Electrochemistry of 9,9'-Spirobifluorene Derivatives: 2-Acetyl- and 2,2'-Diacetyl-9,9'-Spirobifluorene. Preparation of Stereoisomeric 2,3-bis(9,9'-Spirobifluoren-2-yl)butane-2,3-diols

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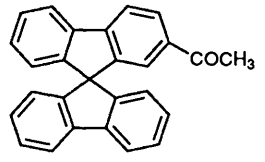
2-Acetyl- and 2,2'-diacetyl-9,9'spirobifluorene **1** and **2** were studied by cyclic voltammetry in dimethylformamide. The corresponding anion radicals show remarkable persistency in aprotic DMF. The (apparent) standard potentials are $E^\circ = -1.77$ V (SCE) and $E^\circ = -1.75$ V for the (quasi-reversible) reduction of **1** and **2** to the anion radicals, respectively. Preparative electrolysis of **1** in DMF–Et_4NClO_4 (0.1 mol dm^{-3}), with excess acetic acid as proton donor, furnished alcohol **3** and the diastereoisomeric pinacols **5** and **6**, which were isolated and characterized. The diastereoisomeric excess, de, as evaluated (NMR) on the electrolyzed solution was only slightly in favour of the (±) compound. Spectroscopic properties of compounds **1**–**6** are, *inter alia*, the ^{13}C NMR chemical shift for the spiro-carbon at $\delta = 65.9$ (TMS), and the fragmentation patterns in the mass spectra, with the 100% relative abundance of the molecular-ion $M^{\bullet+}$ in the case of the aromatic ketones **1** and **2**. Some comments on the influence of conformations of **5** and **6** and of the presence of an intramolecular hydrogen-bond in some intermediates and products are also presented.

Molecules that contain two halves fixed at a 90° angle *via* a σ-bonded network, each half bearing an aromatic, conjugated (proconducting) structure are now actively studied. In fact, they may be used as building blocks for molecular electronic based computing instruments,[1] and, generally, for assembling single compounds that function as a self-contained electronic system.[2] For this reason, we decided to study 9,9'-spirobifluorene,[3] its 2-acetyl and 2,2'-diacetyl derivatives.[4,5] Additional interest in investigating the 9,9'-spirobifluorene compounds is concerned with the effects possibly arising from reciprocal perturbations between the two halves of the spiro-compounds.[6,7] Moreover, functionalized 9,9'-spirobifluorenes are capable of enantio-selective complexation.[8] In this work, electrochemistry has been used by us to determine the redox properties of **1** and **2** and to prepare pinacols **5** and **6**. Electrochemical synthesis of pinacols is a well established procedure.[9] In our case, it was anticipated that electrochemical reduction of compound **1** (A), should furnish the corresponding diols **5** and **6** $(AH)_2$, and possibly also alcohol **3** (AH_2). Both monomeric AH_2 and dimeric $(AH)_2$ should be electrochemically active, at potentials more negative with respect to the corresponding acetyl derivative **1**. As a consequence of the electrochemical behaviour of the aromatic part of **1** and **2**[3] it is crucial that the experiments should be performed at constant potential, not at constant current. In this way, only the C=O bond will be involved in the reduction, while retaining the spiro structure in the resulting compounds. Some observations regarding the importance of the spiro-structure in determining the spectroscopic properties of **1**–**6**, especially NMR and mass spectra, are also reported.



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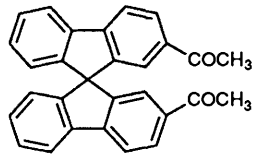

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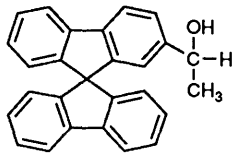

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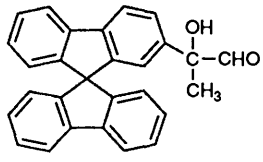

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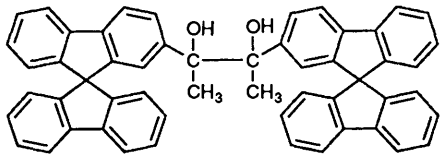
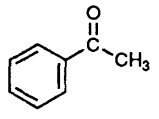


5 *meso*; **6** (±)



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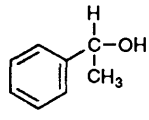

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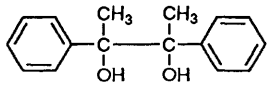


9 *meso*; **10** (±)

Experimental

Apparatus and Procedures.—^1H and ^{13}C NMR spectra were obtained with a Bruker AC 200 spectrometer at 200 and 50 MHz respectively, in $CDCl_3$ solutions. Chemical shifts are reported in ppm downfield from internal $SiMe_4$, locking at the residual $CDCl_3$ signals. The 70 eV mass spectra were obtained in Padova using a Finnigan Incos 50 instrument, with the direct inlet system. EI spectra are reported, unless otherwise stated. HPLC experiments were performed with a Perkin-Elmer Series 2 apparatus, including a LC 75 UV detector. The column was a LiChrosorb Si 60 (7 μm). Column chromatography was performed with silica gel (Si 60 Merck), 0.063–0.200 mm mesh

column. Thin-layer chromatographic separations were of conventional type (Si-60 F254 Merck). Voltammetric experiments were carried out using an Amel Mod. 5000 instrument, equipped with a X-Y Amel Mod. 862/D or 863 recorder. A three-electrode arrangement was used, the working electrode being a vitreous-carbon (GC) disc, inner diameter *ca.* 3 mm, the counter-electrode a platinum wire, and the reference electrode SCE with multiple junctions. The working GC electrode was carefully polished before use by standard methods. For the preparative electrolyses the same Amel 5000 instrumentation was used, with a Metrohm Mod. E 478 recorder. The working electrode was a piece of reticulated vitreous carbon, RVC, 2X1-100S, ERG Oakland. Occasionally, a mercury pool was used. The cathodic compartment of the three electrode arrangement was separated by the anodic one through a porous glass plug in contact with a gelled solution of Et_4NClO_4 in dimethylformamide (DMF). The reference electrode was the same as described before, and the counter-electrode was a platinum gauze cylinder. Melting points were determined with a Büchi or a Kofler apparatus.

Chemicals.—Solvents DMF and Et_4NClO_4 were treated as described previously.[10] The following chemicals were supplied by Aldrich or by Lancaster: fluorenone and 2-iodobiphenyl. Other chemicals and solvents were of the highest purity.

9,9′-*Spirobifluorene*. This compound was prepared following the literature;[11] m.p. (benzene, light petroleum) 197–198 °C (lit.,[11] 198–199 °C) starting from fluorenone and 2-iodobiphenyl. Spectroscopic data were the same as those reported by Haas and Prelog;[12] $\delta_C(CDCl_3)$ 66.0 (spiro-C); 119.9, 124.0, 127.7, 127.8, 141.7 and 148.8; *m/z* 316 (M^+, 100%), 315 (M − H, 60), 313 (30), 289 (10), 157 (20), 150 and 144.

2-*Acetyl*-9,9′-*spirobifluorene* **1**. This substance was prepared following Haas and Prelog[12] from 9,9′-spirobifluorene and CH_3COCl in CS_2. Column chromatography (SiO_2, 10% hexane–ethyl acetate) allowed separation of **1** from **2**. M.p. (**1**) ($CHCl_3$–C_6H_6) 225 °C (lit.,[12] 225 °C). All spectroscopic data reported in ref. 12 were confirmed; $\delta_C(CDCl_3)$ 26.6 (CH_3), 65.9 (spiro-C), 119.9, 120.2, 120.9, 123.9, 124.0, 124.2, 127.8, 127.9, 128.0, 128.7, 129.1, 136.7, 140.3, 141.9, 146.6, 147.8, 149.2, 150.2 and 197.5 (C=O); *m/z* 358 (M^+, 100%), 343 (M − CH_3, 30), 315 (M − CH_3CO), 171, 156, 149 and 143.

2,2′-*Diacetyl*-9,9′-*spirobifluorene* **2**. M.p. (CHCl–AcOEt) 255–257 °C (lit.,[12] 255–257 °C). All spectroscopic data[12] were confirmed; $\delta_C(CDCl_3)$ 26.5, (CH_3), 65.8 (spiro-C), 120.0, 121.1, 123.7, 124.1, 128.2, 129.0, 129.2, 136.8, 140.4, 146.6, 148.3, 149.1 and 197.3 (C=O); *m/z* 400 (M^+, 100%), 385 (M − CH_3, 76), 358 (M − CH_2CO, 44), 357 (M − CH_3CO, 52), 315 (M − 2 × CH_3CO + H, 16), 314 (M − 2 × CH_3CO, 32), 312 (M − 2 × CH_3COH, 52), 185, 156 and 149.

1-(9,9′-*Spirobifluoren*-2-*yl*)*ethanol* **3**. M.p. 125–135 °C (dec.); $\delta_H(CDCl_3)$ 1.33 (3 H, d, *J* 7, CH_3), 1.81 (1 H, s, exch. D_2O, OH), 4.70 (1 H, q, *J* 7, CH) and 6.37–7.86 (15 H, m, ArH); δ_C 25.01 (CH_3), 65.9 (spiro-C), 70.25 (CHOH) and 118.4–149.2 (ArC); *m/z* 360 (M^+, 10%), 358 (M − 2H, 8), 342 (M − H_2O, 100), 326, 315, 314, 172 and 163.

2-*Hydroxy*-2-(9,9′-*Spirobifluoren*-2-*yl*)*propionaldehyde* **4**. M.p. 190–210 °C (dec.); $\delta_H(CDCl_3)$ 1.53 (3 H, s, CH_3), 3.72 (1 H, s, exch. D_2O, OH), 6.70–8.00 (15 H, m, ArH), 9.4 (1 H, s, CHO); δ_C 23.6 (CH_3), 65.9 (spiro-C), 79.1 (COH), 118–149 (ArC) and 199.5 (CO); *m/z* 388 (M^+, 4%), 386 (M − H, 4), 386 (M − 2 H, 8), 371 (M − 2 H − CH_3, 4), 359 (M − CHO, 60), 343 (M − H − CH_3 − CHO, 100), 315 (40), 179, 152 and 157.

meso-2,3-*Bis*(9,9′-*spirobifluoren*-2-*yl*)*butane*-2,3-*diol* **5**. M.p. 145–155 °C; $\delta_H(CDCl_3)$ 1.12 (6 H, s, 2 × CH_3), 2.41 (2 H, s, exch. D_2O, 2 × OH) and 6.43–7.90 (30 H, m, ArH); δ_C 24.56 (CH_3), 65.9 (spiro-C), 78.79 (COH) and 118.4–149.3 (ArC); *m/z* 718 (M^+, 3%), 700 (M − H_2O, 4), 686 (M − CH_3OH, 8), 685 (M − CH_3 − H_2O, 7), 684 (M − 2 × OH, 8), 658 (M − 2 × CH_3OH + 2 H, 10), 447, 411, 387, 373, 359 (M/2, 50) and 343 (100).

(±)-2,3-*Bis*(9,9′-*spirobifluoren*-2-*yl*)*butane*-2,3-*diol* **6**. M.p. 240–270 °C (dec.); $\delta_H(CDCl_3)$ 1.29 (6 H, s, 2 × CH_3), 2.27 (2 H, s, exch. D_2O, 2 × OH) and 6.37–7.80 (15 H, m, ArH); δ_C 24.75 (CH_3), 65.9 (spiro-C), 78.79 (COH) and 118.6–149.4 (ArC); *m/z* 720 (M + 2H, 2%), 700 (M − H_2O, 3), 686 (M − CH_3OH, 10), 685 (8), 504 (57) 430, 429 and 359 (M/2, 100).

The *meso*- and (±) assignments to the diastereoisomeric diols **5** and **6** were made on the basis of the order of elution in the chromatographic experiments and of the R_F values in TLC, considering the *meso*-compound to be less polar than the (±)-compound. This assignment was related to NMR data, see Discussion section.

Computer-generated Models.—These were originated from the MM2 (force-field)[13] based program, with allowance for intramolecular hydrogen bond restraint.[14] In the attempt to identify the most favourable conformation of **5** and **6**, the following criteria were employed: good intramolecular hydrogen-bonded geometry compatible with minimal steric adverse interaction. It followed that unfavourable steric interactions between Ar groups (Ar = 9,9′-spirobifluorenyl) are deleterious to hydrogen bond formation between vicinal OH groups in **5**, whereas less severe CH_3–Ar interactions allow a hydrogen bond to be present in **6**; compare conformation **5b′** of **5** with conformation **6b′** of **6**.[15]

Constant-potential Electrolysis of 2-*Acetyl*-9,9′-*spirobifluorene* **1**.—Cell, electrodes and other usual arrangements were the same as described in ref. 10. Et_4NClO_4–DMF (320 cm^3, 0.1 mol dm^{-3}) solution and 2-acetyl-9,9′-spirobifluorene **1** (1.2 g, 3.35 mmol) solution containing also CH_3CO_2H, mol(acid)/mol (**1**) = *ca.* 10:1, were electrolyzed at the constant potential E_{appl} = −1.90 V *vs.* SCE. Electrolysis was stopped when the current was *ca.* one hundredth of the initial value. Conventional work-up to remove solvent and Et_4NClO_4 was then performed, obtaining 1.2 g of a mixture which was analyzed by TLC and ^1H and ^{13}C NMR. Relative yields of products (identified by the subsequent separation procedure) was thus evaluated by the ^1H NMR spectra.

Column chromatography was then attempted to separate the single substances, using a silica column and an eluent system of 8:2 ethyl acetate–hexane. The five fractions thus obtained consisted, in the order of elution, of: aldehyde **4**, contaminated with **5** and **6**; pinacol **5** contaminated with **4** and **6**; alcohol **3** containing also **5** and traces of **4**; pinacol **6** plus 40% alcohol **3**; and finally, pinacol **6**. The single fractions were then subjected to PTLC, and occasionally, to HPLC. In this way, pinacol **6** was obtained practically pure, pinacol **5** was obtained as a *ca.* 95% pure product (NMR), as well as alcohol **3** (NMR).

It is evident that the spiro structure encourages intermolecular assembling; the presence of hydrogen bonds may further contribute to this situation, thus rendering the separation a very difficult task.

Results and Discussion

Electrochemistry of 2-*Acetyl*-9,9′-*spirobifluorene* **1**.—In cyclic voltammetric experiments (Figs. 1 and 2), 2-acetyl-9,9′-spirobifluorene (**1**) gives a series of reduction peaks, the first one [Fig. 1(*a*)] is reversible; it becomes irreversible [Fig. 1(*b*)] as acetic acid is added. Similar behaviour is observed using various different proton donors of suitable acid strength in DMF. The second reduction peak, Fig. 2, is followed by those of the products, see ref. 3 for reduction of the 9,9′-spirobifluorene nucleus. Thus, radical anion $A^{\bullet -}$ is formed from **1**(A) in the first step, E° = −1.77 V (SCE) in the solvent system used [eqn. (1)].

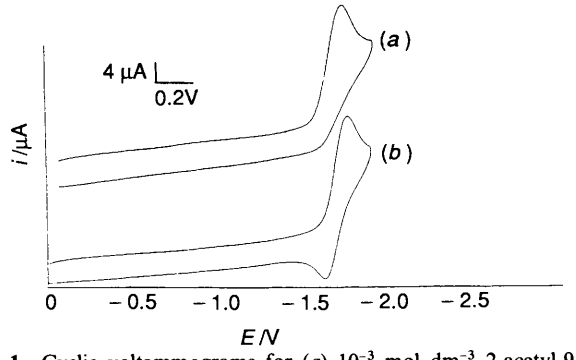


Fig. 1 Cyclic voltammograms for (*a*) 10^{-3} mol dm^{-3} 2-acetyl-9,9′-spirobifluorene **1** dissolved in DMF–Et_4NClO_4 0.1 mol dm^{-3}; (*b*) as (*a*) plus CH_3CO_2H 1:1 mol **1**: mol acid. Sweep rate V = 200 mV s^{-1}. Glassy-carbon electrode. *E*/V *vs.* SCE. Room temperature.

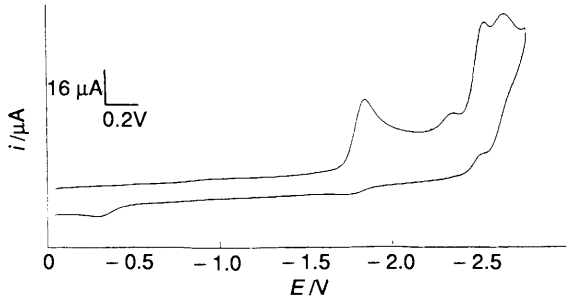


Fig. 2 Cyclic voltammogram for **1**, same conditions as in Fig. 1 (*a*), except sweep return at −2.75 V

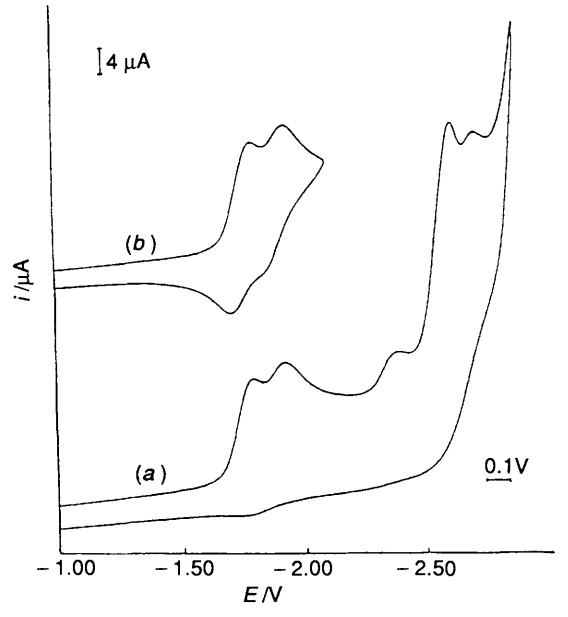


Fig. 3 Cyclic voltammetry for 10^{-3} mol dm^{-3} 2,2′-diacetyl-9,9′-spirobifluorene **2** dissolved in DMF–Et_4NClO_4 0.1 mol dm^{-3}; sweep return (*a*) at −2.9 V; (*b*) at −2.1 V; v = 50 mV s^{-1}; glassy carbon electrode. *E*/V *vs.* SCE.

$$A + e \rightleftharpoons A^{\bullet -} \quad (1)$$

The anion radical $A^{\bullet -}$ is green, and it can be seen during c.p.e. at *ca.* −1.8 V in the absence of added proton donors, and also around the GC electrode during voltammetry, for a few seconds; obviously, the persistency of $A^{\bullet -}$ is related to the proton availability of the solvent. The second (irreversible) reduction step occurs with E_p = −2.3 V (at V = 200 mV s^{-1}) [eqn. (2)]. It

$$A^{\bullet -} + e \rightleftharpoons A^{2-} \quad (2)$$

Table 1 Results of electrochemical reduction of aromatic ketones (A): 2-acetyl-9,9′-spirobifluorene **1** and acetophenone (**7**). Cathode: RVC; solvent system: DMF–Et_4NClO_4(0.1 mol dm^{-3}).

A	Product	Yield (%)[a]	de (%)[b]	n_{app}[c]
1[d]	$A^{\bullet -}$	90[g]		1.1
1[e]	**3**	11.5 (10)		1.5
	4	5		
	5	28.5 (17)		
	6	41.5 (35)	21.5	
	1	13.5		
7[f]	**8**	<5		1.2
	9	14 } (95)		
	10	83 }	72	

[a] Relative yields, crude (NMR); in parentheses, yield of isolated products, based on A. [b] de = diastereomeric excess (NMR), before work-up, from r = (±)/*meso* ratio. [c] Number of Faraday per mol of A consumed in the electrolysis, room temp., E = 1.9 V for **1** and −2.3 V for **7**. [d] No proton donor added. [e] Glacial acetic acid added, *ca.* 10:1 mol acid/mol. A. [g] Before exposure. [f] Dil. HCl added, *ca.* 1:1 mol acid/mol A.

is very interesting to observe that also for the diacetylated derivative **2** this step is located at about the same potential and remains irreversible, see below. No oxidation process is observed for A (to $A^{\bullet +}$) in the potential range available: the same behaviour was remarked in the case of 9,9′-spirobifluorene itself.[3] In order to evaluate the influence of the spirostructure on the heterogeneous electron-transfer constant for reaction (1) k_s,[16] we took acetophenone as a reference compound. Collecting $E_{pa} - E_{pc}$ data for compound **1** and acetophenone **7** under the same experimental conditions, in the range of potential sweep rates 0.05–10 V s^{-1},[17] we found that k_s (**1**)/k_s (**7**) = 1. In other words, the 9,9′-spirobifluorene structure, compared to the phenyl structure, has practically no effect on the electron transfer kinetics, eqn. (1).

Fig. (3) shows the voltammetric characteristics of 2,2′-diacetyl-9,9′-spirobifluorene (**2**). This compound is axially dissymmetric[12] and as a consequence it is present as a (±) mixture, as obtained through the synthesis. The first step, corresponding to the formation of the anion-radical, is again reversible as in the case of the monoacetylated derivative **1**; the main difference is that it is followed by a second reversible electron transfer, Fig. 3(*b*). The appearance of the second electron transfer is favoured at low sweep rates, the first one remaining with peak height i_p pertaining to 1 F mol^{-1} (**2**). The standard potentials $E°$ are: $E°_1$ = −1.75 and $E°_2$ = −1.90 V. Thus, the first step is practically the same as for **1**, occurring at about the same potential, *ca.* 20 mV only in favour of **2**. A detailed study of compound **2** will be reported elsewhere.[18] Formation of a dianion seems to occur at about the same potential as for **1**, E_p = −2.40 V [Fig. 3(*a*)], V = 50 mV s^{-1}. The subsequent reduction processes are those of the products, for which no conjugated C=O group is still present.

Products of the Preparative Electrolysis.—As described in the Experimental section, if a mixture of **1** and acetic acid are electrolyzed at the applied potential E = −1.90 V, using DMF–Et_4NClO_4 as solvent system, and RVC as electrode, a reasonable yield of alcohol **3** and pinacols **5** + **6** are obtained (Table 1). Among the products, the unexpected aldehyde **4** was also present.* With no proton donor added, reduction of **1** consumed *ca.* 1 F mol^{-1} (**1**), giving mainly the anion-radical $A^{\bullet -}$ of **1**; during work-up, $A^{\bullet -}$ is reoxidized by air, so that we finally

* The origin of compound **4** is unknown; it may possibly stem from nucleophilic attack of A^{2-} on the carbonyl group of the solvent dimethylformamide, with subsequent protonation and elimination of dimethylamine. (See later.)

obtained an intractable mixture of **1** and hydrogenated products. The relative yields reported in Table 1 are those obtained on the freshly electrolyzed solution, before isolation of the single products. The diastereoisomeric excess (de) is only slightly in favour of the (±)-pinacol of **1**. The results obtained with acetophenone **7** are also reported in Table 1. Electrochemical reductive dimerization of aromatic carbonyl compounds[9] is known to be a practical method to prepare the corresponding diols. Discussion of the stereochemistry of the process obviously implies a reliable evaluation of the des in the crude mixture of products. This topic has been treated in some cases,[9,19] and likely explanations of the reported des have been offered.

It is clear from our results that, compared to acetophenone, compound **1** is less prone to furnish pinacols under comparable conditions of electrolysis; the anion radical of acetophenone seems to be more basic than the anion radical of **1**, at least as far as kinetic basicity is concerned. At the same time, the bulky aromatic part of **1** seems to discourage dimerization. It is well known that mechanism-oriented studies on aromatic carbonyl compounds are mainly concerned with simple substrates, preferably benzaldehyde[20] or acetophenone, whereas product oriented studies deal with unconventional conditions or substrates.[21] In very few cases attention is paid to elucidate the stereochemical aspects of the pinacol formation.[9,19,21] Conditions, mechanism and stereochemistry are inter-related for a given substrate. Since we were interested only in the preparation of $A^{\bullet -}$ and of diols **5** and **6**, we simply describe the electrode process leading to the anion-radical of **1** by eqn. (1), in the absence of deliberately added proton donors. In the presence of acid, the overall electrode process is mainly that given in eqn. (3)

$$2A + 2e + 2H^+ \longrightarrow (AH)_2 \qquad (3)$$

accompanied by eqn. (4); where $(AH)_2$ represents the mixture of

$$A + 2e + 2H^+ \longrightarrow AH_2 \qquad (4)$$

pinacols and AH_2 the alcohol **3**. The various intermediate steps of reactions (3) and (4), if occurring as separate chemical and electron-transfer reactions, are well described in the literature.[9,19-21]

In the controlled-potential conditions reported here, in the presence of acid, the overall electrode reaction (3) actually results from eqn. (1), thereby anion radical $A^{\bullet -}$ is formed, followed by the solution reaction [eqn. (5)], and coupling [eqns. (6) and (7)], or eqn. (8). Some $AH^{\bullet}$ formed near the electrode

$$A^{\bullet -} + H^+ \longrightarrow AH^{\bullet} \qquad (5)$$

$$A^{\bullet -} + AH^{\bullet} \longrightarrow AAH^- \qquad (6)$$

$$AAH^- + H^+ \longrightarrow (AH)_2 \qquad (7)$$

$$2\,AH^{\bullet} \longrightarrow (AH)_2 \qquad (8)$$

will be reduced at the electrode itself, at the same potential as A [eqns. (9) amd 10)] so that eqns. (1) + (5) + (9) + (10)

$$AH^{\bullet} + e \longrightarrow AH^- \qquad (9)$$

$$AH^- + H^+ \longrightarrow AH_2 \qquad (10)$$

account for the overall 2e process (4).

Finally, the event by which $A^{\bullet -}$ disproportionates [eqn. (11)]

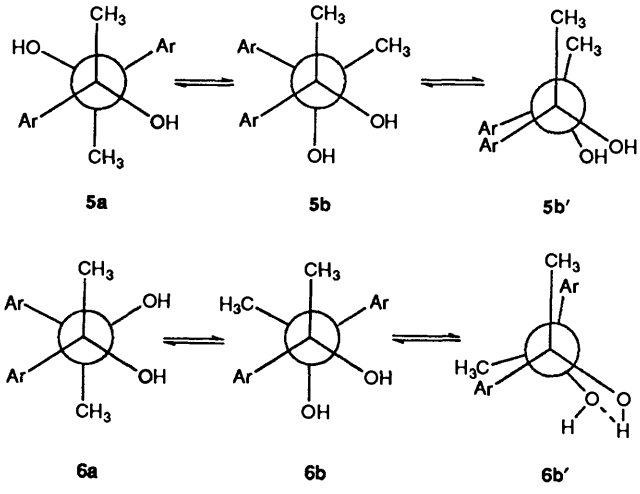
$$2A^{\bullet -} \rightleftharpoons A + A^{2-} \qquad (11)$$

is thermodynamically disfavoured, see the reduction potentials of A and $A^{\bullet -}$. Nevertheless, if A^{2-} interacts with the solvent to give products that decompose, equilibrium (11) may be shifted to the right [eqn. (12)]. The last situation, if confirmed with

$$A^{2-} + DMF \xrightarrow{2H^+} \mathbf{4} + NHMe_2$$

different substrates, will be of some interest with respect to the mechanism of the electrochemical reduction of aromatic carbonyl compounds.

NMR Spectroscopic Properties of Alcohol **3** *and of Diols* **5** *and* **6**.—The less polar *meso*-diol **5** is supposed to prefer the conformation **5a**, whereas for the (±)-diol **6**, in order to avoid



significant Ar–Ar repulsion, the pseudo-axial conformation **6b** is indicated. In addition, intramolecular hydrogen bond may be present in the conformation **6b**, with accompanying adaptation of the torsion angle, as depicted in conformation **6b'**. In the latter event, the two CH_3 groups, as well as the two Ar groups, are *trans* with respect to the O–C–C plane. If the assignment of the diastereoisomeric structures is correct, we observe, in the ^1H NMR spectra of pinacols **5** and **6**, $\delta(CH_3)(meso) < \delta(CH_3)(\pm)$, whereas for acetophenone pinacols $\delta(CH_3)(meso) > \delta(CH_3)(\pm)$. Compounds **5** and **6** have the CH_3 groups more shielded than the CH_3s of acetophenone pinacols, suggesting that the CH_3 protons are located in the shielding cone of one of the two aromatic halves of the spirobifluorene fragment, as indicated by the conformations **5a** and **6b**. Both alcohols **3** and **8** exhibit the CH_3 doublet near the CH_3 singlet of **6** and **10** respectively: $\delta(CH_3)$ (**3**) ~$\delta(CH_3)$ (**6**), as well as $\delta(CH_3)$ (**8**) ~ $\delta(CH_3)$ (**10**). Finally, the ^{13}C signals at δ = 65.9 in all compounds **1–6** as well as in 9,9'-spirobifluorene is indicative of the spiro-carbon; it is of considerable help for the elucidation of the proposed structures.

Selectivity in the Formation of Diastereoisomeric Pinacols.—Inspection of Table 1 reveals that product selectivity, in terms of diastereoisomeric excess, is low (*ca.* 21%) and in favour of the (±) mixture. The same, but more marked trend, is observed for acetophenone pinacols (this work: de = 72%; lit.[22] de = 72% in comparable conditions of electrolysis*). The (±) preference was explained by Bewick assuming the intramolecular hydrogen bond in **10** as the main origin.[22] In our case, the presence of the bulky aromatic groups seems to have a levelling effect in the formation of **5** and **6**, even if the intramolecular hydrogen bond

* Solvent system: DMF + 1500 ppm H_2O, 0.1 mol dm^{-3} TBAP.

may be still be present in **6**. Moreover, we believe that competition between couplings described by eqns. (6) and (8) will further decide about the prevalence of one of the two stereoisomers. In fact, coupling between $^{\bullet}AH$ and $A^{\bullet -}$ as described in eqn. (6) should favour the (±) isomer, through a hydrogen-bonded intermediate: $\dot{C}$–OH . . . $^{-}$O–$\dot{C}$; coupling between neutral radical $^{\bullet}AH$ as described by eqn. (8) should give no de.

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