Syntheses and Thermal Reactions of Cyclic Sulphenium Ylides: 2-Alkyl(or aryl)-1-benzoyl-1*H*-2-thianaphthalen-2-ium-1-ides and 2-Alkyl (or aryl)-1-benzoyl-3,4-dihydro-1*H*-2-thianaphthalen-2-ium-1-ides

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Pummerer cyclisation of phenacyl phenethyl sulphoxide (5) was carried out using trifluoroacetic anhydride to give 1-benzoyl-3,4-dihydro-1*H*-2-thianaphthalene (6) in good yield. Alkylation (or arylation) of 1-benzoyl-1*H*-2-thianaphthalene (1) and the 3,4-dihydro derivative (6) afforded 2-thianaphthalenium salts (2) and 3,4-dihydro-2-thianaphthalenium salts (7), respectively. 2-Alkyl(or aryl)-1-benzoyl-1*H*-2-thianaphthalen-2-ium-1-ides (3) and 3,4-dihydro-1*H*-2-thianaphthalen-2-ium-1-ides (8) were synthesised by deprotonation of the corresponding sulphonium salts (2) and (7) respectively with triethylamine in high yields. The 2-thianaphthalen-2-ium-1-ides (3) underwent a thermal 1,2-rearrangement in refluxing benzene or toluene to give the 1*H*-2-thianaphthalenes (9), while the 3,4-dihydro-2-thianaphthalen-2-ium-1-ides (8) underwent a novel 1,4-rearrangement to afford the enol ethers (10). The 1,4-rearrangement proceeded by two different routes: intermolecularly for *S*-methyl-3,4-dihydro-2-thianaphthaleniumide (8a), and intramolecularly for the *S*-phenyl derivative (8e).

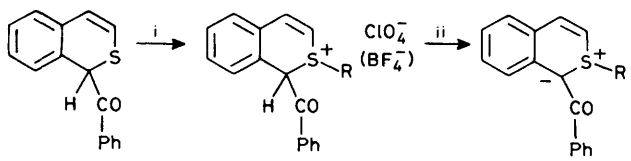
Sulphur ylides containing an electron-withdrawing group have been isolated as stable crystals and their structures and reactivities studied. Although enolisation of a carbonyl group makes a large contribution to the resonance of the benzoyl-stabilised sulphur ylides, as shown by their i.r. spectra, the enolate form played very little part in the reactions.[1]

We have reported on cyclic sulphur ylides related to thiabenzenes; these were formed by deprotonation of the sulphonium salts with base followed by thermal rearrangement.[2] This finding conflicted with the results of the reactions of thiopyrylium salts with phenyl-lithium. Mislow and his co-workers re-examined Price's experiments and concluded that the thiabenzenes claimed by Price were a mixture of oligomers (trimers—hexamers).[3] However, they did not describe the structure of the oligomers at all. We re-examined the reaction of the 9-phenylthioxanthylium salt with phenyl-lithium more closely and showed that the products were not a mixture of oligomers, but a mixture of various monomers and that the reaction was complicated by a radical interaction.[4] Recently the synthesis of stable thiabenzenes and their reactions with electrophiles have been studied.[5]

We report here the synthesis and thermal reactions of 2-substituted 1-benzoyl-1*H*-2-thianaphthalen-2-ium-1-ides and 3,4-dihydro-1*H*-2-thianaphthalene-2-ium-1-ides.[6]

Synthesis of Ylides.—1-Benzoyl-1*H*-2-thianaphthalene (1) was alkylated with alkyl halides and silver perchlorate to give the 2-alkyl-1-benzoyl-1*H*-2-thianaphthalen-2-ium salts (2a—c) (Scheme 1). However, *S*-phenylation of (1), carried out by heating with diphenyliodonium tetrafluoroborate at 120—125 °C, gave 1-benzoyl-2-phenyl-1*H*-2-thianaphthalen-2-ium tetrafluoroborate (2d) in low yield because the starting 1*H*-2-thianaphthalene (1) decomposed under the reaction conditions. The sulphonium salt (2d) was deprotonated without purification to give 1-benzoyl-2-phenyl-1*H*-2-thianaphthalen-2-ium-1-ide (3d) as orange prisms. The alkyl sulphonium salts (2a—c) were similarly deprotonated with triethylamine to yield 2-alkyl-1-benzoyl-1*H*-2-thianaphthalen-2-ium-1-ides (3a—c) in good yields. The yields and analytical data of the sulphonium salts (2a—d) and the ylides (3a—d) are shown in Tables 1 and 2, respectively.

The 3,4-dihydro derivatives were conveniently synthesised by the series of reactions outlined in Scheme 2. Arylcarbonylmethyl phenethyl sulphides (4a—b) prepared from sodium



a; R = Me
b; R = Et
c; R = Pr^n
d; R = Ph

Scheme 1. *Reagents:* i, RI–$AgClO_4$ or Ph_2IBF_4; ii, Et_3N

2-phenylethanethiolate and arylcarbonylmethyl bromide were oxidised with *m*-chloroperbenzoic acid or sodium periodate to give the sulphoxides (5a—b) in high yields. These sulphoxides (5a—b) were converted into the 1-benzoyl-3,4-dihydro-1*H*-2-thianaphthalenes (6a—b) in good yield by Pummerer cyclisation with trifluoroacetic anhydride. Oikawa and Yonemitsu reported the first example of a Pummerer cyclisation of aromatic β-oxosulphoxides (A) to cyclic compounds (B) as shown in Scheme 3.[7] This cyclisation is only applicable to methylsulphinylmethyl arylethyl ketones with an electron-rich aromatic ring such as indolyl or dimethoxyphenyl. In contrast the β-oxosulphoxides used above were readily cyclised under mild conditions even when the sulphoxide (5) had no electron-releasing groups on the aromatic ring. The Pummerer cyclisation reported here is very useful for the synthesis of sulphur-containing heterocycles. Tamura and his co-workers reported a similar synthetic method for (6a), using toluene-*p*-sulphonic acid.[8]

Alkylation of compounds (6a—b) with alkyl halides and silver perchlorate or arylation with diaryliodonium tetrafluoroborate gave the sulphonium salts (7a—i) in high yield, as shown in Table 3. Stereoisomers of the sulphonium salt (7a) were detected in the n.m.r. spectrum, which showed two pairs of singlets, at δ 2.60 (SMe) and 6.81 (1-H) for the major isomer, and at δ 2.45 (SMe) and 6.63 (1-H) for the other; no isomers were found in the other sulphonium salts (7b—e), recrystallised from acetone–ether or dichloromethane–ether. However the *S*-ethyl (7b) and *S*-n-propyl derivatives (7c) were

Table 1. 2-Alkyl(or aryl)-1-benzoyl-1*H*-2-thianaphthalen-2-ium salts (2)

Compound [a]	Yield (%)	M.p. (°C)	Formula	Analysis (%) Required (Found) C	H
(2a) [b]	91.8	158	$C_{17}H_{15}ClO_5S$	55.7 (55.5	4.1 4.2)
(2b) [c]	82.0	167—169 [d]	$C_{18}H_{17}ClO_5S$	56.8 (56.85	4.5 4.4)
(2c) [b]	75.1	139—140 [d]	$C_{19}H_{19}ClO_5S$	57.8 (57.95	4.8 4.8)
(2d) [b]		148—150 [d]	$C_{22}H_{17}BF_4OS$	63.5 (63.5	4.1 4.4)

[a] All obtained as colourless prisms: [b] from CH_2Cl_2–ether; [c] from acetone. [d] With decomposition.

Table 2. 2-Alkyl(or aryl)-1-benzoyl-1*H*-2-thianaphthalen-2-ium-1-ides (3)

Compound	Yield (%)	Appearance (Recryst. solv.)	M.p. (°C)	Formula	Analysis (%) Required (Found) C	H
(3a)	97.7	Orange needles (CH_2Cl_2–ether)	185 [b]	$C_{17}H_{14}OS$	76.6 (76.8	5.3 5.3)
(3b)	75.3	Orange columns (acetone)	133—134 [b]	$C_{18}H_{16}OS$	77.1 (77.0	5.8 5.7)
(3c)	96.3	Orange prisms (acetone–ether)	135—136 [b]	$C_{19}H_{18}OS$	77.5 (77.3	6.2 6.0)
(3d)	18.0 [a]	Orange prisms (acetone–ether)	174—176 [b]	$C_{22}H_{16}OS$	80.5 (80.0	4.9 5.1)

[a] Yield from (1). [b] With decomposition.

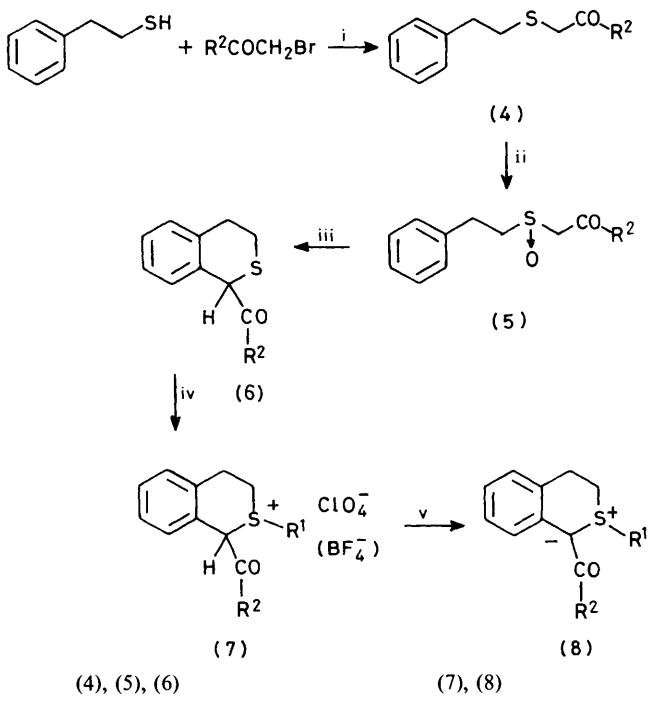
Table 3. 2-Alkyl(or aryl)-1-benzoyl-3,4-dihydro-1*H*-2-thianaphthalen-2-ium salts (7)

Compound [a]	Reagent (equiv.)	Time (h)	Yield (%)	M.p. (°C)	Formula	Analysis (%) Required (Found) C	H
(7a) [b]	MeI (10)	24	95.4	187—189	$C_{17}H_{17}ClO_5S$	55.4 (55.3	4.7 4.7)
(7b) [c]	EtI (10)	70	87.6	168—169	$C_{18}H_{19}ClO_5S$	56.5 (56.3	5.0 5.0)
(7c) [c]	Pr^nI (10)	90	78.3	134—135	$C_{19}H_{21}ClO_5S$	57.5 (57.25	5.3 5.3)
(7d) [c]	Pr^iI (10)	90	71.5	183—184 [d]	$C_{19}H_{21}ClO_5S$	57.5 (57.3	5.3 5.3)
(7e) [c]	Ph_2IBF_4 (1)	3	96.7	185—187	$C_{22}H_{19}BF_4OS$	63.2 (63.0	4.6 4.5)
(7f) [b]	CD_3I (1.36)	8	95.9	188—189	$C_{17}H_{14}D_3ClO_5S$		
(7g) [b]	MeI (10)	24	83.3	214—215	$C_{18}H_{19}ClO_6S$	54.2 (53.95	4.8 4.8)
(7h) [c]	Ph_2IBF_4 (1)	3	79.9	165—166	$C_{23}H_{21}BF_4O_2S$	61.6 (61.4	4.7 4.6)
(7i) [c]	$(p\text{-}MeC_6H_4)_2IBF_4$ (1.5)	3	81.5	151—152	$C_{23}H_{21}BF_4OS$	63.9 (63.6	4.9 4.8)

[a] All obtained as colourless prisms: [b] from CH_2Cl_2–ether; [c] from acetone–ether. [d] With decomposition.

isomerised in trifluoroacetic acid at 60—70 °C. The stereochemistry of the 3,4-dihydro-2-thianaphthalen-2-ium salts will be discussed in detail elsewhere. The desired cyclic sulphur ylides (8a—i) were readily prepared from (7a—i) by deprotonation with triethylamine. The ylides exhibited characteristic broad, strong i.r. absorptions at 1 485—1 528 cm^{-1}, due to the ylidic carbonyl groups. Yields and analytical data are listed in Table 4.

Thermal Rearrangement of the Ylides.—Refluxing ylide (3a) in dry benzene or dry toluene yielded 1-benzoyl-1-methyl-1*H*-2-thianaphthalene (9a) (45.0 or 82.0%, respectively) (Scheme 4). The other *S*-alkyl ylides (3b—c) similarly underwent the thermal 1,2-rearrangement to give the 1*H*-2-thianaphthalenes (9b—c). However, alkyl groups longer than methyl were cleaved by β-elimination and the ylides (3b—c) gave the 1-benzoyl-1*H*-2-thianaphthalenes (1) as the main product. The



(4), (5), (6)

a; R^2 = Ph
b; R^2 = *p*-$MeOC_6H_4$

(7), (8)

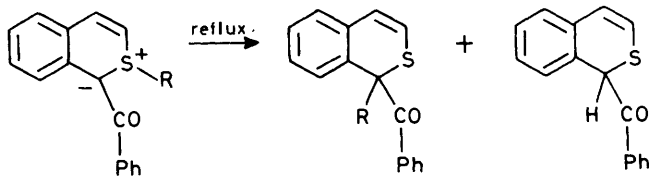
a; R^1 = Me, R^2 = Ph
b; R^1 = Et, R^2 = Ph
c; R^1 = Pr^n, R^2 = Ph
d; R^1 = Pr^i, R^2 = Ph
e; R^1 = R^2 = Ph
f; R^1 = CD_3, R^2 = Ph
g; R^1 = Me, R^2 = *p*-$MeOC_6H_4$
h; R^1 = Ph, R^2 = *p*-$MeOC_6H_4$
i; R^1 = *p*-MeC_6H_4, R^2 = Ph

Scheme 2. *Reagents:* i, EtONa, room temp.; ii, $NaIO_4$, MeOH–H_2O; iii, $(CF_3CO)_2O$, CH_2Cl_2; iv, R^1I–$AgClO_4$ or Ph_2IBF_4, (*p*-$MeC_6H_4)_2IBF_4$; v, Et_3N

Scheme 3.

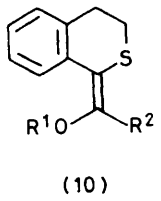
S-phenyl congener (3d) rearranged thermally to the thianaphthalene (9d) in low yield.

The results in Table 5 show that the thermal rearrangements of compounds (3a—d) occurred more effectively under a high temperature for a short period than at low temperatures for a long period. In contrast, 1-benzoyl-2-methyl-3,4-dihydro-1*H*-2-thianaphthalen-2-ium-1-ide (8a) underwent a 1,4-rearrangement of the *S*-methyl group to form the enol ether (10a) in 47.6% yield. The enol ether structure was established from the n.m.r. spectrum, in which a singlet at δ 3.46 was assigned to the protons of the methoxy group, and the i.r. spectrum in which no carbonyl absorption was observed at *ca.* 1 650 cm^{-1}. The other *S*-alkyl ylides (8b—d) were dealkylated *via* β-elimination under similar conditions to give the dihydro-1*H*-2-thianaphthalene (6a) in high yields. The *S*-phenyl derivative (8e) yielded the enol ether (10b) in 14.0 or 45.0% yield when refluxed in dry toluene or in dry xylene, respectively. The *S*-methyl (8f—g) and *S*-aryl analogues (8h—i) rearranged

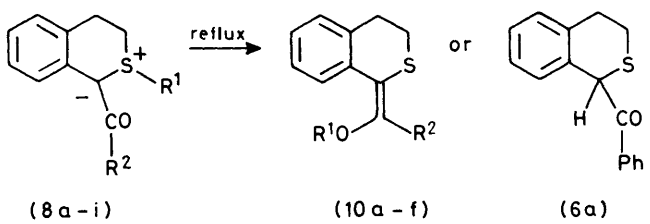


a; R = Me
b; R = Et
c; R = Pr^n
d; R = Ph

Scheme 4.



a; R^1 = Me, R^2 = Ph
b; R^1 = R^2 = Ph
c; R^1 = CD_3, R^2 = Ph
d; R^1 = Me, R^2 = *p*-$MeOC_6H_4$
e; R^1 = Ph, R^2 = *p*-$MeOC_6H_4$
f; R^1 = *p*-MeC_6H_4, R^2 = Ph
g; R^1 = CD_3, R^2 = *p*-$MeOC_6H_4$



Scheme 5.

similarly to form the enol ethers (10c—d) and (10e—f), respectively (Scheme 5, Table 6).

Two isomers (C) and (D) are possible for the enol ethers. The *E*-structure (C) may be more stable than the *Z*-isomer (D) because of the steric hindrance between 8-H and 2′-H (or 6′-H). In the *Z*-structure (D), 8-H may be located above the side-chain benzene ring and an upfield shift of 8-H should be observed in the n.m.r. spectrum. However such an absorption was not observed in the n.m.r. spectra of (10a) and (10b). Therefore we concluded that the enol ethers obtained from (8a,f—i) have the *E*-structure (C).

Crossover experiments were carried out to elucidate the mechanism of the thermal rearrangement. A mixture of 1-benzoyl-2-trideuteriomethyl-3,4-dihydro-1*H*-2-thianaphthalen-2-ium-1-ide (8f) and 1-(*p*-methoxybenzoyl)-2-methyl-3,4-dihydro-1H-2-thianaphthalen-2-ium-1-ide (8g) was refluxed in dry toluene to allow the methyl group to migrate. The mass spectrum of the reaction mixture showed four molecular ion peaks at *m/z* 271, 298, 268, and 301 of (10c), (10d), (10a), and (10g), respectively. The formation of two crossover products, (10a) and (10g), indicated that the 1,4-methyl group migration had proceeded intermolecularly.

The analogous 1,4-migration of an aryl group was investigated by a crossover reaction using 1-(*p*-methoxybenzoyl)-2-

Table 4. 2-Alkyl(or aryl)-1-benzoyl-3,4-dihydro-1*H*-2-thianaphthalen-2-ium-1-ides (8)

Compound	Yield (%)	Appearance (Recryst. solv.)	M.p. (°C) (decomp.)	Formula	Analysis (%) Required (Found) C	H
(8a)	84.5	Yellow prisms (CH_2Cl_2–ether)	170—173	$C_{17}H_{16}OS$	76.1 (76.2	6.0 5.95)
(8b)	86.5	Yellow prisms (acetone)	153—155	$C_{18}H_{18}OS$	76.6 (76.7	6.4 6.3)
(8c)	88.6	Yellow prisms (acetone–ether)	140—141	$C_{19}H_{20}OS$	77.0 (76.8	6.8 6.7)
(8d)	86.5	Yellow prisms (acetone–ether)	119—120	$C_{19}H_{20}OS$	77.0 (76.7	6.8 6.8)
(8e)	93.3	Yellow prisms (CH_2Cl_2–ether)	191—193	$C_{22}H_{18}OS$	80.0 (79.7	5.5 5.6)
(8f)	96.3	Yellow prisms (acetone–ether)	189—190	$C_{17}H_{13}D_3OS$		
(8g)	88.8	Yellow powder (CH_2Cl_2–ether)	179—180	$C_{18}H_{18}O_2S$	72.5 (72.4	6.1 5.9)
(8h)	96.9	Yellow needles (acetone–ether)	175—176	$C_{23}H_{20}O_2S$	76.6 (76.5	5.6 5.45)
(8i)	96.5	Yellow needles (acetone–ether)	196—198	$C_{23}H_{20}OS$	80.2 (80.0	5.9 5.8)

Table 5. Thermal rearrangement of 2-alkyl(or aryl)-1-benzoyl-1*H*-2-thianaphthalen-2-ium-1-ides (3)

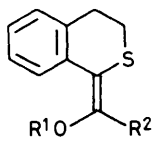
Compd.	Solvent	Time (h)	Product, Yield (%)
(3a)	Benzene	46	(9a) 45.0, (1) 11.6, (3a) 19.0
	Toluene	12	(9a) 82.0, (1) Trace
(3b)	Benzene	10	(9b) 19.0, (1) 77.2
	Toluene	2	(9b) 35.0, (1) 55.1
(3c)	Benzene	8	(9c) 16.0, (1) 67.7
	Toluene	5	(9c) 29.4, (1) 60.7
(3d)	Toluene	18	(9d) 10.0

Table 6. Thermal rearrangements of 2-alkyl(or aryl)-1-benzoyl-3,4-dihydro-1*H*-2-thianaphthalen-2-ium-1-ides (8)

Compound	Solvent	Time (h)	Product, Yield (%)
(8a)	Benzene	12	(8a) 73.3 [a]
	Toluene	12	(10a) 47.6
(8b)	Benzene	12	(6a) 64.3
	Toluene	12	(6a) 67.4
(8c)	Benzene	12	(6a) 76.9
	Toluene	3	(6a) 78.1
(8d)	Benzene	4	(6a) 85.2
	Toluene	2	(6a) 88.5
(8e)	Benzene	12	(8e) 68.3 [a]
	Toluene	12	(8e) 46.0,[a] (10b) 14.0
	Xylene	8	(10b) 45.0
(8h)	Xylene	8	(10c) 26.2
(8i)	Xylene	15	(10d) 25.0

[a] Recovered starting material.

phenyl-3,4-dihydro-1*H*-2-thianaphthalen-2-ium-1-ide (8h) and 1-benzoyl-2-(*p*-tolyl)-3,4-dihydro-1*H*-2-thianaphthalen-2-ium-1-ide (8i). The mass spectrum of the reaction mixture showed two molecular ion peaks, at *m/z* 360 for (10e) and at 344 for (10f). This reaction did not yield crossover products and proceeded intramolecularly. The fact that the *E*-enol ethers (10b,e—f) are formed by an intramolecular reaction of the *S*-aryl ylides (8e,h,i) is very interesting; however, the mechanism is not known as we have been unable to propose



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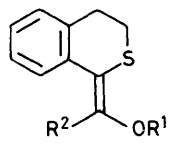

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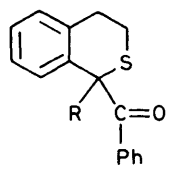

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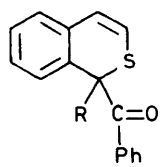

(9)

a reasonable transition state for reaction *via* an intramolecular migration of the *S*-aryl group.

Many rearrangements of sulphonium ylides have been reported; most of these occur by 1,2-, 1,4-, and 2,3-migrations in which the *S*-methylide is transferred to a carbon atom.[9] Exceptionally, a few benzoyl-stabilised sulphur ylides undergo a unique 2,3-rearrangement in which the *S*-methylide migrates to a carbonyl oxygen.[10] The rearrangement of compounds (8a) and (8e—g) described above is the first example of the 1,4-migration of an *S*-substituent to the carbonyl oxygen.

The differences in the thermal rearrangements of 1*H*-2-thianaphthalen-2-ium-3-ides (3a—d) and 3,4-dihydro-1*H*-2-thianaphthalen-2-ium-1-ides (8a,e,h,i) can be explained by the stereochemical characteristics of the products. If the conformation of the 1-substituted 1-benzoyl-3,4-dihydro-1*H*-2-thianaphthalene (11) is such that the C(1) substituent is pseudoaxial, steric hindrance occurs between this substituent and 4-H; when the C(1) substituent occupies a pseudoequatorial position, steric interaction occurs with 8-H. Therefore compound (11) was not obtained, and instead the less crowded product (10) was formed.

These steric repulsions between 4-H and the C(1) substituent are much reduced by the presence of a double bond between C(3) and C(4), and therefore (9) was readily formed.

We have thus shown that in the thermal rearrangement of 2-alkyl(or aryl)-1-benzoyl-1*H*-2-thianaphthaleniumides and 3,4-dihydro-1*H*-2-thianaphthaleniumide derivatives, an *S*-alkyl- (or aryl) group migrates to an adjacent carbanionic carbon in the 2-thianaphthaleniumides, while an *S*-methyl group is transferred intermolecularly to the carbonyl oxygen and an *S*-aryl group rearranges intramolecularly in the 3,4-dihydro-2-thianaphthaleniumides. These thermal reactions may open a new, interesting area in the chemistry of sulphur ylides; studies in this area are in progress.

Experimental

M.p.s were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. I.r. spectra of solids (KBr) and liquids (film) were recorded on a JASCO A-1 spectrophotometer. N.m.r. spectra were obtained for solutions in $CDCl_3$ on a Hitachi R-20B spectrometer with tetramethylsilane as internal standard, unless indicated otherwise. Mass spectra were obtained using a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. All exact mass determinations were obtained on the JMA 2000 on-line system.

2-Alkyl-1-benzoyl-1H-2-thianaphthalen-2-ium Perchlorates (2a—c).—Silver perchlorate (815 mg, 3.54 mmol) was gradually added with stirring to an ice-cooled mixture of 1-benzoyl-1*H*-2-thianaphthalene (1) [2b] (892 mg, 3.54 mmol) and alkyl iodide (35.4 mmol) in dry dichloromethane. The reaction mixture was stirred for 2 or 3 days at room temperature. The precipitate was filtered off and washed with acetone. The washings and the filtrate were combined and evaporated. The residual solid was recrystallised.

1-Benzoyl-2-methyl-1*H*-2-thianaphthalen-2-ium perchlorate (2a) was synthesised by the procedure of ref. 2b. *1-Benzoyl-2-ethyl-1H-2-thianaphthalen-2-ium perchlorate* (2b), $\nu_{max.}$ 1 090 (ClO_4^-), 1 685 cm^{-1} (C=O); δ(CF_3CO_2H) 1.59 (3 H, t, *J* 7.2 Hz, Me), 3.53 (2 H, q, *J* 7.2 Hz, CH_2), 6.58 (1 H, dd, *J* 9.6, 1.8 Hz, 3-H), 6.81 (1 H, d, *J* 1.8 Hz, 1-H), 7.40—7.85 (8 H, m, 4-H and ArH), and 7.95—8.20 (2 H, m, ArH); *1-benzoyl-2-n-propyl-1H-2-thianaphthalen-2-ium perchlorate* (2c), $\nu_{max.}$ 1 090 (ClO_4^-), 1 675 cm^{-1} (C=O); δ(CF_3CO_2H) 1.19 (3 H, t, *J* 7.2 Hz, Me), 1.70—2.35 (2 H, m, CH_2), 3.45 (2 H, t, *J* 7.5 Hz, CH_2), 6.59 (1 H, dd, *J* 1.8, 9.6 Hz, 3-H), 6.79 (1 H, d, *J* 1.8 Hz, 1-H), 7.40—7.80 (8 H, m, 4-H and ArH), and 7.95—8.20 (2 H, m, ArH).

2-Alkyl-1-benzoyl-1H-2-thianaphthalen-2-ium-1-ides (3a—c).—Triethylamine (404 mg, 4.00 mmol) was added with stirring to a suspension of (2) (2.00 mmol) in dry ethanol (30 ml) and allowed to react for 5 h at room temperature. Water (300 ml) was added to the reaction mixture and it was extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated to dryness under reduced pressure. The residual solid was recrystallised. 1-Benzoyl-2-methyl-1*H*-2-thianaphthalen-2-ium-1-ide (3a) was prepared by the procedure in ref. 2*b*. Spectroscopic data are as follows: *1-benzoyl-2-ethyl-1H-2-thianaphthalen-2-ium-1-ide* (3b), $\nu_{max.}$ 1 500 cm^{-1}; δ 1.06 (3 H, t, *J* 7.2 Hz, Me), 2.42 (2 H, q, *J* 7.2 Hz, CH_2), 5.99 (1 H, d, *J* 9.6 Hz, 3-H), and 6.70—7.66 (10 H, m, 4-H and ArH); *m/z* 280; *1-benzoyl-2-n-propyl-1H-2-thianaphthalen-2-ium-1-ide* (3c), $\nu_{max.}$ 1 510 cm^{-1}; δ 0.89 (3 H, t, *J* 6.6 Hz, Me), 1.15—1.80 (2 H, m, CH_2), 2.30—2.70 (2 H, m, CH_2), 5.98 (1 H, *J* 9.0 Hz, 3-H), and 6.70—7.65 (10 H, m, 4-H and ArH); *m/z* 294 (M^+).

1-Benzoyl-2-phenyl-1H-2-thianaphthalen-2-ium-1-ide (3d).—A stirred mixture of (1) [2b] (1.0 g, 3.96 mmol), diphenyliodonium tetrafluoroborate [11] (1.46 g, 3.96 mmol), and a catalytic amount of cupric benzoate was heated at 100—105 °C for 2 h under nitrogen. The mixture was washed several times with ether, and then ethanol (40 ml) was added to the mixture. The ethanol solution was filtered and ether was added to the filtrate. The precipitate (3d) (640 mg) was filtered off and dried. An ice-cooled suspension of the sulphonium salt in absolute ethanol (30 ml) was treated with triethylamine (311 mg, 3.08 mmol) for 3 h at room temperature. The resulting yellow mixture was poured into water (300 ml) and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated to dryness under reduced pressure. The residue was recrystallised, $\nu_{max.}$ 1 530 cm^{-1}; δ 6.22 (1 H, d, *J* 9.6 Hz, 3-H), and 6.75—7.70 (15 H, m, 4-H and ArH); *m/z* 328 (M^+).

Phenacyl Phenethyl Sulphide (4a) *and* p-*Methoxyphenacyl Phenethyl Sulphide* (4b).—A solution of sodium ethoxide in ethanol was prepared by dissolving sodium (1.33 g, 57.8 mmol) in absolute ethanol (15 ml). 2-Phenylethanethiol [12] (8.0 g, 57.8 mmol) was added to the sodium ethoxide solution and then a solution of phenacyl bromide or *p*-methoxyphenacyl bromide (57.8 mmol) in acetonitrile (20 ml) was added dropwise with stirring. After the reaction mixture had been stirred for 2 h at room temperature, the precipitate was filtered off and the filtrate was concentrated. The residue was dissolved in ether and the undissolved material was filtered off. The filtrate was evaporated to give a yellow oil. The products (4a—b) were used without further purification. Phenacyl phenethyl sulphide (4a) (96.6%), $\nu_{max.}$ 1 665 cm^{-1} (C=O); δ 2.84 (4 H, s, $CH_2 \times 2$), 3.76 (2 H, s, CH_2), 7.20 (5 H, s, ArH), 7.38—7.60 (3 H, m, ArH), and 7.58—8.05 (2 H, m, ArH); *m/z* 256 (M^+); *p*-methoxyphenacyl phenethyl sulphide (4b) (90.0%), $\nu_{max.}$ 1 660 cm^{-1} (C=O); δ 2.81 (4 H, s, $CH_2 \times 2$), 3.69 (3 H, s, OMe), 3.74 (2 H, s, CH_2), 6.86 (2 H, d, *J* 9.0 Hz, ArH), 7.18 (5 H, s, ArH), and 7.91 (2 H, d, *J* 9.0 Hz, ArH); *m/z* 286 (M^+).

Phenacyl Phenethyl Sulphoxide (5a) *and* p-*Methoxyphenacyl Phenethyl Sulphoxide* (5b).—An aqueous solution of sodium metaperiodate (9.26 g, 43.3 mmol) in water (150 ml) was added dropwise to an ice-cooled solution of (4a) or (4b) (39.0 mmol) in methanol (500 ml) and then the reaction mixture was stirred for 24 h at room temperature. The precipitate was filtered off and washed several times with dichloromethane. The washings and the filtrate were combined and poured into water (300 ml). The organic layer was separated and the aqueous layer was extracted with dichloromethane. The extracts were dried and evaporated under reduced pressure. The residue was trituated with ether and recrystallised from dichloromethane–ether as colourless needles. *Phenacyl phenethyl sulphoxide* (5a) (79.8%), m.p. 81—83 °C (Found: C, 70.3; H, 6.0. $C_{16}H_{16}O_2S$ requires C, 70.56; H, 5.92%), $\nu_{max.}$ 1 090 (S–O) and 1 670 cm^{-1} (C=O); δ 3.14 (4 H, s, $CH_2 \times 2$), 4.29 (1 H, d, *J* 15.6 Hz, SOCH), 4.39 (1 H, d, *J* 15.6 Hz, SOCH), 7.23 (5 H, s, ArH), 7.30—7.60 (3 H, m, ArH), and 7.85—8.06 (2 H, m, ArH); *m/z* 272 (M^+); p-*methoxyphenacyl phenethyl sulphoxide* (5b) (86.8%), m.p. 124—125 °C (Found: C, 67.3; H, 6.0. $C_{17}H_{18}O_3S$ requires C, 67.71; H, 6.00%), $\nu_{max.}$ 1 035 (S–O), 1 660 cm^{-1} (C=O); δ 3.12 (4 H, s, $CH_2 \times 2$), 3.84 (3 H, s, OMe), 4.24 (1 H, d, *J* 15 Hz, SOCH), 4.34 (1 H, d, *J* 15 Hz, SOCH), 6.93 (2 H, d, *J* 9 Hz, ArH), 7.23 (5 H, s, ArH), and 7.93 (2 H, d, *J* 9 Hz, ArH); *m/z* 302 (M^+).

1-Benzoyl-3,4-dihydro-1H-2-thianaphthalene (6a).—Trifluoroacetic anhydride (12.6 g, 59.9 mmol) was added to an ice-cooled solution of (5a) (10.9 g, 39.9 mmol) in methanol-free dichloromethane (100 ml). The reaction mixture was evaporated under reduced pressure. The residual solid was recrystallised

Table 7. Spectroscopic data of 2-alkyl(or aryl)-1-benzoyl-1*H*-2-thianaphthalen-2-ium salts (7)

Compd.	$\nu_{max.}$ (KBr) (cm^{-1})	δ (CF_3CO_2H)
(7a)	1 090 (ClO_4^-) 1 661 (CO)	2.60 (3 H, s, Me), 2.83—3.60 (3 H, m, 3- and 4-H), 4.21—4.50 (1 H, m, 3-H), 6.81 (1 H, s, 1-H), 7.25—8.20 (9 H, m, ArH)
(7b)	1 090 (ClO_4^-) 1 670 (CO)	1.52 (3 H, t, *J* 7.5 Hz, Me), 2.58—3.63 (5 H, m, 3- and 5-H), 3.96—4.47 (1 H, m, 3-H), 6.84 (1 H, s, 1-H), 7.28—8.28 (9 H, m, ArH)
(7c)	1 090 (ClO_4^-) 1 690 (CO)	1.15 (3 H, t, *J* 7.2 Hz, Me), 1.60—2.28 (2 H, m, CH_2), 2.55—3.65 (5 H, m, CH_2, 3- and 4-H), 3.90—4.47 (1 H, m, 3-H), 6.84 (1 H, s, 1-H), 7.28—8.28 (9 H, m, ArH)
(7d)	1 085 (ClO_4^-) 1 670 (CO)	1.51 (3 H, d, *J* 7.2 Hz, Me), 1.64 (3 H, d, *J* 7.2 Hz, Me), 2.68—3.69 (4 H, m, CH, 3- and 4-H), 3.90—4.50 (1 H, m, 3-H), 6.88 (1 H, s, 1-H), 7.20—8.30 (9 H, m, ArH)
(7e)	1 080 (BF_4^-) 1 680 (CO)	3.06—4.00 (3 H, m, 3- and 4-H), 4.43—4.85 (1 H, m, 3-H), 6.77 (1 H, s, 1-H), 7.14—7.90 (7 H, m, ArH), 7.96—8.22 (2 H, m, ArH)
(7f)	1 095 (ClO_4^-) 1 675 (CO)	2.86—3.70 (3 H, m, 3- and 4-H), 4.21—4.50 (1 H, m, 3-H), 6.82 (1 H, s, 1-H), 7.34—8.28 (9 H, m, ArH)
(7g)	1 090 (ClO_4^-) 1 650 (CO)	2.60 (3 H, s, Me), 2.85—3.60 (3 H, m, 3- and 4-H), 3.96 (3 H, s, OMe), 4.20—4.50 (1 H, m, 3-H), 6.80 (1 H, s, 1-H), 7.08 (2 H, d, *J* 9 Hz, ArH), 7.36—8.02 (4 H, m, ArH), 8.18 (2 H, d, *J* 9 Hz, ArH)
(7h)	1 080 (BF_4^-) 1 655 (CO)	2.80—3.55 (3 H, m, 3- and 4-H), 3.55 (3 H, s, OMe), 4.10—4.50 (1 H, m, 3-H), 6.38 (1 H, s, 1-H), 6.68 (2 H, d, *J* 9 Hz, ArH), 6.80—7.60 (9 H, m, ArH), 7.76 (2 H, d, *J* 9 Hz, ArH)
(7i)	1 060 (BF_4^-) 1 670 (CO)	2.42 (3 H, s, Me), 3.08—3.92 (m, 3- and 4-H), 4.40—4.80 (1 H, m, 3-H), 6.70 (1 H, s, 1-H), 7.00—7.75 (11 H, m, ArH), 7.95—8.20 (2 H, m, ArH)

from ethanol to give colourless needles (8.35 g, 82.2%), m.p. 157—158 °C (Found: C, 75.5; H, 5.5. $C_{16}H_{14}OS$ requires C, 75.56; H, 5.55%), $\nu_{max.}$ 1 650 cm^{-1} (C=O); δ 2.53—3.23 (4 H, m, $CH_2 \times 2$), 5.38 (1 H, s, 1-H), 6.85—7.63 (7 H, m, ArH), and 7.90—8.13 (2 H, m, ArH); *m/z* 254 (M^+).

1-(p-*Methoxybenzoyl*)-3,4-*dihydro*-1H-2-*thianaphthalene* (6b).—Trifluoroacetic anhydride (4.30 g, 20.5 mmol) was added to an ice-cooled solution of (5b) (5.16 g, 17.1 mmol) in methanol-free dichloromethane (50 ml) and the reaction mixture was stirred overnight at room temperature. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel [hexane–ethyl acetate (5 : 1)] and the white solid was recrystallised from dichloromethane–hexane to give colourless prisms (2.30 g, 47.3%), m.p. 117—118 °C (Found: C, 71.7; H, 5.5. $C_{17}H_{16}O_2S$ requires C, 71.80; H, 5.67%), $\nu_{max.}$ 1 650 cm^{-1} (C=O); δ 2.58—3.25 (4 H, m, $CH_2 \times 2$), 3.84 (3 H, s, OMe), 5.38 (1 H, s, 1-H), 6.95 (2 H, d, *J* 9 Hz, ArH), 6.98—7.30 (4 H, m, ArH), and 8.02 (2 H, d, *J* 9 Hz, ArH); *m/z* 284 (M^+).

General Procedure for the Preparation of 2-*Alkyl*-1-*benzoyl*-3,4-*dihydro*-1H-2-*thianaphthalen*-2-*ium Perchlorates* (7a—d, f,g).—Alkyl iodide (10 equiv.) and silver perchlorate (equimolar amount) were added to a solution of (6) (1.0 g) in dry dichloromethane (10 ml). After the period shown in Table 3, the precipitate was filtered off and washed several times with acetone. The washings were combined with the filtrate and evaporated under reduced pressure. The residue was recrystallised. Reaction conditions, yields, analytical data, and spectroscopic data are shown in Tables 3 and 7, respectively.

General Procedure for the 2-*Aryl*-1-*benzoyl*-3,4-*dihydro*-1H-2-*thianaphthalen*-2-*ium Tetrafluoroborates* (7e, h, i).—A mixture of (6) (1.0 g), diaryliodonium tetrafluoroborate, and a catalytic amount of cupric benzoate in *sym*-tetrachloroethane (1 ml) was heated at 120—125 °C for 3 h under nitrogen. Ether was added to the cooled reaction mixture and the resulting precipitate was collected. Reaction conditions, yield, analytical data, and spectroscopic data are summarised in Tables 3 and 7, respectively.

General Procedure for the 2-*Alkyl*(*or aryl*)-1-*benzoyl*-3,4-*dihydro*-1H-2-*thianaphthalen*-2-*ium*-1-*ides* (8a—i).—Triethylamine (2 eq.) was added dropwise to an ice-cooled suspension of (7) (1.0 g) in absolute ethanol (50 ml). After being stirred for 5—7 h at room temperature, the reaction mixture was poured into water (300 ml) and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure; yellow crystals (8a—i) were obtained. The yield, analytical data, and spectroscopic data are shown in Tables 4 and 8, respectively.

Thermal Reactions of 1*H*-2-*Thianaphthalen*-2-*ium*-1-*ides* (3a—d).—A solution of the 1*H*-2-thianaphthalen-2-ium-1-ide (0.1 g) in dry benzene or toluene (20 ml) was refluxed under nitrogen. The solvent was removed under reduced pressure. The residue was separated by preparative t.l.c. on silica gel [hexane–ethyl acetate (5 : 1)]. The following products were isolated: 1-*benzoyl*-1-*methyl*-1H-2-*thianaphthalene* (9a), a yellow oil, $\nu_{max.}$ 1 680 cm^{-1} (C=O); δ (3 H, s, Me), 6.31 (1 H, d, *J* 9.8 Hz, 3-H), 6.70 (1 H, d, *J* 9.8 Hz, 4-H), 6.85—7.45 (7 H, m, ArH), and 7.88—8.15 (2 H, m, ArH); *m/z* 280.0936 ($C_{18}H_{16}OS$ requires 280.0935); 1-*benzoyl*-1-*propyl*-1H-2-*thianaphthalene* (9c), a yellow oil, $\nu_{max.}$ 1 680 cm^{-1} (C=O); δ 0.89 (3 H, t, *J* 6.0 Hz, Me), 1.10—1.90 (2 H, m, CH_2CH_3), 2.16 (2 H, t, *J* 7.2 Hz, CH_2), 6.26 (1 H, d, *J* 9.8 Hz, 3-H), 6.59 (1 H, d, *J* 9.8 Hz, 4-H), 6.80—7.45 (7 H, m, ArH), and 7.85—8.15 (2 H, m, ArH); *m/z* 294.1100 ($C_{19}H_{18}OS$ requires 294.1098); 1-*benzoyl*-1-*phenyl*-1H-2-*thianaphthalene* (9d), a yellow oil, $\nu_{max.}$ 1 680 cm^{-1} (C=O); δ 6.26 (1 H, d, *J* 9.8 Hz, 3-H), 6.61 (1 H, d, *J* 9.8 Hz, 4-H), 6.85—7.85 (12 H, m, ArH), and 7.95—8.15 (2 H, m, ArH); *m/z* 328.0909 ($C_{22}H_{16}OS$ requires 328.0910).

Thermal Reactions of 2-*Alkyl*(*or aryl*)-1-*benzoyl*-3,4-*dihydro*-1H-2-*thianaphthalen*-2-*ium*-1-*ides* (8a—i).—A solution of (8) (0.1 g) in aromatic solvent (20 ml) was refluxed under nitrogen. The solvent was removed under reduced pressure. The residue was separated by preparative t.l.c. on silica gel [hexane–ether (5 : 1) for (10a) and hexane–ethyl acetate (5 : 1) for (10b)]. 1-(α-*Methoxybenzylidene*)-3,4-*dihydro*-1H-2-*thianaphthalene* (10a), a yellow oil, δ 2.75—3.20 (4 H, m, 3-H and 4-H), 3.46 (3 H, s, OMe), and 6.70—7.60 (9 H, m, ArH); *m/z* 268.0871 ($C_{17}H_{16}OS$ requires 268.0876). 1-(α-*Phenoxybenzylidene*)-3,4-*dihydro*-1H-2-*thianaphthalene* (10b), m.p. 132—133 °C, colourless prisms (from dichloromethane–hexane) (Found: C, 79.7; H, 5.4. $C_{22}H_{18}OS$ requires C, 79.97; H, 5.49%); δ 2.70—3.20 (4 H, m, 3-H and 4-H), and 6.75—7.60 (14 H, m, ArH); *m/z* 330 (M^+). 1-(α-*Trideuteriomethoxy*-

Table 8. Spectroscopic data of 2-alkyl(or aryl)-1-benzoyl-3,4-dihydro-1H-2-thianaphthalen-2-ium-1-ides (8)

Compd.	$\nu_{max.}$ (KBr) (cm^{-1})	*m/z*	δ ($CDCl_3$)
(8a)	1 500 (CO)	268 (M^+) 253 (B) [a]	2.55 (3 H, s, Me), 2.80—3.21 (3 H, m, 3- and 4-H), 3.45—3.81 (1 H, m, 3-H), 6.60—7.60 (9 H, m, ArH)
(8b)	1 528	282 (M^+) 149 (B)	1.23 (3 H, s, Me), 2.50—3.27 (5 H, m, CH_2, 3- and 4-H), 3.47—3.90 (1 H, m, 3-H), 6.57—7.90 (9 H, m, ArH)
(8c)	1 502	296 (M^+) 149 (B)	1.02 (3 H, s, Me), 1.30—2.03 (2 H, m, CH_2), 2.10—3.85 (6 H, m, CH_2, 3- and 4-H), 6.52—7.68 (9 H, m, ArH)
(8d)	1 500	296 (M^+) 149 (B)	1.22 (3 H, d, *J* 7.2 Hz, Me), 1.27 (3 H, d, *J* 7.2 Hz, Me), 2.58—3.88 (5 H, m, CH, 3- and 4-H), 6.55—7.60 (9 H, m, ArH)
(8e)	1 485	330 (M^+) 115 (B)	2.77—3.35 (3 H, m, 3- and 4-H), 3.75—4.15 (1 H, m, 3-H), 6.80—7.70 (14 H, m, ArH)
(8f)	1 505	271 (M^+) 149 (B)	2.45—3.92 (4 H, m, 3- and 4-H), 6.10—7.80 (9 H, m, ArH)
(8g)	1 500	298 (M^+) 135 (B)	2.55 (3 H, s, Me), 2.80—3.15 (4 H, m, 3- and 4-H), 3.78 (3 H, s, OMe), 6.60—7.60 (8 H, m, ArH)
(8h)	1 490	360 (M^+) 135 (B)	2.70—3.40 (3 H, m, 3- and 4-H), 3.75 (3 H, s, OMe), 3.80—4.15 (1 H, m, 3-H), 6.72 (2 H, d, *J* 9 Hz, ArH), 6.85—7.65 (11 H, m, ArH)
(8i)	1 490	344 (M^+) 105 (B)	2.55 (3 H, s, Me), 2.80—3.21 (3 H, m, 3- and 4-H), 3.45—3.81 (1 H, m, 3-H), 6.60—7.60 (9 H, m, ArH)

[a] B = base peak.

benzylidene)-3,4-*dihydro*-1H-2-*thianaphthalene* (10c), an oil, δ 2.75—3.20 (4 H, m, 3- and 4-H) and 6.70—7.60 (9 H, m, ArH); *m/z* 271 (M^+). 1-(α,4-*Dimethoxybenzylidene*)-3,4-*dihydro*-1H-2-*thianaphthalene* (10d), an oil, δ 2.76—3.22 (4 H, m, 3- and 4-H), 3.45 (3 H, s, OMe), 3.75 (3 H, s, OMe), and 6.65—7.70 (8 H, m, ArH); *m/z* 298 (M^+); 1-(p-*methoxy*-α-*phenoxybenzylidene*)-3,4-*dihydro*-1H-2-*thianaphthalene* (10e), m.p. 110—112 °C, colourless prisms (from dichloromethane–hexane) (Found: C, 76.4; H, 6.5. $C_{23}H_{20}O_2S$ requires C, 76.64; H, 5.59%); δ 2.70—3.20 (4 H, m, 3- and 4-H), 3.68 (3 H, s, OMe), 6.61 (2 H, d, *J* 9 Hz, ArH), and 6.75—7.80 (11 H, m, ArH); *m/z* 360 (M^+); 1-[α-(p-*tolyloxy*)*benzylidene*]-3,4-*dihydro*-1H-2-*thianaphthalene* (10f), m.p. 147—148 °C, colourless prisms (from dichloromethane–hexane) (Found: C, 79.9; H, 6.0. $C_{23}H_{20}OS$ requires C, 80.20; H, 5.85%), δ 2.21 (3 H, s, Me), 2.70—3.25 (4 H, m, 3- and 4-H), and 6.62—7.50 (13 H, m, ArH); *m/z* 344 (M^+).

Crossover Reaction of 1-(p-*Methoxybenzoyl*)-2-*phenyl*-3,4-*dihydro*-1H-2-*thianaphthalen*-2-*ium*-1-*ide* (8h) *and* 1-*Benzoyl*-2-(p-*tolyl*)-3,4-*dihydro*-1H-2-*thianaphthalen*-2-*ium*-1-*ide* (8i).—The ylides, (8h) (55 mg, 0.153 mmol) and (8i) (61 mg, 0.177 mmol) were dissolved in dry xylene and the solution was refluxed for 15 h under nitrogen. The mass spectrum of the reaction mixture was measured and showed two molecular ion peaks at *m/z* 360 and 344, of (10f) and (10g) respectively.

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