# **Electrochemically induced chain reactions:** the addition of fluorene and indene to aromatic aldehydes initiated by electrochemical reduction

# J.C. Gard, B. Hanquet, L. Roullier, Y. Mugnier, and J. Lessard

Abstract: The electrochemical reduction at  $-30^{\circ}$ C of 2,6-dichlorobenzaldehyde (1*a*), benzaldehyde (1*b*), and terephthalaldehyde (2) in tetrahydrofuran with tetrabutylammonium perchlorate as supporting electrolyte, under an argon atmosphere and in the presence of fluorene or indene, gives carbinols resulting from the addition of fluorene or indene and requires only a catalytic amount of electricity. The chain reaction is initiated by proton abstraction from fluorene or indene by a base electrogenerated by reduction of the aldehyde and the propagation involves the addition of the carbanion to the aldehyde followed by regeneration of the nucleophile by proton transfer from the proton donor to the alkoxide anion (base-catalyzed addition). The voltammetric behavior of the aldehydes in the absence and in the presence of fluorene or indene is also presented.

Key words: electrochemical reduction, aromatic aldehydes, addition of fluorene (indene), base catalysis, chain reaction.

**Résumé** : La réduction électrochimique à  $-30^{\circ}$ C des 2,6-dichlorobenzaldehyde (1*a*), benzaldehyde (1*b*) et terephtalaldehyde (2) dans le tetrahydrofurane contenant du perchlorate de tetrabutylammonium comme électrolyte support, sous atmosphère d'argon et en présence de fluorène ou d'indène, donne des carbinols provenant de l'addition basique du fluorène ou de l'indène et ne nécessite qu'une quantité catalytique d'électrons. La réaction en chaîne est initiée par l'arrachement d'un proton du fluorène ou de l'indène par une base électrogénérée par réduction de l'aldéhyde et les étapes de propagation sont l'addition du carbanion à l'aldéhyde suivie de la regénération du nucléophile par transfert de proton du donneur de proton à l'ion alkoxyde. Le comportement en voltamétrie des aldéhydes, en absence et en présence du fluorène ou d'indène, est également discuté.

*Mots clés* : réduction électrochimique, aldéhydes aromatiques, addition du fluorène (indene), catalyse basique, réaction en chaîne.

## Introduction

Studies on electrochemically induced chain reactions have received considerable attention. Some representative examples are as follows:  $S_{RN}1$  aromatic substitutions initiated by the electroreduction of an aryl halide (1), *cis-trans* isomerization of functionalized olefins (2), oxidation of alcoholates to aldehydes and ketones by aryl halides (3), electrooxidative initiation of triphenyltin hydride promoted radical reactions (4), ligand substitution of organometallic complexes (5), addition of chloroform to aldehydes (6), Michael reactions (7), and addition of fluorene and indene to nitrosobenzene (8). In the last two examples, the initiation step involves the generation of the nucleophile by hydrogen abstraction from a proton donor by a base generated by electroreduction of the electrophile or acceptor.

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In this paper, we present a new example of a chain process involving the addition of a nucleophile initiated by electrochemical reduction of the electrophile: the reaction between a proton donor such as fluorene (FlH<sub>2</sub>) or indene (InH<sub>2</sub>) and an aromatic aldehyde (ArCHO), induced by the electroreduction of the latter in tetrahydrofuran (THF) with *n*-Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte. We describe the results with 2,6dichlorobenzaldehyde (1*a*),<sup>2</sup> benzaldehyde (1*b*), and terephthalaldehyde (2).

## **Results and discussion**

#### Voltammetric reduction

The cyclic voltammogram of 2,6-dichlorobenzaldehyde (1*a*) at  $-30^{\circ}$ C in THF containing  $(n-Bu)_4$ NClO<sub>4</sub> as supporting electrolyte and on a vitreous carbon electrode (Figs. 1a and 2a) shows two reduction peaks A<sub>1</sub> ( $E_p = -1.55$  V vs. SCE) and A<sub>2</sub> ( $E_p = -1.70$  V), and several oxidation peaks. In the presence of FlH<sub>2</sub> (Figs. 1b–1d) or InH<sub>2</sub> (Figs. 2b–2d), the voltammogram at the same sweep rate is modified: both peaks A<sub>1</sub> and A<sub>2</sub> decrease, and peak A<sub>2</sub> more so than peak A<sub>1</sub>. With two to three equivalents of proton donor AH<sub>2</sub> (Figs. 1c and 2c), peak A<sub>2</sub> has disappeared. For peak A<sub>1</sub>, the rapid drop of the current after the peak potential, resulting in a sharp, narrow, and symmetric peak (Figs. 1b–1d and Figs. 2b and 2c), is characteristic

<sup>&</sup>lt;sup>2</sup> Preliminary results on the electroreduction of 1a in the presence of fluorene have been reported (9).

**Fig. 1.** Cyclic voltammogram of 2,6 dichlorobenzaldehyde (1*a*) on a vitreous carbon electrode in THF– $(n-Bu)_4$ NClO<sub>4</sub> (0.2 M) at  $-30^{\circ}$ C: (a) 1*a* alone; (b), (c), and (d), in the presence of 1, 2, and 10 equivalents of FlH<sub>2</sub> respectively. Starting potential: +0.3 V. Sweep rate: 0.02 V s<sup>-1</sup>.



**Fig. 2.** Cyclic voltammogram of 2,6 dichlorobenzaldehyde (1*a*) on a vitreous carbon electrode in THF– $(n-Bu)_4$ NClO<sub>4</sub> (0.2 M) at  $-30^{\circ}$ C: (a) 1*a* alone; (b), (c), in the presence of 1, and 10 equivalents of InH<sub>2</sub>, respectively. Starting potential: +1 V. Sweep rate: 0.02 V s<sup>-1</sup>.



of a catalytic reaction occurring outside the diffusion layer (8, 10). This is further confirmed (*i*) by the fact that when the sweep rate is decreased, peak  $A_1$  becomes smaller, and (*ii*) by the consumption of a catalytic amount of electrons in the controlled potential electrolysis performed on mercury, at  $-30^{\circ}$ C,

**Fig. 3.** Cyclic voltammogram of benzaldehyde (1*b*) on a vitreous carbon electrode in THF– $(n-Bu)_4$ NClO<sub>4</sub> (0.2 M) at  $-30^{\circ}$ C: (a) 1*b* alone; (b) in the presence of 10 equivalents of FlH<sub>2</sub>. Starting potential: -1 V. Sweep rate: 0.02 V s<sup>-1</sup>.



at the potential of peak A<sub>1</sub> and in the presence of 10 equivalents of AH<sub>2</sub> (ca. 0.03 and 0.02 mole of electrons per mole of 1a for FlH<sub>2</sub> and InH<sub>2</sub>, respectively, see below). The voltammetric behavior of benzaldehyde (1b) in the presence of proton donor  $AH_2$  is similar to that of 1a as shown by the cyclic voltammograms of Fig. 3: a decrease of peak A ( $E_p = -2.0$  V vs. SCE) and a change of its morphology in the presence of 10 equivalents of FlH<sub>2</sub> (Fig. 3b), characteristic of a catalytic process. And indeed, the electrolysis of 1b at  $-30^{\circ}$ C, on mercury, in the presence of 20 equivalents of FlH<sub>2</sub> and at the potential of peak A, also consumed a catalytic amount of electron (ca. 0.25 and 0.2 mole of electrons per mole of 1b for FlH<sub>2</sub> and InH<sub>2</sub>, respectively, see below). Peak  $A_1$  in the cyclic voltammogram of 2,6-dichlorobenzaldehyde (1a) (Figs. 1a and 2a) and peak A in the voltammogram of benzaldehyde (1b) correspond to the reduction of the aromatic aldehyde to the radical anion (eq. [1]). This electrogenerated base, in the presence of proton donor AH<sub>2</sub>, abstracts a proton from it to form the anion AH<sup>-</sup> and a neutral radical (eq. [2]). The latter probably disappears in subsequent fast reactions. Reactions [1] and [2] constitute the initiation step of a chain reaction involving, as propagation steps, the nucleophilic addition of AH<sup>-</sup> to the carbonyl (eq. [3]) followed by protonation of the resulting anions (bases) by  $AH_2$  (eq. [4]) to regenerate the nucleophile  $AH^-$  and give a carbinol that has been isolated from the preparative electrolyses (see below). In the case of 1a, the radical anion can be converted to 2-chlorobenzaldehyde (see eqs. [5] and [6]), which is most probably responsible for peak  $A_2$  (eq. [7]) in the voltammograms of 1a (Figs. 1 and 2). In the presence of AH<sub>2</sub>, the elimination of chloride ion from 1a (eq. [5]) competes with its protonation (eq. [2]), leading to the chain process (eqs. [3] and [4]) outside the diffusion layer, and the formation of 2-chlorobenzaldehyde is completely suppressed with two (FlH<sub>2</sub>) to three (InH<sub>2</sub>) equivalents of proton donor (see Figs. 1c and 2c).

The voltammogram of terephthalaldehyde (2) (Fig. 4), recorded under the same conditions as those of 1a and 1b, differs from the latter in showing two redox systems, giving rise to peaks A/A' and B/B' that correspond to the formation of the

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- [1] ArCHO +  $e^- \rightarrow$  [ArCHO]<sup> $\div$ </sup> peak A<sub>1</sub> (Figs. 1 and 2), peak A (Fig. 3)
- [2]  $[ArCHO]^{+} + AH_2 \rightarrow [Ar\dot{C}HOH] + AH^{-}$
- $[3] ArCHO + AH^{-} \rightarrow [ArCH(O^{-})AH] \rightleftharpoons [ArCH(OH)A^{-}]$
- 4]  $[ArCH(OH)A^{-}] + AH_2 \rightarrow ArCH(OH)AH + AH^{-}$



peak A2 (Figs. 1a and 2a)

**Fig. 4.** Cyclic voltammogram of terephthaladehyde (2) on a vitreous carbon electrode in THF– $(n-Bu)_4$ NClO<sub>4</sub> (0.2 M) at  $-30^{\circ}$ C: (a) 2 alone; (b) and (c) in the presence of 5 and 20 equivalents of InH<sub>2</sub>, respectively. Starting potential: 0 V. Sweep rate: 0.02 V s<sup>-1</sup>.



radical anion (eq. [8]) and the dianion (eq. [9]), respectively. In the presence of a proton donor (InH<sub>2</sub>, Figs. 4b and 4f), the radical anion is protonated, the oxidation peak A' and the system B/B' disappear accordingly, and the reduction peak A behaves as peak A<sub>1</sub> in the voltammogram of 1*a* (see Figs. 1b– 1d) and peak A in the voltammogram of 1*b* (see Figs. 1b and 2c): its height decreases with the concentration of AH<sub>2</sub> and its shape is characteristic of a catalytic reduction (see eqs. [1]– [4]). The same behavior was observed with FlH<sub>2</sub> as proton donor. And indeed, the controlled potential electrolysis of **2** at  $-30^{\circ}$ C, on mercury, in the presence of 20 equivalents of FlH<sub>2</sub> and at the potential of peak A (-1.2 V) consumed 0.06–0.12 mole of electrons per mole of **2** and gave products resulting from the addition of FlH<sub>2</sub> to the carbonyl group (see below).

#### **Controlled potential electroreductions**

The controlled potential reductions of aldehydes 1a, 1b, and 2 were carried out at  $-30^{\circ}$ C, on a mercury pool electrode, in



THF- $(n-Bu)_4$ NClO<sub>4</sub> (0.2 M), in the presence of an excess (10-20 equivalents) of proton donor (AH<sub>2</sub>), under an atmosphere of argon and at a potential corresponding to the formation of the radical anion (peak  $A_1$  in Figs. 1 and 2, peak A in Figs. 3 and 4). The solution became colored (see Table 1) and, after the current had dropped to zero, there was no reduction peak in the voltammogram of the electrolyzed solution from 0 to -1.8V.<sup>3</sup> The electrolyzed solution was extracted after the current dropped to zero. The results are reported in Table 1. In the case of 2,6-dichlorobenzaldehyde (1a) (Table 1, entries 1 and 2), the carbinols 3 (Scheme 1) were isolated in very good to excellent yields (74-93%). As already mentioned, the carbinols result from the nucleophilic addition of AH<sup>-</sup> to the aldehyde (eq. [3]) followed by protonation of the resulting anion by  $AH_2$  regenerating  $AH^-$  (eq. [4]), the chain process being initiated by the electrochemical generation of AH<sup>-</sup> (eqs. [1] and [2]). In the case of benzaldehyde (1b) (entries 3 and 4), the yields of isolated carbinols were much lower (14-28%) and the number of moles of electrons per mole of aldehyde consumed was larger (ca. 0.2 for 1b as compared to ca. 0.02 for 1a). The yields reflect the higher reactivity of 1a compared to that of 1b (fewer side products such as glycols and alcohols formed in the case of 1a), most probably due to the electronwithdrawing effect of the two chlorine atoms at the ortho positions of the carbonyl group in 1a.

With terephthalaldehyde (2) and fluorene (Table 1, entry 5), dehydration of the carbinol 4 occurred to a small extent during the electrolysis and (or) during the work-up to give the alkene 6 (1%) (Scheme 2). The total yield of isolated addition products was 33%. The controlled potential electrolysis in the presence of  $InH_2$  was not performed because of the large number of isomeric carbinols possible.

It has long been known that  $FlH_2$  can be added to aldehydes, mainly aromatic aldehydes, in the presence of a basic catalyst (e.g., potassium hydroxide) in refluxing ethanol to form dibenzofulvenes (11). By carrying out the reaction between  $FlH_2$  and benzaldehyde (1b), at room temperature and in sodium ethoxide – ethanol, the carbinol  $3b_1$  was isolated in a 23% yield (12). A dibenzofulvene was obtained in a 45% yield by reaction of benzaldehyde (1b) with  $InH_2$  in refluxing methanolic potassium hydroxide (13). Both FlH<sub>2</sub> and InH<sub>2</sub> were condensed with benzaldehyde (1b) using KF-Al<sub>2</sub>O<sub>3</sub> as the basic catalyst at room temperature (14). With FlH<sub>2</sub>, a mixture of carbinol  $3b_1$  (32%) and a dibenzofulvene (63%) was obtained (14). With InH<sub>2</sub>, a benzofulvene (66%) was isolated together with a product (14%) resulting from the addition of the 3-( $\alpha$ -hydroxyphenyl)-indene to another molecule of benzaldehyde followed by loss of one molecule of water (14). The complex (InH)<sub>2</sub> Ca·NH<sub>3</sub>·THF was reported to react with ben-

<sup>&</sup>lt;sup>3</sup> There was no reaction between  $\text{FlH}_2$  and  $\text{InH}_2$  and any of the aldehydes in the absence of an electron source (no potential applied).

**Table 1.** Controlled potential electroreduction of aromatic aldehydes (ArCHO) in the presence of fluorene (FlH<sub>2</sub>) or indene (InH<sub>2</sub>) as proton donor (AH<sub>2</sub>) on a mercury electrode in THF– $(n-Bu)_4$ ClO<sub>4</sub> (0.2 M) at –30°C followed by immediate extraction.<sup>*a*</sup>

Entry	$\begin{array}{c} E_{w}^{b} \\ \text{ArCHO}  (\text{V}) \qquad \text{AH}_{2} \end{array}$			AH <sub>2</sub> /ArCHO (molar ratio)	Mol of e <sup>-</sup> /mol of ArCHO (×10 <sup>3</sup> )	Solution color	Carbinol(s)	Yield <sup>c</sup> (%)
1	1 <i>a</i>	-1.5	FIH	10	27	Pink	<b>3</b> <i>a</i> .	93
2	1 <i>a</i>	-1.6	InH <sub>2</sub>	10	15	Orange-yellow	$3a_2$	74 <sup>d</sup>
3	1 <i>b</i>	-1.9	FlH,	20	250	Red	$3b_1$	28
4	<b>1</b> <i>b</i>	-2.0	InH,	20	200	Green	$3b_2$	14 <sup>e</sup>
5	2	-1.2	$FlH_2$	20	80	Orange-yellow	4 <sup>-</sup> 5	12 <sup>f</sup> 21

"The electrolyses were carried out under an argon atmosphere and the electrolyzed solution was extracted immediatedly after the current dropped to zero.

<sup>b</sup>Working potential vs. SCE.

'Yield of homogeneous compounds after chromatographic separation and extraction.

<sup>d</sup>The two diastereoisomers RR + SS and RS + SR were separated and isolated in 47% and 27% yield, respectively.

"Only the RS + SR diastereoisomer was isolated.

<sup>1</sup>Alkene 6 resulting from dehydration of 4 was isolated in small amounts (yield <1%).





zaldehyde (15) in liquid ammonia to give the carbinol  $3b_2$  in a 50–55% yield (16). The reaction of terephthalaldehyde (2) with excess FlH<sub>2</sub> in ethanol, with sodium ethoxide as the base and at 60–70°C, was reported to afford a di-(dibenzofulvene) in an 11% yield (15). Finally, Ghera and Spinsak (11) observed that the condensation of FlH<sub>2</sub> and InH<sub>2</sub> with aliphatic aldehydes in pyridine at 0°C, using benzyltrimethylammonium hydroxide (Triton B) as base, gave the corresponding carbinols in substantial yields. At 25°C, in the same medium, the 9-( $\alpha$ -hydroxylalkyl)-fluorenes underwent dehydration to the corresponding bibenzofulvenes, which, in the presence of







Table 2. Mass spectral data.

Product	Molecular ion peak <i>m/z</i> (relative intensity, %)	Other peaks $m/z$ (relative intensity, %)							
<b>3</b> <i>a</i> <sub>1</sub>	340 (5.7)	322 (57) -H <sub>2</sub> O	286 (10.7) -HCl	252 (15) –Cl	175 (65.7) С <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> CHOH	165 (100) FIH			
$3a_2 (RR + SS)$	290 (25)	202 (29.3) -2Cl, -H <sub>2</sub> O	175 (91.4) C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> CHOH	116 (100) InH <sub>2</sub>					
$3a_2(RS+SR)$	290 (34.3)	273 (35) –OH	238 (27.1) Cl	202 (40) -HCl	175 (87.1) С <sub>6</sub> H <sub>3</sub> C <sub>12</sub> CHOH	115 (100) InH			
<b>3</b> <i>b</i> <sub>1</sub>	272 (1.3)	254 (12.8) -H <sub>20</sub>	166 (100) FIH <sub>2</sub>	107 (81.5) C <sub>6</sub> H₅CHOH					
$3b_2 (RS + SR)$	222 (65.7)	204 (45.7) -H <sub>2</sub> O	116 (92.1) InH <sub>2</sub>	107 (100) C <sub>6</sub> H₅CHOH	105 (98.6)?				
4	300 (31.4)	282 (7.8) -H <sub>2</sub> O	253 (11.4) -CHO	165 (100) FIH	135 (65.7) CHOC <sub>6</sub> H <sub>4</sub> CHOH	105 (22.8) CHOC <sub>6</sub> H <sub>4</sub>			
5	466 (0.11)	448 (0.43) –H <sub>2</sub> O	430 (20) -H <sub>2</sub> O	301 (43.6) FI(CHOH) C <sub>6</sub> H <sub>4</sub> (CHOH)	282 (45.7) FI=⊂C(OH) C <sub>6</sub> H₄CH	252 (51.4) FlC(C <sub>6</sub> H <sub>4</sub> )	165 (100) FIH		
6	282 (95.7)	253 (100) -CHO	126 (58.6) ?	113 (23.6) ?					

Table 3. Eluents for chromatographic separation, solvents for recrystallization, melting points, and microanalytical data.

Product	Chroma- tography eluent	Recrystal- lization solvent	Melting point (°C)		Microanalytical data					
				Molecular formula	C Calcd.	(%) Found	H Calcd.	(%) Found	Cl ( Calcd.	%) Found
<b>3</b> <i>a</i> <sub>1</sub>	1: Ether, 4: hexane	Hexane	110	C <sub>20</sub> H <sub>14</sub> Cl <sub>2</sub> O	70.40	70.42	4.14	4.20	20.78	21.26
$\begin{array}{l} 3a_2\\ (RR + SS) \end{array}$	1: Ether, 4: hexane		Oil	$C_{16}H_{12}Cl_{2}O$						
$\begin{array}{l} 3a_2\\ (RS + SR) \end{array}$	1: Ether, 4: hexane	Pentane	98	$C_{16}H_{12}Cl_2O$	66.00	65.44	4.15	4.71	24.35	22.63
$3b_{\mathfrak{l}}$	1: Ether 4: hexane	EtOH	119 (lit. (12) 121–122)	$C_{20}H_{16}O$						
$\frac{3b_2}{(RS + SR)}$	1: Ether, 4: hexane	Heptane	132 (lit. (16) 135)	$C_{16}H_{14}O$						
4	2: Ether, 3: pentane	2: Ether, 3: hexane	126	$C_{21}H_{16}O_2$	83.98	83.69	5.37	5.39		
5	3: Ether 7: hexane	CHCl <sub>3</sub>	>266	$C_{34}H_{26}O_2$	87.52	84.71	5.62	5.50		
6	Hexane	Hexane	Oil	$C_{21}H_{14}O$	89.34	87.24	5.00	4.99		

an excess of  $FlH_2$ , afforded the corresponding 1,1-bis-(9-fluorenyl)-alkanes (11).

#### Structure of products

All compounds were characterized by mass spectrometry (Table 2). The crystalline compounds  $3b_1$  and  $3b_2$  are known

and had melting points close to those reported in the literature (Table 3). Microanalytical data were obtained for all new crystalline compounds (Table 3). The structure of alcohol  $3a_1$  was determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and that of alcohols  $3a_2$  by <sup>1</sup>H NMR spectroscopy. They are shown below.

The complete attribution of the protons of  $3a_1$  was made



using COSY and NOE differential spectroscopy. Alcohol  $3a_1$  exhibits a (<sup>1</sup>H–<sup>1</sup>H) COSY spectrum (Fig. 5) with three sets of protons. The first and the second set (four protons each) concern the fluorene backbone and the third set (three protons), the aryl group. Protons H3' and H5' and H4' appear, respectively, as a broad doublet centered at 7.38 ppm and as a sharp triplet (7.27 ppm). This result indicates a restricted motion around the C1'—C4' axis. Assignment of proton H8 is given by the NOE enhancement observed on this proton by presaturation of the OH. Consequently the set H8, H7, H6, and H5 (ring B) is easily deduced. It should be noticed that the chemical shifts observed for these protons are very similar whereas the important chemical shift difference for the second set of four protons (H1–H4) (ring A) indicates a preferred conformation of the dichlorophenyl ring almost perpendicular to the flu-

orene moiety, leaving H1 *inside* the shielding cone, hence the assignments of H1, H2, H3, and H4. The  $\{{}^{1}H\}{}^{-13}C$  NMR spectrum displays 18 individual resonances for the 20 carbon atoms (C2', C6' and C3' and C5' are broad resonances). The final attribution is made using the  $({}^{1}H{}^{-13}C)$  COSY spectrum (see Fig. 6). The  ${}^{1}H$  and  ${}^{13}C$  NMR data parameters are given in the experimental part.

The stereochemistry of the two diastereoisomeric alcohols  $3a_2$  (*RR* + *SS*) and  $3a_2$  (*RS* + *SR*) was proven by NMR spectroscopy experiments, including homonuclear COSY and NOE differential spectroscopy. From comparison of the normal proton spectra of the two alcohols, it appears that the coupling constants between H<sub>a</sub> and H<sub>b</sub> are very similar (9.3 and 10.5 Hz), indicating an antiperiplanar orientation of the H<sub>a</sub>-C-C-H<sub>b</sub> system in both alcohols. The NMR spectra of Fig. 7

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#### **Fig. 6.** $({}^{1}H-{}^{13}H)$ COSY spectrum of alcohol $3a_{1}$ .



**Fig. 7.** <sup>1</sup>H NMR spectra of  $3a_2(RR + SS)$  and  $3a_2(RS + SR)$ .



show clearly that the dichlorophenyl ring has a different position in the diastereoisomeric alcohols, as illustrated in the structures. The protons on the benzene ring B of the RR + SSdiastereoisomer are in a location analogous to those of the protons of the ring B of alcohol  $3a_1$  and the protons of ring A of the RS + SR diastereoisomer are in a similar location to those of ring A of alcohol  $3a_1$ . Indeed, proton H2 of the RR + SS, being in the shielding cone of the dichlorophenyl group, is strongly shielded with respect to proton H2 of the RS + SR isomer (Fig. 7). For the same reason, protons H7 and H6 of the RS + SR isomer are shielded with respect to these same protons of the RR + SS isomer (Fig. 7) but the shielding is smaller for proton H6 because it is further away from the dichlorophenyl group in the RS + SR isomer. Thus, the stereochemistry RR + SS and RS + SR was attributed respectively to the major (47%) and minor (27%) diastereoisomer of alcohol  $3a_2$ . The chemical shifts and coupling constants for alcohols  $3a_2$  (RR + SS) and  $3a_2$  (RS + SR) are given in the experimental part. Interest-

ingly, carbinol  $3a_2$  exists as the  $\alpha$  form. No sigmatropic rearrangement (17, 18) or base-catalyzed rearrangement (19) to the  $\gamma$ -form was observed (eq. [10]).



## **Experimental part**

#### Reagents

Tetrahydrofuran was purified by distillation under argon from sodium benzophenone ketyl. The supporting electrolyte was tetrabutylammonium perchlorate (0.2 M) in all cases. Fluorene, indene, 2,6 dichlorobenzaldehyde (1a), benzaldehyde (1b), and terephthalaldehyde (2) were all commercial products.

## Apparatus and general procedures

All experiments were carried out under an argon atmosphere. In voltammetry, the working electrode was a vitreous carbon disc (diameter 1.2 mm) and, for the controlled potential electrolyses, a mercury electrode. In all cases, the reference electrode was a saturated calomel electrode (SCE) separated from the solution by a sintered glass disc. The auxiliary electrode was a platinum wire. All reagents in solution in THF were added, with a syringe previously purged with argon, to the THF- $(n-Bu)_4$ NClO<sub>4</sub> solution in the cell. The cyclic voltammetry experiments were conducted with a Tacussel PJT 24-1 potentiostat. The controlled potential electrolyses were carried out with an Amel 552 potentiostat equipped with a Tacussel IG5 integrator. For the experiments carried out at  $-30^{\circ}$ C, the cell was placed in a cooling bath (acetone – liquid nitrogen). Melting points were determined on a Kofler apparatus and are uncorrected. The <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR spectra were recorded from CDCl<sub>3</sub> solutions on a WM400 Bruker NMR spectrometer at the CSMUB (Centre de spectrométrie moléculaire de l'Université de Bourgogne). The chemical shifts ( $\delta$ ) are given in ppm (downfield from TMS) and the coupling constants (J) in hertz. The multiplicities are as follows: s, singlet; d, doublet; t, triplet. Mass spectra were taken on Kratos Concepts spectrometer. Silica gel Merck (280-400 mesh) was used for flash column chromatography and silica gel Merck BOF<sub>254</sub> for thin-layer chromatography. Eluents for chromatographic separation, solvents for recrystallization, melting points, and microanalytical data are recorded in Table 3. The mass spectral and microanalytical data are given in Tables 2 and 3, respectively.

#### **Typical electrolysis procedure**

2,6-Dichlorobenzaldehyde (1*a*) (152.7 mg, 0.87 mmol) was electrolyzed on a mercury electrode at -1.6 V vs. SCE with indene (1 mL, 10 mmol) at  $-30^{\circ}$ C in THF (20 mL) containing  $(n-Bu)_4$ NClO<sub>4</sub> (0.2 M). The electrolysis was stopped when the current dropped to zero (0.0015 electron per molecule of 1*a*). The orange-yellow solution was immediately poured into water and extracted with ether. Chromatography on silica gel with hexane–ether (4:1) as eluent gave two diastereoisomeric 3-[ $\alpha$ -hydroxy-(2',6'-dichloro-phenyl)]-indenes (3*a*<sub>2</sub>). The less

polar RR + SS isomer was isolated as an oil (119 mg, 47%). The more polar RS + SR isomer was recrystallized from pentane, mp 98°C (68 mg, 27%).

## NMR spectral data

Carbinol 3a<sub>1</sub>: <sup>1</sup>H NMR δ (CDCl<sub>3</sub>): 3.28 (s, 1H, OH), 4.87 (d, J = 9.8 Hz, 1H, H9), 5.08 (d, J = 9.8 Hz, 1H,  $H_a$ ), 6.19 (ddd, J =7.6, 1.8, and 0.8 Hz, 1H, H1), 6.96 (ddd, J = 7.6, 7.6, and 1.2 Hz, 1H, H2), 7.27 (t, J = 8.0 Hz, 1H, H4'), 7.30 (ddd, J = 1.8, 7.6, and 7.6 Hz, 1H, H3), 7.35 (ddd, J = 1.7, 7.5, and 7.5 Hz, 1H, *H7*), 7.37 (d, *J* = 8.0 Hz, 2H, *H3'*), 7.44 (ddd, *J* = 7.5, 7.5, and 1.2 Hz, 1H, H6), 7.74 (ddd, J = 0.8, 1.2, and 7.6 Hz, 1H, *H4*), 7.79 (ddd, *J* = 7.5, 1.7, and 0.8 Hz, 1H, *H*5), 7.98 (ddd, *J* = 0.8, 1.2, and 7.5 Hz, 1H, H8).  ${}^{13}$ C NMR  $\delta$  (CDCl<sub>2</sub>): 52.14 (d, 1C, C9), 75.19 (d, 1C, C<sub>a</sub>), 120.34 (d, 1C, C4), 120.45 (d, 1C, C5), 125.71 (d, 1C, C1), 127.12 (d, 1C, C2), 127.52 (d, 1C, C7), 127.59 (d, 1C, C8), 128.11 (d, 1C, C3), 128.33 (d, 1C, C6), 130.04 (d, 2C, C3' and C5'), 130.12 (d, 1C, C4'), 136.14 (s, 2C, C2' and C6'), 137.43 (s, 1C, C1'), 141.83 (s, 1C, C5a), 142.45 (s, 1C, C9a), 142.49 (s, 1C, C4a), 146.12 (s, 1C, C8a). Carbinol  $3a_2$  (RR + SS): <sup>1</sup>H NMR  $\delta$  (CDCl<sub>3</sub>): 3.41 (s, 1H, *OH*), 4.50 ( $\bar{d}$ , J = 10.4 Hz, 1H,  $H_h$ ), 5.02 (d, J = 10.4 Hz, 1H,  $H_a$ , 5.79 (dd, J = 2.0 and 5.6 Hz, 1H, H2), 6.85 (dd, J = 2.0and 5.6 Hz, 1H, H3), 7.20 (t, J = 8.0 Hz, 1H, H4'), 7.25 (dt, J = 1.3 and 7.4 Hz, 1H, H6), 7.36 (dd, J = 8.0 and 8.0 Hz, 1H, H5), 7.36 (d, J = 8.0 Hz, 2H, H3' and H5'), 7.41 (d, J = 7.3 Hz, 1H, H4), 7.94 (d, J = 7.4 Hz, 1H, H7).

*Carbinol*  $3a_2$  (RS + SR): <sup>1</sup>H NMR  $\delta$  (CDCl<sub>3</sub>): 3.25 (d, J = 9.3 Hz, 1H, *OH*), 4.41 (d, J = 9.3 Hz, 1H,  $H_b$ ), 5.17 (dd, J = 9.3 and 9.3 Hz, 1H,  $H_a$ ), 6.42 (d, J = 7.5 Hz, 1H, H7); 6.85 (dd, J = 5.6 and 1.8 Hz, 1H, H2), 6.97 (dd, J = 7.7 and 7.5 Hz, 1H, H6), 6.98 (d, J = 5.6 Hz, 1H, H3), 7.22 (dd, J = 7.5 and 7.5 Hz, 1H, H5), 7.25 (t, J = 7.8 Hz, 1H, H4'), 7.36 (dd, J = 7.5 and 1.8 Hz, 1H, H4), 7.38 (d, J = 7.8 Hz, 2H, H3' and H5').

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