JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2005; **18:** 1145–1160
DOI: 10.1002/poc.986

Radical clocks and electron transfer. Comparison of crown ether effects on the reactivity of potassium and magnesium towards 1-bromo-2-(3-butenyl)benzene. The incidence of homogeneous versus heterogeneous electron transfer on selectivity

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Received 27 April 2005; revised 27 June 2005; accepted 30 June 2005

ABSTRACT: The reaction of the title precursor of the aryl radical clock 1-bromo-2-(3-butenyl)benzene, **1Br**, towards potassium and magnesium in THF was studied in the presence and absence of various additives, at ambient and low temperatures. The additives were *cis*-dicyclohexano-18-crown-6 or *tert*-butyl alcohol; the first one to render soluble potassium by forming its alkalide, the second to distinguish carbanionic from radical cyclization. The addition of **1Br** to a THF stirred suspension of potassium pieces yields remarkably low amounts of products resulting from radical cyclization, in contrast to the amounts reported by Bunnett and Beckwith's group for the reaction in 67% ammonia–33% *tert*-butyl alcohol medium. The amount of cyclized products obtained with potassium pieces in THF is in the same range as that observed in the reaction of magnesium with **1Br** in THF. This similarity allows us to discard the earlier triad hypothesis that we proposed to account for the unexpectedly low amounts of cyclized products of aryl halides radical clocks in Grignard reagent formation. The addition of crown ethers to the THF reaction medium induces contrasting effects for potassium and magnesium. A distinctive increase in the radical cyclization is observed for potassium, whereas the addition of crown inhibits the formation of Grignard reagent more efficiently when the solvent is diethyl ether than when it is THF. The observed effects are explained by putting in perspective the metal reactive dissolution with elementary steps occurring in the vicinity of a cathode. The reaction of potassium pieces or magnesium turnings is comparable to the heterogeneous electron transfer occurring at a cathode whereas the reaction of potassium in the presence of crown ether is comparable to homogeneous conditions of electron transfer obtained in redox catalysis. A discussion of the dianion hypothesis for the Grignard reaction of aryl halides is provided and the importance of considering the reactivity of reactive metal dissolution (or organic corrosion) in the framework of recent progress made in the modelling of electrode reactivity is emphasized. This paper shows that caution should be taken when radical clocks are used to study reactions at the metal–solution interface. More specifically, the non-observation of rearranged products from the radical clock (even for the very rapid ones) under these conditions does not necessary imply that there is no radical intermediate along the dominant reaction channel. This pattern of reactivity strongly contrasts with that usually observed when radical clocks are used in homogeneous media. The leading parameters in the rearranged/unrearranged products ratio seem to be the time that the reactive species (radical anions) created by the first electron transfer spend in the close vicinity of this surface, the rate constant of rearrangement of the radical formed by the cleavage of the radical anion and the redox properties of this radical.

KEYWORDS: Grignard reagent formation; aryl halides; mechanism; crown ethers; homogeneous versus heterogeneous electron transfer; potassium; methodological limits of radical clocks

INTRODUCTION

Dissociative electron transfer from various reducing agents to substituted aromatics and heteroaromatics constitutes an emergent field in physical organic chemistry.[1]

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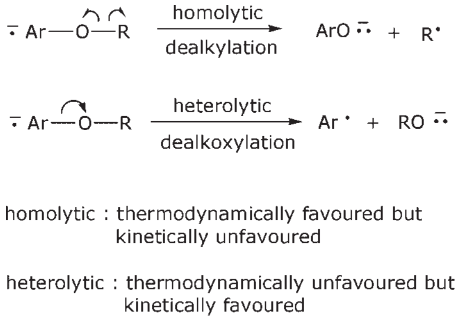
A medley of mechanistic hypotheses have been proposed to account for the experimental observations associated with this field. It is important to recall them because this paper aims to discuss the problem of the mechanisms involved when potassium or magnesium is allowed to react with aryl halides—namely formation of a dianion or a radical from the primary formed radical anion—using appropriate radical clocks.

The reaction of potassium with aromatic ethers or halides has been studied by various authors. Azzena *et al.*[2] reported that anisole reacts with potassium in THF to yield exclusively phenol by demethylation (Scheme 1), regardless of the temperature. In solvents of very low dielectric constant (aliphatic hydrocarbons, toluene, tributylamine, dioxane), however, demethoxylation to benzene was the main reaction pathway, particularly at the lowest temperatures. Neither Li nor Na seems to be able to induce this demethoxylation in these apolar solvents.[2] Nevertheless, in his review on alkali metal induced cleavage of ethers, Maercker reports a different conclusion concerning these two metals.[3]

Casado *et al.*[5] described the dealkylation mode of radical anions as mesolytic homolytic, whereas the dealkoxylation mode was labelled mesolytic heterolytic; the dealkylation mode is the most frequently observed (Scheme 2). From their studies on alkali metal reductions, electrochemical behaviour of substrates and use of substrates with a preformed positive charge in certain positions of their structure, they concluded that the mesolytic heterolytic scission is very much dependent on the electrophilic assistance by the counterion (see also Lazana *et al.*[4]). Hence the mesolytic homolytic scission would be observed in solvent-separated ion pairs (solvating solvent such as dimethoxymethane) and would be especially efficient when the pair has a controlled topology with a tetralkylammonium cation (saturated cation) near the oxygen atom.[5]

Scheme 1



homolytic : thermodynamically favoured but kinetically unfavoured

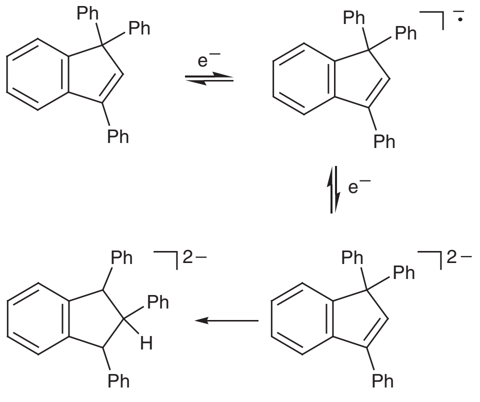
heterolytic : thermodynamically unfavoured but kinetically favoured

Scheme 2

This group recently re-examined this problem, carrying out density functional theory electronic structure calculations of the homolytic/heterolytic C—O fragmentations of a series of radical anions of substituted-phenyl benzyl ethers and substituted-benzyl phenyl ethers. Most of the experimental results could be explained considering only the involvement of radical anions. The calculations for radical anions of nitro-substituted ethers do not account for the experimental results; one possibility advanced to explain this result would be the operation of dianions as key active species. These calculations suggest that homolytic mesolytic cleavages are always thermodynamically favoured versus the corresponding heterolytic mesolytic ones.[6,7] These results give a complementary view to Maslak and Guthrie's early treatment of conservation of local spin density.[8]

For the potassium induced C—O bond cleavage of the three isomers of dimethoxybenzene in THF–dimethoxyethane, Cerri *et al.* observed interesting substituent effects. The addition of dibenzo-18-crown-6 induced the demethoxylation–demethylation switch in the reaction of *o*-dimethoxybenzene: without added crown ether, the major product was the biphenyl radical anion, whereas in the presence of crown ether the dominant product was the *o*-benzodiquinone radical anion. The reaction of the *meta* isomer with potassium yielded dominantly the biphenyl radical anion but, for this isomer, the addition of crown ether did not induce the demethoxylation–demethylation switch. The *para* isomer was transformed into its parent radical anion, which resisted dissociation in the absence or presence of crown ether.[9] Fish and Dupon studied the regioselectivity of the C—O bond cleavage by the alkalide K$^-$, K$^+$(18-crown-6) of a series of aromatic ethers in THF; they observed also drastic differences in the regioselectivity of cleavage depending upon the *ortho* or *para* site of substitution of the methoxy group.[10]

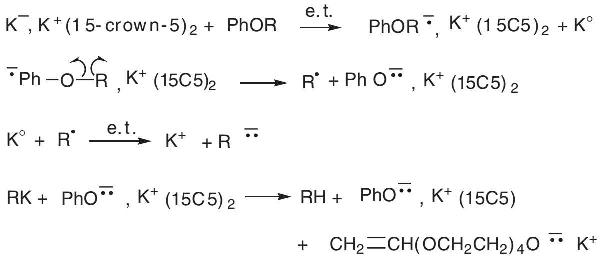
1,1,3-Triphenylindene yields, on reduction at a cathode or by reaction with potassium, the dianion of 1,2,3-triphenyl-2*H*-indene (Scheme 3). Kiesele investigated carefully this type of reaction by cyclic voltammetry in



Scheme 3

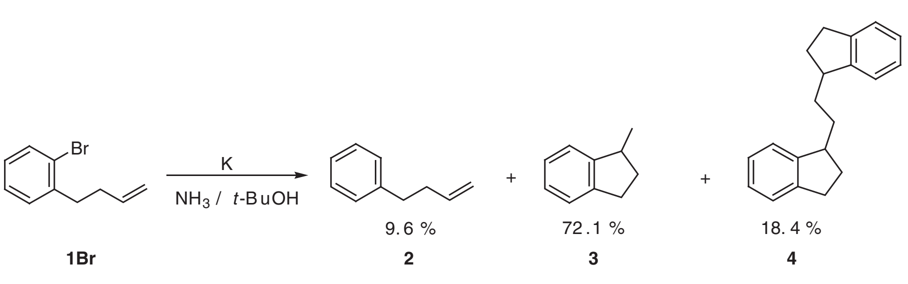
superdry THF–$NaBPh_4$. At room temperature, the rearranging dianion is formed via homogeneous disproportionation, thermodynamically favoured by ion pairing and kinetically supported by the rapid follow-up rearrangement. Ion pairing may be suppressed by making the experiment at lower temperature (0 °C) or by addition of sodium-complexing 15-crown-5. The rearrangement then no longer occurs although the radical anion is still formed. Under these conditions, to induce the rearrangement, one has to apply a much more negative potential. Clearly, for this substrate, the dianion stage has to be reached for the rearrangement to occur.[11,12] Kiesele described more complex examples where C—C bond cleavage may occur either at the radical anion or the dianion stage.[13] The same versatility has been reported by Walsh: radical anions and dianions of 9,9-diarylfluorenes cleave an aryl ring after reduction by alkali metals in ethereal solvents.[14] For the potassium-induced cleavage of ethers, Azzena *et al.* do not favour the intervention of dianions because the reduction potential of aryl ethers is very negative.[2]

The most extensive set of studies using simultaneously potassium metal and crowns to induce unprecedented patterns of reactivity originates from the groups of Jedlinski and Grobelny. Jedlinski *et al.* proposed that solvated electrons, rather than K^- anions, were the initial products of dissolution of potassium by solutions of crown ethers; but controlling the kinetics of metal dissolution makes it possible to obtain alkali metal solutions containing only negligible amounts of solvated electrons.[15] Later, Grobelny and Jedlinski used K-39 NMR spectroscopy to evidence the presence of potassium anions and complexed potassium cations in THF blue potassium solutions containing cryptand [2.2.2]. Spin–lattice and spin–spin relaxation was studied in the temperature range 178–238 K. The comparison of the relaxation behaviour of the investigated system with that of potassium solutions containing 18-crown-6 or tetraglyme instead of cryptand [2.2.2] revealed the major influence of the complexing agent on interactions of K^+ with its counterion.[16–18] Grobelny's group later reached the conclusion that the characteristic blue colour of metal solutions in THF is not connected with the presence of solvated electrons but with metal anions.[19] This conclusion agrees with earlier results concerning the blue solutions of potassium in dimethoxyethane: the blue solution is due to an electron pair attached to K^+, usually referred as K^-. In contrast to this species, the concentration of solvated electron is rather small, as indicated by the low intensity of the pertinent ESR signal.[20] Visible light irradiation of these solutions drastically enhances the concentration of solvated electrons and increases the reducing power of these solutions.[20,21] More recently, Jedlinski proposed that alkali metal supramolecular complexes such as M^+crown, M^- (M = Na or K) are able to transfer two electrons in the anionic polymerization of vinyl monomers to form carbanions as reactive intermediates.[22] Grobelny *et al.* reached the same type of mechanistic conclusion for the selective cleavage of the linear ether bond in benzyl glycidyl ether and triphenylmethyl glycidyl ether by potassium alkalide.[23,24] Grobelny reviewed the chemical methods for ether-bond cleavage by electron-transfer reagents and proposed the course of the reaction of phenyl ethers with alkalides shown in Scheme 4. This route does not involve an aromatic dianion and, in the last step, the ring opening of the crown ether results from its attack by the carbanion R^-. The first electron transfer is proposed to originate from the highly reducing K^- anions rather than from a solvated electron.[25]



Scheme 4

Up to now, radical clocks have been used to gain insight into the mechanisms involved when organic halides react with alkaline earth metals.[26–34] With alkali metals, most of the studies were performed on optically active cyclopropyl halides.[28,35–45] Bunnett and Beckwith's group studied the product ratio variation in reactions of *o*-(3-butenyl)halobenzenes **1** and 6-bromo-1-hexene with alkali metals in ammonia (67%)–*tert*-butyl alcohol (33%) solution (Scheme 5). They rationalized these product variations when the halo group changes as indications of reaction-during-mixing effects.[46] Andrieux and Saveant



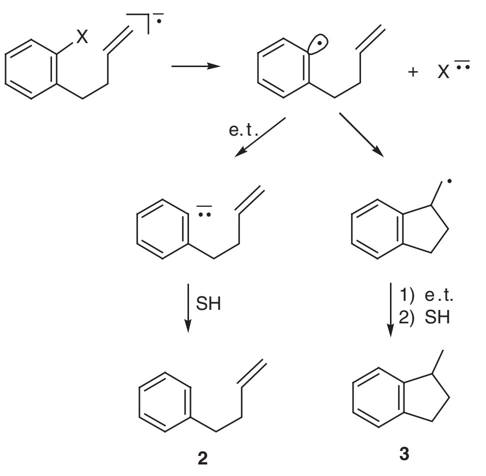
Scheme 5

later proposed a slightly different explanation. Their model allows the quantitative prediction of product distribution. It describes the initial and successive chemical steps as taking place in a thin reaction layer located within the diffusion layer where the two reactants mix. The essential cause of the observed leaving-group effects resides in the decrease in the amount of solvated electrons in the reaction layer as the initiating reaction becomes faster and faster. *o*-(3-butenyl)iodobenzene (**1I**), being the most reactive halobenzene towards solvated electrons, yields the highest amount of cyclized products.[47,48]

In these experiments, it was proposed that the elementary step competing with the rapid cyclization in the radical clock ($k > 10^8\,\mathrm{s}^{-1}$)[49,50] was an electron transfer (Scheme 6). This electron transfer transformed the sigma aryl radical formed from the cleavage of the radical anion into a carbanion whose rate constant of cyclization is considerably slower than the radical one; this step amounts to a quenching of the radical cyclization. The amount of linear product **2** was therefore the result of the competition between a bimolecular reaction (electron transfer) and an intramolecular one (radical cyclization).

As electrochemical studies showed that, at room temperature,[51] the aromatic carbanions cyclize competitively with their radical counterparts, one has to check for the experiments performed at this temperature that the cyclized products do originate exclusively from the radical species. This is done by comparing the ratio of cyclized **3** to linear **2** products in the presence and absence of *tert*-butyl alcohol. If some carbanionic cyclization contributes to the amount of cyclized product, the addition of this alcohol should decrease this ratio (some secondary effects of this alcohol on the formation of cyclized products will be dealt with in another paper).

The starting point of the present study was the observation that, when the Grignard reagents of *o*-(3-butenyl)halobenzenes **1** were formed by their reaction with magnesium in THF, only minor amounts of cyclized product **3** were observed.[30,52] This observation strongly contrasted with the results of Bunnett and Beckwith's group, where the cyclized products dominated (Scheme 5). It was also unexpected because, if the ratio of cyclized to linear products depends on the rate of reaction between the sigma aryl radical and a reducing agent, one would expect that alkali metals, having a higher reducing power than magnesium, would yield more linear products. Furthermore, when Garst *et al.* tried to rationalize the cyclized/linear ratio with the D model, which predicts this ratio accurately for the reaction between magnesium and alkyl halide radical clocks, they obtained startling results. The D model would suggest ~80% of cyclized products when *o*-(3-butenyl)halobenzenes **1** react with magnesium in THF; this prediction contrasted with the experimental value of <3%.[52] The results of Bunnett and Beckwith's group were obtained in liquid ammonia, whereas THF or diethyl ether was the solvent in which the Grignard reagent of aryl radical clocks were prepared. In this work we studied the reaction between potassium and 1-bromo-2-(3-butenyl)benzene (**1Br**) in THF and put the results in perspective with the reaction of magnesium with this radical clock under comparable conditions.



Scheme 6

RESULTS

Table 1 summarizes the results concerning the reactions between potassium and 1-bromo-2-(3-butenyl)benzene (**1Br**) in THF. A general, contrasting feature with respect to the results of Beckwith and Bunnett's group (Table 2)[46] of all the experiments described in this table is the absence of dimeric cyclized structures **4**.

The hydrogen donor ability of THF is far higher than that of NH_3; hence hydrogen abstraction would predominate in the first solvent whereas dimerization would predominate in the second.[53] In THF, without added *cis*-dicyclohexano-18-crown-6 (DCH18C6, entries 1–3), the linear product **2** clearly predominates. Entry 2 suggests that, at room temperature, a considerable part of the cyclized product **3** originates from a carbanionic cyclization. Indeed, addition of *tert*-butyl alcohol decreases the amount of cyclization. This conclusion is confirmed by entry 3: Ross *et al.* reported that carbanionic cyclization does not occur at low temperature.[54] Overall, in the absence of added crown, the radical cyclization is almost absent when this aromatic radical clock reacts with potassium in THF; this strongly differs from the situation reported in ammonia–*tert*-butyl alcohol (Table 2).[46] Entries 4–7 show the results of reacting 1-bromo-2-(3-butenyl)benzene (**1Br**) with a homogeneous blue solution THF of K^+crown, K^-. Comparison of entries 4 and 5 shows that, under these conditions and at room temperature, the presence of *tert*-butyl alcohol increases the amount of cyclization. This effect no longer occurs at low temperature (entries 6 and 7). Furthermore, at low

Table 1. Reaction of 1-bromo-2-(3-butenyl)benzene (**1Br**) with K in THF under various conditions ([**1Br**] = 0.09–0.1 M; K:**1Br** = 3.0–3.7)

Entry	DCH18C6:**1Br**	*t*-BuOH:**1Br**	Temperature (°C)	Time[a]	Conversion (%)[b]	Relative yield (%)[b]	
						3 (cyclized)	**2** (linear)
1[c]	—	—	r.t.	4 h	62	13	87
2[d]	—	6.9	r.t.	21 h	90	3	97
3[e]	—	—	−80/−90	5 h	23	2	98
4[f]	5	—	r.t.	1 min	42	30	70
5[g]	5	2	r.t.	1.5 min	32	49[k]	51[k]
6[h]	5.2	—	−80/−90	2 h[j]	35	21[k]	79[k]
7[i]	5	1.9	−80/−90	13 min	39	22	78

[a] Time after addition of **1Br** (see below).

[b] Estimated from GC analysis.

[c] **1Br** is added to lumps of K in THF.

[d] *t*-BuOH and **1Br** are added successively to lumps of K in THF.

[e] Bath temperature. **1Br** is added to lumps of K in THF.

[f] Lumps of K are added to a solution of DCH18C6 in THF. A dark blue colour is observed. The solution is homogeneous. After 20 min **1Br** is added.

[g] Lumps of K are added to a solution of DCH18C6 in THF. A dark blue colour is observed. After 20 min a mixture of **1Br** and *t*-BuOH is added.

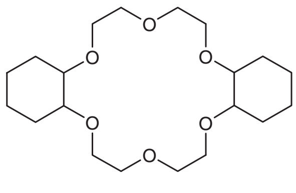
[h] Bath temperature. Lumps of K are added to a solution of DCH18C6 in THF at room temperature. The dark blue solution is cooled to −80 to −90°C and kept at this temperature for 15 min. Then **1Br** is added.

[i] Bath temperature. Lumps of K are added to a solution of DCH18C6 in THF at room temperature. After 13 min the dark blue solution is cooled to −80 to −90 °C and kept at this temperature for 15 min. Then a solution of **1Br** and *t*-BuOH in THF is added.

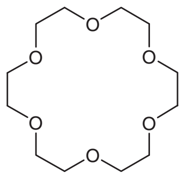
[j] By increasing the reaction time, we tried, unsuccessfully, to improve the conversion compared with entries 4, 5 and 7.

[k] Average of three experiments. Giving this information is meant to say that the several experiments performed were not perfectly reproducible, so that an average had to be taken. When no indication is given, the values have been checked at least twice and a good reproducibility was observed. This remark will hold for all the values presented in the tables in this paper.

temperature, where the carbanionic cyclization does not take place, the presence of crown ether distinctly increases the amount of cyclized products. Overall, the presence of crown ether increases the amount of cyclized products. The presence of crown ether considerably shortens the reaction times (compare entries 1 and 4 or 5, and entries 3 and 7). This is probably due to the fact that, with lumps of K, the contact between the reducing agent and the radical probe (effective concentration) is less favourable than a homogeneous solution of the reducing agent.



DCH18C6



18C6

Table 3 summarizes the results of reaction between 1-bromo-2-(3-butenyl)benzene (**1Br**) and magnesium in THF and diethyl ether (DEE) in the presence of 1,2-dibromoethane.[30,52,55] Table 4 presents the same type of results on the simpler substrate bromobenzene.

Entry 2 in Table 1 and entries 1–3 in Table 3 show that both K and Mg give very low yields of cyclized products when reacted with the same radical clock. Potassium is, thermodynamically, a better reducing agent ($E^\circ = -2.92$ versus NHE in water) than magnesium ($E^\circ = -2.37$ versus NHE in water).[56] Scheme 6 shows that an aryl radical created in a medium of lower reducing power is prone to give more cyclized product. If one considers that 3% (entry 2, Table 1) is significantly greater than 1% (entries 1–3, Table 3) potassium gives more cyclized product than magnesium. From the thermodynamics, this result would seem in the wrong direction. If one admits, with Bickelhaupt and co-workers,[57,58] that the reducing agent of the aryl radicals is magnesium(I), it is possible, as we shall see later in the Discussion section,

Table 2. Reaction of **1Br** and 6-bromo-1-hexene with K in NH$_3$ (67%)–*t*-BuOH (33%) at −28°C[a] described by Bunnett and Beckwith's group[46]

Substrate	Linear (%) '**2** or hexene'	Cyclized (%) '**3** or methylcyclopentane'	Dimer (%)
1Br	**2**: 9.6	**3**: 72.1	**4**: 18.4[b]
6-bromo-1-hexene	Hexene: 63.6	Methylcyclopentane: 0.70	20.7[c]

[a] Conditions: [RX] = 0.1 M; K:RX = 2.2; conversion = 100%. Reaction procedure: RX was added to the solvent 'NH$_3$–*t*-BuOH'. While the reaction mixture was kept at reflux under a nitrogen atmosphere, lumps of K were successively added to the stirred solution. Each lump was added after the previous one had reacted. After the addition was complete, the mixture was stirred for 2 min.

[b] 1,2-Bis(1-indanyl)ethane (mixture of stereoisomers).

[c] 1,11-Dodecadiene.

Table 3. Reaction of 1-bromo-2-(3-butenyl)benzene (**1Br**) with Mg (room temperature; [**1Br**] = 0.14–0.15 M; Mg:**1Br** = 4.4–4.7; $BrCH_2CH_2Br$:**1Br** = 0.38–0.40)

Entry	Solvent	18C6:**1Br**[a]	Time	Conversion (%)[b]	RMgX (%)[c]	Relative yield (%)[b]	
						3 (cyclized)	**2** (linear)
1	THF	0	2 h 5 min	100	96	<1	>99
2	THF	0.1	3 h 18 min	100	95	<1	>99
3	THF	1	3 h	100[d]	65	<1	>99
4	THF	4.9	95 h 35 min	0[e]	—	—	—
5	DEE	0	2 h 5 min	100	84	9	91
6	DEE	0.1	72 h	0[e]	—	—	—

[a] 18C6 is added to Mg with **1Br** and 1,2-dibromoethane in solution in THF or DEE.
[b] Estimated from GC analysis.
[c] Estimated from titration using *o*-phenanthroline and a solution of 2-BuOH in xylenes (0.5 M) as titrant.
[d] With 1 equiv. of 18C6, the reaction sometimes does not take place.
[e] $BrCH_2CH_2Br$, added for entrainment, remains untouched at the end of these experiments: $BrCH_2CH_2Br$:**1Br** = 0.39–0.41 at the end of the reaction from GC analysis.

that the reducing power of this species exceeds that of potassium metal.

The difference between potassium and magnesium is much more significant when it comes to the effect of crown ethers on their reactions with 1-bromo-2-(3-butenyl)benzene (**1Br**). Comparison of entries 5 and 6 in Table 3 shows the inhibiting effect of 18-crown-6 (18C6) for the formation of Grignard reagent in diethyl ether. This is an unprecedented and unexpected effect; therefore, we checked it under a variety of conditions and it was totally reproducible (Tables 3 and 4). Although we shall use the term 'inhibition' in the following discussion, the term partial inhibition would be more appropriate. Entries 6 and 7 in Table 4 show that the effect of the crown ether is to lengthen the induction time. If one waits long enough, however, the reaction occurs. This crown ether effect is unexpected if one puts it into a historical perspective. One may remember that one of the reasons for Grignard meeting with success in the reaction between alkyl halides and magnesium was that he used diethyl ether as a solvent, whereas Lohr, before him, had performed the reaction without solvent.[59] Later, Normant considerably facilitated the access to vinylmagnesium compounds by introducing THF as a new medium for the reaction.[60] Hòrak and co-workers were among the first to take the solvent into account in the formation mechanism.[61,62] These facts gave credence to a driving force brought by oxygenated solvents where the oxygen atoms efficiently coordinate Mg^{2+} and solvate it. One could have thought, therefore, that the six oxygens of 18-crown-6 were well suited for bringing an even better solvation, as shown experimentally by Bickelhaupt's group.[63,64] This solvation should have favoured the formation of the Grignard reagent in place of inhibiting it. This inhibition not only applies to the aryl halides but also to the 1,2-dibromoethane reaction (see footnote e in

Table 4. Reaction of bromobenzene with Mg (room temperature; [RX] = 0.86 M; Mg:RX = 4.2–4.3)

Entry	Solvent	18C6:RX[a]	Time	Conversion (%)[b]	RMgX (%)[c]	Relative yield (%)[d]	
						Biphenyl	Benzene
1	THF	0	20 min	100	96	<1	>99
2	THF	0.1	1 h 13 min	100	95	<1	>99
3	THF	1	58 min	56[e]	42	<1	>99
4	THF	1	1 h 32 min	100[e]	70	<1	>99
5	DEE	0	1 h 5 min	100	87	3	97
6	DEE	0.1	10 h 15 min	0[f]	—	—	—
7	DEE	0.1	23 h 20 min	100[f]	72[g]	3	97

[a] 18C6 is added to Mg with bromobenzene in solution in THF or DEE.
[b] Estimated from GC analysis.
[c] Estimated from titration using *o*-phenanthroline and a solution of 2-BuOH in xylenes (4 M) as titrant.
[d] Estimated from GC analysis: these ratios are equal to the ratios of corrected peak areas.
[e] With 1 equiv. of 18C6 the reaction took place every time but the conversion was not reproducible with respect to the reaction time.
[f] With 0.1 equiv. of 18C6 the reaction starts after various times.
[g] Inaccurate: the end point was not very sharp.

Table 3). The situation could be more subtle. Bock *et al.* showed that in hexacoordinated Na cations the repulsion between the individual ether molecules within the solvent shell can differ considerably, therefore affecting differently the solvation enthalpies.[65] Van Klink reached the same kind of conclusion for magnesium.[66] Tables 3 and 4 seems to point in this direction: the inhibition introduced by the crown ether is far less pronounced in THF than in diethyl ether. Comparison of Tables 3 and 4 shows that the inhibition by 18-crown-6 is less important for bromobenzene than for the more sterically hindered 1-bromo-2-(3-butenyl)benzene (**1Br**). However, within such a perspective, it is not clear why the inhibition should operate in the reaction of 1,2-dibromoethane (footnote e in Table 3) where the steric interactions in the coordination sphere of magnesium are less important. The delicate intricacy of viscosity, basicity and steric effects of the solvent in the Grignard reagent formation was lucidly discussed by van Klink.[66]

A second explanation of this inhibition would be that the crown complexes $MgBr_2$; Garst *et al.* explained the phenomenon of entrainment when they showed that the addition of this salt suppresses the induction period often observed in the Grignard reagent formation; the main effect of 1,2-dibromoethane would therefore be to produce this salt when reacting with magnesium.[67] This explanation does not, however, rationalize the observation that the crown inhibits even the reaction of 1,2-dibromoethane in diethyl ether or THF where no entrainment is needed. Also, for bromobenzene (Table 4), where no $MgBr_2$ is necessary, the inhibiting effect is present.

A third explanation could be that the crown is adsorbed on the active sites present at the surface of magnesium as it seems to do with zinc surfaces.[68] Guijarro *et al.* evidenced the kinetic effect of structural fragments (CN) able to interact attractively with a metallic surface.[69] The oxophilicity of magnesium is well recognized. Crowns have been shown to be as corrosion inhibitors, but it is not clear, however, if these reports are relevant to our observations because not much is said about the possible mechanisms of this action.[70–72] More work is needed to select the best explanation.

DISCUSSION

The experimental data gathered in Tables 1–4 may be commented on via several approaches. The Introduction of this paper showed that the dissociative reduction of substituted aromatics by alkali metals in aprotic solvents has given birth to a variety of molecular schemes: ion pairing versus solvent separated pairs, radical anions versus dianions, electron transfer from the metallic surface or the metal anion versus solvated electrons. If one considers alkaline earth metals one would have to add the possibility of direct insertion of the metal atoms in the C—X bond.[73,74] Finally, with alkalides, one could conceive, although no precedent has been reported, a direct formation of the aryl carbanion by the metal anion effecting a nucleophilic displacement on positive halogen, in a way reminiscent of the halogen dance.[75] Perrin *et al.* discarded, however, the dominant occurrence of simultaneous two-electron transfer possibility in the reaction of K^+crown, K^- with phenylacetyl peroxide making use of the phenylacetoxy radical as a very fast radical clock.[76] We will try to examine successively our set of data in the framework of the various mechanistic schemes which have been proposed in the field of dissociative electron transfer, keeping for the end what we believe to be the most sensible rationalization.

Crown ether effects on ion pairing in radical anions?

Let us first examine the possibility that the main effect of adding crown ether to THF is to transform the dominantly contact ion paired aromatic radical anions, formed when the crown is absent, into dominantly solvent separated ion pairs. This possibility rests on the assumption that the counterion of the aromatic radical anion formed after the first electron transfer is the crown solvated K^+ cation. Simultaneously, in the solution, one should also have K atoms or K clusters. Bock and co-workers studied in depth the characteristics of contact ion-paired aromatic radical anions as well as those of solvent-separated ones;[77,78] Kochi and co-workers recently showed that the information gained from x-ray structural determinations could be used to gain insights into the in-solution reactivity of these ion pairs.[79,80] For large, non-coordinating cations, solvent-separated ion pairs probably cleave faster than their ion-paired counterparts, the effect of the counterion in the contact ion pair, provided that it stays in the vicinity of the aromatic ring rather than that of the halide, being to spread the negative charge over all the aromatic ring, making less easy the intramolecular electron transfer from the aromatic electronic cloud to the sigma antibonding orbital of the C—Br bond.[79,81] Then, in solvent-separated ion pairs, the bromobenzene radical anion would resemble more the very fleeting alkyl halide radical anions.[82] In THF, halo radical clocks where the halide is linked to an sp^3 carbon usually yield much more cyclized products than their aryl counterparts with a similar rate of cyclization.[30] Therefore, the observed increase in cyclization induced by addition of crown (entries 4–7 in Table 1) could be rationalized in this way. Several authors have observed that, as the lifetime of haloaromatic or heteroaromatic radical anions generated at a cathode increases, the quantity of aryl or heteroaryl radicals increases at the expense of the corresponding carbanions.[51,83,84] This discussion holds only for comparing results obtained in the same solvent and radical clocks whose rates of cyclization are not too different. In ammonia–*tert*-butyl alcohol, the amount of cyclized product obtained when potassium reacted with 6-bromo-1-hexene ($k_{cycl} = 4 \times 10^5 s^{-1}$, 37 °C) was very small in comparison with the yields obtained in the reaction of potassium with 1-bromo-2-(3-butenyl)benzene (**1Br**) ($k_{cycl} = 4 \times 10^8 s^{-1}$, 37 °C) in the same solvent (Table 2). This result shows, and we shall return to this point in the conclusion, that the lifetime of radical anions is one of the parameters affecting the cyclized/linear ratio. Therefore, ion pairing could indirectly affect this ratio. If the cation is able to increase the lifetime of the radical anion, it will provide it with a greater probability of escaping from the vicinity of the surface. As the section on the comparison with cathodes will show, this increase in lifetime is associated with higher quantities of cyclized products.

Intervention of dianions?

The bond cleavage induced by electron transfer to aromatic derivatives is generally rationalized at the radical anion stage. In the Introduction, we have seen, however, that when C—C bonds are cleaved, dianions may be the active intermediates.[12,14] Cleavage of the carbon–halogen bond at the dianion stage (as intermediate or transition state) for haloaromatics is, nevertheless, proposed to occur when these substrates react with magnesium to yield a Grignard reagent.[34,52,85] If it had a bearing, the highest quantity of cyclized product obtained when potassium reacts with 1-bromo-2-(3-butenyl)benzene (**1Br**) compared with magnesium in THF (entries 2 in Table 1 and 1 in Table 3) would be rationalized by a less important participation of the dianion route in the alkali metal reaction. Such a dianion route has precedent in the reaction of alkali metal naphthalenides with cyclopropyl halides.[86] As the involvement of dianions seems at variance with most of the reports dealing with dissociative electron transfer to haloaromatics[1,81,84,87–94] it deserves careful discussion.

Could it be that the electrochemical method of measuring the rates of cleavage for radical anion of haloaromatics systematically overestimates these rates? Recent pulse radiolysis studies suggest the opposite, particularly for the fastest cleaving substrates.[95] For the radical anions of iodobenzene and 1-iodo-3-methylbenzene, heterogeneous reduction at a glassy carbon disk electrode, in acetonitrile or *N*,*N*-dimethylformamide as solvents, shows a pattern of cleavage very close to that observed for alkyl halides.[92] Nevertheless, *o*-(3-butenyl)iodobenzene (**1I**) reacts with magnesium in THF yielding far less cyclized product than expected from application of the D model.[52] This argument is weakened, however, by a recent electrochemical study in which the radical anion of iodobenzene was found to be an intermediate in the homogeneous reduction of iodobenzene by appropriate radical anions in *N*,*N*-dimethylformamide.[96]

Could it be that counterion effects increase the lifetime of the radical anion near the magnesium surface, allowing a second electron transfer to occur or catalysing a disproportionation reaction of the radical anion? In solvents with low dielectric constant, ion pairing becomes dominant as the size of the metal cation increases.[97] If one imagines that when magnesium has transferred one electron to the halobenzene it remains a radical cation delocalized on several magnesium atoms, then special counterion effects could be envisioned, particularly if there is some interaction between the metal surface and the radical anion as proposed by the groups of Maslennikov[98–101] and Walborsky.[102]

Could it be that, up to now, theoretical treatments of dissociative electron transfer have overlooked the dianion possibility? Given the variety and the quality of the groups who have attacked this problem, the odds are small. Yanilkin *et al.*, however, recently made an original proposition for an electrochemical mechanism.[103] It is called the EE_D mechanism. This mechanism, applied to bromobenzene, would develop as follows. A first electron transfer from the cathode to bromobenzene would yield the corresponding radical anion and this radical anion, in place of cleaving, would accept a second electron and immediately cleave. As such, the dianion resembles very much to a transition state. The second electron transfer would have the characteristics of the dissociative electron transfer proposed by Saveant:[104] concerted electron transfer and bond cleavage. Two reasons could explain why the second electron transfer is even more rapid than the cleavage of the carbon–halogen bond. The first is that the price of reorganization energy has been paid for effecting the first electron transfer so that no further activation is needed for the second electron transfer. One would be in a situation of inverted potential well illustrated by the cyclooctatetraene reduction.[105] The second is the high driving force provided by the concerted bond cleavage. If this electrochemical scheme were to be extended to the Grignard reaction another recent observation could substantiate it. This observation is that, in homogeneous solution, pulse radiolysis studies show that magnesium(I) is such a strong reducing agent that it would be better described as a magnesium(II)–solvated electron pair.[106] Even if this situation is probably weakened when magnesium(I) is inserted in a metallic matrix, this hints that, with magnesium, the second electron transfer is easier than the first (inverted potentials).[105] As we do not know the precise reduction potential of magnesium(I), we are unable, at this point, to apply this concept to compare entry 2 in Table 1 and entry 1 in Table 3. According to Yanilkin *et al.*, the EE_D mechanism would apply to haloaromatics bearing mildly electron donor substituents. In terms of the current approach of dissociative electron transfer, this raises serious problems because this class of compound would be the ones with the shorter lifetimes.[82] The EE_D scheme, published in the Russian literature, has not yet been discussed by the electrochemists involved in the study of dissociative electron transfer. The same situation applies to Gileadi's even more general proposal, which would also back the participation of dianions.[107]

We will see in the section devoted to electrochemical examples that, up to now, electrochemists studying substrates displaying the structural features of radical clocks and where almost no rearrangement occurs did not resort to the dianion hypothesis to rationalize their observations.

Switch from heterogeneous to homogeneous conditions of electron transfer

In our opinion, the most important difference introduced by using crown ethers with potassium is the *switch from heterogeneous to homogeneous conditions of electron transfer*. Potassium is only slightly soluble in THF,[108] in entry 1 in Table 1 the electron transfer probably takes place from the metal surface to the radical clock probe. In contrast, the blue crown ether solution of potassium (entries 4–7, Table 1) is homogeneous. The first electron transfer probably takes place from the potassium anion to the radical clock probe if one assumes that the unimportant concentration of solvated electron limits its participation in the reaction despite its high reactivity. In the experiments of Beckwith and Bunnett's group performed in NH_3–*tert*-butyl alcohol, the situation is less clear. These authors devoted a complete paragraph to describe the environment in which the first electron transfer takes place. Space is lacking to reproduce this paragraph fully, but some sentences should be quoted. 'When reaction is conducted by adding pieces of alkali metals to a stirred solution of the radical clock probe, we usually see little streaks of blue trailing behind the pieces of metal as they float about, but no more blue than that ... Reaction does not, however, occur uniquely at the metal surface, for we obtained essentially the same results when the metal was provided as a solution in ammonia as when pieces of metals were added ... If the medium were one of uniform solvated electron and substrate concentration, the four radical clock probes differing only by the halogen (F, Cl, Br, I), should not give significantly different product proportions, for the corresponding radical would be formed in essentially the same surroundings regardless of the halogen originally present ... We therefore judge that reaction occurred during mixing in local conditions of strong concentration gradients'.[46] This quotation is highly relevant to our results. Indeed, in ammonia, these authors can control a parameter that we cannot directly control. They can use either homogeneous or heterogeneous solutions of the same metal. In THF we can not. Potassium is only slightly soluble in THF and magnesium is insoluble in this solvent.

Discarding the triad hypothesis for the mechanism of Grignard reagent formation

It may come as a surprise that, for K, under homogeneous conditions, more cyclization is observed than under heterogeneous conditions (Table 1). In Scheme 6, this means that the aryl radical is, overall, subjected to a less reducing medium under homogeneous conditions. This could appear even more striking if one remembers that, under heterogeneous conditions, the reducing agent is the potassium metal surface whereas, under homogeneous conditions, the reducing agent is the potassium anion. It could well be, however, that the concept of inverted potential applies here; potassium anion could be a weaker reducing agent than potassium because, when oxidized, it leads to a cation whose configuration is very stable and whose solvation is more energetic than that of potassium metal.[105] This surprise could lead one to give up the idea that the crossroad of selectivity (where the cyclized: uncyclized ratio sets up) is situated at the radical step (cyclization versus reduction). One would then have to conceive it at the radical anion step (cleavage versus further reduction)[85] or even sooner with the triad hypothesis[109] or with a direct insertion of the metal atom into the carbon–halogen bond taking place.[73,74] The triad hypothesis does not apply for potassium because, when this metal has given up one electron, it yields a diamagnetic cation unable to couple with a radical. The very fact that potassium and magnesium in the same solvent both yield only small amounts of cyclized products when reacting with the same radical clock probe, renders the triad hypothesis obsolete in rationalizing the mechanism of Grignard reagent formation. The section putting in perspective the selectivities observed for K and Mg with those observed at a cathode will clarify the reasons why homogeneous versus heterogeneous electron transfer gives birth to so different selectivities.

Building bridges between the selectivities observed with K or Mg metal and the cathode surface

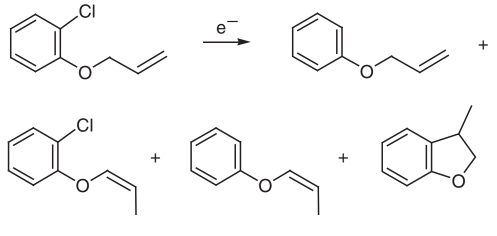
The surprise weakens if one considers what has been reported in electrochemistry, where the switch from heterogeneous to homogeneous electron transfer has been studied in detail from both theoretical[87,110–115] and applied[116–118] points of view. It occurs fairly often that, when at the cathode the first electron transfer induces a cleavage of the substrate rapid enough to create the fragments in the near vicinity of the cathode, if one of the fragments is a better oxidizing agent than the substrate it will be reduced so rapidly that its concentration will remain extremely low. Local conditions of a strong concentration gradient exist in a critical zone near the cathode.[48,119] The advantage of electrochemistry is that one can control experimentally several of the parameters important in this critical zone, whereas in metal corrosion occuring in an organic solvent one undergoes them. To reveal better the radical character of the fragment formed from the radical anion, one has to use an appropriate mediator (indirect electrolysis) which will take one electron from the cathode and transport it to the bulk where the substrate will accept it. The fragment will, this time, be born far enough from the cathode to undergo reactions other than reduction alone and be freed of the concentration gradient present in the close vicinity of the cathode. The situation has been clearly delineated in terms of mapping of the reaction zones.[120]

Three specific examples in which radical clock probes were studied at a cathode can help in answering the following question: 'when very fast radical clock probes, used to study the metal–solution interface, yield very small quantities, if any, of rearranged products, can we draw the conclusion that the mechanism of the scrutinized reaction does not involve paramagnetic intermediates?' The answer is definitely 'No'.

The first example deals with the electrochemical behaviour of 1-bromo-2-(3-butenyl)benzene (**1Br**) at a platinum or mercury cathode in *N*,*N*-dimethylformamide with *tetra-n*-butylammonium perchlorate as supporting electrolyte in the presence or absence of proton or hydrogen atom donor additives.[51] After correction for the carbanionic cyclization, the cyclized to uncyclized ratios are 0.04 and 0.22 at mercury and platinum cathodes, respectively, without mediator. The lower cyclization ratio observed on mercury could arise because radicals react with a mercury cathode.[121,122] In the presence of *m*-toluonitrile as electron mediator, the ratio increased to 9 for both metals. This first example clearly shows the drastic change introduced by the heterogeneous–homogeneous electron transfer switch. It also suggests that in the experiments of Beckwith and Bunnett's group the mixing zone is not far from the bulk because the amounts of cyclization reported by this group and Bartak's group with a mediator are similar for the same radical clock.

The second example deals with the electroreductive dehalogenation of chlorinated aromatic ethers.[123] This work describes the heterogeneous electrochemical reduction of mono- and polychlorinated aromatic ethers at a lead cathode in *N*,*N*-dimethylformamide. The first information provided by this work is that, in the formed radical anion the cleaved bond is always the carbon–halogen bond, and the methoxy substituents remain in the final product of electrolysis. This observation conflicts with the dianion hypothesis for the Grignard formation of aryl halides. From the set of results given in the Introduction, it would seem that, for the cleavage of ethers, most of the experimental results are explained without resorting to the participation of dianions. Why, then, should the dianions be involved for the easier to cleave carbon–halogen bond? This argument, is, however, not totally compelling because one could pretend that the searchers who examined the cleavage of aromatic ethers missed the dianion hypothesis as the electrochemists involved in the dissociative electron transfer possibly did. It adds to other observations discussed in this paper to show that if the dianion hypothesis could be validated its consequences would spread far beyond the mechanism of Grignard reagent formation. The second information comes from the electrochemical behaviour of the radical clock precursor allyl 2-chlorophenyl ether. This substrate yields a faster radical clock ($k = 6.3 \times 10^9\ \mathrm{s}^{-1}$ at 30 °C)[49] than 1-bromo-2-(3-butenyl)benzene (**1Br**). Nevertheless, it reacts at different cathodes to give only traces or small amounts (never more than 4% and often 1% or less) of the expected cyclization product (Scheme 7). Instead, considerable amounts of (*Z*)-enol ethers were obtained depending on the electrodes and experimental conditions. These enol ethers were attributed to the action of electrogenerated bases. On carbon electrodes for which the small amounts of cyclized products appeared, the other main product was the linear counterpart expected for radical clocks (solvent acetonitrile). The experiments in which only traces of cyclized products were observed must be connected with Walter's report.[124] He studied Grignard reagent formation with a similar radical clock probe (iodo in place of chloro in the substrate).[124] He, too, did not observe any traces of cyclized product. It was proposed that a possible complication with these ether radical clocks was complexation of Mg^{2+} to the oxygen.[85] There is no Mg^{2+} in the electrochemical experiments; the explanation for the unexpected behaviour of this very rapid radical clock must be sought elsewhere. A natural explanation, if the EE_D scheme were to be validated, would be that the *O*-alkyl substituents being electron donating, this radical clock probe would be an excellent substrate for full application of the EE_D scheme; the dianion intermediate would allow the aryl radical to be bypassed. In any case, this connection between the chemical and the electrochemical studies *clearly shows that the absence of an isomerized radical clock in a study where electron transfer is studied at the metal–liquid interface cannot be regarded as prima facie evidence of aryl radical absence.*

The third example is probably the most illustrative with respect to this statement even if the dissociative electron transfer that it describes involves an O—O bond rather than a carbon–halogen bond. Workentin *et al.*[133] studied in depth the homogeneous and heterogeneous reductions



Scheme 7

of 9,10-diphenyl-9,10-epidioxyanthracene. The heterogeneous reduction at glassy carbon working electrodes in acetonitrile or *N*,*N*-dimethylformamide yields the corresponding 9,10-dihydroxyanthracene (97%) via the distonic radical anion. In competition with this reaction, a small amount (3%) of 9-phenoxy-10-phenylanthracene is formed under heterogeneous conditions (Scheme 8). Cyclic voltammetric studies show that the starting endoperoxide is the precursor of a very fast radical clock ($k > 5.9 \times 10^{10}\,\mathrm{s}^{-1}$). This radical clock either undergoes the *O*-neophyl-type rearrangement or undergoes more rapidly a second electron transfer at the electrode. The relative yields of 9,10-dihydroxyanthracene and 9-phenoxy-10-phenylanthracene establish that the second electron transfer is more rapid than the *O*-neophyl-type rearrangement. The same substrate was submitted to homogeneous electron transfer with a variety of mediators. With mediators of appropriate reduction potential the *O*-neophyl rearrangement may be made quantitative. Here again, despite the rapidity of the intramolecular rearrangement in the radical clock, the heterogeneous intermolecular electron transfer wins the competition. Given the lability of the O—O bond, it seems difficult to resort to the dianion hypothesis to explain the observed results. A further beauty of this example is that the in-depth electrochemical study provides access to the rate constants of every elementary step involved in this reaction.

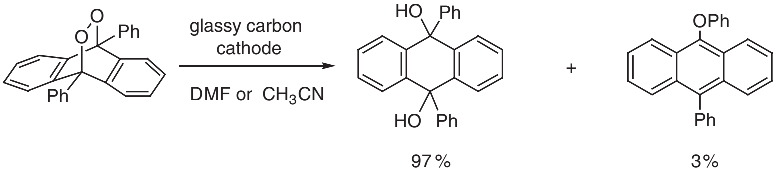
These three examples hint that in the close vicinity of the cathode, but also in the close vicinity of the metallic surface of potassium or magnesium, there exists a thin liquid layer displaying highly reducing properties whose intensity decreases rapidly from the surface to the bulk.[47,48,125] This statement must be made clear to avoid misunderstanding. The decrease in intensity corresponds simply to a decrease in the probability of returning to the metal surface as one continues to increase the distance from this surface where the radical is created.

CONCLUSIONS

This paper draws attention to the special behaviour of radical clock probes used to study electron transfer reactions at the metal–liquid interface. The comparison of two metals reacting with the same radical clock probe and the use of crown ethers showed the difference between homogeneous and heterogeneous electron transfer. Concomitantly, a caveat to possible misuses of radical clock probes in such situations naturally emerged. This is important because these tools recently have been proposed to study more generally the reactivity at metallic surfaces.[126] We have seen that *the absence of an isomerized radical clock in a study where electron transfer is studied at the metal–liquid interface cannot be regarded as prima facie evidence of aryl radical absence.* On the other hand, a long time ago, and because of the possibility of carbanionic cyclization, Koppang *et al.* proposed ‘*Like the alkyl analogues, intramolecular cyclization of a 3-butenylaryl intermediate cannot be regarded as prima facie evidence of aryl radical intermediacy*’.[51]

The very similar behaviour of potassium and magnesium towards the same aromatic radical clock under conditions of heterogeneous electron transfer led us to abandon the triad hypothesis that we had previously proposed to account for the Grignard reagent formation of aryl, cyclopropyl and vinyl halides.[109]

The starting incentive for this work was the question, why is so much cyclized products observed in the experiments of Beckwith and Bunnett’s group and so little in ours when the same starting radical clock probe is used? The answer mainly rests at the level of the solvent: in ammonia the alkali metal is soluble whereas its solubility in THF is very low. Magnesium is insoluble both in ammonia and THF. We shall describe in an other paper how this constraint can be avoided. Bickelhaupt and co-workers were the first to demonstrate the involvement of an aryl carbanion in Grignard reagent formation from aryl halides. They rationalized the formation of these carbanions by the primary formation of aryl radicals rapidly reduced by magnesium(I).[58] Then, both Garst’s group and we confirmed the formation of these carbanions; the structure of our radical clock probe allowed us to show a clear difference between alkyl and aryl halides in the Grignard reaction.[30,52] From their experimental results, Garst *et al.* deduced that there is no aryl radical intermediate along the dominant reaction channel leading to the aryl Grignard reagent. They proposed that the carbanion was directly formed via an aryl halide dianion. From the same experimental results we proposed, in the same line as Bickelhaupt and co-workers, that the carbanion was formed via the aryl radical, the difference with alkyl halides being mainly that the aryl radicals have a higher electron affinity than alkyl radicals.[30,55] *The present paper emphasizes the necessity to treat the reactive dissolution of metals in*



Scheme 8

close connection with the progresses made in the understanding of elementary steps occurring at an electrode.[119,120] Within such a perspective, the difference between alkyl and aryl halides is not limited only to the difference in the electron affinities of alkyl and aryl radicals but involves also the difference in the reduction potentials of the starting halides, the lifetimes of the radical anions formed, their interaction or absence of interaction with the metal surface and more refined parameters such as diffusion coefficients of the species involved.[125] Qualitatively, one could summarize the situation by the following statement: when a given radical probe reacts with a metallic surface, the leading parameters in the rearranged to unrearranged products ratio seem to be the distance from the metallic surface at which the first electron transfer takes place, the time that the reactive species created by this electron transfer spend in the close vicinity of this surface and the reduction potential of these reactive species. This follows from the gradient of reducing power, which rapidly decreases from the surface to the bulk. More quantitative expressions should follow from the application of electrochemical kinetics to the reactive dissolution of metals. Concerning the question of whether one really needs to introduce the participation of dianions to account for the formation of Grignard starting from aryl, vinyl and some cyclopropyl halides, we have provided some new arguments which could back this possibility. We believe, however, that electrochemical experiments and kinetic treatment could explain the experimental results without resorting to dianions. Work along these lines is in progress.

EXPERIMENTAL

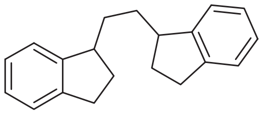
Reactions with potassium

General considerations. THF (SDS, 99.7%) was dried over sodium–benzophenone and distilled from the purple solution prior to use. All glassware and transfer needles were oven-dried at 100 °C. *t*-BuOH (Fluka, >99%) was dried over K_2CO_3 and then distilled. *cis*-Dicyclohexano-18-crown-6 (DCH18C6, Aldrich, 98%, mixture of *syn-cis* and *anti-cis* isomers) was used as received. Teflon-coated stir bars were used. Potassium lumps were first wiped, weighed in a beaker containing xylenes and wiped again. In some experiments, potassium was moreover extensively washed by stirring in a flask containing dry THF. Gas chromatographic (GC) analyses were performed on a Fisons GC 8000 instrument using a BPX5 capillary column (SGE, 25 m × 0.22 mm i.d.) with helium as carrier gas and a flame ionization detector. The following temperature programme was used: injector, 280 °C; detector, 250 °C; 80 °C (0 min) to 250 °C (5 min) at 5 °C min^{-1}. Peak area integrations were performed by electronic integrations on a Spectra-Physics integrator.

1-Bromo-2-(3-butenyl)benzene (**1Br**),[52] an authentic sample of 3-butenylbenzene (**2**)[52] and 1-methylindane (**3**)[52,127] were prepared as described in the literature. We repeated the reaction of **1Br** with potassium in liquid ammonia and isolated 1,2-bis(1-indanyl)ethane (**4**) as a mixture of diastereomers.[46] An authentic sample of (2*E*)-2-butenylbenzene (**7**)[128] was prepared from the reaction of phenylmagnesium bromide with 1-chloro-2-butene in refluxing THF. Similarly, (1*E*)-1-butenylbenzene (**9**)[128] was prepared from reaction of methylmagnesium iodide with cinnamyl bromide. Butylbenzene (**10**) and tetralin (**5**) were commercially available.

Relative yields **2**:**3** and conversions were estimated from GC analysis assuming that the starting bromide and products have similar response factors.[129] The conversion was calculated from the yield of identified products relative to the starting bromide **1Br**. Each experiment was at least duplicated. The conversion can vary but the **2**:**3** ratios remain similar. We limited the reaction times to prevent the possible formation of by-products which could arise from the basic medium (Table 1).

Products **2** and **3** were identified by GC–MS analysis (70 eV) and co-injection of authentic samples.



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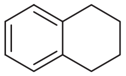

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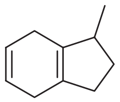

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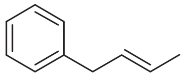

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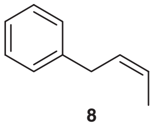

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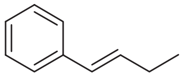

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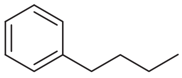

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We found minor by-products **5**–**10**. The reduction of a double bond leads to **6** and **10**; **7**–**9** result from migration of the double bond. Compounds **5**, **7**, **9** and **10** were identified from GC–MS analysis and co-injection of authentic samples. GC–MS analysis suggests the presence of **8** and **6**[130] but we did not prepare authentic samples. Products **5**–**10** were found in the range 0–15% relative to **2** and **3**. In some experiments, with the crown DCH18C6, we observed small amounts of compounds which could result from cleavage of the crown ether in agreement with comparable results in the literature.[131] In only two experiments did we find traces ($\leq$1%) of products which could correspond to **4**.

Reaction of bromide 1Br at room temperature. In a Schlenk tube equipped with a magnetic bar and degassed by three vacuum–nitrogen cycles, THF was introduced by syringe (2 ml). Potassium lumps (0.024 g, 0.614 mmol) were added under a flow of nitrogen. Potassium is not soluble in THF. The Schlenk tube was swept with nitrogen for a few minutes and **1Br** (0.041 g, 0.194 mmol) was added by microsyringe. After 4 h of stirring at room temperature, water was slowly added until complete decomposition of potassium. After dilution with diethyl ether, the mixture was dried ($MgSO_4$) and filtered.

Reaction with *t*-BuOH at room temperature. In a Schlenk tube equipped with a magnetic bar and degassed by three vacuum–nitrogen cycles, THF was introduced by syringe (3 ml). Potassium lumps (0.041 g, 1.048 mmol) were introduced under a flow of nitrogen. The Schlenk tube was swept with nitrogen for a few minutes. Then *t*-BuOH (180 μl, 1.918 mmol) and **1Br** (0.059 g, 0.279 mmol) were successively added by microsyringe. After 21 h of stirring at room temperature, work-up was performed as described below. Only small amount of potassium remained before work-up, probably because of alkoxide formation.

Reaction at low temperature. After introduction of THF (2 ml), potassium lumps (0.026 g, 0.665 mmol) and **1Br** (0.043 g, 0.204 mmol) as described below, the reaction mixture was immediately cooled in a bath kept at −80 to −90 °C and stirred for 5 h. Work-up was performed as described below.

Reaction with crown ether at room temperature. In each experiment involving crown ether DCH18C6, dark blue solutions were obtained and it was difficult to see if potassium was totally dissolved before the addition of **1Br**. Indeed, in some cases, a small amount of metallic potassium was present before work-up.

A Schlenk tube equipped with a magnetic bar and containing DCH18C6 (0.374 g, 1.00 mmol) was degassed by three vacuum–nitrogen cycles. Then DCH18C6 was dissolved in THF added by syringe (2 ml). Potassium lumps (0.023 g, 0.588 mmol) were introduced under a flow of nitrogen. With stirring, potassium started to dissolve and a dark blue colour developed. After 20 min, **1Br** (0.042 g, 0.199 mmol) was added by microsyringe. Then the mixture was stirred for 1 min before the usual work-up.

Reaction with crown ether and *t*-BuOH at room temperature. A Schlenk tube equipped with a magnetic bar and containing crown ether DCH18C6 (0.373 g, 1.00 mmol) was degassed by three vacuum–nitrogen cycles. Then DCH18C6 was dissolved in THF added by syringe (2 ml). Potassium lumps (0.024 g, 0.614 mmol) were introduced under a flow of nitrogen. With stirring, potassium started to dissolve and a dark blue colour developed. After 20 min, a mixture of **1Br** (0.042 g, 0.199 mmol) and *t*-BuOH (38 μl, 0.405 mmol) was added by microsyringe. The mixture was stirred for 1.5 min before the usual work-up.

Reaction with crown ether at low temperature. After introduction of the crown ether DCH18C6 (0.368 g, 0.988 mmol), THF (2 ml) and potassium lumps (0.023 g, 0.588 mmol) as described below, a dark blue colour developed. Then the reaction mixture was cooled in a bath kept at −80 to −90 °C for 15 min and **1Br** (0.040 g, 0.189 mmol) was added by syringe. The reaction mixture was stirred for 2 h before work-up.

Reaction with crown ether and *t*-BuOH at low temperature. After introduction of DCH18C6 (0.374 g, 1.00 mmol), THF (2 ml) and potassium (0.023 g, 0.588 mmol) as described below, a dark blue colour developed. After stirring for 13 min at room temperature, the reaction mixture was cooled in a bath kept at −80 to −90 °C for 15 min. Then a solution of **1Br** (0.042 g, 0.199 mmol) and *t*-BuOH (36 μl, 0.384 mmol) in THF (0.2 ml) was added by microsyringe. The reaction mixture was stirred for 13 min. before work-up.

Reactions with magnesium

General considerations. THF (SDS, 99.7%) and diethyl ether (DEE, SDS, 99.7%) were dried over sodium–benzophenone and distilled from purple solutions prior to use. 2-Butanol was dried over K_2CO_3 and then distilled. Xylenes (mixture of isomers) were distilled from sodium–benzophenone ketyl. All glassware and transfer needles were oven-dried at 100 °C. 18-Crown-6 (18C6, Aldrich, 99%), 1,2-dibromoethane (Acros, 99%) and bromobenzene (Aldrich, 99%) were used as received. Magnesium turnings (99.98%) were purchased from Aldrich. Teflon-coated stir bars were used. Authentic samples of benzene and biphenyl were commercially available. GC analyses were performed on a Fisons GC 8000 instrument using a BPX5 capillary column (SGE, 25 m × 0.22 mm i.d.) with helium as carrier gas and a flame ionization detector. The following temperature programme was used with **1Br**: injector, 280 °C; detector, 250 °C; 80 °C (0 min) to 250 °C

(5 min) at 5 °C min^{-1}. The following temperature programme was used with bromobenzene: injector, 280 °C; detector, 250 °C; 50 °C (10 min) to 160 °C (0 min) at 5 °C min^{-1} and then to 250 °C (5 min) at 10 °C min^{-1}. Peak area integrations were performed by electronic integrations on a Spectra-Physics integrator and, if necessary, corrected using the ECN concept number.[129] Grignard reagents were titrated by Watson and Eastham's method.[132] At the end of the reaction, a solution of *o*-phenanthroline (~1 mg) in THF or DEE (~1 ml) was added by syringe. If the Grignard reagent is present, a purple or red colour develops. The mixture was then titrated to the end-point with a solution of 2-butanol in xylenes (0.5 M or 4 M) and analysed by GC. We checked that the presence of crown ether 18C6 does not interfere with the quantitative titration of the Grignard reagent. Each experiment was at least duplicated.

Reaction of bromide 1Br with magnesium. Magnesium (0.081 g, 3.333 mmol) was introduced into a Schlenk tube equipped with a magnetic bar. The Schlenk tube was successively degassed by three vacuum–nitrogen cycles, flamed under a flow of nitrogen and degassed again. A flask (10 ml) was flushed with nitrogen for 10 min. Then, **1Br** (0.151 g, 0.715 mmol), solvent (THF or diethyl ether, 5 ml) and 1,2-dibromoethane (25 µl, 0.289 mmol) were added by syringe to the flask. The solution obtained was transferred via a canula to the Schlenk tube. After 2 h 5 min of stirring at room temperature, the Grignard reagent was titrated. After dilution with diethyl ether, the reaction mixture was successively washed with 10% ammonium chloride and water, then dried ($MgSO_4$) and filtered.

Reaction of bromide 1Br with magnesium and crown ether. Magnesium (0.032 g, 1.317 mmol) was introduced into a Schlenk tube equipped with a magnetic bar. The Schlenk tube was successively degassed by three vacuum–nitrogen cycles, flamed under a flow of nitrogen and degassed again. A flask (10 ml) containing the crown ether 18C6 (0.1–4.9 equiv.) was flushed with nitrogen for 10 min. Then, solvent (THF or diethyl ether, 2 ml), **1Br** (0.063 g, 0.298 mmol, 1 equiv.) and 1,2-dibromoethane (10 µl, 0.116 mmol) were added by syringe to the flask. The solution obtained was transferred via a canula to the Schlenk tube. After the allocated time of stirring at room temperature, the Grignard reagent was titrated. After dilution with diethyl ether, the reaction mixture was successively washed with 10% ammonium chloride and water, then dried ($MgSO_4$) and filtered.

Reaction of bromobenzene with magnesium. Magnesium (0.485 g, 19.96 mmol) was introduced into a Schlenk tube equipped with a magnetic bar. The Schlenk tube was successively degassed by three vacuum–nitrogen cycles, flamed under a flow of nitrogen and degassed again. A flask (10 ml) was flushed with nitrogen for 10 min. Then, bromobenzene (0.5 ml, 4.748 mmol) and solvent (THF or diethyl ether, 5 ml) were added by syringe in the flask. The solution obtained was transferred via a canula to the Schlenk tube. After the allocated time of stirring at room temperature, the Grignard reagent was titrated. After dilution with diethyl ether, the reaction mixture was successively washed with 10% ammonium chloride and water, then dried ($MgSO_4$) and filtered.

Reaction of bromobenzene with magnesium and crown ether (0.1 equiv.). Magnesium (0.486 g, 20.00 mmol) was introduced into a Schlenk tube equipped with a magnetic bar. The Schlenk tube was successively degassed by three vacuum–nitrogen cycles, flamed under a flow of nitrogen and degassed again. A flask (10 ml) containing crown ether 18C6 (0.126 g, 0.477 mmol) was flushed with nitrogen for 10 min. Then, solvent (THF or diethyl ether, 5 ml) and bromobenzene (0.5 ml, 4.748 mmol) were added by syringe to the flask. The solution obtained was transferred via a canula to the Schlenk tube. After the allocated time of stirring at room temperature, the Grignard reagent was titrated. After dilution with diethyl ether, the reaction mixture was successively washed with 10% ammonium chloride and water, then dried ($MgSO_4$) and filtered.

Reaction of bromobenzene with magnesium and crown ether (1 equiv.). Magnesium (0.10 g, 4.115 mmol) was introduced into a Schlenk tube equipped with a magnetic bar. The Schlenk tube was successively degassed by three vacuum–nitrogen cycles, flamed under a flow of nitrogen and degassed again. A flask (10 ml) containing the crown ether 18C6 (0.269 g, 1.018 mmol) was flushed with nitrogen for 10 min. Then, solvent (THF or diethyl ether, 1 ml) and bromobenzene (0.1 ml, 0.950 mmol) were added by syringe to the flask. The solution obtained was transferred via a canula to the Schlenk tube. After the allocated time of stirring at room temperature, the Grignard reagent was titrated. After dilution with diethyl ether, the reaction mixture was successively washed with 10% ammonium chloride and water, then dried ($MgSO_4$) and filtered.

Acknowledgement

Hassan Hazimeh is grateful to ECOS-Sud for supporting his research training accomplished in Buenos Aires, Argentina. Financial support from the French CNRS, Paul Cezanne University, Buenos Aires University and ECOS-Sud is gratefully acknowledged.

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