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Electron Transfer at the Solid Liquid Interface; New Insights on the Mechanism of Formation of the Grignard Reagent

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Abstract: The strong inhibiting effect of trace quantities of selected compounds on the reaction between ultra fine particles of magnesium and alkyl halides in THF strongly suggests that the generally accepted linear mechanism should be replaced by a chain mechanism.The reactivity of batteries of free radical clocks centered on an aliphatic skeleton displays unexpected leaving group effects. Such effects could be rationalized according to a variety of mechanistic schemes.The main ones are: 1) coexistence of polar and electron transfer routes, 2) participation of solvated electrons in the mechanism, 3) gradient of reactivity starting from the magnesium surface to the bulk solution. A series of experiments aiming at a choice between these possibilities is described.

INTRODUCTION

When Grignard died in 1935, more than 6000 reports in the chemical litterature had used the reaction (Ref. 1) that this author had reported in May 1900 (Ref. 2). Since 1935 more than 30000 reports described the use of this Grignard's reagent to obtain a variety of targets (automatic search in Chemical Abstracts). Despite this considerable importance and the efforts of several excellent teams over long periods of time (Refs. 3-18), the mechanism of formation of this reagent is not fully understood. There is, however general agreement on the proposition that electron transfer from the metallic magnesium to the organic halide seems to represent the first elementary act in this reaction. The mechanism described as generally accepted in the reference books is (Refs. 19-22):

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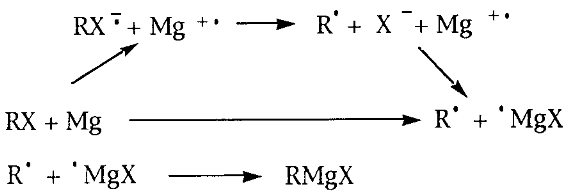


This mechanism is linear: nowhere a catalytic or a chain component does appear. For most of the alkyl halides, it has to be modified because these substrates immediately dissociate upon the addition of an electron (Refs. 23-25). This report describes some new results obtained in our group during the study of this mechanism.

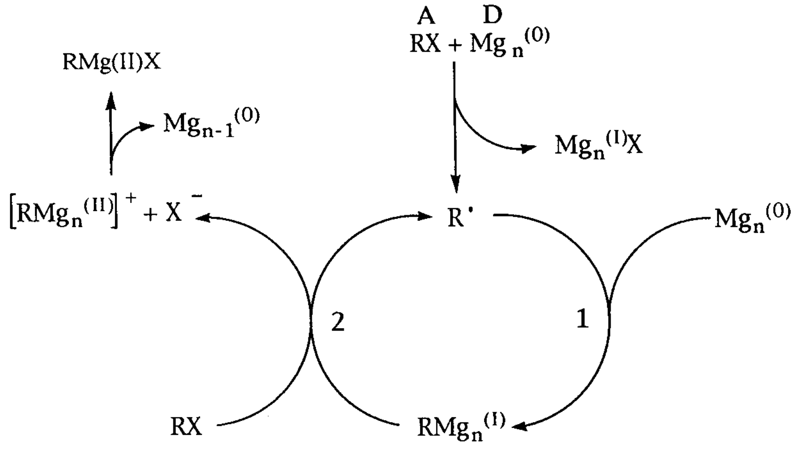
RESULTS AND DISCUSSION

Type of magnesium used

Most of the results reported in this paper have been obtained with a highly reactive form of magnesium. This form of magnesium was prepared thanks to an homebuilt metal vapor atom rotary rector. In such a machine, a 99.9% pure magnesium is vaporized in a crucible and the vapors are condensed at low temperature in a THF solution under the form of ultra fine particles (Ref. 26). Electron microscope measurements of the size of these particules (Ref. 27) show that they are about 4600 times smaller than the ones obtained through Rieke's type of activation (Ref. 28). Klabunde was the first to show the high reactivity of this form of magnesium (Ref. 29) Oppolzer (Ref. 30) and Kundig (Ref. 31) explored some of the synthetic possibilities afforded by this new form of active magnesium (Ref. 32). This form of magnesium is remarkably reactive: for example its reaction at room temperature with the bromo aromatic clock (see below) is over in 90 minutes whereas the trisublimated form of magnesium (kindly provided by Professor Bickelhaupt (Ref. 7) does not react in the same solvent (THF) even when heated at 70° C for more than 10 hours.

Quenching experiments

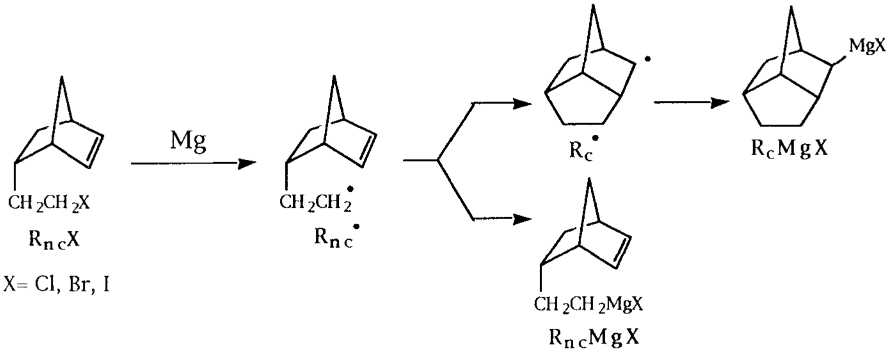
Early results from the litterature (Refs. 33-37) showed that the reaction between turnings of magnesium and alkyl halides could be inhibited by small amounts of selected substances. This quenching was generally admitted to result either from physical coating of surface active sites or from the formation of inactive oxides at the surface of the metal (Ref 21). We have quantitatively revisited the quenching effects exerted by very small amounts of dioxygen, carbon tetrachloride, *para* dinitrobenzene, cupric chloride and benzonitrile when the starting magnesium is the highly divided magnesium described in the preceding paragraph (Ref. 38). The drastic quenchings observed with these ultra fine particules cannot be reconciliated with the classical rationalisation of physical quenching through coating of active sites; a chemical quenching had to be proposed instead. Chemical quenching is one of the most widely used evidences for demonstrating the operation of a chain mechanism in a given reaction (Ref. 39). One of the possible chain mechanisms which can account for chemical quenching effects is (Ref. 38):



In this chain the key active species is the paramagnetic magnesium (I) RMg resulting from the surface reaction between Mg(0) and the alkyl radical formed by the first electron transfer of the mechanism. Fonctional density calculations suggest that this type of species can exist and that they are better reducing agents than Mg(0) clusters or, even more, than metallic magnesium itself (Ref. 40)

Battery of free radical probes (Refs. 41,42)

One of the most conclusive evidences hinting at the active participation of radicals in the formation of Grignard's reagent was provided by experiments using free radical clocks (Ref. 43). These experiments are based on an intramolecular trapping of the postulated transient radical leading to the apparition of rearranged products besides the usual ones if radical intermediates are indeed on the route yielding the products (Ref. 6):

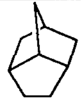


This scheme shows one of the limits of this methodology: the rate of rearrangement must be fast enough to compete with the intermolecular reaction which consumes the radical. Otherwise, the participation of the radical may be missed even if it is an actual intermediate in the reaction. Others possible pitfalls to avoid when using these mechanistic tools are: 1) rearrangements not truly specific of only the radical species searched for (Refs. 44,45), 2) adventitious impurities or side reactions can be responsible for initiation of a radical chain isomerization process misleading the chemist in suggesting that an electron transfer is taking place between a couple of Donor-Acceptor compounds (Ref. 46), 3) search for a radical intermediate within a linear scheme whereas the overall scheme is a chain and the radical is formed in the initiation step by a one electron oxidation of an anion.

The ratio: quantity of rearranged product/quantity of unrearranged product should, in principle, depend only on the relative rates of the intramolecular rearrangement *versus* the rate of the intermolecular reaction. In contrast it should be independant of the nature of X in RX the precursor substrate of the radical species .

Our results, gathered in table I, show that this expectation is not fulfilled with the battery of radical clocks that we used to study the reaction between our reactive magnesium and RX in the reaction:

Tab. 1 . Reaction[a] between Endo-5-(2-haloethyl)-2-norbornene and Mg*[b]

			Yield (%)[c]		
Exp.	X	time (min)[e]			Ratio cycl./uncycl[d].
1	I	90	43.9	56.1	1.3
2	Br	90	63.7	36.3	0.6
3	Cl	90	85.4	14.6	0.2

All the reactions are hydrolysed with a solution of HCl at 10%. Magnesium is in suspension in 10 mL of THF and RX is diluted in 50 mL of THF.

[a] In THF at ambient temperature

[b] Mg* : magnesium activated by vaporization

[c] Relative yields based on the total yields of uncyclized and cyclized products.They are determined by GC with toluen as internal standard.

[d] For all the experiments the total yield (cyclized+uncyclized products) is 98%.The given yields are the average of 3-4 determinations.

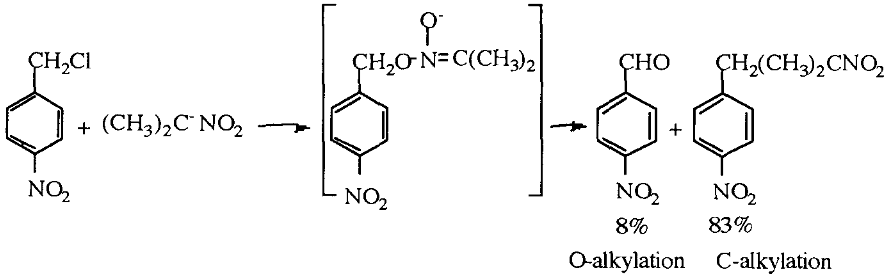
[e] Duration of the reaction: 30 minutes of reaction + 60 minutes of supplementary agitation of reaction .

The iodo substrate clearly displays a higher percentage of rearrangement than the bromo one and the chloro substrate is even less rearranged than these two. How can we explain this unexpected set of results?

Origin of the leaving group effects observed with the free radical clocks

Unexpected leaving group effects have precedents in the chemical litterature. For polar mechanisms they were christened memory effects (Refs. 47-49) and are not fully understood. For electron transfer mechanisms, at least three different mechanistic propositions were formulated to explain their origin.

The first one relies on the coexistence of a polar and a single electron transfer mechanism. It was first proposed by Kornblum (Ref. 50). This author indeed observed that in the reaction between sodium nitronate and various *para* nitrobenzyl halides two main products were formed:



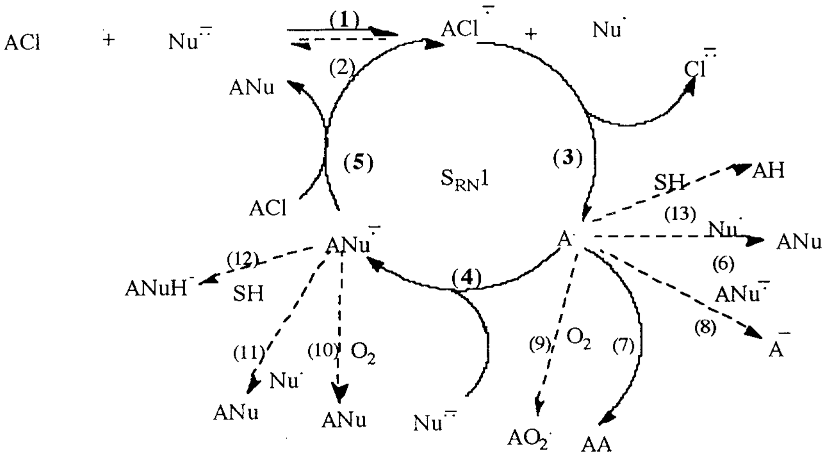
The aldehyde product was proposed to result from a classical SN2 substitution on the benzylic sp3 carbon whereas the product where a C-C bond was formed was proposed to result from a succession of elementary steps triggered by an electron transfer. Even if the original linear mechanism proposed for the electron transfer component of the overall transformation had to be replaced by a chain one two years later (Refs. 52-53) the molecular origin of the selectivity remained the same. It was competition between a polar and a single electron transfer mechanism. In this competition the poorest leaving group on the *para* nitrobenzyl halide was characterized by the highest electron transfer participation.

Tab. 2. Influence of the nature of X in the reaction of $O_2NC_6H_4CH_2X$ with the lithium salt of 2-nitropropane in DMF at -16°C (Ref. 51)

X	C-alk %	O-alk %	$\frac{k \text{ (with } NO_2 \text{ in para)}}{k \text{ (without } NO_2 \text{ in para)}}$
N^+Me_3, I^-	93	0	>100
C_6Cl_5COO	93	0	>100
Cl	95	1	>100
OTos	40	32	8
Br	17	65	6
I	7	81	3

k = rate constant of the global reaction

The highest selectivity in C-C bond formation was observed for the chloro leaving group in the series chloro, bromo, iodo. The overall mechanistic scheme accounting for these observations was a competition between the classical SN2 substitution and the following chain:



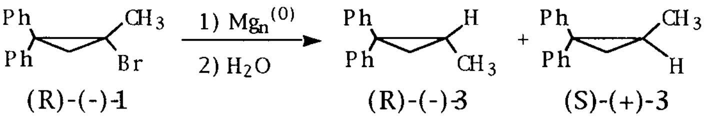
(1) and (2) = Initiation

$$\left.\begin{array}{l}(3) = \text{Dissociation} \\ (4) = \text{Addition} \\ (5) = \text{Transfer}\end{array}\right\} \text{Propagation}$$

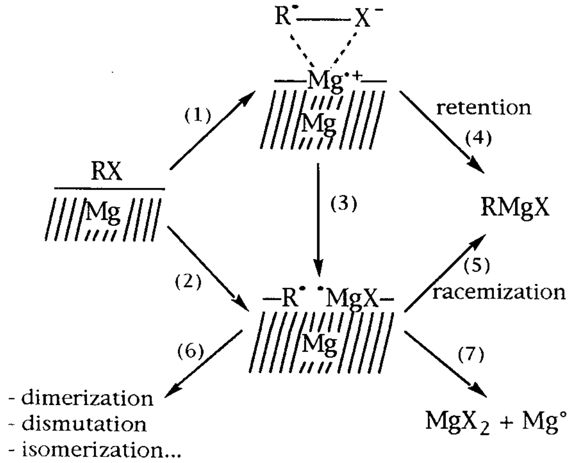
(6),(7),(8),(9),(10),(11),(12) and (13) = Terminations

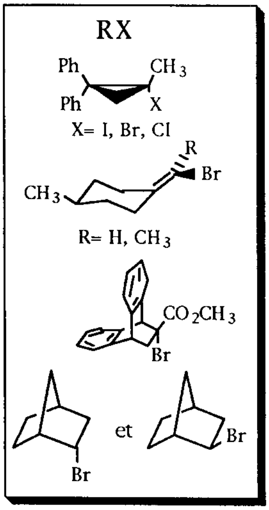
ACl = $p\text{-}O_2NC_6H_4CH_2Cl$
Nu⁻ = $O_2NC(CH_3)_2^-$
ANu = $p\text{-}O_2NC_6H_4CH_2(CH_3)_2NO_2$

One usually admits that the main origin in the change of selectivity is to be searched in the slowest rate of the S_N2 component for the poorest leaving group rather than in a faster rate of electron transfer to the benzyl chloride (Ref. 54). Leaving group effects have also been observed by Ashby's group in the $AlLiH_4$ reduction of hindered alkyl radical clocks. In this work the iodo substrates were yielding the higher proportion of cyclized product in comparison with their bromo homolog (the chloro one being unreactive in this reaction. These results were rationalized by a competition between a polar and a SET pathways (Refs. 55,56).
To explain the stereochemical results for the following reaction and its homologs starting from halogeno substrates (Ref. 57) :



Walborsky proposed also a scheme equivalent to the coexistence of polar and electron transfer pathways in the formation of the Grignard's reagent :





In this scheme, the intimate radical pair displayed at the top corresponds to a polar route. This route would produce a Grignard's reagent with retention of configuration. In contrast, the route centered on solvent separated pairs of radicals - equivalent to the electron transfer mechanism - would lead to racemization in the formed Grignard's reagent. The results reported by Walborsky show that ,within such an explicative framework, the participation of the polar route is more important with the chloride leaving group than with the bromo and even more the iodo. This is the same order as the one shown in table 1 but contrasts with the order found by

Kornblum. Yet, one must notice that the participation of a chain mechanism was never discussed by Walborsky. Such a participation was, before our work, considered only by two authors (Refs. 13,58) .

If one applies the Kornblum's explicative framework to our results and those of Walborsky, one could propose that the reason why the alkyl chloride radical clocks yield less cyclized products than their bromo and iodo counterparts is because the polar route is more important than the electron transfer one for the chloride leaving group. Precedents of the coexistence of polar and electron transfer pathways are known in oxidative additions involving transition metal complexes (Ref. 59). There also, the polar route seems predominant for the chloride in comparison with bromide and iodide (Ref. 60).

In the *para* nitrobenzyl series when small amounts of *para* dinitrobenzene are added to the reaction medium, the electron transfer route is quenched and the only product obtained is the *para* nitrobenzaldehyde (Ref. 50). Thus, if our alkyl halides were behaving equivalently, one should expect that the quenching agents kill the electron transfer route but do not interfere with the polar one. More specifically adding small amounts of carbon tetrachloride to 1-chloro-3-methylbutan should quench only one part of the Grignard's reagent formation. Figure 1, which displays the results of such an experiment of quenching, shows that total quenching can readily be induced in this reaction. Thus the Kornblum's-Walborsky's framework does not seem to apply for rationalizing our leaving group effects.

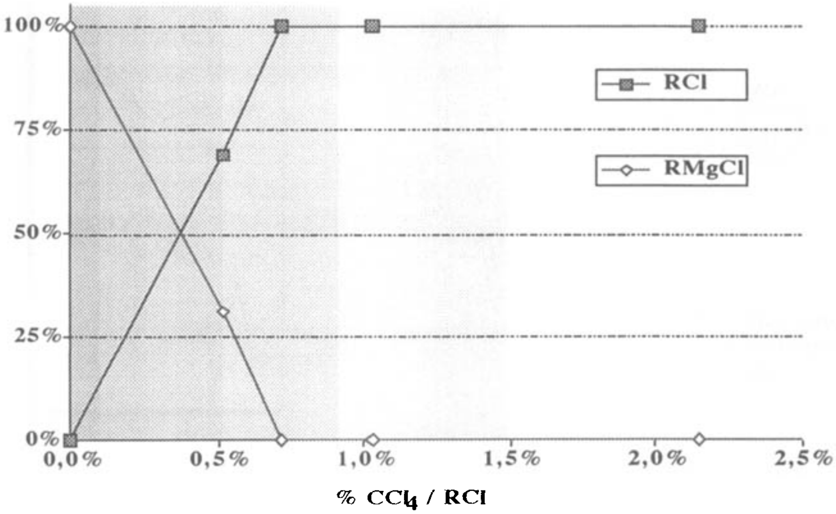
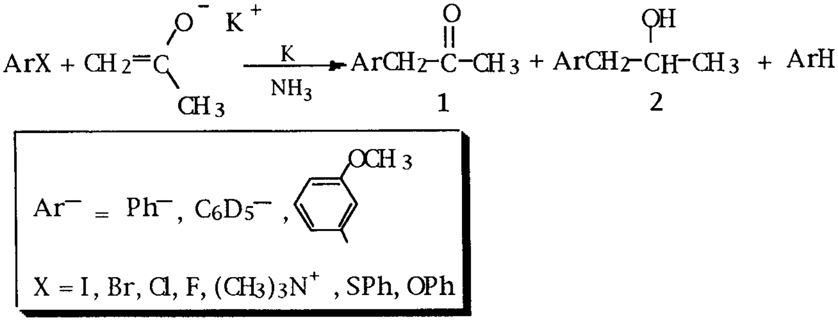
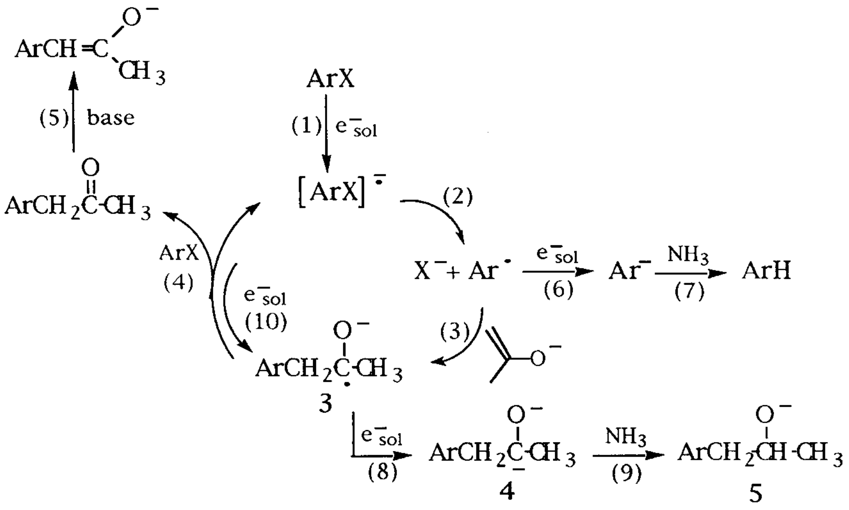


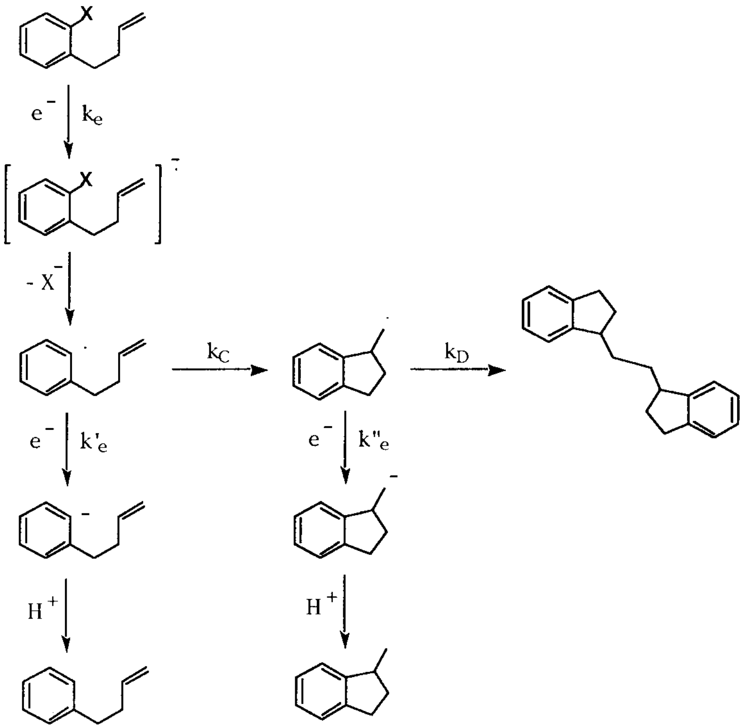
Fig. 1. Quenching effects of CCl_4 on the reaction of magnesium with the chloro aliphatic radical clock

A second type of explanation was initiated by Bunnett's studies on the SRN1 mechanism for aromatic substrates. This author, while studying the reaction of aromatic halides with enolates in liquid ammonia in the presence of metallic potassium, discovered that the quantities of ArH and of the alcohol depended on the nature of X (Refs. 61-62. This was unexpected within a simplistic approach based on the SRN1 mechanism because, in this mechanism, ArH and the alcohol were supposed to be formed in a step chronologically situated *after* the departure of X (step 2) as shown in the mechanistic scheme. Thus the nature of X should have played no role in the relative quantities of these products. Different plausible explanations were examined and the one finally selected was attributing the observed effects to a gradient of concentration of the solvated electrons in the vicinity of metallic potassium particles. This first contribution is also interesting because it contains a critical examination of the possible causes of leaving group effects.



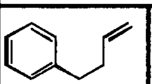
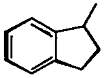
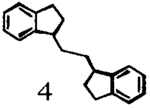


Five years later this author, in collaboration with Beckwith, extended this approach to substrates even closer to the ones presently investigated by our group; indeed these ones were aromatic radical clocks placed in liquid ammonia reacting with any of the three metals K, Na, Li (Ref. 63).



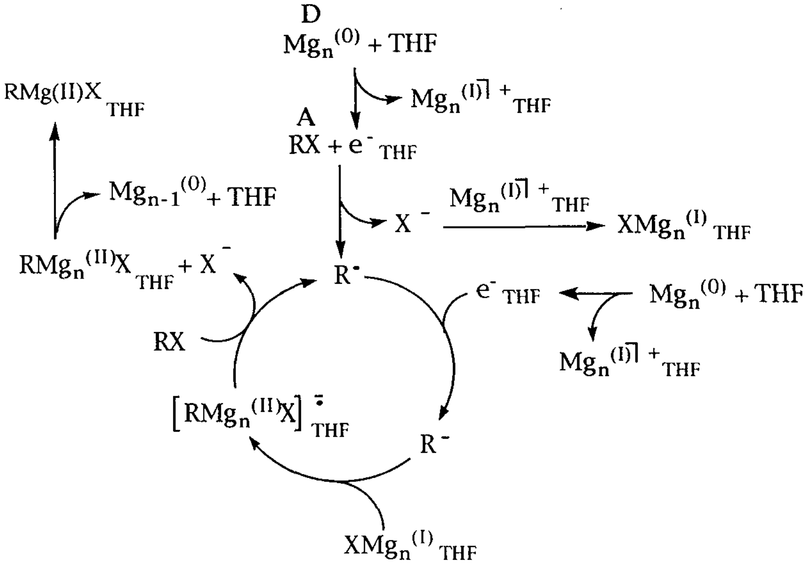
The results, gathered in table 3, closely parallel the ones that we have described in table 1.

Tab. 3 . Reaction between aromatic free radical clocks and the solvated electrons[a]

	Yields (%)				
X	 2	 3	 4	k_e (mol^{-1} s^{-1})	Ratio Cyc (**3** + **4**)/ Uncyc (**2**)
I	7.5	57.7	17.1	2.1 10^{10}	10
Br	9.6	72.1	18.4	1.5 10^{10}	9
Cl	17.6	78.2	3.0	1.9 10^{9}	4.6

[a] 10 mmoles of RX and 22 mmoles of K in 67 ml of NH_3 and 33 ml of *tert*-butylic alcohol at a temperature of -77 °C.

In both series the ratio: concentration of cyclized products/concentration of uncyclized products depends on the nature of X and this ratio is the highest for X=I. To apply the hypothesis of the solvated electron as active species in the formation of the Grignard's reagent one would have to admit that the initial step in the reaction is the solvation of Mg++ and of the electron by THF. One of the possible chains centered on such an hypothesis would be:



Such an hypothesis would provide an interesting explanation of the reason why some Grignard's reagents which could not be directly prepared in diethyl ether were obtained when THF was used as solvent (Ref. 64). Indeed this solvent would better solvate the positive magnesium and would therefore displace the first equilibrium towards the right, increasing therefore the quantity of solvated electrons in solution. The favorable effect of adding amines for the preparation of some Grignard's reagents could also be explained along the same lines (Ref. 65). Furthermore, the more quantitative treatment of the gradient of concentration in solvated electron recently developped by Andrieux and coll. (Ref. 66) would easily explain the trends of reactivity shown in table 1 (Fig.2).

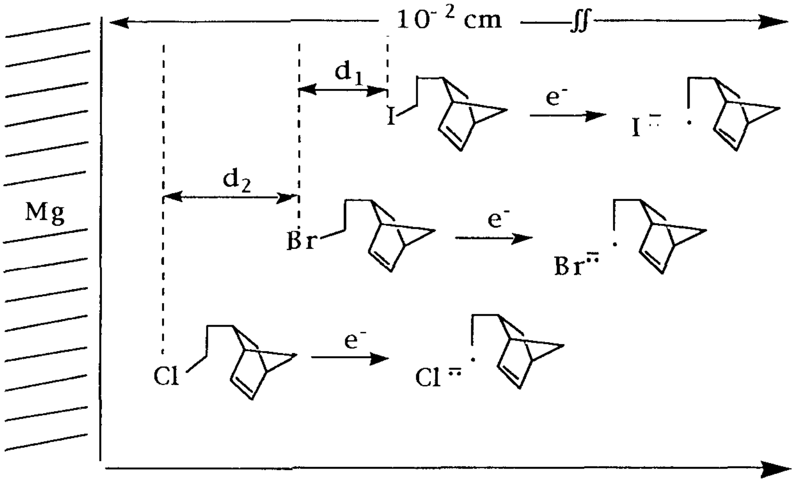
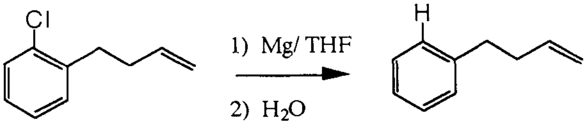


Fig. 2 . Gradient of electrons solvated concentration

In this figure the concentration in solvated electron decreases from the metallic surface to the solution bulk (bottom arrow). Accepting the idea that the iodo derivatives are intrinsically better electron acceptors than bromo, or even more, chloro derivatives (Ref. 66) , the iodo radical clock would be reduced at a larger distance from the magnesium than its bromo and chloro counterparts. The alkyl radical formed from this iodo clock would then be created in a zone of low concentration in solvated electron. The rate of reduction of this alkyl radical would therefore be lower than the rate of reduction of the same alkyl radical created closer to the metallic surface (case of the bromo or even more so of the chloro clocks). The rate constants of cyclization of the carbanions being several orders of magnitude lower than their parent radicals (Ref. 67), the reduction of the radicals with the solvated electron comes to a quenching of the reaction of cyclization for the radical clocks. The quenching being the slower for the iodo radical clock, this one would be the one for which the quantity of cyclized compound is the most important. In agrement with the results shown in table 1.

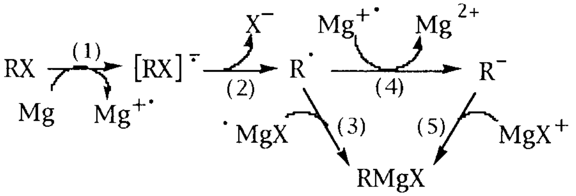
In spite of the preceding attractive features, the solvated electron hypothesis presents some difficulties. The most important one being that whereas solvated electrons have been repeatedly reported in solutions of alkali metals, we are not aware of reports describing solvated electrons in THF solutions of magnesium (Ref. 68). Therefore we prepared the set of radical clocks studied by Bunnett and Beckwith to examine their reactivity in the presence of very active magnesium in THF (Refs. 63,69,70) . The obtained results do not fit with the solvated electron hypothesis. As summarized by the following equation, no cyclized products are formed whatever the leaving group (chloro, bromo, iodo):



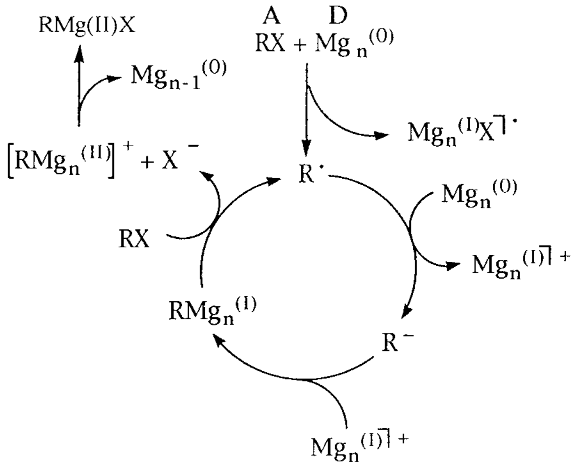
This absence of cyclization products contrasts with the reactivity of the same radical clocks in the presence of alkali metals (Ref. 63). It raises some problems when compared to results on Grignard's reagents obtained from halogenoaromatic crowns by Bickelhaupt (Ref. 71). We are presently investigating these problems in collaboration with Bickelhaupt's group. In any case if the solvated electron were the actual species reducing the aromatic radical clocks when the metallic reagent is magnesium one would have to admit that the formed aromatic radicals are reduced far faster than the aliphatic ones and that the reduction of these aromatic clocks takes place far closer to the metallic surface than it does for their aliphatic homologs. The first proposition would agree with the relative electron affinities of sigma aromatic radicals (EA = 2.2 eV) and aliphatic radicals (EA = 0.89 eV) (Ref. 72). To check it, we are in the process of preparing aromatic radical clocks whose rate constants of cyclization should be higher than the ones described here ($k = 10^8\ s^{-1}$). Yet this first proposition is not sufficient in itself to explain our results. Indeed when the solvated electrons originate from metallic potassium, the same sigma aromatic radicals do find time to cyclize partly before being reduced. Therefore to rationalize the results obtained with active magnesium one has either to add the condition that the aromatic radicals are formed in a zone where the concentration of solvated electrons is far higher (i.e. closer to the metal) or to give up the solvated electron hypothesis.

The third possibility able to account for the leaving group effects observed with our norbornenyl radical clocks relies also on a gradient of reactivity starting from the metal surface to the bulk of solvent. In 1988, Ashby used the 6-halogeno-1-hexene radical clock to study the mechanism of the Grignard's reagent formation in diethyl ether and in THF under sonochemical activation (Ref. 6). He, too, observed leaving group effects in qualitative agreement with the ones reported in the present paper. No connection with Bunnett and Beckwith's previous results was attempted. Ashby proposed that the iodo radical clock,which is the best electron acceptor of the three clocks, is reduced at a larger distance from the metal surface. Thus, the formed radical should have more time to cyclize before reaching the metallic surface where it would react with XMg(I). This approach, obviously expressed in the context of a linear mechanism, may also apply to the chain mechanism that we proposed at the begining of this report. Simply, in this later context, the reaction consuming the radical would be the formation of RMg(I) rather than the direct formation of RMgX. The possible role of distance dependent electron transfer tunneling (Refs. 61,73-75) would provide a possible explanation for the observed leaving group effects. Critical experiments to check this hypothesis are still to be performed.

Comparing the second and third possibilities reveals an important question mark left concerning the fate of the radical formed from the electron transfer to the radical clock. Within the solvated electron hypothesis this radical has the choice between 1) being at once reduced by the solvated electron, 2) starting a travel towards the metallic surface during which it could cyclize; when it would reach the surface it could react either with XMg(I) or with Mg(0). The first choice converges with the recent Bickelhaupt's proposition enonced without any reference to the solvated electron hypothesis (Ref. 71):



The preceding discussion has shown that the solvated electron hypothesis is not compulsory to explain our leaving group effects and it could well be that the reduction of the radical R is more or less rapid depending upon the distance at which the electron created it. One may wonder in any case if the aromatic halides also react following a chain rather than a linear mechanism. The experimental answer to this query is: trace quantities of dioxygen do inhibit the reaction of the chloro aromatic radical clock with our activated magnesium in THF. A possible chain mechanism containing both radical and carbanion intermediates may be proposed. It is shown in the following scheme:



At this point it is difficult to select which chain is the best. Furthermore, fonctional density calculations of clusters of magnesium varying in size suggest that the reducing power of these clusters drastically varies with their size (Refs. 40, 76, 77) In other words when the chemists speak of the reactivity of metallic magnesium as an entity this could correspond to a drastic oversimplification. It could well be that different topographies of active sites (i.e.different sizes of clusters) react with different mechanisms. Such effects were clearly demonstrated in the chemistry of photography by Belloni's group (Ref. 78).

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