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TRANSITION METAL ALKYLS AND HYDRIDES
X*. STRUCTURE OF PRODUCTS FORMED IN THE REACTIONS BETWEEN OLEFINS AND GRIGNARD REAGENTS IN THE PRESENCE OF NICKEL CHLORIDE

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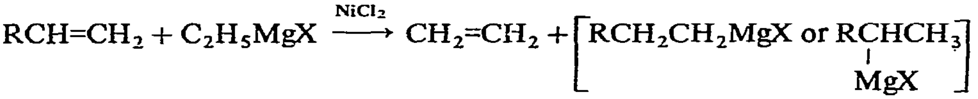
SUMMARY

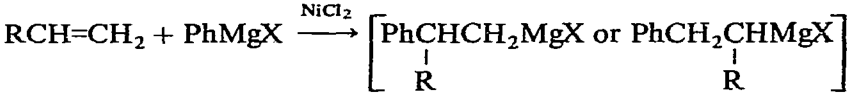
The structures of Grignard compounds formed from olefins and Grignard reagents by alkyl–olefin exchange reaction or olefin insertion under the catalytic influence of anhydrous nickel chloride have been determined. The results indicate that the mechanisms of these reactions involve nucleophilic attack of a hydrogen atom or a phenyl group on a π-complexed olefin within an organonickel intermediate.

INTRODUCTION

α-Olefins were found to react in the presence of nickel chloride with alkyl- and arylmagnesium halides via alkyl–olefin exchange (1) and olefin insertion (2), respectively[2–4]. In the case of ethylene, only one type of organomagnesium halide can be formed, but higher olefins can give rise principally to two isomeric reaction products:



$$RCH{=}CH_2 + C_2H_5MgX \xrightarrow{NiCl_2} CH_2{=}CH_2 + \left[RCH_2CH_2MgX \text{ or } R\underset{MgX}{C}HCH_3\right] \quad (1)$$



$$RCH{=}CH_2 + PhMgX \xrightarrow{NiCl_2} \left[Ph\underset{R}{C}HCH_2MgX \text{ or } PhCH_2\underset{R}{C}HMgX\right] \quad (2)$$

These reactions may be formally regarded as involving addition of the Mg–H and Mg–C entities across the olefinic double bond. The present paper describes an investigation of the direction of the additions.

RESULTS

The structures of the Grignard compounds were determined after oxidation or reaction with acetone, acetaldehyde or formaldehyde and identification of the corresponding alcohols by GLC analysis.

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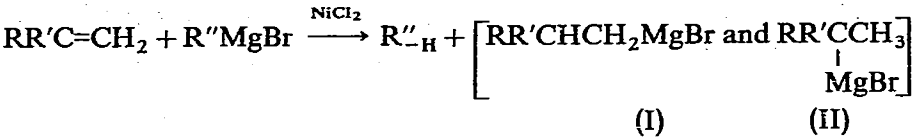
* For Part IX see Ref. 1.

1. *Reaction of propylene, 1-butene, isobutene and styrene with alkylmagnesium bromides*

The reactions investigated are represented by the general scheme (3):



$$RR'C{=}CH_2 + R''MgBr \xrightarrow{NiCl_2} R''_{-H} + \left[\underset{(I)}{RR'CHCH_2MgBr} \text{ and } \underset{(II)}{RR'\underset{\substack{|\\ MgBr}}{C}H_3} \right] \quad (3)$$

(R''_{-H} stands for the olefin formed in the exchange reaction.)

The results are shown in Table 1, it will be seen that formation of the product of type (I) is strongly favoured with aliphatic olefins, the ratios of I/II ranging between 3/1 (propylene, isobutene) and 50/1 or even larger (1-butene).

Styrene, on the other hand yields mainly the Grignard reagent of type (II), *i.e.* (1-phenylethyl)magnesium bromide. With ethylmagnesium bromide, the 2-phenyl derivative could not be detected at all in the product. Grignard reagents with longer alkyl chains always produced some (2-phenylethyl) magnesium bromide too, especially at low catalyst concentrations. An explanation of this will be presented later.

2. *Isomerisation of Grignard reagents by nickel chloride in the presence of olefins*

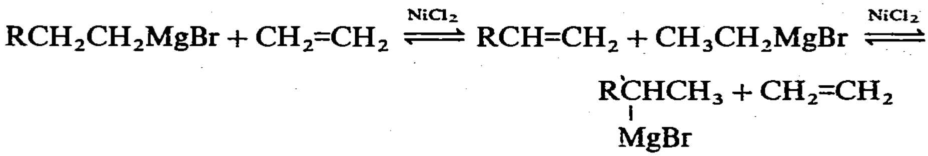
The alkyl–olefin exchange reaction is known to be reversible[2]. Thus the following reaction sequence can lead to the isomerisation of a Grignard compound in the presence of an olefin such as ethylene:

TABLE 1

REACTION OF VARIOUS OLEFINS WITH ETHEREAL ALKYLMAGNESIUM BROMIDES[a]

Olefin	R'' in the Grignard compound	Yield of olefin formation from the Grignard (mole %)	Proportion of primary isomer in the mixture of Grignards formed from olefin (%)
Propylene	C_2H_5	21.5	74.5
	n-C_4H_9	36.6	76.0
	s-C_4H_9	12.0	94.2
1-Butene	C_2H_5	21.0	98.1
	n-C_3H_7	76.0	96.0
	i-C_3H_7	37.0	~100
Isobutene	C_2H_5	58.0	71.0
	n-C_3H_7	84.0	76.0
	i-C_3H_7	54.5	69.0
Styrene	C_2H_5	29.0	0
	n-C_3H_7	36.0	17.1
	i-C_3H_7	38.4	0.8
	n-C_4H_9	35.9	11.7
	s-C_4H_9	43.2	3.3
	i-C_4H_9	51.3	0

[a] Molar ratio Grignard/$NiCl_2$ 10. Reaction time 5 h. Temperature 6°. Grignard concentration in the mixture 1.0 mole/l.



$$\mathrm{RCH_2CH_2MgBr + CH_2{=}CH_2 \overset{NiCl_2}{\rightleftharpoons} RCH{=}CH_2 + CH_3CH_2MgBr \overset{NiCl_2}{\rightleftharpoons} \underset{\displaystyle MgBr}{R\underset{|}{C}HCH_3} + CH_2{=}CH_2} \qquad (4)$$

Since in the systems discussed in Section 1, Grignard compounds and olefins are present simultaneously, the conclusions drawn regarding the direction of addition of the Mg–H entity are only valid if such isomerisation is slow. This question has been investigated for several Grignard compounds and olefins, and the results are presented in Table 2.

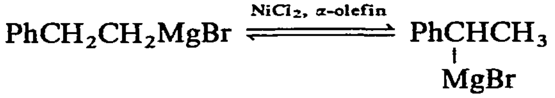
TABLE 2

ISOMERISATION OF GRIGNARD COMPOUNDS BY REPEATED ALKYL–OLEFIN EXCHANGE REACTION[a]

Starting Grignard compound	Olefin	Formation of olefin from the Grignard (mole %)	Yield of isomerisation reaction (mole %)
n-C_3H_7MgBr	Ethylene	5.6	3.5
	1-Butene	76.0	0
	Isobutene	84.0	0
i-C_3H_7MgBr	Ethylene	0.5	4.4
	1-Butene	37.0	6.0
	Isobutene	54.5	3.6
n-C_4H_9MgBr	Ethylene	30.0	0.7
	Propylene	36.6	0
	Styrene	35.9	0
s-C_4H_9MgBr	Ethylene	40.0	0
	Propylene	12.0	16.2
	Styrene	43.2	20.0
i-C_4H_9MgBr	Ethylene	16.0	10.1
	Propylene	10.0	0
	Styrene	51.3	22.4
$PhCH_2CH_2$-MgBr	Ethylene	57.6	42.4
	Propylene	18.5	76.6
	Styrene		73.4

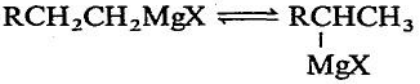
[a] Molar ratio Grignard/$NiCl_2$ 10. Reaction time 5 h. Reaction temperature 6°. Grignard concentration in the reaction mixture 1.0 mole/l.

The isomerisation is obviously very slow in the case of alkylmagnesium halides, but, in contrast, (2-phenylethyl)magnesium bromide is easily isomerized to the 1-phenyl isomer under similar conditions. With high concentrations of catalyst and sufficiently long reaction times, the 2-isomer is completely transformed to the 1-isomer, indicating, that equilibrium (5) lies well over to the right:



$$\mathrm{PhCH_2CH_2MgBr \xrightleftharpoons{NiCl_2,\ \alpha\text{-}olefin} \underset{\displaystyle MgBr}{Ph\underset{|}{C}HCH_3}} \qquad (5)$$

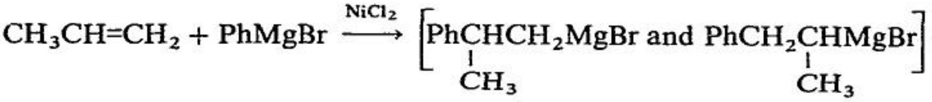
Cooper and Finkbeiner have reported[5], that alkylmagnesium halides are partially isomerized by $TiCl_4$ and that this isomerisation takes place in the sense i-alkyl → n-alkyl. Our experiments with $TiCl_4$ essentially confirmed their results, showing the i-alkyl → n-alkyl isomerisation to be faster than the n-alkyl → i-alkyl route by about two orders of magnitude (Table 3). Thus in the presence of an appropriate catalyst equilibrium (6) probably lies well over to the left, but apparently the $NiCl_2 + \alpha$-olefin catalyst system used in this work appears not to be sufficiently active.



$$RCH_2CH_2MgX \rightleftharpoons \underset{\displaystyle MgX}{\underset{|}{RCHCH_3}} \qquad (6)$$

3. *Reaction of propylene with phenylmagnesium bromide*

The "insertion" of propylene into the Mg–C bond according reaction scheme (7) was found to give (III) as the principal primary product.



$$CH_3CH{=}CH_2 + PhMgBr \xrightarrow{NiCl_2} \left[Ph\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2MgBr \text{ and } PhCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HMgBr \right] \qquad (7)$$

(III) (IV)

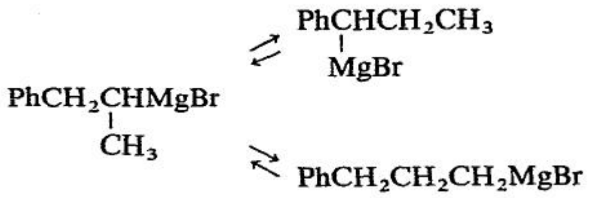
Only the structure of the carbon skeleton of the C_3 group attached to the benzene ring was investigated and no experiments were made to determine the extent of possible secondary isomerisation reactions of Grignard compounds, represented *e.g.* by scheme (8):

TABLE 3

COMPARISON OF THE $TiCl_4$ AND $NiCl_2$ ISOMERISATION CATALYSTS[a]

Catalyst	Grignard compound	Olefin	Formation of olefin from the Grignard (mole %)	Isomer distribution of the residual Grignard compounds (%)	
				$n-C_3H_7MgBr$	$i-C_3H_7MgBr$
$TiCl_4$	$i-C_3H_7MgBr$	None		68	32[b,d]
	$i-C_3H_7MgBr$	None		26	74[c,d]
$TiCl_4$	$n-C_3H_7MgBr$	None		98.8	1.2
	$i-C_3H_7MgBr$	None		62.5	37.5
	$n-C_3H_7MgBr$	Ethylene	13.5	~100	Traces
	$i-C_3H_7MgBr$	Ethylene	51.5	47.0	53.0
	C_2H_5MgBr	Propylene	7.5[e]	~100	Traces
$NiCl_2$	$n-C_3H_7MgBr$	None		98.9	1.1
	$i-C_3H_7MgBr$	None		0	100
	$n-C_3H_7MgBr$	Ethylene	5.6	96.3	3.7
	$i-C_3H_7MgBr$	Ethylene	0.5	4.4	95.6
	C_2H_5MgBr	Propylene	21.5[e]	74.5	25.5

[a] Molar ratio Grignard/catalyst 10. Reaction time 5 h. Reaction temperature 6°. [b] Reaction temperature 0°. Reaction time $1\frac{1}{4}$ h. Molar ratio Grignard/$TiCl_4$ 10. [c] Reaction time 5 h. Molar ratio Grignard/$TiCl_4$ 45. [d] Original results of Cooper and Finkbeiner. [e] Formation of C_3H_7MgBr from propylene, and isomer distribution of the Grignard formed, respectively.



$$PhCH_2\underset{\substack{|\\ CH_3}}{C}HMgBr \begin{array}{l} \rightleftarrows Ph\underset{\substack{|\\ MgBr}}{C}HCH_2CH_3 \\ \rightleftarrows PhCH_2CH_2CH_2MgBr \end{array} \quad (8)$$

The results are shown in Table 4.

TABLE 4

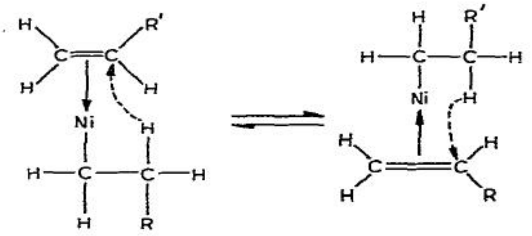
STRUCTURE OF THE PROPYLENE INSERTION PRODUCTS OF PHENYLMAGNESIUM BROMIDE[a]

Molar ratio $PhMgBr/NiCl_2$	Yield of formation of the insertion products (mole %)	Distribution of the insertion products (%)	
		(III)[b]	(IV)[b]
10	4.8	90	10
40	2.0	66	34
100	1.0	60	40

[a] Reaction time 5 h. Temperature 6°. Initial PhMgBr concentration 1.0 mole/l. [b] See eqn. (7).

DISCUSSION

It was previously suggested[2-4] that the alkyl–olefin exchange takes place by β-hydrogen transfer from an alkyl group to a π-complexed olefin within an alkyl-nickel–olefin π-complex:



(9)

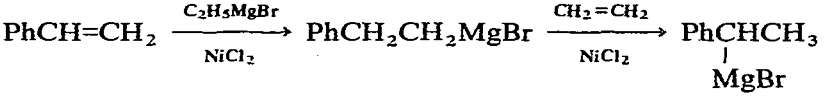
The transfer of alkyl groups between this organonickel intermediate and the alkylmagnesium halides present in excess (the step necessary to give a catalytic cycle)[4] is probably best represented as in (10):

(10)

Such a transfer does not change the structure of the alkyl groups, and thus the structures of the Grignard reagents reflect the processes taking place inside the coordination sphere of the nickel atom.

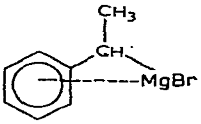
The observation that alkylmagnesium bromides of structure (I) are the chief products in the case of aliphatic olefins (*cf.* Section 1) proves that the hydrogen reacts with the π-complexed olefin by nucleophilic attack at a carbon atom having partial positive character, *i.e.* in accordance with scheme (9). The addition of the Ni–H entity to the olefin to give an alkylnickel derivative can therefore be regarded as a nucleophilic addition to unsaturated carbon.

The results also indicate that the same mechanism also applies to the alkyl–olefin exchange with styrene, and thus (2-phenylethyl)magnesium bromide must be regarded as the primary product. This Grignard reagent rapidly isomerizes to the 1-phenyl derivative, however, which accounts for the preponderant formation of the latter compound when large concentrations of catalyst or long reaction times are used:



$$PhCH{=}CH_2 \xrightarrow[NiCl_2]{C_2H_5MgBr} PhCH_2CH_2MgBr \xrightarrow[NiCl_2]{CH_2=CH_2} \underset{\displaystyle MgBr}{PhCHCH_3} \qquad (11)$$

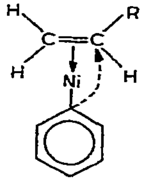
The principal difference between the aliphatic olefins and styrene is, that whereas in the former case the primary alkylmagnesium halide is both the kinetically and thermodynamically controlled product (*cf.* the isomerisation experiments with $TiCl_4$), in the latter case the kinetically controlled primary product [(2-phenylethyl)-magnesium bromide] is transformed in a secondary reaction into the thermodynamically controlled product [(1-phenylethyl)magnesium bromide]. The greater stability of the 1-isomer as compared to the 2-isomer may arise from some interaction between the aromatic ring and the magnesium atom:



(12)

Interactions of this kind are not unknown in organometallic complexes containing the benzyl group [8,9].

The mechanism of the olefin insertion reaction, according to equations (2) and (7), is probably very similar to that of the alkyl–olefin exchange reaction, except that it is the phenyl group which attacks the π-complexed olefin as a nucleophilic reagent:



(13)

The attack of the phenyl group (like that of the hydrogen in the other reaction) is mainly directed towards the olefinic carbon carrying the alkyl group. The fact that the directive influence of the alkyl group on the olefinic carbon atom is not so pronounced as in the case of the alkyl–olefin exchange reaction (*cf.* Tables 1 and 4) may be attributed to steric effects which exert an opposing influence, and are likely to be more important for the migrating phenyl group than for the migrating hydrogen.

The fact that olefin insertion does not take place under similar conditions but with alkyl- instead of arylmagnesium halides, may originate in the significantly weaker nucleophilic character of an alkyl than of an aryl group.

EXPERIMENTAL

The preparation of the anhydrous nickel chloride catalyst and starting Grignard compounds have been described[2–4]. The structures of the starting Grignard reagents were determined by the methods used for the Grignard compounds formed, as described below.

1. *Reaction of Grignard reagents with gaseous olefins*

A thermostatted, jacketed reaction flask attached to a mercury gas burette and equipped with a magnetic stirrer and a side arm for the glass stopper holding a small container for the catalyst, was flushed with the required gas, after the appropriate amount of $NiCl_2$ had been placed in the container. The Grignard solution, the volume of which depended on the quantity of catalyst and the molar ratio, was introduced by means of a syringe through a silicone rubber membrane. The reaction was started with addition of the catalyst by turning the side arm container. The reaction mixture rapidly became black after $NiCl_2$ had been added. Gas absorption was measured as a function of the reaction time.

2. *Reaction of Grignard reagents with liquid olefins*

Reactions of this type were carried out as described before, using dry argon instead of gaseous olefin. The liquid olefin was added from a hypodermic syringe.

3. *Sample handling before analysis*

The experimental samples were divided into two or three parts. One part was treated with water then dissolved in 20% hydrochloric acid. The second part was usually oxidized before hydrolysis by shaking for 3 h under oxygen and then allowing the mixture to stand overnight. Sometimes a third part of the sample was treated with anhydrous acetone before hydrolysis. Several experiments were repeated with treatment of the samples with acetaldehyde and/or formaldehyde instead of acetone.

4. *Product analysis*

Hydrolyzed samples were analyzed by gas liquid chromatography after the ethereal solutions had been dried with Na_2SO_4. Some of the standard compounds were produced by appropriate treatment (oxidation, acetone, etc.) of the corresponding Grignard reagents. 1-Phenyl- and 2-phenylethanols were prepared from phenylmagnesium bromide by treatment with acetaldehyde and ethylene oxide, respectively.

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