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Electrochemical Reduction of β-Aryldehydroamino Acid Derivatives

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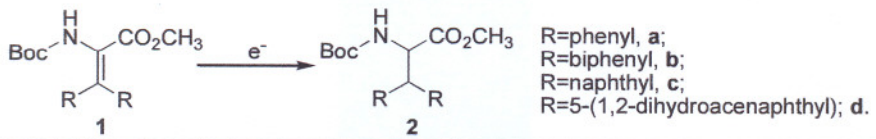
Introduction

The reduction of an isolated double bond is not possible using electrochemical methods, however when the double bond is conjugated with an electron withdrawing group such as a carbonyl it becomes reducible in the accessible potential range [1]. For some years now we have been interested in the synthesis of dehydroamino acid derivatives and in using these compounds as substrates in several types of reactions [2]. As part of this work we have been studying the electrochemical behaviour of dehydroamino acid derivatives. Although there are many reports concerning the chemical reduction of α,β-dehydroamino acids, [3] to the best of our knowledge the electrochemical reduction of β,β-disubstituted dehydroamino acids has not yet been described. Since dehydroamino acids can be considered activated alkenes we decided to study the electrochemical reduction of β,β-diaryldehydroalanines and study the photophysical properties of some of the saturated amino acids prepared and compare them with those of the corresponding β,β-diaryldehydroalanines.

Results and Discussion

Several β,β-diaryldehydroalanines (compounds **1a-d**, Table 1) were prepared from a β,β-dibromoalanine derivative [4] and aryl boronic acids by a Suzuki-Miyaura coupling reaction [5]. The cathodic peak potentials of these compounds were measured by cyclic voltammetry and these were reduced to the corresponding alanine derivatives using controlled potential electrolysis.

Table 1. Cathodic peak potentials obtained by cyclic voltammetry[a] and results obtained in the controlled potential electrolysis[b] of β,β-diaryldehydroalanine derivatives



Reagent	*-Ep / (V vs SCE)*	*Product*	*Yield / %*
1a	1.81	2a	85
1b	1.75	2b	79
1c	1.80	2c	81
1d	1.76	2d	78

[a]Cathode: vitreous carbon. Solvent: dimethylformamide. Supp. electrolyte: Bu_4NBF_4 0.1 mol dm^{-3}. Substrate conc.: ≈0.005 mol dm^{-3}. [b]Solvent: acetonitrile. Supp. electrolyte:Et_4NCl (0.1 mol dm^{-3}); Proton donor:Et_3NHCl (0.04 mol.dm^{-3}).

From the cathodic peak potentials presented, it is possible to observe that all compounds studied have similar reduction potentials. Also when these potentials are compared with that of the methyl ester of *N-tert*-butoxycarbonyl-dehydrophenylalanine (Boc-ΔPhe-OMe, -1.84 V *vs* SCE [6]) it can be concluded that the presence of a second aryl moiety at the β-carbon atom does not significantly influence the reduction potential. Controlled potential electrolysis of compounds **1a-d** gave the corresponding β,β-diarylalanines in good to high yields (**2a-d**). This result is different from those reported for α,β-unsaturated ketones and *N,N*-diprotected dehydroalanines. In the case of α,β-unsaturated ketones the reduction products include the saturated ketone and a dimer [1,7]. *N,N*-Diprotected dehydroalanines give upon electrochemical reduction the corresponding diamino dicarboxylic acids [6]. The results obtained are consistent with the mechanism proposed for the reduction of

α,β-unsaturated ketones in protic media which involves the transfer of an electron to give a radical anion that rapidly protonates and tautomerizes to give an alkyl radical that is more easily reduced than the reagent and is converted into the β,β-diarylalanine [1].

The photophysical properties of compounds **2b** and **2c** were studied in three solvents of different polarity and compared with those of compounds **1b** and **1c** (Table 2).

*Table 2. Maximum absorption (λ_{abs}) and emission wavelengths (λ_{em}), molar absorption coefficients (ε) and fluorescence quantum yields (Φ_F) for compounds **1b**, **1c**, **2b** and **2c***

Solvent	λ_{abs} (nm) ($\varepsilon/10^4$ $M^{-1}cm^{-1}$)				λ_{em} (nm)				Φ_F[a]			
	1b	*1c*	*2b*	*2c*	*1b*	*1c*	*2b*	*2c*	*1b*	*1c*	*2b*	*2c*
Cyclohexane	283 (3.21) 203 (6.38)	298 (1.47) 216 (7.90)	260 (3.32) 206 (6.39)	296 (0.87) 285 (1.12) 274 (0.90) 222 (8.27)	368 382	363	318	328 339	0.067	0.086	0.37	0.13
Acetonitrile	281 (3.41) 204 (6.06)	297 (1.54) 216 (8.39)	262 (3.45) 203 (6.93)	295 (0.90) 285 (1.12) 275 (0.91) 220 (8.52)	368 385	367	318	328 339	0.025	0.044	0.32	0.15
Ethanol	281 (3.09) 201 (6.87)	298 (1.51) 216 (8.31)	261 (3.41) 205 (6.56)	295 (0.91) 285 (1.14) 275 (0.93) 220 (8.45)	369 387	365	319	327 339	0.043	0.035	0.40	0.23

[a]*Relative to anthracene in ethanol (Φ = 0.27 at 25 ºC) [8] for **1b** and **1c**; relative to naphthalene in cyclohexane (Φ_F = 0.23 at 25 ºC) [9].*

The results show that although the dehydroalanines show low quantum yields their reduction products show reasonably high fluorescent yields and could be useful as fluorescent markers.

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