TRANSITION METAL ALKYLS AND HYDRIDES

XI*. EVIDENCE FOR THE EXISTENCE OF HYDRIDO CARBENE NICKEL COMPLEXES

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SUMMARY

In the reaction of ethereal methylmagnesium iodide with anhydrous nickel chloride, ethylene is apparently formed through an intermediate hydrido carbene complex.

RESULTS

As a continuation of our studies on the alkyl-olefin exchange reaction of various Grignard reagents with olefinic hydrocarbons in the presence of anhydrous nickel chloride¹⁻³, we have now examined systems containing ethereal CH₃MgI. In the gas phase above a reaction mixture consisting of CH₃MgI, NiCl₂ and olefins, some ethylene and ethane could always be detected in addition to the chief component, methane. The reaction of CH₃MgI with NiCl₂ in absence of olefin leads to the same result, but ethylene and ethane are not formed when phenyl- or benzylmagnesium halides are used instead of CH₃MgI (Table 1).

DISCUSSION

The formation of methane and ethane can plausibly be explained by the decomposition of methylmetal species (see eqns. (1) and (3)).

The formation of ethylene has been explained by Abraham and Hogarth⁴ by assuming the decomposition of the radical formed from the solvent, diethyl ether:

 $\begin{array}{l} \cdot \mathrm{CH}_3 + \mathrm{C}_2\mathrm{H}_5\mathrm{OC}_2\mathrm{H}_5 \rightarrow \mathrm{CH}_4 + \cdot \mathrm{C}_2\mathrm{H}_4\mathrm{OC}_2\mathrm{H}_5 \\ \cdot \mathrm{C}_2\mathrm{H}_4\mathrm{OC}_2\mathrm{H}_5 \rightarrow \mathrm{C}_2\mathrm{H}_4 + \cdot \mathrm{OC}_2\mathrm{H}_5 \,, \, \mathrm{etc.} \end{array}$

However, the fact that PhMgBr and PhCH₂MgCl give no gaseous product shows that ethylene does not originate from the solvent.

Another possible source of ethylene in systems containing methylmetal derivatives may be transition metal hydrido carbene complexes formed in the reaction

* For Part X see Ref. 3.

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TABLE 1

FORMATION OF GASEOUS HYDROCARBONS FROM $\rm CH_3MgI$ and $\rm NiCl_2$ with or without olefins

Grignærd reagent	Solvent	Olefinic hydrocarbon	Temp. (°C)	Reaction time (h)	Composition of the gas phase (vol. %)			Saturated olefin (male 8()
					C_2H_4	C_2H_6	CH₄	(mole 7 ₆)
PhMgBr	Et,0		Reflux	0.5	0	0	0	
PhMgBr	THF		40	0.5	0	0	0	
PhCH ₂ MgCl	Et ₂ O		Reflux	2	0	0	0	
CH ₃ MgI	Et ₂ O		Reflux	2	1.72	9.20	61.0	
CH ₃ MgI	Et ₂ O	1-Octene	6	2	1.15	6.15	62.5	0.75°
CH ₃ MgI	Et ₂ O	Styrene	6	2	1.67	5.57	52.4	2.2
CH₃MgI	Et ₂ O	Cyclohexene	6	1	0.69	2.72	57.5	0

Molar ratios: $RMgX/NiCl_2 = 10$; RMgX/olefin = 1; initial Grignard concn.: 1 M

^a 14.7 mole % double bond migration.

system; such complexes were suggested by Michman and Zeiss⁵⁻⁷ to be involved in the fragmentation reaction of CD_3MgI and diphenylacetylene in the presence of $CrCl_3$ ·3THF.

Our results (Table 1) make it seem probable that some nickel carbene complex is responsible for the formation of ethylene in the systems containing CH_3MgI and NiCl₂. The process may be visualized either by the interaction of two monomethylene species (eqn. (2)) or by the decomposition of a dimethylene nickel hydride (eqn. (4)).



The nickel hydrides are presumably consumed in a consecutive reaction involving the conversion of olefins into saturated products (Table 1). Since the hydrogen comes from the methyl group this represents a special case of α -hydrogen transfer.

EXPERIMENTAL

The preparations of anhydrous $NiCl_2$ and starting Grignard reagents have been described^{1,3}.

Ethereal CH₃MgI, PhMgBr, or PhCH₂MgCl was stirred at 6° or refluxed for 0.5-2 h in a thermostated reaction flask equipped with a magnetic stirrer and a

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reflux condenser, under nitrogen in the presence of anhydrous nickel chloride. Gas samples were taken with a syringe through a silicone rubber membrane from the gas phase above the reaction mixture before and after the addition of NiCl₂ to the Grignard reagent. The samples were analyzed by GLC on a 1 m activated Al_2O_3 column at 20°. Absolute quantities of the gases evolved were not determined; Table 1 shows the hydrocarbon content of the gas phase in the reaction flask.

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