# Novel Aspects in the Reaction of 2-Diazo-2'-(phenylthio)acetophenone with Arenesulphenyl Chlorides: Formation of α-Ketoaldehyde Thioacetal Chlorides via Cyclic Sulphonium α-(Arylthio)phenacylides

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Under conditions where 2-diazoacetophenone and benzenesulphenyl chloride provide 2-chloro-2-(phenylthio)-acetophenone, 2-diazo-2'-(phenylthio)acetophenone (1a) with 2-nitro- and 2,4-dinitro-benzenesulphenyl chlorides gives, after treatment with water, 2-(2-nitrophenylthio)- and 2-(2,4-dinitrophenylthio)-3-oxo-1-phenyl-benzo[b]thiophenium-2-ides (4b and c) respectively. The structure of these ylides was established by independent syntheses from 3-oxo-1-phenylbenzo[b]thiophenium-2-ide (4a) and the appropriate arenesulphenyl chloride in the presence of triethylamine. In contrast, two molecular proportions of benzenesulphenyl chloride were required to liberate the diazo nitrogen from the phenylthio-diazoketone (1a) when there resulted hydrogen chloride and 2-chloro-2,2,2'-tris(phenylthio)acetophenone (5a). The latter was also prepared from benzenesulphenyl chloride and 3-oxo-1-phenyl-2-(phenylthio)benzo[b]thiophenium-2-ide (4d), which was readily synthesised by condensation of the unsubstituted ylide (4a) with N-(phenylthio)phthalimide in the presence of triethylamine. 2-Chloro-2,2-bis(phenylthio)acetophenones have apparently not been reported previously: evidence in support of such a structure was obtained by hydrolysis, with boiling water, of 2-chloro-2,2,2'-tris(phenylthio)acetophenone (5a) to hydrogen chloride, benzenethiol and S-phenyl [2-(phenylthio)phenyl]thioglyoxylate (8a).

RECENTLY we have shown that 2-diazo-2'-(phenylthio)-acetophenone (1a) with perchloric acid (X = H, Y = ClO_4) provides an acyl-diazonium ion (2a) which cyclises to give the phenacylsulphonium salt (3a); addition of organic base to (3a) affords the cyclic ylide (4a), from which the salt (3a) may be regenerated by addition of perchloric acid (Scheme).[1] It seemed reasonable to expect that analogous reactions might be initiated by electrophilic species other than strong acids. In particular, arenesulphenyl chlorides (X = ArS, Y = Cl) appeared suitable reagents since they are known to react readily with α-diazo-ketones to provide the hemithioacetal chlorides of the corresponding α-ketoaldehydes [e.g., equation (1)].[2,3]

$$PhSCl + PhCOCHN_2 \longrightarrow PhCOCH(SPh)Cl + N_2 \quad (1)$$
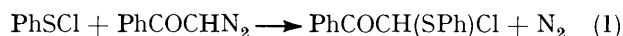
We now report that when equimolar proportions of the diazoketone (1a) and either 2-nitro- or 2,4-dinitro-

benzenesulphenyl chlorides [X = $2\text{-}NO_2C_6H_4S$ or $2,4\text{-}(NO_2)_2C_6H_3S$, Y = Cl] are brought together in acetonitrile, the diazo nitrogen is rapidly and quantitatively evolved to give, after treatment with water, but without addition of base, the ylides (4b and c respectively) in high yield; both these ylides were also synthesised from the unsubstituted ylide (4a) and the appropriate sulphenyl chloride in the presence of triethylamine. The spontaneous deprotonation of the sulphonium salts (3b and c) presumably arises on account of the stabilisation by the arylthio-substituent of the carbanionic centre in the resultant ylides;[4] the enhanced stability of the ylides (4b—e) over that of ylide (4a) is shown by their lack of decomposition on prolonged storage and by their failure to provide a sulphonium salt on addition of perchloric or trifluoromethanesulphonic acids.

However, when the diazo-ketone (1a) is treated with an equimolar proportion of benzenesulphenyl chloride

[1] W. T. Flowers, G. Holt, and M. A. Hope, J.C.S. Perkin I, 1974, 1116.

[2] F. Weygand and H. J. Bestmann, Z. Naturforsch., 1955, 10, 296.

[3] F. Weygand, H. J. Bestmann, and H. Fritzsche, Chem. Ber., 1960, 93, 2340.

[4] Y. Hayasi and H. Nozaki, Bull. Chem. Soc. Japan, 1972, 45, 198.

(X = PhS, Y = Cl) in diethyl ether, the resulting mixture contains unchanged diazo-ketone (1a), either the unsubstituted sulphonium chloride (3d) or its re-arrangement product, the chloro-ketone (5c) apparently in the zwitterionic enol form (6), the thioacetal chloride (5a), and traces of the hemithioacetal chloride (5b) and the chloroketone (5c). Use of acetonitrile as solvent for this reaction led to excessive formation of diphenyl di-sulphide. When the molecular proportions of the sulphenyl chloride to the diazo-ketone are increased to 2 : 1 in either diethyl ether or dichloromethane, evolution of nitrogen is quantitative, and the yields of the thio-acetal chloride (5a) and hydrogen chloride are high [equation (2)]. Similar results were obtained using
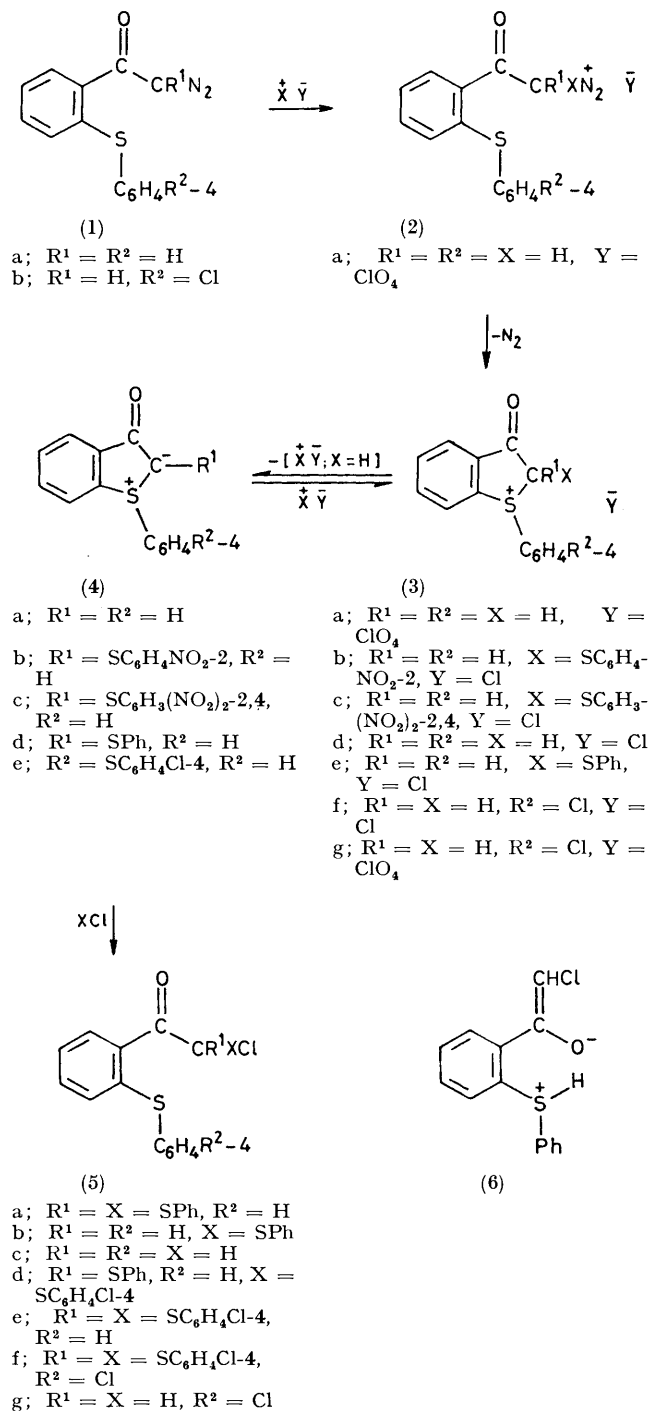
$$Ar^1COCHN_2 + 2Ar^2SCl =$$
$$Ar^1COC(SAr^2)_2Cl + N_2 + HCl \quad (2)$$
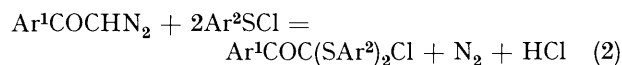
4-chlorobenzenesulphenyl chloride (X = 4-ClC$_6$H$_4$S, Y = Cl).

It thus appeared that, in contrast to its nitro-derivatives, benzenesulphenyl chloride (known to be the more reactive towards enolizable ketones[5] and eno-lates[6]) was reacting with the first-formed ylide (4d) to give the thioacetal chloride (5a). The ylide (4d) was therefore synthesised by reaction of the ylide (4a) and N-(phenylthio)phthalimide; addition of (4d) to an equimolar proportion of benzenesulphenyl chloride did indeed provide the thioacetal chloride (5a) in near-quantitative yield. Furthermore, the unsymmetrical thioacetal chloride (5d) was obtained both from the ylide (4e) and benzenesulphenyl chloride and from the ylide (4d) and 4-chlorobenzenesulphenyl chloride; the (nitrophenylthio)-ylides (4b and c) were unreactive towards sulphenylation by their precursor sulphenyl chlorides.

The only previously reported benzenesulphenylation of a sulphonium ylide appears to be the formation of dimethylsulphonium α-(phenylthio)phenacylide from di-methylsulphonium phenacylide; two molecular pro-portions of the latter were used, presumably to accom-plish *in situ* deprotonation of the intermediate sul-phonium chloride.[4] We therefore investigated the re-actions of the unsubstituted ylide (4a) with equimolar proportions of various sulphenyl chlorides in the absence of base. With 2-nitro- and 2,4-dinitro-benzenesulphenyl chlorides, (4a) affords, after treatment with water, the sulphenylated ylides (4b and c, respectively) in slightly lower yields than when triethylamine was present. When a solution of the ylide (4a) in dichloromethane was treated with benzenesulphenyl chloride the sole product was the hemithioacetal chloride (5b), which was also obtained by the addition of ethereal hydrogen chloride to the sulphenylated ylide (4d). However, when the ylide (4a) was suspended in ethereal benzenesulphenyl chloride, the reaction proved more complex, the isolated compounds being the sulphonium enolate (6) and the thioacetal chloride (5a), indicating that sulphenylation had occurred to give the ylide (4d), but that this had further reacted to provide the thioacetal chloride (5a).

Use of the less-potent sulphenylating agents N-(phenyl-thio)- and N-(4-chlorophenylthio)-phthalimide in the presence of triethylamine afforded the sulphenylated ylides (4d and e, respectively) in excellent yields.
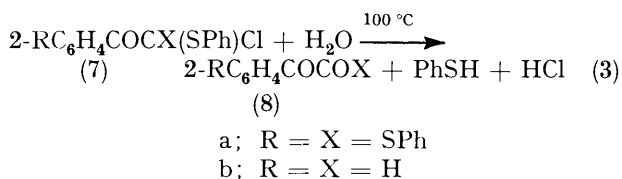

(1)

a; R^1 = R^2 = H
b; R^1 = H, R^2 = Cl

(2)

a; R^1 = R^2 = X = H, Y = ClO$_4$

(4)

a; R^1 = R^2 = H
b; R^1 = SC$_6$H$_4$NO$_2$-2, R^2 = H
c; R^1 = SC$_6$H$_3$(NO$_2$)$_2$-2,4, R^2 = H
d; R^1 = SPh, R^2 = H
e; R^2 = SC$_6$H$_4$Cl-4, R^2 = H

(3)

a; R^1 = R^2 = X = H, Y = ClO$_4$
b; R^1 = R^2 = H, X = SC$_6$H$_4$-NO$_2$-2, Y = Cl
c; R^1 = R^2 = H, X = SC$_6$H$_3$-(NO$_2$)$_2$-2,4, Y = Cl
d; R^1 = R^2 = X = H, Y = Cl
e; R^1 = R^2 = H, X = SPh, Y = Cl
f; R^1 = X = H, R^2 = Cl, Y = Cl
g; R^1 = X = H, R^2 = Cl, Y = ClO$_4$

(5)

a; R^1 = X = SPh, R^2 = H
b; R^1 = R^2 = H, X = SPh
c; R^1 = R^2 = X = H
d; R^1 = SPh, R^2 = H, X = SC$_6$H$_4$Cl-4
e; R^1 = X = SC$_6$H$_4$Cl-4, R^2 = H
f; R^1 = X = SC$_6$H$_4$Cl-4, R^2 = Cl
g; R^1 = X = H, R^2 = Cl

(6)

The above results may be rationalised by suggesting that in the reactions of both the diazo-ketone (1a) and

[5] P. Held, M. Gross, and A. Jumar, *Z. Chem.*, 1970, **10**, 187.
[6] D. Seebach and M. Teschner, *Chem. Ber.*, 1976, **109**, 1601.

the unsubstituted ylide (4a) with arenesulphenyl chlorides there is a common intermediate, the sulphonium chloride (3; $R^1 = R^2 = H$, $X = SAr$, $Y = Cl$), the fate of which is determined by three factors: (i) its ready loss of proton to yield a highly stabilised ylide; (ii) its susceptibility to nucleophilic attack at phenacyl carbon; and (iii) the electrophilic species used to generate it. Thus, both the diazo-ketone (1a) and unsubstituted ylide (4a) react with benzenesulphenyl chloride to afford, initially, the sulphonium chloride (3e), which exists in equilibrium with H^+ and the ylide (4d). The latter is presumably sufficiently nucleophilic to permit reaction with further benzenesulphenyl chloride to provide the thioacetal chloride (5a). 2-Nitro- or 2,4-dinitro-benzene-sulphenyl chloride yield the intermediate sulphonium cation (3b or c respectively), the enhanced acidity of which, over the phenylthio-analogue (3e), favours deprotonation to the corresponding ylide (4b or c respectively); the latter accumulates in the reaction since it does not possess sufficient nucleophilicity to react with further nitrobenzenesulphenyl chloride. In keeping with these suggestions, the phenylthio-ylide (4d) reacts rapidly with hydrogen chloride to provide the hemithioacetal chloride (5b) *via* the transient sulphonium salt (3e) but, under similar conditions, the 2,4-dinitrophenylthio-ylide (4c) is virtually unaffected. The failure of the sulphenylated ylides (4b—e) to undergo analogous reactions with perchloric or trifluoro-methanesulphonic acids may be ascribed to the much lower nucleophilicity of their respective anions compared to chloride ion. The hemithioacetal chloride (5b) [like (10a)] fails to react with benzenesulphenyl chloride and is apparently not therefore the precursor of the thioacetal chloride (5a) in the diazo-ketone reactions.
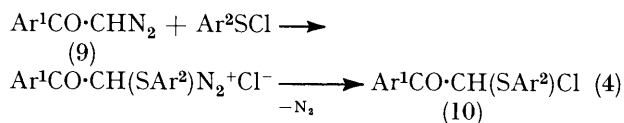
With the exception of brief reference to the unstable chlorobis(phenylthio)methane,[7] thioacetal chlorides and their α-keto-derivatives are classes of compounds which have not apparently been described previously. De-gradative evidence in support of structure was obtained by hydrolysis of the thioacetal chloride (7a) [≡ (5a)] with boiling water and concurrent removal of benzenethiol, as formed *in situ*, by steam distillation; such conditions were similar to those used for the conversion of the hemi-thioacetal chloride (7b) [≡ 10a)] to phenylglyoxal (8b).[2] There then resulted, in near quantitative yields, equi-molar amounts of hydrogen chloride, benzenethiol, and S-phenyl [2-(phenylthio)phenyl]thioglyoxylate (8a), in accord with equation (3).

$$2\text{-}RC_6H_4COCX(SPh)Cl + H_2O \xrightarrow{100\ °C}$$
$$(7) \qquad 2\text{-}RC_6H_4COCOX + PhSH + HCl \quad (3)$$
$$(8)$$

a; R = X = SPh
b; R = X = H

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1977, Index issue. Items less than 10 pp. are supplied as full-size copies.

[7] H. Boehme and J. Roehr, *Annalen*, 1961, **648**, 21.

In contrast to the perchloric acid reactions, the inter-molecular counterpart of the sulphenyl chloride reactions could not be realised. Thus, when typical arene-sulphenyl chlorides were treated with 2-diazoaceto-phenone (9; $Ar^1 = Ph$), or its 4'-nitro-derivative (9; $Ar^1 = 4\text{-}NO_2C_6H_4$), in the presence of dimethyl or methyl phenyl sulphide, there resulted the simple hemithioacetal chlorides (10) in high yield and there was no incorporation of the sulphide [equation (4)]. This result probably reflects the greater nucleophilicity of chloride ion over perchlorate ion and, hence, the superior contribution of the acyldiazonium ion in the latter reactions.

$$Ar^1CO\cdot CHN_2 + Ar^2SCl \longrightarrow$$
$$(9)$$
$$Ar^1CO\cdot CH(SAr^2)N_2{}^+Cl^- \xrightarrow{-N_2} Ar^1CO\cdot CH(SAr^2)Cl \quad (4)$$
$$(10)$$

a; $Ar^1 = Ar^2 = Ph$
b; $Ar^1 = Ph$, $Ar^2 = 2,4\text{-}(NO_2)_2C_6H_3$
c; $Ar^1 = 4\text{-}NO_2C_6H_4$, $Ar^2 = 2\text{-}NO_2C_6H_4$
d; $Ar^1 = 4\text{-}NO_2C_6H_4$, $Ar^2 = 4\text{-}ClC_6H_4$

EXPERIMENTAL

I.r. spectra were recorded on Perkin-Elmer 257 and 621 instruments, ^1H n.m.r. spectra on Perkin-Elmer R20A or Varian HA100 spectrometers, and mass spectra on an A.E.I. MS902 spectrometer. Gas volumes have been reduced to S.T.P. All the known compounds gave satis-factory analytical and spectroscopic data. Physical data for novel 2-chloroacetophenones and 2-(arylthio)-3-oxo-1-phenylbenzo[*b*]thiophenium-2-ylides are given in the Table. For products marked with an asterisk, further spectral data are available in Supplementary Publication No. SUP 22200 (5 pp.).*

Diazo-ketones.—2-Diazoacetophenone [8] (9; $Ar^1 = Ph$), and its 4'-nitro- [9] (9; $Ar^1 = 4\text{-}NO_2C_6H_4$), 2'-(phenylthio)- [1] (1a), and 2'-(4-chlorophenylthio)- [1] (1b) derivatives were prepared from diazomethane and the appropriate benzoyl chloride by standard procedures.[10] Slow recrystallization of the 2'-(phenylthio)-derivative from diethyl ether at −20° provided yellow needles, m.p. 60.0—61.0°, rather than 47.5—48.5° as reported previously.[1]

Arenesulphenyl Chlorides.—Benzenesulphenyl chloride,[11] and its 4-chloro-,[12] 2-nitro-,[13] and 2,4-dinitro-[14] derivatives were prepared by chlorinolysis of the corresponding diaryl disulphide under standard conditions.

N-(*Arylthio*)*phthalimides.*—N-(Phenylthio)- and N-(4-chlorophenylthio)-phthalimide were prepared from the appropriate arenesulphenyl chloride and phthalimide, in the presence of triethylamine, by a standard procedure.[15]

3-*Oxo-1-phenylbenzo*[b]*thiophenium-2-ide* (4a).—Prepared

[8] M. S. Newman and P. Beal III, *J. Amer. Chem. Soc.*, 1949, **71**, 1506.
[9] N. Bradley and G. Schwarzenbach, *J. Chem. Soc.*, 1928, 2907.
[10] See *Org. Reactions*, 1942, **1**, 38, for a compilation of references.
[11] W. E. Truce, H. E. Hill, and M. M. Boudakian, *J. Amer. Chem. Soc.*, 1956, **78**, 2760.
[12] G. H. Schmid and V. M. Csizmadia, *Canad. J. Chem.*, 1966, **44**, 1338.
[13] M. H. Hubacher, *Org. Synth.*, 1943, Coll. Vol. II, 455.
[14] D. D. Lawson and N. Kharasch, *J. Org. Chem.*, 1959, **24**, 857.
[15] M. Behforouz and J. E. Kerwood, *J. Org. Chem.*, 1969, **34**, 51.

from 2,3-dihydro-3-oxo-1-phenylbenzo[*b*]thiophenium perchlorate[1] (3a) and triethylamine under standard conditions,[16] this had m.p. 150.0—152.0° (decomp.) (from acetonitrile) and $v_{max.}$ 1 555s (CO) cm⁻¹, rather than 135—137° [from benzene–light petroleum (b.p. 60—80°)] and 1 594 cm⁻¹, respectively, as reported previously.[1] Its susceptibility to decomposition in a variety of solvents above *ca.* 45° is in marked contrast to the arylthio-ylides

2-nitrobenzenesulphenyl chloride provided 2-(2-*nitrophenylthio*)-3-*oxo*-1-*phenylbenzo*[b]*thiophenium*-2-*ide* * (4b) (62%). Dichloromethane proved equally effective as solvent although no reaction/nitrogen evolution occurred in diethyl ether.

(*b*) When the diazo-ketone (1a) (2.64 g, 10.4 mmol) in dry ether (100 ml) was added, as in (*a*) above, to benzenesulphenyl chloride (3.04 g, 21.0 mmol) in dry ether (60 ml),

Physical data for 2-chloroacetophenones and 2-(arylthio)-3-oxo-1-phenylbenzo[*b*]thiophenium-2-ides

Compound	M.p. °C (solvent)	v_{max}/cm⁻¹ e C=O	NO₂ assymm. (upper) symm. (lower)	τ(CDCl₃)	$M^{+\cdot}$ [ArCO]⁺ m/e (%)	Formula	Found (%) Reqd. (%) C	H	Cl	N	S
				α-Chloro-ketones							
(5c)	73.5—74.5 a	1 687s d		2.4—3.3 (9 H, m, ArH) and 5.43 (2 H, s, COCH₂Cl)	262 (38) 213 (100)	C₁₄H₁₁ClOS	63.9 64.0	4.4 4.2	13.6 13.5		12.3 12.2
(5g)	96.0—98.0 a	1 681s		2.45 (1 H, ArH *ortho* to COR, J_{ortho} 7.0, J_{meta} 2.5 Hz), 2.7—3.3 (7 H, m, ArH), and 5.42 (2 H, s, COCH₂Cl)	296 (55) 247 (100)	C₁₄H₁₀Cl₂OS	56.3 56.6	3.3 3.4	23.4 23.9		10.6 10.8
				Arylglyoxal hemithioacetal chlorides							
(5b)	Oil	1 676s e br		2.3—3.4 (14 H, m, ArH) and 3.63 [1 H, s, CO·CH-(SPh)Cl]	—g	C₂₀H₁₅ClOS₂	64.5 64.8	4.1 4.1	9.7 9.6		17.6 17.3
(10b)	164.5—166.5 MeNO₂	1 687s	1 512s,br 1 338s,br	1.16 (1 H, ArH *ortho* to both NO₂ gps., J_{meta} 2.5 Hz), 1.8—3.0 (7 H, m, ArH), and 3.60 [1 H, s, CO·CH-(SAr)Cl] f	—g 105 (100)	C₁₄H₉ClN₂O₅S	47.5 47.7	2.4 2.6	9.9 10.0	7.8 7.9	9.1 9.1
(10c)	150.0—152.0 MeCN	1 690s	1 514s 1 337, 1 324s	1.74 (4 H, ABq, J_{AB} 9.0 Hz, 4-NO₂C₆H₄CO), 1.9—3.0 (4 H, m, 2-NO₂C₆H₄S) and 3.54 [1 H, s, CO·CH-(SAr)Cl] f	—g 150 (100)	C₁₄H:ClN₂O₅S	47.8 47.7	2.5 2.6	10.2 10.0	7.6 7.9	8.7 9.1
(10d)	120.5—121.0 CCl₄ or EtOH	1 708s	1 525s 1 351s	1.73 (4 H, ABq, J_{AB} 9.0 Hz, 4-NO₂C₆H₄CO), 2.60 (4 H, s, 4-ClC₆H₄S], and 3.70 [1 H, s, CO·CH(SAr)-Cl]	341 (10) 150 (100)	C₁₄H₉Cl₂NO₃S	48.8 49.1	2.5 2.6	20.6 20.7	4.2 4.1	9.3 9.3
				Arylglyoxal thioacetal chlorides							
(5a)	84.0—86.0 b	1 676s		1.8—2.0 (1 H, ArH *ortho* to COR) and 2.4—3.1 (18 H, m, ArH)	—g 213 (44)	C₂₆H₁₉ClOS₃	64.9 65.2	4.3 4.0	7.3 7.4		20.4 20.1
(5d)	94.5—96.0 b	1 670s		1.8—2.1 (1 H, ArH *ortho* to COR) and 2.5—3.3 (17 H, m, ArH)	—g 213 (100)	C₂₆H₁₈Cl₂OS₃	60.7 60.8	3.6 3.5	14.1 13.8		18.6 18.7
(5e)	107.5—108.5 b	1 664s		1.7—1.9 (1 H, ArH *ortho* to COR) and 2.5—3.0 (16 H, m, ArH)	—g 213 (100)	C₂₆H₁₇Cl₃OS₃	56.8 57.0	3.1 3.1	19.3 19.4		18.0 17.6
(5f)	120.0—121.5 b	1 661s		1.6—1.8 (1 H, ArH *ortho* to COR) and 2.4—2.9 (15 H, m, ArH)	—g 247 (76)	C₂₆H₁₆Cl₄OS₃	53.3 53.6	2.9 2.8	24.7 24.7		16.4 16.4
				2-(Arylthio)-3-oxo-1-phenylbenzo[*b*]thiophenium-2-ides							
(4b)	204.0—206.0 MeCN	1 564s	1 513s 1 336s	2.0—2.2 [2 H, ArH *ortho* to COR (J_{ortho} 7.0 Hz) and NO₂ (J_{ortho} 9.0 Hz)], 2.3—3.2 (6 H, m), and 2.67 (5 H, s, Ph S⁺)	379 (1) 213 (100)	C₂₀H₁₃NO₃S₂	63.4 63.3	3.3 3.4		3.7 3.7	16.5 16.9
(4c)	214.5—217.5 MeCN	1 565s	1 527s 1 346s	1.22 (1 H, ArH, *ortho* to both NO₂ gps, J_{meta} 2.5 Hz), 1.9—3.0 (6 H, m, ArH), and 2.64 (5 H, s, Ph S⁺)	—g 213 (94)	C₂₀H₁₂N₂O₅S₂	56.6 56.6	2.7 2.8		6.6 6.6	14.8 15.1
(4d)	198.5—201.0 MeCN	1 568s		2.09 (1 H, ArH *ortho* to COR J_{ortho} 7.0, J_{meta} 2.5 Hz), and 2.4—3.2 (13 H, m, ArH)	334 (5) 213 (34)	C₂₀H₁₄OS₂	71.6 71.8	4.0 4.2			19.0 19.2
(4e)	207.5—209.0 MeCN or CHCl₃	1 565s		2.07 (1 H, ArH *ortho* to COR, J_{ortho} 7.0, J_{meta} 2.5 Hz), 2.3—2.9 (3 H, m,'ArH), 2.71 (5 H, s, Ph S⁺), and 3.03 (4 H, ABq, J_{AB} 9.0 Hz, 4-ClC₆H₄S)	368 (13) 213 (100)	C₂₀H₁₃ClOS₂	64.8 65.1	3.6 3.6	10.0 9.6		17.3 17.4

a From light petroleum (b.p. 60—80°).   *b* From light petroleum (b.p. 60—80°) or Et₂O.   *c* For Nujol or hexachlorobutadiene mulls.   *d* Melt film.   *e* Liquid film.   *f* Solubility was low; decomposition occurred in (CD₃)₂SO.   *g* $M^{+\cdot}$ < 0.1% rel. int.

(4b—e) which, under the same conditions, may be recovered unchanged.

Reaction of 2'-(Arylthio)-2-diazoacetophenones (1) with Arenesulphenyl Chlorides.—(*a*) When 2-diazo-2'-(phenylthio)acetophenone (1a) (2.54 g, 10.0 mmol) in acetonitrile (60 ml) was added with stirring during 20 min to 2,4-dinitrobenzenesulphenyl chloride (2.35 g, 10.0 mmol) in acetonitrile (60 ml), nitrogen (224 ml, 100%) was evolved. Addition of water (100 ml) brought about the precipitation of bis-2,4-dinitrophenyl disulphide (0.19 g, 2%), m.p. *ca.* 265—275° (decomp.) [lit.,[17] 280° (decomp.)], separation of which facilitates crystallization of the product. After the addition of more water (100 ml), the filtrate was extracted with chloroform (3 × 100 ml) and the combined extracts were dried (MgSO₄) before removing the solvent under reduced pressure. The residual solid (4.12 g, 97%) was washed with ether (2 × 50 ml) and recrystallized from acetonitrile to provide 2-(2,4-*dinitrophenylthio*)-3-*oxo*-1-*phenylbenzo*[b]*thiophenium*-2-*ide* * (4c). In the same way,

the diazo-nitrogen (230 ml, 99%) was evolved over 30 min. *Ca.* 2/3 of the solvent was removed under reduced pressure and the resultant solution set aside at −20° for several days. The crude product (3.50 g 70%) was washed with ice-cold, dry ether (2 × 5 ml) and recrystallized from the same solvent or dry light petroleum (b.p. 60—80°) to provide 2-*chloro*-2,2,2'-*tris*(*phenylthio*)*acetophenone* * (5a). When the above experiment was carried out in dry dichloromethane, a slow stream of dry nitrogen was passed through the apparatus for 24 h and the effluent gases were bubbled through 0.20M-sodium hydroxide (100 ml, 20.0 mmol). Back titration with standard acid indicated that 8.15 mmol (78%) of hydrogen chloride had been evolved. The solvent was removed under reduced pressure and the residual oil taken up in dry ether prior to work up as above, when there resulted the thioacetal chloride (5a) (3.38 g, 68%). In the

[16] H. Nozaki, M. Takaku, and K. Kondo, *Tetrahedron*, 1966, **22**, 2145.
[17] H. W. Talen, *Rec. Trav. chim.*, 1928, **47**, 782.

same way, 4-chlorobenzenesulphenyl chloride in ethereal solution provided 2-*chloro*-2,2-*bis*-(4-*chlorophenylthio*)-2′-(*phenylthio*)*acetophenone* * (5e) (73%).

(c) When the above reaction was repeated with equimolar quantities of the diazo-ketone (Ia) and benzenesulphenyl chloride, only 75% of the diazo-nitrogen was evolved and there separated 2,3-*dihydro*-3-*oxo*-1-*phenylbenzo*[b]*thiophenium chloride* (3d) (27%) as a highly hygroscopic solid, m.p. *ca.* 60—70° (decomp.) whose i.r. spectrum was identical with that of the corresponding perchlorate (3a),[1] except for the absence of a perchlorate band at 1 083s,br cm⁻¹. The n.m.r. spectra of the two were identical and the chloride with perchloric acid in acetonitrile at 0° and subsequent treatment with water yielded the perchlorate (92%), m.p. 184.0—186.5° (from acetonitrile–ether at —20°) (lit.,[1] 177—180° from ethanol), spectroscopically identical to that reported previously. The ethereal solution, from which the sulphonium chloride (3d) had been separated, was worked up as in (b) above to provide the thioacetal chloride (5a) (36%). T.l.c. on the mother liquor indicated the presence of unchanged diazoketone (1a), the hemithioacetal chloride (5b), and the chloro-ketone (5c). 4-Chlorobenzenesulphenyl chloride similarly provided the same sulphonium chloride (3d) (25%) and the thioacetal chloride (5e) (38%). Likewise, equimolar proportions of 2′-(4-chlorophenylthio)-2-diazoacetophenone (1b) and 4-chlorobenzenesulphenyl chloride afforded 2-*chloro*-2,2,2′-*tris*-(4-*chlorophenylthio*)*acetophenone* * (5f) (30%) and 1-(4-*chlorophenyl*)-2,3-*dihydro*-3-*oxobenzo*[b]*thiophenium chloride* (3f) (24%) as a hygroscopic solid, m.p. *ca.* 76—79° (decomp.), which by anion exchange gave the known perchlorate (3g) (83%), m.p. 157.5—160.0° (from ethanol) (lit.,[1] 157—160°). Attempted recrystallization of the sulphonium chlorides (3d and f) from hot acetonitrile led to rearrangement to the corresponding α-chloro-ketones, 2-*chloro*-2′-(*phenylthio*)*acetophenone* * (5c) (88%) and 2-*chloro*-2′-(4-*chlorophenylthio*)*acetophenone* * (5g) (94%).

Sulphenylation of 3-*Oxo*-1-*phenylbenzo*[b]*thiophenium*-2-*ide* (4a).—(a) To the ylide (4a) (0.51 g, 2.24 mmol) in dichloromethane (80 ml) was added in one portion 2,4-dinitrobenzenesulphenyl chloride (0.53 g, 2.25 mmol) in dichloromethane (20 ml). After 24 h, the solution was washed with water (3 × 50 ml) to remove hydrogen chloride, dried (MgSO₄), and the solvent removed under reduced pressure. Trituration of the residue with ether (2 × 50 ml) furnished the crude product (0.84 g, 88%), recrystallization of which from acetonitrile provided the ylide (4c). In the same way, 2-nitrobenzenesulphenyl chloride provided the corresponding ylide (4b) (90%). Only a marginal improvement (2—6%) in the yields of ylides (4b and c) was obtained when conducting the above sulphenylations in the presence of triethylamine (2 mol. equiv.).

(b) To benzenesulphenyl chloride (2.24 g, 15.5 mmol) in dry dichloromethane (50 ml) was added in one portion the ylide (4a) (3.48 g, 15.4 mmol) in the same solvent (70 ml) when the colour of the sulphenyl chloride was discharged immediately. After 3 min, the solvent was removed under reduced pressure and residual traces of dichloromethane and hydrogen chloride removed *in vacuo* over solid phosphorus pentaoxide and potassium hydroxide to provide 2-*chloro*-2,2′-*bis*(*phenylthio*)*acetophenone* * (5b) (5.50 g, 96%) as a viscous, yellow oil.

To benzenesulphenyl chloride (0.87 g, 6.05 mmol) in dry ether (15 ml) was added in one portion the ylide (4a) (1.35 g, 5.96 mmol) and the suspension was stirred for 48 h with

exclusion of moisture. The photochromic solid was separated and washed with dry ether (3 × 30 ml) to afford β-*chloro*-o-(*phenylsulphonio*)*styrene*-α-*olate* *,† (6) (0.70 g, 45%) (Found: C, 63.7; H, 4.0; Cl, 13.7; S, 11.9. C₁₄H₁₁ClOS requires C, 64.0; H, 4.2; Cl, 13.5; S, 12.2%), m.p. 130.0—131.5° (dichloromethane-washed), ν_max. 2 530— 2 130s,v.br (max. *ca.* 2 330) (>SH⁺) and 1 546v.s (CO⁻) cm⁻¹, τ[(CD₃)₂SO] (resolution was poor, some degree of decomposition occurred) 1.8—2.8 (9 H, m, ArH) and 4.9—5.2 (2 H, m, >SH⁺ and =CHCl). All attempts to recrystallize this material resulted in its near-quantitative rearrangement to the chloro-ketone (5c). The solution from which the sulphonium enolate (6) had been separated was concentrated under reduced pressure to *ca.* 10 ml and set aside for several days at —20°, when there resulted the thioacetal chloride (5a) (1.17 g, 41%).

(c) To the ylide (4a) (7.58 g, 33.5 mmol) and triethylamine (7.27 g, 71.8 mmol) in dichloromethane (200 ml) was added in one portion N-(phenylthio)phthalimide (8.55 g, 33.5 mmol) in dichloromethane (50 ml). After 24 h, phthalimide (1.17 g, 24%), m.p. and mixed m.p. 233.0— 236.0° (sublim.) was separated and the filtrate was worked up for the ylide as in (a) above. Repeated washing of the crude product with ether removed further phthalimide (2.98 g, 61%) and left the desired ylide (10.04 g, 90%), recrystallization of which from acetonitrile provided 3-*oxo*-1-*phenyl*-2-(*phenylthio*)*benzo*[b]*thiophenium*-2-*ide* * (4d). In the same way, N-(4-chlorophenylthio)phthalimide afforded 2-(4-*chlorophenylthio*)-3-*oxo*-1-*phenylbenzo*[b]*thiophenium*-2-*ide* * (4e) (95%).

Reactions of 3-*Oxo*-1-*phenyl*-2-(*phenylthio*)*benzo*[b]*thiophenium*-2-*ide* (4d).—(a) To the ylide (4d) (3.66 g, 10.9 mmol) suspended in dry ether (10 ml) was added in one portion dry hydrogen chloride (1.28 g, 35.0 mmol) in dry ether (50 ml). After 15 min, the resultant solution was worked up, as in (b) above, to provide the hemithioacetal chloride (5b) (4.05 g, 100%).

(b) To benzenesulphenyl chloride (1.88 g, 13.0 mmol) in dry ether (80 ml) was added in one portion the ylide (4d) (3.99 g, 11.9 mmol) and the suspension was stirred until the solid dissolved (30 min). Concentration under reduced pressure to low bulk furnished the crude product (5.39 g, 94%), recrystallization of which from acetonitrile provided the thioacetal chloride (5a). In the same way, 4-chlorobenzenesulphenyl chloride afforded 2-*chloro*-2-(4-*chlorophenylthio*)-2,2′-*bis*(*phenylthio*)*acetophenone* * (5d) (93%). This unsymmetrical thioacetal chloride (5d) (2.89 g, 99%) was also prepared by the addition of the ylide (5e) (2.08 g, 5.65 mmol) to benzenesulphenyl chloride (0.82 g, 5.67 mmol) under analogous conditions.

Hydrolysis of 2-*Chloro*-2,2,2′-*tris*(*phenylthio*)*acetophenone* (5a).—Steam was passed through a suspension of the thioacetal chloride (5a) (1.51 g, 3.15 mmol) in boiling water (125 ml) until benzenethiol was no longer present in the distillate (7.5 h). The involatile material was extracted with ether (3 × 100 ml) and removal of the solvent under reduced pressure from the dried (MgSO₄), combined extracts provided S-*phenyl* [2-(*phenylthio*)*phenyl*]*thioglyoxylate* * (8a) (1.04 g, 94%) (Found: C, 69.0; H, 3.9;

† Under independent conditions, and in near-quantitative yields (⩾95%), the sulphonium enolate (6) was found to be the product of the reaction of either the diazo-ketone (1a) or the unsubstituted sulphonium ylide (4a) with hydrogen chloride, and the rearrangement product of the unsubstituted sulphonium chloride (3d) when the latter was stirred in ethereal suspension for 24 h.

S, 17.9. $C_{20}H_{14}O_2S_2$ requires C, 68.5; H, 4.0; S, 18.3%) as a viscous, yellow oil, $v_{max.}$ (neat) 1 720—1 650s,br (max. *ca.* 1 691) (CO) cm^{-1}, τ(CDCl$_3$) 2.2—3.2 (m, ArH) only. The aqueous solution from which the thioester had been extracted was concentrated, acidified with nitric acid to pH 4, and treated with silver nitrate solution to provide silver chloride (0.42 g, 93%). The benzenethiol–diphenyl disulphide mixture, isolated from the steam distillate by ether extraction, was treated with ethanol–water–concentrated aqueous ammonia (spec. grav. 0.880) (40 : 40 : 20) and air passed through for 24 h. There then resulted diphenyl disulphide (0.33 g, 97%), m.p. 59.0—60.5° (from ethanol) (lit.,[18] 62.5—63.5°).

Arylglyoxal Hemithioacetal Chlorides.—When the 2-diazoacetophenone (9) (0.01 mol) in dry ether (100 ml) [or in acetonitrile (60 ml) for nitrobenzenesulphenyl chlorides] was added dropwise during 20 min to the arenesulphenyl chloride (0.01 mol) in the same solvent (40 ml), nitrogen evolution was quantitative. The residual, crude product obtained on removal of the solvent under reduced pressure was purified by crystallization or, in one instance, distillation *in vacuo*. The yields of the hemithioacetal chlorides (10) so formed were unaffected by prior mixing of the diazo-ketone with 1 mol. equiv. of either dimethyl or methyl phenyl sulphide. 2-Chloro-2-(phenylthio)acetophenone (10a) (74%) had b.p. 173—175° at 0.025 mmHg (lit.,[2] 166° at 0.01 mmHg), $v_{max.}$ (neat) 1 690s (CO) cm^{-1}, τ(CDCl$_3$) 2.21 (2 H, m, ArH *ortho* to COR, J_{ortho} 8.0, J_{meta} 2.5 Hz), 2.4—3.2 (8 H, m, ArH), and 3.77 [1 H, s, CO·CH(SPh)Cl]. Also prepared were 2-*chloro*-2-(2,4-*dinitrophenylthio*)*acetophenone* * (10b) (90%), 2-*chloro*-4'-*nitro*-2-(2-*nitrophenylthio*)*acetophenone* * (10c) (87%), and 2-*chloro*-2-(4-*chlorophenylthio*)-4'-*nitroacetophenone* * (10d) (92%).

[18] E. Campaigne, J. Tsurugi, and W. W. Meyer, *J. Org. Chem.*, 1961, **22**, 2145.