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# Studies in Sulfoxide Rearrangement: Regioselective Synthesis of Thieno[3,2-*f*]quinolin-7(6*H*)-one Derivatives.#

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***Abstract***: 6-Mercapto-1-methylquinolin-2(1*H*)-one (**3**) was prepared *in situ* by the reductive cleavage of the corresponding disulfide **2** with Zn dust and acid. The disulfide **2** was in turn prepared *via* xanthate after diazotisation of 6-amino-1-methylquinolin-2-(1*H*)-one (**1**). 6-(4-Aryloxybut-2-ynylthio)-1-methylquinolin-2(1*H*)-ones (**5a-e**) were prepared from thiol **3** and 1-aryloxy-4-chlorobut-2-ynes (**4**). The sulfides **5a-e** were then converted into the corresponding sulfoxides **6a-e** by treatment with one equivalent of *m*-CPBA in $CH_2Cl_2$ at 0-5°C for 30 min. The sulfoxides **6a-e** were refluxed in $CCl_4$ for 1 h to give the monothio-hemiacetals **7a-e** in almost quantitative yields which were then converted into the 1-aryloxyacetyl-1,2-dihydro-6-methylthieno[3,2-*f*]quinolin-7(6*H*)-ones (**11a-e**) in almost quantitative yields by simply dissolving in absolute MeOH. Dehydrogenative elimination of product **11a-e** when treated with acid generates 1-acetyl-6-methylthieno[3,2-*f*]quinolin-7(6*H*)-one (**12**) in 70-76% yield.


The construction of the five-membered heterocyclic ring in benzo(*b*)thiophenes and indoles through rearrangements of arylpropynyl sulfoxides[1-3] and arylpropynylamine oxides[4-6] respectively was shown by Thyagarajan and Majumdar to be an excellent high yield one-step process. Later Makisumi et al synthesized naphthothiophenes[7] from allylnaphthyl sulfoxides through the same protocol. This protocol when applied to selenium analogues[8] proceeded with different results. Recently we have reported some applications of the amine oxide rearrangement[9-11] in heterocyclic substrates to the synthesis of a number of tricyclic skeletons. Whilst amine oxide rearranged in $CH_2Cl_2$ at room temperature, the corresponding sulfoxides required refluxing in $CCl_4$. The intermediacy of [2,3] and [3,3] sigmatropic rearrangements in this methodology results in negligible charge build up in the aromatic ring and the reaction proceeds with extreme facility even in the presence of electron-withdrawing groups. We became interested to see whether the five-membered thiophene ring in thienoquinolone system[12-14] could be constructed *via* the aforesaid sulfoxide rearrangement. Here we report the results of this investigation.

The starting materials chosen for this study, 6-(4-aryloxybut-2-ynylthio)-1-methylquinolin-2(1*H*)-ones were prepared in 85-94 % yields by the reaction of 6-mercapto-1-methylquinolin-2(1*H*)-one (**3**) (unstable) with

#This paper is dedicated to Professor (Mrs.) Asima Chatterjee of the University of Calcutta on the occasion of her 80th birth anniversary.

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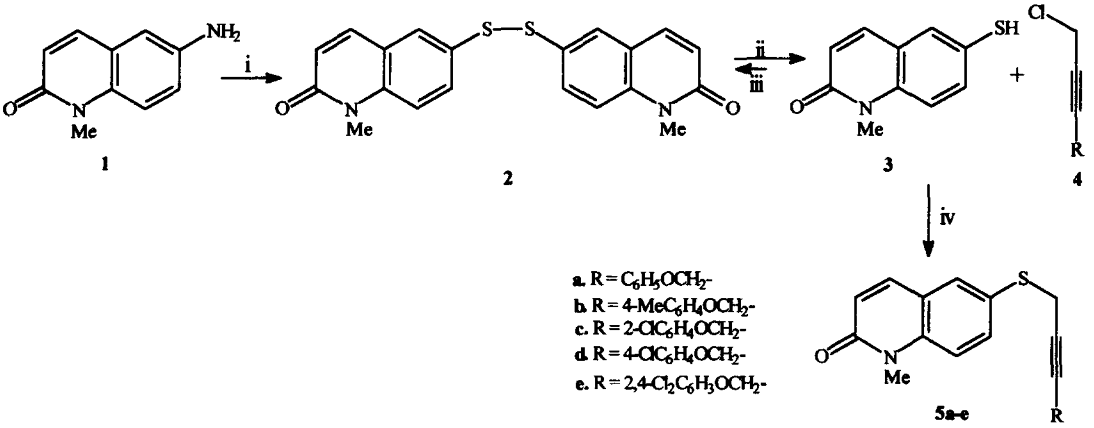
1-aryloxy-4-chlorobut-2-ynes (**4**) in refluxing $Me_2CO$ in the presence of anhyd $K_2CO_3$ and NaI (Finkelstein conditions) for 2 h (Scheme 1). The sulfides were contaminated with the corresponding disulfide, **2** (3-5 %) and were purified by column chromatography over silica gel.

6-Mercapto-1-methylquinolin-2(1*H*)-one was prepared *in situ* by the reductive cleavage of the corresponding disulfide **2** with Zn dust and a mixture of 6N $H_2SO_4$ and acetic acid at 80 $^0$C. The disulfide **2** was in turn prepared from 6-amino-1-methylquinolin-2(1*H*)-one[15] (**1**) by diazotisation and reaction with potassium ethyl xanthate[16] followed by hydrolysis of the xanthate. 6-Mercapto-1-methylquinolin-2(1*H*)-one (**3**) is unstable and converted into disulfide (**2**) on standing at room temperature (Scheme 1).

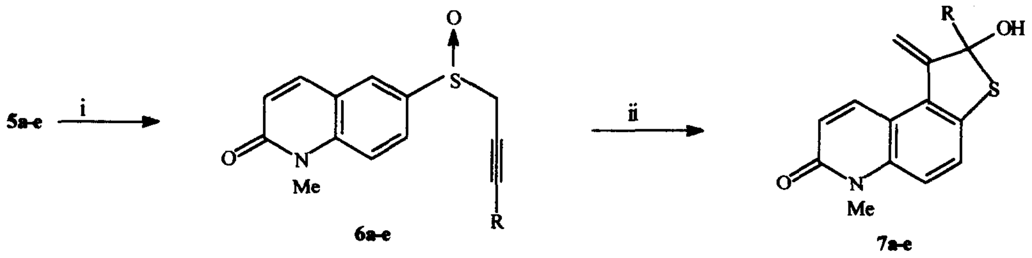



**Reagents:** i. $HCl/NaNO_2$, potassium ethyl xanthate, EtOH-KOH; ii. Zn dust; 6N $H_2SO_4$ + $CH_3COOH$; iii. rt; iv. $Me_2CO_3$-$K_2CO_3$, NaI, refluxed, 2 h.

**Scheme 1**

**Results and Discussion:**

The sulfoxides **6a-e** were prepared by slow addition of one equivalent of *m*-CPBA in $CH_2Cl_2$ to a solution of the sulfides **5a-e** in the same solvent over 30 min (Scheme 2).

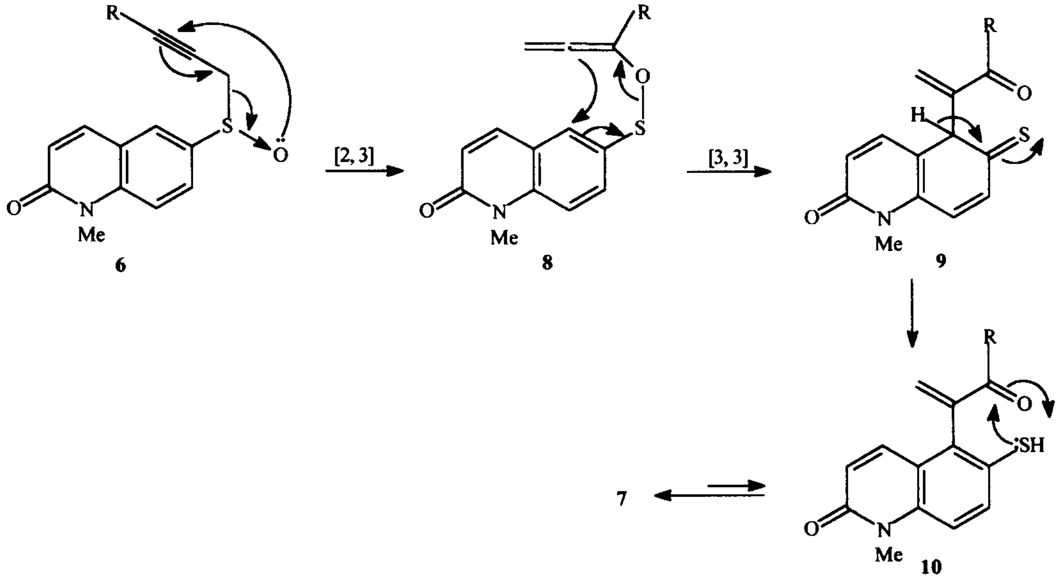


**Reagents:** i. *m*-CPBA, $CH_2Cl_2$, 0-5 $^0$C; ii. $CCl_4$, reflux, 2 h.

**Scheme 2**

Refluxing the sulfoxide **6a** in dry $CCl_4$ effected significant changes in the molecule leading to the quantitative formation of a new compound. Elemental analysis and mass spectral data confirmed that the product was isomeric with the starting sulfoxide. The $^1$H-NMR and IR spectra indicated the presence of a terminal olefin and hydroxyl function but no evidence of the sulfoxide or acetylenic linkage. Monothio-hemiacetal structure **7a** is assigned for the product on the basis of spectral data. The other substrates **6b-e** were also subjected to thermal rearrangement and products **7b-e** were obtained in 93-96 % yields (Scheme 2).

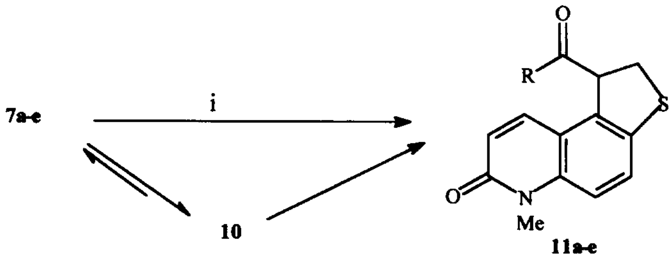
The formation of **7a-e** from the sulfoxides **6a-e** is easily explained by initial [2,3] sigmatropic rearrangement of the sulfoxides **6** to give intermediates **8** which then undergo a [3,3] sigmatropic rearrangement followed by enolisation leading to intermediate thiol **10** containing an enone moiety favorably juxtaposed for the formation of the product monothio-hemiacetals **7** (Scheme 3).




**Scheme 3**

Here the monothio-hemiacetals **7** are stable unlike in the case of the amine oxide rearrangement. The monothio-hemiacetals **7a-e** were easily converted into the corresponding 1-aryloxyacetyl-1,2-dihydro-6-methylthieno[3,2-*f*]quinolin-7(6*H*)-ones (**11a-e**) by simply dissolving in absolute MeOH *via* internal Michael addition of the thiol to the enone moiety in **10** (Scheme 4). The monothio-hemiacetals **7a-e** seem to be reactive towards internal Michael addition. In earlier cases[1,2] trituration with 20 % NaOH was necessary to achieve this internal Michael addition. Here simply dissolution of the monothio-hemiacetals **7** in absolute MeOH is quite satisfactory for carrying out this conversion.

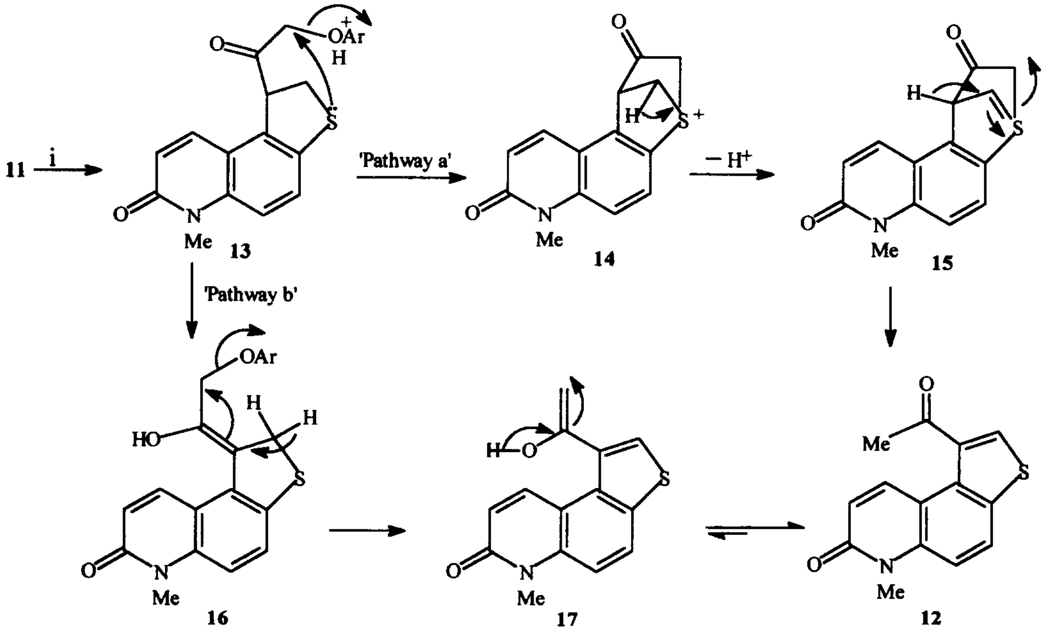
The products **11a-e** upon refluxing in acetic acid with catalytic amount of conc. $H_2SO_4$ for 4 h afforded




**Reagents:** i. MeOH, heat, 30 min.

**Scheme 4**

1-acetyl-6-methylthieno[3,2-*f*]quinolin-7(6*H*)-one (**12**) in 70-76 % yield. The facile loss of the aryloxy moiety by this unusual dehydrogenative elimination[17] is interesting. Different mechanistic pathways could be visualized (Scheme 5). Protonation of aryloxy oxygen and neighbouring group participation of sulfur may lead to intermediate **14** which may finally give product **12** (pathway a) or initial enolization of the ketone on the benzylic carbon side could trigger the loss of proton α to the sulfur and give the product **12** (pathway b).




**Reagents:** i. $CH_3COOH$, $H_2SO_4$, reflux, 4 h.

**Scheme 5**

The peracid does not seem to affect the 3,4-$\pi$ bond of the quinolinone (**5**). The generality of the reaction is demonstrated by the synthesis of a number of thieno[3,2-*f*]quinolin-7(6*H*)-ones **11a-e** utilising this method. Thus in two steps from the sulfoxides, the thieno[3,2-*f*]quinolin-7(6*H*)-ones are obtained in excellent overall yields. This provides an excellent synthetic approach to these compounds. This is also the first application of the sulfoxide rearrangement in a heterocyclic system.

**Experimental:**

Melting points are uncorrected. IR spectra were run for KBr discs. UV absorption spectra were recorded in absolute EtOH. $^1$H-NMR spectra were determined for solutions in $CDCl_3$ with TMS as internal standard. Elemental analyses and recording of mass spectra were carried out by RSIC (CDRI), Lucknow. Silica gel (60-120 mesh) was used for chromatographic separation.

The 1-aryloxy-4-chlorobut-2-ynes were prepared according to the published procedures.[2,5,11,17]

**Procedure for the Preparation of 1-Methylquinolin-2(1*H*)-on-6-yl disulfide:**

In a 100 ml beaker equipped with a stirrer and a thermometer immersed in an ice bath are placed conc. HCl (4 ml, sp. gr. 1.18) and crushed ice (6 g). 6-Amino-1-methylquinolin-2(1*H*)-one (2 g, 11.5 mmol) was slowly added while stirring. The mixture was cooled to 0 $^0$C and a cold solution of $NaNO_2$ (2.5 g) in $H_2O$ (5 ml) was slowly added and the temperature was kept below 4 $^0$C. In a 250 ml flask equipped with magnetic stirrer was placed a solution of potassium ethyl xanthate (5 g) in $H_2O$ (10 ml). This mixture was warmed to 40-45 $^0$C and kept in that range during the slow addition (~2 h) of the cold diazonium solution. It was kept at this temperature for an additional 30 min. to ensure complete decomposition of the intermediate. This reaction mixture was extracted with $CHCl_3$ (3x50 ml) and the extract was washed with $H_2O$ (3x30 ml) and dried ($Na_2SO_4$). Evaporation of $CHCl_3$ gave a crude solid. This was dissolved in EtOH (20 ml) and the solution was boiled and to this hot solution solid KOH (6 g) slowly added so as to keep the solution boiling. The reaction mixture was then refluxed for 1 h. This was then acidified with 6N $H_2SO_4$ (25 ml). This was extracted with $CHCl_3$ (3x50 ml), washed with water (3x30 ml) and dried ($Na_2SO_4$). Evaporation of $CHCl_3$ gave a crude solid, 1-methylquinolin-2(1*H*)-on-6-yl disulfide (**2**). This may be used without further purification in the subsequent reaction for the preparation of sulfides. However, analytical sample was prepared by column chromatographic purification over silica gel. The column was eluted with benzene-ethyl acetate (1:1) to give compound **2**, yield 75 %; mp 222 $^0$C; $\lambda_{max}$/nm 246 (log $\varepsilon$ 4.33), 266 (log $\varepsilon$ 4.10), 340 (log $\varepsilon$ 3.64); $\nu_{max}$/cm$^{-1}$ 1645, 1570, 1412; $\delta_H$ (330 MHz) 3.70 (s, 6H), 6.74 (d, J = 9.5 Hz, 2H), 7.27 (s, 1H), 7.32 (d, J = 9.5 Hz, 2H), 7.59 (d, J = 9.5 Hz, 2H), 7.66 (s, 2H), 7.69 (d, J = 1.5 Hz, 1H); m/z 380 ($M^+$); (Found: C, 62.99; H, 4.07; N, 7.54. $C_{20}H_{16}N_2O_2S_2$ requires C, 63.15; H, 4.24; N, 7.37 %).

**General Procedure for the Preparation of 6-(4-Aryloxybut-2-ynylthio)-1-methylquinolin-2(1*H*)-ones, 5a-e:**

The crude disulfide (1 g, 2.6 mmol) was dissolved in 6N $H_2SO_4$ (20 ml) then added Zn dust (1 g) and acetic acid (15 ml). This reaction mixture was heated on water bath until the reaction mixture became clear. The reaction mixture was extracted with $CHCl_3$ (3x25 ml), then washed with water (3x20 ml) and dried ($Na_2SO_4$). Evaporation of solvent gave a viscous liquid, 6-mercapto-1-methylquinolin-2(1*H*)-one (unstable) which was refluxed with the corresponding 1-aryloxy-4-chlorobut-2-yne (2.5 mmol) in dry $Me_2CO$ (100 ml) in the presence of anhyd $K_2CO_3$ (1 g) and catalytic amount of NaI for 2 h. After cooling, the solvent was removed from the filtrate. The residual mass was extracted with $CHCl_3$ (3x25 ml). The extract was washed with saturated brine (3x20 ml), water (20 ml) and dried ($Na_2SO_4$). Evaporation of $CHCl_3$ gave a crude viscous liquid which was purified by column chromatography over silica gel. The column was eluted with $C_6H_6$-ethyl acetate (3:1) to furnish the sulfides **5a-e**.

**1-Methyl-6-(4-phenoxybut-2-ynylthio)quinolin-2(1*H*)-one (5a),** yield 90 %; Viscous liquid; $\lambda_{max}$/nm 241 (log ε 4.14), 330 (log ε 3.33); $\nu_{max}$/cm$^{-1}$ 3050, 2940, 1640, 1570, 1475, 1410; $\delta_H$ (100 MHz) 3.64 (t, J = 2 Hz, 2H) 3.69 (s, 3H), 4.67 (t, J = 2 Hz, 2H), 6.70 (d, J = 9.5 Hz, 1H), 6.84-7.06 (m, 3H), 7.14-7.37 (m, 3H), 7.44-7.78 (m, 3H); m/z 335 ($M^+$); (Found: C, 71.45; H, 4.97; N, 4.04. $C_{20}H_{17}NO_2S$ requires C, 71.62; H, 5.11; N, 4.18 %).

**1-Methyl-6-[4-(4′-methylphenoxy)but-2-ynylthio]quinolin-2(1*H*)-one (5b),** yield 85 %; Viscous liquid; $\lambda_{max}$/nm 230 (log ε 4.53), 336 (log ε 3.71); $\nu_{max}$/cm$^{-1}$ 3010, 2900, 1640, 1565, 1490, 1403, 1495; $\delta_H$ (100 MHz) 2.26 (s, 3H), 3.63 (t, J = 2 Hz, 2H) 3.68 (s, 3H), 4.63 (t, J = 2 Hz, 2H), 6.69 (d, J = 9.5 Hz, 1H), 6.87 (d, J = 2.5 Hz, 1H), 7.04 (dd, J = 9.5, 2.5 Hz, 2H), 7.22 (d, J = 9.5 Hz, 1H), 7.44-7.71 (m, 4H); m/z 349 ($M^+$); (Found: C, 72.03; H, 5.29; N, 3.89. $C_{21}H_{19}NO_2S$ requires C, 72.18; H, 5.48; N, 4.01 %).

**6-[4-(2′-Chlorophenoxy)but-2-ynylthio]-1-methylquinolin-2(1*H*)-one (5c),** yield 89 %; Viscous liquid; $\lambda_{max}$/nm 237 (log ε 4.35), 336 (log ε 3.55); $\nu_{max}$/cm$^{-1}$ 3055, 2935, 1640, 1570, 1475, 1415; $\delta_H$ (100 MHz) 3.63 (t, J = 2 Hz, 2H) 3.69 (s, 3H), 4.74 (t, J = 2 Hz, 2H), 6.70 (d, J = 9.5 Hz, 1H), 6.84-7.42 (m, 5H), 7.46-7.74 (m, 3H); m/z 371, 369 ($M^+$); (Found: C, 65.14; H, 4.21; N, 3.65. $C_{20}H_{16}ClNO_2S$ requires C, 65.03; H, 4.37; N, 3.79 %).

**6-[4-(4′-Chlorophenoxy)but-2-ynylthio]-1-methylquinolin-2(1*H*)-one (5d),** yield 90 %; Viscous liquid; $\lambda_{max}$/nm 230 (log ε 4.19), 340 (log ε 3.33); $\nu_{max}$/cm$^{-1}$ 3040, 2920, 1640, 1570, 1480, 1410; $\delta_H$ (100 MHz) 3.64 (t, J = 2 Hz, 2H) 3.70 (s, 3H), 4.65 (t, J = 2 Hz, 2H), 6.66-6.90 (m, 3H), 7.12-7.30 (m, 3H), 7.46-7.69 (m, 3H); m/z 371, 369 ($M^+$); (Found: C, 64.89; H, 4.50; N, 3.92. $C_{20}H_{16}ClNO_2S$ requires C, 65.03; H, 4.37; N, 3.79 %).

**6-[4-(2′,4′-Dichlorophenoxy)but-2-ynylthio]-1-methylquinolin-2(1*H*)-one (5e),** yield 92 %; mp 138 $^0$C; $\lambda_{max}$/nm 207 (log ε 4.55), 235 (log ε 4.49), 347 (log ε 3.57); $\nu_{max}$/cm$^{-1}$ 3070, 2930, 1645, 1575, 1475, 1410;

$\delta_H$ (100 MHz) 3.64 (t, J = 2 Hz, 2H) 3.72 (s, 3H), 4.74 (t, J = 2 Hz, 2H), 6.73 (d, J = 9.5 Hz, 1H), 6.86 (d, J = 9.5 Hz, 1H), 7.05 (dd, J = 9.5, 2.5 Hz, 1H), 7.18-7.38 (m, 2H), 7.49-7.69 (m, 3H); m/z 407, 405, 403 ($M^+$); (Found: C, 59.72; H, 3.59; N, 3.61. $C_{20}H_{15}Cl_2NO_2S$ requires C, 59.55; H, 3.75; N, 3.47 %).

**General Procedure for the Oxidation and Rearrangement of 6-(4-Aryloxybut-2-ynylthio)-1-methylquinolin-2(1*H*)-one, 5a-e:**

*m*-CPBA (0.345 g, 50 %, 1 mmol) in $CH_2Cl_2$ (50 ml) was slowly added to a well stirred solution of 6-(4-aryloxybut-2-ynylthio)-methylquinolin-2(1*H*)-one (1 mmol) in $CH_2Cl_2$ (30 ml) at 0-5 $^0$C over a period of 30 min. The mixture was stirred for half an hour more. Some *m*-chlorobenzoic acid separated as insoluble solid at 0 $^0$C. After the completion of the reaction, the solution was washed with 5 % $Na_2CO_3$ solution to remove the organic acid, water (3x50 ml) and dried ($Na_2SO_4$). Removal of solvent gave sulfoxide as a yellow solid which is very unstable. Only one sulfoxide (**6e**) could be secured in pure form, mp 136 $^0$C; $\lambda_{max}$/nm 209 (log ε 4.14), 248 (log ε 4.30), 331 (log ε 3.48); $\nu_{max}$/cm$^{-1}$ 3045, 2940, 1645, 1585, 1485; $\delta_H$ (300 MHz) 3.72 (t, J = 2 Hz, 2H), 3.74 (s, 3H), 4.72 (t, J = 2 Hz, 2H), 6.78 ( d, J = 9.5 Hz, 1H), 6.85 (d, J = 9.5 Hz, 1H), 7.11 (dd, J = 9.5, 2.5 Hz, 1H), 7.34-7.40 (m, 2H), 7.65 (d, J = 9.5 Hz, 1H), 7.73 (dd, J = 9.5, 2.5 Hz, 1H), 7.86 (d, J = 2.5 Hz, 1H). These sulfoxide (yellow solids) were refluxed in $CCl_4$ (20 ml) for 1 h. The solution was cooled, causing a yellow crystalline solid **7a-e** to precipitate in quantitative yield.

**1,2-Dihydro-2-hydroxy-6-methyl-1-methylene-2-(phenoxymethyl)thieno[3,2-*f*]quinolin-7(6*H*)-one (7a),** yield 92 %; mp 160 $^0$C; $\lambda_{max}$/nm 207 (log ε 4.17), 260 (log ε 4.18); $\nu_{max}$/cm$^{-1}$ 3200, 2910, 1622, 1585, 1545, 1400; $\delta_H$ (100 MHz) 3.72 (s, 3H), 3.89 (s, 1H, -**OH**, exchangeable with $D_2O$), 4.26 (d, J = 10 Hz, 1H), 4.38 (d, J = 10 Hz, 1H), 5.92 (s, 1H), 5.98 (s, 1H), 6.76 (d, J = 9.5 Hz, 1H), 6.86-7.07 (m, 3H), 7.19-7.43 (m, 4H), 8.20 (d, J = 9.5 Hz, 1H); m/z 351 ($M^+$); (Found: C, 68.55; H, 5.01; N, 4.12. $C_{20}H_{17}NO_3S$ requires C, 68.36; H, 4.88; N, 3.99 %).

**1,2-Dihydro-2-hydroxy-6-methyl-1-methylene-2-(4′-methylphenoxymethyl)thieno[3,2-*f*]quinolin-7(6*H*)-one (7b),** yield 96 %; mp 140 $^0$C; $\lambda_{max}$/nm 206 (log ε 4.08), 260 (log ε 4.09); $\nu_{max}$/cm$^{-1}$ 3220, 1630, 1590, 1550, 1410; $\delta_H$ (100 MHz) 2.26 (s, 3H), 3.71 (s, 3H), 3.82 (s, 1H, -**OH**, exchangeable with $D_2O$), 4.22 (d, J = 10 Hz, 1H), 4.34 (d, J = 10 Hz, 1H), 5.91 (s, 1H), 5.97 (s, 1H), 6.68-6.88 (m, 3H), 6.99-7.16 (m, 2H), 7.24-7.44 (m, 2H), 8.20 (d, J = 9.5 Hz, 1H); m/z 365 ($M^+$); (Found: C, 69.21; H, 5.41; N, 3.62. $C_{21}H_{19}NO_3S$ requires C, 69.02; H, 5.24; N, 3.84 %).

**2-(2′-Chlorophenoxymethyl)-1,2-dihydro-2-hydroxy-6-methyl-1-methylenethieno[3,2-*f*]quinolin-7(6*H*)-one (7c),** yield 93 %; mp 146 $^0$C; $\lambda_{max}$/nm 206 (log ε 4.21), 254 (log ε 4.10); $\nu_{max}$/cm$^{-1}$ 3230, 1632, 1545, 1470; $\delta_H$ (100 MHz) 3.72 (s, 3H), 3.86 (s, 1H, -**OH**, exchangeable with $D_2O$), 4.28 (d, J = 10 Hz, 1H), 4.44 (d, J = 10 Hz, 1H), 5.93 (s, 1H), 6.02 (s, 1H), 6.68-7.04 (m, 3H), 7.08-7.44 (m, 4H), 8.20 (d, J = 9.5 Hz, 1H); m/z 387, 385 ($M^+$); (Found: C, 62.21; H, 4.00; N, 3.49. $C_{20}H_{16}ClNO_3S$ requires C, 62.33; H, 4.19; N, 3.64 %).

**2-(4$'$-Chlorophenoxymethyl)-1,2-dihydro-2-hydroxy-6-methyl-1-methylenethieno[3,2-*f*]quinolin-7(6*H*)-one (7d)**, yield 96 %; mp 146 $^0$C; $\lambda_{max}$/nm 207 (log ε 4.31), 227 (log ε 4.38), 260 (log ε 4.40), 376 (log ε 3.45; $\nu_{max}$/cm$^{-1}$ 3220, 2910, 1630, 1545, 1475; $\delta_H$ (100 MHz) 3.71 (s, 3H), 3.85 (s, 1H, OH, exchangeable with $D_2O$), 4.25 (d, J = 10 Hz, 1H), 4.38 (d, J = 10 Hz, 1H), 5.92 (s, 1H), 5.99 (s, 1H), 6.68-6.89 (m, 3H), 7.16-7.42 (m, 4H), 8.19 (d, J = 9.5 Hz, 1H); m/z 387, 3.85 ($M^+$); (Found: C, 62.50; H, 4.31; N, 3.79. $C_{20}H_{16}ClNO_3S$ requires C, 62.33; H, 4.19; N, 3.64 %).

**2-(2$'$,4$'$-Dichlorophenoxymethyl)-1,2-dihydro-2-hydroxy-6-methyl-1-methylenethieno[3,2-*f*]quinolin-7(6*H*)-one (7e)**, yield 95 %; mp 188 $^0$C; $\lambda_{max}$/nm 207 (log ε 4.48), 254 (log ε 4.32), 373 (log ε 3.35); $\nu_{max}$/cm$^{-1}$ 3240, 2910, 1630, 1545, 1465; $\delta_H$ (100 MHz) 3.69 (s, 3H), 3.82 (s, 1H, -OH, exchangeable with $D_2O$), 4.24 (d, J = 10 Hz, 1H), 4.39 (d, J = 10 Hz, 1H), 5.92 (s, 1H), 6.01 (s, 1H), 6.72 (d, J = 9.5 Hz, 1H), 6.84 (d, J = 9.5 Hz, 1H), 7.08 (d, J=2.5 1H), 7.16-7.46 (m, 3H), 8.17 (d, J = 9.5 Hz, 1H); m/z 423, 421, 419 ($M^+$); (Found: C, 57.09; H, 3.76; N, 3.46. $C_{20}H_{15}Cl_2NO_3S$ requires C, 57.28; H, 3.61; N, 3.34 %).

**Procedure for Internal Michael addition, Conversion of Product 7 to 11:**

The compounds **7a-e** (1 mmol) were simply refluxed in dry methanol (5 ml) over the period of 30 min. After cooling, the solid crystalline compounds **11a-e** precipitated out in almost quantitative yields.

**1,2-Dihydro-6-methyl-1-(phenoxyacetyl)thieno[3,2-*f*]quinolin-7(6*H*)-one (11a)**, yield 93 %; mp 158 $^0$C; $\lambda_{max}$/ nm 225 (log ε 4.09), 253 (log ε 4.18), 266 (log ε 4.23), 378 (log ε 3.55); $\nu_{max}$/cm$^{-1}$ 1700, 1650, 1570, 1480, 1445; $\delta_H$ (300 MHz) 3.59 (dd, J = 12, 1.5 Hz, 1H), 3.64 (s, 3H), 3.89 (dd, J = 12, 9 Hz, 1H), 4.55 (d, J = 17 Hz, 1H), 4.76 (d, J = 17 Hz, 1H), 4.84 (dd, J = 9, 1.5 Hz, 1H), 6.66 (d, J = 9.5 Hz, 1H), 6.76 (d, J = 9.5 Hz, 2H), 6.88-6.99 (m, 1H), 7.12-7.26 (m, 3H), 7.30-7.42 (m, 2H); m/z 351 ($M^+$); (Found: C, 68.16; H, 5.04; N, 4.13. $C_{20}H_{17}NO_3S$ requires C, 68.36; H, 4.88; N, 3.99 %).

**1,2-Dihydro-6-methyl-1-(4$'$-methylphenoxyacetyl)thieno[3,2-*f*]quinolin-7(6*H*)-one (11b)**, yield 96 %; mp 150 $^0$C; $\lambda_{max}$/nm 224 (log ε 4.31), 252 (log ε 4.33), 266 (log ε 4.37), 378 (log ε 3.61); $\nu_{max}$/cm$^{-1}$ 1710, 1642, 1570, 1500, 1430; $\delta_H$ (300 MHz) 2.31 (s, 3H), 3.67 (dd, J = 12, 1.5 Hz, 1H), 3.78 (s, 3H), 3.86 (dd, J = 12, 9 Hz, 1H), 4.60 (d, J = 17 Hz, 1H), 4.87 (d, J = 17 Hz, 1H), 4.95 (dd, J = 9, 1.5 Hz, 1H), 6.67-6.80 (m, 3H), 7.10 (d, J = 9.5 Hz, 2H), 7.30 (d, J = 9.5 Hz, 1H), 7.40-7.54 (m, 2H); m/z 365 ($M^+$); (Found: C, 69.25; H, 5.39; N, 3.68. $C_{21}H_{19}NO_3S$ requires C, 69.02; H, 5.24; N, 3.84 %).

**1-(2$'$-Chlorophenoxyacetyl)-1,2-dihydro-6-methylthieno[3,2-*f*]quinolin-7(6*H*)-one (11c)**, yield 95 %; mp 178 $^0$C ; $\lambda_{max}$/nm 225 (log ε 4.38), 252 (log ε 4.43), 266 (log ε 4.46), 378 (log ε 3.72); $\nu_{max}$/cm$^{-1}$ 1705, 1640, 1570, 1485, 1440; $\delta_H$ (300 MHz) 3.71 (dd, J = 12, 1.5 Hz, 1H), 3.74 (s, 3H), 4.04 (dd, J = 12, 9 Hz, 1H), 4.70 (d, J = 17 Hz, 1H), 4.87 (d, J = 17 Hz, 1H), 5.10 (dd, J = 9, 1.5 Hz, 1H), 6.77 (d, J = 9.5 Hz, 2H), 6.90-7.05 (m, 1H), 7.15-7.25 (m, 1H), 7.33 (d, J = 9.5 Hz, 1H), 7.42 (dd, J = 9.5, 2.5 Hz, 1H), 7.45-7.52 (m, 2H); m/z 387, 385 ($M^+$); (Found: C, 62.16; H, 3.99; N, 3.81. $C_{20}H_{16}ClNO_3S$ requires C, 62.33; H, 4.19; N, 3.64 %).

**1-(4′-Chlorophenoxyacetyl)-1,2-dihydro-6-methylthieno[3,2-*f*]quinolin-7(6*H*)-one (11d),** yield 95 %; mp 164 $^0$C; $\lambda_{max}$/nm 226 (log ε 4.39), 252 (log ε 4.35), 266 (log ε 4.38), 378 (log ε 3.76); $\nu_{max}$/cm$^{-1}$ 1710, 1645, 1570, 1480, 1435; $\delta_H$ (300 MHz) 3.63 (dd, J = 12, 1.5 Hz, 1H), 3.69 (s, 3H), 3.95 (dd, J = 12, 9 Hz, 1H), 4.55 (d, J = 17 Hz, 1H), 4.78 (d, J = 17 Hz, 1H), 4.83 (dd, J = 9, 1.5 Hz, 1H), 6.69-6.73 (m, 3H), 7.18-7.21 (m, 2H), 7.29 (d, J = 9.5 Hz, 1H), 7.44-7.49 (m, 2H); m/z 387, 385 ($M^+$); (Found: C, 62.52; H, 4.33; N, 3.49. $C_{20}H_{16}ClNO_3S$ requires C, 62.33; H, 4.19; N, 3.64 %).

**1-(2′,4′-Dichlorophenoxyacetyl)-1,2-dihydro-6-methylthieno[3,2-*f*]quinolin-7(6*H*)-one (11e),** yield 94 %; mp 212 $^0$C ; $\lambda_{max}$/nm 226 (log ε 4.06), 252 (log ε 4.08), 267 (log ε 4.12), 378 (log ε 3.67); $\nu_{max}$/cm$^{-1}$ 1700, 1650, 1568, 1475, 1440; $\delta_H$ (300 MHz) 3.62 (d, J = 12 Hz, 1H), 3.65 (s, 3H), 3.95 (dd, J = 12, 9 Hz, 1H), 4.59 (d, J = 17 Hz, 1H), 4.77 (d, J = 17 Hz, 1H), 4.95 (d, J = 9 Hz, 1H), 6.59 (d, J = 9.5 Hz, 1H), 6.70 (d, J = 9.5 Hz, 1H), 7.08 (dd, J = 9.5, 2.5 Hz, 1H), 7.25 (d, J = 9.5 Hz, 1H), 7.33 (d, J = 2.5 Hz, 1H), 7.40 (d, J = 9.5 Hz, 1H), 7.45 (d, J = 9.5 Hz, 1H); m/z 423, 421, 419 ($M^+$); (Found: C, 57.06; H, 3.75; N, 3.50. $C_{20}H_{15}Cl_2NO_3S$ requires C, 57.28; H, 3.61; N, 3.34 %).

**Dehydrogenative Elimination, Conversion of 11a-e to 12:**

The compound **11a-e** (0.5 mmol) was treated with acetic acid (2 ml) and catalytic amount of conc. $H_2SO_4$ (1 drop) for 4 h. After cooling the reaction mixture was poured into ice-water and was extracted with $CHCl_3$ (3x25 ml). The $CHCl_3$ extract was washed with brine (3x20 ml), water (20 ml) and dried ($Na_2SO_4$). The evaporation of solvent gave a crude mass which was subjected to column chromatography over silica gel. The column was eluted with benzene-ethyl acetate (3:1) to furnish product **12** which was recrystalised from $C_6H_6$.

**1-Acetyl-6-methylthieno[3,2-*f*]quinolin-7(6*H*)-one (12),** yield 70-76 %; mp 202 $^0$C; $\lambda_{max}$/nm 244 (log ε 4.04), 295 (log ε 3.95), 347 (log ε 3.65); $\nu_{max}$/cm$^{-1}$ 3035, 2890, 1620, 1525, 1430; $\delta_H$ (300 MHz) 2.78 (s, 3H), 3.84 (s, 3H), 6.78 (d, J = 9.5 Hz, 1H), 7.55 (d, J = 9.5 Hz, 1H), 8.00 (d, J = 9.5 Hz, 1H), 8.29 (s, 1H), 8.65 (d, J = 9.5 Hz, 1H); m/z 257 ($M^+$); (Found: C, 65.55; H, 4.45; N, 5.26. $C_{14}H_{11}NO_2S$ requires C, 65.36; H, 4.31; N, 5.45 %).

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**References.**

1. Majumdar, K. C.; Thyagarajan, B. S. *J. Chem. Soc., Chem. Commun.* **1972**, 83.

2. Majumdar, K. C.; Thyagarajan, B. S. *Int. J. Sulfur Chem., part A* **1972**, *2*, 93.
3. El-osta, B.; Majumdar, K. C.; Thyagarajan, B. S. *J. Heterocycl. Chem.* **1973**, *10*, 107.
4. Thyagarajan, B. S.; Hillard, J. B.; Reddy, K. V.; Majumdar, K. C. *Tetrahedron Lett.* **1974**, 1999.
5. Hillard, J. B.; Reddy, K. V.; Majumdar, K. C.; Thyagarajan, B. S. *J. Heterocyl. Chem.* **1974**, *11*, 369.
6. Majumdar, K. C.; Thyagarajan, B. S. *J. Heterocycl. Chem.*, **1974**, *12*, 43.
7. Makisumi, Y.; Takada, S. *J. Chem. Soc., Chem. Commun.* **1974, 848.**
8. Reich, H. J.; Shah, S. K. *J. Am. Chem. Soc.* **1977**, *99*, 263.
9. Majumdar, K. C.; Chattopadhyay, S. K. *J. Chem. Soc., Chem. Commun.* **1987**, 524.
10. Majumdar, K. C.; Chattopadhyay, S. K.; Khan, A. T. *J. Chem. Soc., Perkin Trans.* 1 **1989**, 1285.
11. Majumdar, K. C.; Ghosh, S. K. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2889.
12. Chapman, N. B.; Clarke, K.; Sharma, K. S. *J. Chem. Soc. (C)* **1970**, 2334.
13. Sharma, K. S.; Parsad, R.; Singh, V. *Indian J. Chem.* **1979**, *17B*, 342.
14. Fries, K.; Heering, H.; Hemmecke, E.; Siebert, G. *Ann.* **1937**, *527*, 83.
15. Majumdar, K. C.; Biswas, P.; Jana, G. H. *J. Chem. Research (S)* **1997**, 310; (M) 2068-2079.
16. Org. Synth. CV (III), page 809.
17. Majumdar, K. C.; Thyagarajan, B. S. *Int. J. Sulfur Chem., part A* **1972**, *2*, 67.