SHORT PAPER

J. Chem. Research (S), 2001, 538–539

Studies in sigmatropic rearrangement: thermal rearrangement of 3-(4′-aryloxybut-2-ynyloxy)thiochromen-4-ones[†]

Krishna C. Majumdar* and Brindaban Roy

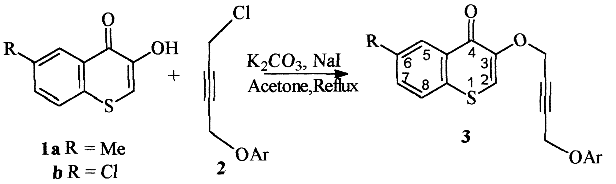
Department of Chemistry, University of Kalyani, Kalyani, 741 235, W. B., India

Reaction of 3-hydroxythiochromen-4-ones **1a,b** with appropriate1-aryloxy-4-chlorobut-2-ynes **2a–f** furnished 3-(4′-aryloxybut-2-ynyloxy)thiochromenones **3a–g** in 80–90% yields. Substrates **3a–g** on refluxing in chlorobenzene for 8–10 h gave 3-aryloxymethyl-2-methylfuro[3,2-*b*]-thiochromen-9-ones in 90–95% yields.

Keywords: Claisen rearrangement, 3-hydroxythiochromen-4-one, 1,4-dichlorobut-2-yne, [3,3] sigmatropic rearrangement, sulfur heterocycle

The thieno[2,3-*b*]thiochromen-4-one system is an intermediate for the synthesis of a series of drugs[1] used against psychotic disturbances. Recently we have reported[2] a simple synthesis for this heterocyclic system. In view of the importance of this system we became interested in modifying the structure of the system by altering ring fusion, the substituents and also replacing the thiophene ring by a furan ring. Interesting results of our recent work[3] on the sigmatropic rearrangement of aryloxybut-2-ynyl ethers of various heterocyclic systems prompted us to undertake a study on the thermal rearrangement of 3-(4′-aryloxybut-2-ynyloxy) thiochromen-4-ones **3a–g**. We report the results of this investigation.

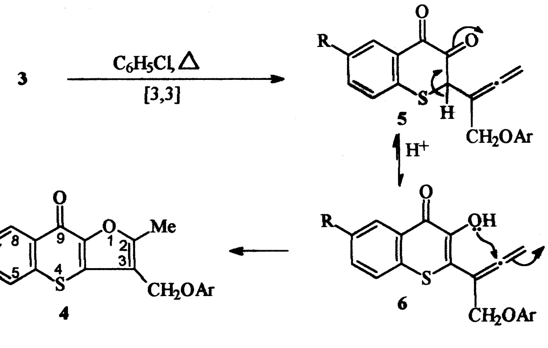
The starting materials, 3-(4′-aryloxybut-2-ynyloxy) thiochromen-4-ones **3a–g** were prepared in 80-90% yields by the reaction of 3-hydroxythiochromen-4-ones[4] **1** and 1-aryloxy-4-chlorobut-2-ynes[5] in refluxing acetone in the presence of anhydrous potassium carbonate and a catalytic amount of sodium iodide (Finkelstein condition, Scheme 1).



	R	OAr
a	Me	4-OMeC_6H_4
b	Me	2-MeC_6H_4
c	Me	4-MeC_6H_4
d	Me	C_6H_5
e	Me	4-ClC_6H_4
f	Me	2-ClC_6H_4
g	Cl	2-ClC_6H_4

Scheme 1

The substrates **3** contain an arylpropargyl ether moiety as well as a propargylvinyl ether moiety. They are prone to [3,3] sigmatropic rearrangement on either part of the molecules. Usually the rearrangement of propargylvinyl ether[6] is more facile than that of the arylpropargyl ether[7] as the latter involves the disruption of aromaticity in the transition state. Substrate **3a** was subjected to thermal rearrangement at a relatively low temperature by refluxing in chlorobenzene (132°C). Monitoring by TLC indicated slow change of the starting material producing a new product. The reaction needed 10 h for the starting material to disappear giving 95% yield of product **4a**. The reaction was then conducted in refluxing *o*-dichlorobenzene (179°C) and as expected the reaction was complete in a much shorter time (30 min). Product **4a** was characterised as 2,7-dimethyl-3-(*p*-methoxyphenylmethyl)furo[3,2-*b*]thiochromen-9-one from its elemental analysis and spectral data. Other substrates **3b–g** were similarly treated to give products **4b–g** in 90-93% yields (**Scheme 2**). Formation of **4** from **3** is explicable[8] by the occurrence of a [3,3] shift in **3** to give **5** and rapid enolization may give **6** which may then undergo a 5-‘exo’ cyclisation to give **4**.



Scheme 2

This result is somewhat different from our earlier observation where we have reported the exclusive formation[2b] of 2*H*-thiopyrano[2,3-*b*]thiochromen-5-ones (**10**) from the thermal [3,3] sigmatropic rearrangement of a number of 2-(4′-aryloxybut-2-ynylthio)thiochromen-4-ones (**9**).

The methodology described here is simple and efficient for the synthesis of furo[3,2-*b*]thiochromen-9-one derivatives.

Experimental

Techniques used : UV absorption spectra were recorded on a Hitachi 200-20 Spectrophotometer for solutions in absolute alcohol. IR spectra were recorded in KBr on a Perkin-Elmer 1330 apparatus. 1H-NMR spectra were recorded for solutions in deuteriochloroform with TMS as an internal standard on a Bruker (300 MHz) instrument. Elemental analyses were recorded on a LECO CHNS-932 instrument and recording of mass spectra were carried out at RSIC (CDRI), Lucknow.

General procedure for the synthesis of 3-(4′-aryloxybut-2-ynyloxy)thiochromen-4-ones **3a–g:** A mixture of 3-hydroxythiochromenones **1** (2.25 mmol) and 4-aryloxybut-2-ynyl chlorides **2** (2.50 mmol) in dry acetone (50 ml) was refluxed in presence of anhydrous K_2CO_3 (2 g) and a catalytic amount of NaI for 4–5 h. The solvent was evaporated, the residual mass was extracted with $CHCl_3$ (3×25 ml) and dried over anhydrous Na_2SO_4. Chloroform was

---

* To receive any correspondence. E-mail: kcm@klyuniv.ernet.in

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

distilled off and the residue was then column chromatographed over silica gel. The products 3-(4′-aryloxybut-2-ynyloxy)thiochromenones **3** were eluted with ethyl acetate-benzene (1:9). Compounds **3a–g** were recrystallised from chloroform-petroleum ether.

Compound **3a.** Yield 90%; m.p. 82°C; λ_{max}/nm 223, 258 and 356; $\nu_{max.}$/cm^{-1} 3050, 2910, 1585 and 1445; δ_H : 8.40 (d, 1H,*J* 1.83, C_5-**H**), 7.51 (d, 1H,*J* 8.26, C_8-**H**), 7.43 (dd, 1H,*J* 8.26,1.83, C_7-**H**), 7.17 (s, 1H, C_2-**H**), 6.76–6.88 (m, 4H, Ar-**H**), 4.85 (t, 2H,*J* 1.65, C_3-OC**H**$_2$), 4.66 (t, 2H,*J* 1.65, ArOC**H**$_2$), 3.73 (s, 3H, ArOC**H**$_3$) and 2.49 (s, 3H, C_6-C**H**$_3$); *m*/*z* (366M$^+$); (Found: C, 68.67; H, 4.87. $C_{21}H_{18}O_4S$ requires C, 68.85; H, 4.92%). *Compound* **3b**. Yield 87%; m.p. 114°C; λ_{max}/nm 218, 258 and 356; $\nu_{max.}$/cm^{-1} 3020, 2900, 1590, 1430, 1350 and 1250; δ_H : 8.41 (s, 1H, C_5-**H**), 7.52 (d, 1H,J 8.28, C_8-**H**), 7.43 (d, 1H,J 8.3, C_7-**H**), 7.18 (s, 1H, C_2-**H**), 7.07-7.14 (m, 2H, Ar-**H**), 6.85–6.89 (m, 2H, Ar-**H**), 4.86 (t, 2H,*J* 1.34, C_3-OC**H**$_2$), 4.74 (t, 2H,*J* 1.48, ArOC**H**$_2$), 2.49 (s, 3H, C_6-C**H**$_3$) and 2.21 (s, 3H, Ar-C**H**$_3$); *m*/*z* (350M$^+$); (Found: C, 72.15; H, 5.07. $C_{21}H_{18}O_3S$ requires C, 72.00; H, 5.14%). *Compound* **3c.** Yield 86%; m.p. 86°C; λ_{max}/nm 221, 258 and 356; $\nu_{max.}$/cm^{-1} 3030, 2900, 1590, 1500, 1440, 1350 and 1235; δ_H: 8.40 (d, 1H,*J* 1.44, C_5-**H**), 7.51 (d, 1H,*J* 8.25, C_8-**H**), 7.42 (dd, 1H,*J* 8.21, 1.44, C_7-**H**), 7.17 (s, 1H, C_2-**H**), 7.03 (d, 2H,*J* 8.23, Ar-**H**), 6.80 (d, 2H,*J* 8.25, Ar-**H**), 4.85 (t, 2H,J 1.62, C_3-OC**H**$_2$), 4.69 (t, 2H,*J* 1.62, ArOC**H**$_2$), 2.49 (s, 3H, C_6-C**H**$_3$) and 2.26 (s, 3H, Ar-C**H**$_3$); *m*/*z* (350M$^+$); (Found: C, 71.87; H, 5.23. $C_{21}H_{18}O_3S$ requires C, 72.00; H, 5.14%). *Compound* **3d.** Yield 84%; m.p. 88°C; λ_{max}/nm 218, 258 and 356; $\nu_{max.}$/cm^{-1} 3025, 2900, 1590, 1435, 1350 and 1240; δ_H : 8.40 (s, 1H, C_5-**H**), 7.52 (d, 1H,*J* 8.25, C_8-*H*), 7.44 (d, 1H,J 8.25, C_7-**H**), 7.18 (s, 1H, C_2-**H**), 6.91–7.01 (m, 5H, Ar-**H**), 4.86 (t, 2H,*J* 1.61, C_3-OC**H**$_2$), 4.72 (t, 2H,*J* 1.61, ArOC**H**$_2$) and 2.49 (s, 3H, C_6-C**H**$_3$); *m*/*z* (336M$^+$); (Found: C, 71.62; H, 4.67. $C_{20}H_{16}O_3S$ requires C, 71.43; H, 4.76%). *Compound* **3e.** Yield 82%; m.p. 130°C; λ_{max}/nm 225, 258 and 356; $\nu_{max.}$/cm^{-1} 3030, 2920, 1595, 1470, 1440, 1340 and 1240; δ_H: 8.40 (d, 1H,*J* 1.75, C_5-*H*), 7.52 (d, 1H,*J* 8.25, C_8-**H**), 7.44 (dd,1H,*J* 8.25,1.75, C_7-**H**), 7.17 (s, 1H, C_2-**H**), 7.14 (m, 2H, Ar-*H*), 6.83 (m, 2H, Ar-**H**), 4.87 (t, 2H,J 1.65, C_3-OC**H**$_2$), 4.68 (t, 2H,*J* 1.65, ArOC**H**2) and 2.49 (s, 3H, C_6-C**H**$_3$); *m*/*z* (370, 372M$^+$); (Found: C, 64.57; H, 4.15.$C_{20}H_{15}O_3SCl$ requires C, 64.78; H, 4.09%). *Compound* **3f.** Yield 80%; m.p. 105°C; λ_{max}/nm 219, 256 and 356; $\nu_{max.}$/cm^{-1} 3030, 2930, 1590, 1460, 1350 and 1235; δ_H: 8.41 (d, 1H,*J* 1.70, C_5-**H**), 7.52 (d, 1H,J 8.26, C_8-**H**), 7.43 (dd, 1H,*J* 8.26, 1.70, C_7-**H**), 7.17 (s, 1H, C_2-**H**), 6.89–7.12 (m, 4H, Ar-**H**), 4.88 (t, 2H,*J* 1.63, C_3-OC**H**$_2$), 4.69 (t, 2H,*J* 1.63, ArOC**H**$_2$) and 2.49 (s, 3H, C_6-C**H**$_3$); *m*/*z* (370, 372M$^+$); (Found: C, 64.63; H, 4.21.$C_{20}H_{15}O_3SCl$ requires C, 64.78; H, 4.09%). *Compound* **3g.** Yield 85%; m.p. 162°C; λ_{max}/nm 225, 273 and 355; $\nu_{max.}$/cm^{-1} 3035, 2930, 1590, 1460, 1400, 1350 and 1235; δ_H: 8.58 (s, 1H, C_5-**H**), 6.57–7.57 (m, 7H, C_8-**H**, C_7-**H**, C_2-**H**, Ar-**H**), 4.87 (s, 2H, C_3-OC**H**$_2$) and 4.81 (s, 2H, ArOC**H**$_2$); *m*/*z* (390, 392, 394M$^+$); (Found: C, 58.41; H, 3.15.$C_{19}H_{12}O_3SCl_2$ requires C, 58.31; H, 3.07%).

Thermal rearrangement of compounds **3a–g** to obtain compounds **4a–g.** Compounds **3** (1 mmol) in *o*-dichlorobenzene (3 ml) were refluxed for 30 mins. Then the reaction mixture was column chromatographed on silica gel. The products 3-aryloxymethyl-2-methylfuro[3,2-*b*]thiochromen-9-ones **4** were eluted with ethyl acetate-benzene (1:3). Compounds **4** were recrystallised from chloroform.

Compound **4a:** Yield 95%; m.p. 160°C; λ_{max}/nm 226, 269, 302 and 353; $\nu_{max.}$/cm^{-1} 3020, 2900, 1595, 1500, 1450 and 1220; δ_H: 8.54 (d, 1H,J 1.9, C_8-**H**), 7.58 (d, 1H,J 8.26, C_5-**H**), 7.44 (dd, 1H,*J* 8.26,1.9, C_6-**H**), 6.92–6.97 (m, 2H, Ar-**H**), 6.84–6.88 (m, 2H, Ar-**H**), 4.99 (s, 2H, ArOC**H**$_2$), 3.78 (s, 3H, OC**H**$_3$), 2.54 (s, 3H, C_2-C**H**$_3$) and 2.50 (s,3H, C_7-C**H**$_3$); *m*/*z* (366M$^+$); (Found: C, 68.73; H, 4.98. $C_{21}H_{18}O_4S$ requires C, 68.85; H, 4.92%). *Compound* **4b:** Yield 92%; m.p. 192°C; λ_{max}/nm 224, 269, 305 and 353; $\nu_{max.}$/cm^{-1} 3030, 2900, 1590, 1450 and 1240; δ_H: 8.54 (d, 1H,*J* 1.96, C_8-**H**), 7.58 (d, 1H,*J* 8.25, C_5-**H**), 7.44 (dd, 1H,*J* 8.28,1.96, C_6-**H**), 7.17–7.22 (m, 2H, Ar-**H**), 6.91–6.96 (m, 2H, Ar-**H**), 5.05 (s, 2H, ArOC**H**$_2$), 2.57 (s, 3H, C_2-C**H**$_3$), 2.51 (s, 3H, C_7-C**H**$_3$) and 2.28 (s, 3H, Ar-C**H**$_3$); *m*/*z* (350M$^+$); (Found: C, 72.15; H, 5.23. $C_{21}H_{18}O_3S$ requires C, 72.00; H, 5.14%). *Compound* **4c:** Yield 90%; m.p. 160°C; λ_{max}/nm 225, 270, 303 and 353; $\nu_{max.}$/cm^{-1} 3020, 2900, 1590, 1500, 1440 and 1230; δ_H: 8.54 (d, 1H,*J* 1.98, C_8-**H**), 7.58 (d, 1H,*J* 8.23, C_5-**H**), 7.43 (dd, 1H,*J* 8.49,1.98, C_6-**H**), 7.12 (d, 2H,*J* 8.18, Ar-**H**), 6.88–6.93 (m, 2H, Ar-**H**), 5.02 (s, 2H, ArOC**H**$_2$), 2.57 (s, 3H, C_2-C**H**$_3$), 2.51 (s, 3H, C_7-C**H**$_3$) and 2.31 (s, 3H, Ar-C**H**$_3$); *m*/*z* (350M$^+$); (Found: C, 72.09; H, 5.25. $C_{21}H_{18}O_3S$ requires C, 72.00; H, 5.14%). *Compound* **4d:** Yield 90%; m.p. 170°C; λ_{max}/nm 220, 269, 304 and 353; $\nu_{max.}$/cm^{-1} 3030, 2900, 1590, 1440 and 1235; δ_H: 8.54 (s, 1H, C_8-**H**), 7.58 (d, 1H,*J* 8.21, C_5-**H**), 7.45 (d, 1H,*J* 1.52, C_6-**H**), 7.31–7.36 (m, 2H, Ar-**H**), 7.00–7.03 (m, 3H, Ar-**H**), 5.05 (s, 2H, ArOC**H**$_2$), 2.57 (s, 3H, C_2-C**H**$_3$), and 2.51 (s, 3H, C_7-C**H**$_3$); *m*/*z* (336M$^+$); (Found: C, 71.60; H, 4.66. $C_{20}H_{16}O_3S$ requires C, 71.43; H, 4.76%). *Compound* **4e:** Yield 88%; m.p. 205°C; λ_{max}/nm 228, 269, 305 and 353; $\nu_{max.}$/cm-1 3050, 2900, 1595, 1490, 1450 and 1240; δ_H: 8.54 (d, 1H,*J* 1.91, C_8-**H**), 7.58 (d, 1H,*J* 8.23, C_5-**H**), 7.44 (dd, 1H,*J* 8.29,1.91, C_6-**H**), 7.28 (dd, 2H, *J* 6.82,2.05, Ar-**H**), 6.94 (dd, 6.82, 2.05 2H, Ar-**H**), 5.02 (s, 2H, ArOC**H**$_2$), 2.56 (s, 3H, C_2-C**H**$_3$) and 2.51 (s, 3H, C_7-C**H**$_3$); *m*/*z* (370, 372M$^+$); (Found: C, 64.53; H, 4.25. $C_{20}H_{15}O_3SCl$ requires C, 64.78; H, 4.09%). *Compound* **4f:** Yield 90%; m.p. 185°C; λ_{max}/nm 222, 270, 305 and 356; $\nu_{max.}$/cm^{-1} 3030, 2920, 1590, 1480 and 1245; δ_H: 8.54 (s, 1H, C_8-**H**), 7.60 (d, 1H,*J* 8.21, C_5-**H**), 7.45 (m, 2H, C_6-**H**, Ar-**H**), 7.24–7.26 (m, 1H, Ar-**H**), 6.98–7.03 (m, 2H, Ar-**H**), 5.11 (s, 2H, ArOC**H**$_2$), 2.57 (s, 3H, C_2-C**H**$_3$) and 2.51 (s, 3H, C_7-C**H**$_3$); *m*/*z* (370, 372M$^+$); (Found: C, 64.64; H, 4.25. $C_{20}H_{15}O_3SCl$ requires C, 64.78; H, 4.09%). *Compound* **4g:** Yield 94%; m.p. 238°C; λ_{max}/nm 219, 273, 307 and 355; $\nu_{max.}$/cm^{-1} 3040, 2920, 1590, 1500, 1480 and 1245; δ_H: 8.70 (d, 1H, *J* 2.5, C_8-**H**), 6.57–7.68 (m, 6H, C_5-**H**, C_6-**H**, Ar-**H**), 5.10 (s, 2H, ArOC**H**$_2$) and 2.59 (s, 3H, C_2-C**H**$_3$); *m*/*z* (390, 392, 394M$^+$); (Found: C, 58.64; H, 4.25. $C_{19}H_{12}O_3SCl_2$ requires C, 58.31; H, 3.07%).

We thank the CSIR (New Delhi) for financial assistance.

Received 18 January 2001; accepted 9 September 2001
Paper 01/707

References:

1 P. Vink, *Neth Appl*, April 9, 1965, 6, 411, 477 (Cl, C 07d), *Swiss Appl*, Oct 8, 1963 and July 29, 1964, 7pp, *Chem Abstr* No. 13265.

2 (a) K.C. Majumdar, A.T. Khan and S. Saha, *Syn. Lett.*, 1991, 595; (b) K.C. Majumdar, A.T. Khan and S. Saha, *Synth. Commun.*, 1992, **22**, 901; (c) K.C. Majumdar, S. Saha and A.T. Khan, *Ind. J. Chem.*, 1994, **33**, 216.

3 (a) K.C. Majumdar, U. Das and N.K. Jana, *J. Org. Chem.*, 1998, **63**, 3550; (b) K.C. Majumdar and U. Das, *Synth. Commun.*, 1997, **27**, 4013; (c) K.C. Majumdar and U. Das, *J. Org. Chem.*, 1998, **63**, 9997; (d) K.C. Majumdar and G.H. Jana, *J. Org. Chem.*, 1997, **62**, 1506; (e) K.C. Majumdar and P. Biswas, *Heterocycles*, 1999, **50**, 1227.

4 E. Bernd and S. Herbert, *Chem. Ber.*, 1963, **96**, 1234.

5 (a) K.C. Majumdar and B.S. Thyagaragan, *Int. J. Sulfur. Chem.*, 1972, **2A**, 93; (b) K.C. Majumdar and B.S. Thyagaragan, *Int. J. Sulfur. Chem.*, 1972, **2A**, 153; (c) J. Hillard, R.V. Reddy, K.C. Majumdar and B.S. Thyagaragan, *J. Heterocyclic Chem.*, 1974, **11**, 369.

6 (a) L. Claisen, *Ber*, 1912, **45**, 3157; (b) K.C. Majumdar, A.T. Khan and R.N. De, *Synth. Commun.*, 1988, **18**, 1589.

7 (a) J. Zsindely and H. Schmidt, *Helv. Chim. Acta.*, 1968, **51**, 1510; (b) K.C. Majumdar, B.S. Thyagaragan and K.K. Balasubramanian, *J. Heterocyclic Chem.*, 1973, **10**, 159; (c) I. Iwai and J. Ide, *Chem. Pharm. Bull. (Japan)*, 1962, **10**, 926.

8 (a) K.C. Majumdar, R.N. De, A.T. Khan, S.K. Chattopadhyay, K. Dey and A. Patra, *J. Chem. Soc. Chem. Commu.*, 1988, 777; (b) K.C. Majumdar and R.N. De, *J. Chem. Soc. Perkin Trans. 1*, 1989, 1901; (c) N. Sarcevic, J. Zsirdely and H. Schmid, *Helv. Chim. Acta.*,1973, *56*, 1467.