A New Route to *o*-Allenylphenols

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Cathodic reduction of 3-bromochromenes led to a ring-opening reaction yielding *o*-allenylphenyl acetates.

Claisen rearrangement of phenyl propynyl ethers is well documented in the literature and is known to proceed through the intermediacy of *o*-allenylphenols.[1,2] All the attempts to trap *o*-allenylphenol have so far been unsuccessful.[3] Although synthesis of a few derivatives of *o*-allenylphenol has been reported,[4,5] no convenient method is available for the preparation of *o*-allenylphenol itself or for the substituted o-allenylphenols. We report herein a concise and facile route to *o*-allenylphenols by the electrochemical ring-opening reaction of 3-bromochromenes.

3-Bromochromenes were prepared by the Claisen rearrangement of the corresponding 2,3-dibromoallyl phenyl ethers in refluxing diethylaniline for 25 h.

The cyclic voltammogram of **1**, (10 mmol dm^{-3}) on a hanging mercury drop electrode at 100 mVs^{-1} sweep rate showed a single irreversible cathodic peak at −2.21 V *vs.* silver quasi reference electrode in acetonitrile containing 0.1 mol dm^{-3} tetraethylammonium perchlorate as supporting electrolyte. The controlled potential electrolysis of **1** was performed on a Hg-pool cathode at −2.4 V in acetonitrile solutions containing 5 equiv. of acetic anhydride. The electrolysis was stopped when the initial current (80 mA) reached a constant minimum value of 5 mA after about 6 h. The catholyte after workup afforded *o*-allenylphenyl acetate **2**† as the major product with chromene **3** in minor amounts (Table 1, Scheme 1).

Interestingly, it was observed that when the electrolysis was carried out in the absence of acetic anhydride only 2-methylbenzofuran, **4**, was obtained as the major product presumably due to the rapid cyclisation of the intermediate, *o*-allenylphenoxide.

While our attempt to prepare *o*-allenyl phenol by saponification of **2** yielded only 2-methylbenzofuran **4**, the acetates **2a–e** could be quantitatively converted to the corresponding phenols **5** by reduction using $LiAlH_4$ in diethyl ether at 0 °C and quenching the lithium salt with acetic acid at 0 °C followed by ether extraction.‡ *o*-Allenylphenol was found to be stable at 0 °C for 24 h as revealed by TLC and NMR analysis. However, after this time it was found to suffer a slow cyclisation to yield the chromene, **3a**.

When 2-bromomethylbenzofuran was subjected to cathodic reductive ring-cleavage reaction at −2.1 V *vs.* silver quasi-reference electrode in acetonitrile solutions, it afforded only the product of simple reduction, namely, 2-methylbenzofuran and not *o*-allenylphenyl acetate. The contrasting behaviour of 2-bromomethylbenzofuran towards this cathodic reaction may be attributed to the aromatic nature of the benzofuran system and also to the stability of the 'benzylic' anion that is formed as compared to the vinylic anion formed in the case of 3-bromochromenes **1**. Separation of **2** and **3** was effected using column chromatography.

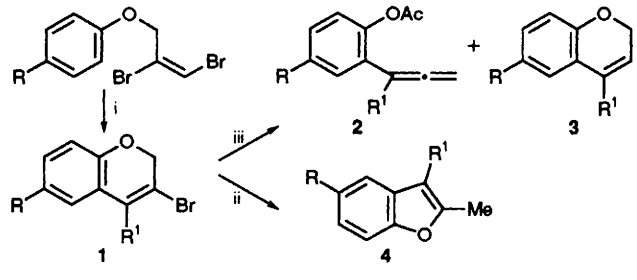
Phenylallenes are prepared generally by isomerisation of propynyl benzene,[6] dehalogenation of *gem* dibromo cyclopropanes[7] and [3,3]-sigmatropic reactions of propynylcyclohexadienols.[8] Allenes undergo a variety of reactions *viz.* [2 + 2] cycloadditions, carbene additions and radical additions.[9] Our electrochemical method provides a convenient entry to the elusive (*o*-hydroxyphenyl)allenes (*o*-allenylphenols) which are important reaction intermediates and potential synthons in organic chemistry.

One of us (N. B.) is grateful to CSIR India for a fellowship. We are thankful to RSIC, Madras for spectral data. M/s BASF, Germany is acknowledged for gift of propynyl alcohol and Bayer AG is thanked for providing free Chem. Inform issues.

Received, 17th February 1994; Com. 4/00977K

Table 1 Product ratios of **2** and **3**

Entry	R	R′	Yield (%)	Ratio of 2 : 3
1a	H	H	75	80 : 20
1b	Me	H	78	78 : 22
1c	Cl	H	72	77 : 23
1d	H	Me	70	75 : 25
1e	Bu^t	H	80	75 : 25



Scheme 1 *Reagents and conditions*: i, $PhNEt_2$, reflux, 25 h; ii, −2.4 V *vs.* Ag electrode, MeCN, 6 h; iii, −2.4 V *vs.* Ag electrode, MeCN, 5 equiv. $(MeCO)_2O$, 6 h

Footnotes

† For **2a**: ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H, $OCOCH_3$), 5.15 (d, 2H, *J* 6.7 Hz, $=CH_2$), 6.2 (t, 1H, *J* 6.7 Hz, –CH=), 7.0–7.4 (m, 4H aromatic); ^{13}C NMR (100.5 MHz, $CDCl_3$) 20.79 (q), 78.40 (t), 88.01 (d), 122.74 (d), 126.21 (d), 127.84 (d), 128.35 (d), 129.73 (s), 147.46 (s), 169.31 (s), 210.61 (s).

‡ For **5a**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.3 (d, 2H, *J* 7 Hz, $=CH_2$), 6.45 (t, 1H, *J* 7 Hz, –CH=), 6.5 (br, s 1H, exchangeable with D_2O, OH), 6.8–7.2 (m, 4H, aromatic); ^{13}C NMR (100.5 MHz, $CDCl_3$) 79.83 (t), 90.69 (d), 116.20 (d), 118.65 (s), 120.63 (d), 128.60 (d), 128.89 (d), 154.51 (s), 209.21 (s).

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