

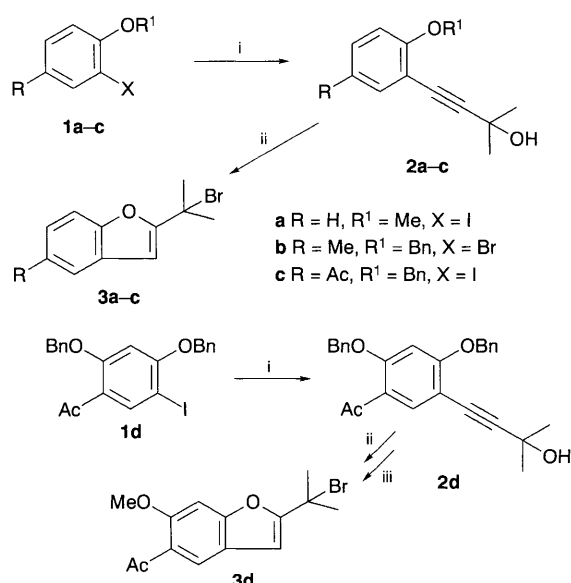
A New Electrosynthesis of 2,2-Dimethylchromenes from 2-(1-Bromo-1-methylethyl)benzofurans

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Electrolytic reduction of 2-(1-bromo-1-methylethyl)benzofurans in acetonitrile affords the corresponding 2,2-dimethylchromenes in good yields even in the absence of a proton donor and comprises the cleavage of a carbon–bromine bond followed by ring expansion.

Chromenes and their modifications are widely distributed in nature;¹ some are useful as pesticides *e.g.* precocenes I and II.² Chromene derivatives are also important as intermediates in organic syntheses and have been synthesized by a variety of methods.^{1a,3} However, as far as we know, there is no direct conversion of benzofurans to benzopyrans.⁴ An electroreductive route has high potential and the electroreduction of benzofurans is of great interest from a mechanistic and synthetic point of view. Here we report the first electrochemical reduction



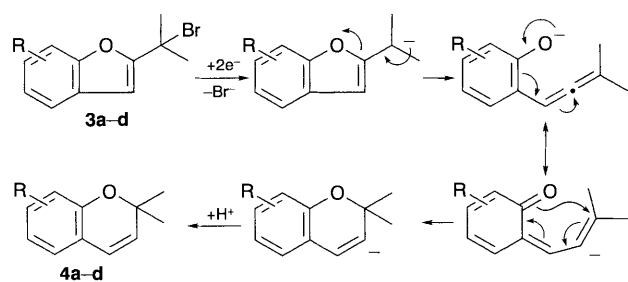
Scheme 1 Reagents and conditions: i, 2-methylbut-3-yn-2-ol (3 mmol), Pd⁰ (3 mol%), Et₃N/DMF, N₂, 50–80 °C, 1–10 h, 90–95%; ii, BBr₃ (2.6–4 mmol), CH₂Cl₂, –70 to 0 °C, 5–10 min, 30–57%; iii, (MeO)₂SO₂, K₂CO₃, MeCOMe, reflux, 96%

of 2-(1-bromo-1-methylethyl)benzofuran derivatives **3a–d**, resulting in the formation of the corresponding 2,2-dimethylchromenes **4a–d**.

The coupling reaction of the halogenated phenols **1** with 2-methylbut-3-yn-2-ol in the presence of Pd⁰ under suitable conditions gave the alkynylphenols **2** in high yields.⁵ The cyclization of **2** with BBr₃ afforded 2-(1-bromo-1-methylethyl)benzofurans **3a–d** in moderate yields (Scheme 1).

An electrolytic cell for macroelectrolysis was composed of three separated compartments. A series of controlled potential macroelectrolyses of **3a–d** were carried out at the Hg pool cathode at the potential of the first reduction wave in acetonitrile (MeCN) containing 0.1 mol dm^{–3} tetraethylammonium toluene-*p*-sulfonate (Et₄NOTs) in the absence or presence of benzoic acid as a proton donor at room temperature. The results of these macroelectrolyses are listed in Table 1, in which the coulometric *n*-values (electrons per molecule) and the half-wave potential (*E*_{1/2}) also are included. The *n*-values were obtained from the amount of substrate added and the quantity of electricity passed until the electrolysis finished. The benzofuran derivatives **3a–d** were electrochemically reduced to afford the corresponding chromenes **4a–d**. The yields of **4** were affected to an extent by the substituent groups of **3**. For example, the electroreduction of **3b** bearing an electron-releasing group such as Me led to **4b** in high yield, as much as **3a**. Although **3c**, and **3d** [bearing an electron-withdrawing group (MeCO)] were reduced more easily than **3a**, **4c** and **4d** were produced in lower yields than **4a**. In spite of the fact that the reduction of **3** to **4** involves the addition of a proton, the addition of a proton donor such as benzoic acid had no significant influence on the yield of **4**. As shown in Table 1, polarography also showed that *E*_{1/2} for the first reduction was not shifted by the addition of benzoic acid, suggesting that the potential-determining transition state does not contain a proton. The *n*-values for the electroreduction of **3a–d** in the absence of the proton donor were about 2, while the *n*-values in the presence of benzoic acid were about 3. The *n*-values of about 2 can be easily understood by the formation of **4**. However, no explanation for the increase in the *n*-values by the addition of benzoic acid can be offered at the present time.

On the basis of our results, a plausible reaction mechanism is proposed for the electroreduction of **3** to **4** as illustrated in Scheme 2.



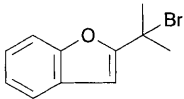
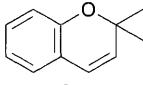
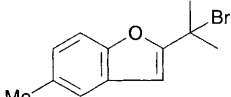
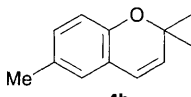
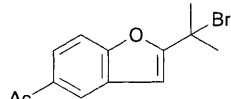
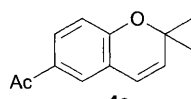
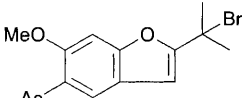
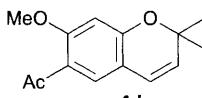
Scheme 2

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Table 1 Controlled potential macroelectrolyses of **3a-d** at the first reduction potential on Hg pool cathode in MeCN/0.1 mol dm⁻³ Et₄NOTs

Entry	Benzofuran	Proton donor (2 equiv.)	$E_{1/2}/V^a$	n -Value	Product ^b (yield, %)	
1		None	-2.6	2.1		87
2	3a	PhCO ₂ H	-2.6	3.0	4a	85
3		None	-2.6	2.1		92
4	3b	PhCO ₂ H	-2.6	2.6	4b	86
5		None	-2.3	1.5		60
6	3c	PhCO ₂ H	-2.3	2.8	4c	63
7		None	-2.4	1.8		73
8	3d	PhCO ₂ H	-2.4	2.8	4d	61

^a The potentials were quoted against an Ag/0.1 mol dm⁻³ AgNO₃ in MeCN reference electrode. ^b All the products are oils. Yields isolated by silica gel column chromatography are given. Identification of all the products was achieved by ¹H NMR evidence and elemental analysis.

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