<u>1,4-Epoxycycloheptane (Vc)</u>. IR spectrum (v, cm⁻¹): 1060 (C-O-C). Proton NMR spectrum (δ , ppm): 1.3-2.1 multiplet (10H, CH₂), 4.4 multiplet (2H, CH-O-CH).

 $\frac{1,4-\text{Epoxycyclooctane (Vd)}}{(\delta, \text{ ppm}): 1.3-2.1 \text{ multiplet (12H, CH}_2), 4.5 \text{ multiplet (2H, CH-O-CH)}. Carbon-13 NMR spectrum (\delta, ppm): 24.4 (C⁶, C⁷), 31.5 (C², C³), 36.1 (C⁵, C⁸), 77.8 (C¹, C⁴).$

CONCLUSIONS

1. The formation of cycloalkoxy, α -hydroxycycloalkyl, and ω -formylalkyl radicals in the oxidation of secondary cycloalkanols by Pb(OAc)₄ was recorded by an EPR method in the presence of spin traps.

2. In the presence of the $Pb(OAc)_4$ -Cu(II) system, the ability of secondary cyclic alcohols to undergo oxidative decyclization with the formation of ω -alkenals decreases in the series cyclopentanol > cycloheptanol > cyclohexanol > cyclooctanol.

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EFFECTIVE REDUCTION OF HALOGEN-CONTAINING HYDROCARBONS BY DIISOBUTYL ALUMINUM HYDRIDE IN THE PRESENCE OF TRANSITION METAL HYDRIDES

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Organometallic compounds: $i-PrMgCl/MnCl_2$ [1], $i-PrMgBr/Cp_2TiCl_2$ [2], and $i-Bu_2AlH\cdot BuLi$ [3] have earlier been proposed as reagents for use in the reduction of halohydrocarbons; however, these reagents are not readily available and are distinguished by low activity with respect to secondary and tertiary alkyl and aryl halides.

We studied the reduction of aryl and alkyl halides using the available i- Bu_2AlH in the presence of transition metal complexes of: Ti, V, Mn, Fe, Co, Ni, Zr, Mo, Ru, Rh, Pd, Nd, Hf, W. To find the optimal reaction conditions we studied in detail the reduction of bromobenzene with i- Bu_2AlH .

The nature of the ethereal solvent (Et₂O, THF, dioxane) in the presence of metal chlorides (NiCl₂, CoCl₂, MnCl₂, WCl₆, HfCl₄, VCl₃, MoCl₅, PdCl₂, FeCl₃, TiCl₄), taken in a ratio relative to the other reagents of MCl_n:PhBr:i-Bu₂AlH = 1:20:30 little influences the yield of benzene (40-60%). In aromatic solvents (toluene, xylene) the formation of traces of benzene is observed. In the absence of a catalyst, the initial bromobenzene is recovered from the reaction mixture entirely unchanged.

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Complex	Yield of benzene, %	
Complex	in dioxane	in Et ₂ O
(<i>n</i> -Bu0), Ti (<i>n</i> -Bu0), Ti **	85 100	25 28
TiCl ₂	100	20
Cp ₂ TiCl ₂ (C ₈ H ₇) ₂ TiCl ₂	100 100	73 *** 48
	47	21
$(C_8H_7)_2 ZrCl_2$	54	24
O HtCl ²	34	29

TABLE 1. Influence of the Nature of Ti, Zr, and Hf Complexes on the Yield of Benzene in the Reduction Reaction with i-Bu₂AlH*

*Reaction conditions: 0.01 mole of PhBr, 0.015 mole of i-Bu₂AlH, 0.16 mmole of the complex, 25 ml of solvent, 36°C, (Et₂O), 80°C (dioxane), 4 h. **0.54 mole of the complex. ***Hexane was formed in an 18% yield.

TABLE 2. Reduction of Aryl Halides with i-Bu₂AlH in the presence of Titanium Compounds*

Con-size	Deceries needuct	Yield, % in the presence of	
Starting compound	Reaction product	(n-BuO)₄Ti	Cp ₂ TiCl ₂
C ₆ H ₅ Cl C ₆ H ₅ Br C ₆ H ₅ I p-CH ₃ C ₆ H ₄ Br m-CH ₃ C ₆ H ₄ Br p-ClC ₆ H ₄ Br p-ClC ₆ H ₄ Br p-BrC ₆ H ₄ Br p-C ₆ H ₅ -C ₆ H ₄ Br α -C ₁₀ H ₇ Br	$\begin{array}{c} C_{6}H_{6} \\ C_{6}H_{6} \\ C_{6}H_{5} \\ CH_{3}C_{6}H_{5} \\ CH_{3}C_{6}H_{5} \\ CH_{5}C_{6}H_{5} \\ CIC_{6}H_{5} \\ BrC_{6}H_{5} \\ C_{6}H_{5} - C_{6}H_{5} \\ C_{10}H_{8} \end{array}$	22 87 100 74 85 91 90 68 74	35 73 ** 68 ** 65 75 75 63 57 57

*Reaction conditions: 0.01 mole of ArX, 0.015 of $i-Bu_2AlH$, 0.16 mmole of the complex, 25 ml of Et₂O, boiling point, 6 h. **n-Hexane was formed in 18% and 21% yields.

When alkoxides and Ti, Zr and Hf complexes are used as catalysts, the yield of benzene can be markedly increased, whereby the Ti and Zr complexes taken in a ratio Ti(Zr, Hf):PhBr: i-Bu₂AlH = 1:60:90, have the highest activity in this reaction (Table 1).

Under selected conditions, mono- and dihaloarenes are readily reduced to the corresponding hydrocarbons in yields of 68-100% (Table 2).

The halohydrocarbons can be arranged in the series RI > RBr > RC1 according to the ease of their reduction. In the case of aryl halides simultaneously containing the C1 and Br atoms, the reduction proceeds selectively, first at the C-Br bond, and then at the C-C1 bond (Table 2).

It was found in the course of the reaction that in the presence of Cp_2TiCl_2 and in an Et_2O solution, PhBr and PhI give on reduction not only benzene, but also a considerable amount of hexane (Table 2), but we were unable to detect in these experiments even traces of cyclohexane. However, in the reaction of bromocyclohexane with i-Bu_AlH in the presence of the above catalyst, cyclohexane and hexane are formed in a ratio of 89:11, in an overall yield of 93%. The mechanism of these previously unknown transformations of halobenzenes or bromocyclohexane, into hexane under mild conditions has not yet been clarified.

TABLE 3. Reduction of Alkyl, Alkenyl and Cyclopropyl Halides with $i-Bu_2AlH$ in the Presence of $(n-Bu0)_4Ti^*$

Starting compound	Reduction products (yield, %)
$\begin{array}{c} n-C_{s}H_{17}Cl \\ n-C_{s}H_{17}Br \\ n-C_{s}H_{17}I \\ C_{6}H_{11}Br \\ Ph \\ Ph \\ Br \\ \end{array}$	$\begin{array}{c ccccc} & n-C_8H_{18} & (31) \\ & n-C_8H_{18} & (100) \\ & n-C_8H_{18} & (100) \\ & C_6H_{12} & (89), \ C_6H_{14} & (11) \\ & Ph \ / & (100) \\ & Ph \ / & (15), \ Ph \ / & (85) \end{array}$
$\begin{array}{c} PI \\ \hline \\ Br \\ C_6H_{13} \\ \hline \\ Br \\ Br \end{array}$	B_{r} $C_{6}H_{13}$ (10), $C_{6}H_{13}$ (90)

*Reaction conditions: 0.01 mole of AlkX, 0.015 mole of i-Bu₂AlH, 0.16 mmole of (n-BuO)₄Ti, 25 ml of dioxane, 80°C, 14 h.

Subsequently we found that not only aryl halides, but also alkyl, alkenyl, and cyclopropyl halides can be effectively reduced by i-Bu₂AlH in the presence of a catalyst to the corresponding saturated, unsaturated or cyclopropane hydrocarbons (Table 3).

EXPERIMENTAL

The halogen-containing hydrocarbons and solvents used were purified according to [4]. Dibromocyclopropane hydrocarbons were obtained according to [5], while i-Bu₂AlH at a concentration of 74% was used without preliminary purification. The metal complexes were obtained according to [6, 7]. The reaction products were analyzed on a LKhM-8MD chromatograph (flame-ionization detector, a 2 m \times 0.3 cm column with SE-30, flow rate of carrier gas 40 ml/min). The PMR spectra were obtained on a Tesla BS-487 spectrometer for solutions in CCl₄, using TMS as internal standard. The IR spectra were recorded on a Specord-75 IR spectrophotometer (in a thin layer), and the mass spectra on a MKh-13-06 spectrometer with the energy of ionizing electrons of 70 eV and an ionization chamber temperature of 200°C.

<u>General Method of Reduction of Halogen-Containing Hydrocarbons with i-Bu₂AlH in the</u> <u>Presence of Complex Catalysts</u>. A 0.54 mmole portion of a chloride or 0.16 mmole of a metal complex, 25 ml of a solvent, 0.01 mole of a haloarene, and 2.88 g (4.5 ml) of a 74% i-Bu₂AlH (0.015 mole) were placed in an argon current in a thermostated glass reactor (V = 35 ml). The mixture was heated for 4-6 h at the boiling point of the solvent, then cooled to 10°C, decomposed with 30 ml of a 10% aqueous HCl solution, extracted with ether, and the extract was dried over Na₂SO₄.

The reduction products were isolated by rectification, and the structure was confirmed by comparison with authentically known preparations [8-10].

<u>Method of Reduction of Bromocyclohexane with i-Bu₂AlH in the Presence of Cp_2TiCl_2 .</u> A 2.88 g portion (4.5 ml, 0.015 mole) of a 74% i-Bu₂AlH was added in an Ar current to a mixture of 1.63 g (0.01 mole) of bromocyclohexane in 25 ml of Et₂O and 0.04 g (0.16 mmole) of Cp_2TiCl_2 . The mixture was heated for 4 h at 40°C, and then treated and analyzed as described above. The yield was 0.76 g (93%) or products containing, according to GLC data (using octane as an internal standard), 0.65 g (89%) of cyclohexane and 0.07 g (11%) of hexane.

CONCLUSIONS

1. An effective reduction of halogen-containing hydrocarbons at the C-Hal bond was carried out by means of $i-Bu_2AlH$ in the presence of catalytic amounts of Ti, Zr, and Hf complexes.

2. A partial transformation of halobenzenes and bromocyclohexane into hexane by the action of i-Bu₂AlH and catalytic amounts of Cp_2TiCl_2 under mild conditions was noted for the first time.

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SYNTHESIS OF ARYL-SUBSTITUTED PYRIDINES BY LIQUID-PHASE CONDENSATION OF ALDEHYDES WITH UREA, CATALYZED BY TRANSITION METAL COMPLEXES

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According to [1-3], the gas-phase condensation of benzaldehyde (BzH) with acetaldehyde (AcH) or butyraldehyde (PrCHO) and NH_3 in the presence of heterogeneous catalysts based on Al_2O_3 impregnated with transition metal complexes, at 300-500°C, results in a mixture of 2- and 4-phenylpyridines in an overall yield of not more than 30%. Attempts to react other substituted aromatic and aliphatic aldehydes, including those containing functional substituents in this manner were unsuccessful.

We have recently developed a highly selective method for the synthesis of pyridine bases by liquid-phase condensation of aliphatic aldehydes with urea at a temperature of 150-200°C by the action of cobalt-containing metallocomplex catalysts [4, 5].

To develop effective methods of synthesis of aryl- and heteroaryl-substituted pyridines and to broaden the scope of their application, we studied the reaction of BzH and substituted benzaldehydes, furfural and 4-pyridinecarboxaldehyde with aliphatic C_4-C_8 aldehydes and urea, catalyzed by low-valency Fe, Co, Ni, V, Cu, Pd, Ti, Zr, Hf, W, Rh complexes.

The complex catalysts were obtained by reducing soluble compounds of these metals by means of AlEt₃, Al(OEt)₂, ClAlEt₂, Cl₂AlEt, MgEt₂, BBu₃, and BPr₃ in a toluene or THF solution, at a temperature of $0-10^{\circ}$ C.

To select the optimal conditions for carrying out the reaction, using the example of the reaction of BzH with PrCHO and urea, we studied the influence of the nature of the catalyst on the yield and composition of the condensation products. It was found that the Co- $(2-\text{ethylhexanoate})_{2-AlR_3}$ system has the highest catalytic activity (Table 1). In its presence, a maximum yield of pyridines (80%) is attained in the course of 4 h at 200°C, and in the mixture obtained, the yield of 2-phenyl-3,5-diethylpyridine (I) and 2-propyl-3,5-diethylpyridine (V) reaches ~95%. In a homocondensation of BzH with urea under the selected conditions, the formation of arylpyridines is not observed. A general scheme of reaction is given below



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