Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

TRANSITION-METAL ALKYLS AND HYDRIDES
III*. ALKYL-OLEFIN EXCHANGE REACTION OF GRIGNARD REAGENTS CATALYZED BY NICKEL CHLORIDE

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(Received June 9th, 1967)

Job and Reich as early as 1924 noticed that a mixture of ethereal phenylmagnesium bromide and nickel chloride absorbs ethylene[2], and this observation seemed worthy of reinvestigation in view of the more recent results achieved with nickel-containing organometallic systems for the oligomerization of ethylene[3]. In this paper we describe results obtained with systems composed of nickel chloride and alkylmagnesium halides. The properties of systems containing arylmagnesium halides will be discussed in a later paper.

The homogeneous, black solutions of anhydrous nickel chloride in ethereal n-octylmagnesium bromide (Mg/Ni ratio about 100 : 1) were found to absorb about 0.6 mole ethylene per mole of Grignard reagent at 6°. Hydrolysis of the reaction product with dilute hydrochloric acid, gave approximately 1 mole of ethane per mole of absorbed ethylene, and the liquid product contained, in addition to n-octane (a hydrolysis product of the Grignard reagent used) 1-octene and *cis*- and *trans*-2-octene.

These results can be explained by the following alkyl-olefin exchange:

$$C_5H_{11}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}MgBr + CH_2{=}CH_2 \xrightarrow{NiCl_2} C_5H_{11}CH_2\text{-}CH{=}CH_2 + C_2H_5MgBr$$

followed by isomerization of the olefin formed:

$$C_5H_{11}\text{-}CH_2\text{-}CH{=}CH_2 \rightarrow C_5H_{11}\text{-}CH{=}CH\text{-}CH_3$$

Similar exchange reactions have been described by Cooper and Finkbeiner[4], who used $TiCl_4$ as catalyst and developed a method for the synthesis of primary alkyl Grignard reagents from vinyl-type olefins and n- or isopropylmagnesium bromide:

$$R\text{-}CH{=}CH_2 + C_3H_7MgBr \xrightarrow{TiCl_4} R\text{-}CH_2\text{-}CH_2\text{-}MgBr + C_3H_6$$

The authors did not investigate nickel compounds as catalysts.

The nickel chloride catalyzed reaction was found to be reversible, since some ethylene was evolved from starting with 1-octene and ethylmagnesium bromide, and after hydrolysis some n-octane was present in the products. The yields obtained in the exchange reactions in both directions were influenced by the ratios of reactants.

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* For part II of this series see Ref. 1.

The results are listed in Table 1.

TABLE 1

REVERSIBILITY OF THE ALKYL–OLEFIN EXCHANGE REACTION

$RMgBr/NiCl_2$ molar ratio 100 : 1.
Ethylene-absorption experiments at 6° for 6 h.
C_2H_5MgBr+1-octene exchange experiments at 35° for 7 h.

Type of experiment	*Mole C_2H_4 absorbed per mole $C_8H_{17}MgBr$*	*Mole C_2H_5MgBr added per mole $C_8H_{17}MgBr$*	*Mole C_2H_5MgBr per mole 1-octene*	*Composition of the C_8 hydrocarbons in product after hydrolysis (mole %)*		
				n-octane	*1-octene*	*2-octene*
Ethylene absorption	0.64			38	58	4
	0.35	1		47	40	13
	0.22	5		81	19	0
	0.27	10		79	21	0
C_2H_5MgBr + 1-octene exchange			1	0.5	94.5	5.0
			3	1.5	88.0	9.5
			5	2.0	87.5	10.5
			10	4.5	80.5	15.0

As can be seen from the data, the reaction rate was appreciably higher with ethylene than with octene. At the same time, the relatively high temperature necessary for the latter olefin to exchange resulted in the generally more extensive olefin isomerization, which was further enhanced by use of high concentrations of Grignard reagents.

The structure of the alkylmagnesium compound formed from higher olefins was investigated in the case of propene. n-Octylmagnesium bromide was brought into reaction with propene, the reaction mixture was treated with carbon dioxide to give as a product thus formed from the propylmagnesium bromide, normal butyric acid (as identified by gas chromatography). No isobutyric acid could be detected, thus proving the propylmagnesium bromide to be the primary isomer:

$$C_8H_{17}MgBr+CH_3CH{=}CH_2 \xrightarrow{NiCl_2} C_8H_{16}+CH_3CH_2CH_2MgBr \xrightarrow{CO_2} CH_3CH_2CH_2COOH$$

The exchange reaction was found to be rather general with vinyl-type olefin and different alkylmagnesium halides. Table 2 and 3 illustrate this point, showing the conversions obtained with some typical combinations of olefins and Grignard reagents. As can be seen from the data, significant conversions could be achieved only with ethylene, propene and styrene, whereas cyclohexene and 2-octene proved to be almost inert under the conditions used, and with 1-octene isomerization was found to be the principal reaction. These results can be understood if we assume that the exchange reaction is effectively confined to α-olefins, but that in the case of α-olefins which can isomerize to internal olefins, this isomerization is the favoured reaction, and gives olefins which are rather inert in the exchange reaction.

The structure of the Grignard reagent has also some influence on the reaction

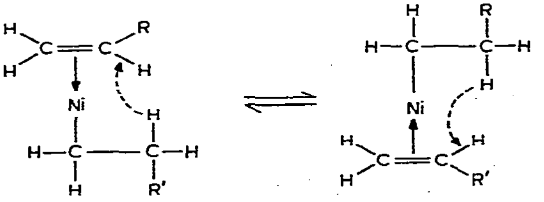
TABLE 2

ALKYL–OLEFIN EXCHANGE REACTION WITH SOME ALKYLMAGNESIUM HALIDES AND GASEOUS OLEFINS

Olefin	*Grignard reagent*	*Molar ratio Grignard to $NiCl_2$*	*Temperature (°C)*	*Reaction time (h)*	*Olefin consumption based on Grignard reagent (%)*
C_2H_4	iso-C_3H_7MgBr	28	6	1.5	0
	n-C_4H_9MgBr	28	6	1	15
		100	6	2	39
	sec-C_4H_9MgBr	100	5	5	27
	n-C_8H_{17}MgBr	42	6.5	5.5	24
		100	−5.5	4	63
		100	6	3	45
		100	16.5	6	36
		150	6	4	42
C_3H_6	n-C_4H_9MgBr	100	6	2	3.2
	n-C_8H_{17}MgBr	42	6.5	5.5	24
		100	5.5	5	23
	n-$C_{10}H_{21}$MgBr	42	6.5	4.5	22
		150	6.5	1.5	4.5

rate, primary alkylmagnesium halides being the most, and tertiary alkylmagnesium halides the least reactive.

Several mechanisms for the exchange reaction can be envisaged and choice between them is not at present possible. The black colour of the reaction mixture is retained under conditions of refluxing only in the presence of higher olefins, and in the absence of such olefins, a black precipitate is formed and the solution becomes colourless. This points to the presence of an olefin–nickel π-complex in these reaction mixtures, and the alkyl–olefin exchange could take place between the π-complexed olefin and the σ-bonded alkyl groups by β-hydrogen elimination.



This hydrogen transfer can be facilitated by the non-bonding orbitals of the nickel atom, in a way which would resemble the intermediate formation of a nickel hydride, but it is not necessary to assume a definite hydride complex.

This hydridic-type intermediate may be responsible for the parallel isomerization reaction also[5]. The scheme above is, however, undoubtedly an oversimplification, since it neglects, among other factors, the role of the organomagnesium species present in the reaction mixture.

TABLE 3

ALKYL–OLEFIN EXCHANGE REACTION WITH SOME ALKYLMAGNESIUM HALIDES AND LIQUID OLEFINS

Reaction temperature: 35°; reaction time: 7 h.

Olefin	*Grignard reagent*	*Molar ratio Grignard to olefin*	*Molar ratio Grignard to $NiCl_2$*	*Conversion of olefin or yield of alkylmagnesium halide (%)*	*Isomerisation of olefin (%)*
1-Octene	CH_3MgI	1	33	0	8
	C_2H_5MgBr	1	33	2.0	14
		1	100	0.5	4
	n-C_4H_9MgBr	1	33	4.0	13
	sec-C_4H_9MgBr	1	33	1.8	20
	tert-C_4H_9MgBr	1	33	1.5	22
2-Octene	C_2H_5MgBr	1	33	< 1	2
	n-C_4H_9MgBr	1	33	2.4	1
	sec-C_4H_9MgBr	1	33	1.3	2.5
Cyclohexene	C_2H_5MgBr	1	33	$\leqslant 1$	
		1	100	0	
		10	100	< 1	
	n-$C_8H_{17}MgBr$	1	33	1.1	
Styrene	C_2H_5MgBr	1	33	12	
		3	33	18	
		10	33	29	
		1	33	7.7[a]	
		10	33	9.8[a]	
		1	100	3.5	
		5	100	4.8	
		10	100	7.3	

[a] Under ethylene.

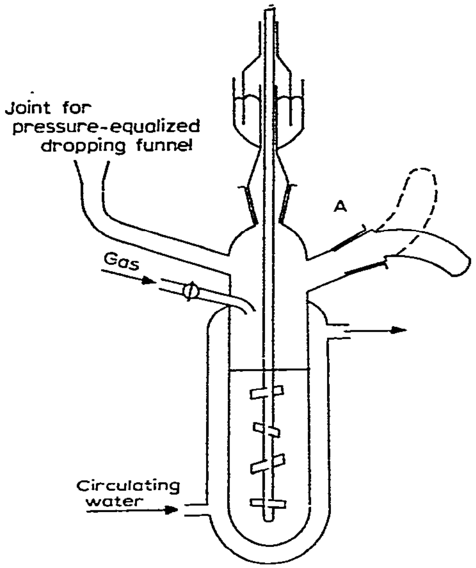
EXPERIMENTAL

1. *Preparation of the $NiCl_2$ catalyst*

Anhydrous nickel chloride was prepared from $NiCl_2 \cdot 6\,H_2O$, by drying at 180–200° for two days, occasionally followed by sublimation in dry nitrogen at 800°. From nickel chloride made by the first method a fraction between 0.063 and 0.25 mm was separated and used as a catalyst, while the sublimed salt was fine enough for immediate use. No essential difference was observed between the reactivities of these products.

2. *Reaction of Grignard reagents with gaseous olefins*

An alkylmagnesium halide (20–30 mmoles), prepared by the usual methods[6] was placed into the dropping funnel of the apparatus on Fig. 1. After chilling the system to the required temperature and flushing with dry nitrogen, the ethereal solution of the Grignard compound was added into the reaction vessel and saturated with ethylene (or propene). After the temperature and vapour pressure of ether reached their final values, the calculated amount of $NiCl_2$ catalyst was added by turning the



side tube "A" of the apparatus. The reaction mixture quickly became black, and a seemingly homogeneous system was formed. Gas absorption set in, the volume of which was measured with a gas burette. Experiments usually lasted 1–6 h, during which time the rate of gas absorption gradually diminished.

3. *Reaction of Grignard reagents with liquid olefins*

The necessary quantity of the proper alkylmagnesium halide was placed into a small flask equipped with an efficient reflux condenser. After addition of the olefin and the $NiCl_2$ catalyst, the mixture was generally refluxed for 7 h, with protection from moisture and air. A black colour appeared as soon as the nickel chloride was added.

4. *Product analysis*

The products were hydrolyzed with 20 % hydrochloric acid, and after separation and drying over anhydrous sodium sulphate were analyzed by gas chromatography. Generally a 4 m long column, packed with 25 % dimethylsulfolane on Celite was used at 50°. For the samples containing styrene or other high boiling components a 1.5 m column of tricresyl phosphate at 150° was used.

SUMMARY

Anhydrous nickel chloride catalyzes the alkyl–olefin exchange reaction between Grignard reagents and α-olefins. The catalyst is especially effective in the case of gaseous olefins and long-chain alkylmagnesium halides. Olefins with internal double bonds do not undergo the reaction, while primary alkylmagnesium halides react more easily than secondary and tertiary ones. The reaction may involve a hydridic transition state or a direct hydride-ion migration between the ligands in the catalyst complex.

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