REDUCTION OF ORGANIC CHLORINE COMPOUNDS BY SYSTEMS CONSISTING OF A HYDROGEN DONOR AND A COMPOUND OF A TRANSITION ELEMENT

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UDC 542.941+547.412.12

In recent years organic compounds containing the trichloromethyl group have become widely available. They are prepared by the telomerization of olefins with carbon tetrachloride or chloroform. The CCl_3 group has been found to be extremely reactive toward radical and electrophilic reagents. Up to now compounds containing a dichloromethyl group have been less accessible, and their preparation by the reduction of trichloromethyl derivatives presents considerable interest. Isolated examples have been reported of the reduction of trichloromethyl to dichloromethyl. Catalytic hydrogenation does not achieve the desired object, for the main process occurring is not the replacement of chlorine by hydrogen, but dechlorination and "dimerization" in accordance with the scheme [1]:

$$2RCCl_3 \xrightarrow[\text{base}]{H_2,\ \text{catalyst}} RCCl_2CCl_2R$$

In a few cases trichloromethyl groups in aliphatic compounds have been reduced electrolytically [2]. We have proposed new methods for the conversion of the trichloromethyl group into dichloromethyl [3, 4]: in these reduction is effected by hydrogen donors (tertiary amines or hydride silanes) in presence of compounds of transition metals as catalysts.

In the present work we studied the selectivity of the reduction and also extended the field of application of the methods. In summary, the results are as follows: polychloro hydrocarbons containing the CCl_3 group are reduced under the action of tertiary amines [3] in presence of small amounts of $Fe(CO)_5$ or $FeCl_3$. Analogous reduction can be effected by hydride silanes in presence of $Fe(CO)_5$ or $H_2PtCl_6 \cdot H_2O$ as catalysts [4].

$$CCl_3CH_2R \xrightarrow[\text{catalyst}]{\text{hydrogen donor}} HCCl_2CH_2R$$

Reduction with the Tertiary Amine – $Fe(CO)_5$ System. The effect of the nature of the amine on the course of the reaction was studied for the case of 1,1,1-trichlorooctane. It was found that, in absence of amines, 1,1,1-trichlorooctane is converted under the action of catalytic amounts of $Fe(CO)_5$ into 1,1-dichloro-1-octene in 90% yield. It was shown by means of GLC that in absence of catalyst N,N-dimethylaniline does not reduce 1,1,1-trichlorooctane, whereas in presence of $Fe(CO)_5$ with the use of a tertiary amine containing an aliphatic group on the nitrogen (triethylamine, N,N-dimethylaniline) 1,1-dichlorooctane is formed in high yield. If pyridine or quinoline is used instead of these amines the yield of reduction product falls to 8-12%.

The reduction of 1,1,1-trichlorooctane with N,N-dimethylaniline in presence of $FeCl_3$ goes as in the presence of $Fe(CO)_5$, but the replacement of the iron compound by chloroplatinic acid leads to a marked diminution in the yield of 1,1-dichloroctane.

In Table 1 we give examples of the reduction of chlorine derivatives with the $(CH_3)_2NC_6H_5 - Fe(CO)_5$ system (Expts. 1-3, 5, 8, 9, 11, 13, and 15).

The reduction of compounds which contain a primary or secondary chlorine atom, alkoxy group, or acetoxy group as well as a trichloromethyl group goes selectively at the trichloromethyl group. The presence of a terminal double bond in 5,5,5-trichloro-1-pentene lowers the yield of reduction product to 20%. In this case the course of the reaction is complex.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1319-1326, June, 1968. Original article submitted October 18, 1967.

TABLE 1. Reduction of Trichloromethyl Derivatives in Presence of $Fe(CO)_5$* $\left(CCl_3R \xrightarrow[Fe(CO)_5]{\text{reducing agent}} CHCl_2R\right)$

Expt.	R	Reducing agent	Yield of $CHCl_2R$, %	Expt.	R	Reducing agent	Yield of $CHCl_2R$, %
1	C_2H_5	DMA**	68	8	$(CH_2)_6Cl$	DMA	49
2	n-C_4H_9	DMA	57	9	$CH_2CHClC_5H_{11}$-n	DMA	44
3	n-C_7H_{15}	DMA	61	10	$CH_2CHClC_3H_7$-n	Et_3SiH	55
4	n-C_8H_{17}	Et_3SiH	62	11	$(CH_2)_2CH=CH_2$	DMA	20
5	CH_2CH_2Cl	DMA	26	12	$(CH_2)_2CH=CH_2$	Et_3SiH	6 ****
6 ***	CH_2CH_2Cl	Cl_3SiH	78	13	$(CH_2)_4OCOCH_3$	DMA	66
7	$(CH_2)_4Cl$	Et_3SiH	83	14	$(CH_2)_4OCOCH_3$	Et_3SiH	69
				15	$(CH_2)_4OC_2H_5$	DMA	61

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*The experimental conditions are stated in Experimental.

†DMA = N,N-dimethylaniline.

‡$H_2PtCl_6 \cdot 6H_2O$ was used instead of $Fe(CO)_5$.

**The degree of conversion of 5,5,5-trichloro-1-pentene was 44%.

The trichloromethyl group is reduced selectively to dichloromethyl under the action of the tertiary amine – $Fe(CO)_5$ system. This conclusion is confirmed by the absence of products of the further reduction of the dichloromethyl group in the reaction mixture and by special experiments: it was established that pentyl chloride, bromide, and iodide are scarcely reduced at all under the given conditions, under which they form quaternary salts with N,N-dimethylaniline, and 1,1-dichloropentane is also not reduced by a tertiary amine – $Fe(CO)_5$ system.

We made use of the reduction of 1,1,1-trichloropropane to elucidate some matters concerning the transformation of the amine reducing agent in the reaction. This case is the most convenient, because the reduction products boil very much lower than N,N-dimethylaniline and can readily be removed from the mixture by fractionation. According to the results of analytical TLC, the main product of the transformation of N,N-dimethylaniline is the diamine $(CH_3)_2NC_6H_4CH_2C_6H_4N(CH_3)_2$ (I). The dimer $(CH_3)_2NC_6H_4CH_2N \cdot (CH_3)C_6H_5$ (II) and the trimer $(CH_3)_2NC_6H_4CH_2N(CH_3)C_6H_4CH_2N(CH_3)C_6H_5$ (III) are present in small amounts. From the reaction mixture, which was subjected to an acid-alkali treatment, we also isolated N-methylaniline in small amount.

It may be supposed that the dimer (II) is formed at first, and, in accord with the data in [5], this then undergoes the following transformations in a weakly acid medium with formation of the diamine (I):

$$C_6H_5N(CH_3)CH_2C_6H_4N(CH_3)_2 + (CH_3)_2NC_6H_5 \xrightarrow{H^+} (CH_3)_2NC_6H_4CH_2C_6H_4N(CH_3)_2 + C_6H_5NH(CH_3) \quad (1)$$

We showed by special experiments that heating of the dimer (II) with N,N-dimethylaniline in presence of N,N-dimethylaniline hydrochloride at 140° (i.e., under the conditions of the reduction experiments) leads to the formation of the diamine (I). However, the reaction (1) should lead to equimolecular amounts of the diamine (I) and N-methylaniline, whereas we isolated very little of the latter. It is possible that in the course of the reaction N-methylaniline undergoes further transformations with formation of condensation products. When N,N-dimethylaniline is heated in presence of $Fe(CO)_5$, none of the above-indicated dimers is formed, but the N,N-dimethylaniline taken is recovered quantitatively.

It was thus shown that the reaction of the trichloromethyl group with N,N-dimethylaniline is brought about at the expense of hydrogen from a methyl group of the N,N-dimethylaniline.

Reduction with the Hydride Silane – Catalyst System. In conjunction with $Fe(CO)_5$ hydride silanes reduced trichloromethyl to dichloromethyl in accordance, for example, with the scheme

$$CCl_3CH_2R + (C_2H_5)_3SiH \xrightarrow{Fe(CO)_5} HCCl_2CH_2R + (C_2H_5)_3SiCl$$

The effectiveness of silanes as reducing agents falls in the series [4]: $(C_2H_5)_3SiH > (C_2H_5O)_3SiH > Cl_3SiH$.

In Table 1 we give examples of the reduction of chlorine derivatives with the $(C_2H_5)_3SiH - Fe(CO)_5$ system (Expts. 4, 7, 10, 12, and 14). Again in this system reduction goes selectively. The presence of a terminal double bond in the trichloromethyl compound prevents reduction (Expt. 12), for, on the one hand, the addition of the hydride silane at the double bond occurs, and, on the other, the total degree of conversion of 5,5,5-trichloro-1-pentene falls to 44%. By special experiments we showed that 1,1-dichloropentane, and also butyl and s-butyl chlorides, are not reduced by the $Fe(CO)_5 + (C_2H_5)_3SiH$ system. t-Butyl chloride is partially dehydrochlorinated under the reduction conditions, but no isobutane is formed.

In both of the methods of reduction (by tertiary amine and by hydride silane) the main side process is dehydrochlorination [3, 4].

$$CCl_3CH_2R \xrightarrow[\text{Fe (CO)}_5]{\text{reducing agent}} \left[\begin{array}{l} \rightarrow CHCl_2CH_2R \\ \rightarrow CCl_2{=}CHR \end{array} \right. \qquad (2)$$

An important difference between hydride silanes and tertiary amines in the reduction reaction is the inability of the former to reduce CCl_3 into $CHCl_2$ in presence of $FeCl_3$ [4]. It was shown [4] that $H_2PtCl_6 \cdot 6H_2O$ also catalyzes the reduction of trichloromethyl groups by hydride silanes, but the following differences from the systems with $Fe(CO)_5$ were noted: in the first place, in presence of $H_2PtCl_6 \cdot 6H_2O$ triethoxy- and trichloro-silanes are effective as reducing agents as well as triethylsilane, and, in the second place, the side reaction of the dehydrochlorination of compounds containing the trichloromethyl group does not occur at all. In the course of this investigation we established that the $H_2PtCl_6 \cdot 6H_2O - X_3SiH$ system reduces the CCl_3 group less selectively than systems with the participation of $Fe(CO)_5$. Thus, in the reduction of 1,1,1,5-tetrachloropentane with trichlorosilane in presence of $H_2PtCl_6 \cdot 6H_2O$ we observed the formation of 1,5-dichloropentane in a yield of about 15-20%. The reduction of 1,1-dichloropentane with the $CH_3Cl_2SiH - H_2PtCl_6 \cdot 6H_2O$ system leads to the formation of pentyl chloride in 20% yield.

The reduction of ethyl 5,5,5-trichloropentyl ether and of 5,5,5-trichloropentyl acetate takes a considerably more complex course than the reactions catalyzed by $Fe(CO)_5$. In the latter case the acetoxy group is also affected by the reduction. As a result a multicomponent mixture of reaction products is formed which contains very little 4,4-dichloropentyl acetate.

EXPERIMENTAL

Preparation of Starting Compounds and Standard Compounds for Use in the Identification of Reduction Products by Means of GLC. 5,5,5-Trichloropentyl acetate and 1,1,1-trichloro-5-iodopentane were prepared by the method described in [6]. A mixture of 5,5,5-trichloro-1-pentene and ethyl 5,5,5-trichloropentyl ether, readily separable by fractional distillation, was prepared by the addition of 1,1,1-trichloro-5-iodopentane to an equimolecular amount of sodium ethoxide with subsequent stirring and heating at 65° for 4 h.

Analogously, from 1,1-dichloro-5-iodopentane we obtained 5,5-dichloropentyl ethyl ether and 5,5-dichloro-1-pentene. The yields, constants, and analyses of all the substances referred to above are given in Table 2. For 5,5,5-trichloro-1-pentene we determined PMR and IR spectra.

The PMR spectrum, determined with a Hitachi H-60 instrument (internal standard hexamethyldisiloxane), contains three groups of multiplets. The vinyl protons give two multiplets with centers at δ = ca. 4.92 and ca. 5.71, characteristic for a terminal double bond. The two methylene groups (α and β relative to CCl_3) give signals in the region $2.25 \leq \delta \leq 3$. The intensity ratio of the three signals (2 : 1 : 0.5) corresponds to the proposed structure. The absence of signals in the region up to 2 p.p.m. confirms the absence of the groups $CCl_3 - CH{=}CH$ and $C_2H_5CH{=}CH$ in the compound under investigation (these could be formed by the migration of the double bond).

The IR spectrum also confirms the proposed structure of 5,5,5-trichloro-1-pentene.

Reduction with the N,N-Dimethylaniline – $Fe(CO)_5$ System

Reduction of 1,1,1-Trichloropropane. A mixture of 0.14 mole of 1,1,1-trichloropropane, 0.35 mole of N,N-dimethylaniline (carefully dried by prolonged standing over NaOH and then distilled over sodium), and 5.4 mmoles of $Fe(CO)_5$ was distributed among four ampules. The ampules were sealed under argon and heated with agitation for 18 h at 140°. Agitation was effected by rotating the ampules in the thermostat. The ampules were opened, and their contents were found to consist of two parts: a mobile liquid

TABLE 2. Yields, Constants, and Analyses of Substances Obtained

Compound	Yield, %	bp, °C(p, mm)	n_D^{20}	d_4^{20}	MR		Found, %			Calculated, %		
					найдено	вычислено	C	H	Cl	C	H	Cl
$CCl_3(CH_2)_2CH{=}CH_2$	31	92(120)	1,4685	1,2138	39,79	39,42	34,79 34,35	4,17 4,15	60,87 60,77	34,61	4,07	61,39
$CCl_3(CH_2)_4OC_2H_5$	47	81(8)	1,4580	1,1648	51,41	50,88	38,25 38,52	6,09 6,04	48,36 48,42	38,31	5,97	48,47
$CHCl_3(CH_2)_4I$	86	97(4)	1,5445	1,7568	48,00	47,90	22,47 22,57	3,43 3,38	74,03 74,21	22,50	3,40	74,1
$CHCl_2(CH_2)_4OC_2H_5$	45	105(25)	1,4495	1,0825	45,91	45,90	45,37 45,37	7,56 7,45	38,48 38,24	45,42	7,62	38,31
$CHCl_2(CH_2)_2CH{=}CH_2$	30	80(115)	1,4540	1,0846	34,71	34,56	43,11 43,25	5,87 5,87	50,14 50,33	43,19	5,80	51,01
$CHCl_2C_8H_{17}$-*n*	62	59(2)	1,4514	0,9895	53,67	53,56	54,82 54,69	9,15 9,28	35,34 35,61	54,82	9,20	35,97
$CHCl_2CH_2CHClC_3H_7$-*n*	55	81(20)	1,4660	1,1741	44,70	44,45	38,31 38,34	5,87 5,87	55,26 55,74	38,02	5,85	56,12
$CHCl_2(CH_2)_4OCOCH_3$	69	72(5)	1,4570	1,1768	46,10	46,01	42,17 41,96	6,16 6,18	35,45 35,46	42,23	6,08	35,62

and a solid resin. Distillation of the liquid part of the reaction mixture yielded the fractions: I, 15.0 g, bp 99-108°, containing 70% of 1,1-dichloropropane (yield 68%); II, 13.0 g, bp 90-130° (620 mm); III, 7 g, resinous residue.

From Fraction I on the preparative chromatograph we obtained pure 1,1-dichloropropane, bp 85.5-86°, n_D^{20} 1.4283, d_4^{20} 1.1342. Found MR 25.65; calculated MR 25.79. The literature [7] gives: bp 86.8-87.6°, n_D^{20} 1.4288, d_4^{20} 1.1321.

According to the results of TLC on alumina with a solvent containing 90% of heptane and 10% of benzene Fraction II consisted mainly of N,N-dimethylaniline, and Fraction III contained the diamine $(CH_3)_2NC_6 \cdot H_4CH_2C_6H_4N(CH_3)_2$ (I) with a small amount of N-methylaniline.

The solid residue from the ampules was dissolved in chloroform and treated with dilute HCl. The hydrochloric acid solution was made strongly alkaline. The organic layer was separated and extracted with chloroform; the extract was dried over Na_2SO_4, solvent was driven off, and the residue was vacuum-distilled. We obtained the fractions: IV, 1 g, bp 50° (20 mm); V, 8.5 g, bp 182-187° (0.7 mm); VI, 4 g, bp 200-280° (0.8 mm). Residue 4.5 g.

According to TLC Fraction IV contained N,N-dimethylaniline and N-methylaniline. Fraction V contained a number of compounds, the main one of which was the diamine (I), while the dimer $(CH_3)_2NC_6H_4CH_2N \cdot (CH_3)C_6H_5$ (II) and the trimer $(CH_3)_2NC_6H_4CH_2N(CH_3)C_6H_4CH_2N(CH_3)C_6H_5$ (III) were present in very small amounts. Fraction VI contained (I) and a number of unidentified substances. The compounds (I), (II), and (III) were identified by comparison with known samples.

Apart from the establishment of the compositions of the fractions by means of TLC, from Fraction IV we prepared the p-tolylsulfonyl derivative of N-methylaniline by Ginsberg's method (0.62 g; mp 91-92°). The literature [8] gives mp 94°. A mixture with a known sample melted without depression.

Reduction of 5,5,5-Trichloropentyl Acetate. By heating a mixture of 0.24 mole of 5,5,5-trichloropentyl acetate, 0.48 mole of N,N-dimethylaniline, and 11 mmoles of $Fe(CO)_5$ for 5 h we obtained 0.16 mole (66%) of 1,1-dichloropentyl acetate, bp 78° (6 mm).

Reduction of Ethyl 5,5,5-Trichloropentyl Ether. Analogously, by heating a mixture of 0.11 mole of ethyl 5,5,5-trichloropentyl ether, 0.23 mole of N,N-dimethylaniline, and 8 mmoles of $Fe(CO)_5$ for 10 h we obtained 0.07 mole (61%) of 1,1-dichloropentyl ethyl ether, bp 80° (15 mm).

Reduction with the $(C_2H_5)_3SiH - Fe(CO)_5$

Reduction of 1,1,1-Trichlorononane. A mixture of 0.15 mole of 1,1,1-trichlorononane, 0.17 mole of triethylsilane, and 9 mmoles of $Fe(CO)_5$ was sealed in several glass ampules in an atmosphere of nitrogen and heated for 5 h at 145° with agitation. The precipitate formed was filtered off, and the reaction mixture was vacuum-fractionated. We obtained 0.09 mole of 1,1-dichlorononane of 95% purity (yield 62%).

Reduction of 1,1,1,3-Tetrachlorohexane. Reaction was between 0.15 mole of 1,1,1,3-tetrachlorohexane, 0.17 mole of triethylsilane, and 9 mmoles of $Fe(CO)_5$ under the same conditions as in the preceding experiment. We isolated 0.08 mole of 1,1,3-trichlorohexane of 95% purity (yield 55%).

Reduction of 5,5,5-Trichloropentyl Acetate. A mixture of 0.2 mole of 5,5,5-trichloropentyl acetate, 0.21 mole of triethylsilane, and 12 mmoles of $Fe(CO)_5$ was heated for 6 h at 140-150° with stirring in a 250-ml stainless steel autoclave. The precipitate was filtered off. Vacuum fractionation of the reaction mixture gave 0.14 mole of 5,5-dichloropentyl acetate of 95% purity. The constants and analyses of the compounds obtained in the last three experiments are given in Table 2 (the substances were distilled through a column with a filling and were pure according to GLC).

DISCUSSION

It should be noted that in the reduction of the trichloromethyl group to dichloromethyl in presence of $Fe(CO)_5$ the hydrogen donor is either an alkyl group attached to the nitrogen of an amine or a hydrogen atom attached to the silicon of a silane.

The ability of tertiary amines containing at least one aliphatic group to serve as a source of hydride hydrogen and reduce certain organic compounds in absence of catalyst has been referred to in the literature in respect to isolated cases [9-14]. Examples of the reducing action of hydride silanes have been examined by us in a previous communication [4]. However, we have found that neither tertiary amines nor hydride silanes will reduce the trichloromethyl group at temperatures of up to 145° and that the reaction goes only in presence of catalytic amounts of $Fe(CO)_5$ or other compounds of transition metals [3, 4]. In recent years compounds of transition metals have found ever wider use as catalysts for various reduction reactions, and together with the extensive literature on hydrogenation with hydrogen more and more data are beginning to appear on the possibility of reduction catalyzed by these compounds at the expense of hydrogen withdrawal from the solvent. Thus, platinum complexes catalyze the hydrogenation of methyl linoleate with methanol [15], and aqueous solutions containing the anions $[Fe(CO)_4]^{2-}$ or $[HFe(CO)_4]^-$ reduce nitrobenzene to aniline, benzil to benzoin, and acetylene to ethylene. In the case of the reaction of $Fe(CO)_5$ with cyclopentadiene, as well as the formation of $(C_5H_5)_2Fe(CO)_4$, the hydrogenation of cyclopentadiene to cyclopentene occurs [16].

It is assumed that in all cases the hydrogen carriers are iron carbonyl hydrides. It is known that hydrides and complex hydrides of nontransition elements reduce the C – Cl bond by two mechanisms. Thus, there are many data in favor of the view that in the case of lithium tetrahydroaluminate and sodium tetrahydroborate reduction is effected by nucleophilic attack by the hydride ion (in the transition complex) on the C – Cl bond [17], whereas the reduction of trialkyl- and triaryl-tins with hydrides has a free-radical character [18].

The data available at present do not favor a free-radical mechanism for reduction catalyzed by $Fe(CO)_5$. Thus, the order of reducing activities of hydride silanes in the reduction reaction concerned – $(C_2H_5)_3SiH > (C_2H_5O)_3SiH > Cl_3SiH$ – corresponds to the order of their activities in ionic reactions and is opposite to the order of the activities of hydride silanes in homolytic processes. Another argument is provided by the occurrence of a heterolytic side process of dehydrochlorination, which usually accompanies other heterolytic transformations of the CCl_3 group [19]. Finally, according to preliminary data in the literature the homolytic reduction of chloroalkanes by hydride silanes initiated by benzoyl peroxide [20] or UV radiation [21-23] is not selective with respect to the CCl_3 group, for not only CCl_3 but also $CHCl_2$ and CH_2Cl groups can be reduced.

In the reduction reactions which we have studied $Fe(CO)_5$ may have two roles. In the first place it may be supposed that $Fe(CO)_5$ participates in the initiation state by activating the C – Cl bond in the transition complex, which also contains a molecule of the hydrogen donor. This view is supported by the fact that in absence of hydrogen donors $Fe(CO)_5$ catalyzes only the dehydrochlorination of the trichloromethyl compound into a dichlorovinyl compound. In presence of hydrogen donors the yield of dehydrochlorination products falls as the hydride mobility of the donor increases, e.g., on transition from $HSiCl_3$ to $(C_2H_5O)_3SiH$ and to $(C_2H_5)_3SiH$ [4]. In the second place $Fe(CO)_5$ may participate in the transfer of hydrogen. The hydride migration of hydrogen may occur either directly from the hydrogen donor, or from an iron carbonyl hydride. The latter may be formed by the reaction of $Fe(CO)_5$ with the hydrogen donor.

Reduction catalyzed by $H_2PtCl_6 \cdot 6H_2O$ probably has a different mechanism, for the side reaction of dehydrochlorination in accordance with the scheme (2) does not occur at all. In this case the activities of the hydride silanes as reducing agents do not depend on the hydride mobility of the Si-hydrogen [4].

In conclusion we compare tertiary amines and hydride silanes from the point of view of the convenience of their application for the preparative reduction of the trichloromethyl group. It is evident that, depending on the substance to be reduced, preference may be given to a particular one of the three systems proposed: N,N-dimethylaniline – $Fe(CO)_5$, $(C_2H_5)_3SiH - Fe(CO)_5$, and $X_3SiH - H_2PtCl_6 \cdot 6H_2O$. Thus, a system containing N,N-dimethylaniline should not be used when a lone chlorine is present in the molecule (see Table 1, expts. 5, 8, and 9), and systems containing $H_2PtCl_6 \cdot 6H_2O$ should not be used when there are oxygen-containing substituents or a terminal double bond. The isolation of a product of reduction of triethylsilane is complicated when the substance boils in the range 100-150° and is therefore difficult to separate from $(C_2H_5)_3SiH$ and the $(C_2H_5)_3SiCl$ formed. It is therefore best to reduce tetrachloroalkanes with the system $X_3SiH - H_2PtCl_6 \cdot 6H_2O$, while the reduction of trichloroalkanes can be conducted both with hydride silanes and with amines. Reduction with triethylsilane in presence of $Fe(CO)_5$ goes most smoothly, and the reaction products are readily isolated by the fractionation of the reaction mixture.

CONCLUSIONS

1. A method was developed for the reduction of the CCl_3 group to the $CHCl_2$ group in various compounds by means of the systems: $Fe(CO)_5 - (CH_3)_2NC_6H_5$; $Fe(CO)_5 - (C_2H_5)_3SiH$, and $H_2PtCl_6 \cdot 6H_2O - HSiX_3$.

2. Reduction by the systems containing $Fe(CO)_5$ goes selectively to the $CHCl_2$ group and does not affect CH_2Cl, CHCl, OC_2H_5, and $OCOCH_3$ groups.

3. The mechanism of reduction catalyzed by $Fe(CO)_5$ is not a free-radical mechanism.

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