

Cation Radical-Induced Claisen Rearrangement of Aryl Allenylmethyl Ethers

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Treatment of aryl allenylmethyl ethers with tris(4-bromophenyl)aminium hexachloroantimonate in acetonitrile at room temperature induces a facile cation radical induced Claisen rearrangement to yield 2-(*o*-hydroxyaryl)buta-1,3-dienes.

Cation radical induced pericyclic reactions have attracted wide attention in recent years.^{1,2} Although the cation radical initiated Cope and related rearrangements have been explored,³ there seems to be no report of the Claisen rearrangement under similar conditions. In view of the unabated interest in Claisen rearrangement,⁴ we began to investigate the behaviour of cation radicals generated from aromatic Claisen systems.⁵ Herein, we describe our results on the behaviour of aromatic 3,3-sigmatropic systems (aryl allyl and aryl allenylmethyl ethers) in the presence of tris-(4-bromophenyl)aminium hexachloroantimonate, **2**.

In a typical reaction, when *p*-methoxyphenyl allenylmethyl ether, **1a** (1 mmol) in dry MeCN (20 ml) was treated with the stable cation radical salt, **2** (0.5 mmol) at room temp.,† a colour change from blue to red was observed. Quenching the reaction mixture after 30 min with NaOMe–MeOH followed by evaporation of MeCN and an aqueous workup afforded a liquid in 95% 'yield'. The analysis of this crude product by TLC, ¹H NMR and HPLC indicated it to be a mixture of the starting material, **1a** and the Claisen rearranged product 2-(2-hydroxy-5-methoxyphenyl)buta-1,3-diene, **3a** (Scheme 1). However, the mixture could be separated chromatographically to afford pure **3a** in 55% yield. Neither the cyclised product, namely, 6-methoxy-4-methyl-2*H*-1-benzopyran nor an appreciable amount of *p*-methoxyphenol (arising from the cleavage of ArO–C bond) was detected in the crude reaction

mixture. This observation is in contrast with the findings encountered for **1a** under thermal conditions.⁶ There was no evidence for the presence of any product due to the formal [1,3] sigmatropic rearrangement.

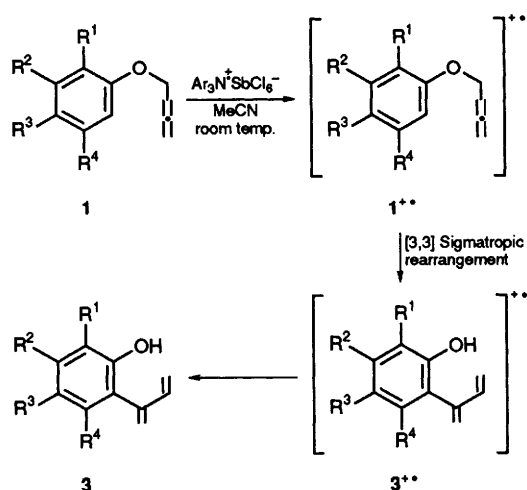
Exposure of **1a** to trifluoroacetic acid, a solvent which was reported to accelerate the Claisen rearrangement of aryl allyl ethers tremendously,⁷ led only to the recovery of starting material. The control experiments of **1a** with hexachloroantimonic acid (HSbCl₆) or with hydrogen chloride did not afford **3a**. This rules out the possibility of a Brønsted acid-catalysed reaction for the above transformation. Further, the photo-induced electron transfer (PET) reaction⁸ of **1a** with dicyanoanthracene in MeCN using a Pyrex filter proved to be unsuccessful. In view of the above observations as well as on the basis of direct EPR evidence‡ we believe the observed Claisen rearrangement occurs through the intermediacy of a cation radical.

Other aryl allenylmethyl ethers, **1b–1e** also underwent the title rearrangement with ease (Table 1). *p*-Methoxyphenyl allyl ether is found to be inactive in the presence of the aminium salt, **2**. The reason can be attributed to the inability of the latter to bring about an electron-transfer owing to its unfavourable oxidation potential.§

The facile nature of the reaction under ambient conditions coupled with the easy accessibility of aryl allenylmethyl ethers render this SET induced process an attractive one for the preparation of 2-(2-hydroxyaryl)buta-1,3-dienes which are potential synthons in Diels–Alder reactions.⁹ Moreover, these reactions appear to represent the first example of cation radical induced Claisen rearrangement though the rearrangement has been well studied under catalytic,^{4c} photochemical,^{4d,4f} mass spectral^{4g} and microwave irradiation^{4g,4h} conditions. The rearranged products in the present investigation were characterized thoroughly by ¹H and ¹³C NMR, IR and HRMS and also by comparison with authentic samples prepared *via* the classical thermal reaction.¶

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Scheme 1

Table 1 Claisen rearrangement of aryl allenylmethyl ethers with the aminium salt^a

Compound No.	R ¹	R ³	R ⁴	Yield ^b (%) of 3
1a	H	OMe	H	55
1b	OMe	H	H	60
1c	OMe	Me	H	65
1d	H	OEt	H	60
1e	H	CH=CH–CH=CH	H	58

^a R² = H. ^b Isolated yield of the product with respect to the reacted starting material.

Footnotes

† Use of the aminium salt less than 0.5 mmol resulted in a slow reaction and lower yield of the product.

‡ After the addition of the aminium salt to **1a** in dry MeCN, the EPR spectra recorded immediately showed two signals—one signal (*g* 1.00215) for the cation radical of the aminium salt (which slowly disappeared with time) and another for that of the allenylmethyl ether **1a** (*g* 2.00335) the intensity of which reaches a maximum after 5 min. In a separate experiment it was observed that the signal due to **3a**⁺ also appears in the same region as that of **1a**⁺.

§ The oxidation potentials of tris(4-bromophenyl)amine, *p*-methoxyphenyl allenylmethyl ether and *p*-methoxyphenyl allyl ether were found to be 0.85, 1.30 and 1.55 V vs. silver quasi-reference electrode, respectively, as observed in cyclic voltammetry at 0.100 V s⁻¹ sweep rate on a platinum micro-electrode in MeCN at room temp.

¶ The spectroscopic data for **3a** are as follows: IR (CHCl₃) ν /cm⁻¹: 3540, 2960, 1610, 1590, 1480, 1220. ¹H NMR (400 MHz, CDCl₃/TMS): 3.76 (s, 3H, OCH₃), 4.9 (bs, exchangeable with D₂O, 1H,

OH), 5.05–5.10 (d, *J* 18 Hz, 1H), 5.24–5.28 (d, *J* 11 Hz, 1H), 5.29 (s, 1H), 5.53 (s, 1H), 6.58–6.60 (dd, *J* 18, *J* 11 Hz, 1H), 6.81–6.9 (m, 3H, aromatic). ¹³C NMR (100.5 MHz CDCl₃): δ 55.753 (q), 114.784 (d), 115.179 (d), 116.302 (d), 118.503 (t), 120.719 (t), 125.834 (s), 137.219 (d), 143.973 (s), 146.584 (s), 153.232 (s). HRMS: *m/z* 176.0833 (calc. C₁₁H₁₂O₆ 176.0837).

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