REDUCTION OF POLYCHLOROALKANES AND POLYCHLOROALKENES WITH A CCl₃ GROUP BY SILICON HYDRIDES IN THE PRESENCE OF METAL CARBONYLS

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Selective reduction of the CCl_3 group in trichloromethyl compounds by the effect of hydrogen donors (HD) - secondary alcohols, mercaptans, tertiary amines, and silicon hydrides with initiation by $Fe(CO)_5$ - is a convenient method of conversion from CCl_3 to the $CHCl_2$ group [1]. The use of other metal carbonyls (MC) for initiation of this reaction has only been investigated on the example of reduction by isopropanol [2] and mercaptans [3].

UDC 542.941.7:547.412:547.413

It was interesting to study the possibility of using $Mo(CO)_6$ and $Mn_2(CO)_{10}$ for initiation of reduction of AlkCCl₃ by secondary alcohols and mercaptans with initiation by the same MC.

Reduction was studied on the example of 1,1,1-trichlorooctane (I). The reaction takes place according to the scheme

 $\underset{(I)}{\overset{C_7H_{15}CCl_3}{\longrightarrow}} + \underset{(II)}{\overset{H_1}{\longrightarrow}} \overset{MC}{C_7H_{15}CHCl_2} + \underset{(II)}{\overset{Et_3}{\longrightarrow}} SiCl_2$

The results obtained are reported in Table 1, which indicates that all of the MC investigated successfully initiate reduction of chloroalkane (I) by the effect of Et_3SiH .

In the case of $Fe(CO)_5$ and $Mo(CO)_6$, the reaction took place at 140°C, while the quantitative yield of the reduced product was attained at 120°C with $Mn_2(CO)_{10}$. In the presence of $Mo(CO)_6$, side dehydrochlorination of (I) with formation of 1,1-dichloro-1-octene (III) played an important role.

In the reduction of higher trichloroalkanes by Et_3SiH or $MeSiCl_2H$ with initiation by $Fe(CO)_5$, it was previously shown that 1,5-H and 1,6-H migration in the intermediate dichloromethyl radical did not take place to a marked degree [1] [formation of $RCCl_2$ radicals in the reactions of $RCCl_3$ with Et_3SiH and MC (cf. [4])]. The absence of 1,5-H and 1,6-H rearrangements was also observed in the reduction of $RCCl_3$ by mercaptans and various MC [3]. On the other hand, in the reduction of trichlorooctane (I) by i-PrOH in the presence of the same MC, the yields of the products of the 1,5-H and 1,6-H rearrangement were 4-27% [5].

We showed that reduction of trichlorooctane (I) by Et_3SiH in the presence of $Mo(CO)_6$ or $Mn_2(CO)_{10}$ was not accompanied by 1,5-H and 1,6-H migrations in the intermediate $C_7H_{15}CCl_2$ radical to any significant degree. Another difference in these MC as initiators of the reduction of RCCl₃ and Et_3SiH from reduction of RCCl₃ with the same MC under the effect of i-PrOH [5] or RSH [3] consists of the fact that an eightfold excess of i-PrOH is required for obtaining the conversion of (I) and the yields of (II) similar to those obtained in the present study (see Table 1). In reduction with RSH, 50 mole % of $Mo(CO)_6$ or $Mn_2(CO)_{10}$ was used per mole of RCCl₃.

The possibility of using $Mo(CO)_6$ or $Mn_2(CO)_{10}$ for initiation of reduction of heme-trichloroalkenes with Et₃SiH or i-PrOH was investigated on the example of 5,5,5-trichloro-l-pentene (IV). It was previously shown that the yields of 1,1-dichloro-l-pentene (V) were, respectively, 6 and 20% in reduction of trichloropentene (IV) in the presence of Fe(CO)₅ by Et₃SiH or Me₂NC₆H₅ [6]. It was found that the reaction of trichloropentene (IV) with i-PrOH or Et₃SiH in the presence of Mo(CO)₆ or Mn₂(CO)₁₀ took place with 60-100% conversion of the starting (IV) and a 7-12% yield of product (V).

The reduction of perchloropropylene (VI), which contains a specific CCl_3 group, was also studied. All of the Cl atoms in the CCl_3 group are in the allyl position, and for this rea-

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A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2061-2064, September, 1984. Original article submitted June 23, 1983.

son, they should be especially easy to reduce. However, the presence of a multiple bond in the molecule could hinder the process. Reduction of perchloropropylene by hydrogen donors in the presence of MC has not been described. In hydrogenation of perchloropropylene in the presence of PtO₂, a duplication product is formed [7]. Similar duplication with the formation of decachlorohexadiene is observed with CuCl in ethanol [8]. Perchlorofulvene can also be obtained as a function of the (VI):CuCl ratio.

The reduction of perchloropropylene by i-PrOH, Et₃SiH, or GKZh-94* in the presence of $Fe(CO)_5$, $Mo(CO)_6$, $Mn_2(CO)_{10}$, and $Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$ was studied. The reaction with i-PrOH in the presence of these MC took place with low conversion of (VI): 3-12%.

The products of the reduction of (VI) were only obtained in the presence of $Fe(CO)_5$ with Et₃SiH or GKZh-94. Two polychloropropenes were formed

$$\begin{array}{c} \text{CCl}_2 = \text{CClCCl}_3 + \text{HSiEt}_3 \xrightarrow{\text{Fe}(\text{CO})_5} \text{CCl}_2 = \text{CClCHCl}_2 + \text{CCl}_2 = \text{CClCH}_2\text{Cl}\\ \text{(VI)} & \text{(VII)} \end{array}$$

In contrast to the selective reduction of the CCl₃ group in heme-trichloroalkanes [for example, in 1,1,1-trichlorooctane (I)], reduction of the CCl₃ group in perchloropropylene took place by steps. Special experiments showed that the reaction began at 80°C, but that a higher temperature was required for attaining higher conversion. It was shown that GKZh-94 and Et₃SiH as the reducing agents produced similar results. It should also be noted that perchloropropene (VI) actively reacted with $Fe(CO)_5$ when poured in, and for this reason, a solution of $Fe(CO)_5$ in Et₃SiH (or GKZh-94) should be added by drops to perchloropropene (VI), heated to the required temperature.

The relative concentration of (VIII) in a mixture of chloropropenes (VII) and (VIII) increased with an increase in the duration of the reaction and the temperature. As a function of the conditions (temperature, ratio of reagents), the reaction can be conducted with predominant formation of (VII) or (VIII) with a yield of 40-50%. Reduction of perchloropropylene (VI) in sealed ampuls or in a closed vessel produces similar results (cf. Experimental, Table 2). Reduction of pentachloropropene (VII) was studied for evidence of the formation of tetrachloropropene (VIII) by the step mechanism

$$\begin{array}{c} \text{CCl}_2 == \text{CClCHCl}_2 + \text{HSiEi}_3 \xrightarrow{\text{Fe}(\text{CO})_5} \text{CCl}_2 == \text{CClCH}_2\text{Cl} + \text{ClSiEt}_3 \\ \text{(VII)} & \text{(VIII)} \end{array}$$

The reaction lasted for 5 h with a 30% yield of tetrachloropropene (VIII) [85% conversion of the starting (VII)]. Reduction of pentachloropropene (VII) with a CHCl₂ group is thus more difficult than reduction of perchloropropene (VI) with a CCl₃ group. Reduction of (VII) requires longer heating and a higher temperature than reduction of (VI). Subsequent reduction of the CH₂Cl group in (VIII) to 1,1,2-trichloro-1-propene (IX) takes place with a yield of ~1%.

 $\overline{}^{*GKZh-94}$ is a siloxane with the structure $\begin{pmatrix} Et \\ -Si-0 \\ H \end{pmatrix}$ and a 1.3-1.4% concentration of active hydrogen.

TABLE 1. Reduction of $C_7H_{15}CCl_3$ (3 mmole) by the Effect of Et₃SiH (4 mmole) in the Presence of MC (0.15 mmole), 3 h

Number of experi- ment	MC	T., °C	Conversion of $C_7H_{15}CC1_3$, %	Yield.of C ₇ H ₁₅ CHCl ₂ , %
1 2 3 * 4 * 5	$\begin{array}{c} \operatorname{Fe}\left(\mathrm{CO}\right)_{5}\\ \operatorname{Fe}\left(\mathrm{CO}\right)_{5}\\ \operatorname{Mo}\left(\mathrm{CO}\right)_{6}\\ \operatorname{Mo}\left(\mathrm{CO}\right)_{6}\\ \operatorname{Mn}_{2}\left(\mathrm{CO}\right)_{10} \end{array}$	$ \begin{array}{r} 120 \\ 140 \\ 120 \\ 140 \\ 120 \end{array} $	62 89 53 97 100	$ \begin{array}{r} 60 \\ 83 \\ 42 \\ 67 \\ 100 \end{array} $

 $*CC1_2=CHC_6H_{13}$ (III) was also obtained with yields of 10 and 30% at 120 and 140°C, respectively.

TABLE 2. Reduction of $CC1_3CC1_2$ (VI) in the Presence of Fe(CO)₅ [5 mole % of (VI)]

Num- ber of experi- ment	Silicon hydride, mmole	(VI), mmole	Т., ℃	Time, h	Conver- sion (VI), %	Yield, %	
						(VII)	(VIII)
1 2 3 4	$Et_{3}SiH, 20$ $Et_{3}SiH, 3$ $GKZh-94 (32)^{*}$ $Et_{3}SiH, 6$	18 3 90 3	$105-110 \\ 120 \\ 140 \\ 140 \\ 140$	7 3 4 6	90 81 100 100	$52 \\ 43 \\ 5 \\ 4$	9 24 43 50
*The	weight is in	ndicated	l in gram	s.			

The structure of chloropropenes (VII) and (VIII) was confirmed by the ¹³C and ¹H NMR spectra. These compounds, synthesized by other methods, are used as intermediate products in the synthesis of pesticides and as fumigants, fireproofing compounds, etc.

EXPERIMENTAL

The GLC analywis was conducted on a LCM-8MD chromatograph with a katharometer, He carrier gas; columns (steel): A) 2 m \times 3 mm, 15% silicone E-301; B) 1 m \times 3 mm, 5% silicone SE-30 on Chromaton N-AW-HMDS (0.15-0.20 mm); C) 1 m \times 9 mm, 20% silicone E-301 on Chromaton N-AW-HMDS (0.20-0.25 mm). A Tsvet-2 instrument with a preparative attachment was used for preparative GLC. The ¹³C NMR spectra were recorded on a Bruker HX-90 for 50% solutions in CHCl₃ and with TMS as the internal standard. See [5] for the preparation of chlorooctane (I) and [6] for the preparation of chloropentene (IV). Perchloropropylene (VI) was prepared by dehydrochlorination of heptachloropropane similar to [10]; pentachloropropene (VII) was prepared by the method in [11].

<u>Reduction of 1,1,1-Trichlorooctane (I) and 5,5,5-Trichloro-1-pentene (IV)</u>. See Table 1 for the conditions of the reduction of (I) by triethylsilane. Reduction of (IV) was conducted in the same conditions with Et_3SiH or i-PrOH. The reactions were conducted in sealed ampuls by the freezing evacuation thawing method in an atmosphere of N₂. The composition of the reaction mixtures was determined by GLC on samples prepared by an independent method [the synthesis is well known: cf. [12] for dichlorooctane (II), and [6] for dichlorooctane (III)]. The conversion of (I) and the yields of (II) and (III) were calculated by GLC analysis based on the internal standard (IS). GLC analysis of (I)-(III) was conducted in column A at 140°C, and the IS was 1,1,1,5-tetrachloropentane (cf. Table 1 for the results); GLC analysis of chloropentenes (IV) and (V) was conducted in column B with temperature programming from 73 to 200°C and 1,1,1-trichloropentane as the IS.

Reduction of Perchloropropylene (VI). Experiments 1 and 3 (see Table 2) were conducted in a flask with a stirrer, a drop funnel, a thermometer, and a reflux condenser. A mixture of the silicon hydride and $Fe(CO)_5$ was added by drops to perchloropropylene (VI) heated to the necessary temperature. The reaction was exothermic. The course of the reaction was monitored by GLC, and formation of tetrachloropropene (VIII) was observed at the beginning of the process.

Experiments 2 and 4 were conducted in sealed glass ampuls similar to reduction of (I) and (IV). The individual $CCl_2=CC1CH_2C1$ (VIII), $n_D^{2^\circ}$, 1.5215, $d_4^{2^\circ}$ (compare [13]) was separated from experiment 3 by distillation and subsequent preparative GLC (column C, 100°C). ¹³C NMR spectrum (δ , ppm): 123.0 (C¹), 128.2 (C²), 44.2 (C³). PMR spectrum (δ , ppm): 4.16 s (CH₂C1).

 $CC1_2=CC1CHC1_2$ (VII) was separated from experiment 1 by distillation and subsequent preparative GLC (column C, 100°C). ¹³C NMR spectrum (δ , ppm): 121.8 (C¹), 130.9 (C²), 66.6 (C³), PMR spectrum (δ , ppm): 7.10 s (CHC1₂).

The yields of polychloropropenes (VII) and (VIII) and the conversion of (VI) were calculated by GLC analysis (column A, 150°C, IS: 1,1,1-trichloropentane).

Reduction of Pentachloropropylene (VII). A mixture of Et_2SiH (30 mmoles) and $Fe(CO)_5$ (1.35 mmole) was added by drops to 18 mmole of (VII) at 140°C over 2 h and maintained at 140°C for another 3 h. The precipitated sediment of iron chlorides was filtered off, the sediment was washed with CHCl₃, and the filtrate was distilled. After distillation of the CHCl₃, the following fractions were obtained: 1) 58-95°C (200 mm), 0.7 g; II) 78-86°C (100 mm), 1.1 g; III) 82-85°C (20 mm), 0.8 g, sediment 1.1 g. The yields of the products were calculated from the chromatograms of the fractions (column B, 90°C) and were: 30% tetrachloropropene (VIII), 1% trichloropropene (IX). The conversion of the starting (VII) was 85%. In the PMR spectrum of alkene (IX), δCH_3 2.30 (s) ppm.

CONCLUSIONS

1. Triethylsilane reduces 1,1,1-trichloroalkane to 1,1-dichloroalkanes with high yields when the reaction is initiated by catalytic quantities of $Fe(CO)_5$, $Mo(CO)_6$, and $Mn_2(CO)_{10}$ at 120-140°C.

2. Triethylsilane or siloxane $[-(Et)Si(H)-O-]_n$ reduce perchloropropylene in the presence of Fe(CO)₅. The reaction takes place nonselectively, and 1,1,2,3,3-pentachloro-1-propene or 1,1,2,3-tetrachloro-1-propene is primarily formed with a yield of up to 50% as a function of the conditions.

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