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Novel Electrochemical Route to 2-(α-Alkoxyallyl)phenols - Cathodic Eliminative Ring Opening Reaction

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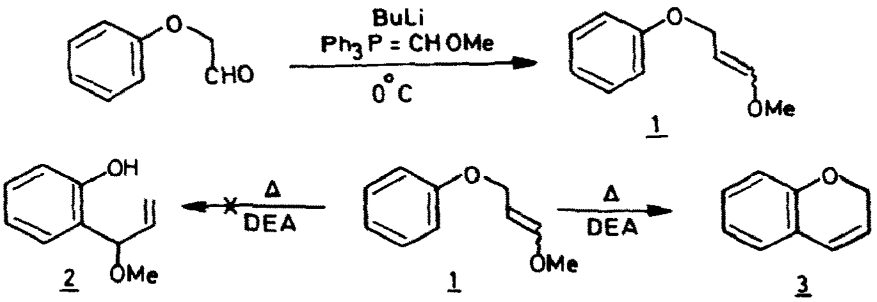
Abstract: Electrochemical reduction of 4-alkoxy-3-bromochromans in acetonitrile led to a facile ring cleavage reaction yielding 2(α-alkoxy- allyl)phenols which are not easily accessible.

In connection with one of our synthetic projects[1,2], we were in need of 2(α-methoxyallyl)phenol, 2b. An obvious entry to this compound would be by the Claisen rearrangement of Γ-methoxyallyl phenyl ether, 1. A survey of literature indicated that conventional method of preparing allyl phenyl ethers failed in this case[3]. We devised a Wittig route to the ether 1, starting from phenoxyacetaldehyde as represented in Scheme-I. However, when the ether 1 was subjected to Claisen rearrangement in refluxing diethylaniline for 3 hr, it furnished only the chromene, 3 and not the required 2(α-methoxyallyl)phenol, 2b. It was evident from this observation that the phenol 2b could not survive the conditions of rearrangement and underwent fast cyclisation to give 3[4].

Scheme - I



In view of this, we were in search of an alternative method which could be carried out at ambient temperature to prevent the cyclisation of 2, and could also be regioselective to furnish only the *o*-isomer. In this context, we envisaged an electrochemical route involving the cathodic eliminative ring opening of 4-alkoxy-3-bromochromans, 4 which could lead to the desired phenols, 2 under mild conditions. Electrochemical reductive ring cleavage of epoxides has been reported recently in the reduction of α-keto epoxides[5]. However, to our knowledge, there is no precedence in the literature on the reductive ring cleavage of stable six membered ring systems under electrochemical conditions.

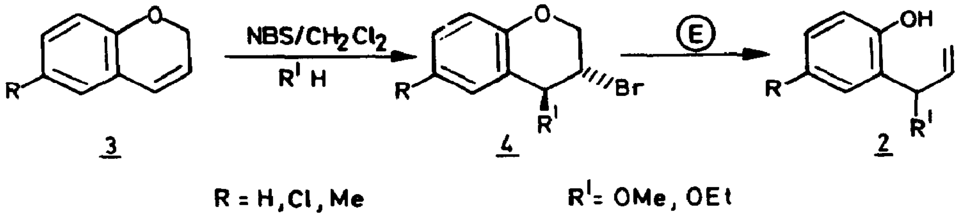
As a model, when controlled-potential macroelectrolysis (CPE)[6] of 3-bromochroman, **4a** was carried out in acetonitrile containing 0.1M tetraethylammonium perchlorate as the supporting electrolyte, it afforded a liquid in 80% yield. It was identified as 2-allylphenol by comparison of its spectral and analytical data with those of an authentic sample. Encouraged by this, a few *trans*-4-alkoxy-3-bromochromans, **4b**-**4e** were prepared by stirring a mixture of the chromene 3 and NBS in dichloromethane at 0°C and then adding 5 equi. of the desired alcohol and stirring the reaction mixture for an additional 2 hr at room temperature. The large scale electrolysis of **4b** afforded straightaway 2(α-methoxyallyl)phenol, **2b**[7,8] in 78% yield. Other alkoxybromo- chromans, **4c**-**4e** also underwent this transformation affording the corresponding 2(α-alkoxyallyl)phenols, **2c**-**2e** in good yields (Scheme-II, Table I).

TABLE I

S.No.	Entry	R	R'	Yield %	Ratio 2 : 3		$-E_{p,c}/V^*$
1.	**4a**	H	H	80	100	0	2.05
2.	**4b**	H	OMe	78	85	15	1.95
3.	**4c**	H	OEt	82	80	20	1.97
4.	**4d**	Me	OMe	75	85	15	1.98
5.	**4e**	Cl	OMe	84	85	15	1.92
6.	**4g**	H	OPh	85	0	100	1.78

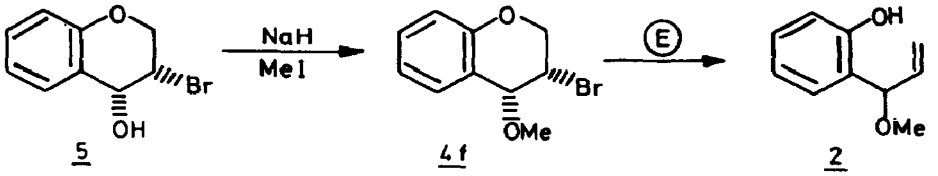
* E are the cathodic peak potentials obtained in cyclic voltammetric experiments carried out in acetonitrile using a HMDE working electrode and silver wire as the reference electrode at 0.10V/s sweep rate.

Scheme - II



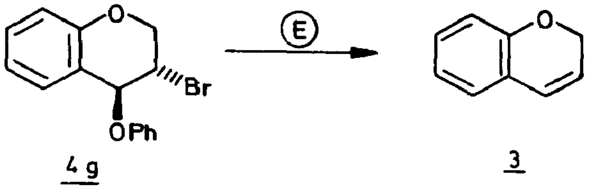
The course of this electrochemical transformation was unaffected by the stereochemistry of the two groups viz. Br and R'. The *cis*- isomer, 4f prepared by methylation of the *cis*- bromohydrin, 5 also afforded the same product, 2b when subjected to electrochemical reduction under the above conditions (Scheme III).

Scheme - III



When the alkoxy group at the 4-position is replaced by a phenoxy group, the major reaction pathway was 1,2-elimination leading to chromene, 3 (Scheme IV) as the only product (Entry 4g, Table I).

Scheme - IV



It is therefore evident that the course of the electrochemical reduction of 3-bromochromans depends upon the leaving group ability of the functional group present at the 4-position. In view of the importance of 2-allylphenols as synthons in organic synthesis, this novel electrochemical method is complimentary to the thermal[9,10] and catalysed[11,12] Claisen rearrangements of phenyl allyl ethers.

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4. The 2(α-methoxyallyl)phenol prepared by electrolysis of **4b** when refluxed in diethylaniline for one hour afforded chromene **3**.
5. Inokuchi,T.; Kusumoto,M.; Torii,S. *J.Org.Chem.*,**1990**,*55*,1548-1553.
6. CPE was carried out in acetonitrile at -2.25V vs. silver quasi-reference electrode. Mercury pool was used as the working electrode (cathode).
7. Spectral data of **2b** ^{1}H NMR (400 MHz, $CDCl_3$) : δ 3.45(s,3H), 4.75(d,1H), 5.3(m,2H), 5.95(m,1H), 6.75-7.30(m,4H), 7.85(s,exchangeable with D_2O).

   ^{13}C NMR (100.5 MHz, $CDCl_3$) 56.80(q), 85.26(d), 118.43(t), 118.93(d), 125.68(s), 130.80(d), 132.07(d), 132.13(d), 135.37(d), 154.64(s).

   HRMS: Cal. 164.08373, Obs. 164.08583. Other compounds also gave satisfactory spectral data.
8. The phenol **2b** has been characterised as its acetate by *in situ* acetylation in the electrolysis and also by acetylation using sodium acetate and acetic anhydride.
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