REDUCTION OF α , α , α - TRICHLOROMETHYL COMPOUNDS IN THE PRESENCE OF METAL CARBONYLS

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We have previously proposed methods for the reduction of the CCl_3 group to a $CHCl_2$ group by the action of secondary alcohols, amines, and silicon hydrides with initiation by $Fe(CO)_5$ [1]. In the case of 1,1,1-triand 1,1,1,5-tetrachloropentanes we studied $Mo(CO)_6$, $W(CO)_6$, $Cr(CO)_6$, and $Mn_2(CO)_{10}$ as initiators for the reduction [2]. The reduction of 1,1,1,5-tetrachloropentane or 1,1,1-triand 1,1,1,7-tetrachloroheptane was accompanied by rearrangement in the intermediate $CCl_2(CH_2)_nR$ radical with 1,5-H and 1,6-H migration [2-4]. The aim of the present research was to investigate the effect of the nature of the metal carbonyl on the reduction.

We investigated the reduction of 1, 1, 1-trichlorooctane (I), 1, 1, 1-trichlorononane (II), 1, 1, 1-trichloroundecane (III), and 1, 1, 1, 2, 2-pentachloroethane (IV).

The participation of an intermediate radical in two competitive processes – reduction and rearrangement – is possible in the reduction of α , α , α -trichloroalkanes I-III. In fact, rearrangement with migration of an H atom to the remote radical center occurs in addition to reduction in the case of alkanes I-III.

In the case of 1,1,1-trichlorooctane (I), which was investigated in greatest detail, the reaction proceeds via the scheme

$$\begin{array}{ccc} \operatorname{CCI}_{3}\mathrm{C}_{7}\mathrm{H}_{15} & \frac{\operatorname{Fe}(\mathrm{CO})^{5}}{\operatorname{i-C_{4}H_{7}OH}} & \dot{\mathrm{CCI}}_{2}\mathrm{C}_{7}\mathrm{H}_{15} & \frac{\mathrm{(a)}}{\mathrm{DH}} & \mathrm{CHCI}_{2}\mathrm{C}_{7}\mathrm{H}_{15} \\ (\mathrm{I}) & & (\mathrm{A}) \\ & & (\mathrm{b}) \\ & & (\mathrm{b}) \\ & & (\mathrm{b}) \\ & & (\mathrm{C}) \\ \end{array} \\ \begin{array}{c} \mathrm{CHCI}_{2}(\mathrm{CH}_{2})_{3}\dot{\mathrm{CHCI}}_{3}\mathrm{H}_{7} + \mathrm{CHCI}_{2}(\mathrm{CH}_{2})_{4}\dot{\mathrm{C}}\mathrm{HC}_{2}\mathrm{H}_{5} \\ & (\mathrm{B}) \\ \end{array} \\ (\mathrm{B}) & & (\mathrm{C}) \end{array} \\ (\mathrm{B}) + (\mathrm{C}) & \xrightarrow{\mathrm{DCI}} & \mathrm{CHCI}_{2}(\mathrm{CH}_{2})_{3}\mathrm{CHCIC}_{3}\mathrm{H}_{7} + \mathrm{CHCI}_{2}(\mathrm{CH}_{2})_{4}\mathrm{CHCIC}_{2}\mathrm{H}_{4}_{5} \\ & (\mathrm{VI}) \\ & & (\mathrm{VI}) \\ \end{array} \\ \end{array}$$

We isolated polychloroalkanes V-VII and established that the relative percentages of the products of rearrangement with 1,5-H and 1,6-H migration in the V-VII mixtures depend on the nature of the metal carbonyl.

Competitive dechlorination via the following scheme takes place in addition to reduction in the reaction of pentachloroethane IV:



The results obtained for various metal carbonyls in the reduction of I and IV under comparable conditions are presented in Table 1. It is apparent from experiments 5 and 6 that $Mn_2(CO)_{10}$ is considerably more effective in the reduction of IV and that its use leads to a higher degree of conversion of the starting compound and a higher yield of the product (VIII) than in the case of $Fe(CO)_5$.

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Expt. No.	RCCI3	Metal car- bonyl, mmole	RCCls i-C3H7OH	Conversion of RCCl ₃ , $\%$	Yield of RCHCl,, %of theor.	Yields of other prods., % of theory	Q , *
1	(I)	Fe (CO) 5,	1:3	71	55	(VI) 10,	27
2	(I)	$Mn_2(CO)_{10}$,	1:3	70	61	(VII) 10 (VI) 2;	8
3	(I)	Fe (CO) 5,	1:3	83	57	(VII) = 3 (VI) = 11;	28
-4	(I)	$Mn_2(CO)_{10}$	1:8	88	79	(VII) 12 (VI) 2; (VII) 2	5
5	(IV)	Fe (CO) 5,	1:8	35	14	(IX) 14	50
6	(IV)	$Mn_2(CO)_{10}$,	1:8	64	40	(IX) 18	30
		1 0,3		I	I.	I	l
* Q=-	(VI)+(VI +(V)+(VI)+	I) .100 Or .	(IX) (XI)+(IIIV)	- •100.			

TABLE 1. Reactions of RCCl₃ with iso-C₃H₇OH Initiated by $Fe(CO)_5$ or $Mn_2(CO)_{10}$ (3 mmole of RCCl₃, 120°C, 3 h)

In this case of the reduction of I, which is accompanied by rearrangement in the intermediate radical (see Scheme 1) the experiments were carried out until the same degree of conversion of I in the presence of both $Fe(CO)_5$ and $Mn_2(CO)_{10}$ was achieved (experiments 1-4 in Table 1); the relative percentage of rearrangement products in the mixture of reaction products (Q) is substantially greater in the case of initiation with $Fe(CO)_5$ (27-28%) than in the case of initiation with $Mn_2(CO)_{10}$ (5-8%).

This difference can be explained in two ways.

It is apparent from Scheme 1 that unrearranged radical A participates in two competitive reactions, viz., detachment of an H atom from the hydrogen donor (DH) (pathway *a*) and isomerization (pathway b). It is possible that the low yield of rearranged products indicates that a stronger hydrogen donor develops when $Mn_2(CO)_{10}$, is present in the reaction medium than when $Fe(CO)_5$ is present.* It might be assumed that $HMn(CO)_5$ (or its complex, which also contains other ligands) is formed under our conditions and that this also shifts the process in direction *a* of Scheme 1. This is also responsible for the decrease in Q. The ability of $HMn(CO)_4PPh_3$ to reduce CCl_4 and $CHCl_3$ at ~ 20°C in the presence of a secondary alcohol was previously noted [6].

The results of the reduction of IV (experiments 5 and 6 in Table 1) serve as evidence in favor of this assumption; under comparable conditions the same intermediate CCl_2CCl_2H radical in the presence of $Mn_2(CO)_{10}$ is stabilized much more easily by detachment of an H atom than by fragmentation with splitting out of a Cl atom (experiment 6), while with $Fe(CO)_5$ the two processes take place to an equal extent. This also indicates the presence of a stronger reducing agent in the case of initiation of the reaction by $Mn_2(CO)_{10}$.

The other explanation is linked with the fact that rearranged radicals B and C obtained in step b can be stabilized in two ways – by detachment of an H or Cl atom from the corresponding donors:

HCCl₂(CH₂)_nĊH(CH₂)_{5-n}CH₃
$$(V)$$

 $n = 3$ (B), $n = 4$ (C).
Scheme 3

The formation of rearrangement products VI and VII is evidently also observed in the case of detachment of a Cl atom by radicals B and C (step d), whereas in the case of detachment of an H atom by the same radicals (step c) product V is identical to the product obtained in step *a* of Scheme 1. Thus, the decrease in the Q values in the reduction of I in the presence of $Mn_2(CO)_{10}$ may be due to the fact that in this case step c is realized more easily than step d of Scheme 3.

Data obtained in similar reactions in the presence of $Mo(CO)_6$, $W(CO)_6$, and $Re_2(CO)_{10}$ are presented in Table 2. For comparison, the results of experiments with $Fe(CO)_5$ at 140°C are also given.

^{*} See [4, 5] for information regarding the effect of the nature of the reducing agent on the relative percentage of rearrangement products in the reaction mixture.

TABLE 2. Reactions of RCCl₃ with iso- C_3H_7OH in the Presence of Metal Carbonyls (3 mmole of RCCl₃, 24 mmole of iso- C_3H_7OH , 0.3 mmole of the Metal Carbonyl, 3 h, 140°C)

Exptl., No.	RCCI.	Metal carbonyl	Conversion of RCC1 ₃ , %	Yield of HCCl ₂ R,% of theory	Yields of other reaction prods., % of theory	Q *, %
1	(I)	Fe (CO) 5	96	75	(VI), 13;	24
2	(1)	Mo(CO) ₆ [†]	93	72	(VII), 11 (VI), 12;	24
3	(I)	W(CO ₆) †	29	24	(VII), 12 (VI), 4,5; (VII), 4,6	11
4 5 6	(I) (IV) (IV)	$\begin{array}{c} \operatorname{Re}_2(\operatorname{CO})_{10} \\ \operatorname{Fe}(\operatorname{CO})_5 \\ \operatorname{Mo}(\operatorname{CO})_6 \end{array}$	14 53 73	12 23 23	(V11), 1, 6 (IX), 27 (IX), 42	54 65

* See the footnote to Table 1.

[†] We used 0.15 mmole, since, according to the data in [2], an increase in the metal carbonyl concentration in this case does not increase the yields of products.

TABLE 3. ¹³C Chemical Shifts for VI and VII

Compound	δ , ppm, found/calculated								
F	Cı	C ²	C ³	C4	C ⁵	C6	C7	C ⁸	
(VI)	73,1	42,9	22,9	37,1	62.8	40.3	19,6	13,4	
(VII)	72,8 73,3 72.8	43.7 <u>43.4</u> <u>43.7</u>	22,4 25,4 25,5	$ \begin{array}{r} 38,2 \\ \underline{25,4} \\ \underline{26,3} \end{array} $	62,6 <u>37,6</u> 38,2	40,8 64,8 65.2	19,6 31,4 34,5	13,6 10,6	

Whereas a comparison of $Fe(CO)_5$ and $Mn_2(CO)_{10}$ revealed a difference in the properties of these metal carbonyls as initiators for the reduction of $RCCl_3$ (see Table 1), no such difference was observed when $Fe(CO)_5$ and $Mo(CO)_6$ were compared (experiments 1 and 2 in Table 2). In this case, the conversion of the starting $RCCl_3$, the yields of reduced $RCHCl_2$, and the relative percentage of products of rearrangement with 1, 5-H and 1, 6-H migration are close. As in the cases described in [2], $W(CO)_6$ and $Re_2(CO)_{10}$ are ineffective in the reduction of $RCCl_3$ to $RCHCl_2$ (experiments 3 and 4). A small difference between $Fe(CO)_5$ and $Mo(CO)_6$ was noted in the reduction of IV. Thus, higher conversion of the starting IV and a somewhat greater degree of dechlorination of the intermediate CCl_2CCl_2H radical are observed with $Mo(CO)_6$ (experiments 5 and 6 in Table 2).

On the basis of the principles that follow from the data in Tables 1 and 2 we carried out the reduction of long-chain trichloroalkanes I-III in the presence of $Fe(CO)_5$, $Mo(CO)_6$, and $Mn_2(CO)_{10}$ on a preparative scale. In the reduction of RCCl₃ in the presence of $Mn_2(CO)_{10}$ and $Mo(CO)_6$ one should use no more of the metal carbonyl than is required for its complete consumption in the process, since otherwise the residual undecomposed catalyst contaminates the reaction products as it sublimes and is difficult to separate from the RCHCl₂. In this respect $Fe(CO)_5$ is superior to $Mo(CO)_6$ and $Mn_2(CO)_{10}$, since excess $Fe(CO)_5$ and Fe salts are easily removed by washing the reaction mixture with 10% HCl.

Products of rearrangement with 1,5-H and 1,6-H migration, viz., VI and VII, are isolated along with V in the reduction of I in the presence of $Fe(CO)_5$. Their structures were confirmed by the ¹³C NMR spectra (Table 3).

We first calculated the chemical shifts of the C atoms in VI and VII via an additive scheme [7]. The calculations showed that the difference in the CH_3 (C^8) signals in the C_2H_5 or C_3H_7 groups is prognostic. The signal from CH_3 in C_2H_5 (10.6 ppm) is found in a region that is free of other signals. The signals from the CHCl (C^5 or C^6) group also differ appreciably for both isomers. Thus, a comparison of the calculated and experimentally found chemical shifts for a given isomer makes it possible to establish the position of the lone Cl atom in the chain, i.e., the site from which the H atom migrated during rearrangement via Scheme 1.

The structures of 1,1,5-trichloro- and 1,1,6-trichlorononane, as well as 1,1,5-trichloro- and 1,1,6-trichloroundecane – the rearrangement products obtained in the reduction of II and III – were similarly proved. The presence of these compounds in the reaction mixtures was confirmed by GLC by comparison with samples obtained by an independent method [8].

Thus, with respect to their effectiveness in the reduction of RCCl₃ to RHCCl₂, the investigated metal carbonyls can be arranged in the order $Mn_2(CO)_{10} > Mo(CO)_6 \simeq Fe(CO)_5 \gg W(CO)_6 > Re_2(CO)_{10}$. With respect to the ease with which they bring about dechlorination (in the case of CCl₃CCl₂H), they can be arranged in the order $Mo(CO)_6 > Fe(CO)_5 > Mn_2(CO)_{10}$, i.e., the nature of the metal carbonyl affects the ratio of the reaction products.

EXPERIMENTAL

Analysis by GLC was carried out with an LKhM-8MD chromatograph with a catharometer, He as the carrier gas, a 2 m by 3 mm steel column filled with 15% E-301 silicone on Chromaton N-AW-HMDS (0.15-0.2 mm) (A), and a 1 m by 9 mm steel column filled with 15% Carbowax 20M on Chromaton N-AW-HMDS (0.20-0.25 mm) (B). A Tsvet-2 chromatograph with a preparative adapter was used for preparative GLC. The ¹³C NMR spectra of 50% solutions of the compounds in CHCl₃ were recorded with a Brucker HX-90 spectrometer with tetramethylsilane as the internal standard. α, α, α -Trichloroalkanes I-III were obtained by the addition of CHCl₃ to the corresponding 1-alkenes in the presence of dicyclohexyl peroxydicarbonate by the method in [9]. The purity of the α, α, α -trichloroalkanes was verified by analysis by GLC. All of the experiments were carried out in sealed ampuls with rotatory stirring. The compositions of the reaction mixtures were determined by GLC with internal standards: 1,1,1,5-tetrachloropentane for the reduction of I (column A, 140°C) and 1,1,1,2-tetrachloroethane for IV (column A, 85°C). Experiments 1-3 (see below) were carried out until 95-100% conversion of the starting I-III was realized.

Reduction of 1,1,1-Trichlorooctane (I) in the Presence of $Fe(CO)_5$ (Experiment 1). A mixture of 4.35 g (20 mmole) of I, 9.6 g (160 mmole) of iso-C₃H₇OH (X), and 0.59 g (3 mmole) of $Fe(CO)_5$ was heated at 120°C for 3 h. The reaction mixtures from five experiments were combined and distilled with collection of the fraction that boiled up to 80°C (iso-C₃H₇OH and its transformation products). The residue was washed with 10% HCl and water and distilled in vacuo to give 12.4 g (65%) of 1,1-dichlorooctane with bp 85-87°C (15 mm), n_D^{20} 1.4430, and d_4^{20} 1.0055 (see [10]). According to GLC data (column A, 140°C), the fraction with bp 97-128°C (10 mm) (4.2 g) contained two substances. Preparative GLC (column B) yielded 1,1,5- and 1,1,6-trichlorooctanes (VI and VII) in the form of 95% enriched fractions containing the second isomer. The parameters of the ¹³C NMR spectra for VI and VII are given in Table 3. Found for the mixture of VI and VII: C 44.11; H 6.80; Cl 48.73%. C₈H₁₅Cl₃. Calculated: C 44.16; H 6.95; Cl 48.89%.

Reduction of 1,1,1-Trichlorononane (II) in the Presence of $Mn_2(CO)_{10}$ (Experiment 2). The reaction was carried out as in experiment 1. A mixture of 20 mmole of II, 160 mmole of X, and 2 mmole of $Mn_2(CO)_{10}$ was heated at 120°C for 3 h. The reaction mixtures from three experiments were combined and worked up to give 9.4 g (68%) of 1,1-dichlorononane with bp 102-104°C (15 mm), n_D^{20} 1.4516, and d_4^{20} 0.9928 (see [9, p. 513]). The undistilled residue (1.6 g) contained 1,1,5- and 1,1,6-trichlorononanes, which were identified by GLC with reference to samples obtained by an independent method [8].

Reduction of 1,1,1-Trichloroundecane in the Presence of $Mo(CO)_6$ (Experiment 3). The reaction was carried out as in experiment 1. A mixture of 20 mmole of III, 160 mmole of X, and 1 mmole of $Mo(CO)_6$ was heated at 140°C for 3 h. The reaction mixtures from five experiments were combined and worked up. Distillation gave 16.6 g (74%) of 1,1-dichloroundecane with bp 101-102°C (2 mm), n_P^{20} 1.4539, and d_4^{20} 0.9710 (see [8]) and a fraction containing, according to GLC data, 3.2 g (16%) of a mixture of 1,1,5- and 1,1,6-trichloroundecanes, which were identified by GLC with reference to samples obtained by an independent method [8].

CONCLUSIONS

1. Iron, molybdenum, and manganese carbonyls can be used successfully as initiators for the reduction of α , α , α -trichloroalkanes (C₈-C₁₁) with isopropyl alcohol.

2. Rearrangement with 1,5-H and 1,6-H migration occurs in the intermediate $CCl_2(CH_2)_nCH_3$ radicals in the presence of all of the investigated metal carbonyls; however, the relative percentage of rearrangement products is greater in the presence of $Fe(CO)_5$ or $Mo(CO)_6$ than in the presence of $Mn_2(CO)_{10}$.

3. Fragmentation of the intermediate CCl_2CCl_2H radical with splitting out of chlorine predominates in the reduction of pentachloroethane in the presence of $Mo(CO)_6$, whereas this radical is stabilized primarily by detachment of hydrogen in the presence of $Mn_2(CO)_{10}$.

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HYDROGEN MIGRATION IN 1,1-DICHLOROALKYL

RADICALS

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In compounds containing a CCl_3 group, rearrangement with 1,5- and 1,6-migration of hydrogen occurs under the action of systems based on $Fe(CO)_5$ in addition to reduction to CH_2Cl [1]. In the case of 1,1,1,3tetrachlorononane in addition to the products of these rearrangements and reduction of the CCl_3 group to $CHCl_2$ there are formed 1,1,3,7- and 1,1,3,8-tetrachlorononanes hypothetically as a result of rearrangement in the intermediate radical with 1,7- and 1,8-migration of hydrogen [2, 3].

In continuation of these investigations, in the present work the action of systems based on $Fe(CO)_5$ in combination with hexamethylphosphoramide (HMPA) or isopropanol on 1,1,1-trichlorononane (Ia) and 1,1,1-trichlorononane (Ib) has been studied. As in [1-3] it is proposed that 1,1-dichloroalkyl radicals (A) are first generated in these reactions. By removal of hydrogen from a hydrogen donor these radicals are converted into 1,1-dichloroalkanes (IIa, b).

Migration of hydrogen in radicals A leads to the formation of the isomeric radicals (B_1, B_2) , the reaction of which with a chlorine donor (CD) form trichloroalkanes (IIIa)-(VIIIa), (IIIb)-(Xb) (Table 1).



Under the selected conditions $(130-140^{\circ}C, 3 h)$ conversion of the initial trichloroalkanes (Ia, b) was closely similar (75-83%), but the yield of 1,1-dichloroalkanes (IIa, b) varied from 44 to 58% and did not in

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