REDUCTION OF TRICHLOROMETHYL GROUP TO THE DICHLOROMETHYL GROUP BY THIOLS IN THE PRESENCE OF METAL CARBONYLS

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Radical reactions of metal carbonyls (MC) are of great interest as a branch of metal complex catalysis [1]. MC of the groups VI-VIII initiate the reduction of trichloroderivatives to dichlorocompounds by secondary alcohols via a free-radical mechanism [2]. Among the hydrogen donors the thiols are of particular interest since they are easily available, they exist in a variety of structures, and they readily homolyze the S-H bond. The example of $Fe(CO)_5$ has been used to demonstrate the efficiency of thiols as hydrogen donors in the reduction of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes [3] and CCl_4 [4].

While investigating the comparative efficiency of MC in the initiation of reductions, we have studied for the first time the reduction of tri-, tetra-, and pentachloroalkanes containing the CCl_3 group by different thiols in the presence of the following MC: $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Fe(CO)_5$. The reduction of 1,1,1,7-tetrachloroheptane (I), 1,1,1,5-tetrachloropentane (II), 1,1,1,9-tetrachlorononane (III), 1,1,7-trichloroheptane (IV), 1,1,1,5-tetrachloro-3-methylhexane (V), and 1,1,1,2,5-pentachloropentane (VI) was achieved. The reducing agents used were n-butyl-, tert-butyl-, and benzylthiols. The reduction of (I) was used to study the influence of the nature and quantity of the initiator, the ratio of the reagents, and the time required for the reaction (Table 1). The data in the table show that the reduction of (I) with n-butylthiol in the presence of 5 mole% Mn, Mo, and W carbonyls proceeds selectively (tests 2-6); however, in distinction from test 1 where $Fe(CO)_5$ was used as the initiator, a low conversion and a low yield of 1,1,7-trichloroheptane (VII) are obtained:

$$CCl_3(CH_2)_5CH_2Cl + n\text{-}BuSH \rightarrow CHCl_2(CH_2)_5CH_2Cl + {}^1/_2(BuS)_2 + HCl$$

An increase in the (I):MC ratio by a factor of 2, and extension of the duration of the reaction to 16 h (tests 8 and 9) result in a certain increase in the conversion of (I) and the yield of (VII) when the reaction is initiated by Mn and Mo carbonyls. The reduction of (I) in the presence of even 10 mole% $W(CO)_6$ proceeds slowly (test 7); with $Re_2(CO)_{10}$ the reaction does not take place at all. An increase in the concentration of n-butylthiol has no

TABLE 1. Reduction of 1,1,1,7-Tetrachloroheptane (I) (1.5 mmole) with n-Butylthiol at 140°C for 4 h

Test No.	Metal carbonyl, mmole	$n\text{-}C_4H_9SH$, mmole	Conversion, %	Yield of 1,1,7-trichloroheptane, %
1	$Fe(CO)_5$, 0,075	4,5	86	83
2	$Mn_2(CO)_{10}$, 0,075	4,5	10	10
3	$Mo(CO)_6$, 0,075	4,5	13	12
4	$W(CO)_6$, 0,075	4,5	9	7
5	$Mn_2(CO)_{10}$, 0,075	13,5	13	10
6	$Mo(CO)_6$, 0,075	13,5	18	11
7	$W(CO)_6$, 0,15	13,5	7	6
8*	$Mn_2(CO)_{10}$, 0,15	4,5	25	15†
9*	$Mo(CO_6)$, 0,15	4,5	36	24†
10*	$Re_2(CO)_{10}$, 0,15	4,5	3	1
11*	$Mn_2(CO)_{10}$, 0,75	4,5	70	63
12*	$Mo(CO)_6$, 0,75	4,5	46	42

*1,1,7-Trichloroheptene-1 is formed in tests 8-12 with a yield of 1-3%.

†Duration of tests 8, 9, and 16 h.

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TABLE 2. Reduction of α,α,α,ω-Tetrachloroalkanes $Cl(CH_2)_nCCl_3$ (n = 4,6,8) with Thiols R^1SH at 140° for 4 h

Test No.	$Cl(CH_2)_nCCl_3$, value of n	R^1	MC	$[Cl(CH_2)_nCCl_3]:[R^1SH]:[MC]$	Conversion, %	Yield, %	
						$Cl(CH_2)_nCHCl_2$	$Cl(CH_2)_{n-1}CH{=}CCl_2$
1	4	$n\text{-}C_4H_9$	$Fe(CO)_5$	1 : 2,9 : 0,17	92	52	7
2	4	$n\text{-}C_4H_9$	$Mn_2(CO)_{10}$	1 : 3,0 : 0,49	77	55	5
3	4	$C_6H_5CH_2$	$Mn_2(CO)_{10}$	1 : 3,0 : 0,49	92	41	3
4	4	$n\text{-}C_4H_9$	$Mo(CO)_6$	1 : 3,0 : 0,48	57	51	6
5	6	$C_6H_5CH_2$	$Mo(CO)_6$	1 : 3,0 : 0,49	74	14	18
6	6	$C_6H_5CH_2$	$Fe(CO)_5$	1 : 3,0 : 0,14	90	69	16
7	6	$C_6H_5CH_2$	$Mn_2(CO)_{10}$	1 : 3,0 : 0,51	86	68	7
8	6	$C_6H_5CH_2$	$Mo(CO)_6$	1 : 3,0 : 0,49	60	17	26
9	8	$n\text{-}C_4H_9$	$Mo(CO)_6$	1 : 3,0 : 0,50	46	42	3
10	8	$n\text{-}C_4H_9$	$Fe(CO)_5$	1 : 3,0 : 0,24	100	79	None
11	8	$n\text{-}C_4H_9$	$Mn_2(CO)_{10}$	1 : 3,2 : 0,49	81	68	»
12	8	$(CH_3)_3C$	$Mn_2(CO)_{10}$	1 : 3,0 : 0,48	100	62	5
13	8	$n\text{-}C_4H_9$	$Mo(CO)_6$	1 : 3,0 : 0,50	62	55	3

effect on the yield of (VII) nor on the conversion of (I). On the other hand, a strong influence of the concentration of the reducing agent on the yield of the reduction product and on the conversion has been observed in the reduction of 1,1,1-trichloropentane [2] with isopropanol. A significant increase in the yield of (VII) and in the conversion of (I) was achieved in the reduction with n-butylthiol only in the presence of 50 mole% Mn and Mo carbonyls (tests 11 and 12). The satisfactory agreement between the data for the conversion of (I) and the yield of (VII) is a sign for the selectivity of the process. The dehydrochlorination of (I) with the formation of 1,1,7-trichloroheptene-1 (VIII) occurs to a small degree as a side reaction. It must be pointed out that a rearrangement of the intermediately formed radicals $\dot{C}Cl_2(CH_2)_6Cl$ and migration of hydrogen has been observed earlier [5] in the reduction of (I) with isopropanol and $Fe(CO)_5$ as the initiator. Such a rearrangement does not occur in the reduction of (I) with n-butylthiol. This is due to the fact that, because of the ease with which the S—H bond is ruptured, thiols represent better hydrogen donors than isopropanol.

It has been demonstrated on the example of the reduction of (I) that the yield of (VII) in moles per mole of MC is equal to 16 in the case of $Fe(CO)_5$ but only close to 1 in the case of $Mo(CO)_6$ and $Mn_2(CO)_{10}$. It has been pointed out in [6] that the reduction of halogen-containing compounds $HMn(CO)_4PPh_3$ is based on a radical mechanism and that the yield of the reduced products is 1 mole per mole of $HMn(CO)_4PPh_3$.

The reaction of polychloroalkanes with thiols, initiated with Mn, Mo, and W carbonyls, can be represented by the scheme 1:

Scheme 1

$$RCCl_3 \xrightarrow{MC} R\dot{C}Cl_2$$

$$R\dot{C}Cl_2 + R^1SH \rightarrow RCHCl_2 + R^1\dot{S}$$

$$2R^1\dot{S} \rightarrow (R^1S)_2$$

With the aim to elucidate further the reduction of the CCl_3 group with thiols and to compare the efficiency of the carbonyls of Mo, Mn, W, and Fe we have studied polychloroalkanes with different structures. The reduction of 1,1,1,5-tetrachloropentane (II) and 1,1,1,9-tetrachlorononane (III) with thiols and initiation of the reaction by Fe, Mn, and Mo carbonyls showed that the reactions proceed in the same way as that observed in the case of (I). For the reduction of (II) and (III) to 1,1,5-trichloropentane (IX) and 1,1,9-trichlorononane (X) it is necessary to take quantities of $Mo(CO)_6$ and $Mn_2(CO)_{10}$ which are higher by a factor of 2-3 than the amount of $Fe(CO)_5$ in order to achieve similar yields of the reduced products (Table 2, tests 1-3 and 10, 11, 13).

The efficiency of thiols as reducing agents for the CCl_3 group was studied on compounds (I)-(III) (see Table 2). The data show that the use of benzylthiol as the reducing agent increased the side reactions. The dependence of the yields of the reduced products and the conversion on the character of the reducing agent was revealed most clearly when comparing the reduction of (I) and (II) with n-butylthiol and benzylthiol, and $Mo(CO)_6$ as the initiator. A comparison of the results obtained in tests 4 and 5, and 9 and 8 showed that in the reduction of (I) and (II) with benzylthiol lower yields of the reduced products (and higher conversions) were obtained than with n-butylthiol as the reducing agent. Besides this, in the tests with benzylthiol significant dehydrochlorination of (I) and (II) took place with the formation of 1,1,7-trichloro-1-pentene (VIII) and 1,1,5-trichloro-1-pentene (XI), respectively. It was shown on the example of (III) that tert-butylthiol also enhances the dehydrochlorination of (III) with the formation of 1,1,9-trichloro-1-nonene (XII) (see Table 2).

The reduction of 1,1,1-trichloroheptane (IV) to 1,1-dichloroheptane (XIII) with n-butylthiol proceeds much more easily when the reaction is initiated with $Fe(CO)_5$ and $Mn_2(CO)_{10}$ than with $Mo(CO)_5$ (Table 3, tests 1-3). The use of benzylthiol as the reducing agent leads to a lower yield of (XIII) (compare tests 3 and 4). The reduction of 1,1,1,5-tetrachloro-3-methylhexane (V) with n-butylthiol and initiation with Mn and Fe carbonyls gives 1,1,5-trichloro-3-methylhexane (XIV); when $Fe(CO)_5$ is used, a noticeable dehydrochlorination occurs besides the reduction with the formation of 1,1,5-trichloro-3-methyl-1-hexene (XV) (see Table 3, tests 5 and 6).

It was of interest to investigate the reduction of 1,1,1,2,5-pentachloropentane (VI), which has a chlorine atom in α-position to the CCl_3 group, since some peculiarities had been

TABLE 3. Reduction of Polychloroalkanes $RCCl_3$ with n-Butylthiol at 140° for 4 h

Test No.	R	MC	$[RCCl_3]$: $[n\text{-}C_4H_9SH]$: [MC]	Conversion, %	Yield of $RCHCl_2$, %
1	$CH_3(CH_2)_4CH_2$ (VI)	$Fe(CO)_5$	1 : 2,9 : 0,16	76	69
2	Same	$Mo(CO)_6$	1 : 3,0 : 0,49	33	24
3	»	$Mn_2(CO)_{10}$	1 : 3,1 : 0,49	90	71
4	»	$Mn_2(CO)_{10}$	1 : 2,8 : 0,49	91	38 *
5	$CH_3CHClCH_2\underset{\mid \atop CH_3}{CH}CH_2$ (V)	$Fe(CO)_5$	1 : 2,7 : 0,15	100	68 †
6	Same	$Mn_2(CO)_{10}$	1 : 2,8 : 0,50	77	59
7	$Cl(CH_2)_3CHCl$ (VI)	$Fe(CO)_5$	1 : 2,9 : 0,16	100	51 ‡
8	Same	$Fe(CO)_5$	1 : 5,6 : 0,18	100	53 ‡
9	»	$Mn_2(CO)_{10}$	1 : 2,7 : 0,48	66	42 ‡

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*Test carried out with $C_6H_5CH_2SH$.

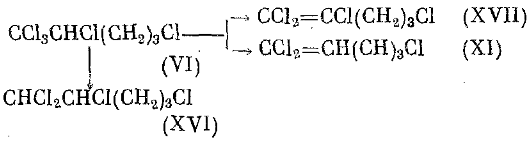
†In test 5 a side reaction leads to the formation of 1,1,5-trichloro-3-methyl-1-hexene (XV) (18%).

‡In tests 7-9, 1,1,2,5-tetrachloro-1-pentene (XVII) (with yields of 5, 4, and 0%, respectively, and 1,1,5-trichloro-1-pentene (XV) (with yields of 42, 30, and 19%, respectively) are formed in side reactions.

observed in its chemical properties [7]. Besides this it has been demonstrated in [8] on the example of the reduction of 1,1,1,2-tetrachloropentane with triethylsilane in the presence of $Fe(CO)_5$ that the presence of a single chlorine atom in the α-position to the CCl_3 group hinders its reduction. This reaction leads to approximately the same yields of reduction and dehydrochlorination products (13 and 15%).

In the reaction of (VI) with n-butylthiol in the presence of $Fe(CO)_5$ (see Table 3, tests 7 and 8) a full conversion of (VI) is achieved in 4 h and a complete balance of the reaction products is available. The reduction of (VI) with the formation of 1,1,2,5-tetrachloropentane (XVI) is accompanied by two competing side reactions: dehydrochlorination with the formation of 1,1,2,5-tetrachloro-1-pentene (XVII) and dechlorination with the formation of 1,1,5-trichloro-1-pentene (XI) (scheme 2):

Scheme 2



The reduction of (VI) with n-butylthiol initiated by $Mn_2(CO)_{10}$ is also accompanied by dechlorination; dehydrochlorination does not take place (see Table 3, test 9).

In conclusion, it must be pointed out that $Mn_2(CO)_{10}$ and $Fe(CO)_5$ are the most effective initiators for the reduction of polychloroalkanes with different structures, while $Mo(CO)_6$ and $W(CO)_6$ are less effective. The reduction of the CCl_3 group with n-butylthiol proceeds more easily than with tert-butyl- and benzylthiols, since the latter lead to a significant degree to side reactions.

EXPERIMENTAL

The reduction of the polychloroalkanes (I)-(VI), initiated by MC, was carried out in glass ampuls according to the procedure described below for the reduction of 1,1,1,2,5-pentachloropentane (VI). The results obtained are presented in Tables 1-3. GLC analyses were performed on an LKhM-8MD chromatograph equipped with a catharometer, with helium as the carrier gas. All products obtained were identified on two stationary phases with different polarity: a column 1 m × 4 mm packed with 6% PEG (20,000) on Chromatone N-AW (0.20-0.25 mm) and a column 2 m × 4 mm packed with SKTFT on Chromatone N-AW (0.16-0.20 mm). The amounts of the components in the reaction mixtures by weight were determined by using internal standards.

Reduction of 1,1,1,2,5-Pentachloropentane (VI). A mixture of 1.76 g (7.2 mmole) of (VI), 2.31 g (25.6 mmole) n-butylthiol, and 0.1 g (0.5 mmole) $Fe(CO)_5$ was heated for 4 h at 140° in an Ar atmosphere in a glass ampul and enclosed in a metal jacket, placed in a thermostat, and mixed by rotation. The reaction mixtures of three parallel experiments were combined and filtered through a layer of silica gel (thickness 20 mm) which was then washed with $CHCl_3$ until complete elution of the reaction products (as checked by GLC). The solvent was stripped off and the residue distilled in vacuum. Preparative GLC (column 1.3 m × 9 mm, packed with 15% Carbowax 20,000 on Chromatone N-AW, 0.25-0.30 mm) isolated the following products from the reaction with bp 109-124°: $Cl(CH_2)_3CHClCHCl_2$ (XVI), n_D^{20} 1.5040, d_4^{20} 1.3940. Found: C 28.67; H 3.89; Cl 67.53%. Calculated: C 28.57; H 3.80; Cl 67.62%, and $Cl(CH_2)_3CH{=}CCl_2$ (XI), n_D^{20} 1.4896, d_4^{20} 1.2757 [9].

CONCLUSIONS

1. The carbonyls $Fe(CO)_5$, $Mn_2(CO)_{10}$, $Mo(CO)_6$, and $W(CO)_6$ initiate the selective reduction of the CCl_3 group to the $CHCl_2$ group by thiols. The reduction systems thiol + Mn, Mo, and W carbonyls have been used for the first time.

2. The reduction of $CCl_3(CH_2)_nCl$ (n = 4, 6, 8), $CCl_3(CH_2)_5CH_3$, $CCl_3CH_2CH(CH_3)CH_2CHCl{-}CH_3$, and $CCl_3CHCl(CH_2)_3Cl$ showed that $Fe(CO)_5$ and $Mn_2(CO)_{10}$ were the most effective initiators.

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