

A Novel and Convenient Mercury(II) Mediated Synthesis of Chroman-4-ones

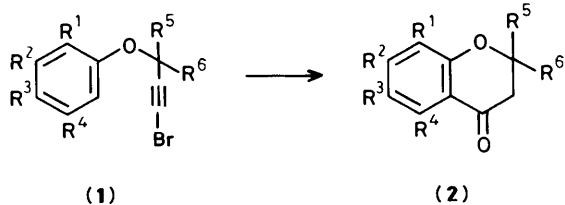
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A simple route to chroman-4-ones from γ -bromopropynyl aryl ethers (**1**) using mercury(II) trifluoroacetate as a catalyst is described.

Benzopyran compounds are widespread in a variety of forms and have interesting properties,¹ e.g. psychotropic constituents (tetrahydrocannabinol), and insecticidal: ageratochromene (Precocene), phytoalexins (pterocarpan), etc. The synthesis of chroman-4-ones,² the synthetic intermediate for this class of compounds, has therefore been the subject of intensive study.³ Most of the existing methodologies for the synthesis of chroman-4-ones involve the cyclisation of aryloxypropionic acids, nitriles, or chlorides, reduction of chromones, or cyclisation of *o*-hydroxychalcones. Herein we report a novel and simple one pot route to chroman-4-ones in high yields, starting from γ -bromoprop-2-ynyl aryl ethers which are easily prepared⁴ in quantitative yield from aryl propynyl ethers.

Refluxing the ether (**1a**) with mercury(II) trifluoroacetate (1 equiv.) in trifluoroacetic acid for 4 h (method 1) afforded directly the chroman-4-one (**2a**)[†] in 62% yield (Scheme 1). The reaction was found to be suitable for synthesis of variously substituted chroman-4-ones (**2a-f**)[‡] in 60–70% yield (see

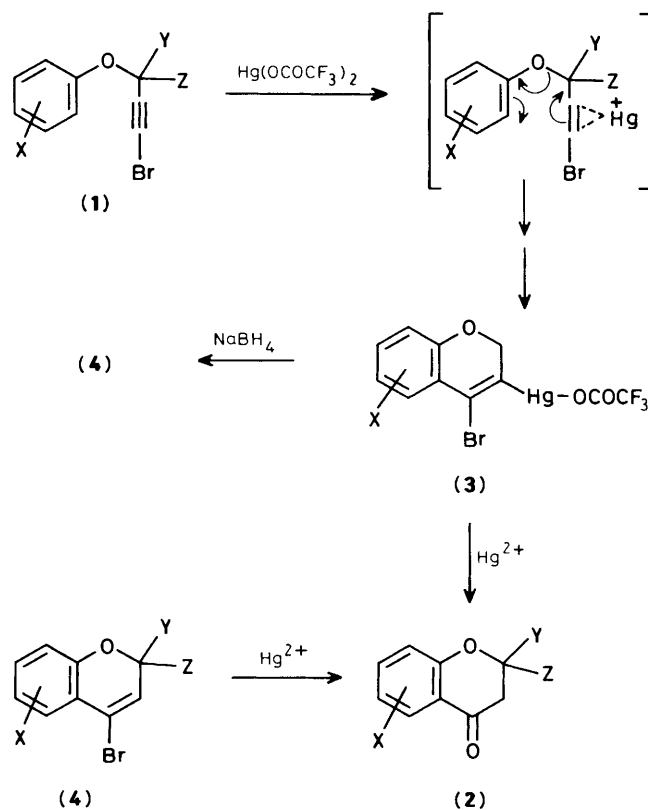


Scheme 1

[†] Structural assignments were based on the combination of physical properties and spectral data of authentic samples.

[‡] The starting material was recovered under the different conditions employed in the case of γ -bromopropynyl *p*-nitro and *p*-acetyl phenyl ethers (**1m**) and (**1n**).

Table 1). To our surprise, when the same methodology was adopted for naphthyl systems (**1**; entries g–j in Table 1), good yields of ketones were obtained even under mild conditions. Thus, treatment of the β -naphthyl ether (**1g**) with mercury(II)



Scheme 2

Table 1.

Entry	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	Method	Yield of (2)
								%
a	H	H	Cl	H	H	H	1	62
b	H	H	H	H	H	H	1	60
c	H	H	Me	H	H	H	1	65
d	H	H	OMe	H	H	H	1	70
e	H	H	Cl	H	Me	H	1	60
f	H	H	OMe	H	Me	H	1	55
g	H	H	-CH=CH-CH=CH-	H	H	H	2	82
h	-CH=CH-CH=CH-	H	H	H	H	H	2	80
i	H	H	-CH=C-CH=CH-	H	H	H	2	88
j	H	H	-CH=CH-CH=CH-	Br	Me	H	2	70
k	H	H	Cl	H	Me	Me	3	40
l	H	H	OMe	H	Me	Me	3	50
m	H	H	NO ₂	H	H	H	1	No reaction
n	H	H	COMe	H	H	H	1	No reaction

trifluoroacetate (1 equiv.) in dichloromethane at room temperature for 6 h (method 2) afforded directly the 2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1-one (**2g**) in 82% yield. When extended to other substituted cases (**2i** and **2j**), this method also gave rise to the respective ketones (**2i** and **2j**) in good yields. Likewise, the α -naphthyl ether (**1h**) was converted to the chromanone (**2h**) in 80% yield.

However, in the case of α,α -dimethyl derivatives, viz. (**1k**) and (**1l**), under the conditions of method 1, significant cleavage of the ether was observed. This was overcome by carrying out the reaction in two steps (method 3). In these cases the benzopyrans (**4**) were isolated by treating the respective ethers with mercury(II) trifluoroacetate (1 equiv.) in dichloromethane at room temperature followed by alkaline sodium borohydride work-up. Refluxing (**4**) in trifluoroacetic acid with a further equivalent of mercury(II) trifluoroacetate afforded the chromanones (**2k**) and (**2l**). The modest yields obtained in these cases were compensated by the economy of the operations.

Our observations are explicable in terms of an initial mercury(II) ion catalysed 3,3-sigmatropic rearrangement⁵ followed by oxymercuration of the resulting benzopyran derivatives[§] (**3**) or (**4**) leading to chroman-4-ones (Scheme 2). We are currently investigating the scope and application of this

reaction for the synthesis of flavanones and spirochromanones, and also thiochromanones and 4-quinolones.

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References

- G. P. Ellis, 'Chromenes, Chromanones and Chromones,' Wiley, New York, 1977; G. P. Ellis and I. M. Lockhart, 'Chromans and Tocopherols,' Wiley, New York, 1981; J. D. Hepworth, in 'Comprehensive Heterocyclic Chemistry,' eds. A. R. Katritzky, C. W. Rees, A. J. Boulton, and A. McKillop, Pergamon Press, Oxford, 1984, vol. 3; B. Loubinoux, J. L. Collin, and B. A. Colin, *Tetrahedron*, 1987, **43**, 93.
- H. J. Kobbe and A. Widdig, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 247.
- S. T. Saengachantara and T. W. Wallace, *J. Chem. Soc., Chem. Commun.*, 1986, 1592; P. J. Cremins and T. W. Wallace, *ibid.*, 1986, 1602.
- L. Brandsma, 'Preparative Acetylenic Chemistry,' Elsevier, New York, 1971.
- R. P. Lutz, *Chem. Rev.*, 1984, **84**, 205; R. C. Larock and L. W. Harrison, *J. Am. Chem. Soc.*, 1984, **106**, 4218; D. K. Bates and M. C. Jones, *J. Org. Chem.*, 1984, **43**, 3856, and references cited therein; G. V. Bindu Madhavan and K. K. Balasubramanian, *Tetrahedron*, 1985, **41**, 111.

§ The intermediate mercurials (**3**) were isolated and characterised.