CATALYZED HYDROMETALATION OF OLEFINS BY ZINC HYDRIDE AS A NEW ROUTE TO THE HIGHER ORGANOZINC COMPOUNDS

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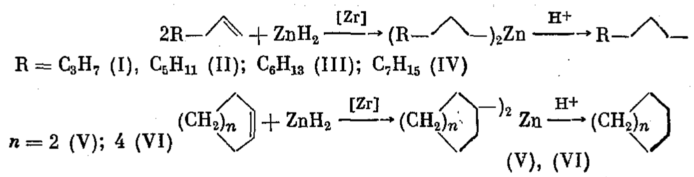
The theoretical possibility of the hydrozincation of 1-hexene using ZnH_2 in the presence of catalytic amounts of $NiCl_2$ and $Cp_2{}^*ZrCl_2$ was shown by us recently [1]. The reaction is run using starting reactants and solvent that have been carefully freed of traces of moisture, O_2, and other impurities. In the opposite case the experimental results are difficultly reproducible.

In order to develop new, highly efficient, and readily available catalysts for the hydrozincation of olefins, and also to expand the application of this reaction for obtaining organozinc compounds, we studied the reaction of ZnH_2 with 1-hexene, 1-octene, 1-nonene, 1-decene, cyclooctene, styrene, and isoprene using transition metal complexes. Of the catalysts studied by us, based on Fe, Co, Ni, Pd, Ti, and Zr compounds, the most active proved to be the complex obtained by the reaction of $ZrCl_4$ with C_4H_9OH.

The highly active ZnH_2 for the experiments was obtained by the reaction of $ZnEt_2$ with $LiAlH_4$ [2]. The optimum condions for the hydrometalation of the mentioned olefins are: temperature 80°C, time 3 h, either aromatic or aliphatic solvents (benzene, toluene, heptane, hexane), and a Zn:olefin:Zr_3 ratio = 50:100:1. In THF as the medium, ZnH_2 decomposes in the presence of Zr catalysts even at 20° to give Zn metal and H_2.

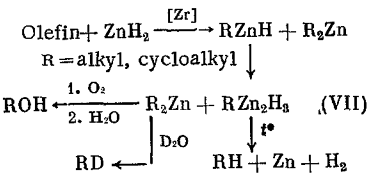
1-Alkenes react with ZnH_2 to give the higher alkyl organozinc compounds (I)-(IV) in 52-65% yields (Table 1). The hydrozincation of cycloolefins by ZnH_2 proceeds to give products (V) and (VI), whose yield does not exceed 20%



The reaction of ZnH_2 with styrene and isoprene leads to the formation of high-molecular compounds.

Together with zinc dialkylates, the corresponding saturated hydrocarbons are formed in all of the experiments, and also Zn metal and H_2. The formation of saturated hydrocarbons during reaction cannot be attributed to the catalytic hydrogenation of the starting olefins by the hydrogen that is liberated during the decomposition of ZnH_2, since it was ascertained by special experiments, run under the conditions of complete ZnH_2 decomposition (either above 100° or in THF as the medium), that hydrogenation of the olefins does not occur here.

Starting with these facts, and also taking into consideration the statement made in [3] that alkyl complexes of the RZn_2H_3 type are unstable even at room temperature, it becomes possible to propose the following scheme for the reaction of ZnH_2 with olefins in the presence of Zr catalysts. Evidently, together with the dialkylzinc, the alkylzinc hydride is formed in the first step, which quickly disproportionates into the dialkylzinc and hydride complex (VII). The latter decomposes under the reaction conditions with the liberation of the alkane RH, H_2, and Zn metal.



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*Cp = cyclopentadienyl.

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TABLE 1. Hydrometalation of Olefins by ZhH_2 Zn :Olefin : Zr Mole Ratio = 50 : 100 :1, 80°C, 3 h, Solvent = Toluene

Olefin	Comp. of deuterolysis products of catalysate, %		
	unreacted olefin	H Alkane	D Alkane (yield of R_2Zn)
1-Hexene	–	35	65
1-Nonene	11	29	60
1-Decene	12	30	58
1-Octene	8	38	54
Cyclohexene	70	10	20
Cyclooctene	79	6	15

It should be mentioned that the hydrometalation of α-olefins by ZnH_2 is exclusively selective at the α-C atom, as was shown by the oxidation of dihexylzinc (I) to n-hexanol.

In our experiments the oxidation of the obtained organozinc compounds by O_2 and subsequent hydrolysis with water gave, instead of the expected alkyl hydroperoxides [4], the corresponding primary alcohols in high yields. Evidently, Zr complexes, under the conditions of oxidizing alkyl organozinc compounds to the corresponding alkyl hydroperoxides, facilitate a conversion of the latter to alcohols. The mechanism of the given conversion is being studied.

EXPERIMENTAL

All of the experiments were run in a dry, O_2-free argon atmosphere. The solvents and olefins prior to use were distilled in an argon stream over $LiAlH_4$. The ZnH_2 was obtained by reducing $ZnEt_2$ as described in [2]. The yields of (I)-(VI) were determined by their deuterolysis products when based on taken olefin. The hydrocarbons in the hydrolysate were identified via the proper standards on a Chrom-5 chromatograph equipped with a flame-ionization detector and a 3.7 m × 3 mm column, packed with 15% PEG-6000 deposited on Chromatone N-AW. The mass spectra were obtained on an MX-1306 instrument, using an electron ionization energy of 70 eV and an ionization chamber temperature of 150°.

To prepare the catalyst we added 4 mmoles of n-butanol to a suspension of 1 mmole of $ZrCl_4$ in 10 ml of dry toluene and stirred the mixture at ~20° until a clear solution was obtained.

Hydrometalation of Olefins. To a suspension of 15 mmoles of freshly prepared ZnH_2 in 5 ml of the solvent were added 30 mmoles of the appropriate olefin and 0.3 ml of catalyst solution, and the reaction mass was stirred for 3 h in a thermostatted reactor at 80°. Then the catalysate was filtered from the deposited Zn, and a part of it was decomposed with either D_2O or H_2O and analyzed either by chromatography or by mass spectrometry. The experimental results are given in Table 1. The remainder of the catalysate was evaporated in vacuo to remove the solvent and unreacted olefin and then oxidized.

Oxidation of Di-n-hexylzinc (I). A slow stream of dry air was passed for 5 h through 25 ml of an ether solution of (I) (5 mmoles), cooled to −10°. After conventional hydrolysis the ether layer, based on the GLC data, contained 4 mmoles of n-hexanol and 1 mmole of hexane. Hydroperoxides were not detected.

CONCLUSIONS

Some higher organozinc compounds were synthesized by reacting ZnH_2 with linear and cyclic olefins in the presence of a catalyst based on $ZrCl_4$ and C_4H_9OH.

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