Studies in sigmatropic rearrangement: synthesis of 3,11a-dimethyl-6a,11a-dihydro-1*H*,6*H*-pyrano[3′,4′:5,6]thiopyrano[4,3-*b*][1]benzofuran-1-one†

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Dedicated to Professor (Mrs.) A. Chatterjee on her 85th birthday

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Abstract

Thermal rearrangement of 4-aryloxymethyl-7-methylthiopyrano-[3,2-*c*]pyran-5-ones **6a-f** afforded a number of hitherto unreported benzofuro[3,2-*c*]-6a,11a-dihydro-3,11a-dimethylthiopyranopyran-1-one **15a-e** in good yields (60-67%) along with the exocyclic derivatives **16d,e,f** as minor products (10-15%). Compounds **6a-f** were in turn synthesized in 72-85% yields by the thermal rearrangement of 4-(4'-aryloxybut-2'-ynylthio)-6-methylpyran-2-ones **5a-f**. Compounds **5a-f** were obtained in (50-55%) yields by the phase-transfer catalyzed alkylation of 4-mercapto-6-methyl-2-pyrone **3** with 1-aryloxy-4-chlorobut-2-yne **4a-f**.

Keywords: Regioselective synthesis, [3,3] sigmatropic rearrangement, sulfur heterocycles, phase-transfer catalysis, 1-aryloxy-4-chlorobut-2-yne, Claisen rearrangement

Introduction

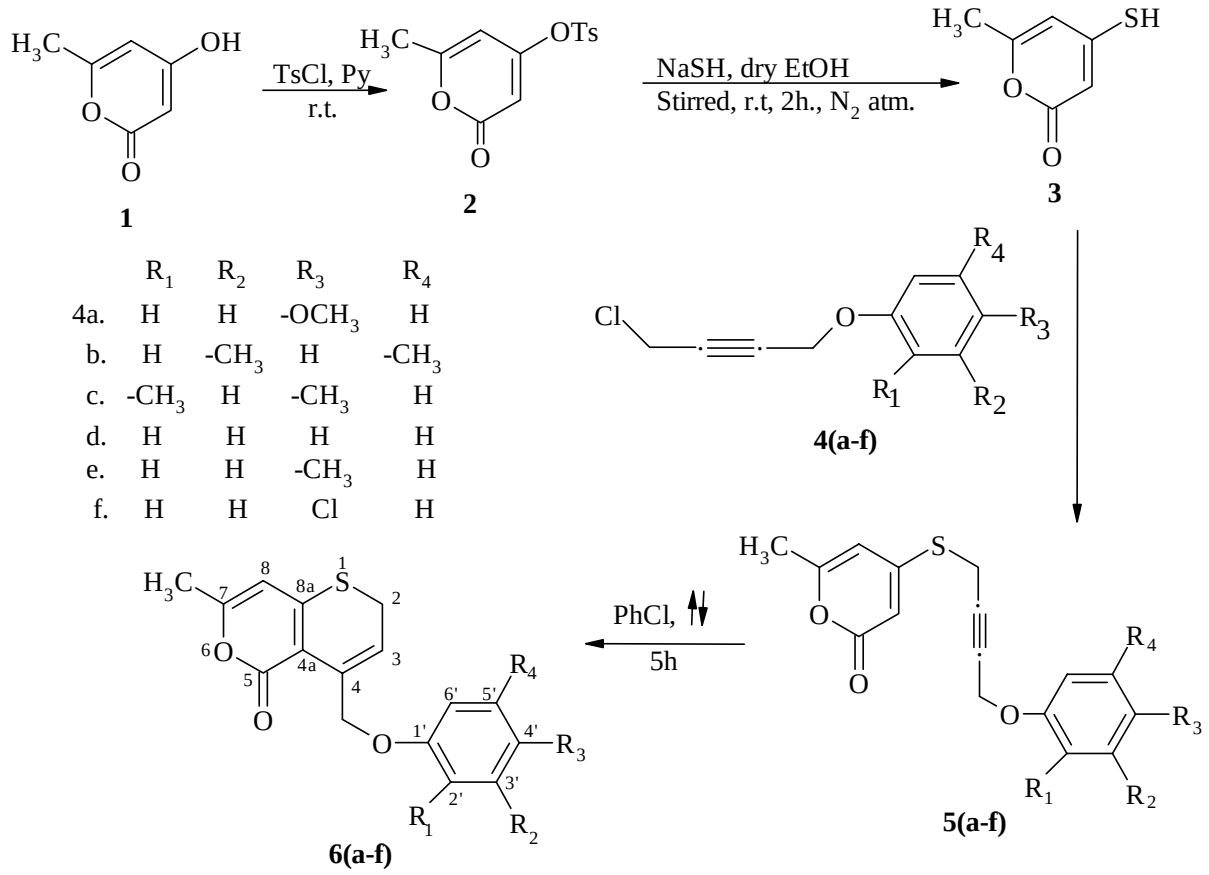
4-Hydroxy-6-methyl-2-pyrone (triacetic acid lactone) **1** is a natural product of polyketide origin.[1] Many naturally occurring compounds[2] contain the basic structural unit of 4-hydroxy(or methoxy)-6-alkyl-2-pyrone. Some of these compounds possess biogenetically plausible groups at C-3 or C-5 or both. Elasnin, isolated from *Steptromices sp*., for example, is a specific inhibitor of human leukocyte elastase, an enzyme involved in inflammatory processes such as pulmonary emphysema.[3] As a logical extension, many more simple pyrones structurally related to elasnin have been synthesized and evaluated as inhibitors of several elastases.[4] Some 4-hydroxy-2-pyrones are known to display the properties of anticoagulant agents.[5] In a continuation of our work on the synthesis of bioactive heterocycles[6] by the application of sigmatropic rearrangements[7], we recently published[8] the synthesis of fused thienopyrone heterocyclic systems. We, then, became interested to find the influence of different substituents in the

benzene nucleus of our substrate 4-aryloxymethyl-7-methylthiopyrano[3,2-*c*]pyran-5-ones, **6a-f** on the course of the rearrangement.

The starting materials for this investigation, 4-(4'-aryloxybut-2'-ynylthio)-6-methylpyran-2-ones **5a-f** were synthesized from 4-mercapto-6-methylpyran-2-ones and 1-aryloxy-4-chlorobut-2-yne by our earlier published procedure.[8] **(Scheme 1)**

Results and Discussion

Substrates **5a-f** contain a propargyl vinyl sulfide moiety as well as aryl propargyl ether segment. Compounds with this structural feature offer an excellent scope for the study of competition between oxy-and thio-Claisen rearrangements as well as the synthesis of new heterocycles through [3,3] Sigmatropic rearrangements.

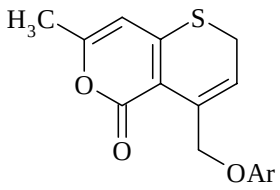


	R_1	R_2	R_3	R_4
4a.	H	H	$-OCH_3$	H
b.	H	$-CH_3$	H	$-CH_3$
c.	$-CH_3$	H	$-CH_3$	H
d.	H	H	H	H
e.	H	H	$-CH_3$	H
f.	H	H	Cl	H

Scheme 1

Occurrence of [3,3] Sigmatropic rearrangement at the vinyl propargyl sulfide segment of compounds **5a-f** may lead to polyheterocycles **6-8** while that at aryl propargyl ether part may generate polyheterocycles **9-11**.

With this end in view, substrate **5a** was refluxed in chlorobenzene (131-132^{o}C) and the isolated product was shown to be compound **6a** from its elemental analysis and spectroscopic data. The ^{1}H-NMR of compound **6a** showed a two-proton doublet at δ 3.34 (*J* 6Hz) assignable to two C_2-H, a two-proton triplet centered at δ 5.96 owing to C_3-H due to (*J* 6Hz), a two-proton broad singlet at δ 5.01 owing to –CH_2OAr, a one-proton singlet at δ 6.01 due to C_8-H, a three proton singlet at δ 2.22 assignable to C_7-CH_3 and two two- proton doublets at δ 6.79 (*J* 9Hz) and δ 6.86 (*J* 9Hz) owing to four aromatic protons.



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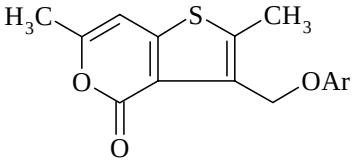

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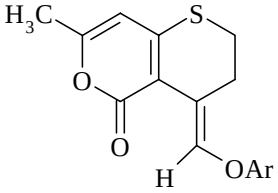

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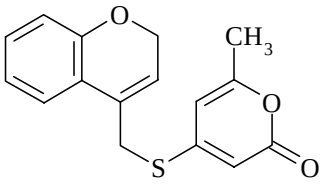

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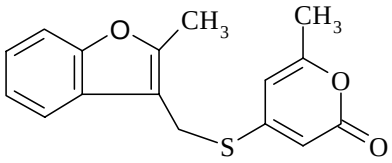

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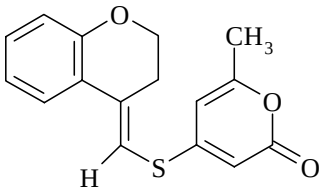

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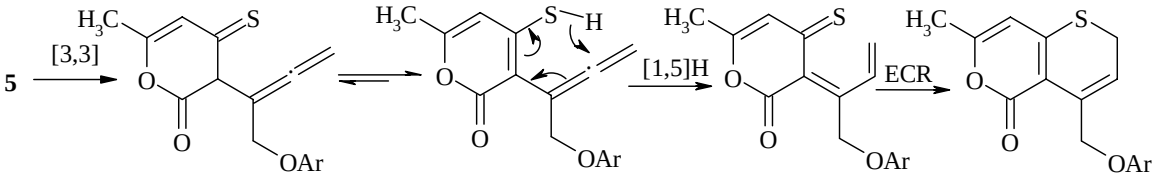
The ^{13}C-NMR spectrum of compound **6a** also strongly supported its structure. The ^{13}C chemical shift of compound **6a** was assigned by DEPT experiments. Multiplicity was also ascertained by DEPT experiment. Substrates **5b-f** were similarly treated to obtained compounds **6b-f**.



12 **13** **14** **6**

Scheme 2

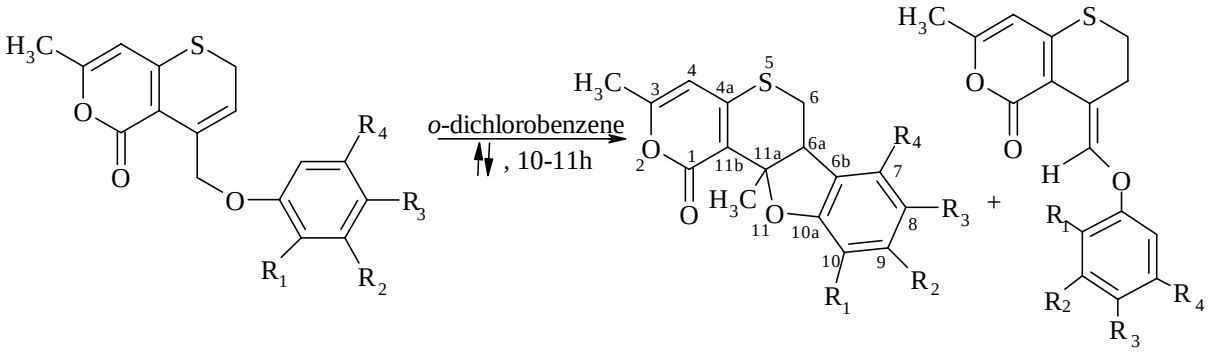
Mechanistic rationalization of the formation of **6** from **5** involves a [3,3] sigmatropic rearrangement at the vinyl propargyl sulfide segment of **5** leading to an allenyl intermediate **12**. Intermediate **12** may undergo tautomerization to furnish **13**. A [1,5]H shift in **13** may give **14** which, on 6π electrocyclic ring-closure, can afford compound **6 (Scheme 2)**.

All the six substrates **5a-f** afforded thiopyranopyrone derivatives **6a-f** exclusively despite the possibility of the formation of other polyheterocycles **7-11**. A lesser energy requirement for the sigmatropic rearrangement in vinyl propargyl systems[9] compared to that in aryl propargyl moieties[10] might be responsible for this excellent regioselectivity.

Presence of an aryl allyl ether segment in compound **6** may enable it to undergo a thermal [3,3] sigmatropic rearrangement. When compound **6a** was subjected to thermal rearrangement in refluxing *o*-dichlorobenzene (179-181^{o}C), the isolated product was shown to be compound **15a** from its elemental analysis and spectral data. Product **15a** was also obtained when the sulfide **5a** was refluxed in *o*-dichlorobenzene for 12h.

The ^{1}H-NMR of compound **15a** showed three one proton doublet of doublets at δ 2.80 (*J* 9.9,13.5Hz), 3.01 (*J* 3.9,13.5Hz) and 3.41 (*J* 3.9,9.9 Hz) indicating the presence of two C_6-H and one C_{6a}-H. This structure of compound **15a** was further confirmed by its ^{13}C-NMR spectrum.

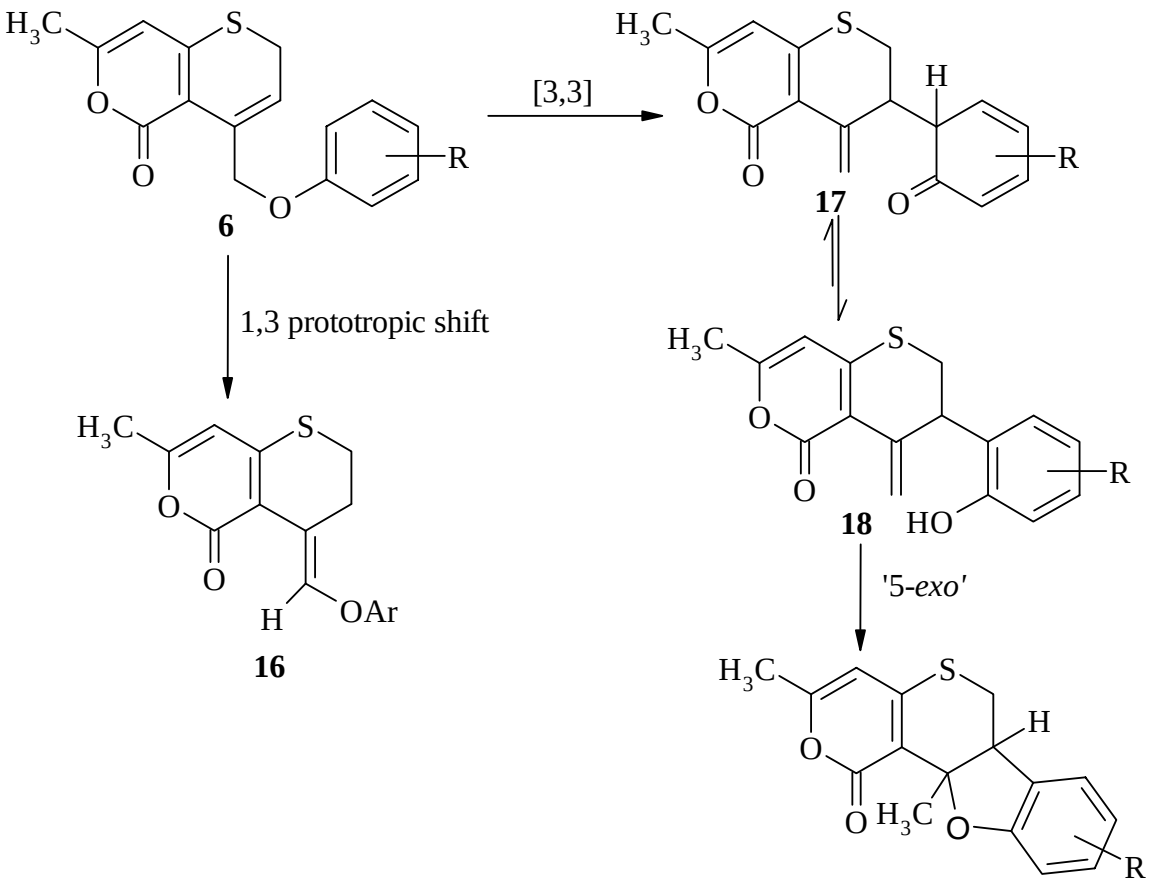
Fused furanothiopyran derivatives **15a,b,c** were obtained as the sole products from the rearrangement of compounds **6a,b,c**. Compounds **6d,e**, however, afforded a mixture of **15d,e** and the exo-cyclic derivatives **16d,e**. Compound **6f** gave only the exo-cyclic product **16f** (**Scheme 3)**. Formation of compound **15** and **16** from **6** can be mechanistically interpreted as outlined in **(Scheme 4).**



6(a-f) **15(a-e)** **16(d,e,f)**

Scheme 3

Compound **6** may undergo [3,3] sigmatropic rearrangement at the aryl allyl ether part to produce intermediate **17**. Tautomerization of **17** may afford **18**, which, on '5-*exo*' ring closure, should furnish compound **15**. Compound **16** can be obtained through a [1,3] prototropic rearrangement in compound **6**.



Scheme 4

Presence of different substituents in the benzene nucleus of compound **6** thus brings about a change in the mode of the rearrangement. However the role of some substituents in the formation of exocyclic derivatives **16d,e,f** is not clear. Here it is noteworthy that in the synthesis of pyranopyrone derivatives from 4-(4'-aryloxybut-2'-ynyloxy)-6-methyl-2-pyrones, only exocyclic products corresponding to **8** were obtained[11]. Synthesis of pyridinopyrone heterocycles from 4-(*N*-4'-aryloxybut-2'-ynyl)-*N*-methylamino-6-methyl-2-pyrones also afforded chiefly the exocyclic products along with the endocyclic compounds as minor products corresponding to **6** only in three cases.[12] In the prsent instance, all the substrate **5a-f** afforded the endocyclic derivatives **6a-f**.

Conclusions

In conclusion, thermal sigmatropic rearrangement has been successfully utilised as an efficient tool for the synthesis of fused furanothiopyran heterocyclic ring systems with moderate regioselectivity. Presence of various substituents in the benzene ring of compound **6** alters the

course of rearrangement in spite of their seemingly remote distance from the site of rearrangement.

Experimental Section

General Procedures. Melting points were determined in an open capillary and are uncorrected. IR spectra were recorded on a Perkin-Elmer L 120-000A spectrometer (ν_{max} in cm^{-1}) using samples as neat liquids and solid samples were recorded in KBr disks and UV absorption spectra were recorded in EtOH on a Shimadzu UV-2401PC spectrophotometer (λ_{max} in nm). ^{1}H NMR (300 MHz, 500 MHz) and ^{13}C NMR (75.5 MHz, 125.7 MHz) spectra were recorded on a Bruker DPX-300 and Bruker DPX-500 spectrometer in $CDCl_3$ (chemical shift in δ) with TMS as internal standard. Elemental analyses and mass spectra were recorded on a JEOL JMS600 instrument. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at Indian Institute of Chemical Biology, Kolkata and Bose Institute, Kolkata. Silica gel [(60-120 mesh), Spectrochem, India] was used for chromatographic separation. Silica gel G[E-Merck (India)] was used for TLC. Petroleum ether refers to the fraction boiling between 60°C and 80°C.

Synthesis of 4-mercapto-6-methylpyran-2-one 3
This compound was synthesized by our earlier published procedure.[8]

General procedure for the synthesis of compounds 5a-f
These compounds were synthesized following a similar procedure published earlier.[8]
4-[4-(4'-Methoxyphenoxybut-2-ynylthio)]-6-methyl-2-pyrone (**5a).** Yield 53%; mp. 76-78 °C; λ_{max} : 230, 268, 291 nm; IR (KBr)ν_{max} : 1715, 1635, 1506, 1221 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.19 (s, 3H, C_6-C**H**$_3$), 3.66 (s, 2H, -SC**H**$_2$), 3.77 (s, 3H, -OC**H**$_3$), 4.63 (s, 2H, -OC**H**$_2$), 5.82 (s, 1H, C_3-**H**), 5.92 (s, 1H ,C_5-**H**), 6.81-6.88 (m, 4H, Ar**H**); MS m/z 316 (M^+). Anal Calcd. For $C_{17}H_{16}O_4S$: C, 64.54; H, 5.09. Found: C, 64.42; 5.21%.
4-[4-(3',5'-Dimethylphenoxybut-2-ynylthio)]-6-methyl-2-pyrone (**5b).** Yield 55%; mp. 82-84 ° C; λ_{max} 230, 268, 302 nm; IR (KBr)ν_{max} : 1717, 1635, 1501, 1221 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.19 (s, 3H, C_6-C**H**$_3$), 2.28 (s, 6H, -C**H**$_3$), 3.67 (s, 2H, -SC**H**$_2$), 4.65 (s, 2H, -OC**H**$_2$), 5.83 (s, 1H, C_3-**H**), 5.93 (s, 1H ,C_5-**H**), 6.55-6.62 (m, 3H, Ar**H**), MS m/z 314 (M^+). Anal Calcd. For $C_{18}H_{18}O_3S$ C, 68.77; H, 5.77. Found: C, 68.62; H, 5.76 %
4-[4-(2',4'-Dimethylphenoxybut-2-ynylthio)]-6-methyl-2-pyrone (**5c).** Yield 55%; mp. 80-82 °C; λ_{max} 230, 268, 302 nm; IR (KBr)ν_{max} : 1716, 1635, 1506, 1221 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.19 (s, 3H, C_6-C**H**$_3$), 2.24 (s, 3H, -C**H**$_3$), 2.27 (s, 3H, -C**H**$_3$), 3.67 (s, 2H, -SC**H**$_2$), 4.65 (s, 2H, -OC**H**$_2$), 5.83 (s, 1H, C_3-**H**), 5.93 (s, 1H, C_5-**H**), 6.55-6.62 (m, 3H, Ar**H**), MS m/z 314 (M^+) Anal Calcd. For $C_{18}H_{18}O_3S$ C, 68.77; H, 5.77 Found: C, 68.68; H, 5.54 %.
4-(4-Phenoxybut-2-ynylthio)-6-methyl-2-pyrone (5d). Yield 52% mp. 78-80 °C; λ_{max} 220, 269, 302 nm; IR (KBr)ν_{max} : 1700, 1610, 1475, 1220 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.19 (s,

3H, C_6-C**H**$_3$), 3.67 (s, 2H, -SC**H**$_2$), 4.69 (s, 2H, -OC**H**$_2$), 5.82 (s, 1H, C_3-**H**), 5.94 (s, 1H, C_5-**H**), 6.91-7.31 (m, 5H, Ar**H**); MS m/z 286 (M^+) Anal Calcd. For $C_{16}H_{14}O_3S$ C, 67.11; H, 4.93. Found: C, 67.32; H, 4.98 %

4-[4-(4'-Methylphenoxybut-2-ynylthio)]-6-methyl-2-pyrone (**5e).** Yield 50%, mp. 71-72 ^oC; λ_{max} 222, 270, 302 nm; IR (KBr)ν_{max} : 1700, 1620, 1485, 1220 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.19 (s, 3H, -C**H**$_3$), 2.28 (s, 3H, -C**H**$_3$), 3.66 (s, 2H, -SC**H**$_2$), 4.66 (s, 2H, -OC**H**$_2$), 5.82 (s, 1H, C_3-**H**), 5.93 (s, 1H, C_5-**H**), 6.81 (d, *J* 9Hz, 2H, Ar**H**), 7.06 (d, *J* 9Hz, 2H, Ar**H**); MS m/z 300 (M^+). Anal Calcd. For $C_{17}H_{16}O_3S$ C, 67.98; H, 5.37 Found: C, 68.11; H, 5.48 %

4-[4-(4'-Chlorophenoxybut-2-ynylthio)]-6-methyl-2-pyrone (**5f).** Yield 52%;, mp. 76-78 ^oC; λ_{max} 224, 271, 303 nm; IR (KBr)ν_{max} : 1700, 1620, 1480, 1215 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.20 (s, 3H, C_6-C**H**$_3$), 3.66 (s, 2H, -SC**H**$_2$), 4.67 (s, 2H, -OC**H**$_2$), 5.81 (s, 1H, C_3-**H**), 5.91 (s, 1H, C_5-**H**), 6.84 (d, *J* 9Hz, 2H, Ar**H**), 7.21 (d, *J* 9Hz, 2H, Ar**H**); MS m/z 320, 322 (M^+). Anal Calcd. For $C_{16}H_{13}ClO_3S$ C, 59.91; H, 4.08 Found: C, 60.12; H, 4.26 %

General procedure for the synthesis of 4-aryloxymethyl-7-methyl thiopyrano[3,2-c]pyran-5-ones 6a-f

Compounds 5a-f (200 mg) were refluxed in chlorobenzene (3 ml) for 5 h. The reaction mixture was then cooled and directly subjected to column chromatography over silica gel. *C*hlorobenzene was eluted out with petroleum ether. Compounds 6a-f were obtained when the column was eluted with benzene-petroleum ether (3:1). These compounds 6a-f were recrystallised from chloroform-petroleum ether.

Compound (6a). Yield 80%; mp. 96-98 ^oC; λ_{max}: 232 , 278, 301 nm; IR (KBr) ν_{max}: 1705, 1626, 1507, 1229 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) : δ 2.22 (s, 3H, C_7-C**H**$_3$), 3.34 (d, *J* 6 Hz, 2H, C_2-**H**), 3.75 (s, 3H, -OC**H**$_3$), 5.01 (brs, 2H, -C**H**$_2$OAr), 5.96 (t, *J* 6 Hz,1H, C_3-**H**), 6.01 (s, 1H, C_8-**H**), 6.79 (d, *J* 9Hz, 2H, Ar**H**), 6.86 (d, *J* 9Hz, 2H, Ar**H**); ^{13}C-NMR ($CDCl_3$, 125.7 MHz): δ 20.03 (C_7-**C**H$_3$), 25.07(C_2), 56.11 (C_4'-O**C**H$_3$), 69.55 (**C**H$_2$OAr), 105.16 (C_8), 114.51 (C_{4a}), 114.74 (C_3), 114.96 (C_2', C_6'), 116.59 (C_3', C_5'), 134.57 (C_4), 153.16 (C_{8a}), 154.36 (C_4'), 155.24 (C_1'), 159.16 (C_7), 159.64 (C_5); m'z 316 (M^+); Anal Calcd. For $C_{17}H_{16}O_4S$: C, 64.54; H, 5.09. Found C, 64.34; H, 5.01 %.

Compound (6b). Yield 83%; mp. 120-122 ^oC; λ_{max}: 248, 302 nm; IR (KBr) ν_{max}: 1708, 1633, 1500, 1255 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) : δ 2.22 (s, 3H, -C**H**$_3$), 2.27 (s, 6H, -C**H**$_3$), 3.34 (d, *J* 6 Hz, 2H, C_2-**H**), 5.02 (brs, 2H, -C**H**$_2$OAr), 5.97 (t, *J* 6 Hz, 1H, C_3-**H**), 6.02 (s, 1H, C_8-**H**), 6.57 (m, 3H, Ar**H**); ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 19.57 (**C**$_7$-**C**H$_3$), 21.39 (C_3',-**C**H$_3$,C_5' -**C**H$_3$), 24.61 (**C**$_2$), 56.11 (**C**$_4$'-O**C**H$_3$), 67.94 (-**C**H$_2$OAr), 104.73 (C_8), 112.69 (**C**$_2$', **C**$_6$'), 114.03 (**C**$_3$), 115.39 (**C**$_{4a}$), 122.58 (**C**$_4$'), 133.97 (**C**$_4$), 139.03 (**C**$_3$', **C**$_5$'), 154.78 (**C**$_{8a}$), 158.53 (**C**$_1$'), 158.75 (**C**$_7$), 159.14 (**C**$_5$); MS m/z 314 (M^+); Anal Calcd. For $C_{18}H_{18}O_3S$: C, 68.77; H, 5.77. Found C, 68.59; H, 5.57 %.

Compound (6c). Yield 85%; mp. 116-118 ^oC; λ_{max}: 223 , 248, 302 nm; IR (KBr) ν_{max}: 1710, 1644, 1533, 1268 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) : δ 2.22 (s, 3H, -C**H**$_3$), 2.27 (s, 6H, C**H**$_3$),

3.35 (d, *J* 6 Hz, 2H, C_2-**H**), 5.02 (brs, 2H, -C**H**$_2$OAr), 5.98 (t, *J* 6 Hz, 1H, C_3-**H**), 6.02 (s, 1H, C_8-**H**), 6.57-6.59 (m, 3H, Ar**H**), m/z 314 (M^+); Anal Calcd. For $C_{18}H_{18}O_3S$: C, 68.77; H, 5.77. Found C, 68.65; H, 5.53 %.

Compound (6d). Yield 72%; gummy mass; λ_{max}: 222 , 247, 299 nm; IR (KBr) ν_{max}: 1690, 1620, 1490, 1250 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) : δ 2.22 (s, 3H, C_7-C**H**$_3$), 3.34 (d, *J* 6 Hz, 2H, C_2-**H**), 5.07 (brs, 2H, -C**H**$_2$OAr), 5.98 (t, *J* 6 Hz,1H, C_3-**H**), 6.02 (s, 1H, C_8-**H**), 6.90-7.32 (m, 5H, Ar**H**); MS m/z 286 (M^+); Anal Calcd. For $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93. Found C, 67.36; H, 5.09%.

Compound (6e). Yield 73%; mp. 97-99 ^{o}C; λ_{max}: 224 , 246, 304 nm; IR (KBr) ν_{max}: 1690, 1620, 1490, 1270 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) : δ 2.22 (s, 3H, -C**H**$_3$), 2.27 (s, 3H, C**H**$_3$), 3.33 (d, *J* 6 Hz, 2H, C_2-**H**), 5.03 (brs, 2H, -C**H**$_2$OAr), 5.97 (t, *J* 6 Hz, 1H, C_3-**H**), 6.01 (s, 1H, C_8-**H**), 6.82 (d, *J* 9Hz, 2H, Ar**H**), 7.04 (d, *J* 9Hz, 2H, Ar**H**); MS m/z 300 (M^+); Anal Calcd. For $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37. Found C, 68.19; H, 5.47 %.

Compound (6f). Yield 80%; mp. 108-109 ^{o}C; λ_{max}: 221 , 247, 302 nm; IR (KBr) ν_{max}: 1690, 1630, 1485, 1255 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) : δ 2.23 (s, 3H, C_7-C**H**$_3$), 3.34 (d, *J* 6 Hz, 2H, C_2-**H**), 5.04 (brs, 2H, -C**H**$_2$OAr), 5.94 (t, *J* 6 Hz,1H, C_3-**H**), 6.02 (s, 1H, C_8-**H**), 6.84 (d, *J* 9Hz, 2H, Ar**H**), 7.19 (d, *J* 9Hz, 2H, Ar**H**); MS m/z 320, 322 (M^+); Anal Calcd. For $C_{16}H_{13}ClO_3S$: C, 59.91; H, 4.08. Found C, 60.15; H, 4.19 %.

General procedure for the synthesis of 3,11a-dimethyl-6a,11a-dihydro-1*H*,6*H*-pyrano[3',4':5,6]thiopyrano[4,3-*b*][1]benzofuran-1-one 15(a-e) and 4-aryloxymethylene-7-methylthio- pyrano[3,2-*c*]pyran-5-ones 16 (d,e,f)

Compounds **6 a-f** (100 mg) were refluxed in *o*-dichlorobenzene (3 ml) for 10-11 h. The reaction mixture was then cooled and directly subjected to column chromatography over silica gel. *o*-Dichlorobenzene was eluted out with petroleum ether. Compounds **16 d,e,f** were obtained when the column was eluted with benzene-petroleum ether (3**:**1). Compounds **15a-e** were obtained when the column was eluted with benzene. Compounds **15 d** and **16 f** appeared as gummy mass. The other compounds were recrystallised from chloroform-petroleum ether.

Compound (15a). Yield 67%; mp. 118-120 ^{o}C; λ_{max}: 219, 232, nm; IR (KBr) ν_{max}: 1708, 1634, 1455, 1220 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) : δ 2.17 (s, 3H, C_3-C**H**$_3$), 1.79 (s, 3H, C_{11a}-C**H**$_3$), 2.80 (dd, *J* 9.9, 13.5 Hz, 1H, C_6-**H**), 3.01 (dd, *J* 3.9, 13.5 Hz, 1H, C_6-**H**), 3.42 (dd, *J* 3.9, 9.9 Hz, 1H, C_{6a}-**H**), 3.76 (s, 3H, -OC**H**$_3$), 5.81 (s, 1H, C_4-**H**), 6.70-6.85 (m, 3H, Ar**H**); ^{13}C-NMR ($CDCl_3$, 125.7 MHz): δ 19.82 (C_3-**C**H$_3$), 24.23(C_{11a}-**C**H$_3$), 28.87 (**C**$_6$), 51.22 (**C**$_{6a}$), 56.39 (C_8-O**C**H$_3$), 84.74 (**C**$_{11a}$), 104.98 (**C**$_4$), 110.91 (**C**$_{10}$), 111.69 (**C**$_9$), 114.28 (**C**$_7$), 115.86 (**C**$_{6b}$), 129.51 (**C**$_{11b}$), 151.90 (**C**$_4$), 154.16 (**C**$_{10a}$), 154.71 (**C**$_8$), 159.40 (**C**$_3$), 159.83 (**C**$_1$); MS m/z 316 (M^+); Anal Calcd. for $C_{17}H_{16}O_4S$: C, 64.54; H, 5.09. Found C, 64.28; H, 5.02%.

Compound (15b). Yield 65%; mp. 110-112 ^{o}C; λ_{max}: 212, 231, nm; IR (KBr) ν_{max}: 1709, 1643, 1441, 1213 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) : δ 2.20 (s, 3H, -C**H**$_3$), 2.27 (s, 3H, -C**H**$_3$), 2.31 (s, 3H, -C**H**$_3$), 1.70 (s, 3H, C_{11a}-C**H**$_3$), 2.58 (dd, *J* 9.9, 13.5 Hz, 1H, C_6-**H**), 2.89 (dd, *J* 3.9, 13.5 Hz,

1H, C_6-**H**), 3.28 (dd, *J* 3.9, 9.9 Hz, 1H, C_{6a}-**H**), 5.88 (s, 1H, C_4-**H**), 6.54-6.62 (m, 2H, Ar**H**), ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 18.13 (C_3-**C**H_3), 19.40(C_{11a}-**C**H_3), 21.52 (C_9-**C**H_3), 23.38 (C_7-**C**H_3), 28.04 (C_6), 49.93 (C_{6a}), 83.67 (C_{11a}), 104.76 (C_4), 109.45 (C_{10}), 122.99 (C_8), 116.12 (C_{6b}), 124.22 (C_{11b}), 133.94 (C_7), 139.38 (C_9), 154.02 (C_{4a}), 157.01 (C_{10a}), 158.94 (C_3), 159.53 (C_1); MS m/z 314 (M^+); Anal Calcd. for $C_{18}H_{18}O_3S$: C, 68.77; H, 5.77. Found C, 68.64; H, 5.58%.

Compound (15c). Yield 67%; mp. 106-108 ^oC; λ_{max}: 205, 233, nm; IR (KBr) ν_{max}: 1704, 1643, 1439, 1222 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) : δ 2.20 (s, 3H, -C**H**$_3$), 2.27 (s, 3H, -C**H**$_3$), 2.31 (s, 3H, -C**H**$_3$), 1.70 (s, 3H, C_{11a}-C**H**$_3$), 2.60 (dd, *J* 9.9, 13.5 Hz, 1H, C_6-**H**), 2.90 (dd, *J* 3.9, 13.5 Hz, 1H, C_6-**H**), 3.29 (dd, *J* 3.9, 9.9 Hz, 1H, C_{6a}-**H**), 5.88 (s, 1H, C_4-**H**), 6.54-6.62 (m, 2H, Ar**H**); MS m/z 314 (M^+); Anal Calcd. for $C_{18}H_{18}O_3S$: C, 68.77; H, 5.77. Found C, 68.59; H, 5.52%.

Compound (15d). Yield 60%; Gummy mass; λ_{max}: 211, 255, nm; IR (KBr) ν_{max}: 1690, 1620, 1430, 1240 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) : δ 2.18 (s, 3H, C_3-C**H**$_3$), 1.81 (s, 3H, C_{11a}-C**H**$_3$), 2.81 (dd, *J* 9.9, 13.5 Hz, 1H, C_6-**H**), 3.02 (dd, *J* 3.9, 13.5 Hz, 1H, C_6-**H**), 3.48 (dd, *J* 3.9, 9.9 Hz, 1H, C_{6a}-**H**), 5.82 (s, 1H, C_4-**H**), 6.93-7.39 (m, 4H, Ar**H**); MS m/z 286 (M^+); Anal Calcd. for $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93. Found C, 67.28; H, 5.02%.

Compound (15e). Yield 63%; mp. 130-131 ^oC; UV(EtOH) λ_{max}: 211, 254, nm; IR (KBr) ν_{max}: 1690, 1620, 1450, 1240 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) : δ 2.17 (s, 3H, -C**H**$_3$), 2.23 (s, 3H, -C**H**$_3$), 1.79 (s, 3H, C_{11a}-C**H**$_3$), 2.76 (dd, *J* 9.9, 13.5 Hz, 1H, C_6-**H**), 2.98 (dd, *J* 3.9, 13.5 Hz, 1H, C_6-**H**), 3.40 (dd, *J* 3.9, 9.9 Hz, 1H, C_{6a}-**H**), 5.82 (s, 1H, C_4-**H**), 6.82-6.84 (m, 1H, Ar**H**), 6.96-7.02 (m, 2H, Ar**H**), MS m/z 300 (M^+); Anal Calcd. for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37. Found C, 68.16; H, 5.22%.

Compound (16d). Yield 10%; mp. 88-89 ^oC; UV(EtOH) λ_{max}: 213, 260, nm; IR (KBr) ν_{max}: 1690, 1620, 1450, 1230 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) : δ 2.19 (s, 3H, -C**H**$_3$), 2.99 (t, *J* 6 Hz, 2H, =CC**H**$_2$), 3.05 (t, *J* 6 Hz, 2H, -SC**H**$_2$), 5.85 (s, 1H, C_8-**H**), 7.05-7.34 (m, 5H, Ar**H**), 8.20 (s, 1H, C=C**H**OAr); MS m/z 286 (M^+); Anal Calcd. for $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93. Found C, 67.27; H, 4.78%.

Compound (16e). Yield 12%; mp. 92-93 ^oC; UV(EtOH) λ_{max}: 213, 259, nm; IR (KBr) ν_{max}: 1690, 1620, 1450, 1230 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) : δ 2.18 (s, 3H, -C**H**$_3$), 2.31 (s, 3H, -C**H**$_3$), 3.01 (t, *J* 6 Hz, 2H, =CC**H**$_2$), 3.04 (t, *J* 6 Hz, 2H, -SC**H**$_2$), 5.84 (s, 1H, C_8-**H**), 6.89-6.99 (m, 2H, Ar**H**), 7.03-7.11 (m, 2H, Ar**H**), 8.16 (s, 1H, C=C**H**OAr); MS m/z 300 (M^+); Anal Calcd. for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37. Found C, 68.17; H, 5.13%.

Compound (16f). Yield 15%; Gummy mass; UV(EtOH) λ_{max}: 213, 259, nm; IR (KBr) ν_{max}: 1690, 1620, 1450, 1230 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) : δ 2.19 (s, 3H, -C**H**$_3$), 2.98 (t, *J* 6 Hz, 2H, =CC**H**$_2$), 3.05 (t, *J* 6 Hz, 2H, -SC**H**$_2$), 5.86 (s, 1H, C_8-**H**), 6.93-7.05 (m, 2H, Ar**H**), 7.14-7.33 (m, 2H, Ar**H**), 8.14 (s, 1H, C=C**H**OAr); MS m/z 320, 322 (M^+); Anal Calcd. for $C_{16}H_{13}ClO_3S$: C, 59.91; H, 4.08. Found C, 59.82; H, 4.22%.

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