

## TRANSITION METAL ALKYL AND HYDRIDES VIII\*. NICKEL CHLORIDE CATALYZED INSERTION OF ETHYLENE INTO ARYLMAGNESIUM HALIDES

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### SUMMARY

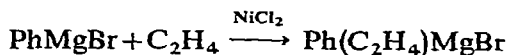
Anhydrous nickel chloride catalyses the insertion of ethylene into the C-Mg-bond of arylmagnesium bromides and also the subsequent alkyl-olefin exchange reaction of the primary aralkyl metal derivatives. Other transition metal halides are less active. (2-Phenylethyl)magnesium bromide isomerises under these conditions to the 1-isomer, and this isomerization is promoted by olefins. The nickel catalyst complex probably contains both  $\sigma$ -alkyl (aralkyl or aryl) and  $\pi$ -olefin ligands, and direct hydride migration between these ligands is proposed as the mechanism for the exchange and isomerization in the presence of certain olefins.

### INTRODUCTION

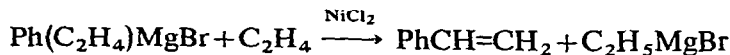
In previous papers<sup>2</sup> we reported our results connected with the alkyl-olefin exchange reaction of arylmagnesium halides catalyzed by anhydrous nickel chloride. Now we discuss studies of ethylene insertion reactions of aryl Grignard reagents, which are followed by such exchange reactions.

Job and coworkers first studied the reaction between ethereal phenylmagnesium bromide and unsaturated compounds in the presence of anhydrous nickel chloride<sup>3</sup>. When ethylene was absorbed by the catalyst system consisting of PhMgBr and NiCl<sub>2</sub>, ethylbenzene and styrene were formed, in addition to benzene<sup>4</sup>, but the nature of the reaction was not discussed.

In the light of information on the so-called alkyl-olefin exchange reaction<sup>2,5</sup> and the olefin insertion reaction<sup>6,7</sup> in presence of similar catalysts, we thought it likely the first step of the reaction between PhMgBr and ethylene would be an olefin insertion:



and that this would be followed by the exchange reaction:



\* For Part VII see ref. 1.

## RESULTS

## 1. Olefin insertion and alkyl-olefin exchange

First the effect of several variables on the quantity of ethylene absorbed, on the degree of conversion of PhMgBr, and on the yields of ethylbenzene and styrene were investigated. Such data were obtained by GLC analysis of the product (after hydrolysis) and from the volume of ethylene consumed in the reaction, it being assumed that possible side reactions consume no ethylene; the yields in the first (insertion) and the second (exchange) step could thus be separately determined. Relative rates of ethylene consumption were determined from the initial slopes of the gas absorption curves ( $\text{tg } \alpha$ ).

The results listed in Table 1–3 show the effects of varying separately the concentrations of  $\text{MgBr}_2 \cdot \text{etherate}$ , PhMgBr, and  $\text{NiCl}_2$ . Table 4 shows the effects of temperature on both the insertion and exchange reactions. It can be seen that ethylene consumption and the yield of the ethylene insertion reaction are strongly influenced by the concentration of PhMgBr,  $\text{NiCl}_2$  and  $\text{MgBr}_2 \cdot \text{etherate}$ , whereas the yield of the exchange reaction is nearly constant (60–80%). The rate of reaction is enhanced by increasing the catalyst concentration, but this does not lead to a high yield because of rapid deactivation of the catalyst.

Some other transition metal chlorides were found to be active, but less so than nickel chloride (Table 5). No reaction took place in the presence of ferric chloride.

The system consisting of PhMgBr,  $\text{NiCl}_2$  and ethylene is moderately sensitive to water and oxygen. Admission of pure oxygen into the reaction flask before the reaction slightly diminished the volume of ethylene consumed, but even 0.3 equivalents of oxygen per equivalent of PhMgBr did not stop the catalytic process. Two equivalents of water decreased the ethylene consumption to about one tenth.

Some coupling also occurred, the products generally containing a small amount of biphenyl. (Phenylethyl)magnesium bromide, the first intermediate product, gives practically no second insertion reaction with ethylene, since only in a few

TABLE 1

ETHYLENE INSERTION AND EXCHANGE REACTION WITH PhMgBr AND  $\text{NiCl}_2$ . EFFECT OF  $\text{MgBr}_2$  ETHERATE (IN ETHEREAL SOLUTION)

Reaction temperature: 7°. Molar ratio PhMgBr/ $\text{NiCl}_2$  = 42. PhMgBr concentration in the mixture: 0.94 mole/l.

Molar ratio $\text{MgBr}_2$ to PhMgBr	Ethylene consumption $\left( \frac{\text{mole C}_2\text{H}_4}{\text{mole PhMgBr}} \right)$	PhMgBr conversion (mole %)	Yield of insertion based on total PhMgBr (mole %)	Yields of exchange reaction based on		$\text{tg } \alpha \cdot 10^2$ $\left( \frac{\text{mole C}_2\text{H}_4}{\text{mole PhMgBr} \cdot \text{min}} \right)$
				Total PhMgBr (mole %)	Ethylene inserted (mole %)	
0	0.74	78	46	28	61	0.67
0.2	1.08	79	63	45	71	0.79
0.5	0.76	78	45	31	69	1.14
1.0	0.62	71	36	26	72	0.92
2.0	0.29	66	17	12	70	0.21

TABLE 2

ETHYLENE INSERTION AND EXCHANGE REACTION WITH ETHERIAL PhMgBr AND NiCl<sub>2</sub>. EFFECT OF THE GRIGNARD REAGENT CONCENTRATION  
 Reaction temperature: 7°. Molar ratio PhMgBr/NiCl<sub>2</sub> = 42. Molar ratio MgBr<sub>2</sub>/PhMgBr = 0.2.

PhMgBr concentration in the reaction mixture (mole/l)	Calculated NiCl <sub>2</sub> concentration (mmole/l)	Ethylene consumption $\left(\frac{\text{mole C}_2\text{H}_4}{\text{mole PhMgBr}}\right)$	PhMgBr conversion (mole %)	Yield of insertion based on total PhMgBr (mole %)	Yield of exchange reaction based on		$\lg \alpha \cdot 10^2 \left(\frac{\text{mole C}_2\text{H}_4}{\text{mole PhMgBr} \cdot \text{min}}\right)$
					Total PhMgBr (mole %)	Ethylene inserted (mole %)	
0.30	7.1	0.40		21	19	93	0.68
0.51	12.2	0.73	73	40	33	83	1.06
0.69	16.4	0.87	67	50	37	75	1.25
0.94	22.4	1.08	79	63	45	71	0.79
1.18	28.1	0.91	85	55	35	63	0.66

TABLE 3

ETHYLENE INSERTION AND EXCHANGE REACTION WITH ETHERIAL PhMgBr AND NiCl<sub>2</sub>. EFFECT OF THE PhMgBr/NiCl<sub>2</sub> MOLAR RATIO  
 Reaction temperature: 7°. Molar ratio MgBr<sub>2</sub>/PhMgBr = 0.2. PhMgBr concentration in the mixture: 0.94 mole/l.

Molar ratio PhMgBr to NiCl <sub>2</sub>	Calculated NiCl <sub>2</sub> concentration (mmole/l)	Ethylene consumption $\left(\frac{\text{mole C}_2\text{H}_4}{\text{mole PhMgBr}}\right)$	PhMgBr conversion (mole %)	Yield of insertion based on total PhMgBr (mole %)	Yield of exchange reaction based on		$\lg \alpha \cdot 10^2 \left(\frac{\text{mole C}_2\text{H}_4}{\text{mole PhMgBr} \cdot \text{min}}\right)$
					Total PhMgBr (mole %)	Ethylene inserted (mole %)	
27	34.9	0.88	77	54	34	63	0.99
42	22.4	1.08	79	63	45	71	0.79
70	13.4	1.20	84	70	50	71	0.59
100	9.4	1.25	81	74	50	68	0.37
200	4.7	1.13	79	69	44	64	0.13

TABLE 4

ETHYLENE INSERTION AND EXCHANGE REACTION WITH ETHEREAL PhMgBr AND NiCl<sub>2</sub>. EFFECT OF TEMPERATUREMolar ratio PhMgBr/NiCl<sub>2</sub>=42. Molar ratio MgBr<sub>2</sub>/PhMgBr=0.2. PhMgBr concentration in the mixture: 0.94 mole/l.

Temp. (°C)	Ethylene consumption $\left(\frac{\text{mole C}_2\text{H}_4}{\text{mole PhMgBr}}\right)$	PhMgBr conversion (mole %)	Yield of insertion based on total PhMgBr (mole %)	Yields of exchange reaction based on		$\text{tg } \alpha \cdot 10^2$ $\left(\frac{\text{mole C}_2\text{H}_4}{\text{mole PhMgBr} \cdot \text{min}}\right)$
				Total PhMgBr (mole %)	Ethylene inserted (mole %)	
-10.5	1.04					0.24
+ 0.5	1.11	81	68	43	64	0.52
+ 7.0	1.08	79	63	45	71	0.79
+14.5	0.97	74	56	41	73	0.85
+20.0	0.37					0.75

TABLE 5

REACTION OF ETHYLENE WITH ETHEREAL PhMgBr. COMPARISON OF SOME TRANSITION METAL CHLORIDES AS CATALYSTS

Reaction temperature: 6-7°. Molar ratio MgBr<sub>2</sub>/PhMgBr=0.2. PhMgBr concentration in the mixture: 0.94 mole/l.

Transition metal chloride MX <sub>n</sub>	Molar ratio PhMgBr to MX <sub>n</sub>	Ethylene consumption $\left(\frac{\text{mole C}_2\text{H}_4}{\text{mole PhMgBr}}\right)$	$\text{tg } \alpha \cdot 10^2$ $\left(\frac{\text{mole C}_2\text{H}_4}{\text{mole PhMgBr} \cdot \text{min}}\right)$
TiCl <sub>4</sub>	42	0.18	0.19
NiCl <sub>2</sub>	42	1.08	0.79
CoCl <sub>2</sub>	100	0.05	0.026
NiCl <sub>2</sub>	100	1.25	0.37

samples could butylbenzenes be detected in trace quantities\*. This is in accordance with our previous findings<sup>2</sup> that in the case of alkyl Grignard reagents olefin exchange is the main reaction.

The formation of ethylmagnesium bromide in the second reaction step has been proved by collecting the gas evolved during hydrolysis by means of a Töppler pump at -30°, and analysis for ethane and ethylene by gas chromatography. Quantitative analysis showed the amount of ethane to be about 65% of the theoretical.

As one of the possible processes leading to by-products, the reaction of styrene (formed in the second reaction step) and PhMgBr in the presence of NiCl<sub>2</sub> was studied. In experiments with different amounts of catalyst, it was found that about 2 moles of ethylbenzene and 0.5 mole of 1,1-diphenylethylene were formed for each mole of NiCl<sub>2</sub>. In view of the relatively small amount of the insertion product formed,

\* Using TiCl<sub>4</sub> as catalyst in a larger amount this product is generally detectable<sup>5</sup>.

it seems that only about 25% of the ethylbenzene could have been formed by alkyl-olefin exchange. Some additional source of hydrogen must thus be assumed to be present.

Reactions of ethylene with arylmagnesium bromides having different alkyl groups on the aromatic ring were also studied. Values of gas consumption and their initial velocities are given in Table 6. As can be seen from these data, alkyl groups in the *ortho*-position of the benzene ring increase the overall rate of the reaction, but the same groups in *para*-position decrease it.

TABLE 6

REACTION OF ETHYLENE WITH VARIOUS ARYLMAGNESIUM BROMIDES

Reaction temperature: 6°. Grignard reagent concentration in the mixture: 1.0 mole/l. Molar ratio of Grignard reagent to NiCl<sub>2</sub>=40. (Without MgBr<sub>2</sub> etherate.)

Grignard reagent	Ethylene consumption $\left(\frac{\text{mole C}_2\text{H}_4}{\text{mole Grignard}}\right)$	$\text{tg } \alpha \cdot 10^2$ $\left(\frac{\text{mole C}_2\text{H}_4}{\text{mole Grignard} \cdot \text{min}}\right)$	Yield of ethylene insertion, based on Grignard reagent converted (mole %)
C <sub>6</sub> H <sub>5</sub> MgBr	1.21	0.25	93
<i>o</i> -MeC <sub>6</sub> H <sub>4</sub> MgBr	1.55	0.61	81
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> MgBr	0.36	0.06	
<i>p</i> -EtC <sub>6</sub> H <sub>4</sub> MgBr	1.41	0.06	
Mesityl-MgBr	1.23	1.91	
1-Naphthyl-MgBr	0.79	1.36	49
2-Naphthyl-MgBr	1.23	0.24	96

## 2. Isomerization of (phenylethyl)magnesium bromide

In some ethylene-insertion experiments, the products were oxidized before hydrolysis. Subsequent GLC analysis showed both 1- and 2-phenylethanol to be present (Table 7). This shows that the formed (phenylethyl)magnesium bromide is

TABLE 7

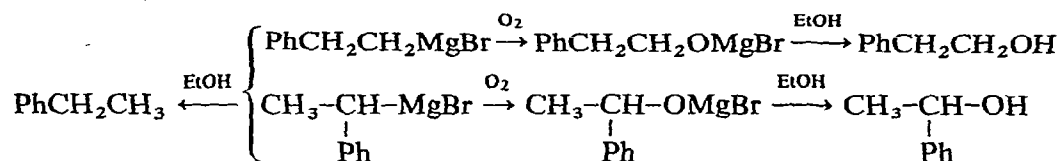
STRUCTURE OF Ph(C<sub>2</sub>H<sub>4</sub>)MgBr FORMED IN THE SYSTEM PhMgBr/ETHYLENE/NiCl<sub>2</sub> (IN ETHEREAL SOLUTION)

Reaction temperature: 6°. (Without MgBr<sub>2</sub> etherate.)

Molar ratio PhMgBr to NiCl <sub>2</sub>	Ethylene consumption $\left(\frac{\text{mole C}_2\text{H}_4}{\text{mole PhMgBr}}\right)$	$\text{tg } \alpha \cdot 10^2$ $\left(\frac{\text{mole C}_2\text{H}_4}{\text{mole PhMgBr} \cdot \text{min}}\right)$	Ratio of phenyl ethanol isomers in the oxidized reaction mixture 1-/2-
10	0.96	1.04	∞
40	1.21	0.25	4.2
42 <sup>a</sup>	0.91	0.58	45
100	0.79	0.05	3.0

<sup>a</sup> MgBr<sub>2</sub>/PhMgBr=0.2.

a mixture of 1- and 2-phenyl derivatives:



(2-Phenylethyl)magnesium bromide was found to be isomerized by nickel chloride to the 1-phenyl derivative (Table 8). This isomerisation is strongly promoted at low temperatures by ethylene and styrene, but propylene has practically no effect.

TABLE 8

ISOMERIZATION OF (2-PHENYLETHYL)MAGNESIUM BROMIDE

Molar ratio  $\text{PhCH}_2\text{CH}_2\text{MgBr}/\text{NiCl}_2 = 33$ .

Olefin added	Molar ratio olefin to $\text{NiCl}_2$	Temp. (°C)	Reaction time (h)	Ratio of phenyl-ethanol isomers 1-/2-
		Reflux	5	<sup>a</sup>
		6	5	0.021
$\text{C}_2\text{H}_4$	Excess	Reflux	5	0.025
$\text{C}_2\text{H}_4$	Excess	5.5	2	3.1
$\text{C}_3\text{H}_6$	Excess	Reflux	5	0.024
$\text{C}_3\text{H}_6$	Excess	5.5	5	0.034
Styrene	33	Reflux	7	0.16
Styrene	33	6	5	0.73

<sup>a</sup> Traces of 1-isomer.

In all the experiments giving (partial) isomerization of the Grignard compound, some styrene was formed. Part of this styrene appears to be formed by the dehydration of 1-phenylethanol, probably during the hydrolysis of the product, but parallel experiments without oxidation showed that a significant amount of styrene is formed directly from the Grignard reagent.

### 3. The nature of the catalyst

No reaction occurs between Grignard reagents and olefins in the absence of nickel chloride. Just after addition of the nickel chloride to the Grignard-olefin system a black, seemingly homogeneous reaction mixture is formed. Since some residual  $\text{NiCl}_2$  can be removed from this mixture by centrifugation, the actual amount of nickel in the mixture is somewhat less than that taken.

Information on the nature of the catalyst complex was obtained by studying the effect of centrifugation and of the order of mixing of reagents on the alkyl-olefin exchange reaction<sup>2</sup>

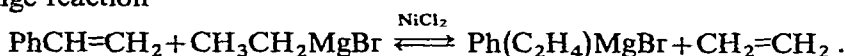


TABLE 9

## CHARACTERIZATION OF THE CATALYST BY CENTRIFUGATION

EtMgBr/Olefin/NiCl<sub>2</sub> system with benzene as internal standard (for GLC analysis) in ethereal solution. Molar ratio: EtMgBr/NiCl<sub>2</sub> = 10; EtMgBr/olefin = 1; EtMgBr/standard = 1. EtMgBr concentration: 1.0 mole/l.

No. of experiment	Order of mixing					Olefin conversion (mole %)
	1.	2.	3.	4.	5.	
1	NiCl <sub>2</sub>	EtMgBr	Standard	Styrene		27
2	NiCl <sub>2</sub>	EtMgBr	Standard	Styrene	Centrifug.	26
3	NiCl <sub>2</sub>	EtMgBr	Standard	Centrifug.	Styrene	3.8
4	NiCl <sub>2</sub>	EtMgBr	Standard	Centrifug.	Styrene	3.9
5	NiCl <sub>2</sub>	EtMgBr	Centrifug.	Standard	Styrene	1.8
6	NiCl <sub>2</sub>	Styrene	Standard	Centrifug.	EtMgBr	1.5

From the results, shown in Table 9, it can be seen that the effective catalyst must be in solution, since the removal of the residual nickel chloride by centrifugation has no effect on the yields (Table 9, Exp. 1 and 2). When the olefin and/or the Grignard reagent is added to the mixture *after* centrifugation, practically no reaction takes place (Exp. 3-6), which indicates that both the olefin and Grignard reagent are required for the formation of the catalyst. Evidently the catalyst consists of some nickel complex containing both  $\sigma$ -bonded alkyl or aryl group(s) (from the Grignard reagent) and  $\pi$ -bonded olefin(s).

## DISCUSSION

A reaction scheme is outlined in Fig. 1. The process must start with the formation of a complex phenylnickel derivative (1), as no reaction occurs without

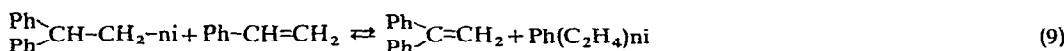
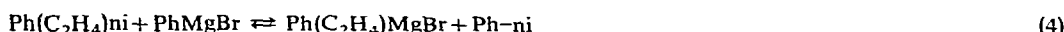
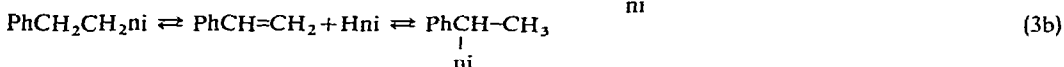
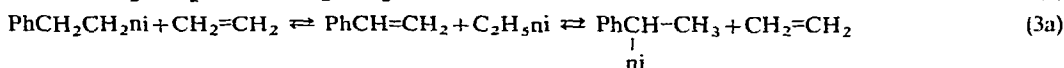
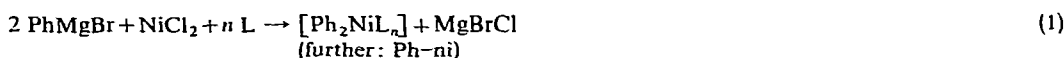
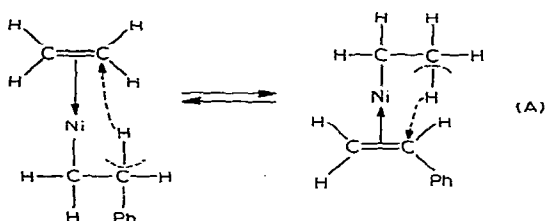


Fig. 1. Scheme of reactions of ethylene with PhMgBr.

nickel chloride. Ethylene insertion, (2), leads to a complex 2-phenylethyl derivative of nickel. The equilibrium (3a) represents an alkyl-olefin exchange yielding styrene, which can be transformed into the 1-isomer of the organometallic compound mentioned above. Equilibria (4) and (5) lead to regeneration of the catalyst. Reactions (6) and (7) take place during hydrolysis of the reaction mixture to give ethane and ethylbenzene, the latter, one of the main products of the reaction, being formed from both (1-phenylethyl)- and (2-phenylethyl)magnesium bromides. Reactions (8) and (9) account for the formation of by-product 1,1-diphenylethylene and [combined with reactions (4) and (7)] for part of the ethylbenzene formation in the reaction between  $\text{PhMgBr}$  and styrene.

The alkyl-olefin exchange equilibrium (3a) is thought to proceed by the mechanism previously proposed<sup>2</sup>, *i.e.* by hydrogen migration within the organonickel complex *without* formation of a definite nickel hydride [scheme (A)]:



This type of intermediate in the catalytic process is indicated by the following facts:

- (a) ethylene and styrene significantly increase the rate of (2-phenylethyl)magnesium bromide isomerization;
- (b) the formation of a homogeneous catalyst complex needs the presence of an olefin.

An alternative mechanism for both the alkyl-olefin exchange and the Grignard reagent isomerization would be the formation of a nickel hydride complex, as shown in reactions (3b) and (3c). This mechanism would also account for the formation of styrene in the reaction between (phenylethyl)magnesium bromide and  $\text{NiCl}_2$ . An alkyl-olefin hydride-shift inside the organonickel complex [scheme (A)] seems more probable in those cases in which an "active" olefin (*e.g.* ethylene or styrene) is present. "Active" olefins are those which [according to scheme (A)] readily accept the hydridic hydrogen. For this they must not contain groups with positive inductive effect, and thus propylene, with its  $+I$  methyl group is not a co-catalyst for the Grignard isomerization.

As the alkyl-olefin hydride-shift mechanism of scheme (A) involves intermediates of very similar enthalpy and entropy (which is not the case if a definite transition-metal hydride is formed), the increase of reaction rate by olefin  $\pi$ -complexation is not unexpected. Since the splitting off of a 2-hydrogen atom is a rather general elementary step in reactions of olefins catalysed by transition metal complexes, this effect of a  $\pi$ -bonded olefin may be a common phenomenon<sup>8</sup>.

Finally, the role of reactions (4) and (5) in the catalytic character of the overall process is considered. The extent of these exchange reactions determines whether the whole reaction sequence takes place catalytically or only stoichiometrically. The



phenyl group seems to enhance the catalytic cycle, perhaps because its electron-withdrawing character facilitates the dipolar exchange of the two organometallic species in the following process [scheme (B)]:



This may explain the observations that primary alkyl metal derivatives react less easily than aryl or alkylaryl ones and that secondary or tertiary alkyl Grignard reagents generally give no catalytic reaction<sup>2</sup>.

Experiments with higher olefins and aromatic Grignard reagents are in progress to provide a more detailed insight into the mechanism of the olefin insertion reaction, which will be discussed therefore in a later paper.

#### EXPERIMENTAL

The methods of preparation of the anhydrous nickel chloride catalyst and the reactions of different Grignard reagents with ethylene have been described<sup>2</sup>.

##### 1. Preparation of starting materials

Grignard reagents were generally prepared by the usual methods<sup>9</sup> using magnesium in a relatively large excess (20%) to minimize the coupling reaction.

2-Phenylethyl bromide was obtained by bromination of 2-phenylethanol prepared from PhMgBr and ethylene oxide according to Huston and Agett<sup>10</sup>.

Magnesium bromide etherate was prepared by adding bromine to magnesium turnings under ether<sup>11</sup>. The concentration of the ethereal solution was about 2.5 mole/l.

##### 2. Reaction of Grignard reagents with liquid olefins

The necessary quantity (about 20 mmoles) of the appropriate Grignard reagent (PhMgBr, PhCH<sub>2</sub>CH<sub>2</sub>MgBr or C<sub>2</sub>H<sub>5</sub>MgBr) was placed in a small reaction flask equipped with an efficient reflux condenser and with a water jacket attached to an ultrathermostat. After addition of the olefin and the NiCl<sub>2</sub> catalyst, the mixture was magnetically stirred, usually for 5 h at the required temperature, with protection from moisture and air.

##### 3. Oxidation procedure

Samples were shaken with oxygen for 3 h and then allowed to stand overnight under oxygen before hydrolysis.

##### 4. Product analysis

The products were hydrolyzed with 20% hydrochloric acid and after separation and drying (Na<sub>2</sub>SO<sub>4</sub>) were analyzed by gas chromatography. The starting Grignard reagents used were also analyzed after hydrolysis. Columns with 25% tricresyl

phosphate on Celite at 145–155°, and 25% Apiezon L on Celite at 155° were used.

Some internal standards not commercially available were prepared for the GLC analysis. 1,1-Diphenylethylene was obtained by dehydration of 1,1-diphenylethanol (prepared after Klages<sup>12</sup> from benzophenone and MeMgI). 1,1- and 1,2-diphenylethanes were produced by catalytic hydrogenation of the corresponding unsaturated compounds with Raney nickel in methanol solution.

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