

REDUCTION OF UNSATURATED COMPOUNDS WITH
HYDROGEN TRANSFER FROM ALCOHOL IN THE
PRESENCE OF TRANSITION METAL SALTS

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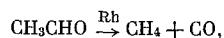
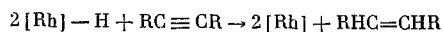
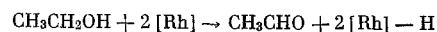
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It is known that the salts of the metals of the platinum group cleave hydrogen from alcohols; here, depending on the nature of the alcohol, are formed either the aldehyde or the ketone as one of the reaction products [1-4], i.e., the reaction of alcohol dehydrogenation takes place. The hydrogen from the alcohol can go for the formation of the hydride complexes of the transition metals (in the presence of ligands, which stabilize the metal-hydrogen bond). At the same time, it is known that the hydride complexes of the transition metals can transfer hydrogen to the double bond of olefins, or to other organic compounds, with the formation of their hydrogenation products.

It is possible to assume that compounds of the transition metals, cleaving hydrogen from the alcohol with the formation of the hydride complex, will be capable of transferring this hydrogen to the organic substrate. Actually, when unsaturated compounds are heated in ethanol, in the presence of Rh and Ru salts, the unsaturated compounds are reduced (Table 1) under homogeneous conditions.

The reduction of unsaturated compounds can occur not only under the influence of ethanol, but also of other alcohols which have an α -hydrogen atom (*n*-propyl and isopropyl alcohols). However, the reduction practically fails to go in *tert*-butyl and methyl alcohols.

It was natural to expect that acetaldehyde will be formed during the process of ethanol hydrogenation. However, we were unable to detect it in the reaction medium in the presence of RhCl_3 , while methane was detected in the gas phase, which makes it possible to depict the reaction by the scheme:



Here Rh is the catalytically active rhodium compound.

TABLE 1

Catalyst	Hydrogenated compound	Hydrogenation product	Yield, mole/1mole of salt
$\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ Ethanol	3-Hexene	3-Hexene	3.2
	Cyclopentadiene	Cyclopentene	0.3
	5-Vinyldicyclo-[2,2,1]-heptene-2	2-Vinyldicyclo-[2,2,1]-heptane	20
	5-Methyldicyclo-[2,2,1]-heptene-2	2-Methyldicyclo-[2,2,1]-heptane	12
RuCl_3 Ethanol	Hexene-1, 1-methylcyclopentene, cyclohexene	Nonhydrolyzed (metallic precipitate)	
	5-Vinyldicyclo-[2,2,1]-heptene-2	2-Vinyldicyclo-[2,2,1]-heptane	18

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It is significant that the formation of methane and carbon monoxide was observed in [5] when the phosphine complexes of ruthenium are reacted with ethanol. The reaction of hydrogen transfer from potassium benzylate in benzyl alcohol to the olefin employing the rhodium complex $(\text{Rh}_3\text{P})_2\text{RhCl}$ is known [6].

EXPERIMENTAL METHOD

The experiments on the reduction of unsaturated compounds was run in sealed ampuls. The reactants were taken in the ratio catalyst: substrate = 1:50, at a catalyst concentration of 0.05 M. After opening the ampul the reaction mixture was cooled well and analyzed by GLC.

CONCLUSIONS

The reduction of some unsaturated compounds was accomplished in the presence of transition metal salts using alcohol as the hydrogen donor.

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