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Further Evidence for the Radical Chain Character of Grignard's Reagent Formation. Use of Free Radical Clock in Conjunction with Changes in Concentration of Active Mg.

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Abstract: The reaction of endo-5-(2'-haloethyl)-2-norbornene (X=I, Br, Cl) with active Mg obtained by metal vaporization yields both cyclized and uncyclized organomagnesium compounds. The ratio cyclized / uncyclized increases in the order Cl < Br < I. This ratio decreases when the ratio Mg / RX increases suggesting that the radicals formed by E.T. from Mg to RX may be trapped by Mg at a rate competitive with the rate of cyclization of a norbornenyl radical.

INTRODUCTION

Kinetic and product analysis (including stereochemistry) as well as the study of magnesium surfaces have resulted in the proposition of different mechanisms for the Grignard reagent formation [1-15]. There is a general agreement that the reaction involves the intermediacy of free radicals[16-25] (**Scheme 1**) but there is disagreement concerning the mobility of these radicals during the reaction[26-28].

$$RX + Mg \longrightarrow R^{\cdot} + MgX^{\cdot}$$
$$R^{\cdot} + MgX^{\cdot} \longrightarrow RMgX$$

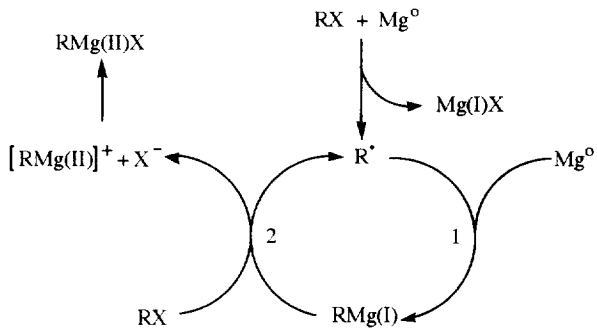
Scheme 1

The question of whether these radicals are adsorbed on the magnesium surface or diffuse freely in solution has currently been discussed[29,30]. Two classes of mechanisms for the Grignard reagent formation, D-model[31] (diffusion) and A-model[29,32] (adsorption), are still under active consideration.

Garst, Deutch and Whitesides[28] have reported that all the radicals diffuse from the magnesium surface into solution and thus are not necessarily adsorbed onto the magnesium surface prior to the formation of RMgX. Their D-model[27,33,34] is based on a mathematical kinetic analysis carried out with existing kinetic data in the literature[35] obtained under homogeneous solution conditions. This kinetic model does not integrate the possibility of a chain mechanism in the production of the Grignard reagent.

Walborsky[29,36,37] has studied the reactions of optically active alkyl halides with magnesium and based his adsorption mechanism on product distributions and stereochemistries observed during the formation of the Grignard reagent. He proposed that the generated radicals could partially maintain their configuration by interaction with the surface of magnesium for some RX. His studies also establish that a given RMgX may be formed simultaneously by two pathways. The first one comes to a direct insertion of magnesium into carbon-halogen bond (polar mechanism). The second one involves radical intermediates which can be directly monitored and lead to a loss of configuration of the carbon linked to X when RX is optically active (SET mechanism). This coexistence of mechanisms will not be addressed in the present report; this does not mean that this duality is not present here but that the radical clocks that we have used lack the structural features necessary to bring information on this point.

Recently, we published the results of the addition of selected inhibitors in the reaction between an alkyl halide and active magnesium obtained by vaporization of metal[38]. For all the selected inhibitors, the inhibition of the Grignard reagent formation was shown by the total absence of consumption of the alkyl halide. The highly reactive form of magnesium and the catalytic quantities of inhibitors used in the reaction allowed us to propose the participation of the following new chain pathway (**Scheme 2**).



Scheme 2

This new perspective may be viewed as an extension of the A-model. Once adsorbed, these radicals would, however, produce an intermediate RMg(I) that could be a better reducing agent than the magnesium surface itself.

The formation of RMg(I) may be viewed as a reversible reaction with an equilibrium constant K, varying widely depending upon the structure of R· and, possibly, the solvent. This reversibility would make possible a mobility of R· from cluster to cluster, or, when a metallic surface is considered would lead to a surface mobility varying with K.

Within Scheme 2 the action of inhibitors may be viewed at the level of the initiation step or any reaction able to compete with steps 1 or 2. For a long time, the action of inhibitors was viewed as a "surface poisoning" effect. We have measured the size of particles obtained in our preparation. The size corresponds to clusters of Mg containing 5 to 30 atoms. This comes to having a concentrate of "active sites" in our solution. Under such circumstances, the old explanation of "surface poisoning" can no longer be applied.

In the initiation step Mg(I)X is formed and this paramagnetic specie is probably able to initiate itself other chain by an S_H2 reaction on RX. The lifetime of these species should widely vary with the nature of X and this point is currently being studied in our group.

We now wish to report further results designed to confirm the formation of the intermediate RMg(I) from the radical R·.

RESULTS AND DISCUSSION

The aim of our work is to carry out the Grignard reaction between alkenyl halide "mechanistic probes" and pure, alkali free, extremely reactive magnesium obtained by vaporization of metal in THF.

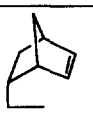
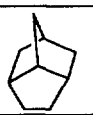
This highly reactive form of magnesium[39] made possible the Grignard reagent formation at low temperature with the advantage of immediate reaction initiation in every case. This outstanding reactivity of magnesium is believed to be due to the "metal surface" (slurry in solution) in the most pure form (absence of metal salts), to the important number of active sites and also, to the conditions of rigorous elimination of oxygen excluding the presence of MgO which could poison the active sites.

The use of cyclizable radical probes has been carried out in order to obtain more informations about the intermediates displayed in scheme 2. Furthermore, the ratio of rearranged to unrearranged products in the reaction, with our active magnesium, could be used as a radical chain indicator by a direct analogy to the ratio obtained in the chain mechanisms established for the reduction of alkyl halides by Bu_3SnH[40-43].

The cyclization of the 5-hexenyl radical to a cyclopentylmethyl radical has been widely used as a mechanistic probe and kinetic standard[35,44]. This probe is known to cyclize irreversibly with a rate constant $k_c=1.0 \times 10^5\ s^{-1}$.

Ashby proposed a faster free radical clock centered on the norbornenyl system[41]. Therefore, we examined the reaction of endo-5-(2-haloethyl)-2-norbornene with magnesium in THF (**Table 1**).

Table 1. Reaction[a] of Endo-5-(2'-haloethyl)-2-norbornene with Mg[b] in THF at Room Temperature

			% relative yields[d]		Ratio of products
expt	X	Time (min)[c]			(uncyc./ cyc.)
1	I	90	43.9	56.1	0.78
2	Br	90	63.7	36.3	1.75
3	Cl	90	85.4	14.6	5.85

[a] All reactions carried out were 4 mmoles of Mg, 1 mmol of halide and then quenched with 10% HCl

[b] Mg activated by vaporization

[c] Reaction time : addition (30 min) + stirring (60 min)

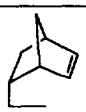
[d] Relative yields were based on the total yields of cyclized and uncyclized products[e] and were determined by GC with toluene as internal standard

[e] In all experiments, cyclized and uncyclized products resulted in 98 ± 2 % yield. Yields correspond to an average value obtained by 3-4 determinations

The cyclization rate of the endo-5-ethyl-2-norbornene radical was calculated to be approximately 1.0×10^7 s^{-1} by Ashby and Pham[41]. So, we were not surprised to find that endo-5-(2-haloethyl)-2-norbornenes give large proportions of cyclization product. The extent of formation of cyclized hydrocarbon follows the order RI > RBr > RCl which could be consistent with a S.E.T. initiation[15,45,46] and, possibly, with a competition polar versus SET process with the former being the most important for RCl.

A critical test for the high reactivity of our magnesium involves the quenching of the reaction immediately after the addition of endo-5-(2-iodoethyl)-2-norbornene (expt. 1, **table 2**). This quenching shows that within 3 minutes, the reaction of Grignard reagent formation is over. Entries 3 and 4 show that this reagent stays stable within the time of our experiments. This result converges with Kossa' s report[47] which studied the rates of cyclization in formed Grignard reagents and found constants in the range of 10^{-6} s^{-1}.

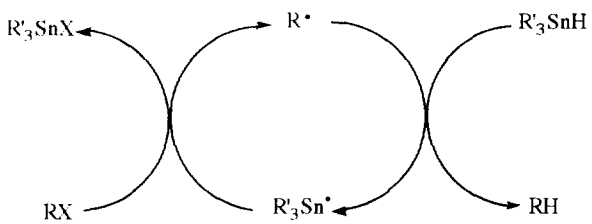
Table 2. Effect of Time on the Reaction[a] of Endo-5-(2'-iodoethyl)-2-norbornene with Mg[b] in THF at Room Temperature

		% relative yields[d]		Ratio of products
expt	Time (min)[c]			(uncyc./ cyc.)
1	<3[f]	44	56	0.79
2	30	44	56	0.79
3	60	43.8	56.2	0.78
4	90	43.9	56.1	0.78

a,b,c,d,e see footnote in Table 1

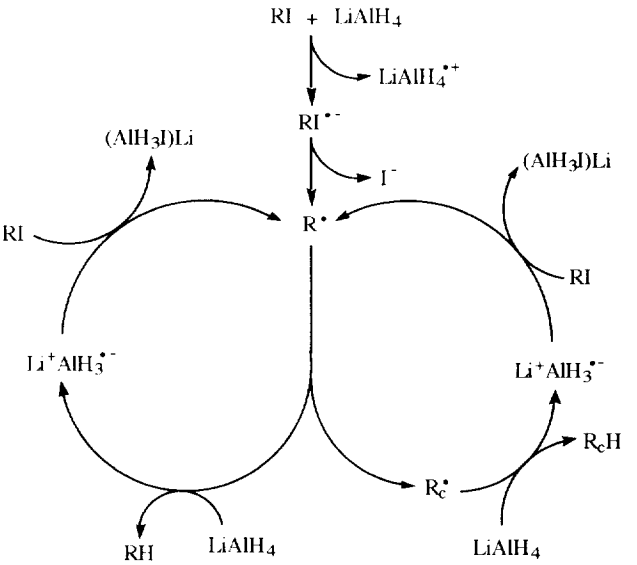
[f] After addition, the reaction was quenched immediately

In a report by Whitesides[40,43], rate-structure profiles were compared for the reduction of alkyl chlorides with tri-n-butyltin hydride and for the heterogeneous reaction of the same alkyl chlorides with magnesium. Linear correlations of the relative rate constants of reactions between alkyl chlorides of changing reactivity and magnesium with the relative rate constants of reactions between the same alkyl chlorides and tri-n-butyltin hydride were obtained. The similarity of the rate-structure profiles obtained in both cases, suggested that the carbon-halogen bond is significantly broken in the transition state for both types of reactions. Although the report by Whitesides did not propose a chain mechanism for Grignard reagent formation, these results could also hint at a similarity between the established R'_3SnH chain mechanism (**Scheme 3**) and a chain mechanism for the reaction of magnesium with the studied alkyl halides (**Scheme 2**).



Scheme 3

On the other hand, Ashby[45] proposed a chain mechanism (**Scheme 4**) for the reduction of the 5,5-dimethyl-6-iodo-1-hexene (RI) by $LiAlH_4$.



Scheme 4

The support for the hydrogen atom abstraction radical chain process was based on the increased amount of RH (3.3% to 9.4% to 15.2%) with respect to that of R_cH as the $LiAlH_4$:RI ratio was increased from 0.1:1 to 1:1 to 1:5, showing that the radical $R^\bullet$ is quenched with $LiAlH_4$ at a faster rate than the cyclization of $R^\bullet \longrightarrow R_c^\bullet$.

The results gathered in table 3 are compatible with a mechanism for the reaction of RX with Mg (**Scheme 2**) occurring by a chain process comparable to the one shown in scheme 4. If the interception of initially formed radicals by Mg were competitive with cyclization, the increase of the magnesium to alkyl halide (RX) ratio should increase the number of sites at which $R^\bullet$ can react, and should then increase the amount of uncyclized product. The faster the reaction 1 (**Scheme 2**), the smaller would the amount of uncyclized product be.

The uncyclized / cyclized product ratio (**Table 3**) follows an approximately linear dependence on the amount of magnesium. This evidence, taken alone, is not necessarily compelling as pointed out by one of the referees. Indeed, Bickelhaupt[48] recently showed that a possible fate for a radical $R^\bullet$ (scheme 2) is further reduction to R^- by Mg°. If this reaction applies to our radical clocks, when higher amounts of magnesium are present in the medium, higher concentrations of R^- should be formed. As Richey and Rees[49] showed that cyclization rates of R^- are far smaller than the rates of cyclization of the corresponding $R^\bullet$, the overall result would also be smaller concentration of cyclized RMgX. We believe, however, that the convergence of our radical chain mechanism with the effects of inhibitors, added to the report by Whitesides[50] which indicates that free carbanions are not intermediates in the formation of the Grignard reagent suggest that our explanation (chain

mechanism) still fits better with the overall set of known facts. We are presently searching specific intermolecular traps able to definitely settle this point.

Table 3. Effect of Ratio Mg/RX on the Reaction of Endo-5-(2'-haloethyl)-2-norbornene with Mg[b] in THF at Room Temperature

				% relative yields[d]		Ratio of products
expt	X	Time (min)[c]	Ratio Mg/RX			(uncyc./ cyc.)
1[a]	I	90	0.8	4.8	95.2	0.05
2	I	90	4	43.9	56.1	0.78
3[a]	Br	90	0.8	42	58	0.72
4	Br	90	4	63.7	36.3	1.75
5	Br	90	10	80.1	19.9	4.03

[a] Yields were based on the percent of endo-5-(2'-haloethyl)-2-norbornene that reached ≈80%
b,c,d,e see footnote in Table 1

When the magnesium / RX ratio is 0.8:1 (expt. 1,3), the major product is the cyclic one (95.2 % and 58 %, respectively, for RI and RBr). Increasing the magnesium / RX ratio to 4:1, leads to an increase of yield of the straight-chain product (expt. 2,4). If even more magnesium is employed (ratio of Mg / RX = 10:1) (entry 5), the uncyclized product proportion increases even more. This behaviour is similar to the one reported by Barreau and Julia[51] for the archetype of electron transfer induced chain reactions. In the reaction between the nitronate anion and a para-nitrobenzylic chloride including a free radical trap linked to the benzylic carbon, these authors could not find cyclized products despite of the clear participation of a para-nitrobenzylic radical in this reaction. This observation was rationalized by suggesting that this radical was reacting faster intermoleculary with the nitronate anion than it was reacting intramoleculary on the double bond. This interpretation was confirmed by performing the same reaction under phase transfer conditions; then the relative amount of nitronate was considerably decreased in the organic phase. Under these conditions, the product resulting from the intramolecular cyclization of radical intermediate was formed in higher amounts.

These results strongly suggest that RMg(I) is an intermediate in the chain mechanism proposed for the Grignard reagent formation (**scheme 2**). The proposed chain is probably rather long because radical-radical coupling products were never observed under our conditions. Although RMg(I) species have not yet been observed spectroscopically, preliminary calculations based on the functional density approach suggest not only that such species may have a finite lifetime but also that they should be better reducing agents than the homologous clusters of Mg.

Acknowledgment. We thank Prof. E.C. Ashby for providing us with the private communication on the synthesis of the endo 5-(2-haloethyl)-2-norbornene. This work was supported by an EC grant in the programme Science.

EXPERIMENTAL SECTION

GENERAL

^1H NMR (200 MHz) spectra were recorded in $CDCl_3$ solution, unless specified on a Bruker AC200. All chemical shifts are reported in ppm (δ) downfield from internal tetramethylsilane (TMS).

Fully decoupled ^{13}C NMR (50 MHz) spectra were recorded in $CDCl_3$ solution on a Bruker AC200. The center peak of $CDCl_3$ (77.0 ppm) was used as the internal reference.

IR spectra were recorded on a FT-IR Nicolet MX-S instrument.

The GC analysis were performed on a Carlo Erba Model GC 8000 chromatograph using a DB1 capillary column (J & W Scientific, 30m x 0.32mm ID) with nitrogen as carrier gas, a flame ionization detector; toluene was used as internal standard. Peak areas integrations were performed by electronic integration on a Spectra Physics Chromjet integrator. All analysis results were corrected by the calculation of flame ionization detector relative response factors using the effective carbon number concept[52].

Liquid chromatographic purifications were performed by flash column chromatography using glass columns packed with Merck silica gel 60 (70-200 μm).

Low temperatures were obtained by utilizing liquid air / methylcyclohexane baths.

The prepurified grade argon (Linde) was further purified by passage over a column of molecular sieves (3Å), a BASF R3-11 catalyst column at 150 °C and a phosphorus pentoxide column (Mallinckrodt® aquasorb®).

For the reaction without oxygen, all liquid substrates and solvents were degassed by freeze-pump-thaw cycles before being used in the reaction.

All manipulations were conducted under an atmosphere of purified argon by standard Schlenk techniques. All glassware and transfer needles were oven-dried at 150 °C and cooled on a dual manifold vacuum / argon system just prior to use.

Tetrahydrofuran (S.D.S., 99.5%), diethylether (S.D.S., 99.7%) and benzene (Carlo Erba, 99.5%) were dried by refluxing and distilling from sodium under an atmosphere of purified argon immediately before use.

Pyridine (Carlo Erba, 99.6%) was dried by reflux and distillation from KOH before use.

Paraformaldehyde (Aldrich, 95%) was dried over P_2O_5 before use.

Acetone (S.D.S., >99.7%) and dichloromethane (S.D.S., 99.9%) were dried on $CaCl_2$ and distilled. 6-Bromo-1-hexene (Aldrich, 98%) and methyl acrylate (Aldrich, 99%) were fractionnaly distilled before use. $LiAlH_4$ (Fluka, >97%), p-toluene sulfonyl chloride (Aldrich, 99+%), $AlCl_3$ (Aldrich, 99%), LiBr (Aldrich, 99+%), NaI (Aldrich, 99+%), LiCl (Aldrich, 99+%), AIBN (Jansen, 98%) and n-Bu_3SnH (Aldrich, 97%, under argon) were used as received. Magnesium chips (Aldrich, 99.95%) and magnesium pieces (Cerac, 99.99%, 0.4-1.7 mm) were stored under argon.

Cyclopentadiene was obtained by distillation from dicyclopentadiene (Aldrich, 95%). It was used immediately or stored in the ice compartment of a refrigerator overnight.

The endo-5-(2-haloethyl)-2-norbornene (X= I, Br, Cl) were prepared by use of published procedure[41].

Authentic samples of the reaction products (endo-5-ethyl-2-norbornene and tricyclo [4.2.1.0^{3-9}] nonane were obtained from published procedures[53].

1 Description of the rotary metal atom reactor

Extremely reactive small-sized magnesium clusters were obtained by vaporization of the metal in a rotary metal atom reactor.

Our home-made apparatus, derived from the Green's reactor[54] is a small-sized "bench top" type model equipped with a three-liters round-bottom flask. Pitch of the vessel is adjustable from 45° (cocondensation reactions) through about 20° (solution reactions) to the horizontal (recovery of reaction mixtures). The speed of rotation is controllable from 6 to 80 rpm. The 100 mm i.d. ("Borex" equipped with o-ring flange) of the flask allows us the installation of water-cooled shields to stop in five directions the radiant heat emitted by the crucible.

Good vacuum performances were obtained by the utilization of a 200 l / s oil diffusion pump, with a 63 mm butterfly valve, backed by a two stage 15 m^3 / h mechanical vacuum pump. The liquid nitrogen-cooled glass trap, between the diffusion pump and the reactor, was specially designed to obtain a high speed pumping. The built-in rotary sealing system includes two 55 mm i.d. proprietary graphite-teflon rotary seals with differential pumping.

All the feedthroughs were specially designed and utilize viton o-rings. A continuous temperature monitoring system allows one to follow and adjust the temperature of the liquid reaction mixture inside the reactor. Reactants can be injected into the reaction vessel as gas or liquid by means of two 1/4" inlet lines.

For the vaporization of magnesium, we utilized a 2.1 ml alumina-coated Sylvania integral crucible (CS-1011).

2 Procedure for preparation of Mg/THF slurry

In a typical experiment, the crucible was loaded with up to 3 g of magnesium pieces, the round-bottom flask fitted on the stainless steel rotary flange was evacuated to 66 10^{-3} mbars.

Then, 200 ml of distilled and degassed THF were injected, under static vacuum, into the reactor rotated at 20 rpm and was cooled to -110 °C with a methylcyclohexane bath cooled by liquid nitrogen circulating in a heat exchanger.

A new liquid film cooling system of the upper part of the reactor makes it possible to maintain a low vapor pressure of the THF and largely reduces pyrolysis from the source. This allows the formation of clean, extremely reactive magnesium clusters.

The butterfly valve was opened when the temperature inside the reactor was below -105 °C.

The metal was evaporated by resistive heating (21 amp) of the crucible within one hour and a half under a 66.10^{-5} mbars pressure. At the end of the vaporization, the reactor was isolated and returned to atmospheric pressure with purified argon. The dark-black suspension of magnesium clusters in THF was transferred to the storage Schlenck tube (equipped with greaseless stopcock and teflon screwcap) via a 1/4" teflon transfer tube under positive argon pressure.

The so-obtained finely divided and extremely reactive magnesium can be stored in solution under argon for months at room or lower temperature.

3 Manipulation of the active Mg under inert atmosphere

For the reactions using the Mg/THF slurry, it was possible to determine exactly the amount of magnesium. The first time, a rough estimate of the magnesium transferred to the weighed Grignard reaction Schlenck tube was done by shaking the Mg/THF slurry vigorously and quickly pouring off a known volume (with a large teflon transfer needle). Since the total Mg in the total Mg/THF slurry was known, and the total volume of the slurry was known, then the estimate could be made (with the assumption that the Mg was evenly dispersed after violent agitation). The exact determination was done by pumping off the THF, followed by reweighing of the Grignard reaction Schlenck tube and then a known volume of dry, degassed THF was introduced into the Schlenck tube to obtain again a Mg/THF slurry.

4 Grignard reaction of endo-5-(2-haloethyl)-2-norbornene with Mg*

To a dry Schlenk tube equipped with a magnetic stirring bar and flushed with argon, were added a slurry of magnesium (4 mmol) and THF (10 ml). The solution was maintained at room temperature, and a solution of endo-5-(2-haloethyl)-2-norbornene (1 mmol) in THF (50 ml) was added dropwise.
After 30 min of addition, the reaction mixture was stirred for an additional hour and then quenched with 10% HCl. Then, the solution was dried over molecular sieves (4 Å) and analyzed by GC.

5 Effect of time on the Grignard reaction of endo-5-(2-iodoethyl)-2-norbornene with Mg*

In a similar Grignard reaction, the endo-5-(2-iodoethyl)-2-norbornene was added into the Schlenk tube containing the slurry of magnesium (4 mmol).
Aliquots were taken at appropriate times by transferring approximately 1/3 of the reaction mixture by cannula into a vial, capped with a rubber septum stopper, filled with a quenching solution of 10% hydrochloric acid.
The organic layer was separated, dried (molecular sieves 4Å) and analysed by GC.

6 Effect of ratio Mg/RX on the Grignard reaction of endo-5-(2'-haloethyl)-2-norbornene with active Mg

The degassed solution of endo-5-(2'-haloethyl)-2-norbornene (1 mmol) in THF (50 ml) was introduced into the reaction Schlenck tube equipped with a magnetic stirring bar. The required quantity of slurry of active magnesium in THF (10 ml) was added slowly dropwise with a transfer needle into the halide solution at room temperature. The reaction mixture was stirred at room temperature for an additional 1 hour, and then quenched with 10% HCl. The mixture was saturated with NaCl and the organic layer was separated, dried over molecular sieves (4Å). An aliquot of organic layer was analyzed by GC with toluene as internal standard.

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