REDUCTION OF THE CCl_3 GROUP IN POLYCHLOROALKANES BY HYDRIDE COMPLEXES OF CYCLOPENTADIENYL DERIVATIVES OF ZIRCONIUM

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In recent years, there have been intensive study of the hydride complexes of cyclopentadienyl derivatives of transition metals [1]. A number of methods have been developed for the synthesis of xirconium hydride complexes containing Cp ligands and the chemical transformations of these compounds are the subject of active study [1-3]. Investigations have been carried out on the reduction of the carbon–halogen bond by these complexes for several polychloromethanes [4, 5] and MeI [6] and for chlorocyclohexane and haloalkenes [7]. In our previous work [5], we showed that the hydride complexes of Zr and Hf of the type Cp_3MH and $Cp_2Zr(Cl)H$ ($Cp = C_5H_5$) reduce CCl_4 and $CHCl_3$ under mild conditions to $CHCl_3$ and CH_2Cl_2, respectively. Various hydrogen donors such as hydrides of Si, Sn, and Ge, secondary alcohols, amines and mercaptans are used to reduce the CCl_3 group (see our previous review [8]).

In the present work, we studied the possibility of using hydride complexes of Zr to reduce the CCl_3 group in 1,1,1-trichlorooctane (I), 1,1,1,2,2-pentachloroethane (II), and 1,1,1,3-tetrachloropropane (III). Cp_3ZrH (IV), Cp_2ZrH_2 (V) and $Cp_2Zr(Cl)H$ (VI) were used as the reducing agents.

The action of zirconium hydrides (IV)-(VI) on polychloroalkanes (I)-(III) gave the reduction of the CCl_3 group to $CHCl_2$ under mild conditions using an excess of the polychloroalkane in toluene (the product yield is lower for the reduction without toluene or in benzene [5]).

The reduction of (I) and (II) by 2-propanol in the presence of metal carbonyls is accompanied by side reactions. Thus, in addition to reduction of the CCl_3 group in (I), rearragnement occurs with 1,5 and 1,6 hydrogen migration in the intermediate radical, while (II) dechlorinates to give trichloroethylene [9]. Under the conditions selected, such side reactions do not occur in the reduction of (I) and (II) by zirconium hydrides. The reaction proceeds by the scheme.

$$RCCl_3 + \diagdown\!\!\!-ZrH \rightarrow RCHCl_2 + \diagdown\!\!\!-ZrCl$$

$R = C_7H_{15}$, $CHCl_2$, CH_2CH_2Cl.

Zirconium hydrides are converted to the corresponding chlorides. Thus, in the reduction of polyhaloalkanes by complex (IV), we isolated tetracyclopentadienyl dichloride dizirconoxane $(Cp_2ZrCl)_2O$ which may form from the extremely labile complex Cp_3ZrCl as a result of uncontrolled absorption of traces of moisture. A mixture of biscyclopentadienylzirconium dichloride and unreacted (VI) was isolated in most cases of the reactions of polyhaloalkanes with complexes (V) and (VI).

Table 1 shows that, independently of the structure of the starting polychloroalkane, hydride (IV) is a more effective reducing agent than (VI). Apparently, the introduction of a chlorine atom into the zirconium hydride lowers its effectiveness as a reducing agent. The formation of 1,1-dichlorooctane in yields above 100% upon reduction by dihydride (V) indicates that (V) may react with two hydrogen atoms in this reaction. We may assume that the reaction of (V) with polychloroalkanes proceeds by the following scheme.

$$RCCl_3 + Cp_2ZrH_2 \rightarrow RCHCl_2 + Cp_2Zr(Cl)H \quad (1)$$

$$Cp_2Zr(Cl)H + RCCl_3 \rightarrow RCHCl_2 + Cp_2ZrCl_2 \quad (2)$$

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TABLE 1. Reduction of Polychloroalkanes $RCCl_3$ by Zirconium Hydrides at 20°C over 5-6 h in Toluene (argon atmosphere, $[RCCl_3]:[\rangle ZrH] = 10:1$)

Reducing agent	Yield of $RCHCl_2$, % relative to hydride		
	$CHCl_2C_7H_{15}$	$CHCl_2CHCl_2$	$CHCl_2CH_2CH_2Cl$
$(C_5H_5)_3ZrH$ (IV)	94	76	72
$(C_5H_5)_2ZrH_2$ (V)	126	81	83
$(C_5H_5)_2Zr(Cl)H$ (VI)	45	12	35

We should also note that the introduction of chlorine atoms in the α and β position relative to the CCl_3 group leads to some diminution in the yield of the reduction product. Thus, the greatest yields of $RCHCl_2$ are achieved in the reduction of haloalkane (I).

EXPERIMENTAL

The gas–liquid chromatograhic analysis was carried out on an LKhM-8MD chromatograph with helium gas carrier and a katharometer detector using stainless steel columns packed with Chromatone N-AW-HMDS (0.16-0.20 mm) as the solid support. Column 1 (1 m × 3 mm) was packed with 15% SE-30, while column 2 (2 m × 3 mm) was packed with 15% silicone E-301. Column 3 (1 m × 3 mm) was packed with Carbowax 20M. The chromatographically pure samples of the polychloroalkanes and toluene were dried and redistilled in an argon stream. The $LiAlH_4$ sample was recrystallized from toluene–ether in an argon atmosphere. The following internal standards were used for the gas–liquid chromatographic analysis: 1,1,1,5-tetrachloropentane for $CCl_3C_7H_{15}$ and 1,1,1,2-tetrachloroethane for $CCl_3CH_2CH_2Cl$ and CCl_3CHCl_2. The IR spectra were taken on a UR-20 spectrometer. A sample of Cp_3ZrH was synthesized according to our previous procedure [10] and a sample of the complex $Cp_2ZrCl(H)$ was prepared according to Kautzner et al. [11], mp 161-164°C (dec.).

Preparation of Cp_2ZrH_2. A solution of 0.07 g (1.73 mmoles) $LiAlH_4$ in 20 ml THF was added dropwise to a solution of 1 g (3.4 mmoles) Cp_2ZrCl_2 in 12 ml THF. The reaction was carried out for 40 min at 20°C in an argon stream. The white infusible powder was washed and dried to yield 0.54 g (70.4%) Cp_2ZrH_2. Found: C 53.8; H 5.59; Zr 39.56%. Calculated for $C_{10}H_{12}Zr$: C 53.76; H 5.41; Zr 40.82%. The compound did not contain chlorine; Al < 10^{-2}%. The IR spectrum showed the presence of Cp ligands: 3075, 1445, 1375, 1128, 1070, 1020, 920, 810-840, 605 cm^{-1} and contained bands at 1535 and 1330 cm^{-1} corresponding to the Zr–H bond.

Reduction of Polychloroalkanes (I)-(III). The yields of the reduction products are given in Table 1.

a) By the action of Cp_3ZrH (IV). A sample of 9.8 mmoles (I) was added to a suspension of 0.98 mmoles (IV) in 10 ml dry toluene and the mixture was stirred for 5 h at 20°C in an argon atmosphere and then left for 12 h at 0° to obtain complete deposition of the precipitate. Pressing was used to separate the liquid portion from the precipitate (conversion products of zirconium hydrides). The filtrate contained 0.90 mmoles $CHCl_2C_7H_{15}$ as indicated by gas–liquid chromatography.

Comparison of the retention times in the gas–liquid chromatographic analysis of the products obtained in the reduction of (I) by complexes (IV)-(VI) with the retention times of 1,1,5- and 1,1,6-trichlorooctanes obtained according to our previous work [9] on columns 2 and 3 showed that, under the given conditions, products of the rearrangement of (I) with 1,5- and 1,6 hydrogen migration are not formed.

Analogously, the reduction of 39 mmoles (II) by the action of 2.4 mmoles (IV) gives 1.9 mmole $CHCl_2CHCl_2$. The precipitate formed (0.4 g, mp 270-280°C) contained $[Cp_2ZrCl]_2O$. The IR spectrum shows the presence of Cp groups and the Zr–O–Zr group.

In the reaction mixtures obtained in the reduction of (II) by hydrides (IV)-(VI), gas–liquid chromatography on columns 2 and 3 did not reveal significant amounts of trichloroethylene, which may be formed by the dechlorination of starting (II).

The reduction of (III) was carried out by analogy using 1.84 mmole (IV), 19.3 mmoles (III) and 10 ml toluene. The reaction mixture contained 1.3 mmole $CHCl_2CH_2CH_2Cl$.

b) By the action of Cp_2Zr_2 (V). The procedure for carrying out this reduction was similar to that given above using 2.6 mmoles (V) and 25 mmoles (I). Gas–liquid chromatographic analysis showed 3.1 mmoles $CHCl_2C_7H_{15}$. Analogously, 2.5 mmoles (V) and 25 mmoles (III) gave 2.2 mmoles $CHCl_2CH_2CH_2Cl$ and 2.4 mmoles (V) and 24 mmoles (II) gave 1.73 mmole $CHCl_2CHCl_2$.

c) By the action of $Cp_2Zr(H)Cl$ (VI). By analogy to the previous procedure, 1.6 mmole (VI) and 16 mmoles (I) gave 0.98 mmole $CHCl_2C_7H_{15}$, 2.6 mmoles (VI) and 26 mmoles (III) gave 0.92 mmoles $CHCl_2CH_2CH_2Cl$, and 1.5 mmole (VI) and 15 mmoles (II) gave 0.19 mmole $CHCl_2CHCl_2$. A precipitate of 0.15 g Cp_2ZrCl_2 was also obtained, mp 225-231°C which does not give a depressed mixed melting point with an authentic sample.

CONCLUSIONS

Zirconium hydride complexes Cp_3ZrH, Cp_2ZrH_2, and $CpZr(Cl)H$ selectively reduce the CCl_3 group in 1,1,1-trichlorooctane, 1,1,1,3-tetrachloropropane, and 1,1,1,2,2,-pentachloroethane at 20°C with the formation of the corresponding dichloromethyl derivatives.

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PREPARATION OF PYRAZOLES AND PYRAZOLINES BY THE REACTION OF CHLOROCYCLOPROPANOLS WITH HYDRAZINES IN THE PRESENCE OF CROWN ETHERS

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Pyrazoles have been prepared by the reaction of gem-dichlorocyclopropyl acetates with hydrozines [1, 2]. It has been assumed that this reaction proceeds through unsaturated α-chloroketones which are formed as intermediates by the initial attack of the carbonyl carbon by hydrazine. However, according to Kitaev and Buzykin [3], the reaction of N_2H_4 with RR'CO involves the formation of a carbinol $RR'C(OH)NHNH_2$ and, thus, there is no basis for considering α-chloroketones as intermediates in this reaction. Hence, we propose that corresponding nitrogen heterocycles may be obtained not only in reactions of halocyclopropanes containing carbonyl groups but also in reactions of the corresponding cyclopropanols.

In the present work, we studied the reaction of gem-dichlorocyclopropanol (I) with hydrazine and $PhNHNH_2$ and of cis- and trans-chlorocyclopropanols (II) with $PhNHNH_2$. Heating (I) or (II) with hydrazines in absolute ethanol at 50-70°C for 15-17 h leads to the corresponding pyrazoles or pyrazolines with yields $\leqslant$20%. Since hydrazines in the presence of crown

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