

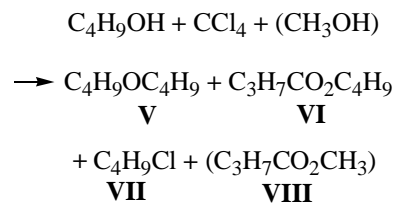
Below the ethanol conversion and the ratio of reaction products are given at various molar ratios of the reagents.

EtOH:CCl ₄	EtOH conversion, %	(III):(IV)
1:1	38	1:2
1:2	59	1:2
2:1	44	1:1.5

Since the iodometric titration of the reaction mixture reveals the presence of an active chlorine, it is presumable that ethanol is first through the formation of ethyl hypochlorite (EtOCl) oxidized to acetic aldehyde which in its turn in the acid medium gives acetal with excess alcohol.

The acetic aldehyde is further oxidized to acetic acid that forms ester with the alcohol.

The oxidation of primary C₄–C₅ alcohols (1-butanol, 1-pentanol, 3-methyl-1-butanol) occurs along a similar scheme.



The reaction was carried out in the presence of methanol, for it had been previously established that methanol fast underwent oxidation with tetrachloromethane into methyl hypochlorite, an active oxidant. Actually, the reaction of butanol with CCl₄ in the presence of methanol at 170°C within 3 h at molar ratio 1:2:2 resulted in butanol conversion of 39%, and alongside butyl butyrate (VI) and 1-chlorobutane (VII) methyl butyrate (VIII) was obtained (in a ratio 1:2:1).

The use of methanol easily generating methyl hypochlorite acting as an oxidant permitted a reduction of the process temperature to 130°C and exclusion of chlorinated products, but butanol conversion decreased therewith to 22%, although the reaction time was increased to 8 h.

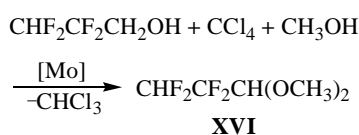
Reaction of isoamyl alcohol with CCl₄ taken in equimolar amounts occurred in the presence of Mo(CO)₆ at 150°C in 3 h with the alcohol conversion of 61% and

Table 1. Effect of reaction conditions on conversion of primary alcohols and yields of reaction products

Oxidized alcohol RCH ₂ OH	Molar ratio of reagents Mo:RCH ₂ OH:CCl ₄ : (CH ₃ OH)	Conversion of alcohol, %	Reaction temperature, °C (time, h)	Yields, % ^a			
				RCH ₂ Cl	RCOOCH ₃	RCH ₂ OCH ₂ R	RCOOCH ₂ R
1-Butanol R = Pr	1:200:400:(400)	22	130 (8)	–	61	–	39
	1:100:100(200)	22	140 (3)	28	35	–	37
	1:100:200:(200)	10	140 (3)	24	39	–	36
	1:100:100:(200)	24	140 (6)	48	34	–	17
	1:200:200:(400)	27	160 (3)	38	43	–	18
	1:200:200:(400)	36	160 (6)	55	7.1	–	37
	1:200:200:(400)	39	170 (3)	25	24	–	50
	1:200:400	78	170 (3)	67	–	17	16
3-Methyl-1- butanol R = <i>i</i> -Bu	1:100:100	30	140 (6)	57	–	30	13
	1:100:100	61	150 (3)	66	–	18	16
	1:100:200	50	160 (3)	55	–	20	25
	1:100:200:(200)	32	160 (3)	19	46	–	34
1-Pentanol R = Bu	1:100:200:(100)	18	150 (3)	66	–	12	22
	1:100:200:(200)	55	150 (3)	14	25	8	53
	1:100:200	15	150 (3)	64	–	18	18
	1:100:200	55	160 (4)	46	–	26	28

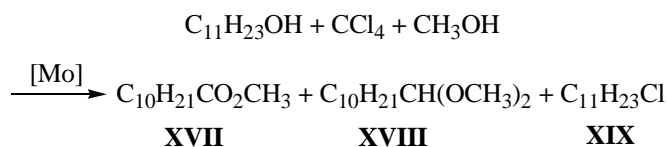
^a Calculated on reacted alcohol.

formation of 1-chloro-3-methyl butane (**IX**) (66%, main product) and also of isoamyl isovalerate (**X**) (16%), and diisoamyl ether (**XI**) (18%). A similar reaction of amyl alcohol proceeded to 55% conversion leading to the formation of the following reaction products: 1-chloropentane (**XII**), 46%, amyl valerate (**XIII**), 28%, and diamyl ether (**XIV**), 26%. All our attempts to increase the yield of the oxidation products by raising the temperature (to 160°C) and the time of reaction (to 4 h) were unsuccessful. Only the use of methanol in the reactions of isoamyl and amyl alcohols with CCl₄ permitted increasing the amount of oxidation products to the following values: **X**, 34%; **XIII**, 53%; and methyl valerate (**XV**), 25%.

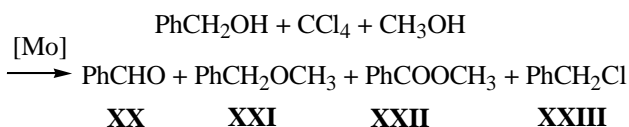


For special attention calls the high selectivity in oxidizing 2,2,3,3-tetrafluoropropanol by the system CCl₄–MeOH–Mo(CO)₆, 1:0.5:1. The single reaction product is 1,1-dimethoxy-2,2,3,3-tetrafluoropropane (**XVI**), but its yield does not exceed 14% even at prolonging the process to 6 h (160°C). In the absence of methanol the fluorinated alcohol is not consumed and the only reaction product is hexachloroethane.

With growing length of the alkyl chain of the alcohols their activity in oxidation with CCl₄ gradually diminished. For instance, 1-undecanol reacted with the system CCl₄–CH₃OH in the presence of Mo(CO)₆ to 18% conversion to form methyl undecanoate (**XVII**), 1,1-dimethoxyundecane (**XVIII**), and 1-chloroundecane (**XIX**) in a ratio 1.5:1:14.



Benzyl alcohol is oxidized with tetrachloromethane at 160°C virtually to 100% giving benzaldehyde (**XX**), α-methoxytoluene (**XXI**), methyl benzoate (**XXII**), and benzyl chloride (**XXIII**) in a ratio depending mainly on the concentration of the initial reagents.

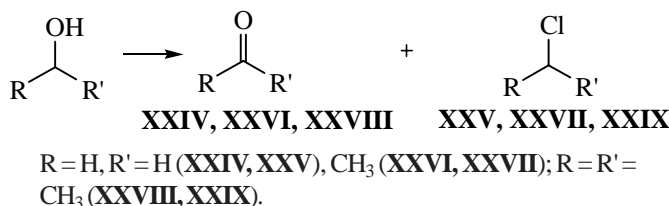


The ratio of reaction products obtained from benzyl alcohol at various molar ratios of reagents are given below.

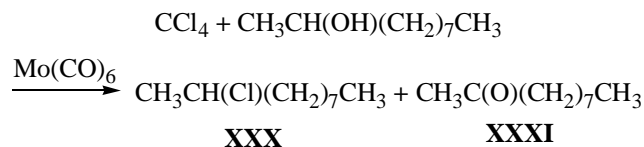
PhCH ₂ OH:CCl ₄ : CH ₃ OH	PhCH ₂ OH conversion, %	XX:XXI: XXII:XXIII
1:1:1	100	4:4:1:2
1:2:1	100	3:2:1:3
1:1:2	100	7:6:1:0.5
1:1:3	100	3:3:1:0.2

Further research demonstrated that generation of alkyl hypochlorites in the presence of molybdenum compounds and subsequent oxidation reactions with them are characteristic not only of primary, but also of secondary alcohols which as expected are oxidized into ketones. However the dominant direction (4:1) of reaction between secondary alcohols and CCl₄ in the presence of Mo(CO)₆ was the substitution of OH group by chlorine. The conversion of alcohols at 150–160°C was 60–80% in 3 h.

In reaction with secondary alcohols like with primary alcohols among the tested molybdenum compounds [MoCl₅, MoO₂(C₅H₇O₂)₂, MoO₃, Mo(CO)₆] Mo(CO)₆ proved to be the most active. Whereas CCl₄ is simultaneously reagent and solvent it is reasonable to use it in a great excess with respect to alcohol (ROH:CCl₄=1:2–5). The reaction of secondary alcohols with CCl₄ is completed within 3 h, at a longer heating formation of ethers of the initial alcohols and chlorinated ketones is observed.



The optimum concentrations of the components of the catalytic system and of reagents and also the recommended reaction conditions are as follows: Mo(CO)₆ : ROH : CCl₄ = 1:100–200:200–500, 150–160°C, 3–6 h. Under these conditions the conversion of alcohols is complete, but the ratio of the formed ketones and chloroalkanes is practically independent of the alcohol structure.



For instance, reaction of 1 mol of 2-decanol with 2 mol of CCl₄ yielded as products 2-chlorodecane (**XXX**)

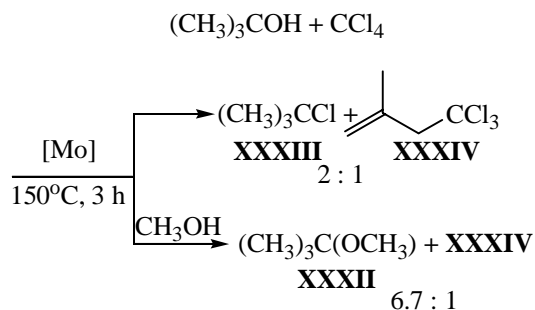
Table 2. Effect of reaction conditions on conversion of 2,3-butanediol and yields of reaction products

Molar ratio Mo:diol:CCl ₄	Reaction temperature, °C (time, h)	Conversion of initial diol, %	Yields, % ^a	
			XXXV	XXXVI
1:200:200	130 (3)	95	21	79
1:200:400	130 (6)	99	33	67
1:200:200	140 (3)	98	31	69
1:200:400	130 (3)	76	14	86

^a Calculated on reacted diol.

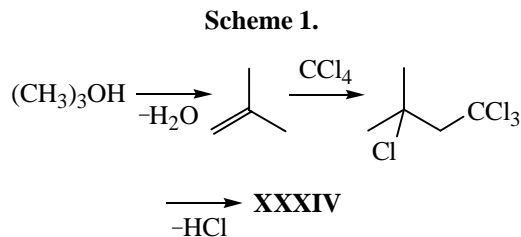
and 2-decanone (**XXXI**), the former prevailing. At 150°C in 3 h the conversion was 70%, at 140°C in 6 h, 96%, ratio of compounds **XXX:XXXI** was 2:1.

We succeeded in increasing the reaction selectivity with respect to ketone **XXXI** by introducing into the system methanol which was actively oxidized with CCl₄ forming methyl hypochlorite. It turned out that the result of the process depended on two factors, namely, on the nature of the initial substrate, and on the reaction time. For instance, at the molar ratio secondary alcohol:CH₃OH:CCl₄:Mo(CO)₆ 100:300:300:1 (150°C, 3 h) the selectivity of reaction with respect to 2-decanone (**XXXI**) at conversion 53–87% can attain 90%.

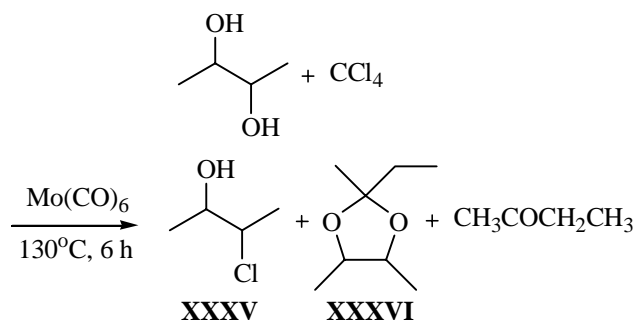


Tertiary alcohol, *tert*-butanol, reacted with the system CH₃OH–CCl₄ in the presence of Mo(CO)₆ leading to the formation of methyl *tert*-butyl ether (**XXXII**) as major product (87%). In the absence of methanol the *tert*-butanol suffered substitution chlorination giving *tert*-butyl chloride (**XXXIII**) in 66% yield. In both cases alongside compounds **XXXII** and **XXXIII** the reaction mixture contained 4,4,4-trichloro-2-methyl-1-butene (**XXXIV**) and traces of isobutylene indicating that presumably compound **XXXIV** formed in three stages by Scheme 1.

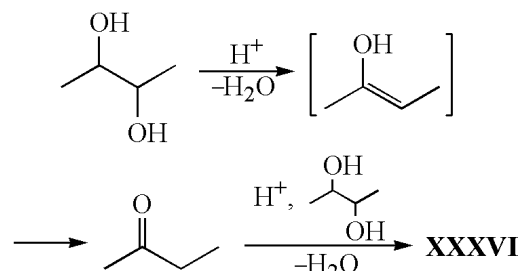
Molybdenum hexacarbonyl catalyzes also diols oxidation with CCl₄. The reaction direction is governed mainly by the structure of diol and also depends on CCl₄



concentration and reaction conditions. For instance, 2,3-butanediol in reaction with 2 mol of CCl₄ at a quantitative conversion provided a mixture of two products: 3-chlorobutanol (**XXXV**) and 2,4,5-trimethyl-2-ethyl-1,3-dioxolane (**XXXVI**) in a 2:1 ratio (Table 2).



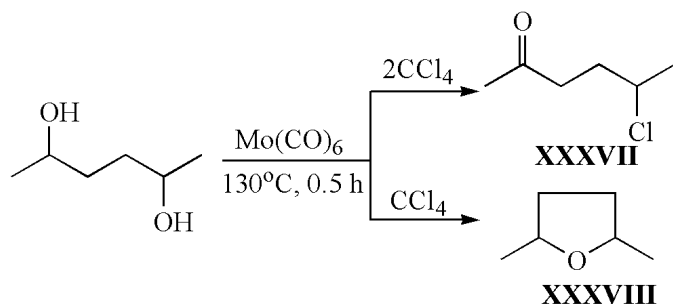
Based on published data [4] the following probable scheme of dioxolane **XXXVI** formation can be suggested.



The process starts by dehydration of the initial glycol resulting first in the formation of 2-butanone which undergoes acetalization with the second diol molecule. The content of 2-butanone to the end of the reaction was 3–5% (detected by GLC and GC-MS methods).

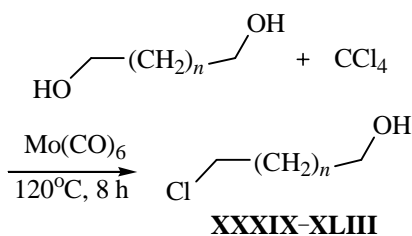
At reduced CCl₄ concentration (CCl₄:diol = 1:1) dioxolane **XXXVI** becomes the major reaction product. No reaction is observed in the absence of Mo(CO)₆ or CCl₄.

2,5-Hexanediol under similar conditions is converted in 80% yield into chloroketone **XXXVII**, resulting from the diol oxidation at one of the hydroxy groups and substitution chlorination at the other. At diminished concentration of CCl₄ the main product isolated from the



reaction mixture in 87% yield was 2,5-dimethyltetrahydrofuran (**XXXVIII**), the product of intramolecular dehydration of 2,5-hexanediol. The influence of reaction conditions on the yield of products is presented in Table 3.

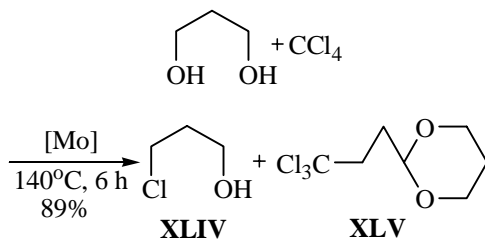
The reaction of CCl_4 with α,ω -diols occurs by the type of substitution chlorination at one of the hydroxy groups giving in high yields α,ω -chlorohydrins and thus is of significant preparative interest.



$n = 3$ (**XXXIX**, 95%), 4 (**XL**, 98%), 5 (**XLI**, 87%), 7 (**XLII**, 74%), 10 (**XLIII**, 48%).

On increasing temperature to 150°C (3 h) hexachloroethane formation is observed whose yield can reach 40–45%.

In contrast to the other α,ω -diols the reaction of 1,3-propyleneglycol with CCl_4 under the effect of $\text{Mo}(\text{CO})_6$ is not selective. In the reaction mixture alongside 3-chloro-1-propanol (**XLIV**) is also present 2-(3,3,3-trichloro-propyl)-1,3-dioxane (**XLV**) (27%).



The probable route of compound **XLV** formation may involve 4 stages: dehydration of diola to allyl alcohol, its telomerization with CCl_4 , elimination of HCl from the

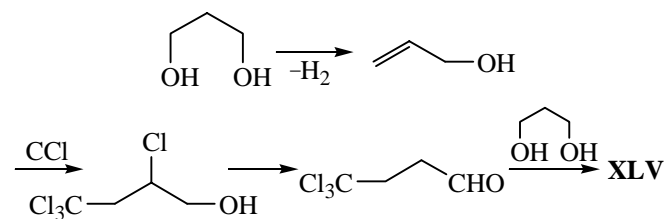
Table 3. Effect of reaction conditions on conversion of 2,5-hexanediol and yields of reaction products

Molar ratio Mo:diol: CCl_4	Reaction temperature, $^\circ\text{C}$ (time, h)	Conversion of initial diol, %	Yields, % ^a	
			XXXVII	XXXVIII
1:100:100	20 (144)	22	–	100
1:100:100	100 (3)	100	10	90
1:200:200	100 (3)	100	6	94
1:100:100	120 (3)	100	19	81
1:100:100	130 (0.5)	80	13	87
1:100:100	130 (3)	100	82	18
1:100:200	130 (3)	90	93	7
1:100:300	130 (3)	100	67	38
1:100:400	130 (3)	100	14	86
^b	130 (3)	77	–	100
^c	130 (3)	77	–	100

^a Calculated on reacted diol. ^b Diol without $\text{Mo}(\text{CO})_6$ and CCl_4 .

^c Diol with $\text{Mo}(\text{CO})_6$ in a ratio 100:1 without CCl_4 .

arising chlorohydrin to give 4,4,4-trichlorobutyric aldehyde which provides acetal **XLV** with diol excess.



Thus we established that $\text{Mo}(\text{CO})_6$ catalyzes oxidation of alcohols and diol with CCl_4 leading to the formation of aldehydes, ketones, chloroketones, and esters.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer UR-75 from KBr pellets or thin films. ^1H and ^{13}C NMR spectra were registered on a spectrometer JEOL FX-90 Q at 89.55 (^1H) and 22.5 MHz (^{13}C) in CDCl_3 , chemical shifts were reported relative to TMS. Mass spectra were measured on a GC-MS instrument Finnigan-4021 (electron impact, 70 eV, 200°C , direct admission into the ion source). GLC was carried out on a chromatograph Chrom-5, column 1.200×3 mm, stationary phase silicone SE-30 (5%), on Chromaton N-AW-HMDS (0.125–0.160 mm), carrier gas helium (47 ml/min), ramp from 50 to 250°C at a rate 8 deg/min. Hypochlorite concentration was determined iodometrically [5].

Molybdenum compounds $\text{Mo}(\text{CO})_6$, MoCl_5 , $\text{MoO}_2(\text{C}_3\text{H}_7\text{O}_2)_2$, MoO_3 were commercial products, dried in a vacuum-desiccator before use.

General procedure of alcohols and diols oxidation. Into a pressure microreactor of stainless steel or a glass ampule (the results of parallel runs are virtually identical) were charged under an argon atmosphere 0.1 mmol of $\text{MO}(\text{CO})_6$, 20 mmol of an appropriate alcohol (or 10 mmol of diol), and 20–40 mmol of CCl_4 , and the reactor was air-tight closed (the ampule was sealed). The reaction was carried out at constant stirring for 1–6 h at 120–150°C. Then the reactor was cooled to room temperature, the reaction mixture was filtered through a silica gel bed (eluent hexane–ether, 1:1). The solvent was distilled off, the residue was distilled under the atmospheric pressure or in a vacuum. The yields are given with respect to consumed alcohol (GLC, internal reference). The structure of compounds obtained was proved by spectral methods and by comparison with authentic samples and reference data [6–11].

1,1-Dimethoxy-2,2,3,3-tetrafluoropropane (XVI). Yield 14%. Mass spectrum, m/z (I_{rel} , %): 87 (26), 85 (31), 74 (100), 59 (28), 57 (19), 56 (10), 55 (19), 43 (63), 42 (10), 39 (14), 31 (5), 29 (57). Found, %: C 34.12; H 4.47; F 43.17. $\text{C}_5\text{H}_8\text{F}_4\text{O}_2$. Calculated, %: C 34.09; H 4.58; F 43.15.

Methyl undecenoate (XVII). Yield 3%. Mass spectrum, m/z (I_{rel} , %): 200 [M]⁺ (3), 169 (5), 157 (8), 143 (7), 101 (5), 87 (5), 75 (11), 74 (100), 69 (10), 59 (13), 57 (12), 56 (5), 55 (31), 43 (18), 42 (12), 41 (41), 39 (8), 29 (32). Found, %: C 71.91; H 11.97. $\text{C}_{12}\text{H}_{24}\text{O}_2$. Calculated, %: C 71.95; H 12.08.

1,1-Dimethoxyundecene (XVIII). Yield 2%. Mass spectrum, m/z (I_{rel} , %): 185 (5), 75 (100), 71 (13), 69 (5), 58 (6), 55 (8), 53 (5), 47 (8), 45 (8), 43 (11), 41 (17), 31 (5), 29 (16). Found, %: C 72.07; H 12.95. $\text{C}_{13}\text{H}_{28}\text{O}_2$. Calculated, %: C 72.16; H 13.04.

1-Chloroundecene (XIX). Yield 32%, bp 97°C (20 mm Hg). Mass spectrum, m/z (I_{rel} , %): 105 (10), 97 (7), 93 (13), 91 (48), 85 (5), 84 (5), 83 (12), 71 (13), 70 (17), 69 (37), 68 (7), 67 (10), 57 (57), 56 (24), 55 (64), 54 (6), 53 (5), 43 (100), 42 (23), 41 (87), 39 (17), 31 (7), 39 (66). Found, %: C 69.19; H 12.14; Cl 18.67. $\text{C}_{11}\text{H}_{23}\text{Cl}$. Calculated, %: C 69.26; H 12.15; Cl 18.59.

2-Chlorodecene (XXX). Yield 64%, bp 105°C (10 mm Hg). Mass spectrum, m/z (I_{rel} , %): 140 (5), 112 (11), 111 (18), 105 (7), 98 (14), 97 (25), 96 (6), 85 (7), 84 (25), 83 (24), 82 (10), 71 (16), 70 (60), 69 (67), 68 (7), 67 (7), 63 (7), 57 (23), 56 (41), 55 (81), 54 (8), 53 (6), 43 (100), 42 (36), 41 (89), 40 (5), 39 (22), 29 (48). Found, %: C 56.49; H 9.91; Cl 33.60. $\text{C}_{10}\text{H}_{21}\text{Cl}$. Calculated, %: C 56.60; H 9.97; Cl 33.43.

Decene-2-one (XXXI). Yield 90%, bp 81°C (15 mm Hg). Mass spectrum, m/z (I_{rel} , %): 156 [M]⁺ (5), 71 (25), 59 (25), 58 (100), 57 (12), 55 (8), 43 (90), 42 (5), 41 (19), 39 (5), 29 (12). Found, %: C 75.82; H 13.86. $\text{C}_6\text{H}_{10}\text{O}$. Calculated, %: C 76.92; H 12.82.

4,4,4-Trichloro-2-methylbut-1-ene (XXXIV). Yield 47%, bp 60–61°C (75 mm Hg). ¹H NMR spectrum, δ , ppm: 5.05–5.30 d (2H, CH_2), 3.42 s (2H, CH_2), 2.01 s (3H, CH_3). ¹³C NMR spectrum, δ , ppm: 98.33 (C^4), 61.69 (C^3), 138.25 (C^2), 120.08 (C^1), 23.66 (C^5). Mass spectrum, m/z (I_{rel} , %): 172 [M]⁺ (6), 139 (10), 137 (14), 127 (10), 125 (60), 124 (7), 123 (95), 122 (6), 109 (5), 103 (5), 101 (6), 98 (5), 96 (6), 89 (5), 87 (16), 85 (5), 78 (12), 76 (36), 75 (7), 73 (5), 65 (35), 63 (8), 61 (14), 55 (61), 53 (10), 51 (17), 50 (11), 49 (6), 41 (78), 40 (30), 39 (100), 38 (14), 37 (6), 29 (4). Found, %: C 28.68; H 3.30; Cl 68.02. $\text{C}_5\text{H}_7\text{Cl}_3$. Calculated, %: C 28.71; H 3.34; Cl 67.95.

3-Chlorobutan-2-ol (XXXV). Yield 33%. Mass spectrum, m/z (I_{rel} , %): 57 (5), 55 (5), 45 (100), 43 (10), 29 (17). Found, %: C 44.16; H 8.31; Cl 32.50. $\text{C}_4\text{H}_9\text{ClO}$. Calculated, %: C 44.25; H 8.35; Cl 32.66.

2,4,5-Trimethyl-2-ethyl-1,3-dioxolane (XXXVI). Isolated by preparative GLC. Yield 95%. IR spectrum, ν , cm^{-1} : 1050, 1370, 1400, 2900–2960. ¹H NMR spectrum, δ , ppm: 0.75–1.1 t (3H, CH_3), 1.3 s (9H, 3 CH_3), 1.5–1.8 q (2H, CH_2), 3.5–3.7 m (2H, 2CH). ¹³C NMR spectrum, δ , ppm: 109.6 (C^2), 78.89 (C^4), 78.04 (C^5), 25.19 (C^6), 33.14 (C^7), 8.13 (C^8), 16.78 (C^9), 16.40 (C^{10}). Mass spectrum, m/z (I_{rel} , %): 129 (11), 115 (47), 100 (11), 73 (23), 72 (25), 57 (48), 56 (18), 55 (28), 45 (7), 43 (100), 41 (17), 39 (6), 29 (24). Found, %: C 66.50; H 11.14. $\text{C}_8\text{H}_{16}\text{O}_2$. Calculated, %: C 66.63; H 11.18.

2-Chlorohexan-5-one (XXXVII). Isolated by preparative GLC. Yield 85%. Mass spectrum, m/z (I_{rel} , %): 134 [M]⁺ (5), 58 (41), 57 (14), 56 (8), 55 (16), 43 (100), 42 (29), 41 (10), 39 (6), 29 (6). Found, %: C 53.50; H 8.21; Cl 26.35. $\text{C}_6\text{H}_{11}\text{ClO}$. Calculated, %: C 53.59; H 8.24; Cl 26.37.

2,5-Dimethyltetrahydrofuran (XXXVIII). Yield ~100%, bp 91–92°C. IR spectrum, ν , cm^{-1} : 1090, 1370, 1450, 2850–2950. ¹H NMR spectrum, δ , ppm, *trans*-isomer: 1.20 d (6H, 2 CH_3), 3.86 m (2H, 2CH), 1.68 m (4H, 2 CH_2); *cis*-isomer: 1.125 d (2 CH_3), 4.02 m (2H, 2CH), 1.68 m (4H, 2 CH_2). ¹³C NMR spectrum, δ , ppm, *trans*-isomer: 21.38 (C^6 , C^7), 74.49 (C^2 , C^5), 33.04 (C^3 , C^4); *cis*-isomer: 21.38 (C^6 , C^7), 75.34 (C^2 , C^5), 34.15 (C^3 , C^4). Mass spectrum, m/z (I_{rel} , %): 100 [M]⁺ (6), 73 (23),

72 (25), 57 (48), 56 (18), 55 (28), 45 (7), 43 (100), 41 (17), 39 (6), 29 (24). Found, %: C 71.86; H 12.06. $C_6H_{12}O$. Calculated, %: C 71.95; H 12.08.

5-Chloropentanol (XXXIX). Yield 95%, bp 57–58°C (1 mm Hg). ^{13}C NMR spectrum, δ , ppm: 62.28 (C^1), 32.08 (C^2), 23.07 (C^3), 32.30 (C^4), 44.25 (C^5). Found, %: C 49.05; H 9.11; Cl 29.01. $C_5H_{11}ClO$. Calculated, %: C 48.98; H 9.04; Cl 28.92.

6-Chlorohexanol (XL). Yield 98%, bp 97°C (10 mm Hg). 1H NMR spectrum, δ , ppm: 1.10–1.92 (8H, 4 CH_2), 3.42–3.80 m (4H, CH_2Cl , CH_2OH). ^{13}C NMR spectrum, δ , ppm: 62.99 (C^1), 32.49 (C^2), 26.59 (C^3), 25.00 (C^4), 32.07 (C^5), 45.03 (C^6). Mass spectrum, m/z (I_{rel} , %): 92 (10), 90 (12), 83 (12), 82 (30), 81 (5), 76 (5), 70 (8), 69 (65), 68 (8), 67 (47), 63 (5), 57 (11), 56 (40), 55 (100), 54 (29), 53 (8), 49 (5), 45 (5), 44 (7), 43 (34), 42 (76), 41 (99), 40 (12), 39 (28), 31 (77), 30 (7), 29 (41). Found, %: C 52.70; H 9.56; Cl 26.08. $C_6H_{13}ClO$. Calculated, %: C 52.74; H 9.59; Cl 25.95.

7-Chloroheptanol (XLI). Yield 87%, bp 80°C (15 mm Hg). 1H NMR spectrum, δ , ppm: 1.15–2.0 m (10H, 5 CH_2), 3.25–3.75 m (4H, CH_2Cl , CH_2OH). ^{13}C NMR spectrum, δ , ppm: 62.69 (C^1), 32.39 (C^2), 25.57 (C^3), 27.69 (C^4), 28.02 (C^5), 30.63 (C^6), 44.54 (C^7). Found, %: C 55.74; H 10.10; Cl 23.68. $C_7H_{15}ClO$. Calculated, %: C 55.81; H 10.04; Cl 23.53.

9-Chlorononanol (XLII). Yield 74%, bp 142–143°C (20 mm Hg). 1H , δ , ppm: 1.2–2.0 m (14H, 7 CH_2), 3.40–3.65 m (4H, CH_2Cl , CH_2OH). ^{13}C , δ , ppm: 62.79 (C^1), 32.50 (C^2), 26.17 (C^3), 27.55 (C^4), 27.23 (C^5), 27.89 (C^6), 28.00 (C^7), 28.74 (C^8), 44.40 (C^9). Found, %: C 60.12; H 10.54; Cl 19.76. $C_9H_{19}ClO$. Calculated, %: C 60.48; H 10.72; Cl 19.84.

12-Chlorododecanol (XLIII). Isolated by column chromatography (eluent ether–hexane, 1:2). Yield 48%. 1H NMR spectrum, δ , ppm: 1.31–1.95 (20H, 10 CH_2), 3.42–3.64 m (4H, CH_2Cl , CH_2OH). ^{13}C NMR spectrum, δ , ppm: 62.87 (C^1), 32.81 (C^2), 26.28 (C^3), 27.55 (C^4), 27.76 (C^5), 27.22 (C^6), 27.89 (C^7), 28.02 (C^8), 28.64 (C^9), 28.70 (C^{10}), 29.36 (C^{11}), 45.05 (C^{12}). Found, %: C 65.32; H 14.30; Cl 15.67. $C_{12}H_{25}ClO$. Calculated, %: C 65.57; H 14.46; Cl 15.68.

3-Chloropropanol (XLIV). Yield 73%, bp 82°C (80 mm Hg). ^{13}C NMR spectrum, δ , ppm: 59.49 (C^1), 34.87 (C^2), 43.30 (C^3). Mass spectrum, m/z (I_{rel} , %):

76 (11), 58 (72), 57 (48), 41 (16), 39 (8), 31 (100), 30 (36), 29 (55).

2-(3,3,3-Trichloropropyl)-1,3-dioxane (XLV). Yield 27%. 1H NMR spectrum, δ , ppm: 1.20–1.42 m (2H, CH_2), 2.00–2.15 m (2H, CH_2), 2.78–2.85 t (2H, CH_2), 3.70–4.12 m (4H, 2 CH_2), 4.61–4.68 t (1H, CH). ^{13}C NMR spectrum, δ , ppm: 99.99 (C^2), 66.77 (C^4 , C^6), 25.75 (C^5), 32.06 (C^7), 49.32 (C^8), 99.79 (C^9). Mass spectrum, m/z (I_{rel} , %): 233 [M]⁺ (8), 231 (10), 141 (5), 139 (7), 111 (5), 109 (7), 88 (5), 87 (100), 85 (5), 77 (5), 75 (13), 59 (13), 42 (8), 41 (7), 39 (5), 31 (16), 29 (10). Found, %: C 36.02; H 4.63; Cl 45.72. $C_7H_{11}Cl_3O_2$. Calculated, %: C 35.99; H 4.75; Cl 45.55.

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