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3-METHYLTHIO-1,2-DITHIOLYLIUM SALTS

REACTION WITH 4-HYDROXY-6-METHYL-2H-PYRAN-2-ONE AND 4-HYDROXYCOUMARIN

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Abstract—The reaction of 4- and 5-aryl-3-methylthio-1,2-dithiolylium iodides with 4-hydroxy-6-methyl-2H-pyran-2-one and 4-hydroxycoumarin has been studied. 4-Substituted salts yielded 3-aryl-7-methyl-2-thioxo-2H,5H-pyrano[3,2-*c*]pyran-5-ones and 3-aryl-2-thioxo-2H,5H-pyrano[3,2-*c*]benzo[*e*]pyran-5-ones, respectively, whereas 5-substituted salts gave rise to 3-(5'-aryl-1',2'-dithiol-3'-ylidene)-6-methyl-2H-pyran-2,4-diones and 3-(5'-aryl-1',2'-dithiol-3'-ylidene)-2H-benzo[*b*]-pyran-2,4-diones.

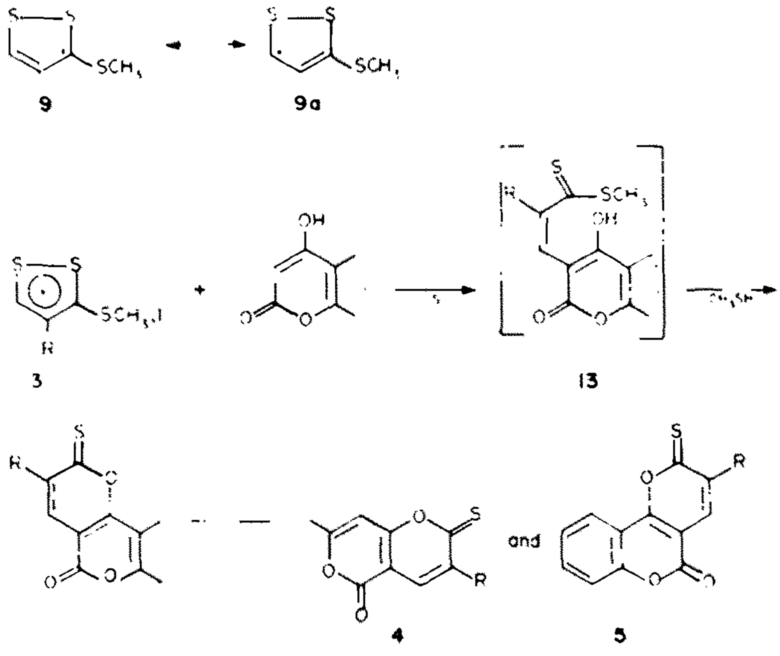
5-Aryl-3-methylthio-1,2-dithiolylium salts condense with compounds containing an activated methylene group to give α-(1',2'-dithiol-3'-ylidene)ketones.[1] Salts with a *tertiary* alkyl group attached to C atom 5 react as the aryl substituted compounds, whereas salts with a *primary* or *secondary* alkyl group give rise to intensively coloured selfcondensation products of unknown structure.[2] Reactions of salts without a substituent in position 5 have hitherto not been reported.

We have studied the reaction of 4- and 5-aryl-3-methylthio-1,2-dithiolylium iodides with 4-hydroxy-6-methyl-2H-pyran-2-one (**1**) and 4-hydroxycoumarin (**2**). 4-Aryl-1,2-dithiolylium iodies (**3**) gave rise to 3-aryl-7-methyl-2-thioxo-2H,5H-pyrano[3,2-*c*]pyfan-5-ones (**4**) and 3-aryl-2-thioxo-2H,5H-pyrano[3,2-*c*]benzo[*e*]pyran-5-ones (**5**), respectively, whereas 5-aryl-3-methylthio-1,2-dithiolylium iodides (**6**) yielded 3-(5'-aryl-1',2'-dithiol-3'-ylidene)-6-methyl-2H-pyran-2,4-diones (**7**) and 3-(5'-aryl-1',2'-dithiol-3'-ylidene)-2H-benzo[*b*]pyran-2, 4-diones (**8**).[1] **7** and **8** may be useful starting material for preparation of the rather inaccessible extended structures related to trithiapentalenes (see Ref. 1).

RESULTS AND DISCUSSION

Reaction of 4-aryl-3-methylthio-1,2-dithiolylium iodides with 4-hydroxy-6-methyl-2H-pyran-2-one and 4-hydroxycoumarin

The 3-methylthio-1,2-dithiolylium cation can be regarded as a hybride of several mesomeric forms such as **9** and **9a** (Scheme 1). 5-Aryl-substituted salts bear the most bulky substitutent at C atom 5 (C5) and the reaction course of these salts can be predicted on the basis of **9**.[1] In contrast, salts with a H atom attached to C5 should from steric arguments preferentially react according to **9a**. In

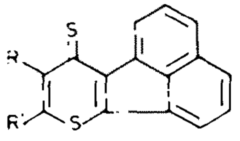


R = phenyl or p-tolyl

Scheme 1.

agreement with this assumption, we have found that the reaction of **3** with **1** and **2** gave rise to **4** and **9**, respectively (see Scheme 1).

The reactions were performed in N,N-dimethylformamide (*ca.* 25°, method A), glacial acetic acid (reflux, method B) and dichloromethane (reflux, method C) with pyridine as base. Whereas **5** was isolated in good yields when either of the methods A, B or C was used, only method A gave satisfactory yields of **4** (see Experimental).



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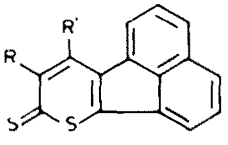

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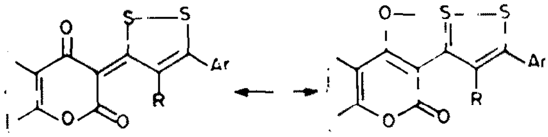
A French group has studied the reaction of 4-aryl-1,2-dithiole-3-thiones (**10**) with some carbanions and enamines. Mollier and Lozac'h[4] assigned structure **11** to the product from the reaction of **10** with acenaphthone, but later studies by Kim Son *et al.*[5] showed that the right structure was the isomeric **12**. In a similar reaction Patris[6] prepared some substituted 2H-thiopyran-2-thiones from **10** and the anion derived from ethyl cyanoacetate. Finally, Ishii *et al.*[7] found that the reaction of **10** with enamines gave rise to 2H-thiopyran-2-thiones.

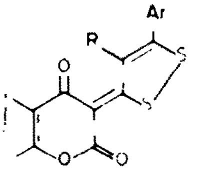
In these cases the formation of the products could be explained by assuming (*i*) a nucleophilic attack at C5 in the dithiole ring and cleavage of the C5–S bond, (*ii*) sulphur extrusion with formation of a dithioacid anion and (*iii*) attack of this anion at a CO- or masked CO group. The formation of **4** and **5** can be explained by a similar reaction mechanism (see Scheme 1). (*i*) and (*ii*) give the intermediate **13** which by elimination of methanethiol is converted to **4** and **5**.†

Reaction of 5-aryl-3-methylthio-1,2-dithiolylium iodides with 4-hydroxy-6-methyl-2H-pyran-2-one and 4-hydroxycoumarin

Normally, condensation of 5-aryl-3-methylthio-1,2-dithiolylium iodides with compounds containing an activated methylene group has been performed in refluxing glacial acetic acid with pyridine as base.[1] In addition to the condensation reaction, demethylation initiated by pyridine is reported to occur. During this investigation it was observed, that refluxing three salts (**6b**,**d** and **e**) in glacial acetic acid without pyridine resulted in conversion of the salts to the corresponding thiones within 0.5–2 hr.‡ The progress of the demethylation was easily followed by TLC and quantitative yields of the thiones were isolated. Thus, three reactions have to be considered under the reaction conditions normally employed. When the salt is unsubstituted in position 4, the condensation reaction apparently is favoured (Table 1, **7a**, **7b**, **8a** and **8b**). However, under these reaction conditions 4,5-diphenyl-3-methylthio-1,2-dithiolylium iodide gave unsatisfactory yields of the condensation products (Table 2). Probably steric interaction between the 2-CO group in the pyrone molecule and the 4-Ph group in the salt favours the demethylation reaction at the expense of the condensation reaction. In dichloromethane and N,N-dimethylformamide the side reactions proceeded slower than the condensation reaction and good yields of the desired products (**7e** and **8e**) were isolated (see Table 2). Other 4-substituted salts also gave rise to high yields of the condensation products when the reaction was performed in dichloromethane (Table 1).



14 14a



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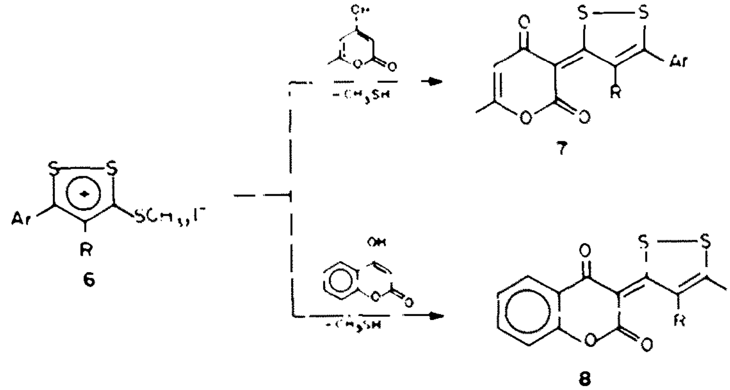
Two isomeric structures **14** and **15** may be assigned to the reaction products. In view of the known preference for ketonic oxygen to participate in heterapentalene



Compound number	**6a**	**6b**	**6c**	**6d**	**6e**	**6f**
R	H	H	H	CH_3	C_6H_5	
Ar	C_6H_5	p-$C_6H_4OCH_3$	p-C_6H_4F	C_6H_5	C_6H_5	–HC=CH·HC=CH·

Scheme 2.

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† A related reaction has been reported for 4-aryl-1,2-dithiolylium salts.[14]

‡ Probably the iodide ion acts as nucleophile.

Table 1. 3-(5'-Aryl-1',2'-dithiol-3'-ylidene)-6-methyl-2H-pyran-2,4-diones and 3-(5'-aryl-1',2'-dithiol-3'-ylidene)-2H-benzo[*b*]pyran-2,4-diones

Compound^a	R	Ar	Method^b	Yield (%)	M.p. (°C)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	p-[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	p-[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	Cf. Table 2	Cf. Table 2	[illegible]
[illegible]	-CH=CH-CH=CH-		[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
[illegible]	[illegible]	p-[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	p-[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	Cf. Table 2	Cf. Table 2	[illegible]
[illegible]	-CH=CH-CH=CH-		[illegible]	[illegible]	[illegible]

^{a}Cf. Scheme 1. ^{b}Cf. Experimental. ^{c}Recrystallized from [illegible]. ^{d}Recrystallized from [illegible] 2-methoxyethanol. ^{e}Recrystallized from [illegible]-methoxyethanol [illegible]. ^{f}Recrystallized from [illegible]-methoxyethanol water [illegible].

Table 2. A comparison of different reaction conditions for preparation of 3-(4',5'-diphenyl-1',2'-dithiol-3'-ylidene)-6-methyl-2H-pyran-2,4-diones (**7e**) and 3-(4',5'-diphenyl-1',2'-dithiol-3'-ylidene)-2H-benzo[*b*]pyran-2,4-dione (**8e**)

Reaction conditions^a	Yield (%)		
	[illegible]	[illegible]	[illegible]^b
A	[illegible]	-	[illegible]
B	[illegible]	[illegible]	-
C	[illegible]	[illegible]	-
D	[illegible]	-	[illegible]
	[illegible]	[illegible]	[illegible]^b
A	[illegible]	-	[illegible]
B	[illegible]	[illegible]	-
C	[illegible]	[illegible]	-
D	[illegible]	-	[illegible]

^{a}Cf. Experimental.

^{b}[illegible]: 4,5-Diphenyl-1,2-dithiole-3-thione.

formation when ester oxygen is also available,[8] structure **14** is considered most likely.

The almost identical frequency (*ca.* 1700 cm^{-1}, see Experimental) of the lactonic band in **7**, **8**, 3-aryl-4-hydroxy-6-methyl-2H-pyran-2-ones[9] and 3-aryl-4-hydroxycoumarins[10] excludes structure **15** as a distinct displacement of the carbonyl vibration is observed in all cases where a carbonyl group is situated *cis* to the dithiole ring and the established *cis*-interaction is operative (**14a** and **16**).†

The contribution of the mesoionic form exemplified with **16** in the description of α-(1',2'-dithiol-3'-ylidene)ketones has been discussed.[5] Recently, Lindberg *et al.*[11] have established that a correlation between the ^{19}F NMR chemical shifts of 5-(4'-fluorophenyl)-1,2-dithiole compounds and the S2p electron energies measured by ESCA exists. Therefore, a convenient evaluation of the positive charge taken by the dithiole ring in **7** and **8** might be obtained by measuring the ^{19}F chemical shifts of compounds **7c** and **8c**. The values found are 107.5 and 107.2 ppm, respectively. For compounds **17**, **18** and **19** the ^{19}F NMR chemical shifts reported[11] are 109.6, 109.1 and 107.8 ppm. Accordingly, the charge distribution in **7**, **8** and **19** is similar. On the basis of an IR investigation it is concluded,[12] that the non-polar resonance form **19a** only contributes slightly (*ca.* 8%) to the description of 2-(5'-aryl-1',2'-dithiol-3'-ylio)phenolates (**19**). However, in contrast to **19** it is possible to convert **7** and **8** to the corresponding 1,6,6aλ^4-trithiapentalenes (**20**) by reaction with phosphorus pentasulfide[3,13] and this observation indicates that the non-polar form is more important in the series **7** and **8**. A difference in importance of the non-polar form can be expected since the 2H-pyran-2-one and coumarin ring systems are only quasiaromatic.

EXPERIMENTAL

Microanalysis were carried out by Mr. P. Hansen, Microanalytical Department of the University of Copenhagen.

Instrumentation. IR: Perkin Elmer 457. MS: AEI MS-902. ^{1}H NMR: JEOL JNM-Fx 60. ^{19}F NMR: Bruker Hx 60.

The m.ps are uncorrected.

The 3-methylthio-1,2-dithiolylium iodides were prepared from the appropriate 1,2-dithiole-3-thiones.[14]

3-Aryl-7-methyl-2-thioxo-2H-5H-pyrano[3,2-c]pyran-5-ones (**4**) *and 3-aryl-2-thioxo-2H,5H-pyrano[3,2-c]benzo[e]pyran-5-ones* (**5**) (cf. Scheme 1)

Method A. The appropriate 4-aryl-3-methylthio-1,2-dithiolylium iodide (5 × 10^{-3} mol), 4-hydroxy-6-methyl-2H-pyran-2-one or

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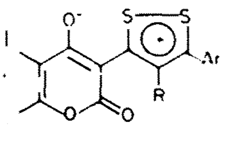
†In diethyl 2-(5'-(*p*-methoxyphenyl)-1',2'-dithiol-3'-ylidene)-malonate the *cis* CO group absorbs at 1605 cm^{-1} and the *trans* at 1677 cm^{-1}.[11]



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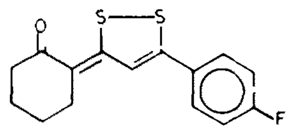

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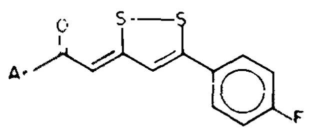

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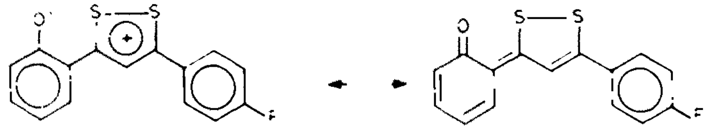
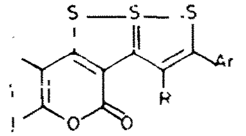


19 19a



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4-hydroxycoumarin (5×10^{-3} mol) and pyridine (4 ml) in N,N-dimethylformamide (80 ml) were stirred at room temp. for *ca.* 24 hr. The mixture was poured on water and the separated crystals were collected.

Method B. 4-Aryl-3-methylthio-1,2-dithiolylium iodide (2×10^{-2} mol), 4-hydroxycoumarin (2×10^{-2} mol) and pyridine (60 ml) in glacial AcOH (625 ml) were refluxed for 1 hr. The precipitated crystals were collected and recrystallized.

Method C (cf. Method B). The reactants (5×10^{-3} mol) and pyridine (15 ml) in dichloromethane (250 ml) were refluxed for 1 hr. Evaporation *in vacuo* gave crystals which were recrystallized.

3-*Phenyl-7-methyl-2-thioxo-2H,5H-pyrano*[3,2-c]*pyran-5-one*

Method A. Purified by preparative layer chromatography (silica, chloroform, 3 times). Orange crystals (yield = 49%, m.p. = 216–219°C d). ^1H NMR (60 MHz, $CDCl_3$): 2.40 (3H), 6.31 (1H), 7.41 (5H) and 7.62 (1H). IR (KBr): 1720 cm^{-1}. MS: *m/e* (%) = 270 (62, M^+), 269 (100), 242 (4) and 227 (22). (Found: C, 66.50; H, 3.70; S, 11.68. $C_{15}H_{10}SO_3$ requires: C, 66.67; H, 3.73; S, 11.85%).

3-(p-*Tolyl*)-7-*methyl-2-thioxo-2H,5H-pyrano*[3,2-c]*pyran-5-one*

Method A. Purified by preparative layer chromatography (silica, chloroform, 3 times). Orange crystals (yield = 45%, m.p. = 242–247°C d.). ^1H NMR (60 MHz, $CDCl_3$): 2.40 (6H), 6.33 (1H), 7.13–7.50 (4H) and 7.63 (1H). IR (KBr): 1735 cm^{-1}. MS: *m/e* (%) = 284 (100, M^+), 283 (86), 269 (72), 256 (8) and 241 (22). (Found: C, 67.85; H, 4.55; S, 11.42. $C_{16}H_{12}SO_3$ requires: C, 67.61; H, 4.27; S, 11.26%).

3-*Phenyl-2-thioxo-5H,5H-pyrano*[3,2-c]*benzo*[e]*pyran-5-one*

Method A, B and C. Orange crystals (yields = 72% (A), 77% (B) and 74% (C)). Recrystallized from 2-methoxyethanol or benzene (m.p. = 256–257°C). ^1H NMR (60 MHz, $CDCl_3$): 7.3–7.9 (9H) and 8.28 (1H). IR (KBr): 1720 cm^{-1}. MS: *m/e* (%) = 306 (80, M^+), 305 (14) and 288 (100). (Found: C, 70.59; H, 3.29; S, 10.45. $C_{18}H_{10}SO_3$ requires: C, 70.55; H, 3.28; S, 10.53%).

3-(p-*Tolyl*)-2-*thioxo-2H,5H-pyrano*[3,2-c]*benzo*[e]*pyran-5-one*

Method A and B. Orange crystals (yields = 81% (A) and 65% (B)). Recrystallized from 2-methoxyethanol or purified by preparative layer chromatography (silica, chloroform, 3 times) (m.p. = 262–264°). ^1H NMR (60 MHz, $CDCl_3$): 2.40 (3H, 7.1–7.8 (8H) and 8.28 (1H). IR (KBr): 1730 cm^{-1}. MS: *m/e* (%) = 320 (100, M^+), 319 (84), 305 (92) and 292 (53). (Found: C, 71.15; H, 3.92; S, 9.77. $C_{19}H_{12}SO_3$ requires: C, 71.25; H, 3.75; S, 10.00%).

3-(5'-*aryl*-1',2'-*dithiol*-3'-*ylidene*)-6-*methyl*-2H-*pyran*-2,4-*diones and* 3-(5'-*aryl*-1',2'-*dithiol*-3'-*ylidene*)-2H-*benzo*[b]*pyran*-2,4-*diones* (see Table 1).

Method A'. The appropriate 5-aryl-3-methylthio-1,2-dithiolylium iodide (2×10^{-2} mol), 6-methyl-4-hydroxy-2H-pyran-2-one or 4-hydroxy-coumarin (2×10^{-2} mol) and pyridine (60 ml) in glacial acetic acid (625 ml) were refluxed for *ca.* 2.5 hr. If crystals separated on cooling to room temp. they were collected. The filtrate was evaporated and the residue was extracted with boiling cyclohexane (250 ml) followed by boiling benzene (2 × 250 ml). In some cases crystals separated from the cyclohexane soln and they were collected. The benzene solution was evaporated and the residue together with the crystals previously collected were recrystallized (see Table 1).

Method B' (see Method A'). The reactants (5×10^{-3} mol) and pyridine (15 ml) in dichloromethane (250 ml) were refluxed for 6 hr. Purification as above.

Method C'. As method B', but the refluxing time was extended to *ca.* 21 hr.

Method D' (see Method A'). The reactants (5×10^{-3} mol) and pyridine (2 ml) in N,N-dimethylformamide (40 ml) were stirred at room temp. for 48–72 hr. After filtration the mixture was poured on water (160 ml). The crystals were collected, washed with water, dried and recrystallized (see Table 1).

IR (KBr): In both series **7** and **8** the lactonic CO band was observed within the range 1700–1715 cm^{-1}. ^1H NMR (60 MHz, DMSO-d_6): The signal from the 4-dithiole proton in compounds **7a** to **7c** (δ = *ca.* 9.5) and **8a** to **8c** (δ = *ca.* 9.1) was found at unusually low field due to anisotropic deshielding from the lactonic CO group. The positions and couplings of the other protons were as expected for compounds with structures **7** and **8**.[1] MS: The molecular ions gave rise to the base peaks in most cases. Analyses: **7a** (Found: C, 59.35; H, 3.48; S, 21.10. $C_{15}H_{10}S_2O_3$ requires: C, 59.61; H, 3.34; S, 21.19%). **7b** (Found: C, 57.95; H, 3.77; S, 19.29. $C_{16}H_{12}S_2O_4$ requires: C, 57.84; H, 3.64; S, 19.20%). **7c** (Found: C, 56.20; H, 3.00; S, 19.90. $C_{15}H_9S_2O_3F$ requires: C, 56.25; H, 2.81; S, 20.00%). **7d** (Found: C, 60.90; H, 3.71; S, 20.20. $C_{16}H_{12}S_2O_3$ requires: C, 60.76; H, 3.82; S, 20.25%). **7e** (Found: C, 66.55; H, 3.75; S, 16.80. $C_{21}H_{14}S_2O_3$ requires: C, 66.67; H, 3.73; S, 16.93%). **7f** (Found: C, 56.35; H, 2.95; S, 22.93. $C_{13}H_8S_2O_3$ requires: C, 56.53; H, 2.92; S, 23.18%). **8a** (Found: C, 64.00; H, 3.03; S, 19.05. $C_{18}H_{10}S_2O_3$ requires: C, 63.91; H, 2.98; S, 18.93%). **8b** (Found: C, 62.00; H, 3.32; S, 17.48. $C_{19}H_{12}S_2O_4$ requires: C, 61.96; H, 3.29; S, 17.38%). **8c** (Found: C, 60.50; H, 2.71; S, 17.95. $C_{18}H_9S_2O_3F$ requires: C, 60.67; H, 2.53; S, 17.98%). **8d** (Found: C, 64.80; H, 3.58; S, 18.12. $C_{19}H_{12}S_2O_3$ requires: C, 64.77; H, 3.43; S, 18.18%), **8e** (Found: C, 69.75; H, 3.34; S, 15.40. $C_{24}H_{14}S_2O_3$ requires: C, 69.56; H, 3.41; S, 15.46%) and **8f** (Found: C, 61.65; H, 2.74; S, 20.53. $C_{16}H_8S_2O_3$ requires: C, 61.55; H, 2.58; S, 20.51%)

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