Pergamon

Tetrahedron Letters 43 (2002) 2123–2125

TETRAHEDRON LETTERS

Studies on sulfoxide rearrangements: regioselective synthesis of 3-(aryloxyacetyl)-2,3-dihydrothieno[3,2-*c*][1]benzopyran-4-ones

K. C. Majumdar* and S. K. Ghosh

Department of Chemistry, University of Kalyani, Kalyani 741235, West Bengal, India

Received 19 November 2001; accepted 24 January 2002

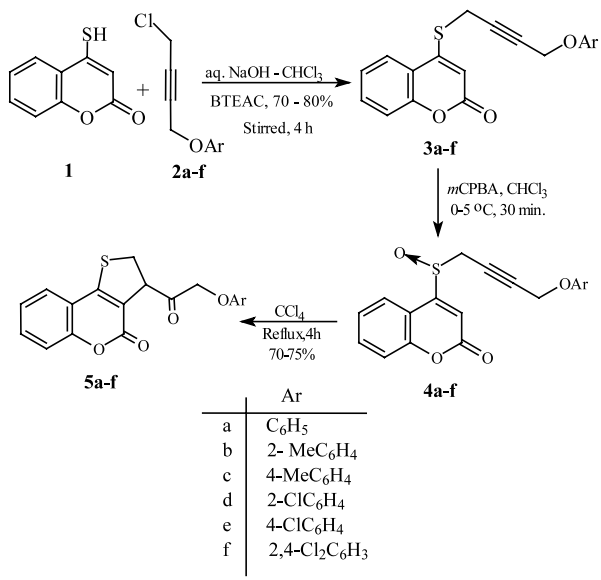
Abstract—Hitherto unreported 3-(aryloxyacetyl)-2,3-dihydrothieno[3,2-*c*][1] benzopyran-4-ones **5a**–**f** were synthesised in 70–75% yields by the application of the sulfoxide rearrangement of 4-(4-aryloxybut-2-ynylthio)[1]benzopyran-2-ones **4a**–**f**. The substrates **4a**–**f** were synthesised by phase-transfer-catalysed alkylation of previously unreported 4-mercaptocoumarin.

Some thienocoumarins are known to possess anti-inflammatory, antipyretic and antiallergic properties.[1] The construction of the five-membered heterocyclic rings in benzo(*b*)thiophenes and indoles through sulfoxide[2–5] and amine oxide[6–8] rearrangements, respectively, was reported by Majumdar and Thyagarajan. This protocol when applied to selenium analogues[9] proceeded with different results. Application of the amine oxide rearrangement[10–12] in heterocyclic substrates[13,14] for the synthesis of a number of tricyclic skeletons has been reported from this laboratory. Whilst amine oxides rearrange in dichloromethane at room temperature, the corresponding sulfoxides require refluxing in carbon tetrachloride. Both the amine oxide and sulfoxide rearrangement involve the intermediacy of a [2,3] and a [3,3] sigmatropic rearrangement. Very recently Majumdar et al. reported the regioselective synthesis of thieno[2,3-*f*]quinolin-7(6*H*)-one and pyrano[3,2-*f*]benzo-[b]thiophene derivatives[15,16] by the application of sulfoxide rearrangements.

This exceedingly facile and simple reaction for the construction of five-membered heterocyclic rings motivated us to undertake a study to synthesise heterocyclic compounds from 4-(4-aryloxybut-2-ynylthio)[1]benzopyran-2-ones **3a**–**f** for the synthesis of new heterocyclic compounds. We now report our results.

The substrates 4-(4-aryloxybut-2-ynylthio)[1]benzopyran-2-ones **3a**–**f** for this study were prepared by phase-transfer catalysed alkylation of 4-mercaptocoumarin **1** with 1-chloro-4-aryloxy-but-2-yne **2a**–**f** using benzyltriethyl ammonium chloride (BTEAC) in aqueous NaOH and chloroform. The PTC alkylation is faster and gives a higher yield of the *S*-alkylated products (**3a**–**f**, 70–80%) over the classical alkylation using K_2CO_3 and acetone. Classical alkylation in the case of **3e** gave a 55% yield but in other cases a tendency to decompose was observed (Scheme 1).

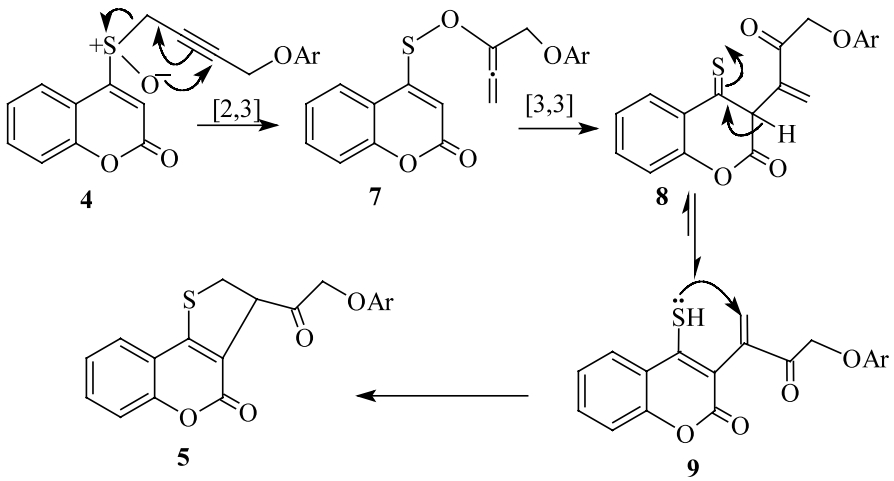
Compounds **3a**–**f** are all solids and were characterised from their elemental analyses and spectroscopic data.[17]



Scheme 1.

* Corresponding author. Fax: 0091-33-5828282; e-mail: kcm@klyuniv.ernet.in

0040-4039/02/$ - see front matter
PII: S0040-4039(02)00200-9



Scheme 2.

The sulphides **3a–f** were oxidised to the corresponding sulfoxides **4a–f** by slow addition of 1 equiv. of *m*-chloroperoxybenzoic acid in chloroform at 0–5°C over 30 min. The formation of a new product was indicated by a single spot (TLC monitoring) and by the disappearance of the starting sulphide (Scheme 1).

The sulfoxides **4a–f** are quite unstable. They rearrange even during work up of the reaction mixture. Therefore, no attempt was made to characterise them. They were directly subjected to thermal rearrangement without further purification. The sulfoxide **4a** was refluxed in carbon tetrachloride to give the compound **5a** in 70% yield (Scheme 1). Compound **5a** was characterised from its elemental analysis and spectroscopic data.[18]

To test the generality of the reaction five other substrates **4b–f** were subjected to sulfoxide rearrangement under the same reaction conditions. All the substrates gave similar products **5b–f** in 70–75% yields. In the ^{1}H NMR spectra of **5a–f** except for **5d**, one of the -S-C**H**$_2$- protons appeared as triplet. However, in the ^{1}H NMR spectrum of **5d** these two protons appeared as two double doublets.

The formation of products **5a–f** from the sulfoxides **4a–f** may be rationalised by an initial [2,3] sigmatropic rearrangement of the sulfoxides **4** to give the intermediate allenylsulphenates **7** followed by a [3,3] sigmatropic rearragement and enolisation leading to the intermediates **9** containing an enone moiety favourably juxtaposed to a -SH function for an internal Michael addition of the thiol to the enone to yield **5a–f** (Scheme 2).

This method is found to be general for the synthesis of 3 - (aryloxyacetyl) - 2,3 - dihydrothieno[3,2 - *c*][1]benzopyran-4-ones (**5a–f)** in good yields. This is also an example of the application of a sulfoxide rearrangement in heterocyclic substrates to furnish polyheterocycles.

Acknowledgements

We are thankful to CSIR (New Delhi) for financial assistance. One of us (S.K.G) is grateful to CSIR for a fellowship.

References

1. Makisumi, Y. *Jpn Kokai*, 73, 00,597 (cl. 16E622), 1972; *Chem. Abstr*. **1973**, *78*, 72097.
2. Thyagarajan, B. S.; Majumdar, K. C. *J. Chem. Soc., Chem. Commun*. **1972**, 83.
3. Majumdar, K. C.; Thyagarajan, B. S. *Int. J. Sulfur Chem*. **1972**, *2A*, 93.
4. Majumdar, K. C.; Thyagarajan, B. S. *Int. J. Sulfur Chem*. **1972**, *2A*, 67.
5. El-Osta, B.; Majumdar, K. C.; Thyagarajan, B. S. *J. Heterocyclic Chem*. **1973**, *10*, 107.
6. Hillard, J. B.; Thyagarajan, B. S.; Reddy, K. V.; Majumdar, K. C. *Tetrahedron Lett*. **1974**, 1999.
7. Hillard, J. B.; Reddy, K. V.; Majumdar, K. C.; Thyaragajan, B. S. *J. Heterocyclic Chem*. **1974**, *11*, 369.
8. Thyagarajan, B. S.; Majumdar, K. C. *J. Heterocyclic Chem*. **1975**, *12*, 43.
9. Reich, H. J.; Shah, S. K. *J. Am. Chem. Soc*. **1977**, *99*, 263.
10. Majumdar, K. C.; Chattopadhyay, S. K. *J. Chem. Soc., Chem. Commun*. **1987**, 524.
11. Majumdar, K. C.; Chattopadhyay, S. K.; Khan, A. T. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1285.
12. Majumdar, K. C.; Ghosh, S. K. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2889.
13. Majumdar, K. C.; Das, U.; Jana, N. K. *J. Org. Chem*. **1998**, *63*, 3550.
14. Majumdar, K. C.; Biswas, P.; Jana, G. H. *J. Chem. Res. (S)* **1997**. 310; *(M)* **1997**, 2068.
15. Majumdar, K. C.; Biswas, P. *Tetrahedron* **1998**, *54*, 11603.

16. Majumdar, K. C.; Biswas, P. *Tetrahedron* **1999**, *55*, 1449.
17. **Compound 4a**: mp 108°C; yield 75%; UV (EtOH) λ_{max}: 218, 271 nm; IR (KBr) ν_{max}: 1690, 1580, 1230 cm^{-1}; ^1H NMR (300 MHz): δ 3.82 (t, 2H, $J=2$ Hz), 4.71 (t, 2H, $J=2$ Hz), 6.28 (s, 1H), 6.92–7.73 (m, 9H); m/z 322 (M^+). Anal. calcd for $C_{19}H_{14}O_3S$: C, 70.80; H, 4.35. Found: C, 70.67; H, 4.19%.
18. **Compound 5a**: mp 138°C; yield 70%; UV (EtOH) λ_{max}: 217, 270, 329 nm; IR (KBr) ν_{max}: 1715, 1700, 1590, 1250 cm^{-1}; ^1H NMR (500 MHz): δ 3.73 (dd, 1H, $J=9$, 12 Hz), 3.82 (dd, 1H, $J=6$, 12 Hz), 4.86 (dd, 1H, $J=6$, 9 Hz), 4.95 (d, 1H, $J=15$ Hz), 4.99 (d, 1H, $J=15$ Hz), 6.93–7.58 (m, 9H); m/z 338 (M^+). Anal. calcd for $C_{19}H_{14}O_4S$: C, 67.45; H, 4.14. Found: C, 67.58; H, 4.23%.