Thermal Claisen Rearrangement of Aryl Allenylmethyl Ethers: Synthesis of 2-(*o*-Hydroxyaryl)buta-1,3-dienes and 4-Methyl-2*H*-1-benzopyrans

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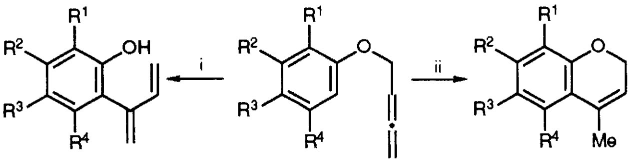
Thermal Claisen rearrangement of aryl allenylmethyl ethers in diethylene glycol afforded 2-(*o*-hydroxyaryl)buta-1,3-dienes and 4-methyl-2*H*-1-benzopyrans in good yield.

Few classical named reactions have been studied so extensively from synthetic, stereochemical, mechanistic and theoretical aspects as the Claisen rearrangement. The many exhaustive reviews surveying the rapid development of this reaction illustrate the attention it continues to receive.[1] Though a large number of reports on the Claisen rearrangement of non-cumulated double bond systems are available in the literature,[1,2] only a few examples can be found for allenes.[3] In particular, the thermal behaviour of aryl allenylmethyl (buta-2,3-dienyl) ethers has remained virtually uninvestigated till recently[4,5] in contrast to that of the isomeric aryl prop-2-ynyl ethers which has been studied extensively.[1,6] Herein, we report a simple route to 4-methyl-2*H*-1-benzopyrans and an expedient synthesis of 2-(*o*-hydroxyaryl)buta-1,3-dienes by the thermal Claisen rearrangement of aryl allenylmethyl ethers.

Heating the 2-naphthyl allenylmethyl ether **1e** (2 mmol) in diethylene glycol (DEG) (5 ml) at 160–165 °C (bath temperature) for 20 min afforded the 2-(2-hydroxy-1-naphthyl)-buta-1,3-diene **2e** as a colourless liquid in 82% yield.† Other aryl allenylmethyl ethers **1a–d** and **1f** were also found to undergo this [3,3] sigmatropic rearrangement furnishing the respective 2-(*o*-hydroxyaryl)buta-1,3-dienes **2a–d** and **2f** in good yield‡ (Scheme 1, Table 1).

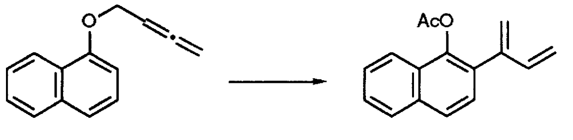


2 **1** **3**

Scheme 1 *Conditions* (in DEG under N$_2$): i, heat, shorter time; ii, reflux, longer time

The 1-naphthyl allenylmethyl ether **1f** rearranged faster than the isomeric ether **1e** (Table 1, Entries 5 and 6). The lower yield of **2f** in the case of the 1-naphthyl allenylmethyl ether is due to its fast rearrangement and a more rapid cyclisation of the intermediate phenolic product, *viz.*, **2f**, to the naphthopyran **3f**. This cyclisation can be avoided by trapping the 2-(1-hydroxy-2-naphthyl)buta-1,3-diene as its acetate **4f**. Refluxing the 1-naphthyl allenylmethyl ether **1f** (2 mmol) in a mixture of *o*-dichlorobenzene (*o*DCB) (5 ml) and acetic anhydride (1 ml) in the presence of a catalytic amount of 4-*N*,*N*-dimethylamino-pyridine (DMAP) for 8 h afforded the 2-(1-acetoxyl-2-naphthyl)buta-1,3-diene **4f** as a colourless liquid in 80% yield§ (Scheme 2). The 2-arylbuta-1,3-dienes are useful synthons in Diels–Alder reactions and there is no good method for their synthesis.[7] The thermal Claisen rearrangement of aryl allenylmethyl ethers thus provides a convenient method for the preparation of these compounds.

Benzopyran compounds are widespread in a variety of natural products and have interesting properties, *e.g.*, psychotropic (tetrahydrocannabinol), and insecticidal: ageratochromene (precocene), phytoalexins (pterocarpans) *etc.*[8] Claisen rearrangement of aryl prop-2-ynyl ethers is a good method for the synthesis of benzopyrans.[9] Surprisingly the utility of thermal Claisen rearrangement of aryl allenylmethyl ethers for the synthesis of benzopyrans has not been explored. In the present study, 4-methyl-2*H*-1-benzopyrans **3a–f** were



1f **4f**

Scheme 2 *Conditions:* (MeCO)$_2$O, DMAP, *o*DCB, reflux, 8 h, under N$_2$

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† The duration of heating was found to be critical: after short times unreacted starting material was present to a considerable extent whereas heating for a long period led to a lower yield of **2e**.

‡ All the new compounds reported in this communication were thoroughly characterised by spectral and HRMS data.

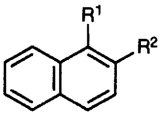
§ Other aryl allenylmethyl ethers were also trapped as acetates in 62–82% yield.

Table 1 Synthesis of 2-(*o*-hydroxyaryl)buta-1,3-dienes **2** and 4-methyl-2*H*-1-benzopyrans **3**

Entry	Starting ether	R^1	R^2	R^3	R^4	Conditions for **2**	Yield of **2** (%)	Time at reflux for **3**	Yield of **3** (%)
1	**1a**	H	H	OMe	H	200–210 °C, 12 min	78	30 min	86
2	**1b**	H	H	Me	H	200–210 °C, 16 min	72	40 min	82
3	**1c**	H	H	H	H	200–210 °C, 20 min	66	40 min	80
4	**1d**	H	H	Cl	H	200–210 °C, 20 min	62	40 min	80
5	**1e**	H	H	Benzo		160–165 °C, 20 min	82	5 min	88
6	**1f**	Benzo		H	H	140–145 °C, 12 min	52[a]	5 min	88

[a] The rest of the product was 4-methyl-2*H*-1-naphthopyran and starting material.

Table 2 Comparison of the ease of rearrangement of allenylmethyl, allyl, prop-2-ynyl and but-2-ynyl ethers of 1-naphthol and 2-naphthol **A**[a]



A

Entry	Compound	R^1 in **A**	R^2 in **A**	*t*/min	Unreacted (%)	Products
1	**1e**	H	$OCH_2CH{=}C{=}CH_2$	20	0	**2e** + **3e**
2	**5**	H	$OCH_2CH{=}CH_2$	20	66	1-Allyl-2-naphthol
3	**6**	H	$OCH_2C{\equiv}CH$	20	95	3*H*-Naphtho[2,1-*b*]pyran
4	**7**	H	$OCH_2C{\equiv}CMe$	20	100	—
5	**1f**	$OCH_2CH{=}C{=}CH_2$	H	8	0	**2f** + **3f**
6	**8**	$OCH_2CH{=}CH_2$	H	8	63	2-Allyl-1-naphthol
7	**9**	$OCH_2C{\equiv}CH$	H	8	94	2*H*-Naphtho[1,2-*b*]pyran
8	**10**	$OCH_2C{\equiv}CMe$	H	8	100	—

[a] In DEG at 160–165 °C.

obtained in good yield by refluxing the aryl allenylmethyl ethers **1a–f** in diethylene glycol for 5–40 min (Scheme 1 and Table 1).

Since substituent effects on Claisen rearrangement have been the subject of several theoretical studies in recent years,[10] it was of interest to compare the relative ease of rearrangement of allenylmethyl, allyl, prop-2-ynyl and but-2-ynyl ethers of 1-naphthol as well as of 2-naphthol (Table 2). The results from our preliminary study indicate that the allenylmethyl ethers rearrange much faster than the other ethers, in both the 1-naphthyl (Table 2, Entries 5–8) and the 2-naphthyl (Table 2, Entries 1–4) systems. This is in good agreement with the calculations of Jorgensen *et al.*[11] from their theoretical studies on [3,3] sigmatropic reactions. They have shown that a terminus which is part of a cumulene lowers the E_a by 25 kJ mol^{-1}. In all these cases 1-naphthyl ethers were observed to rearrange faster than the corresponding 2-naphthyl ethers. Also, the possibility of fast prototropic rearrangement of **1e** to the propynylic derivative **7**, prior to the Claisen rearrangement step, is ruled out (Table 2, Entries 1 and 4).

Our successful thermal Claisen rearrangement of aryl allenylmethyl ethers to 2-(*o*-hydroxyaryl)buta-1,3-dienes after a short time and to 4-methyl-2*H*-1-benzopyrans after a longer time is in marked contrast to the recent report of Dikshit *et al.*[4] who observed the thermal rearrangement of *p*-methoxyphenyl allenylmethyl ether in refluxing *N*,*N*-diethylaniline (b.p. 217 °C) or diethylene glycol (b.p. 245 °C) led to a complex mixture. It is evident that the products had decomposed under their experimental conditions.¶

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¶ Reaction time is not mentioned, and only one aryl allenylmethyl ether was tried by the authors.