The Synthesis of some Heterocyclic Sulphonium Salts

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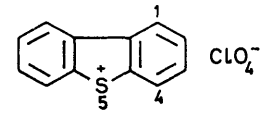
A number of heterocyclic sulphur compounds and their sulphoxides have been *S*- and *O*-alkylated respectively, with silver perchlorate and alkyl halides. 5-Methoxydibenzothiophenium and 10-methoxyphenoxathiinium perchlorates reacted with amines to give 5- and 10-aminosulphonium salts, respectively, and with certain carbanions to give zwitterionic compounds.

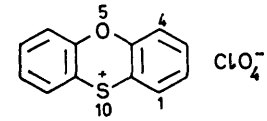
WHEREAS aliphatic sulphides react readily with alkyl halides to give stable sulphonium salts, aromatic and heterocyclic sulphides are much less nucleophilic. A partial order of reactivity [1,2] is $Me_2S > Ph_2S >$ phenoxathiin > dibenzothiophen > benzothiophen > thiophen. The less reactive compounds may be alkylated by the use of trialkyloxonium tetrafluoroborates or by alkyl halides in the presence of silver salts.[2] The sulphonium salts then produced are themselves alkylating agents, and are toxic, probably for this reason. In connection with possible biological applications it was hoped to prepare sulphonium salts which would be weaker, more selective, alkylating agents than the *S*-alkylthiophenium salts prepared earlier.[2]

Silver perchlorate, or its complex with acetonitrile, was used in dichloroethane to effect the alkylation of dibenzothiophen, phenoxathiin, thioxanthene, and *N*-acetyl- and *N*-phenyl-phenothiazine. Because of the risk of explosion,[2] silver perchlorate was only used when its acetonitrile complex proved ineffective. Neither reagent was effective in attempts to cyclise compound (31) or (32) to a sulphonium salt. Unlike the u.v. spectra of *S*-alkylbenzothiophenium salts,[2] the spectra of our *S*-alkylsulphonium salts in cold water or alcohol were unchanged after 24 h, showing the stability of the compounds under these conditions. Compounds (24) and (25) were observed to alkylate hexadeuteriodimethyl sulphoxide; the n.m.r. spectra of solutions in this solvent changed rapidly to that of a mixture of *N*-acetylphenothiazine and the corresponding alkoxydimethylsulphonium salt.

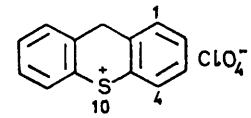
For compounds (10)—(30), if a non-coplanar ring-system is assumed and the bonds to sulphur are arranged trigonally, as in the case of 1-alkylbenzothiophenium salts,[2] the possibility of two configurations occurs, the



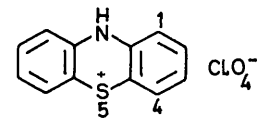
(1) 5-CH_2I
(2) 5-$CH_2{\cdot}CO_2Me$
(3) 5-PPh_2
(4) 5-OMe
(5) 5-OEt
(6) 5-O·$CH_2{\cdot}$CH(O)$-CH_2$
(7) 5-N·$[CH_2]_4{\cdot}CH_2$
(8) 5-NH·$CH_2{\cdot}CH_2Ph$
(9) 5-NH·$CH_2{\cdot}CH_2{\cdot}\overset{+}{N}HEt_2$ ClO_4^-



(10) 10-Me
(11) 10-Et
(12) 10-CH_2I
(13) 10-$CH_2{\cdot}CO_2Me$
(14) 10-$CH_2{\cdot}CH_2Br$
(15) 10-$[CH_2]_3$-10′
(16) 10-Et-2,8-Br_2
(17) 10-CH_2I-2,8-Br_2
(18) 10-OMe
(19) 10-NH·$[CH_2]_3{\cdot}NEt_2$
(20) 10-NH·$CH_2{\cdot}CH_2{\cdot}\overset{+}{N}HEt_2$ ClO_4^-



(21) 10-CH_2I
(22) 10-$CH_2{\cdot}CO_2Me$
(23) 10-$CH_2{\cdot}CO{\cdot}NH_2$

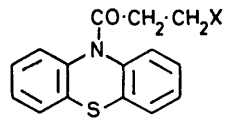


(24) 5-Me-10-Ac
(25) 5-Et-10-Ac
(26) 5-Me-10-Ph
(27) 5-Et-10-Ph
(28) 5-CH_2I-10-Ph
(29) 5-$CH_2{\cdot}CO_2Me$-10-Ph
(30) 5-Et-10-(*p*-$O_2N{\cdot}C_6H_4$)

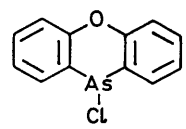
[1] ' Methoden der Organischen Chemie,' vol. 9, ed. E. Muller, Georg Thieme, Stuttgart, 1955, pp. 175, 176.
[2] R. M. Acheson and D. R. Harrison, *J. Chem. Soc.* (*C*), 1970, 1764.

S-alkyl group being ' axial ' or ' equatorial '. However, in polar solvents the inversion rate of these compounds appears to be rapid; according to Andersen *et al.*[3] the n.m.r. signal due to the methylene group of *S*-methylthioxanthenium tetrafluoroborate appears as a doublet in tetrachloroethane, but as a singlet in acetonitrile. The n.m.r. spectrum of compound (18) in chloroform showed the methyl signal as two peaks (Δ 3·6 Hz) of similar height, but as a singlet in acetonitrile or in trifluoroacetic acid solution. No splitting was observed with compounds (10)—(17) and (21)—(23), whose n.m.r. spectra were recorded for solutions in polar solvents for solubility reasons.

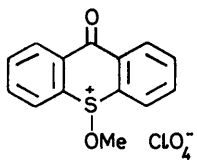
Phenothiazine is reported[4] to give a salt on heating with 10-chlorophenoxarsine (33). Unsuccessful attempts were made to extend this reaction of (33) to form salts with dibenzothiophen or phenoxathiin by the use of



(31) X = Br
(32) X = I



(33)



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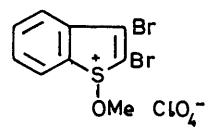

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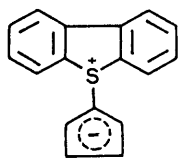

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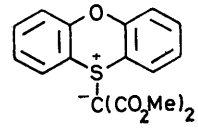

(37)

silver perchlorate. These failures suggest that the phenothiazine derivative of 10-chlorophenoxarsine is closer to a π-complex than a salt. However, chlorodiphenylphosphine reacted at low temperature with dibenzothiophen and silver perchlorate to give a low yield of the phosphinosulphonium salt (3).

Sulphoxides are sufficiently nucleophilic to be alkylated at the oxygen atom by the reagents mentioned above; for example dimethyl sulphoxide is methylated by methyl iodide and silver perchlorate[5] and diaryl sulphoxides are ethylated by triethyloxonium tetrafluoroborate.[3,6] Dibenzothiophen 5-oxide reacted readily with a number of alkyl halides in the presence of silver perchlorate (acetonitrile complex). The salts (4) and (5) were stable in a dry atmosphere, but salt (6) decomposed within a few weeks, and the products from phenethyl bromide and from ethyl bromoacetate decomposed rapidly to the sulphoxide on exposure to the atmosphere. The sulphoxides of phenoxathiin, thioxanthone, and dibromobenzothiophen suffer alkylation similarly. From their behaviour in trial experiments the alkoxysulphonium salts produced appeared to be hydrolysed much faster than the corresponding alkylsulphonium salts, giving the sulphoxides.

Whereas alkylsulphonium salts are hydrolysed by an S_N1 process in neutral solution, or by nucleophilic attack on the carbon atom,[2] alkoxysulphonium salts appear to be hydrolysed by nucleophilic attack on the sulphur atom. This is shown by the inversion of configuration which occurs on alkaline hydrolysis.[6] The reaction of Grignard reagents with diar[illegible]thoxysulphonium salts to give triarylsulphonium salts[3] clearly involves nucleophilic attack at the sulphur atom.

It was therefore of interest to treat some other bases with the alkoxysulphonium salts. The 5-methoxydibenzothiophenium salt (4) was recovered from treatment with aniline, hydrazine, or phenylhydrazine at room temperature, but the compounds (4) and (18) reacted readily with aliphatic amines, the methoxy-group being displaced to give, respectively, the aminosulphonium salts (7), (8), and (9), and (19) and (20). The salts showed the strong i.r. absorption near 1100 cm^{-1} characteristic of the perchlorate ion. The n.m.r. spectrum of the piperidine derivative (7) in hexadeuteriodimethyl sulphoxide showed the piperidyl protons as two broad signals at τ 7·08 and 8·53, corresponding to four and six protons, respectively. The aromatic region was similar to that of 5-alkyldibenzothiophenium salts,[2] and was simulated to 0·1 Hz accuracy by use of the seven-spin n.m.r. computer program of Klopfenstein.[7] Compounds (34) and (35), and methoxydimethylsulphonium perchlorate gave only the sulphoxides when treated with piperidine. In the last case, piperidinium perchlorate (not *N*-methylpiperidinium perchlorate) was isolated, suggesting the intermediate formation and hydrolysis of an aminosulphonium salt.

5-Methoxydibenzothiophenium perchlorate (4), on treatment with sodium cyclopentadienide, gave a zwitterionic compound (36), and the salt (18) similarly reacted with dimethyl sodiomalonate to give the ylide (37), methanol being eliminated in each case. The n.m.r. spectra showed the replacement of the original methoxy-signal by a narrow, symmetrical four-proton multiplet in the cyclopentadienide (36), and by a relatively high-field six-proton singlet for the ester methyl groups in the ylide (37). Compound (36) was thermally unstable and difficult to purify, but (37) formed salt-like crystals of

[3] K. K. Andersen, M. Cinquini, and N. E. Papanikolaou, *J. Org. Chem.*, 1970, **35**, 706.
[4] S. J. Strycker, U.S.P. 3,117,123/1964 (*Chem. Abs.*, 1964, **61**, 667).
[5] N. J. Leonard and C. R. Johnson, *J. Amer. Chem. Soc.*, 1962, **84**, 3704.
[6] C. R. Johnson and D. McCants, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 5404.
[7] C. L. Wilkins and C. E. Klopfenstein, *J. Chem. Educ.*, 1966, **43**, 10; translated into Egtran by P. C. Bell, Part II, Thesis, Oxford University, 1967.

high m.p. Some related sulphonium methylides, prepared by other methods, have been described.[8,9]

EXPERIMENTAL

N.m.r. spectra were measured with a Perkin-Elmer R12 instrument at 60 MHz. U.v. absorption spectra were measured with a Perkin-Elmer Ultracord instrument. I.r. spectra were measured with a Perkin-Elmer 257 spectrophotometer for Nujol mulls. All the perchlorate salts showed characteristic intense absorption near 1100 cm^{-1}; other peaks of interest and the peaks in the region 1000—650 cm^{-1} are recorded. M.p.s were measured with a Reichert hot-stage apparatus. Acetonitrile and dichloroethane were dried by refluxing for 1 h with 2% (w/w) of powdered calcium hydride, and distilled.

General Procedures for Alkylations.—(*A*) Silver perchlorate (0·1 mol) and the sulphur-containing compound (0·11—0·18 mol) were stirred in dichloroethane (300 ml) and the alkyl halide (0·2—0·6 mol) was added dropwise. Stirring was continued for a day or longer; the precipitate of silver halide was then filtered off and washed with acetonitrile. The combined filtrates were concentrated *in vacuo* and the residue triturated with ether. The solid was filtered off, washed with a little water to remove silver perchlorate, dried thoroughly, and recrystallised by dissolving in acetonitrile (treating with charcoal if necessary), filtering, and diluting slowly with ether. When the solution became slightly turbid, it was seeded and set aside to crystallise.

(*B*) Silver perchlorate–acetonitrile complex (1 : 4 molar; prepared as described [10]) (0·1 mol) and the sulphur-containing compound (0·1 mol) were dissolved in dichloroethane

TABLE 1

N.m.r. spectra (τ values; *J* in Hz; Me_4Si as internal standard)

Compound	Solvent	ArH	Substituents
(1)	MeCN	1·6—2·4 (8H, m)	4·79 (2H, CH_2I)
	$(CD_3)_2SO$	1·5—2·6 (8H, m)	4·50 (2H, CH_2I)
(2)	MeCN	1·7—2·45 (8H, m)	5·41 (2H, CH_2); 6·25 (3H, O·CH_3)
(3)	$(CD_3)_2SO$	0·85—3·0 (18H, m)	
(4)	$PhNO_2$		6·28 (3H, O·CH_3)
(5)	$PhNO_2$		5·80 (2H, q, O·CH_2); 8·60 (3H, t, CH_3)
(6)	$(CD_3)_2SO$	1·5—2·5 (8H, m)	5·55 (1H, q, H_a); 6·23 (1H, q, H_b); 6·78 (1H, m, H_c); 7·21 (1H, t, H_d); 7·42 (1H, q, H_e); $J_{a,b}$ 8·7; $J_{a,c}$ 2·1; $J_{b,c}$ 7·2; $J_{c,d}$ 7·0; $J_{d,e}$ 7·0
(7) [a]	$(CD_3)_2SO$	1·6—2·5 (8H, m)	7·08 (4H, m); 8·53 (6H, m)
(8)	$CDCl_3$	1·86—3·1 (13H, m)	3·35br (1H, NH); 7·26 (4H, apparent s, aliphatic H)
(9)	$(CD_3)_2SO$	1·55—2·4 (8H, m)	7·04 (4H, q, N·CH_2·CH_3); 7·09 (4H, apparent s, aliphatic H); 8·95 (6H, t, N·CH_2·CH_3)
(10)	CH_2Cl_2	1·95—2·7 (8H, m)	6·74 (3H, CH_3)
(11)	CH_2Cl_2	1·9—2·7 (8H, m)	6·41 (2H, q, CH_2); 8·73 (3H, t, CH_3); *J* 7·0
(12)	$(CD_3)_2SO$	1·8—2·65 (8H, m)	4·91 (2H, CH_2I)
(13)	$CDCl_3$	1·7—2·6 (8H, m)	5·41 (2H, CH_2); 6·26 (3H, O·CH_3)
(14)	MeCN	1·9—2·65 (8H, m)	6·02 (2H, t, CH_2·CH_2Br); 6·56 (2H, t, CH_2·CH_2Br); *J* 6·5
(15)	$(CD_3)_2SO$	1·9—2·7 (16H, m)	6·37 (4H, m, aliphatic H); 8·57 (2H, m, aliphatic H)
(16)	$(CD_3)_2SO$	2·51 (2H, d, 1-, 9-H); 2·64 (2H, q, 3-, 7-H); 3·03 (2H, d, 4-, 6-H); $J_{3,4}$ 8·4; $J_{1,3}$ 2·5	5·72 (2H, q, CH_2); 8·69 (3H, t, CH_3); *J* 7·2
(17)	MeCN	1·86 (2H, d, 1-, 9-H); 1·94 (2H, q, 3-, 7-H, 2·49 (2H, d, 4-, 6-H), $J_{3,4}$ 8·8; $J_{1,3}$ 2·4	5·12 (2H, CH_2I)
(18)	$CDCl_3$	1·65—2·5 (8H, m)	6·52, 6·58 (3H, apparent d, O·CH_3)
	MeCN	1·6—2·45 (8H, m)	6·66 (3H, O·CH_3)
	CF_3·CO_2H	1·6—2·35 (8H, m)	6·63 (3H, O·CH_3)
(19)	$CDCl_3$	2·05—2·7 (8H, m)	1·08 (1H, NH); 7·08 (4H, q); 7·18 (2H, t); 7·54 (2H, t); 8·38 (2H, m); 8·80 (6H, t); *J ca.* 7 in each case
(20)	$(CD_3)_2SO$	1·8—2·6 (8H, m)	7·04 (4H, apparent s, aliphatic H); 7·08 (4H, q, N·CH_2·CH_3); 8·98 (6H, t, N·CH_2·CH_3); *J* 7·0
(21)	MeCN	1·85—2·5 (8H, m)	5·28 (2H, CH_2I); 5·51 (2H, 9-H_2)
(22)	MeCN	1·8—2·53 (8H, m)	5·48 (2H, CH_2); 5·50 (2H, 9-H_2); 6·23 (3H, O·CH_3)
(23)	MeCN	1·9—2·6 (8H, m)	3·7br (2H, NH_2); 5·56 (4H, apparent s, CH_2 and 9-H_2)
(24)	$(CD_3)_2SO$	1·8—2·8 (8H, m)	6·51 (3H, CH_3); 7·60 (3H, CO·CH_3)
(25)	$(CD_3)_2SO$	1·8—2·8 (8H, m)	6·42 (2H, CH_2); 7·60 (3H, CO·CH_3); 8·74 (3H, t, CH_3); *J* 7·5
(26)	MeCN	2·0—2·9 (11H, m); 3·25 (2H, q); *J* 8 and 2	7·06 (3H, CH_3)
(27)	CH_2Cl_2	2·0—2·7 (11H, m); 3·25 (2H, q); *J* 8 and 2	6·56 (2H, q, CH_2); 8·72 (3H, t, CH_3); *J* 7·2
	MeCN	2·0—2·9 (11H, m); 3·27 (2H, q); *J* 8 and 2	6·62 (2H, q, CH_2); 8·83 (3H, t, CH_3); *J* 7 and 2
(28)	MeCN	2·0—2·7 (11H, m); 3·22 (2H, q); *J* 8 and 2	5·38 (2H, CH_2I)
(29)	MeCN	1·95—2·8 (11H, m); 3·22 (2H, q); *J* 8 and 2	5·68 (2H, CH_2); 6·33 (3H, O·CH_3)
(30)	MeCN	1·88—2·8 (8H, m); 1·45 (2H, d); 3·38 (2H, d); *J* 9	6·43 (2H, q, CH_2); 8·88 (3H, t, CH_3); *J* 7·2
(31)	$CDCl_3$	2·4—2·9 (8H, m)	6·43 (2H, t); 7·01 (2H, t); *J* 6·7
(32)	$CDCl_3$	2·4—2·9 (8H, m)	6·93 (4H, m)
(34)	$(CD_3)_2SO$	1·65—2·25 (8H, m)	6·29 (3H, O·CH_3)
(35)	$(CD_3)_2SO$	1·9—2·6 (4H, m)	6·36 (3H, O·CH_3)
(36)	$CDCl_3$	1·95—2·7 (8H, m)	3·80 (4H, m)
(37)	$CDCl_3$	2·36—3·0 (8H, m)	6·44 (6H, O·CH_3)

[a] The aromatic region (acetonitrile as solvent; 100 MHz) was simulated to 0·1 Hz accuracy by use of the folowing parameters: τ 1·8[illegible]-H), 2·256 (2-H), 2·087 (3-H), 1·824 (4-H): $J_{1,2}$ 7·8, $J_{1,3}$ 1·2, $J_{1,4}$ 0·6, $J_{2,3}$ 7·7, $J_{2,4}$ 1·4, $J_{3,4}$ 7·7.

[8] G. Seitz, *Chem. Ber.*, 1968, **101**, 585.

[9] H. Nozaki, D. Tunemoto, S. Matabara, and K. Kondo, *Tetrahedron*, 1967, **23**, 545.

[10] T. E. Young and R. A. Lazarus, *J. Org. Chem.*, 1968, **33**, 3774 (footnote).

(250 ml) and the alkyl halide was added dropwise. When the reaction was complete, the product was isolated as in procedure *A* except that it was unnecessary to wash with water.

The halides used were: di-iodomethane, methyl bromoacetate, chlorodiphenylphosphine, methyl iodide, ethyl iodide, 1,2-epoxy-3-iodopropane, 1,2-dibromoethane, and 1,3-di-iodopropane.

TABLE 2

U.v. absorption spectra (solutions in methanol)

Compound	$\lambda_{max.}$/nm ($10^{-4}\varepsilon$)
(1)	211 (3·3), 241 (3·3), 270infl (0·74), 324 (0·2)
(2)	211 (4·0), 233 (2·7), 264 (1·8), 315 (0·21)
(3)	213 (4·2), 239 (5·3), 269 (3·7), 213infl (0·8)
(4), (5)	207 (2·1), 222 (2·6), 244infl (3·4), 249 (3·5), 281 (0·32), 356 (0·13)
(7)	209 (2·4), 238infl (2·8), 242 (3·1), 266 (0·63), 333 (0·13)
(8)	209 (4·0), 239 (3·6), 332 (0·17)
(9)	210 (2·9), 232infl (2·8), 238 (3·1). 328 (0·16)
(10)	213 (3·7), 287 (0·61)
(11)	214 (3·4), 290 (0·50)
(12)	213 (4·7), 294 (0·53)
(13)	212 (4·3), 280 (0·87)
(15)	212 (6·6), 292 (0·84)
(16)	217 (4·0), 250infl (1·2), 300 (0·46)
(17)	220 (4·8), 258 (1·6), 310 (0·63)
(18)	212 (2·8), 224 (3·2), 304 (0·37), 317 (0·37)
(19)	212 (4·5), 281infl (0·31), 301 (0·46)
(20)	212 (4·7), 286infl (0·32), 302 (0·48)
(21)	210 (2·7), 266 (0·90)
(22)	212 (2·1), 268 (1·3)
(23)	212(2·0), 270 (1·3)
(24)	212 (2·9), 278 (0·44), 293 (0·45)
(26)	218 (3·6), 275 (0·87), 326 (0·88)
(28)	222 (5·4), 277 (1·0), 337 (1·1)
(29)	218 (4·0), 265 (0·78), 329 (0·82)
(32)	215 (2·2), 228 (2·1), 262 (1·1)
(35)	230 (2·9), 328 (0·37)
(36)	211 (2·7), 227 (1·8), 234 (1·9), 264 (1·7), 285infl (1·4)
(37)	210 (2·2), 247 (0·68)

5-Alkylaminodibenzo[bd]*thiophenium Perchlorates.*—5-Methoxydibenzothiophenium perchlorate (4) (0·315 g) was dissolved in acetonitrile (2—3 ml) and stirred in a carbon dioxide–carbon tetrachloride cooling bath; a solution of piperidine (85 mg) in acetonitrile (1 ml) was added, and the mixture was allowed to warm to room temperature. After 0·5 h, dry ether was added slowly and the crystalline precipitate was filtered off and recrystallised, by dissolving in acetonitrile and adding ether, to give the *perchlorate* (7) (0·26 g, 70%), plates, m.p. 174° (decomp.). Similarly phenethylamine (121 mg) gave the *perchlorate* (8) (0·24 g, 60%), needles, m.p. 133—133·5°, and 2-(diethylamino)-ethylamine (116 mg) gave 5-(2-*diethylaminoethylamino*)*dibenzothiophenium perchlorate hydroperchlorate* (9) (0·18 g, 36%), rhombs, m.p. 210—212°.

10-Alkylaminophenoxathiinium Perchlorates.—These were prepared by the method used for compound (7): 10-methoxyphenoxathiinium perchlorate (18) (0·66 g) and 3-(diethylamino)propylamine (0·26 g) in acetonitrile (4 ml), mixed at −30° and left overnight at room temperature, gave the *perchlorate* (19) (0·64 g, 74%), needles, m.p. 104°. Similarly 2-(diethylamino)ethylamine (116 mg) gave 10-(2-*diethylaminoethylamino*)*phenoxathiinium perchlorate hydroperchlorate* (20) (0·1 g, 20%), needles, m.p. 155—156°.

10-(3-Bromopropionyl)phenothiazine (31).—Recrystallised phenothiazine (2·0 g), anhydrous sodium carbonate (4·0 g), and 3-bromopropionyl chloride (2·5 g) were stirred in dry dioxan (50 ml) at 100° for 45 min; the mixture was then cooled, diluted, and neutralised. The crude product was filtered off and recrystallised from ethanol to give compound (31) (2·6 g, 77%) pale yellow plates, m.p. 141—142° (lit.,[11] 144—145°).

10-(3-Iodopropionyl)phenothiazine (32).—10-(3-Bromopropionyl)phenothiazine (31) (3·0 g) and sodium iodide (10 g) in AnalaR acetone (40 ml) were stirred and refluxed for 12 h; the hot solution was then diluted and allowed to cool. Recrystallisation of the precipitate from ethanol gave the *phenothiazine* (32) (2·5 g) as yellow-green needles, m.p. 147—148°.

Thioxanthen-5-one 10-Oxide.—Thioxanthen-5-one has been oxidised to the sulphoxide with iodosylbenzene diacetate,[12] but controlled oxidation with hydrogen peroxide was found to be more convenient. Thioxanthen-5-one (9·0 g) in glacial acetic acid (100 ml) was stirred and refluxed vigorously on an oil-bath (bath temp. 140°), and 30% hydrogen peroxide (18 ml) was added through the condenser. The mixture soon became homogeneous; it was refluxed vigorously for 2 min and then poured into hot water (500 ml) and cooled. The precipitate was filtered off, dried (8·5 g), dissolved in chloroform (40 ml), and applied to a column of silica (300 ml) prepared in benzene. Elution with benzene gave first thioxanthen-5-one (2·0 g), $\nu_{max.}$ 1645 cm^{-1}, then thioxanthen-5-one sulphone (*ca.* 1 g), $\nu_{max.}$ 1680 cm^{-1}. Elution with chloroform gave thioxanthen-5-one 10-oxide (4·8 g), m.p. 201—202° (lit.,[12] 202—204°), $\nu_{max.}$ 1670 cm^{-1} (CO).

TABLE 3

Alkylation products

Product	Procedure	Reaction time (days)	Yield (%)	M.p. (°C)	Description
(1)	*A*	3	40	160—164 †	Plates
(2)	*A*	8	59	136 †	Plates
(3)	*B* [a]	1	6	277—279	Pale yellow prisms
(4)	*B*	1	70	144—145	Pale yellow plates
(5)	*B*	1	77	152—153	Pale yellow prisms
(6)	*B*	1	22	157—158	Pale yellow plates
(10)	*B*	1	86	198 †	Prisms
(11)	*B*	3	58	131—132 †	Prisms
(12)	*A*	6	45	214 †	Prisms
(13)	*A*	7	80	173 †	Prisms
(14)	*A*	13	29	154—155 †	Prisms
(15)	*A* [b]	3	41	196—197 †	Needles
(16)	*A*	5	<10	170—175 †	Prisms
(17)	*A*	19	13	195 †	Prisms
(18)	*B*	1	67	117	Plates
(21)	*A*	7	<10	216—217 †	Needles
(22)	*A*	9	19	198 †	Needles
(23)	*A*	2	48	175 †	Prisms
(24)	*B*	2	24	175 †	Needles
(25)	*A*	1	29	141 †	Needles
(26)	*B*	2	76	183—184 †	Prisms
(27)	*B*	2	39	181—182 †	Prisms
(28)	*A*	10	65	220 †	Prisms
(29)	*A*	10	77	190 †	Prisms
(30)	*B*	6	40	195—200 †	Pale green needles
(34)	*B*	2	67	155—160 †	Needles
(35)	*B*	1	46	122 †	Yellow prisms

[a] Mixed at −70°. [b] Proportions used: di-iodopropane (1), silver perchlorates (3), phenoxathiin (5).
† Decomp.

[11] R. Dahlbom, *Acta Chem. Scand.*, 1953, **7**, 873.
[12] J. P. A. Castrillon and H. H. Szmant, *J. Org. Chem.*, 1967, **32**, 976.

2,3-*Dibromobenzo*[b]*thiophen* 1-*Oxide*.—This was prepared as described in ref. 13 and had m.p. 156° (from benzene) (lit.,[13] 156·5—157·5°).

Dibenzothiophenium Cyclopentadienide (36).—5-Methoxydibenzothiophenium perchlorate (4) (1·58 g) dissolved in acetonitrile (10 ml) was cooled to −20°, and a solution of cyclopentadiene (0·5 g) in methanol (5 ml) containing sodium (115 mg) was added slowly. After 20 min at −20° the mixture was allowed to warm slowly to room temperature, and the product precipitated. After 0·5 h the mixture was cooled, water (2 ml) was added, and the crude *cyclopentadienide* was filtered off and dried. Recrystallisation from acetonitrile gave yellow-brown needles (0·5 g, 40%), m.p. *ca.* 114° (decomp.).

10-*Phenoxathiinium Bis(methoxycarbonyl)methylide* (37).—10-Methoxyphenoxathiinium perchlorate (18) (0·66 g) dissolved in acetonitrile (2 ml) was cooled to −20° and a solution of dimethyl malonate (0·3 ml) in methanol (3 ml) containing sodium (46 mg) was added slowly. The mixture was kept for 20 min at −20° and for 20 min at room temperature, then an excess of water was added to precipitate the product. Recrystallisation from methanol gave the *methylide* (37) (0·48 g, 72%), cubic crystals, m.p. 225°.

TABLE 4

Analyses and i.r. spectra

Compound	Formula	Found (%) C	H	N	S	Required (%) C	H	N	S	$\nu_{max.}$/cm^{-1}
(1)	$C_{13}H_{10}ClIO_4S$	36·8	2·6			36·7	2·4			782w, 762, 758, 706w
(2)	$C_{15}H_{13}ClO_6S$	50·5	3·8		9·2	50·5	3·6		9·0	1731, 975, 955, 912, 893, 780w, 760, 750w, 705
(3)	$C_{24}H_{18}ClO_4PS$	61·6	3·4		7·0	61·5	3·8		6·8	810, 781, 760, 739, 721, 704
(4)	$C_{13}H_{11}ClO_5S$	50·0	4·0		10·2	49·6	3·5		10·2	949, 792w, 771, 762, 722, 710, 688w
(5)	$C_{14}H_{13}ClO_5S$	51·1	4·5		10·2	51·2	4·0		9·75	985, 870, 780w, 770, 761, 745, 708
(6)	$C_{15}H_{13}ClO_6S$	51·0	3·9		9·1	50·5	3·6		9·0	917, 901, 870, 862, 784, 772, 762w, 710
(7)	$C_{17}H_{18}ClNO_4S$	55·9	5·0	4·0		55·5	4·9	3·8		960w, 940w, 918w, 858, 837w, 764, 760, 710
(8)	$C_{20}H_{18}ClNO_4S$	59·7	4·6	3·7		59·5	4·5	3·5		3190 (NH), 930, 893w, 763, 739, 711w, 698
(9)	$C_{18}H_{24}Cl_2N_2O_8S$	43·6	4·9	5·8		43·3	4·8	5·6		3180, 3120 (NH), 955, 932, 760, 709
(10)	$C_{13}H_{11}ClO_5S$	50·3	3·6		10·4	49·9	3·5		10·2	990w, 885, 820w, 767
(11)	$C_{14}H_{13}ClO_5S$	51·4	3·8		10·0	51·2	4·0		9·75	968w, 959w, 930w, 880, 871w, 812w, 780w, 768, 709w
(12)	$C_{13}H_{10}ClIO_5S$	35·9	2·5			35·5	2·3			890, 806w, 770w, 762
(13)	$C_{15}H_{13}ClO_7S$	48·8	3·6		8·9	48·4	3·5		8·6	1735, 987w, 913w, 891, 882, 817w, 782, 764, 754w
(14)	$C_{14}H_{12}BrClO_5S$	42·0	3·0			41·3	3·0			958w, 883, 839w, 815w, 776, 763
(15)	$C_{27}H_{22}Cl_2O_{10}S_2$	50·7	3·7		12·5	50·5	3·4		10·0	955w, 887, 881, 813w, 770, 761
(16)	$C_{14}H_{11}Br_2ClO_5S$	34·8	2·3			34·5	2·3			965w, 913w, 870w, 851, 840, 825, 783w, 762, 732
(17)	$C_{13}H_8Br_2ClIO_5S$	26·5	1·6			26·1	1·3			870w, 841, 823, 732
(18)	$C_{13}H_{11}ClO_6S$	47·5	3·6		10·1	47·2	3·3		9·7	952, 940, 893, 777, 770, 720, 710, 675
(19)	$C_{19}H_{25}ClN_2O_5S$	53·4	5·9	6·7		53·2	5·8	6·5		2420 (NH), 992, 887, 848, 770w, 752
(20)	$C_{18}H_{24}Cl_2N_2O_9S$	42·1	4·9	5·6		42·0	4·7	5·4		3200, 3110 (NH), 955w, 930, 892, 753
(21)	$C_{14}H_{12}ClIO_4S$	38·8	2·6		7·6	38·4	2·7		7·3	828w, 800w, 755
(22)	$C_{16}H_{15}ClO_6S$	52·1	3·8		8·9	51·8	4·0		8·6	1733, 983, 969w, 927w, 914, 896, 830, 768, 751, 711w
(23)	$C_{15}H_{14}ClNO_5S$	50·6	4·0	4·0		50·6	3·9	3·9		3400, 3300, 3240 (NH), 1680, 980w, 915w, 830w, 777, 770
(24)	$C_{15}H_{14}ClNO_5S$	51·0	4·1		8·9	50·6	3·9		9·0	1690, 993w, 982w, 791, 758
(25)	$C_{16}H_{16}ClNO_5S$	52·2	4·4	3·8		52·0	4·3	3·8		1683, 902w, 778, 758, 733w
(26)	$C_{19}H_{16}ClNO_4S$	54·7	4·2	3·4		58·5	4·1	3·6		972w, 760, 722, 709
(27)	$C_{20}H_{18}ClNO_4S$	60·5	4·6	3·6		59·5	4·5	3·5		910w, 781, 763, 723, 711, 702
(28)	$C_{19}H_{15}ClINO_4S$	45·1	3·1			44·2	2·9			942w, 910w, 800w, 793w, 759, 768, 722, 711, 700w
(29)	$C_{21}H_{18}ClNO_6S$	56·2	4·5			56·4	4·0			1740, 989, 942w, 909, 892, 783, 762, 722, 710, 696
(30)	$C_{20}H_{17}ClN_2O_6S$	53·5	3·9	6·5		53·5	3·8	6·2		920, 850, 755, 720, 704
(31)										1673, 946w, 872w, 772, 766, 753, 733, 724w, 697w
(32)	$C_{15}H_{12}INOS$	47·6	3·3	3·6		47·3	3·2	3·7		1681, 980w, 920, 850w, 769, 753, 732
(34)	$C_{14}H_{11}ClO_6S$	49·1	3·1		9·8	49·1	3·2		9·4	1678, 942, 935w, 810, 771, 760, 752, 732, 685, 672
(35)	$C_9H_7Br_2ClO_5S$	26·0	1·8			25·6	1·7			981w, 935, 765, 721w
(36)	$C_{17}H_{12}S$				12·7				12·9	753, 705
(37)	$C_{17}H_{14}O_5S$	62·1	4·3			61·8	4·2			1679, 1648, 965, 940w, 853w, 782, 751, 743

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[13] H. D. Hartough and S. L. Meisel, ' Condensed Thiophenes,' Interscience, New York, 1954, p. 155.