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Attempted Simmons-Smith Reaction on α-Oxoketene Dithioacetals: A New General Route to 3,4-Substituted and Annelated Thiophenes

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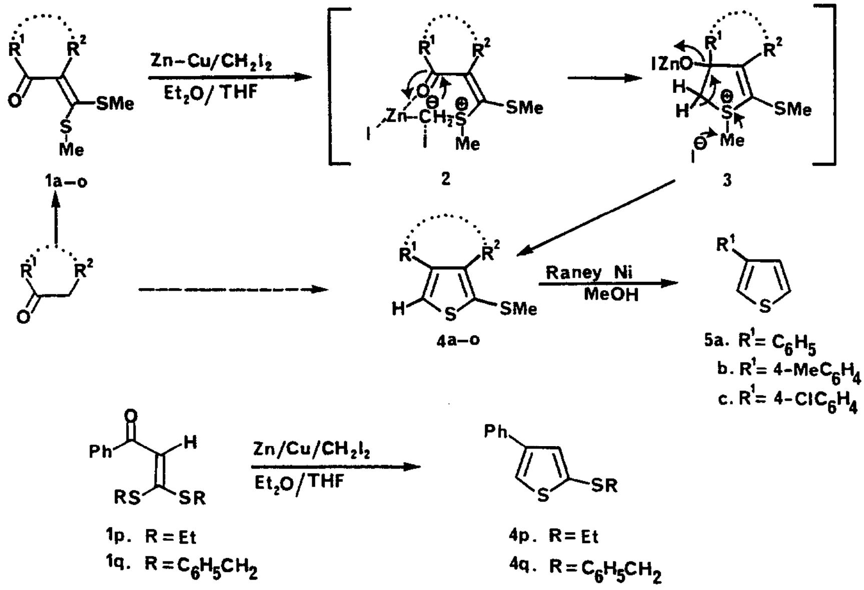
Abstract: *A new general synthesis of 3- and 3,4-substituted* ***4a-q****, 3,4-annelated* ***7a-d*** *and condensed tricyclic* ***9a-e*** *thiophenes has been developed through Simmons-Smith reaction on the respective α-oxoketene dithioacetals. Extension of the reaction to α-cinnamoylketene dithioacetals* ***10a-e*** *and its higher enyl analogs* ***13a-d, 15a-c*** *gave the corresponding 3-styryl* ***11a-e*** *and 3-di- and trienyl* ***14a-d, 16a-c*** *thiophenes in highly regioselective manner. A probable mechanism involving an unusual intramolecular aldol condensation of sulphonium ylid formed through carbenoid methylene insertion on divalent sulfur has been suggested.*

The Simmons-Smith cyclopropanation of olefins carrying a variety of functional groups including heteroatoms is well documented.[1] Thus vinyl ethers, enamines and ketene O,O-acetals are known to undergo facile cyclopropanation under these conditions.[2-3] However, the corresponding sulphur analogs such as vinyl sulphides and ketene S,S-acetals[3,4] have not similarly been examined, though the vinylsulphones appear to be the only sulfur substituted olefins which have been cyclopropanated under Simmons-Smith conditions. One reason for the lack of examples in this area could be attributed to the facile formation of sulfur ylids by electrophilic addition of carbenes and carbenoids to the divalent sulfur which may deviate the course of reaction from intended cyclopropanation of double bond.[5] As a part of our interest in the chemistry of α-oxoketene dithioacetals, we had discovered that these acetals under Simmons-Smith reaction condition, yield the corresponding thiophenes in high yields instead of the expected cyclopropanes or the products thereof. Apparantly, the divalent sulfur adds to carbenoid intermediate to form the corresponding ylid 2, which on intramolecular aldol type of addition-elimination sequence followed by demethylation of the quaternary sulphonium salt yields the product thiophenes (Scheme 1). These results were published in a preliminary communication [6] and in the present paper, we describe the full details of our studies on this new thiophene synthesis.

RESULTS AND DISCUSSION

In a typical experiment, **1a** was reacted with Simmons-Smith reagent prepared from methylene iodide/Zn-Cu couple in Et_2O/THF mixture to afford a pale yellow solid characterized as 2-methylthio-4-phenylthiophene **4a** in 61% yield. The structure and regiochemistry of **4a** was established by its spectral and analytical data and also by its independent synthesis according to the reported procedure by Marino and co-workers.[7] Raney Nickel dethiomethylation of **4a** under controlled

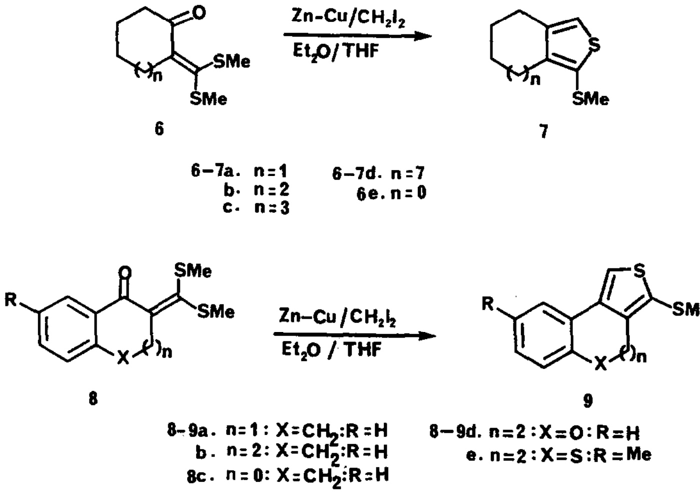


Scheme 1

Table 1. Synthesis of 3,4-Alkyl/Aryl-2-MethylthioThiophenes **4a-o**

Entry	St.material	Product	R^1	R^2	Yield %
1	1a	4a	C_6H_5	H	61
2	1b	4b	4-MeC_6H_4	H	64
3	1c	4c	4-ClC_6H_4	H	65
4	1d	4d	2-Furyl	H	58
5	1e	4e	2-Thienyl	H	63
6	1f	4f	C_6H_5	Me	59
7	1g	4g	C_6H_5	Et	58
8	1h	4h	C_6H_5	n-Pr	59
9	1i	4i	4-ClC_6H_4	$C_6H_5CH_2$	58
10	1j	4j	C_6H_5	C_6H_5	54
11	1k	4k	Me	H	53
12	1l	4l	Me	Me	56
13	1m	4m	Et	Me	58
14	1n	4n	Me	n-Bu	62
15	1o	4o	C_6H_5	Allyl	60

conditions, to the known thiophene **5a** further confirmed the structural assignment.[8] The other 4-aryl **4b-c**, 4-(2-furyl) **4d**, 4-(2-thienyl) **4e** thiophenes were similarly obtained from the respective ketene dithioacetals **1b-e** in good yields (Table 1). The thiophenes **4b-c** could also be dethiomethylated in the presence of Raney Nickel in good yields under controlled conditions. Entries 6-10 represent the extension of this methodology for the synthesis of 4-aryl-3-alkyl/arylthiophenes **4f-j** in 54-59% overall yields (Table 1) from the respective ketene dithioacetals. Similarly the ketene dithioacetal **1k-n** derived from aliphatic ketones gave the corresponding 4-methyl **4k** and 3,4-dialkylthiophenes **4l-n** in good yields (entries 11-14). Interestingly the isolated double bond in **1o** was not affected under the described reaction conditions and was carried over in the product thiophene **4o** (entry 15). Simmons-Smith reaction on the S-ethyl **1p** and S-benzyl **1q** ketene dithioacetals also followed similar course yielding 2-ethylthio **4p** and 2-benzylthio **4q** thiophenes in good yields (Scheme 1).



6–7a. n=1
b. n=2
c. n=3

6–7d. n=7
6e. n=0

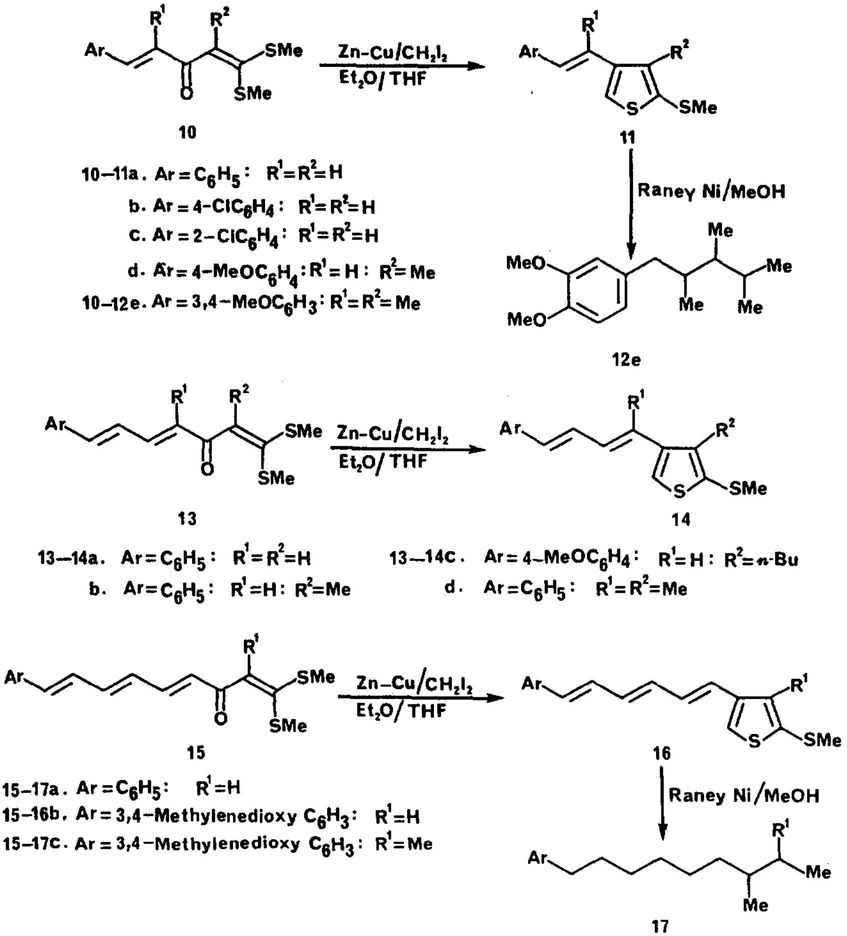
8–9a. n=1 : X=CH$_2$:R=H
b. n=2: X=CH$_2$:R=H
8c. n=0: X=CH$_2$:R=H

8–9d. n=2 :X=O:R=H
e. n=2 :X=S:R=Me

Scheme 2

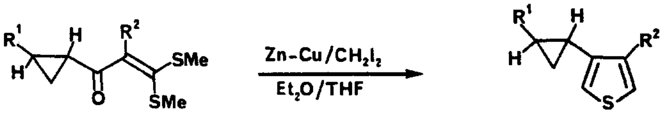
The methodology was found quite suitable for the synthesis of 3,4- annelated thiophenes (Scheme 2). The literature methods for the synthesis of 3,4-fused thiophenes are quite unsatisfactory involving multistep synthetic sequence with overall poor yields.[9,10] The present method should therefore prove superior since a large number of cyclic ketones could be converted into the corresponding annelated thiophenes. Thus **6a** derived from cyclohexanone underwent thiophene ring formation to afford 3,4-tetramethylene thiophene **7a** in 65% yield. Similarly the dithioacetals **6b-d** derived from cycloheptanone, cyclooctanone and cyclododecanone respectively yielded the corresponding 3,4-annelated thiophenes **7b-d** in 62-66% overall yields under the described conditions. The other condensed thiophenes **9a-b** and **9d-e** were similarly prepared from the corresponding **8a-b** and **8d-e** (Scheme 2) in good yields. It may be noted that the dithioacetal **8e** underwent a highly chemoselective participation of sulfur from mercapto functionality and no ring sulfur participation with the Simmons-Smith reagent was observed. The method however was found to be inefficient for thiophene annelation on a five membered ring. The dithioacetals **6e** and **8c** derived from cyclopentanone and indanone failed to give the annelated thiophenes and no tractable product could be isolated from the reaction mixture.

Interestingly, the presence of additional double bond(s) did not interfere in the described thiophene synthesis. Thus α-cinnamoylketene dithioacetals and its higher enyl analogs of the general formula **10**, **13** and **15** were examined. The choice of these substrates is of particular interest since the α,β-unsaturated ketones are known to undergo cyclopropanation under Simmons-Smith reaction.[11] Thus **10a** was reacted with Simmons-Smith reagent, when the corresponding thiophene **11a** was formed in



Scheme 3

58% yield confirming that the presence of additional double bond(s) did not interfere in the thiophene synthesis. The other substituted cinnamoylketene dithioacetals **10b-d** similarly gave the corresponding thiophenes **11b-d** in 66-68% overall yields (Scheme 3). The dithioacetal **10e** needs special comment as it afforded the thiophene **11e** having methyl substituent in 3-position as well as in side chain. The thiophene **11e** underwent complete reductive desulphurization by W-2 Raney Nickel in methanol at room temperature to give the saturated hydrocarbon **12e** (Scheme 3). The styrylthiophenes constitute an important group of dienes often required for cycloaddition reactions to make condensed thiophenes.[10] The above reaction sequence could successfully be extended to 5-aryl-2,4-pentadienoylketene dithioacetals **13a-d** when the corresponding thiophenes **14a-d** with arylbutadienyl side chains could be obtained in 58-65% overall yields. These thiophenes are important as they could provide interesting photoinduced transformations,[12] and there appears to be no general method in the literature for the synthesis of these class of thiophenes. The 7-aryl-2,4,6-heptatrienoylketene dithioacetals **15a-c** also underwent facile cyclization under Simmons-Smith reaction conditions in highly regiospecific fashion to afford the corresponding 1-aryl-6-(4-thienyl)-1,3,5-hexatrienes **16a-c** in 68-70% overall yields (Scheme 3). The thiophenes **16a** and **16c** underwent complete reductive desulphurization in the presence of Raney-Nickel/methanol at room temperature to afford the saturated hydrocarbons **17a** and **17c** respectively in good yields (Scheme 3).

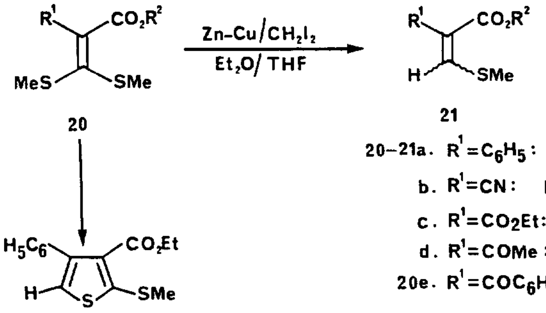


18 19

18-19a. R^1= C$_6$H$_5$: R^2= H
b. R^1= C$_6$H$_5$CH=CH- : R^2=H
c. R^1=C$_6$H$_5$(CH=CH)$_2$-:R^2=H

Scheme 4

Finally, the α-oxoketene dithioacetals **18a-c** with a preconstructed cyclopropane ring **18a**, cyclopropane ring with styryl **18b** and phenylbutadienyl **18c** side chains were selected in the present study. These compounds were obtained by regiospecific cyclopropanation of the respective enoyl ketene dithioacetals with dimethylsulphoxonium methylide using phase transfer catalyst.[13] The thiophenes **19a-c** thus obtained are of interest for the possibility of their undergoing skeletal rearrangement. Also, the dithioacetals **18b-c** possess structural feature in which the double bond is insulated from the carbonyl group by a cyclopropyl ring and behaves as an isolated double bond. Under Simmons-Smith conditions, these molecules reacted as expected, without double bond participation, although the thiophenes **19a-c** were obtained in comparatively lower yields (Scheme 4).



20 21 22

20–21a. R^1=C$_6$H$_5$: R^2=Et
b. R^1=CN: R^2=Et
c. R^1=CO$_2$Et: R^2=Et
d. R^1=COMe : R^2=Me
20e. R^1=COC$_6$H$_5$: R^2=Et

Scheme 5

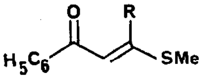
The doubly activated α-carboalkoxyketene dithioacetals **20a-e** were next investigated with a view to study the effect of changing carbonyl moiety, whether the reaction could be extended for the synthesis of 3-hydroxy/aminothiophenes. However, when **20a-d** were examined under the above reaction conditions, the corresponding dethiomethylated products **21a-d** were isolated in 56-82% overall yields. The formation of expected thiophene **22** in lower yield was observed only from the dithioacetal **20e** carrying a α-benzoyl group (Scheme 5).

MECHANISM

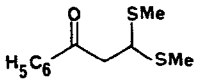
The probable mechanism of thiophene formation from α-oxoketene dithioacetals is shown in the Scheme 1. Apparently the attack of carbenoid methylene on one of the sulfur atoms (cis to carbonyl group) of **1** to give an initially formed ylid appears to be the first step in this transformation. The carbenes are known to react with sulfides nearly four times faster than double bond,[5] which is evidently demonstrated in the many examples examined in the present study. Also to our knowledge, there is no report on the formation of ylid from the interaction of sulfides with Simmons-Smith carbenoid species. The intermediate sulphur ylid **2** undergoes intramolecular nucleophilic addition elimination on carbonyl group which is probably assisted by coordination of zinc with carbonyl oxygen lone pair. The resulting S-methylthiophenium salt rapidly undergoes demethylation probably assisted by iodide ion. The overall process thus represents an intramolecular aldol condensation of sulfur ylid on a carbonyl group which itself is unprecedented with only few exceptions.[14] The mechanism of formation of dethiomethylated products **21a-d** from doubly activated α-carboalkoxyketene dithioacetals **20a-d** under Simmons-Smith conditions appears to be not very clear (Scheme 5). The combination of Zn-Cu/methylene iodide was necessary for this transformation since the starting material was recovered unchanged when **20a** was refluxed with Zn-Cu couple alone in THF under identical conditions. Reductive desulphurization of α-phenylthioketones with Zn in the presence of trimethylsilyl chloride is reported in the literature.[15] The methylthio group in these doubly activated ketene dithioacetals is more labile and less nucleophilic, therefore the reaction appears to take different course under these conditions causing reductive dethiomethylation of the substrates. However, the details of mechanism and the nature of the actual reducing species are under investigation.

CONCLUSION

In conclusion, a new synthetically useful, mechanistically interesting, efficient two step methodology for not so easily accessible 3- and 3,4-disubstituted/annelated thiophenes from active methylene ketones through their α-oxoketene dithioacetals has been developed. The reaction conditions are mild and the proven regioselectivity promises wide structural variation in the product thiophenes. Despite plethora of reports for the synthesis of thiophenes, very few methods are reported in the literature that lead to 3-substituted or 3,4-disubstituted/annelated thiophenes.[9,16] The only interesting approach close to the present methodology is due to Marino and Kostusyk[7] involving deprotonation of **1** by LDA/HMPA to generate thiomethyl anion which on intramolecular addition elimination sequence leads to the corresponding thiophene in overall 22-42% yields except in one case where the yield is improved to 55%. The method also suffers from limitations of its scope, since aliphatic oxoketene dithioacetals undergo undesirable competative deprotonation. The structural limitation for 3,4-annelated thiophenes are also evident from representative cyclic α-oxoketene dithioacetals selected in their study, while no examples were studied with olefinic side chains. The present methodology is thus free from all these limitations. However, the thiomethyl group could not be removed efficiently by Raney-Nickel desulphurization without affecting the thiophene ring in most of the cases. Similarly, attempted Simmons-Smith reaction on ß-methylthioenones **23a-b** to give either 2,5-unsubstituted or 2-methylthiophenes was not successful and only the starting materials were recovered unchanged. This is probably due to *trans* disposition of methylthio and benzoyl group resulting in the failure of intramolecular aldol condensation of the intermediate sulphur ylid. Similarly the ß-ketodithioacetal **24** underwent dethiomethylation to give only **23a** under the described conditions.



23a. R=H
b. R=Me



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EXPERIMENTAL

Melting points were determined on a 'Thomas Hoover' capillary melting point apparatus and are uncorrected. IR spectra were obtained on a Perkin-Elmer 297 spectrophotometer. The ^{1}H NMR spectra were recorded on a Varian EM-390 (90 MHz) spectrometer in $CDCl_3$ or CCl_4 using TMS as iternal standard, while ^{13}C NMR spectra were recorded on a Brucker WM-400 spectrometer and chemical shifts are expressed in δ(PPM) units downfield from TMS. Mass spectra were obtained on a Jeol JMS-D-300 spectrometer. Elemental analysis were performed on a Heraeus CHN-O-Rapid Elemental Analyzer.

All the starting α-oxoketene dithioacetals were prepared according to the earlier reported procedures.[17a,b]

General procedure for Simmons-Smith reaction; Synthesis of thiophenes:

To a well stirred suspension of zinc-copper couple (4.0g, 30 mmol) in dry ether (25 ml), under nitrogen atmosphere, a small crystal of iodine and methylene iodide (6.70g, 25 mmol) were added and the reaction mixture was refluxed for 45 minutes. A solution of the α-oxoketene dithioacetals (10 mmol) in dry THF (25 ml) was added to the reaction mixture which was further refluxed with stirring for 8-12 hr (monitored by t.l.c.). The solvent was removed under reduced pressure and the residue was diluted with chloroform (150 ml) and water (200 ml). The extract was filtered to remove unreacted Zn-Cu couple and the residue was washed with chloroform (2x25ml). The chloroform layer was separated and washed with saturated NH_4Cl solution, water, dried (Na_2SO_4) and concentrated to give the crude thiophenes which were purified by column chromatography over silica gel using hexane as eluent.

2-Methylthio-4-phenylthiophene (4a). Pale yellow crystals (hexane); 61%; m.p. 42°C (lit[7] m.p. 92 °C); IR(KBr) 1597, 1482, 1443, 1300cm^{-1}; δ_H($CDCl_3$) 2.43 (3H,s,SCH_3), 7.10-7.59(7H, m, *arom*, *H*-3 and *H*-5); δ_c($CDCl_3$) 21.32 (SCH_3), 122.56 (*C-5*), 125.61, 126.42, 129.00 (*CH arom*), 130.02 (*C-3*), 135.35 (*C*-1' *arom*) 138.28 (*C*-2), 144.42 (*C*-4); m/z 206 (M^+, 100%), 191(32), 147(23). (Anal. Calcd. for $C_{11}H_{10}S_2$: C, 64.03; H, 4.88. Found: C, 64.32; H, 4.65%).

2-Methylthio-4-(4-methylphenyl)thiophene (4b). Spectral data given in ref.6

2-Methylthio-4-(4-chlorophenyl)thiophene (4c). Pale yellow crystals (hexane); 65%; m.p. 64°C; IR (KBr) 1596, 1485, 1356cm^{-1}; δ_H($CDCl_3$) 2.44 (3H, s, SCH_3), 7.13-7.25(2H, m, *H*-3 and *H*-5), 7.26-7.45(4H, m, *arom*); δ_C($CDCl_3$) 21.88(SCH_3), 122.57(*C*-5), 129.51 (*C*-3), 127.36, 128.29(*CH arom*), 133.01 133.84(*C*-1' and *C*-4' *arom*), 138.63, 141.20 (*C*-2 and *C*-4); m/z 242 and 240 (M^+, 45 and 100%). Anal. Calcd. for $C_{11}H_9ClS_2$: C, 54.87; H, 3.77. Found: C, 54.66; H, 3.93%).

4-(2-Furyl)-2-methylthiothiophene (4d). Colorless viscous liquid; 58%; IR (Neat) 1600, 1520, 1474, 1418 cm^{-1}, δ_H(CCl_4) 2.46(3H, s, SCH_3), 6.33(2H, brs, *H-3'* and *H-5' furyl*), 7.19(1H, brs, *H-4' furyl*), 7.36(2H, brs, *H-3 and H-5*); m/z 196 (M^+, 100%). (Anal.Calcd for $C_9H_8OS_2$: C, 55.07; H, 4.11. Found : C, 54.82; H, 4.32%).

2-Methylthio-4-(2-thienyl)thiophene (4e). Pale yellow viscous liquid; 63%; IR (neat) 1498, 1427, 1410cm^{-1}; δ_H(CCl_4) 2.47 (3H, s, SCH_3) 6.87-7.28(5H, m, *thienyl, H-3* and *H-5*); m/z 212 (M^+, 100%) 197(45), 153(58). (Anal. Calcd. for $C_9H_8S_3$: C, 50.90; H, 3.80. Found: C, 51.17; H, 4.02%).

3-Methyl-2-methylthio-4-phenylthiophene (4f). Pale yellow viscous liquid ; 59%; IR (neat) 1599, 1576, 1484 cm^{-1} : δ_H(CCl_4) 2.20(3H, s, SCH_3), 2.31(3H, s, CH_3), 7.05(1H, s, *H*-5), 7.26(5H, s, *arom*); m/z 220 (M^+, 100%), 205 (35). (Anal. Calcd. for $C_{12}H_{12}S_2$: C, 65.41; H, 5.49. Found : C, 65.22; H, 5.38%).

3-Ethyl--2-methylthio-4-phenylthiophene (4g). Pale yellow viscous liquid; 58% ; IR (neat) 1598, 1574, 1482, 1440 cm^{-1}; δ_H(CCl_4) 0.97 (3H, t, J=7Hz, CH_2CH_3), 2.41 (3H, s, SCH_3), 2.66 (2H, q, J=7Hz, CH_2CH_3), 7.09 (1H, s, *H-5*), 7.31 (5H, s, *arom*); m/z 234 (M^+, 21%). (Anal. Calcd. for $C_{13}H_{14}S_2$: C, 66.62 ; H, 6.02. Found : C, 66.49; H, 5.98%).

2-Methylthio-4-phenyl-3-propylthiophene (4h). Pale yellow viscous liquid; 59%; IR(neat) 1595, 1573, 1520, 1487, 1440, 1360 cm^{-1}; δ_H(CCl_4) 0.79 (3H,t, J=7Hz, $CH_2CH_2CH_3$), 1.30 (2H, sext, J=7.0Hz, $CH_2CH_2CH_3$), 2.42 (3H, s, SCH_3), 2.66 (2H, t, J=7.0Hz, $CH_2CH_2CH_3$), 7.09 (1H, s, *H-5*), 7.32 (5H, s, *arom*); m/z 248 (M^+, 100%), 219 (75), 172 (49). (Anal.Calcd. for $C_{14}H_{16}S_2$: C, 67.69; H, 6.49. Found : C, 67.83; H, 6.72%).

3-Benzyl-4-(4-chlorophenyl)-2-methylthiothiophene (4i). Brown viscous liquid ; 58%; IR(neat) 1591, 1520, 1477, 1419 cm^{-1}; δ_H($CDCl_3$) 2.25 (3H, s, SCH_3), 4.01 (2H, s, $CH_2C_6H_5$), 6.78-7.29(10H, m, *arom* and *H-5*); m/z 332 and 330 (M^+, 100%), (Anal.Calcd. for $C_{18}H_{15}ClS_2$: C, 65.34; H, 4.57. Found : C, 65.21, H, 4.52%).

3,4-Diphenyl-2-methylthiothiophene (4j). Colorless crystal (hexane); 54%; m.p. 99-100°C; IR (KBr) 1598, 1479, 1435, 1428 cm^{-1}; $\delta_H(CDCl_3)$ 2.34 (3H, s, SCH_3), 6.97-7.40 (11H, m, *arom* and *H-5*); m/z 282 (M^+, 100%), 267(29), 234(52). (Anal. Calcd. for $C_{17}H_{14}S_2$: C, 72.30; H, 5.00. Found: C, 72.19; H, 4.92%).

4-Methyl-2-methylthiothiophene (4k). Colorless viscous liquid; 53%; IR(neat) 1593, 1510, 1473, 1410 cm^{-1}; $\delta_H(CCl_4)$ 2.20 (3H, brs, CH_3), 2.41 (3H, s, SCH_3), 6.80 (2H, s, *H-3* and *H-5*); m/z 144 (M^+ 100%). (Anal. Calcd. for $C_6H_8S_2$: C, 49.96; H, 5.59. Found : C, 50.21; H, 5.83%).

3,4-Dimethyl-2-methylthiothiophene (4l). Pale yellow viscous liquid; 56%; IR(neat) 1430, 1380, 1363 cm^{-1}; $\delta_H(CCl_4)$ 2.10 (3H, s, CH_3-*3*), 2.13 (3H, s, CH_3-*4*), 2.29 (3H, s, SCH_3), 6.80 (1H, s, *H-5*); m/z 158 (M^+, 100%). (Anal. Calcd. for $C_7H_{10}S_2$: C, 53.12; H, 6.37. Found : C, 53.39; H, 6.58%).

4-Ethyl-3-methyl-2-methylthiothiophene (4m). Pale yellow viscous liquid; 58%; IR(neat) 1599, 1458, 1428, 1376 cm^{-1}; $\delta_H(CCl_4)$ 1.19 (3H, t, J=7.5Hz, CH_2CH_3), 2.16 (3H, s, CH_3-*3*), 2.29 (3H, s, SCH_3), 2.48 (2H, q, CH_2CH_3), 6.81 (1H, s, *H-5*); m/z 172 (M^+, 15%). (Anal. Calcd. for $C_8H_{12}S_2$: C, 55.76; H, 7.02. Found : C, 55.82; H, 7.12%).

3-Butyl-4-methyl-2-methylthiothiophene (4n). Pale yellow viscous liquid; 62%; IR(neat) 1440, 1379, 1309, 1179 cm^{-1}; $\delta_H(CCl_4)$ 0.95 [3H, distorted t, $CH_2(CH_2)_2CH_3$], 1.23-1.54 [4H, m, $CH_2(CH_2)_2CH_3$], 2.17 (3H, s, CH_3-*3*), 2.36 (3H, s, SCH_3), 2.61 [2H, t, $CH_2(CH_2)_2CH_3$), 6.82 (1H, s, *H-5*); m/z 200 (M^+, 64%), 157 (100) (Anal. Calcd. for $C_{10}H_{16}S_2$: C, 59.95; H, 8.05. Found : C, 60.24; H, 8.33%).

3-Allyl-2-methylthio-4-phenylthiophene (4o). Pale yellow viscous liquid; 60%; IR(neat) 1599, 1490, 1443, 1425 cm^{-1}; δ_H (CCl_4) 2.37 (3H, s, SCH_3), 3.39 (2H, d, J=4.5Hz, CH_2-CH=CH_2), 4.84-5.07 (2H, m, CH_2-CH=CH_2), 5.56-5.97 (1H, m, CH_2-*CH*=CH_2), 7.12 (1H, s, *H-5*), 7.31 (5H, s, *arom*); m/z 246 (M^+ 100%) 231 (86). (Anal. Calcd. for $C_{14}H_{14}S_2$: C, 68.25; H, 5.73. Found : C, 68.51; H, 6.01%).

2-Ethylthio-4-phenylthiophene (4p). Yellow viscous liquid; 62%; IR(neat) 1570, 1468, 1300, 1240 cm^{-1}; $\delta_H(CDCl_3)$ 1.30 (3H, t, J=6Hz, SCH_2CH_3), 2.79 (2H, q, J=6Hz, SCH_2CH_3), 7.03-7.58 (5H, m, *arom*); m/z 220 (M^+, 100%). (Anal. Calcd. for $C_{12}H_{12}S_2$: C, 65.41; H, 5.49. Found : C, 65.68; H, 5.72%).

2-Benzylthio-4-phenylthiophene (4q). Pale yellow solid ($CHCl_3$/hexane); 64%; m.p. 93-94°C; IR(KBr) 1605, 1495, 1458, 1352, 1208 cm^{-1}; δ_H $(CDCl_3)$ 4.0 (2H, s, $SCH_2C_6H_5$), 7.04-7.65 (12H, m, *arom*, *H*-3 and *H*-5); m/z 282 (M^+, 100%). (Anal. Calcd. for $C_{17}H_{14}S_2$: C, 72.30; H, 5.00. Found : C, 72.49; H, 5.28%).

2-Methylthiocyclohexa[c]thiophene (7a). Colourless viscous liquid; 65%; IR(neat) 1543, 1437, 1388 cm^{-1}; $\delta_H(CCl_4)$ 1.55-1.84 (4H, m, CH_2), 2.34 (3H, s, SCH_3), 2.60-2.82 (4H, m, CH_2), 6.76 (1H, s, *H-5*); m/z 184 (M^+ 100%), 169 (42). (Anal. Calcd. for $C_9H_{12}S_2$: C, 58.65; H, 6.57, Found : C, 58.90; H, 6.83%).

2-Methylthiocyclohepta[c]thiophene (7b). Colourless viscous liquid; 62%; IR(neat), 1442, 1428, 1382, 1309 cm^{-1}; $\delta_H(CCl_4)$ 1.43-1.90 (6H, m, CH_2), 2.30 (3H, s, SCH_3), 2.57-2.89 (4H, m, CH_2), 6.73 (1H, s, *H-5*); m/z 198 (M^+, 100%), 183 (38). (Anal. Calcd. for $C_{10}H_{14}S_2$: C, 60.56; H, 7.11. Found : 60.28; H, 7.40%).

2-Methylthiocycloocta[c]thiophene (7c). Colourless viscous liquid; 66%; IR(neat) 1459, 1442, 1390 cm^{-1}; $\delta_H(CCl_4)$ 1.18-1.76 (8H, m, CH_2), 2.33 (3H, s, SCH_3), 2.47-2.88 (4H, m, CH_2), 6.82 (1H, s, *H-5*); m/z 212 (M^+, 100%). (Anal. Calcd. for $C_{11}H_{16}S_2$: C, 62.21; H, 7.60. Found : C, 62.39; H, 7.84%).

2-Methylthiocyclododeca[c]thiophene (7d). Colourless viscous liquid; 64%; IR(neat) 1467, 1444, 1422, 1383 cm^{-1}; $\delta_H(CCl_4)$ 1.16-1.88 (16H, m, CH_2), 2.35 (3H, s, SCH_3), 2.43-2.75 (4H, m, CH_2) 6.96 (1H, s, *H-5*); m/z 267 (M^+, 100%) 220 (24). (Anal. Calcd. for $C_{15}H_{24}S_2$: C, 67.10; H, 9.01. Found : C, 67.32; H, 9.27%).

2-Methylthio-3,4-dihydronaphtho[2,1-c]thiophene (9a). Pale yellow viscous liquid; 57%; IR(neat) 1599, 1479, 1454, 1420 cm^{-1}; $\delta_H(CDCl_3)$ 2.32 (3H, s, SCH_3), 2.79 (4H, s, CH_2), 6.93-7.18 (3H, m, *arom*), 7.28

(1H, s, *H-5*), 7.32-7.50 (1H, m, *arom*); m/z 232 (M^+, 100%), 217(22). (Anal.Calcd. for $C_{13}H_{12}S_2$: C, 67.20; H, 5.21. Found : C, 67.38; H, 5.41%).

2-Methylthio-4,5-dihydro-3H-benzocyclohepta[2,1-c]thiophene (9b). Pale yellow viscous liquid; 60%; IR(neat) 1524, 1476, 1439, 1360 cm^{-1}; δ_H (CCl_4) 1.83-2.24 (2H, quint, CH_2), 2.31 (3H, s, SCH_3), 2.38-2.71 (4H, m, CH_2), 7.00-7.24 (5H, m, *arom* and *H-5*); m/z 246(M^+, 100%), 231 (11). (Anal Calcd. for $C_{14}H_{14}S_2$: C, 68.25; H, 5.73. Found : C, 68.52; H, 5.91%).

2-Methylthio-3,4-dihydrobenzooxepino[2,1-c]thiophene (9d). Yellow viscous liquid; 61%; IR(neat) 1596, 1563, 1479, 1441 cm^{-1}; δ_H($CDCl_3$) 2.27 (3H, s, SCH_3), 2.89 (2H, t, CH_2) 4.24 (2H, t, CH_2), 6.78-7.18 (3H, m, *arom*), 7.20 (1H, s, *H-5*), 7.25-7.41 (1H, m, *arom*); m/z 248 (M^+, 100%), 233(44). (Anal. Calcd. for $C_{13}H_{12}OS_2$: C, 62.87; H,4.87. Found : C, 62.62; H,5.13%).

8-Methyl-2-methylthio-3,4-dihydrobenzothiepino[2,1-c]thiophene (9e). Brown viscous liquid; 62%; IR(neat) 1595, 1532, 1480, 1421 cm^{-1}; δ_H ($CDCl_3$) 2.32 (3H, s, CH_3), 2.38 (3H, s, SCH_3), 2.91-3.12 (2H, m, CH_2), 3.21-3.39 (2H, m, CH_2), 7.20-7.33 (3H, m, *arom* and *H-5*), 7.53 (1H, brs, *arom*); m/z 278 (M^+, 100%), 263 (31). (Anal.Calcd. for $C_{14}H_{14}S_3$; C, 60.39; H, 5.07. Found : C, 60.21; H, 5.18%).

2-Methylthio-4-styrylthiophene (11a). Pale yellow crystals (hexane); 58%; m.p. 58.59°C; IR(KBr) 1600, 1580, 1498, 1453, 1425 cm^{-1}; δ_H($CDCl_3$) 2.48 (3H, s, SCH_3), 6.88 (2H, brs, $=CH$), 7.01-7.48 (7H, m, *arom*, *H-3* and *H-5*); m/z 232 (M^+, 86%) 184 (100). (Anal.Calcd. for $C_{13}H_{12}S_2$: C, 67.20; H, 5.21. Found : C, 67.28; H, 5.33%).

2-Methylthio-4-(4-chlorostyryl)thiophene (11b). Pale yellow crystals (hexane); 68%; m.p. 79-80°C; IR (KBr) 1585, 1481, 1403, 1391 cm^{-1}; δ_H($CDCl_3$) 2.48 (3H, s, SCH_3), 6.82 (2H, brs, $=CH$), 7.01-7.33 (6H, m, *arom*, *H*-3 and *H-5*); m/z 268 and 266 (M^+, 44, 100%), 184(58). (Anal. Calcd. for $C_{13}H_{11}ClS_2$: C, 58.52; H, 4.16. Found : C, 58.58; H, 4.01%).

2-Methylthio-4-(2-chlorostyryl)thiophene (11c). Yellow viscous liquid; 66%; IR(neat) 1628, 1585, 1463, 1436 cm^{-1}; δ_H($CDCl_3$) 2.49 (3H, s, SCH_3), 6.79-7.66 (8H, m, *arom*, $=CH$, *H-3* and *H-5*); m/z 268 and 266 (M^+,15,100%). (Anal. Calcd. for $C_{13}H_{11}ClS_2$; C, 58.52; H, 4.16. Found : C, 58.41; H, 3.99%).

3-Methyl-2-methylthio-4-(4-methoxystyryl)thiophene (11d). Pale yellow solid (hexane); 68%; m.p. 85-86°C; IR(KBr) 1591, 1560, 1498, 1426 cm^{-1}; δ_H($CDCl_3$) 2.30 (3H, s, CH_3), 2.32 (3H, s, SCH_3), 3.75 (3H, s, OCH_3), 6.67-6.83 (4H, m, *arom* and $=CH$), 7.16-7.38 (3H,m, *arom* and *H-5*); m/z 276 (M^+, 100%) 228 (58). (Anal. Calcd. for $C_{15}H_{16}OS_2$: C, 65.18; H, 5.84. Found : C, 65.06; H, 5.90%).

3-Methyl-2-methylthio-4-[3-(3,4-dimethoxyphenyl)-2-propenyl]thiophene (11e). Colorless solid (hexane); 61%; m.p. 64-65°C; IR (KBr) 1604, 1586, 1517, 1462, 1440 cm^{-1}; δ_H($CDCl_3$) 2.21 (3H, brs, CH_3), 2.34 (3H, s, CH_3-3), 2.42 (3H, s, SCH_3), 3.94 (6H, s, OCH_3), 6.49 (1H, brs, *arom*), 6.94 (3H, brs, *arom* and $=CH$). 7.14 (1H, s, *H-5*); m/z 320 (M^+, 100%), 258 (49). (Anal. Calcd. for $C_{17}H_{20}O_2S_2$: C,63.71; H,6.29. Found: C, 63.80; H,6.32%).

2-Methylthio-4-(4-phenyl-1,3-butadienyl)thiophene (14a). Colorless solid (hexane); 65%, m.p. 89-90; IR (KBr) 1479, 1440, 1303 cm^{-1}; δ_H ($CDCl_3$) 2.47 (3H, s, SCH_3), 6.50-6.80 (4H, m, $=CH$), 7.03-7.40 (7H, m, *arom*, *H*-3 and *H-5*); m/z. 258 (M^+,100%), 210 (77). (Anal. Calcd. for $C_{15}H_{14}S_2$: C, 69.72; H,5.46. Found: C,69.80; H, 5.58%).

3-Methyl-2-methylthio-4-(4-phenyl-1,3-butadienyl)thiophene (14b). Pale yellow crystals (hexane); 62%; m.p. 98-99°C; IR(KBr) 1584, 1489, 1479, 1426 cm^{-1}; δ_H($CDCl_3$) 2.30 (3H, s, CH_3-3), 2.35 (3H, s, SCH_3), 6.59-6.99 (4H, m, $=CH$), 7.20-7.52 (6H, m, *arom* and *H-5*); m/z 272 (M^+, 100%) 224 (73) (Anal. Calcd. for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92. Found: C, 70.52; H, 5.99%).

3-Butyl-2-methylthio-4-[(4-methoxyphenyl)-1,3-butadienyl]thiophene (14c). Pale yellow solid (hexane);

60%; m.p. 79-80°C; IR(KBr) 1598, 1508, 1460, 1438 cm^{-1}; δ_H($CDCl_3$) 0.95 [3H, distorted t, $CH_2(CH_2)_2\mathit{CH_3}$], 1.25-1.62 [4H, m,$CH_2(\mathit{CH_2})_2CH_3$], 2.36 (3H, s, $\mathit{SCH_3}$), 2.73 [2H, distorted t, $\mathit{CH_2}(CH_2)_2CH_3$], 3.77 (3H, s, $\mathit{OCH_3}$), 6.34-6.91(6H, m, *arom* and =*CH*), 7.28-7.43(3H, m, *arom* and *H*-5); m/z 344 (M$^+$, 100%). (Anal. Calcd. for $C_{20}H_{24}OS_2$: C, 69.72; H, 7.02. Found : C, 69.82; H, 7.08%).

3-Methyl-2-methylthio-4-(5-phenyl-2,4-pentadienyl)thiophene (14d). Yellow viscous liquid; 58%; IR(neat) 1589, 1483, 1440, 1425, 1370, 1309 cm^{-1}; δ_H($CDCl_3$) 2.10 (3H, brs, $\mathit{CH_3}$), 2.24 (3H, s, $\mathit{CH_3}$-3), 2.26 (3H, s, $\mathit{SCH_3}$, 6.10-6.59 (3H, m, =*CH*), 6.88-7.39 (6H, m, *arom* and *H*-5); m/z 286 (M$^+$, 100%), 238(39), 224(40). (Anal. Calcd. for $C_{17}H_{18}S_2$: C, 71.28; H, 6.33. Found : C, 71.40; H, 6.42%).

2-Methylthio-4-(6-phenyl-1,3,5-hexatrienyl)thiophene (16a). Pale yellow crystals (CH_2Cl_2/hexane); 69%; m.p. 133-134°C; IR(KBr) 1612, 1580, 1479, 1439, 1410 cm^{-1}; δ_H ($CDCl_3$: 400 MHz) 2.46 (3H, s, $\mathit{SCH_3}$), 6.40-6.52 (3H, m, =*CH*), 6.58 (1H, d, J=12 Hz, =*CH*), 7.09 (1H, brs, *H*-3), 7.20 (1H, brs, *H*-5), 7.18-7.25 (1H, m, *arom*), 7.31 (2H, t, J=8.5Hz, *arom*), 7.40 (2H, d, J=8.5Hz *arom*); m/z 284 (M$^+$, 100%). (Anal. Calcd. for $C_{17}H_{16}S_2$: C, 71.78; H, 5.67. Found : C, 71.62; H, 5.72%).

2-Methylthio-4-[6-(3,4-methylenedioxyphenyl)-1,3,5-hexatrienyl]thiophene (16b). Yellow crystals (CH_2Cl_2/hexane); 68%; m.p. 142-143°C; IR(KBr) 1628, 1509, 1498, 1451, 1260 cm^{-1}; δ_H ($CDCl_3$) 2.48 (3H, s, $\mathit{SCH_3}$), 5.95 (2H, s, $\mathit{OCH_2O}$), 6.24-6.63 (6H, m, =*CH*), 6.72-7.27 (5H, m, *arom*, *H*-3 and *H*-5); m/z 328 (M$^+$,100%). (Anal. Calcd. for $C_{18}H_{16}O_2S_2$: C, 65.82; H, 4.91. Found : C, 65.69; H, 4.82%).

3-Methyl-2-methylthio-4-[6-(3,4-methylenedioxyphenyl)-1,3,5-hexatrienyl] thiophene (16c). Yellow crystals (CH_2Cl_2/hexane); 70%; m.p. 109°C; IR(KBr) 1661, 1480, 1435, 1352, 1251 cm^{-1}; δ_H($CDCl_3$), 2.29 (3H, s, $\mathit{CH_3}$-3), 2.36 (3H, s, $\mathit{SCH_3}$), 5.92 (2H, s, $\mathit{OCH_2O}$), 6.311-6.99 (9H, m, =*CH* and *arom*), 7.27 (1H, s, *H*-5); m/z 342 (M$^+$, 100%). (Anal. Calcd. for $C_{19}H_{18}O_2S_2$: C, 66.63; H, 5.30. Found : C, 66.72; H, 5.21%).

2-Methylthio-4-(2-phenylcyclopropyl)thiophene (19a). Yellow viscous liquid; 57%; IR(neat) 1600, 1531, 1492, 1459, 1412 cm^{-1}; δ_H ($CDCl_3$) 1.24 (2H, distorted t, J=7.0Hz, $\mathit{CH_2}$), 2.00 (2H, t, J=7.0Hz, *CH*), 2.37 (3H, s, $\mathit{SCH_3}$), 6.76 (2H, brs, *H*-3 and *H*-5), 6.93-7.29 (5H, m, *arom*); m/z 246 (M$^+$, 100%) .(Anal. Calcd. for $C_{14}H_{14}S_2$: C, 68.25; H, 5.73. Found : C, 68.54; H, 5.97%).

2-Methylthio-4-(2-styrylcyclopropyl)thiophene (19b). Yellow viscous liquid; 54%; IR(neat) 1640, 1597, 1530, 1487, 1440, 1410 cm^{-1}; δ_H ($CDCl_3$) 0.92-1.21 (2H, m, $\mathit{CH_2}$), 1.45-1.91 (2H, m, *CH*), 2.31 (3H, s, $\mathit{SCH_3}$), 5.64 (1H, dd, J=16 and 7.5Hz, =*CH*), 6.31 (1H, d, J=16Hz, =*CH*), 6.63 (1H, brs, *H*-3), 7.06 (6H, brs, *arom* and *H*-5); m/z 272 (M$^+$, 100%), 225(22). (Anal. Calcd. for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92. Found : C, 70.74; H, 6.13%).

2-Methylthio-4-[2-(4-phenyl-1,3-butadienyl)cyclopropyl]thiophene (19c). Yellow viscous liquid; 56%; IR(neat) 1636, 1590, 1530, 1458, 1410 cm^{-1}; δ_H ($CDCl_3$) 0.80-1.23 (2H, m, $\mathit{CH_2}$), 1.37-1.89 (2H, m, *CH*), 2.31 (3H, s, $\mathit{SCH_3}$), 5.27 (1H, dd, J=16Hz and 7.5Hz, =*CH*), 5.95-6.63 (3H, m, =*CH*), 6.72 (1H, s, *H*-3), 6.88-7.27 (6H, m, *arom* and *H*-5); m/z 298 (M$^+$, 84%). (Anal. Calcd. for $C_{18}H_{18}S_2$: C, 72.44; H, 6.08. Found : C, 72.73; H, 6.32%).

Ethyl 3-methylthio-2-phenylpropenoate (21a). Yellow viscous liquid; 79%; IR(neat) 1710, 1570, 1230 cm^{-1}; δ_H(CCl_4) 1.10 (3H, t, J=6Hz, $OCH_2\mathit{CH_3}$), 2.27 (3H, s, $\mathit{SCH_3}$), 4.30 (2H, q, J=6Hz, $O\mathit{CH_2}CH_3$), 7.27 (5H, m, *arom*), 7.61 (1H, s, =CH); m/z 222 (M$^+$, 100%), 175(60). (Anal. Calcd. for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35. Found : C, 65.11; H, 6.61%).

Ethyl 2-cyano-3-methylthiopropenoate (21b). Yellow crystal ($CHCl_3$/hexane); 82%; m.p. 51-52°C; IR(KBr) 2218, 1712, 1540, 1300, 1245 cm^{-1}; δ_H ($CDCl_3$) 1.34 (3H, t, J=6Hz, $OCH_2\mathit{CH_3}$), 2.68 (3H, s, $\mathit{SCH_3}$), 4.28 (2H, q, J=6Hz, $O\mathit{CH_2}CH_3$), 8.50 (1H, s, =*CH*); m/z 171 (M$^+$, 100%). (Anal. Calcd. for $C_7H_9NO_2S$: C, 49.10; H, 5.30. Found : C, 49.37; H, 5.56%).

Ethyl 2-carboethoxy-3-methylthiopropenoate (21c). Yellow viscous liquid; 56%; IR(neat) 1710, 1554, 1242 cm^{-1}; δ_H(CCl_4) 1.08-1.43(6H, m, OCH_2CH_3), 2.40 (3H, s, SCH_3) 3.89-4.32(4H, m, OCH_2CH_3), 7.90 (1H, s, =*CH*); m/z 218 (M^+, 100%). (Anal. Calcd. for $C_9H_{14}O_4S$: C, 49.52; H, 6.46. Found : C, 49.81; H, 6.73%).

Methyl 2-acetyl-3-methylthiopropenoate (21d). Pale yellow crystal ($CHCl_3$/hexane); 69%; m.p. 57°C; IR(KBr) 1711, 1644, 1493, 1343, 1201 cm^{-1}; δ_H ($CDCl_3$) 2.48 (3H, s, SCH_3), 3.80 (3H, s, OCH_3), 8.50 (1H, s, =*CH*); m/z 174 (M^+, 100). (Anal. Calcd. for $C_7H_{10}O_3S$: C, 48.26; H, 5.79. Found : C, 48.51; H, 6.02%).

Ethyl 2-Methylthio-4-phenylthiophene-3-carboxylate(22). Pale Yellow viscous liquid;51%; IR(neat) 1710, 1600, 1482, 1420, 1310, 1245 cm^{-1}; δ_H 1.03 (3H, t, J=6Hz, OCH_2CH_3), 2.57 (3H, s, SCH_3), 4.08 (2H, q, J=6Hz, OCH_2CH_3), 6.97 (1H, s, *H*-5), 7.28 (5H, s, *arom*); m/z 278 (M^+, 100%), (Anal. Calcd. for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.07. Found : C, 60.67; H, 5.35%).

Desulphurization of thiophenes (4a-c, 11e, 16a,c); General Procedure:

To a solution of methylthiothiophene (0.004 mol) in methanol (30 ml) was added Raney-Nickel (W-2) (10 times by weight) and the mixture was stirred at room temperature for 3-5 hr (monitored by t.l.c.).The reaction mixture was filtered and the residue was washed with hot methanol (3x20 ml). The bulk of the methanol was removed under reduced pressure and chloroform (30 ml) was added. The solution was washed with water (2x50 ml), dried (Na_2SO_4) and evaporated. Analytically pure compounds were obtained by passing through short length silica gel column using pentane as eluent.

3-Phenylthiophene (5a). Colourless cyrstals (pentane); 52%; m.p. 89-90°C (lit.[18] m.p. 90-91); IR, NMR and mass spectral data in agreement with those reported.[18]

3-(4-Methylphenyl)thiophene (5b). Colorless crystals (pentane); 58%; m.p. 108-109°C(lit.[18] m.p.113-114); IR, NMR and mass spectral data in agreement with those reported.[18]

3-(4-Chlorophenyl)thiophene (5c). Colourless crystals (pentane); 59%; m.p. 95-96°C(lit.[18] m.p. 104-105); IR, NMR and mass spectral data in agreement with those reported.[18]

5-(3,4-Dimethoxyphenyl)-2,3,4-trimethylpentane (12e). Colourless viscous liquid; 72%; IR(neat) 1600, 1580, 1505, 1460, 1411 cm^{-1}; δ_H(CCl_4) 0.67-1.17(9H, m, CH_3), 1.41-2.05(8H, m, CH_2, CH_3 and *CH*), 3.79 (6H, brs, OCH_3), 6.51-6.77 (3H, m, *arom*); m/z 250 (M^+, 15%). (Anal. Calcd. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found : C, 76.89; H, 10.61%).

3-Methyl-9-phenylnonane (17a). Colourless viscous liquid; 70%; IR(neat) 1601, 1545, 1490, 1450 cm^{-1}; δ_H (CCl_4) 0.72-0.96(6H, m, CH_3), 1.11-1.73(12H, m, CH_2), 1.79-2.06(1H, m, *CH*), 2.56 (2H, t, J=7.5 Hz, $CH_2C_6H_5$), 7.10 (5H, brs, *arom*); m/z 218 (M^+, 51%). (Anal. Calcd. for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found : C, 88.21; H, 12.15%).

2,3-Dimethyl-9-(3,4-methylenedioxyphenyl)nonane (17c). Colourless viscous liquid, 71%; IR(neat) 1499, 1482, 1439, 1240 cm^{-1}; δ_H(CCl_4) 0.70-1.04 (6H, m, CH_3), 1.12-1.66(13H, m, CH_2 and CH_3), 1.77-2.20 (2H, m, *CH*), 2.48 (2H, t, J=7.5Hz, $CH_2C_6H_5$), 5.84 (2H, s, OCH_2O), 6.51-6.64(3H, m, *arom*); m/z 276 (M^+, 39%). (Anal. Calcd. for $C_{18}H_{28}O_2$: C, 78.24; H, 10.21. Found : C, 78.11; H, 10.23%).

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