

# Versatile electrochemically based preparation of unusual Grignard reagents containing electrophilic substituents

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## Abstract

Upon electrochemical reduction of potassium perchlorate in dimethyl sulfoxide to potassium the strong dimethyl sulfoxide base (i.e. the conjugate base of dimethyl sulfoxide) is formed in the reaction of the alkali metal with the solvent. The electrolysis is performed in an undivided cell with a magnesium rod serving as sacrificial anode, thereby generating magnesium ions, which stabilize the generated dimethyl sulfoxide base through ion-pair formation. In a second non-electrochemical step, Grignard type reagents  $R_2Mg$  are obtained simply by letting the magnesium salt of dimethyl sulfoxide base deprotonate weakly acidic substrates ( $pK_a < 26$  in dimethyl sulfoxide) added to the solution. The advantage of generating these reagents through a deprotonation route rather than by reduction of halogen-substituted compounds as in the classical approach is that the substrates may contain electrophilic groups, such as halogen, carbonyl or cyano. The  $R_2Mg$  reagents react with electrophiles akin to ordinary Grignard reagents as illustrated by the preparation of several substituted benzyldienefluorenes in nucleophilic addition reactions. The electrochemical properties of the products were investigated and a reasonable linear correlation of the first reduction potentials with the Hammett substituent coefficient  $\sigma^-$  was found.

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**Keywords:** Electrogenerated bases; Grignard type reagent; Sacrificial anode; Nucleophilic addition; Synthetic methods

## 1. Introduction

Grignard reagents have for a century been important species employed in organic chemistry. The reagent is most often described as  $RMgX$  although in reality there will be a Schlenk equilibrium between  $R_2Mg$ ,  $MgX_2$ ,  $RMgX$  and adsorbed species at magnesium [1,2]. In the classical approach, the reagent is formed in a reaction between an organic halide and magnesium in an inert solvent, generally, an ether. Although extremely useful, this approach has some limitations, as it prohibits the presence of other reactive and reducible functional groups in the same molecule. Electrophilic groups, such as carbonyl, nitro and cyano, along with acidic groups, such as alcohols, amines, thiols

and carboxylic acids, must be avoided because of their high reactivity towards the Grignard functionality [3].

Grignard reagents may be prepared in other ways than the classical one, such as employing highly reactive magnesium slurries in THF at  $-78^\circ C$  [4], using an iodide-magnesium exchange reaction by treating *o*-iodonitrobenzene with phenylmagnesium chloride in THF at  $-40^\circ C$  [5], or reacting an alkenyl iodide with isopropylmagnesium chloride and lithium chloride in dry THF [6]. Using these methods cyano groups, esters and even nitro groups [5] may be allowed in the Grignard reagent.

The aim of the present paper is to present another way of preparing Grignard type reagents which allows the presence of certain electrophilic groups. The first step in the new approach is an electrochemical generation of the strong dimethyl sulfoxide base (i.e. the conjugated base of dimethyl sulfoxide, DMSO) accomplished through a reduction of a potassium salt to the reactive and strongly reducing potassium metal in

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DMSO. This electrolysis is carried out in an undivided cell with a magnesium rod serving as sacrificial anode in order to prepare simultaneously the other important constituent of Grignard reagents, i.e. magnesium ions. In a second non-electrochemical step, this dimsyl base (now ion-paired with magnesium) is used to deprotonate weakly acidic substrates, thereby generating the target molecule in terms of a Grignard type reagent of the form  $R_2Mg$ . The great advantage of this procedure is that it allows the formation of  $R_2Mg$  reagents containing electrophilic substituents, such as halogen, carbonyl and cyano, which otherwise would be reduced by magnesium in the classical procedure for preparing such reactants.

A somewhat similar procedure has been used in forming strong bases from compounds having an N–H bond. Thus, electrochemical reduction of hexamethyldisilazane (HMDS) in DME containing 15% HMPA in an undivided cell with a sacrificial magnesium anode and a stainless steel grid cathode produced  $[(Me_3Si)_2N]_2Mg$  which could deprotonate ketones having an  $\alpha$ -hydrogen [7]. 2-Pyrrolidone and HMDS were similarly reduced at transition metal cathodes with a sacrificial magnesium anode. It was found that 2-pyrrolidone with  $pK_a = 24.2$  (DMSO) [8] was reduced by a diffusion-controlled direct dissociative discharge mechanism, whereas the reduction of HMDS with  $pK_a = 26$  (DMSO), involved a reduction of the solvent followed by a slow evolution of hydrogen from HMDS [9].

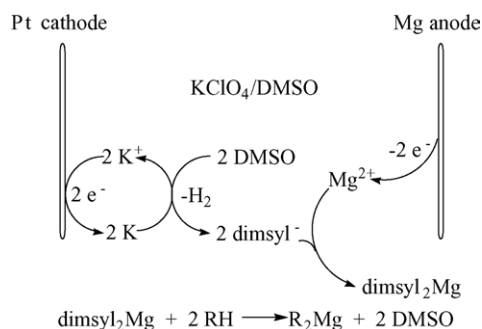
In the present paper, we have prepared Grignard reagents from fluorene, halogen-substituted fluorenes, acetophenone and phenylacetonitrile. The reagents have been employed in nucleophilic addition reactions involving carbonyl compounds, in most cases substituted benzaldehydes.

## 2. Results and discussion

One of the most useful strong bases employed within the organic chemistry community is the deprotonated DMSO, dimsyl. In principle, this base (along with hydrogen) may be prepared chemically by reacting an alkali metal (K, Na) or an alkali metal hydride (KH, NaH) with DMSO [10]. However, the latter procedure is somewhat hazardous and certainly for industrial purposes it will be associated with safety problems.

From this perspective, it would be desirable if the alkali metal could be generated in situ from the corresponding alkali ions. An attractive route is presented by the electrochemical approach outlined in Scheme 1. The electrochemical reduction of  $KClO_4$  in DMSO in an undivided electrochemical cell using magnesium as anode produces in the first step the dimsyl base ion-paired with the magnesium ions generated at the anode.

The use of a galvanostatic (i.e. constant current) set-up is advantageous as this allows easy control of the amount of base produced simply through adjustment of the current and the electrolysis time. The current efficiency is close to 100%



Scheme 1. Proposed mechanism for the generation of the Grignard type reagent  $R_2Mg$  in the electrochemical approach.

as deduced from titration of the amounts of base produced. Note that if electrophilic impurities should be present in the solution, other and weaker bases might be generated along with dimsyl. In order to evaluate roughly the strength of the base(s) present we let the electrogenerated solution react with a weak acid, such as fluorene ( $pK_a = 22.6$  in DMSO) [8]. The conversion of fluorene to fluorenone was found to be higher than 90% as determined from the recording of UV–vis spectra of the latter species (see Section 6). This result does not only illustrate the high efficiency of the electrochemical procedure outlined but also that electrogenerated dimsyl has a high stability in solution in the absence of electrophiles. In the synthetic applications described below we usually choose to employ a small excess of base. At the same time the set-up is simple requiring only two rods as electrodes and a power supply. The stabilizing effect exerted by magnesium ions on dimsyl is important because the further attack by potassium on DMSO [11] then is diminished. If the electrolysis were carried out in a divided cell the more reactive potassium salt of dimsyl would rather be produced. On the basis of the cyclic voltammograms of electrochemically generated dimsyl collected in Fig. 1 it is seen that the anodic peak potential is about 0.3 V less negative when dimsyl is ion-paired with  $Mg^{2+}$  than

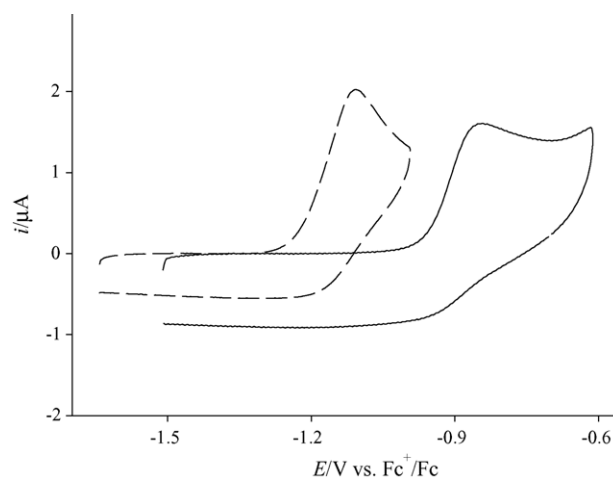


Fig. 1. Cyclic voltammograms of 2 mM magnesium ion-paired dimsyl (—) and 2 mM potassium ion-paired dimsyl (---) in 0.3 M  $KClO_4$ /DMSO recorded at a scan rate of  $0.5 V s^{-1}$ .

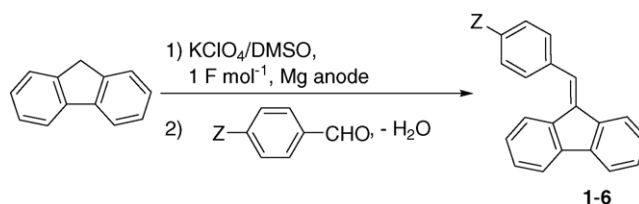
with  $K^+$ . Such a potential difference would translate to a difference in basicity of about 5  $pK_a$  units [12].

The above procedure presents the first electrochemical approach for generating such a strong base as dimsyl. Previously basic anions have been prepared by reducing weakly acidic compounds at a platinum electrode in different aprotic media [7,9,13–19]. The formation of the anions is accompanied by evolution of hydrogen originating either from the direct discharge of the acidic compound or from the reduction of protons formed in a pre-dissociation reaction of the acidic compound. Alternatively, anions may be generated from a two-electron reduction of halogen compounds [20,21]. Several papers and reviews dealing with the properties and applications of electrochemical bases have been published [22–25].

With the electrochemical generation of the magnesium salt of dimsyl, the target molecules in terms of Grignard type reagents (formally of the form  $R_2Mg$ ) can easily be generated in a second non-electrochemical step upon adding an acid RH to the solution (see Scheme 1). Because of the strong base strength of dimsyl it is expected that even rather weak acids RH may be used. A limiting  $pK_a$  value can roughly be determined to be about 27, employing a  $pK_a$  value of 32 for DMSO (in DMSO) [8] and taking into account that the base strength of dimsyl is lowered by approximately 5  $pK_a$  units because of the ion-pairing with  $Mg^{2+}$ . In this investigation, we have selected the following acids with the listed  $pK_a$  values all referring to DMSO: fluorene ( $pK_a = 22.6$ ), 2-bromofluorene ( $pK_a = 20.0$ ), 2,7-dibromofluorene ( $pK_a \leq 20.0$ ), acetophenone ( $pK_a = 24.7$ ) and phenylacetonitrile ( $pK_a = 21.9$ ) [8]. As seen, some of the Grignard type reagents thus formed will be quite unusual as they contain reducible groups, such as bromine, carbonyl and cyano. The applicability of these reagents will be illustrated through classical nucleophilic addition reactions involving mainly benzaldehydes [26].

### 2.1. Synthetic aspects

Yields of the isolated addition products are collected in Table 1. For the first six entries fluorene was used



Scheme 2. Reaction of fluorene with dimsyl $_2$ Mg and 4'-substituted benzaldehydes (Z = H, CN, CH $_3$ O, Me $_2$ N, NO $_2$  and Br, respectively) affording 1–6, respectively.

as the weak acid RH while the electrophile employed in the nucleophilic addition reaction was varied, i.e. benzaldehyde, 4-cyanobenzaldehyde, 4-methoxybenzaldehyde, 4-(*N,N*-dimethylamino)benzaldehyde, 4-nitrobenzaldehyde and 4-bromobenzaldehyde (see Scheme 2).

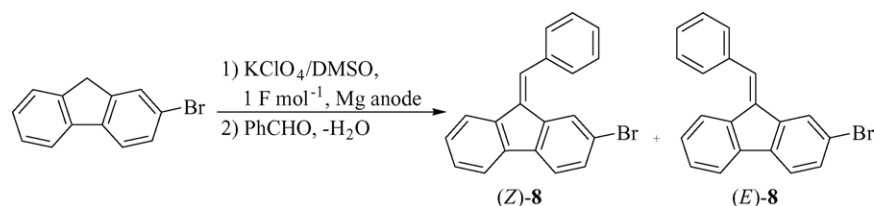
In all reactions, the corresponding benzylidene fluorenes 1–6 were obtained in fair to good yields, although a small portion of the nitro derivative 5 was reduced by the base to afford small amounts of 9-(4'-aminobenzylidene)fluorene as detected by GC–MS. The product 9-(4'-*N,N*-dimethylaminobenzylidene)fluorene (4) can easily be converted to 9-(4'-*N,N,N*-trimethylammoniumbenzylidene)fluorene iodide (7) through a methylation reaction using methyl iodide in acetonitrile. In some of the reactions, fluorenone is found in the product mixture due to the air oxidation of residual fluorenone, a well-known reaction previously described in literature [27]. In general, it may thus be concluded that electron-withdrawing substituents positioned on the carbonyl-containing compound are not exposed to reactions with the Grignard-type reagents but rather enhance the efficiency of the nucleophilic addition to the carbonyl group. For the nucleophilic addition to benzaldehyde containing electron-donating substituents the yields are somewhat lower.

In the literature, similar procedures employing deprotonation of fluorene and further reaction with benzaldehydes have produced comparable yields. The bases used were aqueous sodium hydroxide in phase transfer catalysis [28], sodium alcoholates [29–33], aluminum oxide [34] and alkaline earth hydroxides or potassium [35–37]. One example employing

Table 1  
Product yields for the reaction of Grignard type reagents generated from the acids RH with different electrophiles

Acid (RH)	Electrophile	Products	Yield (%) <sup>a</sup>
Fluorene	Benzaldehyde	9-Benzylidene fluorene (1)	89
Fluorene	4-Cyanobenzaldehyde	9-(4'-Cyanobenzylidene)fluorene (2)	87
Fluorene	4-Methoxybenzaldehyde	9-(4'-Methoxybenzylidene)fluorene (3)	61
Fluorene	4-( <i>N,N</i> -Dimethylamino)-benzaldehyde	9-(4'- <i>N,N</i> -Dimethylamino-benzylidene)fluorene (4)	42
Fluorene	4-Nitrobenzaldehyde	9-(4'-Nitrobenzylidene)fluorene (5)	51
Fluorene	4-Bromobenzaldehyde	9-(4'-Bromobenzylidene)fluorene (6)	61
2-Bromo-fluorene	Benzaldehyde	9-Benzylidene-2-bromo-fluorene (8)	75
2,7-Dibromo-fluorene	Benzaldehyde	9-Benzylidene-2,7-dibromo-fluorene (9)	84
2,7-Dibromo-fluorene	4-Bromobenzaldehyde	9-(4'-Bromobenzylidene)-2,7-dibromofluorene (10)	84
Fluorene	2,2,2-Trifluoro-acetophenone	1-(9'-Fluorenyl)-2,2,2-trifluoro-1-phenylethanol (11)	62
Acetophenone	Benzaldehyde	( <i>E</i> )-1,3-Diphenyl-2-propenone (12)	57
Phenyl-acetonitrile	Benzaldehyde	( <i>Z</i> )-2,3-Diphenylacrylonitrile (13)	92

<sup>a</sup> Isolated yield.



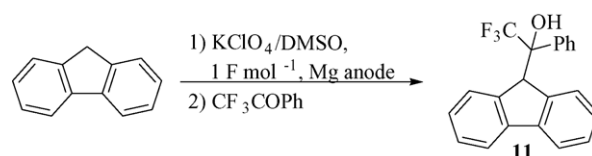
Scheme 3. Reaction of 2-bromofluorene with  $\text{dimethyl}_2\text{Mg}$  and benzaldehyde affording a 1:1 mixture of (*E*)- and (*Z*)-benzylidene-2-bromofluorene (**8**).

thiouronium fluorenylides as reactants has also been published [38]. In another approach, the reactants were circumvented in the sense that phosphoniumylides were allowed to react with 9-fluorenone [39]. No reports have appeared, in which the Grignard reagent, 9-fluorenylmagnesium bromide, was reacted with benzaldehyde. 9-Fluorenylmagnesium bromide cannot be obtained using the classical approach involving Mg and 9-bromofluorene but has to be obtained through a reaction between ethylmagnesium bromide and fluorene [40–43]. Even then, the nucleophilic addition reaction with benzaldehyde was not successful in our hands as the products obtained mostly consisted of 9-ethylfluorene, 1-phenylpropan-1-ol accompanied by detectable amounts of 9-benzylidene fluorene. The approach described herein thus presents a convenient alternative route for generating this kind of Grignard type reagents.

Using 2-bromofluorene rather than fluorene as the weak acid and benzaldehyde as the electrophile in the outlined reaction protocol results in the formation of a mixture of (*Z*)- and (*E*)-9-benzylidene-2-bromofluorene (**8**) in essentially equal amounts (see Scheme 3). The identification of the products was facilitated by the fact that one of the isomers crystallized and its structure could be solved on the basis of an X-ray analysis to be the (*E*)-isomer [44]. The most important feature to note about this reaction is that the bromine in the 2-position is retained, which strongly underlines the advantage of generating the Grignard reagent through the new procedure outlined herein. In the classical approach, it would certainly be difficult to prepare a Grignard reagent containing a reducible bromine, so in a previous preparation of **8** (as an oil) the reactants had to be circumvented in the sense that benzylmagnesium chloride was allowed to act on 2-bromofluorenone [45].

If 2,7-dibromofluorene is used as the weak acid and benzaldehyde or 4-bromobenzaldehyde as the electrophile a high yield (84% in both cases) of 9-benzylidene-2,7-dibromofluorene (**9**) and 9-(4'-bromobenzylidene)-2,7-dibromofluorene (**10**), respectively, is isolated. An X-ray structure determination of the latter product indicated that the phenyl group is located at an angle of  $48^\circ$  compared with the planar fluorene methylene moiety [44,46].

While the magnesium salt of fluorenylides is found to react readily with benzaldehyde (see above) no addition product can be isolated if acetophenone is used as the electrophile. On the other hand, we found that 2,2,2-trifluoroacetophenone reacts quite effectively with formation of 2,2,2-trifluoro-1-



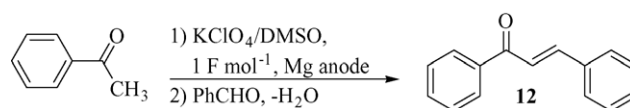
Scheme 4. Reaction of fluorene with  $\text{dimethyl}_2\text{Mg}$  and 2,2,2-trifluoroacetophenone affording **11**.

(9'-fluorenyl)-1-phenylethanol (**11**) in an acceptable yield of 62% (see Scheme 4).

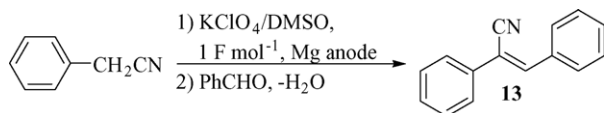
The failure of acetophenone can be attributed to a lower reactivity of the carbonyl group along with the possibility of having a deprotonation reaction involving the acidic  $\alpha$ -hydrogens, which would lead to the formation of a magnesium enolate salt with low reactivity. Although acetophenone is less acidic than fluorene by two  $\text{p}K_a$  units as measured in DMSO [8] the presence of the magnesium ions might exert a compensating effect in that the enolate ion would enjoy a larger stabilization from ion-pairing than fluorenylides.

So far, we have shown that the presence of a bromine substituent in an aromatic system is no hindrance for the formation of a Grignard-type reagent. The next question is, can other groups such as carbonyl be introduced as well? In order to test this point we selected acetophenone as the weak acid ( $\text{p}K_a = 24.7$ ) and upon generating the pertinent Grignard reagent it was reacted with benzaldehyde to afford (*E*)-1,3-diphenyl-2-propen-1-one (**12**) in a smooth reaction (see Scheme 5). Only a trace of the base-catalyzed self-condensation product of acetophenone, 1,3-diphenyl-2-buten-1-one (dypnone), could be detected by GC indicating that the conversion of acetophenone to its magnesium enolate had been almost complete.

In this context, it might be mentioned that electrochemical reduction of acetophenone in  $\text{KClO}_4/\text{DMSO}$  in a divided cell results among other products in a low yield of 1,3,5-triphenylbenzene (36%), obtained by self-condensation of three molecules of acetophenone. Furthermore, 1,3,5-triphenylbenzene may also be obtained



Scheme 5. Reaction of acetophenone with  $\text{dimethyl}_2\text{Mg}$  and benzaldehyde affording **12**.



Scheme 6. Reaction of phenylacetonitrile with dimethylmagnesium and benzaldehyde affording **13**.

directly from acetophenone by both base and acid catalysis [47–49].

Just as a keto group alpha to acidic hydrogens presents no hindrance for the formation of a Grignard-type reagent (i.e. a magnesium enolate in this case) the same is true for a cyano group. As shown in Scheme 6, addition of phenylacetonitrile (pK<sub>a</sub> = 21.9) [8] to a dimethylmagnesium solution produces the expected reagent, which further can react with benzaldehyde to give (Z)-1,2-diphenylacrylonitrile (**13**).

If an even weaker acid such as 4-benzylpyridine (pK<sub>a</sub> = 26.7) [8] is used the procedure outlined does not work simply because no deprotonation takes place in the reaction with the magnesium salt of dimethyl. As no such problems were observed for acetophenone (pK<sub>a</sub> = 24.7), the upper pK<sub>a</sub> limit for the applicability of the method can be set at 25–26 in good agreement with the above-mentioned value of ca. 27 estimated on the basis of the recorded voltammograms in the presence and absence of magnesium ions (see Fig. 1). The nucleophilic addition reaction works best for the aromatic carbonyls without α-hydrogens, while for carbonyl-containing substrates having an α-hydrogen, the main pathway rather consists of condensation reactions because of the formation of enolate ions. For instance, with propanal a maximum of 15% 9-propylidene-fluorene is formed, so in this case the addition product can be prepared much more conveniently from a reaction between propylmagnesium bromide and 9-fluorenone [50]. In order to increase the reactivity of the generated nucleophiles we attempted to improve the procedure by not having magnesium ions present – carrying out the electrolysis in a divided cell – but the result was a disappointing diminish in the yield, in the case of **1** from 89 to 27%.

## 2.2. Mechanistic aspects

Mechanistically, the reaction between a Grignard reagent and a carbonyl compound may proceed either as a polar “two-electron” nucleophilic addition to the carbon–oxygen double bond or as an electron transfer process with the Grignard reagent acting as an electron donor. In particular, in the case of aromatic ketones strong evidence has been presented in favor of the electron transfer pathway through the detection of magnesium-coordinated radical anion intermediates [51–53]. From a thermodynamic point of view, the feasibility of the electron transfer pathway can easily be judged from a measurement of the oxidation potential of the nucleophile and the reduction potential of the electrophile. For this reason, it became of interest to measure relevant potentials of some of the reactants involved in the reactions of Scheme 2.

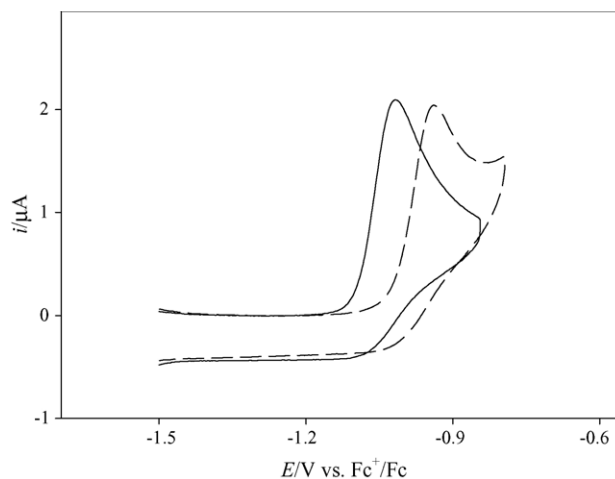


Fig. 2. Cyclic voltammograms of 2 mM potassium ion-paired fluorenone anion (—) and magnesium ion-paired fluorenone anion (---) in 0.3 M KClO<sub>4</sub>/DMSO recorded at a scan rate of 0.5 V s<sup>-1</sup>.

## 2.3. Electrochemical aspects

Fig. 2 shows a cyclic voltammogram of the Grignard reagent R<sub>2</sub>Mg of fluorenone, i.e. the magnesium salt of fluorenone generated from the reaction of fluorenone with the magnesium salt of dimethyl, along with the corresponding potassium salt of fluorenone, generated from the reaction of fluorenone with the potassium salt of dimethyl. In general, from previous studies it would be expected that while the ion-pairing effect of K<sup>+</sup> is small and comparable with that of the tetrabutylammonium ion [54,55] it should be substantially larger for Mg<sup>2+</sup> [56,57]. Indeed, the oxidation peak of fluorenone appears at a potential that is about 100 mV less negative, when it is ion-paired with magnesium, i.e. R<sub>2</sub>Mg, compared with potassium, i.e. RK (peak potential ≈ -1.0 V versus Fc<sup>+</sup>/Fc). Such a positive shift in the oxidation potential would be expected to be transposed into a slightly lower basicity and nucleophilic reactivity of R<sub>2</sub>Mg as compared with RK.

In comparison, the reduction peak potential of benzaldehyde employed as electrophile in the very first reaction of Scheme 2 is equal to -2.14 V versus Fc<sup>+</sup>/Fc in DMSO [58] (recorded at a sweep rate of 1 V s<sup>-1</sup>). This shows that an outer-sphere electron transfer to benzaldehyde will be an up-hill reaction of more than 1.0 eV (≈99 kJ mol<sup>-1</sup>). For this reason, this pathway may be excluded and there seems to be no doubt that the mechanism must follow the polar nucleophilic addition pathway. Of the substituents considered in Scheme 2 an electron transfer will present a feasible pathway only in the case of 4-nitrobenzaldehyde having a reduction potential of -1.15 V versus Fc<sup>+</sup>/Fc which gives an up-hill barrier of about 0.1 eV (≈9 kJ mol<sup>-1</sup>). Actually, this is presumably the reason why reduction and dimerization products such as 4-aminobenzylidene-fluorenone and 9,9'-bi-9H-fluorene were detected in GC-MS in this case.

In Table 2, we have collected all reduction peak and standard potentials of the products **1–10** measured by

Table 2  
Standard or peak potentials measured at a glassy carbon electrode at a sweep rate of  $1 \text{ V s}^{-1}$

Products	$E_p$ (V) <sup>a</sup>	$E^0$ (V) <sup>a</sup>
9-Benzylidene fluorene ( <b>1</b> )		-2.00 (-2.06)
9-(4'-Cyanobenzylidene)fluorene ( <b>2</b> )		-1.72 (-1.77)
9-(4'-Methoxybenzylidene)fluorene ( <b>3</b> )		-2.07 (-2.14)
9-(4'- <i>N,N</i> -Dimethylaminobenzylidene)fluorene ( <b>4</b> )		-2.13 (-2.19)
9-(4'-Nitrobenzylidene)fluorene ( <b>5</b> )		-1.29 (-1.38)
9-(4'-Bromobenzylidene)fluorene ( <b>6</b> )	-1.94 (-1.99)	
9-(4'- <i>N,N,N</i> -Trimethylammoniumbenzylidene)fluorene iodide ( <b>7</b> ) <sup>b</sup>	-1.86 (-1.90)	
9-Benzylidene-2-bromofluorene ( <b>8</b> )		-1.90 (-1.95)
9-Benzylidene-2,7-dibromofluorene ( <b>9</b> )	-1.82 (-1.86)	
9-(4'-Bromobenzylidene)-2,7-dibromofluorene ( <b>10</b> )	-1.76 (-1.78)	

<sup>a</sup> Measured in 0.3 M  $\text{KClO}_4/\text{DMSO}$  vs.  $\text{Fc}^+/\text{Fc}$ . Values given in parentheses pertain to 0.1 M  $\text{Bu}_4\text{NBF}_4/\text{DMF}$ .

<sup>b</sup> Product was obtained by methylation of **4** in 95% yield.

cyclic voltammetry in DMSO and *N,N*-dimethylformamide (DMF). Three illustrative examples of cyclic voltammograms recorded for benzylidene fluorene (**1**), 9-(4'-cyanobenzylidene)fluorene (**2**) and 9-(4'-bromobenzylidene)fluorene (**6**) are shown in Fig. 3. While the reduction process of **1** is reversible, the cyclic voltammetric reduction feature of **6** consists of an irreversible wave attributed to the two-electron reduction of the C–Br bond followed by the reversible reduction of the thus generated **1** (after protonation). The difference between the peak potentials of **6** and that of **1** is about 100 mV at a sweep rate of  $1 \text{ V s}^{-1}$ , while at higher sweep rates the peak potential of **6** becomes gradually more negative and the peak merges with that of **1**.

The voltammograms of **2** and **5** each consists of two reversible electrode processes having a potential difference of 200–300 mV. Such an unusually small potential difference between the two waves might be indicative of some major geometrical changes going on during the reduction steps. As an X-ray crystallographic analysis of **2** shows that the plane of the phenyl ring is about  $48^\circ$  [44] out of the fluorenylidene plane one could easily imagine that the angle between the planes of the two moieties would become smaller upon

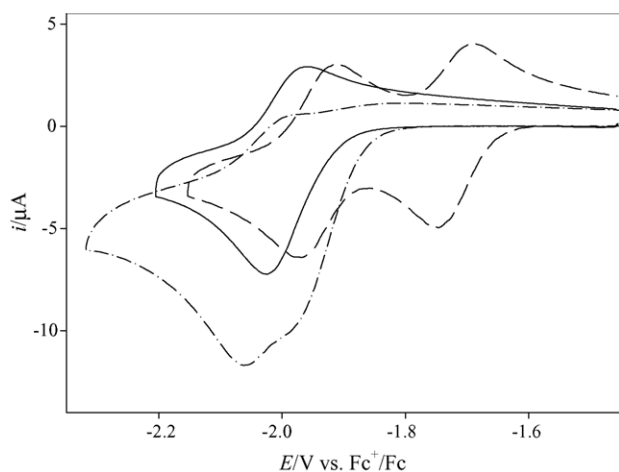


Fig. 3. Cyclic voltammograms of 2 mM **1** (—), **2** (---) and **6** (- · -) in 0.3 M  $\text{KClO}_4/\text{DMSO}$  recorded at a scan rate of  $1 \text{ V s}^{-1}$ .

reduction to allow for extended conjugation in the radical anion and dianion.

The peak (recorded at a sweep rate of  $1 \text{ V s}^{-1}$ ) and standard potentials for the 4'-substituted benzylidene fluorenes exhibit a reasonable linear dependency on the Hammett substituent coefficients  $\sigma^-$  with slopes  $\rho$  of 0.30 V for DMSO and 0.32 V for DMF as shown in Fig. 4.

If  $\sigma$  is used as the correlation parameter, a slightly worse correlation is obtained with slopes of 0.28 and 0.32 for DMSO and DMF, respectively. It may seem surprising that the potentials fit so well considering that they are a mixture of reversible and irreversible potentials but this is not without precedent as a Hammett relation with  $\rho = 0.23 \text{ V}$  also has been found in a study of the polarographic reduction potentials of benzylidene fluorenes in 68% methanol, using  $\sigma$  as the correlation parameter [59]. The additive nature of the substituent effects is substantiated by the fact that the value of  $\sigma^-$  [60] used here for the bromo derivatives **6**, **8–10** is the usual value for a bromine substituent ( $\sigma^- = 0.25$ ) times the number of bromines present in the 2-, 7- and/or 4'-positions.

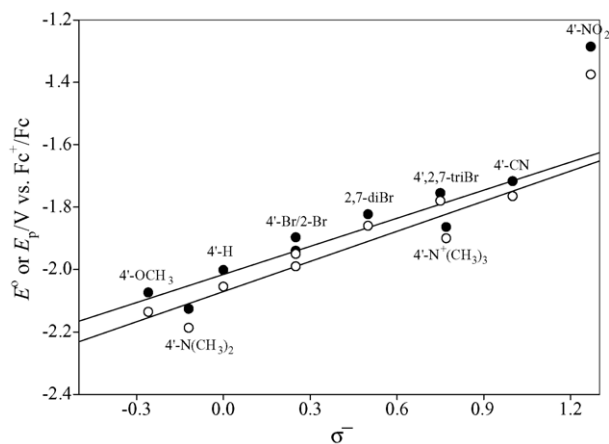


Fig. 4. Hammett plot for standard or peak potentials (recorded at a scan rate of  $1 \text{ V s}^{-1}$ ) of 4'-substituted benzylidene fluorenes in 0.3 M  $\text{KClO}_4/\text{DMSO}$  (●) and 0.1 M  $\text{Bu}_4\text{NBF}_4/\text{DMF}$  (○). The following  $\sigma^-$  values were used: **3**, -0.26; **4**, -0.12; **1**, 0.00; **8**, 0.25; **6**, 0.25; **9**, 0.50; **10**, 0.75; **7**, 0.77; **2**, 1.00; **5**, 1.27. The points for **5** were excluded from the regression analysis.

Three exceptions from the general trend are presented by the dimethylamino and trimethylammonium groups and, in particular, the nitro group; the nitro-substituted substrate is much more easily reduced than predicted by its  $\sigma^-$  value by several hundred mV. While there is no obvious reason for the deviation observed for the dimethylamino group, the behavior of the nitro-substituted compounds is not unusual. In this case, the standard potential merely reflects the reduction of the nitro-substituent rather than the benzylidene-fluorene unit. Concerning the trimethylammonium substituent it has a  $\sigma^-$  value of 0.77 [60] but nevertheless **7** is reduced at a potential that is 140 mV more negative than that of the cyano derivative **2** with  $\sigma^- = 1.00$ . In order to test the generality of this observation we measured a number of potentials for a different trimethylammonium- and cyano-substituted benzaldehydes, pyridines and ethyl benzoates. In all cases, the peak potentials recorded for the trimethylammonium substituent were indeed found to be 200–300 mV more negative than the standard potential of the pertinent cyano-substituted compounds. These results confirm the view expressed previously on the basis of electrostatic equations [61] that charged substituents cannot be included along with dipolar groups in one general scale of electronic substituent effects.

### 3. Conclusion

A new methodology for preparing Grignard type reagents has been developed. The first step is based on an electrochemical generation of the magnesium salt of dimsyl through electrolysis of potassium perchlorate in DMSO and with a magnesium rod serving as sacrificial anode. The strong dimsyl base can be obtained in the desired concentration simply by adjusting the current and the electrolysis time. Furthermore, this procedure eliminates the need of using hazardous potassium or potassium hydride in the reaction with DMSO [62]. The rather strong dimsyl base can deprotonate acidic substrates added to the solution as long as its  $\text{p}K_{\text{a}} < 26$  (in DMSO) thereby forming a Grignard type reagent. The latter can further react with suitable electrophiles, such as aromatic carbonyls, without  $\alpha$ -hydrogens in classical nucleophilic addition reactions to afford, e.g. substituted benzylidenes. The great advantage of generating the Grignard reagent through a deprotonation of a weak acid rather than reduction of a halogen-substituted compound by magnesium as known from the classical approach is that the substrate may contain reducible substituents, such as halogens and carbonyl or cyano alpha to the acidic site.

The electrochemical properties of the products, i.e. substituted benzylidenes, and the reagents were investigated as well. The reaction mechanism of fluorenone and benzaldehyde is a nucleophilic addition reaction since the electron transfer is an up-hill reaction of 99  $\text{kJ mol}^{-1}$ . Further it was found that the reduction peak potentials of the benzylidene-fluorenes exhibited a reasonable linear dependence on the

Hammett substituent coefficients  $\sigma^-$  with a slope  $\rho$  of 0.30 V in DMSO and 0.32 V in DMF, excluding the deviating behavior of the nitro-substituent.

## 4. Experimental

### 4.1. Materials

Dimethyl sulfoxide (Fluka, >99.5%) was handled under argon using normal syringe procedures and dimethylformamide (Lab Scan) was dried over activated alumina (ICN Alumina-I-Super) prior to use. Potassium perchlorate (Merck p.a.), potassium iodide (Riedel de Haën) and tetrabutylammonium iodide,  $\text{Bu}_4\text{NI}$  (Chemische Fabrik Berg GmbH), were used as received. Tetrabutylammonium tetrafluoroborate,  $\text{Bu}_4\text{NBF}_4$ , was synthesized according to standard procedures and dried under vacuum at 60 °C for 24 h. The magnesium rods were purchased from Aldrich (+99.9%). All other substrates were purchased from Aldrich, Fluka or Merck except for 2-bromofluorene [63] and 2,7-dibromofluorene [64], which were prepared according to the references given. Fluorene, 2-bromofluorene and 2,7-dibromofluorene were recrystallized prior to use, while all other reagents were used as received.

### 4.2. Equipment

The GC–MS analyses were carried out on a Hewlett Packard 5890A gas chromatograph equipped with a 5971A MSD mass-selective detector. The GC column was an HP5 25 m with 0.25 mm internal diameter. The injection temperature was 250 °C, helium flow 1.0  $\text{mL min}^{-1}$ , temperature program 40 °C for 5 min to 230 °C, rate 15 °C  $\text{min}^{-1}$ . The  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectra were recorded on a Varian 400 MHz with  $\text{CDCl}_3$  ( $\delta = 7.26$  and 77.16 ppm) or DMSO ( $\delta = 2.50$  and 39.60 ppm) as reference. The UV–vis experiments were recorded by means of a fiber-optic spectrometer S1000 (dip-probe) from Ocean Optics. The cyclic voltammetric experiments were performed with a three-electrode cell set-up with a glassy carbon (Sigradur® G,  $\text{Ø} = 1$  mm) working electrode, a platinum wire and an Ag/AgI electrode (silver wire in either 0.1 M potassium iodide in DMSO or 0.1 M tetrabutylammonium iodide in DMF separated from the solution by a ceramic frit) served as counter and reference electrode, respectively. All potentials are referenced against the ferrocenium/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) redox couple. The ohmic drop was compensated with a positive feedback system incorporated in the home-built potentiostat.

## 5. Procedures

A typical experiment was performed using the following parameters. Potassium perchlorate (1.6 g) was dissolved in

dry DMSO (40 mL). The solution was added to an undivided electrochemical cell containing a platinum cathode and a magnesium anode. The solution was deaerated with dry argon and a current of 100 mA was passed through it for 1 h thereby generating 3.7 mmol dimsyl. The substrate (3.3 mmol) was subsequently dissolved in the electrolyzed solution, and after an additional 5 min the carbonyl-containing compound (3.3 mmol) was added. The reaction was stirred for 2 h at room temperature, acidified with dilute sulfuric acid and diluted with water. The product was extracted with petroleum ether or diethylether. The collected ether phases were washed thoroughly with water and a saturated solution of sodium hydrogencarbonate. The ether phase was dried with magnesium sulfate and evaporated in vacuo. The following products were synthesized.

**9-Benzylidene fluorene (1):** m.p. 74–75 °C (recrystallized from ethanol) [39];  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.05 (dt,  $J$  = 7.5, 1.4 Hz, 1 H), 7.24–7.50 (m, 6 H), 7.53–7.61 (m, 3 H), 7.68–7.74 (m, 3 H), 7.79 (dt,  $J$  = 7.5, 1 Hz, 1 H);  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 119.9, 120.0, 120.5, 124.7, 126.9, 127.3, 127.5, 128.3, 128.5, 128.8 (2C), 129.5 (3C), 136.7, 136.8, 137.2, 139.5, 139.8, 141.5; MS (70 eV, EI):  $m/z$  (%): 255 (19), 254 (87), 253 (100), 252 (65), 250 (24), 239 (7), 226 (6), 200 (3), 166 (5), 126 (20), 125 (9), 113 (9).

**9-(4'-Cyanobenzylidene) fluorene (2):** m.p. 150 °C (recrystallized from isopropanol) [39];  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.07 (dt,  $J$  = 7.6, 1.2 Hz, 1 H), 7.25–7.43 (m, 4 H), 7.57 (s, 1 H), 7.66–7.78 (m, 7 H);  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 77.5, 111.7, 119.0, 120.0, 120.3, 120.7, 124.5, 127.1, 127.5, 129.2, 129.6, 130.3 (2C), 132.6 (2C), 136.1, 138.7, 139.2, 139.7, 141.9, 142.1; IR (KCl):  $\nu$  = 2226  $\text{cm}^{-1}$  (C $\equiv$ N); MS (70 eV, EI):  $m/z$  (%): 280 (18), 279 (86), 278 (100), 277 (46), 250 (9), 165 (5), 139 (8), 125 (13), 112 (4).

**9-(4'-Methoxybenzylidene) fluorene (3):** m.p. 129.5–130 °C (recrystallized from 2-propanol,  $\text{CH}_2\text{Cl}_2$ /pentane) [65];  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.82 (s, 3 H), 6.99 (dt,  $J$  = 8.9, 2.0 Hz, 2 H), 7.09 (dt,  $J$  = 7.6, 1.1 Hz, 1 H), 7.29–7.39 (m, 3 H), 7.55 (dt,  $J$  = 8.9, 1.9 Hz, 2 H), 7.68–7.76 (m, 4 H), 7.78 (d,  $J$  = 7.5 Hz, 1 H);  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 55.4, 114.0 (2C), 119.6, 119.8, 120.2, 124.3, 126.7, 127.0, 127.5, 128.0, 128.4, 129.2, 131.0 (2C), 135.6, 136.7, 139.1, 139.8, 141.2, 159.7; MS (70 eV, EI):  $m/z$  (%): 285 (23), 284 (100), 283 (19), 269 (17), 253 (19), 240 (20), 239 (44), 226 (8), 213 (4), 120 (11).

**9-(4'-*N,N*-Dimethylaminobenzylidene) fluorene (4):** m.p. 135 °C (recrystallized from ethanol) [45];  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.07 (s, 6 H;  $\text{CH}_3$ ), 6.82 (d,  $J$  = 8.5 Hz, 2 H), 7.23 (t,  $J$  = 8.0 Hz, 1 H), 7.40 (m, 3 H), 7.64 (d,  $J$  = 8.5 Hz, 2 H), 7.74 (s, 1 H), 7.83 (m, 3 H), 8.10 (d,  $J$  = 8.0 Hz, 1 H);  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 40.4 (2C), 111.9 (2C), 119.5, 119.7, 120.0, 124.1, 124.3, 126.6, 126.8, 127.4, 127.9, 128.8, 131.2 (2C), 133.5, 137.0, 138.7, 140.3, 140.9, 150.4; MS (70 eV, EI):  $m/z$  (%): 298 (25), 297 (100), 296 (20), 253 (20), 252 (30), 149 (8), 148 (9), 126 (13).

**9-(4'-Nitrobenzylidene) fluorene (5):** m.p. 166–167 °C (recrystallized from ethanol) [38];  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.07 (dt,  $J$  = 7.6, 1.2 Hz, 1 H), 7.35–7.48 (m, 5H), 7.59 (bs, 1 H), 7.68–7.82 (m, 5 H), 8.31 (dt,  $J$  = 8.8, 2 Hz, 1 H);  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 120.0, 120.3, 120.8, 124.0, 124.1 (2C), 124.6, 127.0, 127.2, 127.5, 129.3, 129.7, 130.5 (2C), 136.1, 139.1, 139.2, 139.8, 142.0, 144.2; MS (70 eV, EI):  $m/z$  (%): 300 (18), 299 (72), 253 (41), 252 (100), 250 (36), 239 (20), 226 (11), 200 (6), 165 (11), 126 (12), 125 (10), 113 (9).

**9-(4'-Bromobenzylidene) fluorene (6):** m.p. 144–145 °C (recrystallized from acetic acid) [32];  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.08 (dt,  $J$  = 7.7, 1.1 Hz, 1H), 7.33 (dt,  $J$  = 7.4, 1.2 Hz, 2 H), 7.39 (dt,  $J$  = 7.7, 1.2 Hz, 1 H), 7.46 (d,  $J$  = 8.1 Hz, 2 H), 7.52 (d,  $J$  = 7.4 Hz, 1 H), 7.56–7.50 (m, 3 H), 7.71 (d,  $J$  = 8.1 Hz, 2 H), 7.76 (d,  $J$  = 7.4 Hz, 1 H);  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 119.8, 120.0, 120.4, 122.2, 124.4, 125.7, 126.9, 127.2, 128.5, 128.9, 131.1 (2C), 131.8 (2C), 135.9, 136.4, 137.2, 139.35, 139.37, 141.5; MS (70 eV, EI):  $m/z$  (%): 335 (10), 334 (50), 333 (15), 332 (51), 254 (15), 253 (81), 252 (100), 250 (32), 126 (28), 125 (18), 113 (13).

**9-(4'-*N,N,N*-Trimethylammoniumbenzylidene) fluorene iodide (7):** Treatment of 9-(4'-*N,N*-dimethylamino-benzylidene) fluorene with methyl iodide in acetonitrile gave **7** in 95% yield. m.p. 179–180 °C (recrystallized from acetonitrile/ether);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  = 3.72 (s, 9 H), 7.14 (t,  $J$  = 7.6 Hz, 1 H), 7.39 (m, 3 H), 7.49 (d,  $J$  = 7.7 Hz, 1 H), 7.86 (m, 4 H), 7.92 (s, 1 H), 7.99 (d,  $J$  = 7.6 Hz, 1 H), 8.11 (d,  $J$  = 8.4 Hz, 2 H);  $^{13}\text{C NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  = 56.4 (3C), 119.9, 120.4, 120.9 (2C), 121.0, 123.7, 126.0, 127.0, 127.3, 128.8, 129.3, 130.6 (2C), 135.3, 136.7, 138.0, 138.4, 138.6, 141.0, 146.6. HRMS (FAB):  $m/z$ : 312.1761  $\pm$  0.0016; calculated for the cation  $\text{C}_{23}\text{H}_{22}\text{N}^+$ : 312.1752.

**9-Benzylidene-2-bromofluorene (8):** A mixture of approximately 1:1 of the *E* and the *Z* isomer was isolated as a solid.

**(*E*)-9-Benzylidene-2-bromofluorene:** m.p. 133–134 °C (recrystallized from ethanol);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.01 (t,  $J$  = 7.6 Hz, 1 H), 7.25 (t,  $J$  = 7.2 Hz, 1 H), 7.30–7.44 (m, 4 H), 7.46–7.52 (m, 4 H), 7.58–7.63 (m, 2 H), 7.83 (d,  $J$  = 1.6 Hz, 1 H);  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 120.0, 121.0, 121.1, 123.8, 124.6, 127.3, 128.6, 128.78, 128.83 (2C), 129.0, 129.4, 131.2 (2C), 135.7, 136.5, 136.6, 138.2, 140.5, 141.6;  $^{13}\text{C NMR}$  (*Z*)-isomer (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 119.9, 120.55, 120.62, 121.2, 127.60, 127.65, 128.6, 128.8, 128.9 (2C), 129.5 (2C), 131.5, 136.4, 138.5, 138.6, 139.5, 140.3 two signals are missing because of overlap; the same MS was observed for both stereoisomers (70 eV, EI):  $m/z$  (%): 335 (10), 334 (41), 333 (11), 332 (41), 254 (14), 253 (71), 252 (100), 250 (37), 226 (5), 224 (6), 200 (3), 126 (26), 125 (18), 113 (12), 112 (7).

**9-Benzylidene-2,7-dibromofluorene (9):** m.p. 99–100 °C (recrystallized from acetonitrile) [32];  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.42–7.58 (m, 9 H), 7.68 (d,  $J$  = 1.6 Hz, 1 H), 7.71 (s, 1 H), 7.90 (d,  $J$  = 1.6 Hz, 1



H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 121.0, 121.1, 121.2, 121.4, 123.9, 127.6, 129.0 (2C), 129.1, 129.4 (2C), 130.2, 131.4, 131.7, 134.7, 135.9, 137.2, 138.2, 139.3, 141.3; MS (70 eV, EI):  $m/z$  (%): 415 (10), 414 (49), 413 (22), 412 (97), 411 (11), 410 (50), 333 (3), 332 (9), 331(3), 330 (9), 254 (3), 253 (22), 252 (100), 251 (15), 250 (49), 249 (7), 248 (9), 224 (6), 126 (32), 125 (26), 124 (9), 113 (8), 112 (8).

**9-(4'-Bromobenzylidene)-2,7-dibromofluorene (10):** m.p. 231–233 °C (recrystallized from DMSO) [66];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.42–7.58 (m, 7 H), 7.62 (dt,  $J$  = 8.0, 2.4 Hz, 2 H), 7.69 (d,  $J$  = 1.6 Hz, 1 H), 7.87 (d,  $J$  = 1.6 Hz, 1 H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 121.1, 121.2, 121.4, 121.5, 123.2, 124.0, 127.5, 128.6, 131.1 (2C), 131.6, 132.0, 132.2 (2C), 134.8, 135.2, 137.3, 138.0, 139.5, 141.1; MS (70 eV, EI):  $m/z$  (%): 495 (6), 494 (26), 493 (17), 492 (77), 491 (18), 490 (78), 488 (26), 412 (5), 410 (6), 333 (13), 332 (54), 331 (13), 330 (54), 251 (33), 250 (100), 249 (18), 248 (25), 224 (12), 200 (5), 166 (23), 165 (25), 125 (58), 124 (22), 112 (13).

**1-(9'-Fluorenyl)-2,2,2-trifluoro-1-phenylethanol (11):** The reaction time was increased to 4 h and the temperature to 40 °C. Up to 15% of the dehydrated product, 9-( $\alpha$ -trifluoromethylbenzylidene)fluorene, was detected by GC–MS in the crude product mixture. m.p. 140–141 °C (recrystallized from from toluene/pentane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.35 (s, 1 H), 4.80 (s, 1 H), 6.42 (d,  $J$  = 7.9 Hz, 1 H), 7.04 (t,  $J$  = 7.4 Hz, 1 H), 7.30 (t,  $J$  = 7.4 Hz, 1 H), 7.36 (t,  $J$  = 7.4 Hz, 1 H), 7.39–7.46 (m, 4 H), 7.53–7.58 (m, 2 H), 7.66 (d,  $J$  = 7.9 Hz, 1 H), 7.71 (dd,  $J$  = 7.8, 4.0 Hz, 2 H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 54.4, 119.8, 119.9, 124.5, 126.6, 126.7, 126.8, 127.3, 128.04 ( $\text{CF}_3$ ), 128.07 ( $\text{CF}_3$ ), 128.1 ( $\text{CF}_3$ ), 128.13 ( $\text{CF}_3$ ), 128.47 (2C), 128.50 (2C), 128.8, 129.0, 137.6, 140.0, 141.3, 142.5, 143.0; MS (70 eV, EI):  $m/z$  (%): 340 (5), 167 (12), 166 (91), 165 (100), 139 (4), 105 (11), 77 (5). HRMS(FAB):  $m/z$ : 339.1088  $\pm$  0.0016; calculated for the anion  $\text{C}_{21}\text{H}_{14}\text{F}_3\text{O}^-$ : 339.1075.

**9-( $\alpha$ -Trifluoromethylbenzylidene)fluorene:** MS (70 eV, EI):  $m/z$  (%): 323 (13), 322 (60), 254 (20), 253 (100), 252 (65), 250 (18), 126 (14), 113 (6).

**(E)-1,3-Diphenyl-2-propen-1-one (12):** m.p. 57–59 °C (recrystallized from ethanol);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.43 (m, 3 H), 7.48–7.62 (m, 4 H), 7.65 (dd,  $J$  = 6, 2.4 Hz, 2 H), 7.82 (d,  $J$  = 16 Hz, 1 H), 8.02 (d,  $J$  = 7.2 Hz, 2 H); MS (70 eV, EI);  $m/z$  (%): 209 (12), 208 (78), 207 (100), 179 (24), 178 (13), 165 (11), 131 (33), 105 (25), 103 (30), 77 (64), 51 (24).

**(Z)-2,3-Diphenylacrylonitrile (13):** The reaction was left over night to improve the yield to 92% from 66% as achieved after 2 h of reaction. m.p. 83–84 °C (recrystallized from ethanol) [67];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.35–7.51 (m, 6 H), 7.55 (s, 1 H), 7.69 (d,  $J$  = 7.2 Hz, 2 H), 7.90 (d,  $J$  = 7.2 Hz, 2 H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 111.9, 118.2, 126.2 (2C), 129.2 (2C), 129.3 (2C), 129.4, 129.5 (2C), 130.8, 134.0, 134.7, 142.5; MS (70 eV, EI):  $m/z$  (%): 206 (16),

205 (100), 204 (87), 203 (25), 190 (42), 178 (17), 177 (20), 176 (17), 165 (12), 151 (8), 149 (14), 105 (6).

## 6. Grignard reaction of fluorenylmagnesium bromide with benzaldehyde

Ethyl bromide (6.83 g, 63 mmol) in dry diethylether (15 mL) was added dropwise to magnesium (1.5 g, 63 mmol). The reaction was heated to 45 °C until all magnesium had reacted. Ethylmagnesium bromide was added to a solution of fluorene (4.15 g, 25 mmol) in *o*-xylene (25 mL) and heated to 125 °C for 2.5 h. Diethylether was evaporated prior to the addition of benzaldehyde (2.65 g, 25 mmol). The reaction was heated to 60 °C for 2.5 h and subsequently cooled on ice before addition of hydrochloric acid. The products were extracted with ether, washed with sodium hydrogensulfite, dried over sodium sulfate and evaporated in vacuo. The products were identified with GC–MS.

### 6.1. Titration of $\text{dimethyl}_2\text{Mg}$

During the constant current electrolysis (100 mA) of potassium perchlorate (2.0 g) in dry and deaerated DMSO (50 mL) in an undivided cell using a platinum cathode and a magnesium anode, samples (1 mL) of the electrolyzed solution were collected at different times until 80 min. Hydrochloric acid (0.0096 M, 10–20 mL) was added and then titrated with sodium hydroxide (0.01 M) using methyl red as indicator. The charge passed through the electrolyzed solution was at the same time measured by a coulometer. In this manner, it was found that the current efficiency for base formation was close to 100%. However, it should be mentioned that the titration procedure may be hampered severely for samples collected at the longer electrolysis times, unless the solutions are filtered. Presumably this is due to the presence of elemental magnesium, which is liberated from the anode upon prolonged electrolysis because of corrosion.

### 6.2. UV–vis detection of fluorenyl

The concentration of fluorenyl formed in the reaction between the electrogenerated magnesium ion-paired dimethyl solutions and excess fluorene could be determined by measuring the absorption at 360 nm. In these calculations an extinction coefficient of 14860  $\text{M}^{-1} \text{cm}^{-1}$  was used [68].

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- [58] Note that the standard potential of benzaldehyde was measured in the absence of magnesium ions. It is expected that the presence of magnesium ions would induce a shift in the cyclic voltammetric wave in a positive direction by a few hundred mV as observed by Pletcher and Slevin [56] in their study of methyl benzoate. This will result in an increase of the reaction driving force by approximately  $20 \text{ kJ mol}^{-1}$ .
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