 63 (11), 84 (48), 85 (11). Found, *% :* C 59.66; H 10.81; Cl 29.53. $C_6H_{13}Cl$. Calculated, % : C 59.74; H 10.86; Cl 29.40. *M* 120.60.

1-Chlorodecane (IIa). Yield 8%, bp 105°C (10 mm Hg) (bp 233°C [15]). Mass spectrum, *m/z* (I_{rel}, %) : 29 (38), 39 (14), 40 (13), 41 (70), 42 (31), 43 (100), 54 (11), 55 (53), 56 (25), 63 (7), 67 (7), 68 (7), 69 (67), 70 (60), 71 (16), 82 (10), 83 (24), 84 (25), 85 (7), 96 (6), 97 (25), 98 (14), 105 (7), 111 (18), 112 (11), 140 (5). Found, % : C 67.48; H 11.90; Cl 20.62. $C_{10}H_{21}Cl$. Calculated, % : C 67.96; H 11.98; Cl 20.06. *M* 176.726.

2-Chlorodecane (IIb). Yield 33%, bp 105°C (10 mm Hg) (bp 238°C [15]). ^{13}C NMR spectrum, δ, ppm : 14.10 (C^{10}), 22.73 (C^9), 24.75 (C^4), 26.00 (C^1), 27.94 (C^5), 28.32 (C^6), 28.92 (C^7), 31.95 (C^8), 40.37 (C^3), 57.26 (C^2). Mass spectrum, *m/z* (I_{rel}, %) : 29 (48), 39 (22), 40 (5), 41 (89), 42 (36), 43 (100), 53 (6), 54 (8), 55 (81), 56 (41), 63 (7), 67 (7), 68 (7), 69 (67), 70 (60), 71 (16), 82 (10), 83 (24), 84 (25), 85 (7), 96 (6), 97 (25), 98 (14), 105 (7), 111 (18), 112 (11), 140 (5). Found, % : C 67.48; H 11.90; Cl 20.62. $C_{10}H_{21}Cl$. Calculated, %: C 67.96; H 11.98; Cl 20.06. M 176.726.

3-Chlorodecane (IIc). Yield 15%. Mass spectrum, *m/z* (I_{rel}, %) : 29 (48), 39 (19), 40 (20), 41 (90), 42 (55), 43 (97), 53 (6), 54 (24), 55 (100), 51 (90), 52 (46), 67 (7), 68 (17), 69 (67), 70 (67), 71 (16), 82 (13), 83 (31), 84 (31), 85 (10), 96 (12), 97 (35), 98 (17), 110 (6), 111 (22), 112 (12), 140 (8). Found, % : C 67.90; H 11.90; Cl 20.20. $C_{10}H_{21}Cl$. Calculated, % : C 67.96; H 11.98; Cl 20.06. *M* 176.726.

1-Chlorododecane (IIIa). Yield 29%, bp 128°C (10 mm Hg) {130°C (15 mm Hg) [16]}. ^{13}C NMR spectrum, δ, ppm : 13.63 (C^{12}), 22.54 (C^{11}), 28.95 (C^3), 28.98 (C^2), 29.00 (C^4), 29.16 (C^5), 29.27 (C^6), 29.40 (C^7), 29.98 (C^8), 30.00 (C^9), 31.77 (C^{10}), 40.75 (C^1). Mass spectrum, *m/z* (I_{rel}, %) : 29 (32), 39 (10), 40 (8), 41 (60), 42 (29), 43 (100), 54 (10), 55 (48), 56 (26), 57 (82), 68 (8), 69 (32), 70 (13), 71 (28), 82 (5), 83 (13), 84 (6), 85 (12), 90 (13), 91 (66), 92 (7), 93 (19), 97 (7), 104 (5), 105 (14), 107 (5). Found, % : C 70.31; H 12.27; Cl 17.42. $C_{12}H_{25}Cl$. Calculated, % : C 70.38; H 12.31; Cl 17.31. *M* 204.78.

2-Chlorododecane (IIIb). Yield 71%, bp 121°C (10 mm Hg). ^{13}C NMR spectrum, δ, ppm: 14.15 (C^{12}), 23.00 (C^{11}), 26.83 (C^1), 28.98 (C^4), 28.99 (C^5), 29.09 (C^6), 29.11 (C^7), 32.14 (C^8), 32.21 (C^9), 32.30 (C^{10}), 38.93 (C^3), 57.79 (C^2). Mass spectrum, *m/z* (I_{rel}, %) : 39 (20), 41 (100), 43 (98), 55 (85), 69 (59), 83 (37), 97 (29), 111 (20), 125 (7), 140 (5), 168 (12). Found, % : C 70.48; H 12.50; Cl 17.02. $C_{12}H_{25}Cl$. Calculated, % : C 70.38; H 12.31; Cl 17.31. *M* 204.78.

3-Chlorododecane (IIIc). Yield 24%. Mass spectrum, m/z (I_{rel}, %) : 29 (51), 39 (14), 40 (13), 41 (89), 42 (43), 43 (100), 53 (7), 54 (23), 55 (93), 56 (87), 57 (67), 67 (10), 68 (20), 69 (81), 70 (66), 71 (22), 81 (6), 82 (20), 83 (51), 84 (35), 85 (10), 96 (13), 97 (36), 98 (18), 110 (8), 111 (22), 112 (10), 125 (11), 126 (5), 135 (7), 168 (8). Found, %: C 70.34; H 13.25; Cl 16.41. $C_{12}H_{25}Cl$. Calculated, % : C 70.38; H 12.31; Cl 17.31. *M* 204.78.

1-Chlorooctadecane (IVa). Yield 28%, bp 126°C (10 mm Hg) (bp 260°C [16]). ^{13}C NMR spectrum, δ, ppm: 13.63 (C^{18}), 22.54 (C^{17}), 28.65 (C^2), 28.71 (C^3), 28.80 (C^4), 28.96 (C^5), 29.00 (C^6), 29.10 (C^7), 29.19 (C^8), 29.22 (C^9), 29.34 (C^{10}), 29.42 (C^{11}), 29.49 (C^{12}), 29.53 (C^{13}), 29.56 (C^{14}), 29.62 (C^{15}), 29.69 (C^{16}), 40.62 (C^1). Mass spectrum, *m/z* (I_{rel}, %) : 39 (19), 41 (74), 43 (100), 55 (70), 57 (74), 69 (51), 83 (44), 97 (42), 111 (25), 125 (12), 139 (5), 153 (4), 167 (3), 224 (3), 252 (7). Found, % : C 75.30; H 12.20; Cl 12.50. $C_{18}H_{37}Cl$. Calculated, % : C 74.82; H 12.91; Cl 12.27. *M* 288.939.

2-Chlorooctadecene (IVb). Yield 72%, bp 120°C (10 mm Hg). ^{13}C NMR spectrum, δ, ppm : 13.57 (C^{18}), 22.28 (C^{17}), 25.34 (C^4), 25.96 (C^5), 26.10 (C^6), 26.19 (C^7), 26.27 (C^8), 26.37 (C^9), 26.44 (C^{10}), 26.49 (C^{11}), 26.51 (C^1), 26.53 (C^{12}), 26.57 (C^{13}), 26.61 (C^{14}), 26.68 (C^{15}), 26.70 (C^{16}), 40.36 (C^3), 58.50 (C^2). Mass spectrum, *m/z* (I_{rel}, %) : 39 (10), 41 (83), 43 (100), 55 (73), 57 (71), 69 (56), 83 (49), 97 (41), 111 (22), 125 (15), 139 (7), 153 (6), 252 (10). Found, % : C 74.18; H 12.80; Cl 13.02. $C_{18}H_{37}Cl$. Calculated, % : C 74.82; H 12.91; Cl 12.27. *M* 288.939.

Chlorocyclopentane (V). Yield 98%, bp 114°C (bp 112°C [15]). ^{13}C NMR spectrum, δ, ppm : 22.43

($C^{3,4}$), 38.61 ($C^{2,5}$), 60.13 (C^{1}). Mass spectrum, *m/z* (I_{rel}, %) : $[M]^+$ 102 (2), 41 (39), 42 (30), 51 (3), 53 (7), 55 (5), 62 (5), 67 (55), 68 (100), 69 (32), 75 (4), 76 (5). Found, % : C 57.40; H 8.63; Cl 33.97. C_5H_9Cl. Calculated, % : C 57.42; H 8.67; Cl 33.91. *M* 104.577.

Chlorocyclohexane (VI). Yield 79%, bp 140–141°C (bp 142°C [14]). ^{1}H NMR spectrum, δ, ppm *:* 3.97 t (1H, CHCl), 1.77 m (10H, $5CH_2$). ^{13}C NMR spectrum, δ, ppm: 24.69 ($C^{3,5}$), 25.08 (C^4), 36.52 (C^2), 36.59 (C^6), 59.74 (C^1). Mass spectrum, *m/z* (I_{rel}, %) : $[M]^+$ 118 (2), 83 (24), 82 (62), 81 (11), 68 (6), 67 (100), 66 (9), 56 (9), 55 (45), 54 (36), 53 (11), 51 (5), 43 (2), 42 (7), 41 (51), 40 (7), 39 (28), 38 (5). Found, % : C 60.65; H 9.75; Cl 29.60. $C_6H_{11}Cl$. Calculated, % : C 60.75; H 9.35; Cl 29.90. *M* 118.604.

Chlorocyclooctane (VII). Yield 82%, bp 60–62°C (6 mm Hg) {bp 85–86°C (21 mm Hg) [17]}. ^{13}C NMR spectrum, δ, ppm : 23.86 ($C^{3,7}$), 25.59 (C^5), 28.19 ($C^{4,6}$), 35.13 ($C^{2,8}$), 62.13 (C^1). Найде- но, % : C 65.60; H 10.25; Cl 24.15. $C_8H_{15}Cl$. Calculated, % : C 65.52; H 10.31; Cl 24.17.

Chlorocyclododecane (VIII). Yield 38%, bp 92–94°C (3 mm Hg) {bp 87–90°C (0.4–0.5 mm Hg) [17]}. ^{13}C NMR spectrum, δ, ppm : 24.87 ($C^{3,11}$), 28.29 ($C^{4,10}$), 28.82 ($C^{5,6,7,8,9}$), 40.07 ($C^{2,12}$), 62.64 (C^1). Mass spectrum, *m/z* (I_{rel}, %) : $[M]^+$ 200 (2), 39 (56), 40 (11), 41 (100), 42 (21), 43(11), 51 (10), 53 (34), 54 (28), 55 (55), 65 (25), 66 (11), 67 (78), 68 (22), 69 (20), 77 (28), 79 (54), 80 (24), 88 (27), 91 (15), 93 (18), 94 (14), 95 (36), 96 (16), 109 (23), 110 (4), 121 (22), 135 (13), 164 (6). Found, %: C 71.28; H 11.40; Cl 17.32. $C_{12}H_{23}Cl$. Calculated, % : C 71.08; H 11.44; Cl 17.48. M 202.764.

Chlorination of adamantane with tetrachloromethane in the presence of alcohols. Into a pressure microreactor of stainless steel of 17 mL capacity or into a glass ampule of 20 mL capacity (the results of parallel runs materially coincide) under an argon atmosphere was charged 0.03 mmol of catalyst [$Fe(acac)_3$, $Fe(C_5H_5)_2$, $Fe_2(CO)_9$], 1 mmol of adamantane, 2 mmol of CCl_4, and 1 mmol of alcohol. The reactor was pressure-tight closed (the ampule was sealed), and the reaction mixture was heated at 160°C for 6 h. On the completion of the reaction the reactor (ampule) was cooled to ~20°C, opened, the solvent was distilled off, the residue was recrystallized from methanol.

Chlorination of adamantane with tetrachloromethane in the presence of water. Into a pressure microreactor of stainless steel of 17 mL capacity or into a glass ampule of 20 mL capacity (the results of parallel runs materially coincide) under an argon atmosphere was charged 0.01–0.1 mmol of $Fe(C_5H_5)_2$, 0.02 mmol of diethylamine, 1 mmol of adamantane (**IX**), 2 mmol of CCl_4, and 1 mmol of water воды. The reactor was pressure-tight closed (the ampule was sealed), and the reaction mixture was heated at 140°C for 6 h. On the completion of the reaction the reactor (ampule) was cooled to ~20°C, opened, the solvent was distilled off, the residue was recrystallized from methanol.

Chloroadamantane (IXa). Yield 90%, mp 165–166°C {mp 166°C (ethanol) [13]}. ^{13}C NMR spectrum, δ, ppm : 31.49 (C^3, C^5, C^7), 35.75 (C^4, C^6, C^{10}), 47.77 (C^2, C^8, C^9), 68.21 (C^1). Found, % : C 70.34; H 8.84; Cl 20.82. $C_{10}H_{15}Cl$. Calculated, % : C 70.37; H 8.86; Cl 20.77.

1,3-Dichloroadamantane (IXb. Yield 98%, mp 130–132°C {mp 129.5–130°C (ethanol) [13]}. ^{13}C NMR spectrum, δ, ppm : 33.35 (C^6), 33.65 (C^5, C^7), 45.71 (C^4, C^8, C^9, C^{10}), 56.51 (C^2), 66.74 (C^1, C^3). Found, % : C 58.54; H 6.84; Cl 34.62. $C_{10}H_{14}Cl_2$. Calculated, % : C 58.55; H 6.87; Cl 34.56.

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REFERENCES

1. Stteter, V.H., Krause, M., and Last, W.D., *Angew. Chem*., 1968, p. 970.
2. Kovacic, P. and Chang, J., *J. Org. Chem*., 1971, vol. 36, p. 3138.
3. Schreiner, P.R., Lauenstein, O., Kolomitsin, I.V., and Fokin, A.A., *Angew. Chem., Int. Ed*., 1998, vol. 37, p. 1895.
4. Vedernikov, A.N., Scharifullin, R.R., and Solomonov, B.N., *Mendeleev Commun.*, 1996, p. 54.
5. Vedernikov, A.N., Kuramshin, A.I., Sayakhov, M.D., Soba-, nov, A.A., and Solomonov, B.N.*, Russ. J. Org. Chem.,* 1997, vol. 33, p. 39.
6. Vedernikov, A.N., Sayakhov, M.D., Zazybin, A.G., and Solomonov, B.N.*, Russ. J. Org. Chem.,* 1998, vol. 34, p. 812.
7. Golubeva, E.N., Nevskaya, S.M., Vorontsov, V.V., and Abdrashitov, Ya.M., *Izv. Akad. Nauk, Ser. Khim.,* 1997, 1835.
8. Smirnov, V.V., Nevskaya, S.M., and Golubeva, E.N., *Neftekhimiya, 20*02, vol. 42, p. 22.
9. Khusnutdinov, R.I., Shchadneva, N.A., Baiguzina, A.R., Lavrent'eva, Yu.Yu., and Dzhemilev, U.M., *Izv. Akad. Nauk,*

Ser. Khim., 2002, p. 1919.

10. Khusnutdinov, R.I., Shchadneva, N.A., Baiguzina, A.R., and Dzhemilev, U.M., *Izv. Akad. Nauk, Ser. Khim.*, 2002, p. 979.
11. Smirnov, V.V., Zelikman, V.M., Beletskaya, I.P., Golubeva, E.N., Tsvetkov, D.S., Levitskii, M.M., and Kazankova, M.A., *Russ. J. Org. Chem.,* 2002, vol. 38, p. 1004.
12. Bagrii, E.I., *Adamantany, poluchenie, svoistva, primenenie* (Adamantanes: Synthesis, Properties, Application), Moscow: Nauka, 1989.
13. Khusnutdinov, R.I., Shchadneva, N.A., Baiguzina, A.R., Lavrent'eva, Yu.Yu., Burangulova, R.Yu., and Dzhemilev, U.M., *Neftekhimiya*, 2004, vol. 44, p. 148.
14. *Fluka. Khimicheskie reaktivy dlya laboratornykh i analiticheskikh rabot* (Chemicals for Laboratory and Analytical Researches), Rossiya, 2009–2010, 1748 p.
15. *Aldrich. Catalog. Handbook of Fine Ghemicals*, 2009–2010.
16. *Dictionary of Organic Compounds*, Buckingham, J., Ed., New York: London–Toronto: Chapman and Hall, 1982.
17. Asscher, M. and Vofsi, D., *J. Am. Chem. Soc.,* 1961.