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Regioselectivity in the intramolecular allyl transfer reaction catalysed by electrogenerated nickel complexes: influence of metal ions

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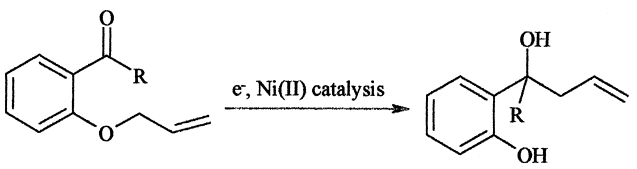
Abstract—The intramolecular transfer of allyl moieties from substituted allyl aryl ethers to carbonyl groups has been studied by electrosynthesis, in a nickel-catalysed reaction. The influence of metal ions such as Mg^{2+}, Zn^{2+} and Al^{3+} has been examined. Regioselectivity towards the branched isomer was better with Zn^{2+} than with Mg^{2+} ions, but it was higher in the absence of added metal ions.

1. Introduction

The allylation of carbonyl compounds is a widely used reaction for C–C bond formation. Generally, a previously prepared allylic organometallic reagent is added to a carbonyl group to form the homoallylic alcohol.[1] In the presence of non-symmetrically substituted allyl groups, branched or linear regioisomers can be obtained, depending on the nature of the metal reagent and on the reaction conditions.[2] Thus, high regioselectivities towards the branched isomer have been reported with allyl Grignard reagents and with most of the allylic organometallic reagents,[3,4] although a reversed regioselectivity has been observed with allyltin[5] or allylbarium reagents.[6,7] The addition of metal ions can influence,[3] and even reverse[8] the regioselectivity.

In the field of electrosynthesis, we have been interested in the intramolecular allylation of carbonyl compounds. The electrochemical allylation of carbonyl compounds with allyl chlorides and acetates has been reported.[9,10] Regioselectivity has been examined in the case of the direct electrochemical allylation,[10] as well as in the case of the nickel-catalysed allylation in the presence of a Zn anode.[11] In both cases, the branched regioisomer was predominant.

We studied an intramolecular version of the electrochemical allylation of carbonyl compounds in which the allyl moiety is issued from the cleavage of allyl ethers as summarised in compound **1a** (Eq. (1)).[12]



1a **2a** 42-87% (1)

This allyl transfer reaction allows the synthesis of alcohol–phenol derivatives in moderate to good yields. These highly functionalised compounds can undergo further reactivity, such as the intramolecular cyclisation to benzopyrans. The allyl transfer is catalysed by an electrogenerated Ni(0) complex, formed from the in situ reduction of the cationic Ni(II) complex, $Ni(bipy)_3^{2+}$, $2BF_4^-$ ((bipy=2,2′-bipyridine).[13] The homoallylic alcohol–phenol, **2a**, was obtained in up to 87% yield.

The influence of metal ions such as Mg^{2+}, Zn^{2+} or Al^{3+}on the regioselectivity of the intramolecular allyl transfer process has not been addressed before. We present here our results on the regioselectivity of the electrochemical intramolecular allylation process with derivatives of type **1**, with non-symmetrically substituted allyl groups. We also present the study of the influence of several metal ions, such as Mg^{2+}, Zn^{2+} and Al^{3+}, on the regioselective outcome of the reaction.

Keywords: allylation; electrochemical; regioselectivity; nickel; metal ions.
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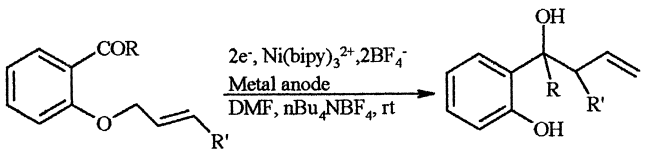
2. Results and discussion

Allyl ethers **1b**–**1f** were used as model compounds and were prepared by allylation of *ortho*-hydroxybenzaldehyde and *ortho*-hydroxyacetophenone with the corresponding allyl bromides in K_2CO_3/DMF. The electrolyses were carried out in a single-compartment cell at room temperature, with 10 mol% of the Ni(II) catalyst with respect to the substrate.

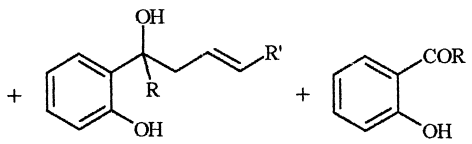
2.1. Allylation in the presence of Mg^{2+} ions

The $[Ni(bipy)_3]^{2+}2BF_4^-$-catalysed electrolysis of substrate **1b** in the presence of a Mg anode and a stainless-steel cathode led to a 53% yield of intramolecular allyl transfer compounds, with a 85:15 ratio of branched/linear regioisomers, **2b** and **3b** (Eq. (2) and Table 1). The reaction was run in DMF, at room temperature and at constant current intensity. The complete consumption of **1b** was reached after 2.4 F mol^{-1} electrolysis and the main by-product was salicylaldehyde **4**, formed in 14% yield. Compound **4** is issued from a Ni-catalysed deallylation process but without allyl transfer. The presence of the nickel catalyst was essential for the reaction; in its absence, the elecroreduction of **1a**, **1b** or **1c** led mainly to **4**, with low conversions. These results are summarised in Table 1.



1b-1f **2b-2f**

R = H, Me
R' = Me, Ph



3b-3f **4** R=H **5** R=Me

(2)

The electrochemical procedure in a single-compartment cell is a one-step allyl ether cleavage—allyl transfer process, in which there is no need for the previous preparation of the metal-allyl species. At the anode, a magnesium rod is oxidised to Mg^{2+} ions, and at the cathode the Ni(II) catalyst precursor is reduced to Ni(0), the active catalytic species. The mechanistic aspects of this reaction are discussed hereafter.

The electrolysis of the cinnamyl ether derivative, **1c**, under the same conditions, led to **2c** and **3c** in 70% yield, with a 67:33 ratio of branched to linear regioisomers. Only traces of **4** were obtained.

The electrolysis of **1d** led to an almost quantitative allyl transfer reaction (yield of 99%) with a ratio **2d/3d** of 99:1. In this case a very selective process occurred. The branched regioisomer **2d** was obtained as a 45:55 mixture of stereoisomers.

The electrolysis of methyl ketones **1e** and **1f**, with a Mg/stainless steel couple of electrodes, afforded no allylated compound. Only the C–O cleavage of the allyl group occurred, with the formation of **5** in 90 and 50% yields, respectively.

The results in Table 1 indicate that the main regioisomer corresponds to the branched compound **2**, and the regioselectivities are highly dependent on the type of substituent. The cinnamyl group presents the lower selectivity, whereas the presence of a single methyl substituent in the crotyl group of **1d** affords almost exclusively the branched isomer.

When comparing our data with the regioselective outcome of the reaction of allyl Grignards with carbonyl compounds,[2] the results of the chemical and the electrochemical reactions are similar: the formation of the branched regioisomer is favoured in both cases, with slightly better regioselectivities in the Ni-catalysed electrochemical process.

2.2. Allylation in the presence of Zn^{2+} ions

In order to compare the influence of the nature of the metal ions issued from the anodic oxidation and present in solution, several electrochemical intramolecular allylation reactions were carried out with substrates **1** in the presence of Zn and Al anodes. The results are presented in Tables 2 and 3.

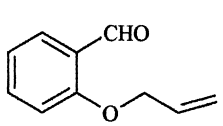
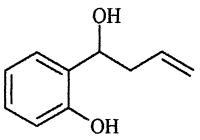
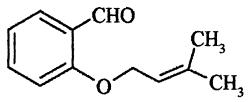
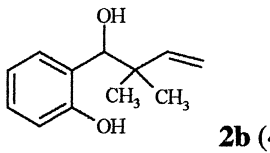
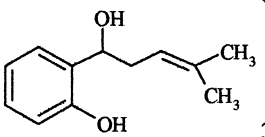
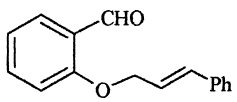
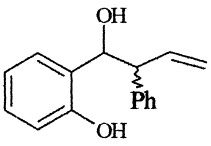
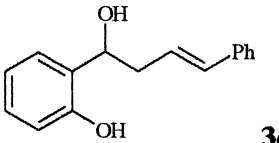
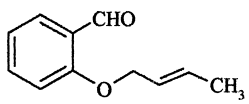
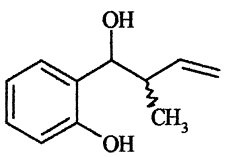
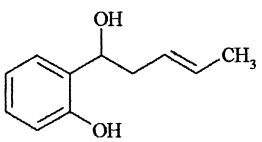
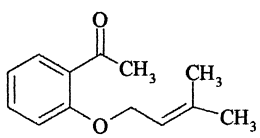
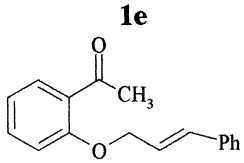
The use of a Zn anode also enabled the process of allyl transfer from ethers **1**, as shown in entry 1, Table 2, with the formation of **2a** in 63% yield. Some elimination from the homoallyl alcohol **2a** to the diene **6a** occurred, resulting in an overall allyl transfer of 90% from **1a**.

The electrolysis of **1b** (entry 2) led to a 90% allyl transfer with a **2b/3b** ratio of 89:11. Cinnamyl derivative **1c** afforded 91% allylation with a **2c/3c** ratio of 83:17 (entry 4). The electrolysis of the crotyl ether derivative **1d** with a Zn anode led mainly to **2d**, in a 99:1 regioselectivity (entry 6). Compound **2d** was obtained as a 79:21 mixture of stereoisomers.

With a Zn anode, the ratios towards the branched isomer increased in the reactions involving **1b**–**1d**, as compared to the use of a Mg anode, and regioselectivities higher than 83% were attained for isomer **2**.

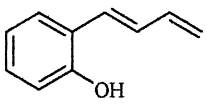
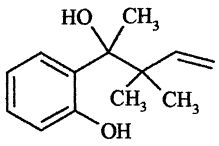
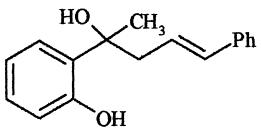
To check if the concentration of Zn^{2+} ions in solution had a beneficial effect on the regioselective outcome of the allyl transfer, the electrolysis of **1b** was carried out in the presence of an excess of Zn^{2+}. Thus, a pre-electrolysis of a DMF solution of 1,2-dibromoethane with *n*-$Bu_4N^+BF_4^-$ in the presence of a Zn anode for 1.85 equiv. of Zn^{2+} towards **1b**, was followed by the standard electrolysis. The results (entry 3) led to a ratio of branched to linear isomers of 89:11. However, the reaction was not complete until the

Table 1. Nickel-catalysed electrochemical allyl transfer from substrates **1** in DMF, with a Mg/stainless steel couple of electrodes

Entry	Substrate	F mol^{-1}	Products (%)	Yield of allyl transfer (**2**+**3**) (%)	Ratio **2/3**
1	 **1a**	2.1	 **2a** (87%) + **4** (3%)	87	–
2	 **1b**	2.4	 **2b** (45%)  **3b** (8%) + **4** (14%)	53	85:15
3	 **1c**	2.5	 **2c** (47%)[b]  **3c** (23%) + **4** (traces)	70	67:33
4	 **1d**	2.9	 **2d** (98%)[c]  **3d** (1%) + **4** (traces)	99	99:1
5	 **1e**	3.0	**5** (90%)	–	–
6	 **1f**	2.0	**5** (50%)	–	–

See Section 4. [b]One indeterminated diastereoisomer. [c] **2d** as a 45:55 ratio of stereoisomers.

Table 2. Nickel-catalysed electrochemical allyl transfer from substrates **1** in DMF, with a Zn/stainless steel couple of electrodes

Entry	Substrate	F mol^{-1}	Products (%)	Yield of allyl transfer (**2**+**3**) (%)	Ratio **2**/**3**
1	**1a**	4.6	**2a** (63%)  **6a** (27%)	90	–
2	**1b**	3.0	**2b** (80%) **3b** (10%)	90	88:12
3	**1b**[a]	3.7	**2b** (80%)[b] **3b** (10%) **4** (traces)	90	89:11
4	**1c**	2.6	**2c** (75%)[c] **3c** (16%) **4** (7%)	91	83:17
5	**1c**[d]	2.0	**2c** (51%)[e] **3c** (22%) **4** (27%)	73	70:30
6	**1d**	5.0	**2d** (86%)[f] **3d** (1%) **4** (13%)	87	99:1
7	**1e**	2.7	 **2e** (40%) **5** (55%)	40	>99:1
8	**1f**	3.3	 **3f** (19%) **5** (37%)	19	<1:99

See Section 4.
[a] Reaction with the addition of 1.85 equiv. of Zn^{2+} to the reaction medium before electrolysis.
[b] **2b** was found partially under its reduced form on the double bond, ratio 60:20.
[c] **2c** obtained together with the corresponding dehydrated product in a 73:27 ratio.
[d] Reaction run in two-compartment cell with the addition of 5 equiv. of Zn^{2+} to the reaction medium before electrolysis.
[e] **2c** obtained together with the corresponding dehydrated product in a 20:80 ratio.
[f] **2d** as a 79:21 mixture of diastereomers.

passage of 3.7 F mol^{-1}. Thus, comparing entries 2 and 3, the effect of the added Zn^{2+} ions does not seem to influence the regioselectivity.

The high electricity consumption in several reactions run in the presence of a Zn anode is most probably due to the parallel process of reduction of the Zn^{2+} ions present in the medium. Indeed, the reduction potentials of Ni(II) and Zn^{2+} are close enough (-1.2 and -1.4 V, respectively) to reduce the Zn^{2+} ions when their concentration progressively increases.

A different electrolysis was carried out in the presence of excess Zn^{2+} ions, in a two-compartment cell at controlled potential of -1.3 V vs SCE, corresponding to the reduction potential of the Ni(II) species. Allyl ether **1c** was thus electrolysed in the presence of 5 equiv. of added Zn^{2+} ions at the cathodic compartment (entry 5). The branched to linear ratio of allylated compounds reached 70:30. The excess of Zn^{2+} ions did not allow to get a higher ratio of **2c** (compare entries 4 and 5). Moreover, under these conditions the reaction was less selective: compound **4** was obtained in 27% yield and the branched regioisomer **2c** was partially dehydrated to the corresponding diene. We could conclude that the excess of Zn^{2+} ions did not favour the selectivity of the allyl transfer.

The partial dehydration of isomer **2** was observed in the case of **2a** (entry 1) and **2c** (entry 5) with a Zn anode, but not with a Mg anode. For **2c**, out of the 75% of the branched isomer formed, 55% of **2c** and 20% of the corresponding dehydrated diene were obtained after 2.6 F mol^{-1} electrolysis.

The intramolecular allyl transfer from allyl ethers to ketone groups could be obtained in the presence of a Zn anode

Table 3. Nickel-catalysed electrochemical allyl transfer from substrates **1** in DMF, with a Al/stainless steel couple of electrodes

Entry	Substrate	F mol^{-1}	Products (%)	Yield of allyl transfer (**2**+**3**) (%)	Ratio **2/3**
1	**1a**	4.3	**2a** (90%) **4** (traces)	90	–
2	**1b**[a]	3.3	**2b** (24%) **3b** (37%) **4** (4%)	61	39:61
3	**1c**	2.0	**2c** (25%) **3c** (15%) **4** (30%)	40	62:38
4	**1d**	4.0	**2d** (40%) **3d** (traces) **4** (22%)	40	99:1

See Section 4.
[a] Recovered **1b**, 9%.

(entries 7 and 8, Table 2). Thus, compounds **1e** and **1f** could be allylated regioselectively. In the case of **1e**, only the branched **2e** was obtained in 40% yield, together with non-allylated **5**. In contrast, the electrolysis of **1f** led to linear **3f** and to **5** in 19 and 37% yields, respectively. This result is in sharp contrast with the regioselectivity obtained in the case of **1c**. A high regioselectivity towards the linear isomer in the case of cinnamyl derivatives has already been reported for the coupling of diethyl ketone and cinnamyl chloride in the presence of a Zn anode.[11] On the other hand, the crotyl or the prenyl zinc reagents when reacting with aliphatic or aromatic aldehydes form almost exclusively the branched alcohol.[2]

2.3. Allylation in the presence of Al^{3+} ions

The electrolyses of **1a**–**1d** were also carried out in the presence of a consumable Al anode, giving rise to Al^{3+} ions in solution. The results are shown in Table 3. The allyl transfer from **1a** to **2a** was efficient, affording 90% yield of **2a** (entry 1), although passivation of the Al anode could occur in some cases. The reaction of **1b** with an Al rod as the anode led to a 39:61 ratio of branched to linear isomers in 61% yield. Unexpectedly, the presence of Al^{3+} ions reversed the regioselectivity as compared to the effect of Mg^{2+} or Zn^{2+} ions for the same substrate.

With substrate **1c** the yield of intramolecular allylation was of 40% with a branched to linear ratio of 62:38, and 30% of **4** were also obtained. The same reaction with **1d** allowed a very selective allylation process (99% regioselectivity) in 40% yield, with 22% of **4**.

Intramolecular allyl transfer to ketones was not efficient with an Al anode. Unless for **1a**, the reactions carried out with an Al anode were less efficient from the point of view of the allylation yields. The regioselectivities were very dependent on the nature of the substrate. Whereas substrate **1d** afforded almost exclusively the branched regioisomer in the presence or either Mg^{2+}, Zn^{2+} or Al^{3+} ions, with **1b** and **1c** the results were influenced by the different ions, even allowing for a reversal of the regioselectivity in the case of **1b** and Al^{3+}.

We also carried out the electrolysis of **1b** in the presence of the nickel catalyst but in the absence of other metal ions. Such reaction was run in a two-compartment cell at −1.3 V vs SCE, for 2 F mol^{-1}. The yield of the allyl transfer products **2b** and **3b** was of 89% and the ratio **2b/3b** was 91:9. This result is interesting and reveals that high regioselectivity can be obtained in the absence of metal ions such as Mg^{2+}, Zn^{2+} or Al^{3+}. However, from the points of view of the simplicity and time of the electrolysis, the reactions carried out in a one-compartment cell with a metal anode under constant intensity conditions are more efficient.

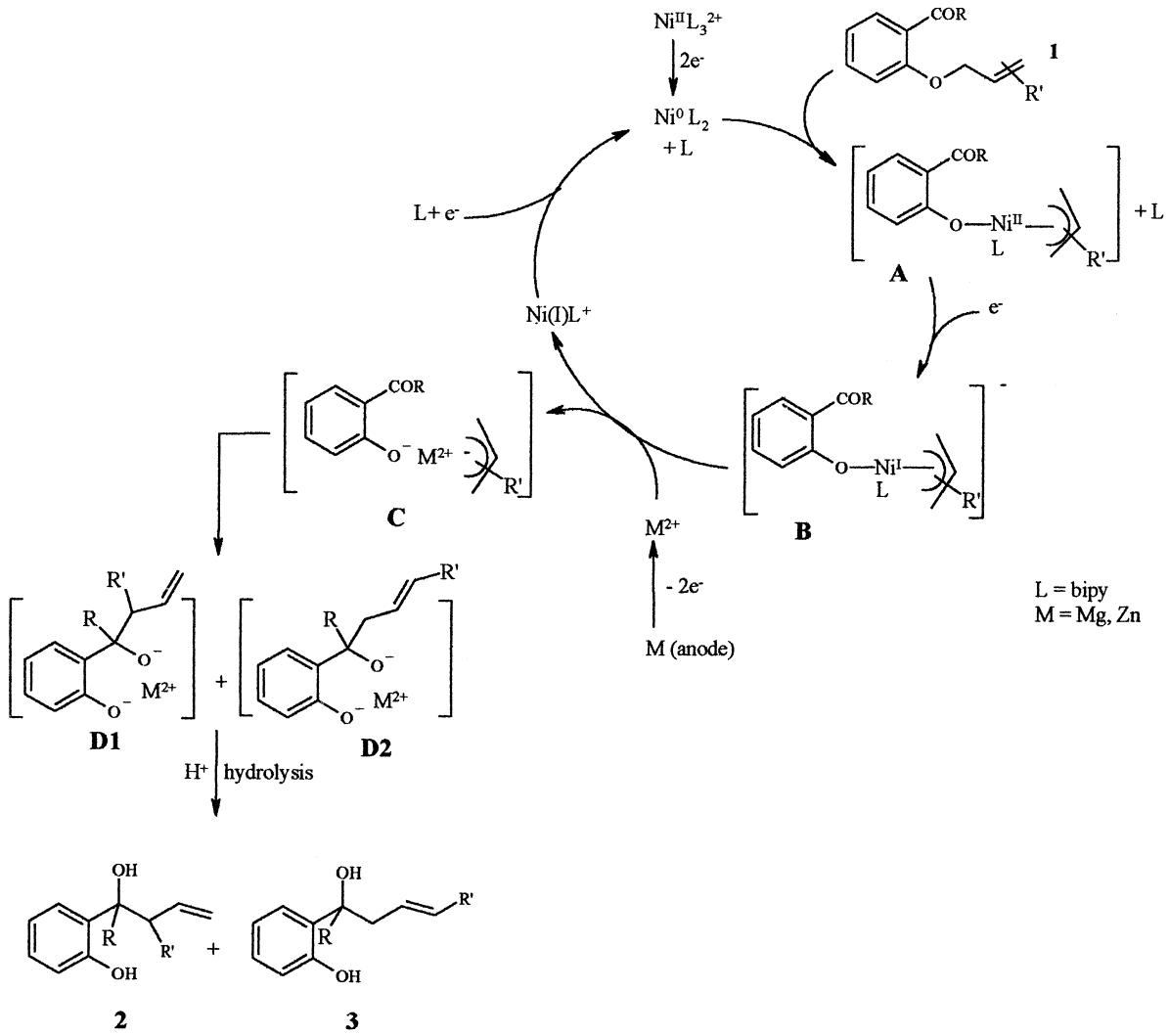
Other controlled-potential electrolyses were carried out in order to better evaluate the role of the metal ions in the efficiency of the reaction and/or in the recycling of the nickel species. Thus, the controlled-potential electrolysis of a 1:1 mixture of Ni(II) and **1a** was carried out at −1.46 V in DMF, in a two-compartment cell in the absence of other metal ions. The reaction was run up to the consumption of 2 F mol^{-1} of **1a**, and **2a** was obtained in 36% yield. A similar but catalytic controlled-potential electrolysis with a 1:10 molar ratio of Ni(II) to **1a** at −1.75 V led to 32% of **2a**. The same catalytic electrolysis in the presence of Mg^{2+} ions (one equiv. vs **1a**) led to 85% of **2a** after 2 F mol^{-1}. These results indicate that the presence of Mg^{2+} ions facilitate the recycling of the nickel species and enhance the overall efficiency of the catalytic reaction.

2.4. Mechanistic aspects

From a mechanistic point of view, chemical, electrochemical and theoretical studies on the nickel-catalysed cleavage of allyl ethers in substrates such as **1a**, with a further intramolecular allyl transfer process, have been recently described in the presence of a Mg anode.[14] However, no indication on the role of the anodically generated metal cations (e.g. Mg^{2+}) in the catalytic cycle has been reported. The Mg^{2+} ions were proposed be involved in a transmetallation step after the allylation, thus enabling the recycling of the nickel species.[14] The experimental results presented here, concerning the effect of metal ions on the regioselectivity of the allyl transfer, clearly indicate that these different cations have to be present and play an important role in the allyl transfer step.

Cyclic voltammetry of the Ni(II) system was carried out and revealed that the Ni(II)/Ni(0) reduction step occurs reversibly at −1.2 V vs SCE in a DMF/*n*-Bu_4BF_4 solution. The direct reduction of substrates **1** in the absence of the Ni(II) complex takes place beyond −2.0 V. This reduction potential is in agreement with the observed low reduction potential of some functionalised allyl ethers (−2.4 V)[15] or that of benzyl ethers (−2.3 V).[16] The addition of **1a** to the Ni(II) solution caused irreversibility of the NI(II)/Ni(0) reduction peak and a further one-electron reduction peak appeared, among other changes, at −1.4 V.

According to these data, we propose the mechanism as shown in Scheme 1. The active complex Ni(0) species formed by a two-electron reduction of the Ni(II)$(bipy)_3^{2+}$ complex react with substrate **1** to form a (π-allyl)Ni(II) intermediate, **A**. Intermediate **A** is further reduced by one electron (at −1.4 V) to afford a (π-allyl)Ni(I)$^-$ complex,



Scheme 1.

B.[14] A transmetallation is proposed to occur between the anodically generated species M^{2+} (Zn^{2+}, Mg^{2+} or Al^{3+}) and **B** to give **C**. This transmetallation is proposed before the intramolecular allylation of the carbonyl fragment occurs. The $Ni(I)^{+}$ species is liberated and can regenerate the active catalytic species Ni(0) after one-electron electroreduction. The (π-allyl)M^{2+}(phenate) intermediate **C** undergoes allyl transfer to the carbonyl group to give the branched and linear homoallylic alcoholate-phenates **D-1** and **D-2**, respectively. The final hydrolysis step affords the regioisomers **2** and **3**. The possibility of a mixed mechanism in which a bimetallic Ni(I)/M^{2+} species would be involved in the allyl transfer step cannot be ruled out.

3. Conclusions

In conclusion, the nickel-catalysed intramolecular transfer of allyl groups from substituted allyl ethers to carbonyl compounds affords regioselectively the branched isomer in almost all cases. The best regioselectivities were obtained without added metal ions or in the presence of Zn^{2+}. The presence of Al^{3+} afforded the lower yields and selectivities, and could even reverse the ratio of branched to linear isomers. The reaction was very sensitive to the nature of the allyl substituents and thus, the crotyl group could be transferred regiospecifically under the different conditions tested.

Our results indicated on one hand that the presence of metal ions favoured the efficiency of the reaction and the regeneration of the catalyst. However, concerning the regioselective outcome of the allyl transfer, the reactions run in the absence of metal ions afforded the highest regioselectivity.

4. Experimental

4.1. General procedure for one-compartment cell electrolyses

In a glass cell such as described in Ref. 17 were introduced 20 ml of freshly distilled DMF, n-$Bu_4N^+BF_4^-$ (10^{-2} M), $[Ni(bipy)_3]^{2+}$, $2BF_4^-$ (0.1 mmol) and the substrate **1** (1 mmol), prepared from the corresponding

ortho-hydroxybenzaldehyde or *ortho*-hydroxyacetophenone by stirring at 50°C with the corresponding substituted allyl bromide and potassium carbonate in DMF. The solution was stirred at room temperature and electrolysed at constant current of 60 mA (current density of 0.2 A dm^{-2} and 5–15 V between the rod anode (Mg, Zn or Al electrode) and a stainless steel cathode, up to the total consumption of the starting material (checked by GC analysis of aliquots), unless electrode passivation occurred. After evaporation of the DMF under vacuum, the crude mixture was hydrolysed with HCl 0.1 M saturated with NaCl, up to pH 1–2 and extracted with Et_2O. The organic layers, dried over $MgSO_4$, were filtered off and evaporated. The major products **2** and **3** were purified by SiO_2 column chromatography with pentane–ether (90/10) as eluent and analysed by NMR, mass spectroscopy and IR.

4.2. General procedure for two-compartment cell electrolyses

Both compartments were filled with a DMF solution (50 ml each) of *n*-$Bu_4N^+BF_4^-$ (1 g, 3 mmol) under inert atmosphere. The Ni(II) complex (0.1 mmol) and **1b** (0.1 mmol) were added to the cathodic compartment. The electrolyses were run at 20°C at the desired controlled potential (−1.3 V vs SCE) and was stopped when the current was negligible. The work-up was the same as described above, the reaction being followed by GC.

4.2.1. 2-(1′-Hydroxybut-3′-enyl)phenol, 2a. To facilitate analysis, **2a** was also converted into its methyl ether by treatment of the crude mixture with methyl iodide. ^{1}H NMR ($CDCl_3$, 200 MHz; relative integration, multiplicity, coupling constants in Hz): 7.90 (1H; s); 7.10 (1H; ddd; *J*=16.3, 1.7, 1.7 Hz); 6.90 (1H; dd; *J*=16.8, 1.5 Hz); 6.85–6.70 (2H; m); 5.84 (1H; dddd; *J*=17.1, 10.5, 7.1, 7.1 Hz); 5.3 (1H; dd; *J*=10.9, 1.1 Hz); 5.25 (1H; *J*=17.1, 1.1 Hz); 4.87 (1H; dd; *J*=7.5, 7.5 Hz); 2.90 (1H; s); 2.60 (2H; dd; *J*=7.6, 7.7 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): 155.5; 134.0; 129.0; 127.2; 126.6; 119.9; 119.3; 117.3; 74.7; 42.2. MS: *m/z* 164(M^+); 146; 131; 121; 107; 91; 77; 65; 43(100%). IR (KBr): 3366; 3071; 1235; 755 cm^{-1}. HRMS calcd for $C_{10}H_{12}O_2$: 164.083730; found: 164.083091.

4.2.2. 2-(2′,2′-Dimethyl-1′-hydroxybut-3′-enyl)phenol, 2b. ^{1}H NMR ($CDCl_3$, 200 MHz): 7.9 (1H; s); 7.9–7.7 (3H; m); 7.1 (1H; ddd; *J*=8, 2.1 Hz); 5.9–5.75 (1H; dd; *J*=13, 10 Hz); 5.3 (1H; dd; *J*=13, 1.1 Hz); 5.25 (1H; dd; *J*=10, 1.1 Hz); 4.5 (1H; s); 3.1 (1H; s); 1.1 (3H; s); 1.0 (3H; s). ^{13}C NMR ($CDCl_3$, 50.3 MHz): 156.6; 144.9; 130.0; 129.0; 128.9; 122.1; 118.7; 117.5; 115.2; 92.4; 83.0; 24.7; 20.2. MS: *m/z* 174(M^+-18); 159; 144; 123; 95; 77; 65; 51; 39(100%). IR (KBr): 3363; 2963; 2931; 2874; 1499; 1456; 1288; 1246; 754 cm^{-1}.

4.2.3. 2-(2′,2′-Dimethyl-1′-hydroxybutyl)phenol (reduced form of 2b). ^{1}H NMR ($CDCl_3$, 200 MHz): 8.38 (1H; s large); 7.26–6.70 (4H; m); 4.65 (1H; s); 1.43 (2H; q; 7.5); 0.95 (3H; s); 0.90 (3H; s); 0.88 (3H; t; 7.5). ^{13}C NMR ($CDCl_3$, 50.33 MHz): 129.7; 129.4; 128.8; 120.0; 118.7; 117.4; 84.0; 40.0; 30.7; 22.6; 22.3; 8.3. MS: *m/z* 194(M^+); 176; 161; 147; 123(100%); 107; 91; 77; 65; 51; 43; 27.

4.2.4. 2-(1′-Hydroxy-4′-methylpent-3′-enyl)phenol, 3b. ^{1}H NMR ($CDCl_3$, 200 MHz): 7.68 (1H; s large); 7.20–6.66 (4H; m); 6.05 (1H; d; *J*=9.0 Hz); 4.93 (1H; dd; *J*=7.0, 7.0 Hz); 4.75 (1H; s large); 4.64 (1H; s large); 2.50 (2H; dd; *J*=9.0, 7.0 Hz); 1.72 (3H; s); 1.61 (3H; s). ^{13}C NMR ($CDCl_3$, 50.3 MHz): 167.9; 142.2; 132.6; 129.7; 128.4; 117.4; 113.8; 111.6; 82.9; 47.9; 38.9; 30.5. MS: *m/z* 192(M^+); 174; 157; 145; 122(100%); 104; 77; 65; 51; 39.

4.2.5. 2-(1′-Hydroxy-2′-phenylbut-3′-enol)phenol, 2c. ^{1}H NMR ($CDCl_3$, 200 MHz): 7.92 (1H; s large); 7.85–6.8 (9H; m); 5.91 (1H; ddd; *J*=17.0, 10.2, 7.8 Hz); 5.02 (1H; dd; *J*=10.2, 1.4 Hz); 4.88 (1H; dd; *J*=17.0, 1.4 Hz); 4.82 (1H; d; *J*=17.0 Hz); 3.83 (1H; dd; *J*=8.6, 8.2 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): 155.6; 141.1; 137.9; 129.2; 129.1; 129.0; 128.7; 128.5; 127.4; 126.8; 126.6; 119.9; 117.6; 117.2; 78.2; 57.1. MS: *m/z* 222(M^+-18); 145; 115; 91; 77; 63; 51; 39(100%).

4.2.6. 2-(2′-Phenylbut-1′,3′-diene)phenol (dehydrated form of 2c). ^{1}H NMR ($CDCl_3$, 200 MHz): 7.98 (1H; s large); 7.85–6.8 (9H; m); 6.45 (1H; s); 6.40 (1H; m); 5.0 (1H; dd; *J*=10.2, 1.5 Hz); 4.92 (1H; dd; *J*=17.2, 1.5 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): 163.6; 155.4; 141.1; 137.6; 133.5; 129.2; 129.1; 129.0; 128.7; 128.5; 127.4; 126.8; 126.6; 119.9; 117.6; 117.2. MS: *m/z* 222(M^+); 145; 115; 91; 77; 63; 51; 39(100%).

4.2.7. 2-(1′-Hydroxy-4′-phenylbut-3′-enol)phenol, 3c. ^{1}H NMR ($CDCl_3$, 200 MHz): 8.28 (1H; s large); 7.85–6.8 (9H; m); 6.57 (1H; d; *J*=17.0 Hz); 6.41–6.12 (1H; m); 4.92 (1H; dd; *J*=7.1, 7.1 Hz); 3.55 (1H; s); 2.75 (2H; m). ^{13}C NMR ($CDCl_3$, 50.3 MHz): 155.3; 141.0; 138.0; 137.8; 130.8; 130.3; 129.1; 127.6; 127.0; 125.8; 120.3; 119.7; 118.7; 117.0; 74.5; 57.3. MS: *m/z* 222(M^+-18); 194; 165; 145; 128; 107; 91; 77; 63; 51; 39(100%).

4.2.8. 2-(1′-Hydroxy-2′-methylbut-3′-enol)phenol, 2d (mixture of diastereomers 54:45). *First diastereomer*: ^{1}H NMR ($CDCl_3$, 200 MHz): 9.20 (1H; s); 7.20–6.65 (4H; m); 5.92–5.71 (1H; ddd; *J*=16.6, 10.1, 6.8 Hz); 5.28 (1H; d; *J*=10.1 Hz); 5.09 (1H; d; *J*=16.6 Hz); 4.78 (1H; d; *J*=5.4 Hz); 2.68 (1H; qd; *J*=6.8, 5.4 Hz); 1.45 (1H; s); 1.10 (3H; d; *J*=6.8 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): 156.1; 140.4; 129.0; 126.8; 126.3; 120.5; 119.6; 117.8; 77.2; 44.8; 16.9. MS: *m/z* 160(M^+-18); 145; 131; 123 (100%); 115; 107; 95; 77; 65; 51; 39; 27; 18.

Second diastereomer: ^{1}H NMR ($CDCl_3$, 200 MHz): 9.20 (1H; s); 7.20–6.65 (4H; m); 5.92–5.71 (1H; ddd; *J*=16.6, 10.1, 4.7 Hz); 5.28 (1H; d; *J*=10.1 Hz); 5.09 (1H; d; *J*=16.6 Hz); 4.49 (1H; d; *J*=8.5 Hz); 2.63 (1H; qd; *J*=8.5, 4.7 Hz); 1.45 (1H; s); 0.90 (3H; d; *J*=4.7 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): 155.8; 140.2; 128.9; 128.4; 125.3; 128.1; 119.6; 117.3; 79.3; 44.5; 13.8. MS: *m/z* 178 (M^+); 160; 145; 131; 123 (100%); 115; 105; 95; 77; 65; 51.

4.2.9. 2-(1′-Hydroxy-1′-methyl-2-2′-dimethyl-3′-butenyl)phenol, 2e. ^{1}H NMR ($CDCl_3$, 200 MHz): 9.59 (1H; s large); 7.16–7.12 (1H; m); 6.99–6.95 (1H; m); 6.79–6.85 (2H; m); 6.02 (1H; dd; *J*=17.4, 10.9 Hz); 5.21 (1H; dd; *J*=10.9, 1.3 Hz); 5.16 (1H; dd; *J*=17.4, 1.3 Hz); 2.75 (1H; s large); 1.65 (3H; s); 1.08 (3H; s); 1.07 (3H; s). ^{13}C NMR

($CDCl_3$, 50.3 MHz): 156.8; 144.1; 129.2; 128.9; 126.9; 118.4; 117.6; 115.1; 83.3; 46.3.

4.2.10. 2-(Buta-1′,3′-dienyl)phenol, 6a. ^1H NMR ($CDCl_3$, 200 MHz): relative integration, multiplicity, coupling constants in Hz) 8.80 (1H; s large); 7.85–6.8 (4H; m); 6.60 (1H; d; 17.1); 6.26 (1H; ddd; J=17.0, 10.2, 7.1 Hz); 5.44 (1H; dd; J=17.1, 7.1 Hz); 5.24 (1H; dd; J=17.0, 1.5 Hz); 5.07 (1H; dd; J=10.2, 1.5 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): 163.5; 155.5; 134.0; 129.0; 127.2; 126.6; 119.9; 119.3; 117.3; 111.8. MS: m/z 146(M^+); 133(100%); 115; 105; 91; 77; 65; 51.

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