

THE FORMATION OF GRIGNARD COMPOUNDS—II<sup>1</sup>

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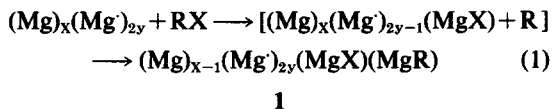
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**Abstract**—Detailed investigations of CIDNP phenomena during Grignard formation reactions are reported. CIDNP was found in the main product RMgX, as well as in the byproducts R(H) and R(-H) and in one case in the starting halide, *i*-C<sub>3</sub>H<sub>7</sub>I. The radical pair  $\bar{R} \cdot \bar{R}$  is shown to be involved in the formation of the polarized products. Furthermore it is proposed that the first step in the reaction sequence is a one electron transfer from magnesium to the organic halide to form the radical anion R-X<sup>⊖</sup> which dissociates rapidly to furnish radical R.

## INTRODUCTION

Based on chemical and physical evidence, it is generally accepted that radicals occur during the Grignard formation reaction, i.e. the reaction of magnesium with organic halides in ethereal solvents.<sup>2-7</sup> However, in all these reports neither the first reaction step between magnesium and halide nor further details of the mechanism leading to these radicals are well defined or clearly described.

Kharasch and Reinmuth<sup>3</sup> suggest, based on earlier experimental evidence, the existence of "points of unsaturation" on the magnesium surface, (Mg)<sub>x</sub>(Mg)<sub>2y</sub> with  $x \geq 2y$ , which cause the following reaction:



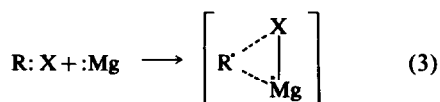
The authors probably suggest the occurrence of a transient stage (1) with two independent species containing unpaired electrons, which on reaction regenerate the points of insaturation.

Anteunis and Van Schoote<sup>5</sup> describe the first step at an "active" site of magnesium as the transfer of one electron to the absorbed organic halide molecule:

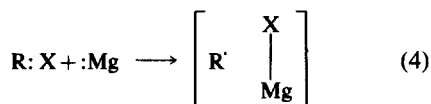


thus generating a phenyl radical and a bromine anion.

Similarly Walborsky and Young<sup>6</sup> suggest that magnesium either transfers an electron to the alkyl halide absorbed on the magnesium surface to give a "tight radical pair":



or reacts directly with the alkyl halide to give a "loose radical pair":



It should be mentioned however that the "tight radical pair" in Eq. (3) is not the direct product of a one electron transfer from magnesium to the halide as stated by the authors, but must be formed in a reaction step following electron transfer. In fact Anteunis and Van Schoote<sup>5</sup> do postulate such a one electron transfer, but their formulation in Eq. (2) is not at all clear.

In a preliminary report<sup>1</sup> we presented direct proof for the occurrence of radicals in the Grignard reaction by means of Chemically Induced Dynamic Nuclear Polarization (CIDNP). From the radical pair theory of CIDNP<sup>8</sup> it is clear that CIDNP phenomena in reaction products are a proof for the occurrence of radical pairs as intermediates for these products. Contrary to ESR spectroscopy CIDNP phenomena reflect properties of products derived from radicals and they can be observed during a period which is much longer than the lifetime of the radicals. In fact, in spite of many attempts, radicals in Grignard reactions have never been measured by means of ESR spectroscopy, presumably due to their low steady state concentration; therefore CIDNP provides the first direct physical method to detect these transient radicals.

We now wish to report the results of more detailed investigations of CIDNP phenomena during Grignard reactions and based on these results, we propose a detailed scheme for the reactions leading to Grignard compounds as well as to by-products.

## RESULTS AND DISCUSSION

Chemical evidence for the occurrence of radicals during the formation of Grignard compounds\* is provided amongst others by the formation of combination and disproportionation products of the alkyl entities, i.e. R-R, R(H) and R(-H).

During the reaction of magnesium with organic halides a multiplet effect is observed in the  $^1\text{H-NMR}$  spectra of the Grignard compounds as well

\*For the sake of simplicity of the discussion at this stage no distinction is made between the possibilities that the Grignard compound  $\text{RMgX}$  is formed directly or via  $\text{R}_2\text{Mg-MgX}_2$ .

as of several other products. Table 1 presents the results obtained with different halides in tetrahydrofuran (THF) and in di-n-butyl ether (DBE).

In Fig 1 a typical  $^1\text{H-NMR}$  spectrum is given in which CIDNP is observable in the  $\alpha$ -protons of n-propylmagnesium iodide and in the olefinic protons of propene during the reaction of 1-iodopropane with magnesium in DBE, (run 4, Table 1).

The absence of CIDNP signals in  $\text{RMgX}$  in solutions containing both Grignard reagent and alkyl halide as well as the fact that the signals subside immediately after the magnesium crystals have been used up by an excess of alkyl halide prove that the observed signals are in fact directly

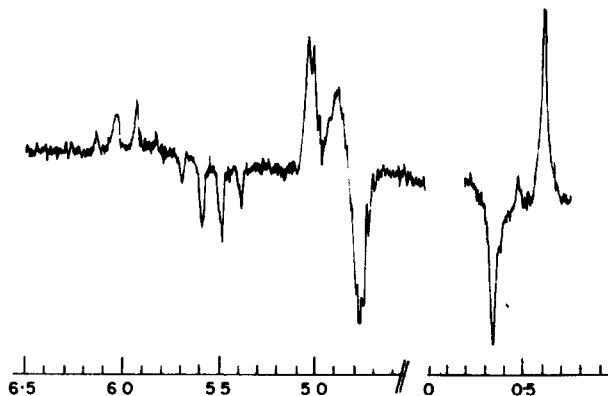


Fig 1. 60 MHz  $^1\text{H-NMR}$  spectrum obtained during the reaction of 1-iodopropane with magnesium in DBE,  $\delta(-0.35)$ - $(-0.65)$ :  $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr}$ ;  $\delta 4.70$ - $6.15$ :  $\text{CH}_2=\text{CH}-\text{CH}_3$ .

Table 1. Characteristics of the 60 MHz CIDNP spectra obtained during the reaction of magnesium with organic halides in THF or DBE

Run	Halide	Solvent	RMgX		R-R	R-H	R(-H)	R-X
			RMgX	Yield in %				
1	MeI	DBE	$\text{CH}_3\text{MgI}$	N 95	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>
2	EtBr	DBE	$-\text{CH}_2\text{MgBr}$ ,	E/A 90 (DBE)	— <sup>a</sup>	— <sup>a</sup>	$\text{CH}_2=\text{CH}_2$ , N	— <sup>a</sup>
		and THF	$\text{CH}_3-$ ,	E/A <sup>b</sup> 93 (THF)				
3	EtI	DBE	$-\text{CH}_2\text{MgI}$ ,	E/A 86	— <sup>a</sup>	— <sup>a</sup>	$\text{CH}_2=\text{CH}_2$ , N	$-\text{CH}_2\text{I}$ , N
4	PrI	DBE	$-\text{CH}_2\text{MgI}$ ,	E/A 86	— <sup>a</sup>	— <sup>a</sup>	$\text{CH}_3\text{CH}=\text{CH}_2$ , A/E	$-\text{CH}_2\text{I}$ , N
5	i-PrI	DBE	$-\text{CH}(\text{MgI})-$ ,	E/A 71	— <sup>a</sup>	— <sup>a</sup>	$\text{CH}_3\text{CH}=\text{CH}_2$ , A/E	$-\text{CH}(\text{I})-$ , E/A <sup>c</sup>
6	n-BuI	DBE	$-\text{CH}_2\text{MgI}$ ,	E/A 71	— <sup>a</sup>	— <sup>a</sup>	$\text{C}_2\text{H}_5\text{CH}=\text{CH}_2$ , A/E	$-\text{CH}_2\text{I}$ , N
7	i-BuI	DBE	$-\text{CH}_2\text{MgBr}$ ,	E/A 71 (DBE)	— <sup>a</sup>	$(\text{CH}_3)_2\text{CH}$ , A/E	$(\text{CH}_3)_2\text{C}=\text{CH}_2$ , A/E	$-\text{CH}_2\text{Br}$ , N
		and THF		67 (THF)				
8	MeCH(Br)Et	THF	$-\text{CH}(\text{MgBr})-$ ,	E/A 71	— <sup>a</sup>	— <sup>a</sup>	$\text{C}_2\text{H}_5\text{CH}=\text{CH}_2$ , A/E	$-\text{CH}(\text{Br})-$ , N
9	PhBr	THF	$\text{C}_6\text{H}_5\text{MgBr}$ ,	N 96	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
10	PhCH <sub>2</sub> CH <sub>2</sub> Br	THF	$-\text{CH}_2\text{MgBr}$ ,	E/A 98	— <sup>d</sup>	— <sup>d</sup>	— <sup>d</sup>	— <sup>d</sup>

The phase of the multiplets given concerns the spectra of the underlined protons. The positions of the signals are given in the experimental part. N indicates that no polarization was found.

<sup>a</sup>Spectrum coincides with other signals (e.g. signals of the solvent).

<sup>b</sup>This experiment was performed in THF-*d*<sub>6</sub>.

<sup>c</sup>The same results were obtained when I<sub>2</sub> was added; CIDNP was much stronger in that case (Fig 2).

<sup>d</sup>That particular part of the spectrum was not investigated.

<sup>e</sup>No indication of CIDNP was obtained, although the interpretation of the aromatic region was complicated by coincidence of signals.

connected with the formation reaction and are not due to secondary reactions such as metal halogen exchange.<sup>9,10</sup>

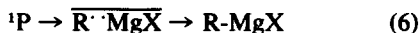
Kaptein, Closs and Lawler<sup>8,11</sup> have formulated rules to predict the phase of CIDNP spectra which are valid only for spectra run in a high magnetic field. The phase of the multiplet (absorption at low field and emission at high field: A/E, or the reverse: E/A) is given by the sign of the product of six parameters,\* each of which can be positive or negative:<sup>8a, 8b, 11</sup>

$$\Gamma_m = \mu \cdot \epsilon \cdot A_i \cdot A_j \cdot J_U \cdot \sigma_U \quad (5)$$

If  $\Gamma_m$  is positive the phase of the multiplet will be A/E and if  $\Gamma_m$  is negative E/A.

For the <sup>1</sup>H-NMR spectra of the Grignard compounds listed in Table 1,  $A_i$ <sup>12</sup> is negative whereas  $A_j$ <sup>12</sup>,  $J_U$ <sup>13</sup> and  $\sigma_U$  are positive. The experiments show that the phase of the multiplet spectra is E/A, so  $\Gamma_m$  is positive and from Eq. 5 it follows that  $\mu \cdot \epsilon$  is negative (+ =  $\mu \cdot \epsilon \cdot - \cdot + \cdot + \cdot +$ ).

Consequently, two different cases for the radical pair involved have to be considered. In the first case polarized RMgX is formed by a combination reaction of a radical pair ( $\epsilon$  is positive) with a singlet precursor state (<sup>1</sup>P) of this radical pair ( $\mu$  is negative). So the radical pair involved has to be  $\overline{R \cdot} \cdot \text{MgX}$  or  $\overline{\text{RMg} \cdot} \cdot \text{X}$ , according to Eqs. 6 and 7:



As it is unlikely that the difference in  $g$ -factor,  $\Delta g$ , in any of the radical pairs will be nearly zero,† a net effect should be observed in this case.

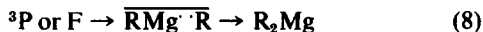
In none of the spectra, in particular not in the spectrum of MeMgI for which a multiplet effect

\*We adopt here the representation of Eq. 5 as given by Kaptein:<sup>8b, 11</sup>  $\mu$  is positive for pairs from triplet precursors or from free radicals and  $\mu$  is negative for singlet precursors.  $\epsilon$  is positive for combination and disproportionation reactions and  $\epsilon$  is negative for transfer reactions.  $\sigma_U$  is positive when the nuclei belong to the same radical and negative when this is not the case.  $A_i$  and  $A_j$  are hyperfine coupling constants and  $J_U$  is the corresponding spin coupling constant in the product.

†The only available  $g$ -factor of magnesian halides is that of FMg<sup>14</sup> ( $g_{\parallel} = 2.0020$  and  $g_{\perp} = 2.0010$ ). Here the  $g$ -value lies close to the value for the free spin. Going to the heavier halogens one would expect a larger  $g$ -value because the electron can be better delocalised in these cases. In fact in the gas phase reaction of Mg and I<sub>2</sub>, the ESR-spectrum of the solid, deposited on the magnesium crystals, consisted of 6 lines, all of the same intensity, with  $A = 35.5$  gauss and with  $g = 2.0069$  (we thank H. H. Grootveld, T. H. Gerner, and C. Gooijer for the communication of these unpublished results). There was no anisotropy in the spectrum. It is not clear at the moment whether this spectrum is due to IMg.

is precluded, we have ever observed any indication of what might be interpreted as a net effect. On the basis of this evidence it is highly unlikely that the polarization of the alkyl entity takes place in the radical pairs of Eqs. 6 or 7.

In the second case the radical pair has a triplet precursor state (<sup>3</sup>P) or was formed from free radicals (F), ( $\mu$  is positive). Apart from the radical pairs given in Eqs. 6 and 7 (but now with a triplet precursor state or formed from free radicals) two other possibilities have to be considered:

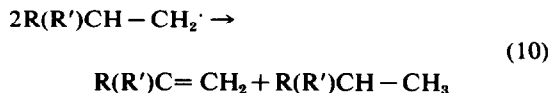


As outlined in the discussion of the first case, radical pairs as given in Eqs. 6 and 7 can be excluded on the base of the lack of a net effect, the same being true for the radical pair given in Eq. 8. The radical pair given in Eq. 9 can be excluded because it represents a disproportionation reaction ( $\epsilon$  is positive) and not a transfer reaction ( $\epsilon$  is negative) as required by the negative sign of  $\mu \cdot \epsilon$ . So the only possibility left, which can account for the polarization of the alkyl entity, is the occurrence of the radical pair  $\overline{R \cdot} \cdot \overline{R}$ .

From the CIDNP spectra of the olefins it can be distinguished whether the radical pair had a triplet precursor state or was formed from free radicals. Each of the <sup>1</sup>H-NMR spectra of propene, 1-butene and 2-methylpropene as well as of the only observable hydrocarbon 2-methylpropane shows the phase A/E, so  $\Gamma_m$  is negative.

Taking propane as an example (Fig 1), it is known that in the  $n$ -propyl radical<sup>12</sup>  $A_{(\alpha\text{-CH}_2)}$  is negative and  $A_{(\beta\text{-CH}_2)}$  is positive and that in propene<sup>13</sup>  $J_{13}$  and  $J_{23}$  are positive,  $J_{12}$  is positive but small and  $J_{14}$  is negative but small, so that as a net result  $J_U$  in Eq. 5 is positive. This leads to:  $- = \mu \cdot \epsilon \cdot - \cdot + \cdot + \cdot +$ , so that  $\mu \cdot \epsilon$  is positive. Using the appropriate parameters for 1-butene, 2-methylpropene and 2-methylpropane the same conclusion can be obtained.

It is well known that two alkyl radicals can form olefins in a disproportionation reaction ( $\epsilon$  is positive):



As in this case a triplet precursor state of the radical pair involved is impossible, the radical pair  $\overline{R \cdot} \cdot \overline{R}$  has to be formed from free radicals ( $\mu$  is positive).

That the polarization in RMgX and in the olefins do arise from a selection process of the same radical pair  $\overline{R \cdot} \cdot \overline{R}$  can be concluded from the sign

reversal of the phase of the multiplet going from the olefins (A/E, disproportionation reaction of the radicals in the radical pair) to the Grignard compounds (E/A, transfer reactions of radicals escaped from the radical pair).

From the intensity of the CIDNP spectra of the Grignard compounds it is impossible to draw conclusions on the amount of  $\text{RMgX}$  formed *via* radical pairs. Since the radical pairs are formed from free radicals they will exist for 25% in the singlet state  $S$  and for 25% in each of the three triplet states  $T_+$ ,  $T_0$  and  $T_-$ . In high magnetic fields only  $S-T_0$  mixing will occur. These two states are equally distributed in the radical pairs, so no net intersystem crossing between  $S$  and  $T_0$  can occur. Only when the singlet state will be depleted, as in our case by reactions leading to  $R-R$ ,  $R(H)$  and  $R(H)$ , the remaining pairs will have more triplet character, giving rise to  $T_0-S$  transitions. The radicals escaping from these pairs will lead to CIDNP in  $\text{RMgX}$ . However these radicals can undergo, apart from the reaction to  $\text{RMgX}$ , other transfer reactions, i.e. hydrogen and halogen abstraction from the solvent or starting halides which makes it impossible to make a quantitative correlation between the polarized Grignard compound on one hand and the polarized disproportionation and recombination products (olefins and hydrocarbons) on the other by means of the intensity of the CIDNP spectra.

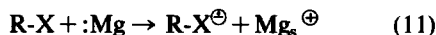
The question arises to what extent radical pairs  $\overline{R} \overline{R}$  are formed. It appears that the polarization of  $\text{RMgX}$  in the weakly basic DBE is 5 to 30 times stronger than in the much more basic THF, whereas titration of the reaction products indicated that the amount of Grignard compound formed are roughly equal in both ethers (Table 1). A reasonable interpretation of these observations is that an increase in basicity of the ether favours solvation of magnesium species which have to be withdrawn from the metal surface to react with a radical  $R\cdot$ . Therefore in weakly basic ethers the possibility of the formation of the radical pair  $\overline{R} \overline{R}$  increases, leading to a stronger polarization in the end product.

It turned out to be difficult to obtain equal intensities in the multiplets in different experiments run under apparently identical conditions. One of the reasons is that relaxation of the CIDNP spectra of the Grignard compounds is very fast, as was evidenced by the asymmetries of the spectra introduced by reversing the scanning direction. Furthermore the reproducibility of the spectra is affected by the heterogeneity of the reactions: the product must diffuse from the metal surface into the solution and further be transported into the cavity. The transport of material by convection depends to a large extent on the boiling of the solvent and on gas evolution, which are quite irregular.

#### MECHANISM AND DISCUSSION

The previous results indicate that radical processes play an important role in the Grignard formation reaction. Based on these results we suggest the following scheme.

The first step in the reaction of an organic halide  $\text{RX}$  with magnesium is the transfer of one electron from the metal to the halide with formation of a radical anion  $\text{R-X}^{\ominus}$  and unipositive magnesium which remains part of the metal surface, as expressed in the notation  $\text{Mg}_s^{\oplus}$ :



Such a one electron transfer will preferably take place on what Kharasch calls "points of unsaturation"<sup>13</sup> and what in more modern terms might be described as points of high electron density at the surface due to irregularities in the crystal lattice. The transfer of one electron to the halide is also assumed by Garst<sup>15</sup> as a first step in the reaction of organic halides with sodium naphthalene solutions and by Hush and Segal<sup>16</sup> for the electrolytic reduction of organic halides. In the latter case it was proposed that an electron is transferred from the metal to the lowest  $\sigma$ -anti bonding orbital of the carbon-halogen bond. According to Lambert<sup>17</sup> during this transfer the carbon-halogen bond has to be parallel to the metal surface. The rate constants of the electrolytic reduction of bromides and iodides appear to be comparable, but the rate constants for the chlorides are many orders of magnitude smaller,<sup>16</sup> a trend in reactivity which parallels that of organic halides with magnesium.

We assume that the radical anion is absorbed at the metal surface e.g. by electrostatic interaction and that it rapidly decomposes according to Eq. 12.  $\text{X}^{\ominus}$  will react with the unipositive magnesium to form the magnesium halide  $\text{XMg}_s$ .



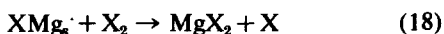
When the radical  $R\cdot$  is still present at the site of electron transfer  $\text{XMg}_s$  will react with it to form the Grignard compound, according to Eq. 14:



It should be noted that the discussion of the CIDNP spectra of the Grignard compounds has made clear that polarization does not arise from radical pairs  $\overline{R}\cdot \overline{\text{MgX}}$ . A reasonable explanation might be that  $\text{XMg}_s$  lacks the required degrees of freedom to take part in singlet triplet mixing in a radical pair  $\overline{R}\cdot \overline{\text{MgX}}$ : this is why we employ the subscript "s" in the radical  $\text{XMg}_s$  to describe it as a surface-bound "non free" radical.

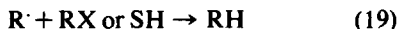
From the solvent effect in the CIDNP spectra mentioned earlier, it seems likely that  $\text{XMg}_6$  is drawn out of the surface by the ether before or during the formation of the carbon-magnesium bond. The reaction to  $\text{RMgX}$  should then be so fast that the conditions for radical pair polarisation are not fulfilled.

When radical  $\text{R}^\cdot$  diffuses away from the site of electron transfer radical  $\text{XMg}_6^\cdot$  may in principle undergo the following reactions:



Comparing the bond energies in the different products and also the reactivity of the radicals  $\text{R}^\cdot$  and  $\text{X}^\cdot$ , one can come to the conclusion that Eq. 15 will be by far more important than Eq. 16. The radicals  $\text{R}$  formed according to Eq. 15 cannot be distinguished from those formed from the radical anion  $\text{R-X}^\ominus$ .

The radical  $\text{R}^\cdot$  which has diffused away from the site of its formation can either abstract hydrogen or halogen from an appropriate molecule:



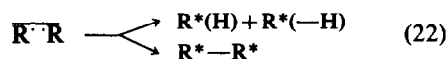
or it can meet another radical  $\text{R}$  to form a radical pair  $\overline{\text{R}^\cdot \text{R}^\cdot}$ , which is responsible for all polarization

observed:



Hydrogen abstraction, Eq. 19, is much more important than halogen abstraction, Eq. 20, because of the larger amount of hydrogen available. In most cases  $\text{X}_2$  will only be present when used as an entrainer for the reaction.

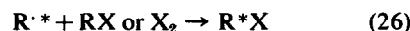
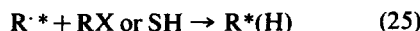
The formation of the radical pair  $\overline{\text{R}^\cdot \text{R}^\cdot}$  in Eq. 21 may lead to combination and disproportionation products, in which CIDNP can be observed, marked by the notation  $\text{R}^*$ :



If no reaction occurs in the radical pair, the radicals will diffuse apart:

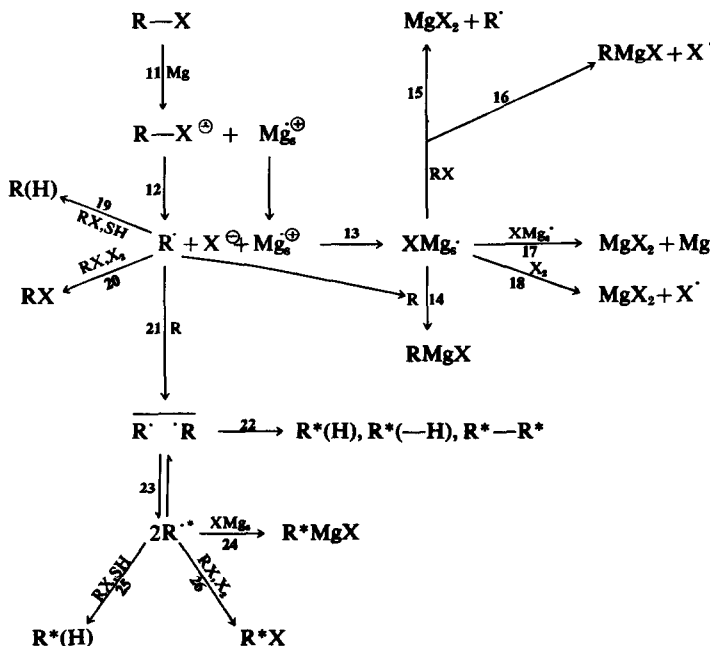


These free radicals may react according to the following transfer reactions:



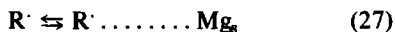
The reality of Eq. 26 is proved by run 5 in Table 1, where polarized  $\text{RX}$  was observed.

The complex of reactions discussed so far is summarized in Scheme 1 (the numbers refer to the equations in the text).

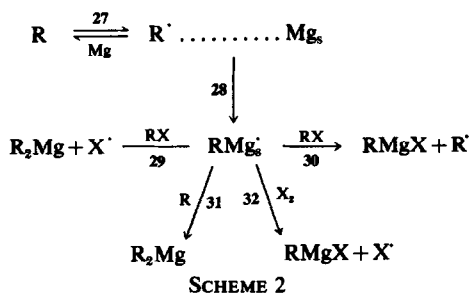


SCHEME 1

Apart from the reactions represented in Scheme 1 it is conceivable that radicals R which do not react immediately further *via* Eqs. (14), (19), (20) or (21) can become attached to the metal with non-localized bonds:



This will be a reversible process because of the small bonding energy, unless a real sigma bond is formed [Eq. 28]. Presumably in the same sense Kharasch<sup>3</sup> discusses the "surface mobility" of radicals. RMg<sub>s</sub> formed in this way will be a short living intermediate which will react immediately as indicated in Scheme 2. The same scheme applies to polarized radicals having escaped from the radical pair  $\bar{R}^{\cdot}R^{\cdot}$ †



In none of the Grignard compounds under investigation could a distinction be made by NMR between RMgX and R<sub>2</sub>Mg. Therefore from the CIDNP spectra we cannot differentiate between the different possible reactions leading to polarized Grignard compounds, especially not between those of Eqs. 24 and 31.

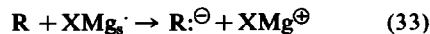
From Schemes 1 and 2, representing a multitude of reactions, it is not easy to decide which of these are to be considered as the major pathways to the different products. Moreover, as stated before, no quantitative conclusions can be drawn from the CIDNP experiments. We feel that the direct reaction at the site of electron transfer [Eqs. 11, 12, 13 and 14] is by far the most important route leading to the Grignard compound.

The following arguments support this statement. In the first place in most cases the yields of RMgX are high, up to 98%, despite the fact that reaction conditions are not what would be considered optimal in a preparative reaction (Experimental). If all of the RMgX was formed *via* radical pairs  $\bar{R}^{\cdot}R^{\cdot}$  one would expect a much lower yield of RMgX because loss of radicals R in combination and disproportionation reactions would be considerable. Secondly, if radical R' does not

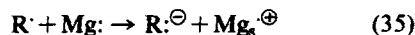
react directly at the site of electron transfer, one would expect much more loss by transfer reactions with hydrogen and halogen [Eqs. 19 and 20]. The only possibility left is that radical R of Scheme 1 is not free, but surface-bound and that the formation of Grignard compound takes place to a large extent *via* reactions represented in Scheme 2. This would imply that the intermediate RMg<sub>s</sub> plays an important role in the Grignard formation reaction. An analogy may be found in the work of Reutov,<sup>18,19</sup> who reported that surface bound RHg radicals do occur during the reduction of RHgX and R<sub>2</sub>Hg at the mercury surface. However, the formation of RMg<sub>s</sub> from a radical R' and the metal surface [27 and 28] will be energetically less favourable than the direct formation of RMgX according to Eq. 14. An argument in favour of this interpretation is provided by the solvent effect in the CIDNP spectra of the Grignard compounds which is more likely in the formation of RMgX according to Eq. 24, than according to the reactions in Scheme 2.

The possibility that polarized R\*MgX is formed by reaction of polarized R\*X with magnesium should not be overlooked. Polarized R\*X is found only in the case of isopropyl iodide with and without addition of I<sub>2</sub> (Table 1 and Fig 2). Therefore, at least in this particular case, it cannot be excluded that this is indeed a source of polarized R\*MgX.

A final remark has to be made concerning the possibility of an ionic character of the Grignard reaction. Prévost *et al.*<sup>20</sup> have considered such an ionic mechanism without the intermediacy of radicals; based on the evidence for radical intermediates we feel that this is not an important pathway to RMgX. However, it is feasible that the reaction of a radical R' with magnesium halide, [Eqs. 14 or 24], takes place either as a one step or as a two step reaction. In the latter case [Eqs. 33 and 34] an ionic mechanism is evident:



Electron transfer to radical R' might of course also take place from the metal surface followed by reaction of the carbanion with magnesium halide:



There is an analogy between the reactions given in Eqs. 33, 34, 35 and 36 and the formation of Grignard compounds in the reaction of organic halides with sodium naphthalene solutions in the presence of MgBr<sub>2</sub>, as investigated by Bank and Bank.<sup>21</sup> Although such an ionic pathway is felt to

†For Eqs. (29), (30), (31) and (32) the same considerations apply as is discussed for (16), (15), (14) and (18) respectively.

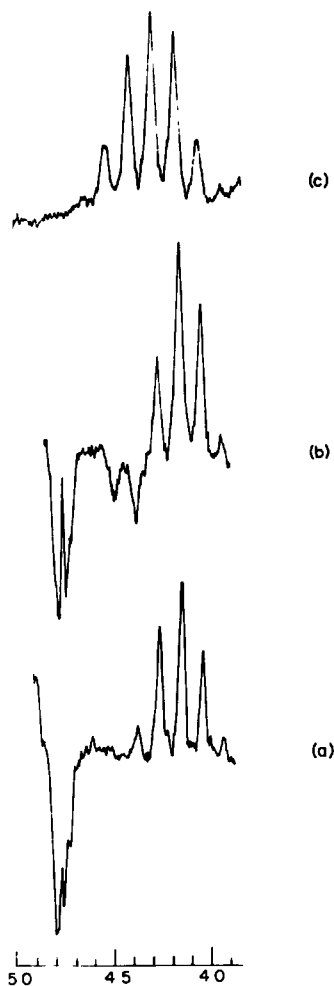


Fig 2. 60 MHz  $^1\text{H-NMR}$  spectrum of *i*-PrI obtained during the reaction of *i*-PrI with magnesium in DBE; A: without addition of  $\text{I}_2$ ; B: with addition of  $\text{I}_2$ ; C: normal spectrum of *i*-PrI in DBE. The emission signals at  $\delta$  4.80 are caused by propene (Fig 1).

be less likely in the normal Grignard reaction, it cannot be excluded at this stage.

The stereochemistry of the Grignard reaction has been investigated and aptly discussed by Walborsky.<sup>6</sup> In general his results can be considered as support for some of the reactions of Schemes 1 and 2.

#### EXPERIMENTAL

For the reactions use was made of magnesium crystals (Specpure<sup>®</sup> from Johnson and Matthey, Chemicals Ltd. London). The organic halides were distilled before use and dried on  $\text{CaCl}_2$ . Tetrahydrofuran (THF) and di-*n*-butyl ether (DBE) were freed from water by distillation from sodium in a sealed apparatus and stored on molecular sieves. In a characteristic run 0.3–1.0 mg-atom magnesium and 0.5 ml of the solvent were introduced into an NMR tube. After  $\text{N}_2$  was led through the ether,

a twofold excess of halide was added, the tube closed (cotton wool, plug or plastic cap) and placed in a Varian A-60 NMR spectrometer. Usually there was an induction period before reaction started. Thus an entrainer ( $\text{I}_2$  or  $\text{C}_2\text{H}_4\text{Br}_2$ ) was sometimes used. Spectra were taken in scans of approximately 30 sec. It was difficult to reproduce the CIDNP spectra exactly because the initiation rate of the reaction and sometimes the reaction rate itself was irreproducible. Moreover, if the rate of the reaction was too high the reproducibility was impaired due to strong gas evolution, boiling of the solvent and the appearance of magnesium particles in the cavity. No use was made of sealed tubes because explosions occasionally occur in the spectrometer. The CIDNP spectra of the olefins could be observed for slightly longer, probably because in this case no underlying normal spectrum was present since the amount of olefin formed was much smaller and, moreover, the olefin rapidly evaporated.

The positions of the protons of the compounds in Table 1, given in  $\delta$  (ppm) relative to TMS, are:  $\text{MeMgI}$ , DBE,  $\delta$  1.30 (s, 3H);  $\text{EtMgBr}$ , THF,  $\delta$  0.64 (q, 2H),  $\delta$  1.18 (t, 3H), DBE,  $\delta$  0.56 (q, 2H);  $\text{C}_2\text{H}_4$ , THF,  $\delta$  5.37 (s, 4H), DBE,  $\delta$  5.27 (s, 4H);  $\text{EtMgI}$ , DBE,  $\delta$  0.62 (q, 2H); *n*-PrMgI, DBE,  $\delta$  0.50 (t, 2H); *n*-PrI, DBE,  $\delta$  3.09 (t, 2H);  $\text{CH}_2=\text{CHMe}$ , DBE,  $\delta$  4.70–5.10 (m, 2H),  $\delta$  5.30–6.15 (m, 1H); *i*-PrMgI, DBE,  $\delta$  0.38 (sept, 1H); *i*-PrI, DBE,  $\delta$  3.95–4.60 (sept, 1H); *n*-BuMgI, DBE,  $\delta$  0.50 (t, 2H); *n*-BuI, DBE,  $\delta$  3.13 (t, 2H); 1-butene, DBE,  $\delta$  4.44–5.02 (m, 2H),  $\delta$  5.23–6.13 (m, 1H), THF,  $\delta$  4.72–5.12 (m, 2H),  $\delta$  5.47–6.22 (m, 1H); *i*-BuMgBr, DBE,  $\delta$  0.25 (d, 2H), THF,  $\delta$  0.33 (d, 2H); *i*-BuBr, THF,  $\delta$  3.51 (d, 2H); isobutane, THF,  $\delta$  0.85 (d, 2H), isobutene, DBE,  $\delta$  4.55 (d, 2H), THF,  $\delta$  4.65 (d, 2H); *sec*-BuMgBr, THF,  $\delta$  0.33 (sext, 1H); *sec*-BuBr, THF,  $\delta$  4.02 (sext, 1H);  $\text{PhMgBr}$ , THF,  $\delta$  7.68 (m, 2H, *ortho*),  $\delta$  7.03 (d, 2H, *meta*),  $\delta$  6.95 (d, 1H, *para*);  $\text{C}_6\text{H}_6$ , THF,  $\delta$  7.25 (s, 6H); biphenyl, THF,  $\delta$  7.20 (s);  $\beta$ -phenylethylmagnesium bromide, THF,  $\delta$  0.22 (t, 2H).

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