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DARZEN'S REACTION ON OXOKETENE DITHIOACETALS: A NEW VERSATILE SYNTHESIS OF SUBSTITUTED AND ANNELATED FURAN-2-CARBOXYLATES

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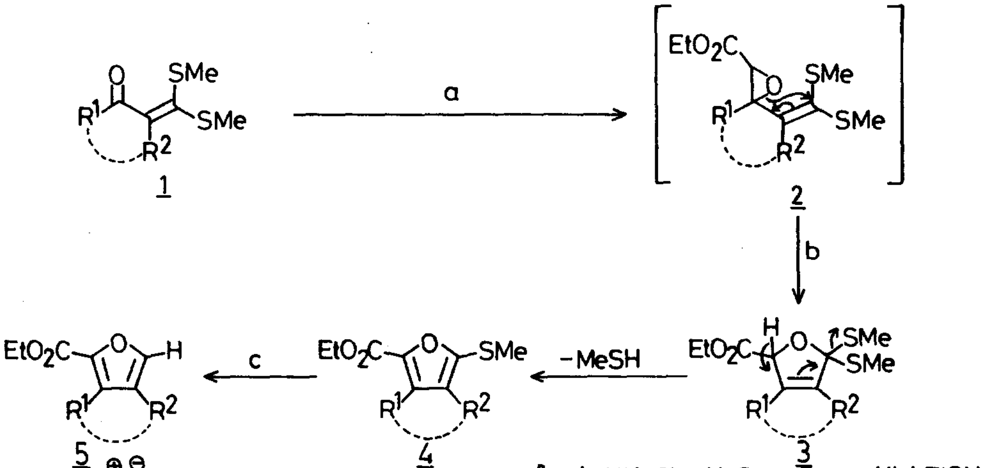
Abstract: Darzen's condensation of lithiobromoacetate with α-oxoketene dithioacetals affords the title furans 4 in moderate to good yields. A few of the 5-methylthio furan-2-carboxylates were desulphurized to yield 5-unsubstituted derivatives 5 in good yields. The reaction of α-cinnamoylketene dithioacetals 6 with lithiobromoacetate under identical conditions yielded the corresponding 5-methylthio-3-styryl furan-2-carboxylates 7 along with 3-(2-carbethoxy-3-aryl cycloprop-1-yl)-5-methylthio furan-2-carboxylates 8 which are shown to be formed by conjugate addition elimination of lithiobromoacetate on 7. The corresponding α-(5-aryl-2,4-pentadienoyl)-(9a-b) and α-(7-aryl-2,4,6-heptatrienoyl)-(11a-b) ketene dithioacetals gave the corresponding 3-(4-aryl-1,3-butadienyl)-(10a-b) and 3-(6-aryl-1,3,5-hexatrienyl)-(12a-b) 5-methylthio furan-2-carboxylates exclusively in good yields.

Methodologies for efficient synthesis of substituted furan rings are of practical importance since many furans containing compounds exist in nature and some of them exhibit interesting biological activities[1]. In a programmed research on α-oxoketene dithioacetals, we have extensively exploited their regioselective C-C bond forming reactions and developed efficient new synthetic methods for a number of carbocyclic and heterocyclic ring systems[2]. We further considered of interest to study these systems under Darzen's glycidic ester synthesis conditions with a view to utilize these intermediates to develop simple and short method for a number of substituted and annelated furan-2-carboxylates (Scheme 1). The α-oxoketene dithioacetals have been utilized in past for the construction of furan ring by reacting them with dimethylsulphonium methylide to afford initially the corresponding 2,2-bis(methylthio)-2,5-dihydrofurans, which on acid treatment yielded the respective 2-methylthiofurans in good yields[3,4]. In the present studies, we have explored the reaction of widely available α-oxoketene dithioacetals with bromoacetate carbanion to afford 3- or 3,4-substituted/annelated-furan-2-carboxylates in good yields. The reaction is applicable to wide structural variants of active methylene ketones via their α-oxoketene dithioacetals thus providing a facile route for these furans.

RESULTS AND DISCUSSION

Darzen's glycidic ester condensation has been extensively investigated under different basic reaction conditions[5]. Our attempts to condense α-oxoketene dithioacetals with bromoacetate in the presence of different bases such as sodium ethoxide, sodium t-butoxide and butyllithium failed to yield the expected condensation products. However, when the bromoacetate anion was generated by using lithium hexamethyldisilazide (HMDS) as base, the reaction followed the satisfactory course to yield the desired furans (Scheme 1). In a typical experiment, when 1a (1 eqv) was reacted with lithiobromoacetate (2 eqv) derived from HMDS at -78°C, the reaction mixture after work-up afforded the product which was characterized as ethyl 3-methyl-5-methylthio furan-2-carboxylate (4a) (57%) (Table 1). The structure and regiochemistry of 4a was established by its spectral and analytical data (experimental). Its unequivocal structural proof was further obtained by subjecting it to Raney nickel desulphurization to yield the known[6] ethyl 3-methyl-furan-2-carboxylate (5a) (Scheme 1) which was found identical in all respects (superimposable i.r. and n.m.r. spectra). The other acyclic 3-substituted furan-2-carboxylates 4b-f were similarly obtained in 55-65% overall yields from the respective dithioacetals 1b-f (Table 1). However, the corresponding 3,4-dimethyl (4g) and 3-aryl-4-methyl (4h) derivatives were obtained in comparative lower yields under identical reaction conditions (Table 1).



a. $Li^{\oplus}N^{\ominus}(SiMe_3)_2$ / $BrCH_2CO_2Et$, THF, -78°C, b. NH_4Cl / H_2O c. RaneyNi / EtOH

Scheme 1

When the reaction was extended to cyclic ketene dithioacetals 1i-p (Table 2), the corresponding 3,4-annelated-5-methylthio-furan-2-carboxylates 4i-4p were obtained in 52-69% overall yields. In all these reactions, the regiochemistry of the furans 4a-p was unequivocally dictated by the structure of the starting dithioacetals 1. Some of the thiomethylfurans 4 were dethiomethylated to the corresponding sulphur free furans 5 in high yields (Scheme 1,Table 1,2).

The reaction most probably proceeds by way of the intermediates 2 and 3 (Scheme 1) analogous to those proposed by Okazaki in the addition of dimethylsulphonium methylide to 1[3a,b]. However our attempts to isolate either glycidic ester 2 or the dihydrofuran 3 in any of these experiments were not successful. The reaction was next extended to α-cinnamoyl (6a-f), α-butenoyl (6g) ketene dithioacetals and their higher enoyl homologs 9a-b and 11a-b (Schemes 2,4,5).

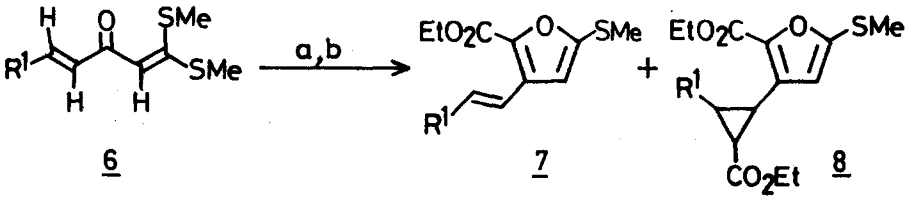
Table 1: Synthesis of Ethyl 3,4-substituted furan-2-carboxylates 4 and 5

Entry	Starting material	Product 4, 5	R^1	R^2	% Yield[a]
1	1a	4a	Me	H	57
2	1b	4b	Et	H	55
3	1c	4c	Ph	H	62
4	1d	4d	2-naphthyl	H	61
5	1e	4e	2-furyl	H	65
6	1f	4f	2-thienyl	H	63
7	1g	4g	Me	Me	45
8	1h	4h	$4\text{-}MeOC_6H_4$	Me	40
9	4a	5a[b]	Me	H	83
10	4b	5b[b]	Et	H	82
11	4c	5c[b]	Ph	H	87
12	4e	5e[b]	2-furyl	H	76

[a] Yield of pure isolated product; [b]Product of Raney Nickel desulphurization of 4

When 6a (1 eqv) was reacted with lithiobromoacetate, two products were isolated which were characterized as ethyl 5-methylthio-3-styryl furan-2-carboxylate (7a) (20%) and ethyl 5-methylthio-3-(2-carbethoxy-3-phenylcycloprop-1-yl)furan-2-carboxylate (8a) in 42% yield. Apparently, the cyclopropylfuran 8a is formed by conjugate addition elimination sequence of lithiobromoacetate on the highly electrophilic β-carbon of styryl group in 7a (Scheme 2). This was further confirmed by reacting 7d with lithiobromoacetate to afford 8d in 36% yield. The other substituted cinnamoylketene dithioacetals 6b-e similarly afforded the mixture of the corresponding 7b-e and 8b-e in varying proportions (Scheme 2). However the corresponding 4-chloro (6f) and the α-butenoyl (6g) ketene dithioacetals yielded only the corresponding cyclopropylfurans 8f and 8g in good yields. When the conjugation was further extended the cyclopropylfurans were not formed and the corresponding 3-enylfuran-2-carboxylates were the only products isolated. Thus the reaction of α-(5-aryl 2,4-pentadienoyl) (9a-b) and α-(7-aryl-2,4,6-heptatrienoyl) (11a-b) ketene dithioacetals with lithiobromoacetate yielded only the corresponding 3-(4-aryl-1,3-butadienyl)-(10a-b) and 3-(6-aryl-1,3,5-hexatrienyl)-(12a-b)furan-2-carboxylates in 49-61% overall yields (Scheme 4 and 5).

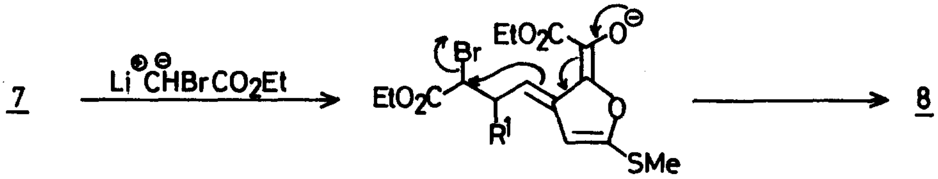
The α-oxoketene dithioacetals,thus serve as useful 3-carbon substrates for the synthesis of regioselectively substituted and annelated furan-2-carboxylates under the Darzen's glycidic ester condensation conditions in one pot reaction. It is pertinent to note that methyl 3-methyl furan-2-carboxylate and the corresponding 3-phenyl derivative have been synthesized earlier in two steps through Darzen's condensation on the respective β-ketoacetals and subsequent thermal rearrangement of the resulting glycidic esters[6a]. However the generality of the reaction has not been studied probably due to nonavailability of β-ketoacetals which are not easily accessible. Therefore the present method is more versatile and provides greater



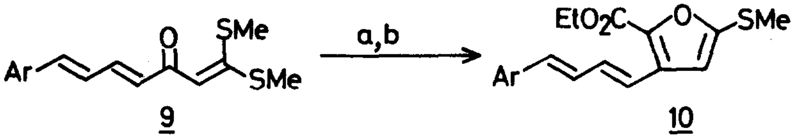
6–8	R^1	% yield (7)	% yield (8)
a	C_6H_5	20	42
b	$4\text{-}MeOC_6H_4$	25	48
c	$3,4\text{-}(MeO)_2C_6H_3$	55	28
d	$3,4,5\text{-}(MeO)_3C_6H_2$	60	30
e	3,4-methylene-dioxyC_6H_3	22	43
f	$4\text{-}ClC_6H_4$	–	67
g	Me	–	67

a. $Li^{\oplus}N^{\ominus}(SiMe_3)_2$ / $BrCH_2CO_2Et$, THF, −78°C ; b. NH_4Cl / H_2O

Scheme 2



Scheme 3

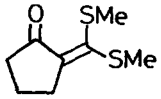
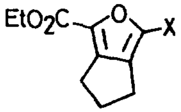
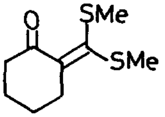
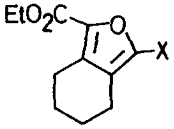
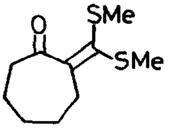
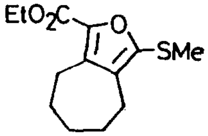
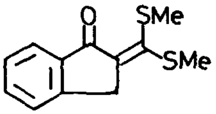
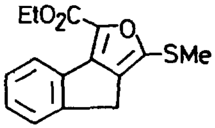
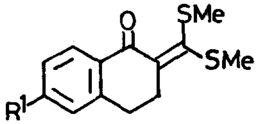
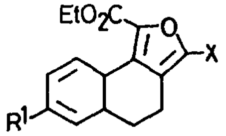
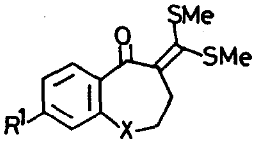
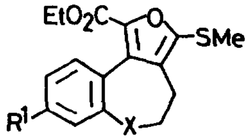


9,10 a, Ar=C_6H_5 , 52%

b, Ar=$4\text{-}MeOC_6H_4$, 51%

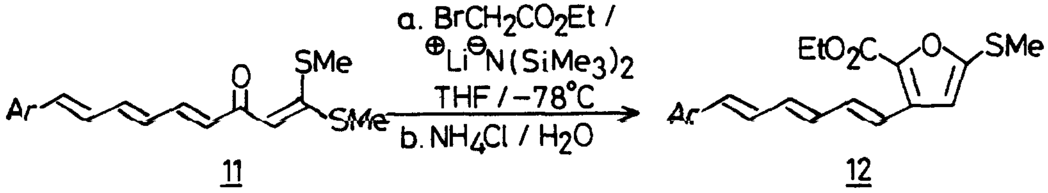
Scheme 4

Table 2: Synthesis of Ethyl 3,4-annelated furan-2-carboxylates (4) and (5)

Entry	Starting material	Product 4, 5	% Yield
			
1	1i	4i, X=SMe	58
2[a]	4i	5i, X=H	70
			
3	1j	4j, X=SMe	60
4[a]	4j	5j, X=H	85
			
5	1k	4k	59
			
6	1l	4l	56
			
7	1m, R^1= H	4m, R^1= H; X= SMe	67
8[a]	4m	5m, R^1= H; X= H	80
9	1n, R^1=MeO	4n, R^1= MeO; X=SMe	69
			
10	1o, R^1=H; X= CH$_2$	4o, R^1=H; X=CH$_2$	55
11	1p, R^1=Me, X=S	4p, R^1=Me; X=S	52

[a] Desulphurization of 4 with Raney Nickel

flexibility in the choice of dithioacetals easily accessible from a variety of active methylene ketones.



11,12 a, Ar = C_6H_5 , 58%

b, Ar = 4-$MeOC_6H_4$, 49 %

Scheme 5

EXPERIMENTAL SECTION

Melting points were determined on a Thomas Hoover apparatus and are uncorrected. The i.r. spectra were obtained on a Perkin Elmer 297 spectrophotometer. ^{1}H n.m.r. spectra were recorded on Varian EM-390 spectrometer and are reported in δ units downfield from Me_4Si. Mass spectra were obtained on Jeol D-600 spectrometer.

All the ketene dithioacetals 1a-p, 6a-g, 9a,b and 11a,b were prepared according to earlier reported procedure[7a-f].

General Procedure for the synthesis of Ethyl 3,4-substituted and annelated-5-methylthio furan-2-carboxylates (4a-p, 7a-e, 8a-g, 10a,b, 12a,b):

To a nitrogen flushed 100 ml three necked flask equipped with nitrogen inlet, septum inlet and magnetic stirrer was added a solution of lithium bis(trimethylsilyl)amide[8] (3.4g, 0.02 m) in dry THF (15 mL) and the flask was cooled to -78°C. A solution of ethyl α-bromoacetate (3.2g, 0.02m) in dry THF (10 mL) was then added dropwise (5 min) to the cooled mixture and stirred for 10 min. The corresponding dithioacetal (0.01 m) dissolved in dry THF (20 mL) was then added over a period of 10 min. and the mixture was stirred at -78°C for 30 min. followed by further stirring at room temperature for 12 h. The reaction mixture was then poured over saturated aqueous ammonium chloride (100 mL), extracted with ether (3x50 mL), the combined organic layer washed with water (1x100 mL), dried (anhyd. Na_2SO_4) and the solvent was removed to give the crude product which was further purified by passing through neutral alumina column. Elution with hexane yielded the pure product in good yield.

Ethyl 3-methyl-5-methylthio furan-2-carboxylate (4a); viscous liquid; IR: ν_{max} (CCl_4): 1710 cm^{-1} ^{1}H NMR (CCl_4): 1.33(t,J=6Hz,3H,CH_2CH_3); 2.23(s,3H,CH_3); 2.45(s,3H,SCH_3); 4.24(q,J=6H,2H,CH_2CH_3); 6.09(s,1H,H-4). (Found: C,53.82; H,6.00. Calc. for $C_9H_{12}O_3S$: C,53.97; H,6.04%). m/z 200(100%,M^+)

Ethyl 3-ethyl-5-methylthio furan-2-carboxylate (**4b**); viscous liquid; IR: $\nu_{max}(CCl_4)$; 1700 cm^{-1}; ^1H NMR(CCl_4): 1.03-1.53(m,6H,$CH_2C\underline{H}_3$); 2.46(s,3H,$SC\underline{H}_3$); 2.76(q,J=7Hz,2H,$C\underline{H}_2CH_3$); 4.22(q,J=7Hz, 2H,$C\underline{H}_2CH_3$); 6.05(s,1H,$\underline{H}$-4). (Found: C,56.15; H,6.60. Calc. for $C_{10}H_{14}O_3S$: C,56.05; H,6.58%). m/z 214 (100%,M^+).

Ethyl 3-phenyl-5-methylthio furan-2-carboxylate (**4c**); white solid ($CHCl_3$); m.p. 52°C; IR: $\nu_{max}(CCl_4)$; 1700 cm^{-1}; ^1H NMR(CCl_4): 1.22(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 2.50(s,3H,$SC\underline{H}_3$); 4.22(q,J=6Hz, 2H, $C\underline{H}_2CH_3$); 6.42(s,1H,$\underline{H}$-4); 7.22-7.60(m,5H arom). (Found: C,64.22; H,5.31. Calc. for $C_{14}H_{14}O_3S$ C,64 .09; H,5.37%). m/z 262(100%,M^+).

Ethyl 3-(2-naphthyl)-5-methylthio furan-2-carboxylate (**4d**); viscous liquid; IR: ν_{max} (CCl_4); 1720 cm^{-1}; ^1H NMR (CCl_4): 1.24(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 2.54(s,3H,$SC\underline{H}_3$); 4.22(q,J=6Hz,2H,$CH_2C\underline{H}_3$); 6.52(s,1H,$\underline{H}$-4); 7.32-8.02(m,7H arom). (Found: C,69.35; H,5.10. Calc. for $C_{18}H_{16}O_3S$: C,69.20; H,5.16%). m/z 312(100%,M^+).

Ethyl 3- 2-furyl -5-methylthio furan-2-carboxylate (**4e**); viscous liquid; IR: $\nu_{max}(CCl_4)$;1720 cm^{-1}; ^1H NMR(CCl_4): 1.36(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 2.46(s,3H,$SC\underline{H}_3$); 4.32(q,J=6Hz,2H,$C\underline{H}_2CH_3$); 6.36-6.40(d,J=2Hz,1H,$\underline{H}$-4'); 6.66(s,1H,$\underline{H}$-4); 7.34(d,J=2Hz,$\underline{H}$-3'); 7.54(d,J=3Hz,1H,$\underline{H}$-5'). (Found: C, 57.28; H,4.72. Calc. for $C_{12}H_{12}O_4S$: C,57.12; H,4.79%). m/z 252(100%,M^+).

Ethyl 3-(2-thienyl)-5-methylthio furan-2-carboxylate (**4f**); viscous liquid; IR: $\nu_{max}(CCl_4)$; 1715 cm^{-1}; ^1H NMR(CCl_4); 1.36(t,J=7Hz,3H,$CH_2C\underline{H}_3$); 2.46(s,3H,$SC\underline{H}_3$); 4.36(q,J=6Hz,2H,$C\underline{H}_2CH_3$); 6.56(s,1H,$\underline{H}$-4); 7.06(m,1H,$\underline{H}$-4'); 7.35(d,J=2Hz,1H,$\underline{H}$-3'); 7.76(d,J=2Hz,1H,$\underline{H}$-5'). (Found: C, 53.81; H,4.46. Calc. for $C_{12}H_{12}O_3S_2$: C,53.70; H,4.50%). m/z 268(100%,M^+).

Ethyl 3,4-dimethyl-5-methylthio furan-2-carboxylate (**4g**); viscous liquid; IR: $\nu_{max}(CCl_4)$; 1710 cm^{-1}; ^1H NMR(CCl_4): 1.40(t,J=7Hz,3H,$CH_2C\underline{H}_3$); 2.18(s,3H,$C\underline{H}_3$); 2.48(s,6H,$SC\underline{H}_3$,$C\underline{H}_3$); 4.20(q,J=7Hz, 2H,$C\underline{H}_2CH_3$). (Found: C,56.13; H,6.52. Calc. for $C_{10}H_{14}O_3S$: C,56.05; H,6.58%). m/z 214(100%,M^+).

Ethyl 3-(4-methoxyphenyl)-4-methyl-5-methylthio furan-2-carboxylate (**4h**); viscous liquid; IR: $\nu_{max}(CCl_4)$; 1715 cm^{-1}; ^1H NMR(CCl_4); 1.21(t,J=7Hz,3H,$CH_2C\underline{H}_3$); 1.90(s,3H,$C\underline{H}_3$); 2.48(s,3H,$SC\underline{H}_3$); 3.78(s,3H,$OC\underline{H}_3$); 4.10(q,J=7Hz,2H,$C\underline{H}_2CH_3$); 6.79-7.20(m,4H arom). (Found: C,62.88; H,5.90. Calc. for $C_{16}H_{18}O_4S$: C,62.72; H,5.92%). m/z 306(100%,M^+).

Ethyl 6-methylthio-cyclopenta[c]furan-2-carboxylate (**4i**); viscous liquid; IR: $\nu_{max}(CCl_4)$; 1710 cm^{-1}; ^1H NMR(CCl_4): 1.39(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 2.29-2.99(m,6H, ring $C\underline{H}_2$); 2.49(s,3H,$SC\underline{H}_3$); 4.28(q,J=6Hz,2H,$C\underline{H}_2CH_3$). (Found: C,58.48; H,6.26. Calc. for $C_{11}H_{14}O_3S$: C,58.32; H,6.28%). m/z 226(100%,M^+).

Ethyl 7-methylthio-cyclohexa[c] furan-2-carboxylate (**4j**); white solid ($CHCl_3$); m.p. 45-47°C; IR: ν_{max}(KBr) 1690 cm^{-1}; ^1H NMR(CCl_4): 1.34(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 1.60-1.82(m,4H,ring $C\underline{H}_2$); 2.42 (s,3H,$SC\underline{H}_3$); 2.31-2.82(m,4H,ring $C\underline{H}_2$); 4.20(q,J=6Hz,2H,$C\underline{H}_2CH_3$). (Found: C,59.82; H,6.68. Calc. for $C_{12}H_{16}O_3S$: C,59.97; H,6.71%). m/z 240(100%,M^+).

Ethyl 8-methylthio-cyclohepta[c]-furan-2-carboxylate (**4k**); viscous liquid; IR: $\nu_{max}(CCl_4)$; 1710 cm^{-1}; ^1H NMR(CCl_4): 1.36(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 1.44-1.86(m,6H,ring $C\underline{H}_2$); 2.42(s,3H,$SC\underline{H}_3$); 2.42-2.62(m,2H,ring $C\underline{H}_2$); 2.84-3.02(m,2H,ring $C\underline{H}_2$); 4.26(q,J=6Hz,2H,$C\underline{H}_2CH_3$). (Found: C,61.49; H,7.10. Calc. for $C_{13}H_{18}O_3S$: C,61.38; H,7.13%). m/z 254(100%,M^+).

Ethyl 2-methylthio(3H)indano[2,1-c] furan-8-carboxylate (**4l**); viscous liquid; IR: $\nu_{max}(CCl_4)$; 1710 cm^{-1}; ^1H NMR(CCl_4): 1.44(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 2.56(s,3H,$SC\underline{H}_3$); 3.70(s,2H,ring $C\underline{H}_2$); 4.44 (q,J=6Hz,2H,$C\underline{H}_2CH_3$); 7.20-7.46(m,3H,arom); 8.13-8.23(m,1H,arom). (Found: C,65.57; H,5.12. Calc. for $C_{15}H_{14}O_3S$: C,65.67; H,5.14%). m/z 274(100%,M^+).

Ethyl 2-methylthio-3,4-dihydronaphtho[2,1-c]furan-9-carboxylate (**4m**); viscous liquid; IR: $\nu_{max}(CCl_4)$; 1710 cm^{-1}; ^1H NMR($CDCl_3$): 1.34(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 2.44(s,3H,$SC\underline{H}_3$); 2.52-2.94(m, 4H,ring $C\underline{H}_2$); 4.36(q,J=6Hz,2H,$C\underline{H}_2CH_3$); 7.14-7.46(m,3H arom); 8.46-8.64(m,1H arom). (Found: C,66.79; H,5.53. Calc. for $C_{16}H_{16}O_3S$: C,66.64; H,5.59%). m/z 288(100%,M^+).

Ethyl 2-methylthio-6-methoxy-3,4-dihydronaphtho[2,1-c]furan-9-carboxylate (**4n**); viscous liquid; IR: $\nu_{max}(CCl_4)$; 1700 cm^{-1}; ^1H NMR(CCl_4); 1.36(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 2.42(s,3H,$SC\underline{H}_3$); 2.53-2.88 (m,4H,ring $C\underline{H}_2$); 3.72(s,3H,$OC\underline{H}_3$); 4.30(q,J=6Hz,2H,$C\underline{H}_2CH_3$); 6.58-6.85(m,2H arom); 8.46-8.60(m, 1H arom). (Found: C,64.20; H,5.62. Calc. for $C_{17}H_{18}O_4S$: C,64.15; H,5.65%). m/z 318(100%,M^+).

Ethyl 2-methylthio-4,5-dihydro(3H)benzocyclohepta[2,1-c]furan-9-carboxylate (**4o**); viscous liquid; IR: $\nu_{max}(CCl_4)$; 1700 cm^{-1}; ^1H NMR(CCl_4): 1.30(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 1.78-2.24(m,2H,ring $C\underline{H}_2$); 2.16-2.64(M,4H,ring $C\underline{H}_2$); 2.50(s,3H,$SC\underline{H}_3$); 4.20(q,J=6Hz,2H,$C\underline{H}_2CH_3$); 7.24-7.32(m,3H arom);

7.44-7.64(m,1H arom). (Found: C,67.68; H,5.90. Calc. for $C_{17}H_{18}O_3S$: C,67.52; H,5.99%). m/z 302(100%,M$^+$).

Ethyl 2-methylthio-7-methyl-3,4-dihydro-[1]benzthiepino[4,5-c] furan-10-carboxylate (4p); viscous liquid; IR: ν_{max} (CCl$_4$) 1710 cm^{-1}; ^{1}H NMR(CDCl$_3$): 1.31(t,J=6Hz,3H,CH$_2$CH$_3$); 2.36(s,3H,CH$_3$); 2.50(s,3H,SCH$_3$); 2.57-2.71(m,2H,ring,CH$_2$); 2.81-3.36(m,2H,SCH$_2$); 4.31(q,J=6Hz,2H,CH$_2$CH$_3$); 7.01-7.72(m,3H arom).(Found: C,61.21; H,5.38. Calc. for $C_{17}H_{18}O_3S_2$: C,61.05; H,5.42%). m/z 334(100%,M$^+$).

General Procedure for Raney Nickel Desulphurization of Furans 4a-c,e,i-j,m :

To a solution of the appropriate methylthiofuran (0.005 m) in ethanol (25 ml) freshly prepared W$_4$ Raney Nickel (~5g) was added and the reaction mixture stirred at room temperature for 1 hr. It was then filtered through Kieselguhr, washed with hot chloroform (3x15 ml), and the solvent is evaporated from the combined filtrate to give the crude desulphurized product,which was further purified by passing through neutral alumina column (elution with hexane). The spectral and analytical data of furans thus obtained are given below.

Ethyl 3-methyl furan-2-carboxylate (5a)[6b];viscous liquid; IR: ν_{max}(CCl$_4$) 1700 cm^{-1}; ^{1}H NMR (CCl$_4$): 1.36(t,J=6Hz,3H,CH$_2$CH$_3$); 2.30(s,3H,CH$_3$); 4.30(q,J=6Hz,2H,CH$_2$CH$_3$); 6.26(d,J=3Hz,1H, H-4); 7.36(d,J=3Hz,1H,H-5).

Ethyl 3-ethyl furan-2-carboxylate (5b); viscous liquid; IR: ν_{max} (CCl$_4$) 1710 cm^{-1}; ^{1}H NMR (CDCl$_3$): 1.03-1.66(m,6H,CH$_2$CH$_3$); 2.83(q,J=7Hz,2H,CH$_2$CH$_3$); 4.30(q,J=7Hz,CH$_2$CH$_3$); 6.36(d,J=3Hz, 1H,H-4); 7.43(d,J=3Hz,1H,H-5). (Found: C,64.38; H,7.09. Calc. for $C_9H_{12}O_3$: C,64.26; H,7.19%). m/z 168(25%,M$^+$).

Ethyl 3-phenyl furan-2-carboxylate (5c); viscous liquid; IR: ν_{max} (CCl$_4$) 1705 cm^{-1}; ^{1}H NMR (CDCl$_3$); 1.26(t,J=6Hz,3H,CH$_2$CH$_3$); 4.36(q,J=6Hz,2H,CH$_2$CH$_3$); 6.63(d,J=2Hz,1H,H-4); 7.36(d,J=2Hz, 1H,H-5); 7.43-7.70(m,5H arom). (Found: C,72.38; H,5.54. Calc. for $C_{13}H_{12}O_3$: C,72.20; H,5.59%). m/z 216(95%,M$^+$).

Ethyl 3-(2-furyl) furan-2-carboxylate (5e); viscous liquid; IR: ν_{max}(CCl$_4$) 1710 cm^{-1}; ^{1}H NMR (CDCl$_3$); 1.36(t,J=6Hz,3H,CH$_2$CH$_3$); 4.33(q,J=6Hz,2H,CH$_2$CH$_3$); 6.33-6.56(m,1H,H-4'); 6.83(d,J=3Hz, H-4); 7.40(d,J=3Hz,2H,H-3',H-5); 7.50(d,J=3Hz,1H,H-5). (Found: C,64.22; H,4.79. Calc. for $C_{11}H_{10}O_4$: C,64.07; H,4.88%). m/z 206(100%,M$^+$).

Ethyl cyclopenta[c]furan-2-carboxylate (5i); viscous liquid; IR: ν_{max}(CCl$_4$) 1710 cm^{-1}; ^{1}H NMR (CCl$_4$); 1.33(t,J=6Hz,3H,CH$_2$CH$_3$); 2.23-2.93(m,6H,ring CH$_2$); 4.20(q,J=6Hz,2H,CH$_2$CH$_3$); 7.10 (s,1H olefinic). (Found: C,66.78; H,6.68. Calc. for $C_{10}H_{12}O_3$: C,66.64; H,6.71%). m/z 180 (41%,M$^+$).

Ethyl cyclohexa[c]furan-2-carboxylate (5j); viscous liquid; IR: ν_{max} (CCl$_4$) 1700 cm^{-1};^{1}H NMR (CDCl$_3$); 1.36(t,J=6Hz,3H,CH$_2$CH$_3$); 1.50-1.86(m,4H,ring CH$_2$); 2.40-2.63(m,2H,ring CH$_2$); 2.73-2.93(m,2H,ring CH$_2$); 4.33(q,J=6Hz,2H,CH$_2$CH$_3$); 7.26(s,1H olefinic). (Found: C,68.11; H,7.06. Calc. for $C_{11}H_{14}O_3$: C,68.02; H,7.26%).

Ethyl-3,4-dihydronaphtho[2,1-c]furan-2-carboxylate (5m); viscous liquid; IR: ν_{max} (CCl$_4$) 1700 cm^{-1}; ^{1}H NMR(CDCl$_3$); 1.36(t,J=6Hz,3H,CH$_2$CH$_3$); 2.53-2.93(m,4H,ring CH$_2$); 4.33(q,J=6Hz,2H, CH$_2$CH$_3$); 7.03-7.33(m,3H arom, 1H olefinic); 8.36-8.63(m,1H arom). (Found: C,74.25; H,5.80. Calc. for $C_{15}H_{14}O_3$: C,74.36; H,5.82%). m/z 242(100%,M$^+$).

Ethyl 3-styryl-5-methylthio furan-2-carboxylate (7a); viscous liquid; IR: ν_{max}(CCl$_4$); 1690, 1600 cm^{-1}; ^{1}H NMR(CCl$_4$); 1.33(t,J=6Hz,3H,CH$_2$CH$_3$); 2.46(s,3H,SCH$_3$); 4.33(q,J=6Hz,2H,CH$_2$CH$_3$); 6.56(s,1H,H-4); 6.83(d,J=16Hz,1H olefinic); 7.16-7.56(m,5H arom); 7.60(d,J=16Hz,1H olefinic). (Found: C,66.49; H,5.50. Calc. for $C_{16}H_{16}O_3S$: C,66.64; H,5.59%). m/z 288(100%,M$^+$).

Ethyl 3-(4-methoxystyryl)-5-methylthio furan-2-carboxylate (7b); viscous liquid; IR: ν_{max} (CCl$_4$); 1669 cm^{-1}; ^{1}H NMR(CDCl$_3$): 1.43(t,J=7Hz,3H,CH$_2$CH$_3$); 2.53(s,3H,SCH$_3$); 3.86(s,3H,OCH$_3$); 4.40(q,J=7Hz,2H,CH$_2$CH$_3$); 6.66(s,1H,H-4); 6.83-7.03(m,2H arom + 1H olefinic); 7.33-7.60(m, 2H arom + 1H olefinic). (Found: C,64.21; H,5.63. Calc. for $C_{17}H_{18}O_4S$: C,64.12; H,5.69%). m/z 318(21%,M$^+$).

Ethyl 3-(3,4-dimethoxystyryl)-5-methylthio furan-2-carboxylate (7c); white solid (CHCl$_3$);

2H,$C\underline{H}_2CH_3$); 6.60(s,1H,$\underline{H}$-4); 6.73-7.13(m,3H,1H arom+2H olefinic); 7.26-7.63(m,4H arom+2H olefinic). (Found: C,68.70; H,5.74. Calc. for $C_{18}H_{18}O_3S$: C,68.76; H,5.77%). m/z 314(79%,M^+).

Ethyl 3-[4-(4-methoxyphenyl)-1,3-butadienyl]-5-methylthio furan-2-carboxylate (10b);viscous liquid; IR: ν_{max} (CCl_4) 1710 cm^{-1}; ^1H NMR($CDCl_3$): 1.40(t,J=7Hz,3H,$CH_2C\underline{H}_3$); 2.53(s,3H,$SC\underline{H}_3$); 3.83(s,3H,$OC\underline{H}_3$); 4.43(q,J=7Hz,2H,$C\underline{H}_2CH_3$); 6.60(s,1H,$\underline{H}$-4); 6.66-6.96(m,2H arom+2H olefinic); 7.26-7.50(m,2H arom+2H olefinic). (Found: C,66.15; H,5.82. Calc. for $C_{19}H_{20}O_4S$: C,66.25; H, 5.85%). m/z 344(17%,M^+).

Ethyl 3-(6-phenyl-1,3,5-hexatrienyl)-5-methylthio furan-2-carboxylate (12a); viscous liquid; IR: ν_{max} (CCl_4) 1700 cm^{-1}; ^1H NMR($CDCl_3$): 1.36(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 2.50(s,3H,$SC\underline{H}_3$); 4.36(q, J=6Hz,2H,$C\underline{H}_2CH_3$); 6.36-6.96(m,7H olefinic); 7.23-7.63(m,5H arom). (Found: C,70.44; H,5.88. Calc. for $C_{20}H_{20}O_3S$: C,70.55; H,5.92%). m/z 340(44%,M^+).

Ethyl 3-[6-(4-methoxyphenyl)-1,3,5-hexatrienyl]furan-2-carboxylate (12b); viscous liquid; IR: ν_{max} (CCl_4) 1705 cm^{-1}; ^1H NMR($CDCl_3$): 1.36(t,J=7Hz,3H,$CH_2C\underline{H}_3$); 2.46(s,3H,$SC\underline{H}_3$); 3.76(s, 3H,$OC\underline{H}_3$); 4.36(q,J=7Hz,2H,$CH_2C\underline{H}_3$); 6.36-6.93(m,5H olefinic+3H arom); 7.05-7.06(m,2H arom+1H olefinic). (Found: C,67.28; H,5.96.Calc. for $C_{21}H_{22}O_4S$: C,67.08; H,5.98%). m/z 370(15%,M^+).

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m.p. 98°C; IR: ν_{max}(KBr): 1680 cm^{-1}; ^1H NMR($CDCl_3$): 1.30(t,J=7Hz,3H,$CH_2C\underline{H}_3$); 2.40(s,3H,$SC\underline{H}_3$); 3.76(s,6H,$OC\underline{H}_3$); 4.33(q,J=7Hz,2H,$C\underline{H}_2CH_3$); 6.66(s,1H,$\underline{H}$-4); 6.80-7.53(m,3H arom + 1H olefinic); 7.86(d,J=16Hz,1H olefinic). (Found: C,62.19; H,5.72. Calc. for $C_{18}H_{20}O_5S$: C,62.04; H,5.78%). m/z 348(73%,M^+).

Ethyl 3-(3,4,5-trimethoxystyryl)-5-methylthio furan-2-carboxylate (7d); white solid ($CHCl_3$); m.p. 100°C; IR: ν_{max}(KBr): 1680 cm^{-1}; ^1H NMR($CDCl_3$): 1.36(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 2.46(s,3H,$SC\underline{H}_3$); 3.86(s,3H,$OC\underline{H}_3$); 3.90(s,6H,$OC\underline{H}_3$); 4.43(q,J=6Hz,2H,$C\underline{H}_2CH_3$); 6.66(s,1H,$\underline{H}$-4); 6.76-6.89(m,2H arom); 6.86(d,J=16Hz,1H olefinic). 7.90(d,J=16Hz,1H olefinic). (Found: C,60.18; H,5.77. Calc. for $C_{19}H_{22}O_6S$: C,60.29; H,5.86%). m/z 378(100%,M^+).

Ethyl 3-(3,4-methylenedioxystyryl)-5-methylthio furan-2-carboxylate (7e); viscous liquid;IR: ν_{max}(CCl_4): 1720 cm^{-1}; ^1H NMR($CDCl_3$); 1.46(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 2.46(s,3H,$SC\underline{H}_3$); 4.36(q,J=6Hz, 2H,$C\underline{H}_2CH_3$); 5.93(s,2H,O-$C\underline{H}_2$-O); 6.56(s,1H,$\underline{H}$-4); 6.66-7.33(m,3H arom + 1H olefinic). 7.50(d, J=16Hz,1H cyclopropyl). (Found: C,61.32; H,4.76. Calc. for $C_{17}H_{16}O_5S$: C,61.43; H,4.85%). m/z 332(100%,M^+).

Ethyl 3-[2-carbethoxy-3-phenylcycloprop-1-yl]-5-methylthiofuran-2-carboxylate (8a); viscous liquid; IR: ν_{max} (CCl_4) 1720 cm^{-1}; ^1H NMR($CDCl_3$): 1.13-1.56(m,6H,$CH_2C\underline{H}_3$); 2.50(s,3H,$SC\underline{H}_3$); 2.26-2.43(m,1H,cyclopropyl); 2.83-3.03(m,1H, cyclopropyl); 3.23-3.46(m,1H,cyclopropyl); 6.46 (s,1H,$\underline{H}$-4); 7.13-7.46(brs,5H arom). (Found: C,64.05; H,5.83. Calc. for $C_{20}H_{22}O_5S$: C,64.15; H,6.22%). m/z 374(24%,M^+).

Ethyl 3-{2-carbethoxy-3-(4-methoxyphenyl)cycloprop-1-yl}-5-methylthio furan-2-carboxylate(8b); viscous liquid; IR: ν_{max} (CCl_4) 1710 cm^{-1}; ^1H NMR($CDCl_3$): 0.93(t,J=7Hz,3H,$CH_2C\underline{H}_3$); 1.23(t, J=7Hz,3H,$CH_2C\underline{H}_3$); 2.03(m,1H,cyclopropyl); 2.43(s,3H,$SC\underline{H}_3$); 2.53-2.73(m,1H,cyclopropyl); 3.56-3.73(m,1H,cyclopropyl); 3.76(s,3H,$OC\underline{H}_3$); 3.80(q,J=7Hz,2H,$C\underline{H}_2CH_3$); 4.36(q,J=7Hz,2H,$C\underline{H}_2CH_3$); 6.10(s,1H,$\underline{H}$-4);; 6.83(d,J=7Hz,A_2B_2,2H arom); 7.30(d,J=7Hz,A_2B_2,2H arom). (Found: C,62.24; H, 5.94. Calc. for $C_{21}H_{24}O_6S$:C,62.35; H,5.98%). m/z 404(100%, M^+).

Ethyl 3-{2-carbethoxy-3-(3,4-dimethoxyphenyl)cycloprop-1-yl}-5-methylthio furan-2-carboxylate (8c); viscous liquid; IR: ν_{max} (CCl_4) 1720 cm^{-1}; ^1H NMR($CDCl_3$); 1.03(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 1.33 (t,J=6Hz,3H,$CH_2C\underline{H}_3$); 2.33-2.40(m,1H,cyclopropyl); 2.46(s,3H,$SC\underline{H}_3$); 2.83-2.96(m,1H,cyclopropyl); 3.60-3.73(m,1H,cyclopropyl); 3.53-4.03(m,2H,$C\underline{H}_2CH_3$+6H,$OC\underline{H}_3$); 4.33(q,J=7Hz,2H,$C\underline{H}_2CH_3$); 6.16(s, 1H,$\underline{H}$-4); 6.73-7.06(m,3H arom). (Found: C,60.69; H,6.00. Calc. for $C_{22}H_{26}O_7S$: C,60.81; H,6.03%). m/z 434(16%,M^+).

Ethyl 3-[2-carbethoxy-3-(3,4,5-trimethoxyphenyl)cycloprop-1-yl]-5-methylthio furan-2-carboxylate (8d); white solid; m.p. 110°C; IR: ν_{max}(KBr): 1715 cm^{-1}; ^1H NMR(CCl_4); 1.03(t,J=6Hz,3H, $CH_2C\underline{H}_3$); 1.43(t,J=6Hz,3H,$CH_2C\underline{H}_3$); 2.00-2.26(m,1H,cyclopropyl); 2.46(s,3H,$SC\underline{H}_3$); 2.60-2.83(m, 1H,cyclopropyl); 3.13-3.53(m,1H,cyclopropyl); 3.63-4.16(m,9H,$(OCH_3)_3$+2H,$C\underline{H}_2CH_3$); 4.46(q,J=6Hz, 2H,$C\underline{H}_2CH_3$); 6.16(s,1H,$\underline{H}$-4); 6.66(brs,2H arom). (Found: C,59.35; H,6.01. Calc. for $C_{23}H_{28}O_8S$: C,59.46; H,6.07%). m/z 464(74%,M^+).

Ethyl 3-[2-carbethoxy-3-(3,4 -methylenedioxyphenyl)cycloprop-1-yl]-5-methylthio furan-2-carboxylate (8e); viscous liquid; IR: ν_{max}(CCl_4) 1710 cm^{-1}; ^1H NMR(CCl_4); 1.03(t,J=7Hz,3H,$C\underline{H}_2CH_3$); 1.36(t,J=7Hz,3H,$CH_2C\underline{H}_3$); 2.10-2.30(m,1H,cyclopropyl); 2.46(s,3H,$SC\underline{H}_3$); 2.53-2.70(m,1H,cyclopropyl); 3.50-3.73(m,1H,cyclopropyl); 3.86(q,J=7Hz,2H,$CH_2C\underline{H}_3$); 4.40(q,J=7Hz,2H,$C\underline{H}_2CH_3$); 5.96 (s,2H,methylene $OC\underline{H}_2O$); 6.13(s,1H,$\underline{H}$-4); 6.66-6.96(m,3H arom). (Found: C,60.15; H,5.28. Calc. for $C_{21}H_{22}O_7S$: C,60.27; H,5.30%). m/z 418(100%,M^+).

Ethyl 3-[2-carbethoxy-3-(4-chlorophenyl)cycloprop-1-yl]-5-methylthio furan-2-carboxylate(8f); viscous liquid; IR: ν_{max}(CCl_4) 1720 cm^{-1}; ^1H NMR(CCl_4); 1.00(t,J=7Hz,3H,$CH_2C\underline{H}_3$); 1.36(t,J=7Hz, 3H,$C\underline{H}_2CH_3$); 2.13-2.33(m,1H,cyclopropyl); 2.46(s,3H,$SC\underline{H}_3$); 2.53-2.76(m,1H,cyclopropyl); 3.56-3.76(m,1H,cyclopropyl); 3.96(q,J=7Hz,2H,$CH_2C\underline{H}_3$); 4.36(q,J=7Hz,2H,$C\underline{H}_2CH_3$); 6.13(s,1H,$\underline{H}$-4); 7.20-7.43(brs,4H arom). (Found: C,64.21; H,5.57. Calc. for $C_{20}H_{21}ClO_5S$: C,64.32; H,5.66%).m/z 408, 410(59, 23%,M^+).

Ethyl 3-[2-carbethoxy-3-(4-methyl)cycloprop-1-yl]-5-methylthio furan-2-carboxylate (8g);viscous liquid; IR: ν_{max}(CCl_4) 1720 cm^{-1}; ^1H NMR(CCl_4): 1.13-1.63(m,6H,$C\underline{H}_2CH_3$+3H,$C\underline{H}_3$); 1.63-2.03(m, 1H,cyclopropyl); 2.46(s,3H,$SC\underline{H}_3$); 2.76-2.96(m,1H,cyclopropyl); 3.93-4.53(m,4H,$C\underline{H}_2CH_3$); 5.93 (s,1H,$\underline{H}$-4). (Found: C,57.60; H,6.42. Calc. for $C_{15}H_{20}O_5S$: C,57.71; H,6.45%). m/z 312(62%,M^+).

Ethyl 3-(4-phenyl-1,3-butadienyl)-5-methylthio furan-2-carboxylate (10a); viscous liquid;IR: ν_{max}(CCl_4) 1710 cm^{-1}; ^1H NMR($CDCl_3$): 1.43(t,J=6Hz,3H,CH2C$\underline{H}_3$); 2.50(s,3H,$SC\underline{H}_3$); 4.40(q,J=6Hz,