Synthesis of Bioactive Heterocycles: Aza-Claisen Rearrangement of 4-*N*-(4'-Aryloxybut-2'-ynyl),*N*- methylamino[1]benzothiopyran-2-ones

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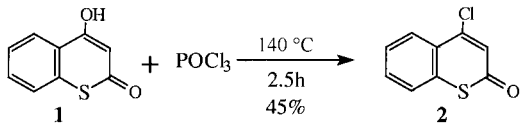
Received 20 July 2001; revised 2 October 2001

Abstract: The hitherto unreported 4-(aryloxymethylene-1-methyl-1,2,3-trihydropyrido[3,2-*c*]benzothiopyran-5-ones are synthesized in 60–90% yield by the thermal aza-Claisen rearrangement of 4-*N*-(4'-aryloxybut-2'-ynyl),*N*-methylamino[1]benzothiopyran-2-ones in refluxing 1,2-dichlorobenzene. 4-*N*-(4'-Aryloxybut-2'-ynyl),*N*-methylamino[1]benzothiopyran-2-ones were prepared in 80–90% yields by the reaction of 4-chloro[1]benzothiopyan-2-one and appropriate 1-aryloxy-*N*-methylaminobut-2-ynes in refluxing ethanol. 4-Chloro[1]benzothiopyran-2-ones was in turn synthesised from 4-hydroxythiocoumarin by reaction with phosphorous oxychloride at 140 °C.

Key words: aza-Claisen rearrangement, sigmatropic rearrangement, heterocycles, pyrido[3,2-*c*][1]benzothiopyran-5-ones, 4-chlorothiocoumarin, 4-hydroxythiocoumarin

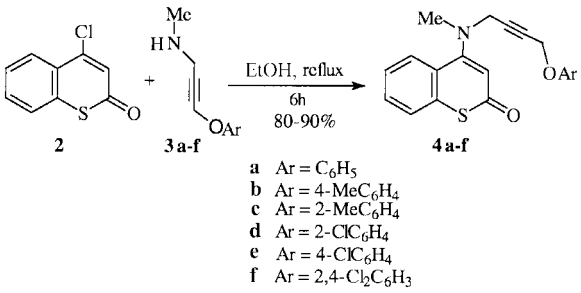
Synthesis of different derivatives of coumarin has been of interest due to their biological activity,[1] namely anthelminatic, hypnotic, insecticidal, antifungal and photodynamic activities, anticoagulant effect on blood and diuretic property. Extensive work has been done on the synthesis[2] of these class of compounds. We have recently reported a simple methodology for the regioselective synthesis of pyrano- and furocoumarins by the application of [3,3] sigmatropic rearrangement.[3] We have also extended this methodology to other systems[4] for the regioselective synthesis of pyrano- and furo heterocycles. However, very little work has been reported on the synthesis of pyrrolo- and pyridino- analogs of these heterocycles. This prompted us to undertake a study on the thermal rearrangement of 4-*N*-(4'-aryloxybut-2'-ynyl),*N*-methylamino[1]benzothiopyran-2-ones and the results are reported here.

4-Chlorothiocoumarin (**2**) was prepared in 45% yield by heating the 4-hydroxy thiocoumarin (**1**) with $POCl_3$ at 140 °C for 2.5 hours (Scheme 1).



Scheme 1

The 4-(*N*-4'-aryloxybut-2'-ynyl),*N*-methylaminothiocoumarins **4a**–**f** were prepared in 80–90% yields by the reaction of 4-chlorothiocoumarin (**2**) and the corresponding *N*-(4'-aryloxybut-2'-ynyl),*N*-methylamines **3a**–**f** in refluxing ethanol for 6 hours (Scheme 2). The IR spectrum of **4a** showed a peak at 1610 cm^{-1} due to the presence of carbonyl group. The ^1H NMR spectrum of **4a** showed a three proton singlet at δ = 2.9 due to NCH_3, two sets of two proton triplets at δ = 4.0 (*J* = 1.6 Hz) and 4.75 (*J* = 1.6 Hz) due to NCH_2 and OCH_2, respectively. A one proton singlet appeared at δ = 6.2 due to H-3 of thiocoumarin moiety. Mass spectrum of **4a** showed a molecular ion peak at *m*/*z* = 335 (M^+).



Scheme 2

The substrates **4a**–**f** are unique, possessing two different sites for Claisen rearrangement. The aryloxypropargyl moiety may undergo an oxy-Claisen rearrangement. There is also a scope for an amino-Claisen rearrangement at the *N*-methyl, *N*-propargyl, *N*-(4'-thiocoumarinyl) moiety of the same substrate **4a**. Hence these substrates are suitable for studying competitive [3,3] rearrangements. The result of the competition is difficult to guess prior to performing the actual experiments. It is already reported in literature that the amino-Claisen rearrangement[5] demands higher activation energy than oxy-Claisen rearrangement. Again the activation energy required for arylpropargyl ether[6] rearrangement is much higher than that of propargyl vinyl ether rearrangement.[7]

The substrate **4a** was heated in refluxing chlorobenzene but very little change of starting material was observed even after 10 hours. Then the reaction was tried in refluxing 1,2-dichlorobenzene at 180 °C for 8 hours. But the yield of the product was lowered due to the formation of untractable mass. The reaction was optimized to 4 hours when the yield of the product **5a** was found to be maxi-

Synthesis 2002, No. 1, 28 12 2001. Article Identifier:
1437-210X,E;2002,0,01,0121,0125,ftx,en;Z08501SS.pdf.

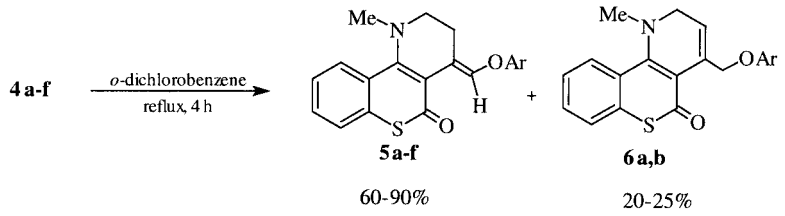
ISSN 0039-7881

mum. However, a fairly large quantity of starting material **4a** (20%) was found to remain unchanged. This was recovered and subjected to rearrangement in order to obtain more of **5a**. The product was found to be a mixture of two components. The major component was isolated in pure form as a viscus liquid (65%) by column chromatography over silica gel and was characterised as 4-aryloxymethylene-1-methyl-1,2,3-trihydro[3,2-*c*][1]benzothiopyran-5-one (**5a**) from its elemental analysis and spectral data (Scheme 3). The IR spectrum of **5a** has an absorption at 2960 cm^{-1} due to aromatic C–H stretching and at 1710 cm^{-1} for the carbonyl group. The ^1H NMR spectrum exhibited a two proton triplet at δ = 2.8 (*J* = 6 Hz) for CH_2CH_2N, a two proton triplet at δ = 3.38 (*J* = 6 Hz) due to NCH_2CH_2 and a one proton singlet at δ = 8.24, for =CHOAr. Proton decoupling also supported this assignment. The mass spectrum showed a molecular ion peak at *m*/*z* = 335 (M^+). To test the generality of the reaction the thermal rearrangement of five other substrates **4b**–**f** were similarly carried out. Substrate **4b** gave a mixture from which **5b** was isolated in 62% yield. Substrates **4c**–**f** furnished products **5c**–**f** in 75–85% yield.

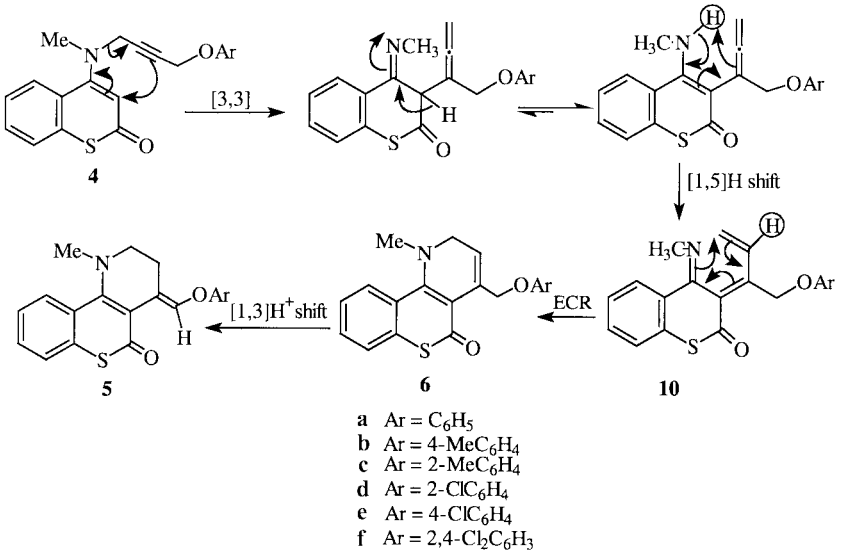
From the earlier literature reports we could have expected to get 4-aryloxymethylpyrido[3,2-*c*][1]benzothiopyran-5-one skeleton **6** or pyrrolo[3,2-*c*][1]benzothio pyran-4-one derivative **7**, via usual occurrence of the amino-Claisen rearrangement of substrates **4a**–**f**. The usual event of the oxygen-Claisen rearrangement of substrates **4a**–**f** would have produced **8** and **9** (Figure). All the substrates **4a**–**f** indicated the formation of endocyclic products **6** on TLC in the crude reaction mixture at the beginning of the reaction. However, we were able to isolate relatively pure **6a** and **6b** from the reaction mixture of substrates **4a** and **4b**, respectively. These two products exhibited a one proton triplet at δ = 5.88 (*J* = 4.6 Hz), a two proton doublet at δ = 5.1 (*J* = 1.4Hz) and a two proton doublet at δ = 3.7 (*J* = 4.6 Hz) to definitely show that the endocyclic products are actually formed during the reaction.

The formation of the products **5** from **4** is easily explicable by an initial [3,3] sigmatropic rearrangement at the propargyl vinyl amine moiety of the substrate **4** to give first an allene intermediate, followed by tautomerization, [1,5] H shift, 6π-electrocyclic ring closure leading to the unstable endocyclic intermediate **6**. [1,3] Prototropic shift in **6** then gives the final product **5**. This pathway derives additional support from the fact that endocyclic products **6a** and **6b** when heated under the same reaction conditions gave only the exocyclic products **5a** and **5b**, respectively (Scheme 4).

At present the aza-Claisen rearrangement gives exclusively the unusual products **5a**–**f** containing exocyclic double bond . The occurrence of [3,3] sigmatropic rearrangement at the propargyl vinylamine moiety in preference to aryl propargyl ether moiety in all the substrates **4a**–**f** studied so far is certainly noteworthy.



Scheme 3



Scheme 4

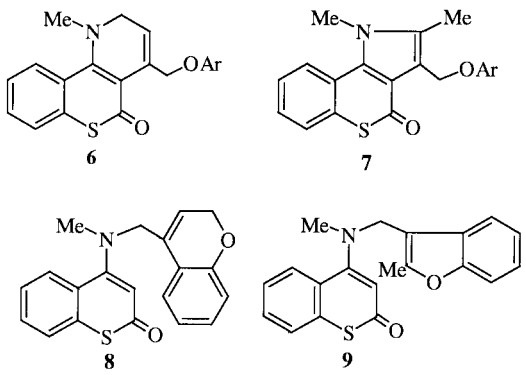


Figure Structures of compounds **6–9**

Melting points were measured on a sulfuric acid bath and are uncorrected. UV absorption spectra were recorded on a Perkin-Elmer UV/Vis spectrophotometer, Lamda 20 nm in EtOH. IR spectra were run on a Perkin-Elmer 1330 apparatus as a film between NaCl plates. ^{1}H NMR spectra were determined for solutions in $CDCl_3$ with TMS as internal standard on a Bruker 300 (300 MHz) instrument. Elemental analyses and recording of mass spectra were carried out by RSIC (CDRI) Lucknow on a [Jeol D-300 (El)] instrument. Silica gel [(60–120 mesh), Spectrochem, India] was used for chromatographic separations. Silica gel G [E. Merck (India)] was used for TLC. Petroleum ether refers to the fraction boiling between 60 °C and 80 °C. 1-Aryloxy-4-*N*-methylaminobut-2-ynes **3a–f** were prepared according to our earlier published procedure.[8]

4-Chlorothiocoumarin (2)

4-Hydroxythiocoumarin (**1**; 5g, 28 mmol) was refluxed in $POCl_3$ (35 mL) for 2.5 h. The mixture was cooled and slowly poured into crushed ice (250 g) and was extracted with $CHCl_3$ (150 mL). The $CHCl_3$ layer was washed with aq sat. Na_2CO_3 solution (3 × 30 mL), brine (3 × 40 mL), H_2O (2 × 25mL) and dried (Na_2SO_4). Evaporation of $CHCl_3$ left a gummy residue. Purification of this residue by column chromatography over silica gel using benzene–petroleum ether (1:1) as eluent afforded **2** as a white crystalline solid; yield: 45%; white crystals; mp 92 °C; R_f 0.3 (benzene–petroleum ether, 1:1).

UV (EtOH): λ_{max} (log ε) = 230 (4.1), 293 (3.6), 350 nm (3.3).

IR (KBr): 940, 1200, 1350, 1630, 3040 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.89 (s, 1 H, H-3) 7.2–7.5 (m, 3 H, ArH), 8.2 (d, *J* = 8 Hz, 1 H, H-5).

MS *m*/*z*: 196, 198 (M^+).

Anal. Calcd for C_8H_5ClOS: C, 55.2; H, 2.41. Found: C, 55.10; H, 2.55.

Compounds 4a–f; General Procedure

A mixture of 1-aryloxy-4-*N*-methylaminobut-2-yne **3** (5 mmol) and 4-chloro-thiocoumarin (**2**; 0.50 g, 2.55 mmol) in anhyd EtOH (50 mL) was refluxed for 4 h in a water bath. EtOH was removed by distillation and the residual mass was dissolved in $CHCl_3$ (50 mL). The $CHCl_3$ solution was washed with brine (2 × 25 mL), H_2O (2 × 25 mL) and dried (Na_2SO_4). Evaporation of $CHCl_3$ afforded a gummy mass which was subjected to column chromatography over silica gel. Elution of the column with benzene gave compounds **4a–f**.

4a

Yield: 80%; viscous liquid; R_f 0.3 (benzene).

UV (EtOH): λ_{max} (log ε) = 236 (4.4), 330 nm (4.02).

IR (film): 1100, 1220, 1380, 1610, 2950, 3020 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.92 (s, 3 H, NCH_3), 4.00 (t, *J* = 1.6 Hz, 2 H, NCH_2), 4.75 (t, *J* = 1.6 Hz, 2 H, OCH_2), 6.20 (s, 1 H, H-3), 6.92–7.4 (m, 8 H, ArH), 7.9 (d, *J* = 8 Hz, 1 H, H-5).

MS *m*/*z*: = 335 (M^+).

Anal. Calcd for $C_{20}H_{17}NO_2S$: C, 71.64; H, 5.07; N, 4.17. Found: C, 71.35; H, 4.9; N, 3.98.

4b

Yield: 85%; viscous liquid; R_f 0.3 (benzene).

UV (EtOH): λ_{max} (log ε) = 236 (4.32), 265 (3.99), 330 nm (3.89).

IR (film): 1130, 1240,1390, 1620, 2950, 3030 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.25 (s, 3 H, ArC*H*$_3$), 2.9 (s, 3 H, NCH_3) 3.99 (t, *J* = 1.6 Hz, 2 H, NCH_2), 4.76 (t, *J* = 1.6 Hz, 2 H, OCH_2), 6.2 (s, 1 H, H-3), 6.9–7.4 (m, 7 H, ArH), 7.9 (d, *J* = 8 Hz, 1 H, H-5).

MS *m*/*z*: = 349 (M^+).

Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.2; H, 5.44; N, 4.0. Found: C, 72; H, 5.21; N, 3.9.

4c

Yield 90%; viscous liquid; R_f 0.3 (benzene).

UV (EtOH): λ_{max} (log ε) = 236 (4.48), 330 nm (4).

IR (film): 1110, 1210, 1380, 1620, 2960, 3010 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.29 (s, 3 H, ArC*H*$_3$), 2.92 (s, 3 H, NCH_3), 3.99 (t, *J* = 1.6 Hz, 2 H, NCH_2), 4.7 (t, *J* = 1.6 Hz, 2 H, OCH_2), 6.2 (s, 1 H, H-3), 6.8–7.4 (m, 7 H, ArH), 7.9 (d, *J* = 8 Hz, 1 H, H-5).

MS *m*/*z*: = 349 (M^+).

Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.2; H, 5.44; N, 4.0. Found C, 72.10; H, 5.21; N, 3.93.

4d

Yield: 89%; viscous liquid; R_f 0.3 (benzene)

UV (EtOH): λ_{max} (log ε) 236 (4.2), 330 nm (3.8).

IR (film): 1110, 1240, 1380, 1620, 2960, 3020 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.91 (s, 3 H, NCH_3), 4.0 (t, *J* = 1.6 Hz, 2 H, NCH_2), 4.8 (t, *J* = 1.6 Hz, 2 H, OCH_2), 6.1 (s, 1 H, H-3), 6.9–7.4 (m, 7 H, ArH), 7.9 (d, *J* = 8 Hz, 1 H, H-5).

MS *m*/*z*: 369, 371 (M^+).

Anal. Calcd for $C_{20}H_{16}ClNO_2S$: C, 65.0; H, 4.3; N, 3.79. Found C, 64.91; H, 4.11; N, 3.61.

4e

Yield: 85%; viscous liquid; Rf 0.3 (benzene).

UV(EtOH): λ_{max} (log ε) = 232 (4.3), 330 nm (3.8).

IR (film): 1130, 1220, 1380, 1620, 2960, 3020 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.91 (s, 3 H, NCH_3), 4.01 (t, *J* = 1.6 Hz, 2 H, NCH_2), 4.60 (t, *J* = 1.6 Hz, 2 H, OCH_2), 6.20 (s, 1 H, H-3), 6.8–7.4 (m, 7 H, ArH), 7.9 (d, *J* = 8 Hz, 1 H, H-5).

MS *m*/*z*: 369, 371 (M^+).

Anal. Calcd for $C_{20}H_{16}ClNO_2S$: C, 65.0; H, 4.3; N, 3.9. Found C, 64.95; H, 4.13; N, 3.61.

4f

Yield: 81%; viscous liquid; R_f 0.3 (benzene).

UV(EtOH): λ_{max} (log ε) 236 (4.20), 330 nm (3.9).

IR (film): 1140, 1250, 1330, 1610, 2950, 3030 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.91 (s, 3 H, NCH_3), 4.01 (t, *J* = 1.6 Hz, 2 H, NCH_2), 4.8 (t, *J* = 1.6 Hz, 2 H, OCH_2), 6.20 (s, 1 H, H-3), 6.9–7.4 (m, 6 H, ArH), 7.8 (d, *J* = 8 Hz, 1 H, H-5).

MS *m*/*z*: 404, 408, 406 (M^+).

Anal. Calcd for $C_{20}H_{15}Cl_2NO_2S$: C,59.4, H, 3.71, N, 3.46. Found C, 59.12; H, 3.52; N, 3.21.

Compounds 5a–f and 6a,b; General Procedure

Compounds **4a**–**f** (0.2 g, 0.59 mmol) were refluxed in 1,2-dichlorobenzene (2 mL) for 2 h. The mixture was then cooled and directly subjected to column chromatography over silica gel. 1,2-Dichlorobenzene was eluted out with petroleum ether. All the products **5a–f** were obtained when the column was eluted with petroleum ether–benzene (3:1). Compounds **6a**,**b** followed compounds **5a**,**b** in the same eluent and were carefully separated. Unchanged starting materials **4a**–**f** were also carefully eluted out with benzene. The yields were calculated on the basis of actual conversion of starting materials.

5a

Yield: 65%; viscous liquid; R_f 0.4 (benzene–petroleum ether,1:3).

UV (EtOH): λ_{max} (log ε) 223 (4.4), 269 (4.2), 397 nm (4).

IR (film): 1240, 1460, 1570, 1710, 2960 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.8 (t, *J* = 6 Hz, 2 H, NCH_2CH_2), 3.0 (s, 3 H, NCH_3), 3.37 (t, *J* = 6 Hz, 2 H, NCH_2), 7.0–7.5 (m, 8 H, ArH), 7.7 (d, *J* = 8 Hz, 1 H, H-10), 8.2 (s, 1 H, =C*H*OAr).

MS *m*/*z*: 335 (M^+);

Anal. Calcd for $C_{20}H_{17}NO_2S$: C, 71.64; H, 5.07; N, 4.17. Found C, 71.39; H, 4.81; N, 3.87.

5b

Yield 62%; viscous liquid; R_f 0.4 (benzene–petroleum ether, 1:3).

UV(EtOH): λ_{max} (log ε) 224 (4.4), 269 (4.1), 379 nm (3.8).

IR (Film): 1230, 1500, 1600, 1710, 2960 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.25 (s, 3 H, $ArCH_3$), 2.8 (t, *J* = 6 Hz, 2 H, NCH_2CH_2), 3.0 (s, 3 H, NCH_3), 3.3 (t, *J* = 6 Hz, 2 H, NCH_2), 6.9–7.3 (m, 7 H, ArH), 7.8 (d, *J* = 8 Hz, 1 H, H-10), 8.2 (s, 1 H, =C*H*OAr).

MS *m*/*z*: 349 (M^+).

Anal. Calcd for $C_{21}H_{19}O_2NS$: C, 72.20; H, 5.44; N, 4.0. Found C, 71.82; H, 5.31; N, 3.89.

5c

Yield: 85%; viscous liquid; R_f 0.4 (benzene–petroleum ether, 1:3).

UV (EtOH): λ_{max} (log ε) 221 (4.3), 359 nm (3.66).

IR (film): 1240, 1490, 1590, 1710, 2970 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.27 (s, 3 H, $ArCH_3$), 2.8 (t, *J* = 6 Hz, 2 H, NCH_2CH_2), 3.0 (s, 3 H, NCH_3), 3.3 (t, *J* = 6 Hz, 2 H, NCH_2), 6.91–7.3 (m, 7 H, ArH), 7.8 (d, *J* = 8 Hz, 1 H, H-10), 8.2 (s, 1 H, =C*H*OAr).

MS *m*/*z*: 349 (M^+).

Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.20; H, 5.44; N, 4.0. Found C, 71.88; H, 5.31; N, 3.72.

5d

Yield: 82%; viscous liquid; R_f 0.4 (benzene–petroleum ether, 1:3).

UV (EtOH): λ_{max} (log ε) 232 (4.4), 292 (3.9), 374 nm (3.5).

IR (film): 1240, 1470, 1710, 2960 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.8 (t, *J* = 6 Hz, 2 H, NCH_2CH_2), 3.0 (s, 3 H, NCH_3), 3.3 (t, *J* = 6 Hz, 2 H, NCH_2), 6.7–7.4 (m, 7 H, ArH), 7.7 (d, *J* = 8 Hz, 1 H, H-10), 8.1 (s, 1 H, =C*H*OAr).

MS *m*/*z*: 369, 371 (M^+).

Anal. Calcd for $C_{20}H_{16}ClNO_2S$: C, 65; H, 4.3; N, 3.79. Found C, 64.82; H, 4.19; N, 3.51.

5e

Yield: 81%; viscous liquid; R_f 0.4 (benzene–petroleum ether, 1:3).

UV(EtOH): λ_{max} (log ε) 227 (4.4), 264 (4.0), 352 nm (3.6).

IR (film): 1230, 1480, 1590, 1710, 2970 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.9 (t, *J* = 6 Hz, 2 H, NCH_2CH_2), 3.1 (s, 3 H, NCH_3), 3.4 (t, *J* = 6 Hz, 2 H, NCH_2), 7.2–7.5 (m, 7 H, ArH), 7.7 (d, *J* = 8 Hz, 1 H, H-10), 8.2 (s, 1 H, =C*H*OAr).

MS *m*/*z*: 369, 371 (M^+).

Anal. Calcd for $C_{20}H_{16}ClNSO_2$: C, 65.00; H, 4.30; N, 3.79. Found C, 64.89; H, 4.18; N, 3.48.

5f

Yield: 75%; viscous liquid; R_f 0.4 (benzene–petroleum ether, 1:3).

UV (EtOH): λ_{max} (log ε) = 232 (4.4), 292 (3.9), 347 nm (3.5).

IR (film): 1250, 1470, 1580, 1710, 2950 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.9 (t, *J* = 6 Hz, 2 H, NCH_2CH_2), 3.1 (s, 3 H, NCH_3), 3.4 (t, *J* = 6 Hz, 2 H, NCH_2), 7.1–7.3 (m, 7 H, ArH), 7.7 (d, *J* = 8 Hz, 1 H, H-10), 8.1 (s, 1 H, =C*H*OAr).

MS *m*/*z*: 404, 408, 406 (M^+).

Anal. Calcd for $C_{20}H_{15}Cl_2NO_2S$: C, 59.4, H, 3.71, N, 3.46. Found C, 59.29; H, 3.62; N, 3.25.

6a

Yield: 25%; viscous liquid; R_f 0.3 (benzene–petroleum ether, 1:3).

UV (EtOH): λ_{max} (log ε) = 220 (4.4), 347 nm (3.6).

IR (film): 1230, 1480, 1600, 2960 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.9 (s, 3 H, NCH_3), 3.7 (d, *J* = 4.6 Hz, 2 H, NCH_2), 5.1 (d, *J* = 1.4 Hz, 2 H, OCH_2), 5.8 (t, *J* = 4.6 Hz, 1 H, NCH_2CH), 6.9–7.3 (m, 8 H, ArH), 7.9 (d, *J* = 8 Hz, 1 H, H-10).

MS *m*/*z*: 335 (M^+).

Anal. Calcd for $C_{20}H_{17}SNO_2$: C, 71.64; H, 5.07; N, 4.17. Found C, 71.45; H, 4.91; N, 3.90.

6b

Yield: 20%; viscous liquid; R_f 0.3 (benzene–petroleum ether, 1:3).

UV (EtOH): λ_{max} (log ε) = 224 (4.21), 359 nm (3.6).

IR (film): 1240, 1490, 1600, 2960 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.26 (s, 3 H, $ArCH_3$), 2.9 (s, 3 H, NCH_3), 3.7 (d, *J* = 4.6 Hz, 2 H, NCH_2), 5.0 (d, *J* = 1.4 Hz, 2 H, OCH_2), 5.8 (t, *J* = 4.6 Hz, 1 H, NCH_2CH), 6.8–7.4 (m, 7 H, ArH), 7.9 (d, *J* = 8 Hz, 1 H, H-10).

MS *m*/*z*: 349 (M^+).

Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.20; H, 5.44; N, 4.00. Found C, 72.05; H, 5.21; N, 3.84.

Acknowledgement

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

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