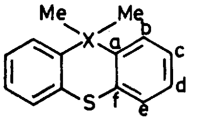
Group IVB Heterocyclic Compounds. Oxidation Rates, Carbon-13 Nuclear Magnetic Resonance, and Photoelectron Spectra of 10,10-Dimethylphenothia-silin, -germin, and -stannin Derivatives and of 9,9-Dimethylthioxanthen

By **Alfredo Ricci,*** Istituto di Chimica Organica dell'Università, Via G. Capponi 9, 50121 Firenze, Italy
Domenico Pietropaolo, Giuseppe Distefano, Dante Macciantelli, and **Francesco P. Colonna,** Laboratorio dei Composti del Carbonio contenenti Eteroatomi e loro Applicazioni del C.N.R., Ozzano Emilia, Bologna, Italy.

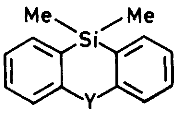
10,10-Dimethylphenothia-silin and -germin have been prepared for the first time and their properties compared with those of the corresponding tin derivative and of 9,9-dimethylthioxanthen. The ^{13}C n.m.r. spectra of these compounds suggest increasing strain in the heterocyclic framework on going down Group IVB. The oxidation rates of sulphur to sulphinyl group with perbenzoic acid have been measured in carbon tetrachloride. The first few bands in the photoelectron (He^{I}) spectra are assigned by comparison with the spectra of related compounds. The reactivity sequence and the ionization energy data indicate that, for geometrical changes along the series, the interaction between the sulphur lone pair and the benzene rings decreases on going towards the Sn derivative.

MUCH interest has recently been centred on the synthesis and some spectroscopic properties of heterocyclic compounds containing C–X–C linkages (X = Si or Sn) and oxygen,[1,2] sulphur,[2] or nitrogen[3] in the ring, but no information is available on the way in which a change of X (Group IVB element) affects the chemical and spectroscopic behaviour of these compounds. Since replacement of an annular carbon by silicon, germanium, or tin changes the dimensions of the non-benzenoid ring, it is important to assess any effect that this may have on the properties of these compounds.

We report here the results of a study of the series of heterocycles (1)—(4), two of them previously unknown.



(1) X = C
(2) X = Si
(3) X = Ge
(4) X = Sn



(5) Y = O
(6) Y = NMe

We have investigated the kinetics of the oxidation of sulphur to the sulphinyl group, ^{13}C chemical shifts, and the photoelectron (He^{I}) spectra of these compounds.

RESULTS AND DISCUSSION

^{13}C N.m.r. Spectra and Oxidation Rates.—The general procedure of Noltes[2] has been used with slight modifications (see Experimental section) for the synthesis of the silicon (2) and germanium (3) derivatives previously unreported. The new compounds were obtained in good yield and gave correct elemental and mass spectrometric analyses and their structure was further proved by their ^{1}H n.m.r. spectra.

As for 9,9-dimethylthioxanthen (1) and 10,10-dimethylphenothiastannin (4),[2] at the probe temperature (*ca.* 30°), the ^{1}H n.m.r. spectra of (2) and (3) exhibit a single sharp resonance for the methyl group consistent with a rapid conformational interchange. Furthermore the only change observed in the n.m.r. spectra on decreasing the temperature, is a slight downfield shift which suggests, in line with previous results,[4] a tendency at *ca.* −150° to take up a conformation with a methyl group in a pseudoequatorial position. This form is populated only to a minor extent even at very low temperatures as shown by the magnitude of the effects (0.05 and 0.09 p.p.m. for the tin and silicon derivatives respectively).

To a first approximation changes in the Group IVB element might cause substantial differences in the ground and transition state as a consequence of changes in the geometry and properties of the heterocyclic ring due to the lengthening of the carbon–metal bond and to the increased metallic character of the heavier elements. These differences are likely to reflect conformational and geometrical differences as well as purely electronic effects within the series (1)—(4) and any analysis of the chemical shifts would therefore require a detailed knowledge of structural parameters unavailable at the present time.†

However some information on the geometry of compounds (1)—(4) can be obtained by using known bond lengths and angles and from inspection of Dreiding models. These in fact clearly indicate that the lengthening of the C–X bond in the heaviest derivatives is associated with a C–S–C bond angle deformation [a rough estimate based on Dreiding models indicates an increase of this angle from *ca.* 106° for (1), to *ca.* 120° for the tin derivative (4)] and with an increase in strain of the heterocyclic ring.

Since ^{13}C n.m.r. spectroscopy has been shown[5] to be a useful tool for the investigation of charge density differences in the ground state within homogeneous series, we

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† An *X*-ray diffraction study of these compounds is now in progress.

[1] C. H. S. Hitchock, F. G. Mann, and A. Vanterpool, *J. Chem. Soc.*, 1957, 4537.

[2] H. A. Meinema and J. G. Noltes, *J. Organometallic Chem.*, 1973, **63**, 243; E. J. Kupchik and J. A. Ursino, *Chem. and Ind.*, 1965, 794.

[3] D. Wassermann, R. E. Jones, S. A. Robinson, and S. D. Garber, *J. Org. Chem.*, 1965, **30**, 3248.

[4] A. L. Ternay, jun., L. Ens, J. Herrmann, and S. Evans, *J. Org. Chem.*, 1968, **34**, 940.

[5] G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, 1972, **94**, 3089.

have recorded the ^{13}C n.m.r. spectra of compounds (1)—(4) in [^{2}H$_6$]dimethyl sulphoxide and the results are given in Table 1. Assignments of carbon resonances in Table 1 were based on well established criteria such as relative intensities of chemical shifts. The off-resonance technique was employed for distinguishing ^{13}C resonances of the bridgehead and unsubstituted carbons in 10,10-dimethylphenothiasilin where certain peaks overlapped.

TABLE 1

^{13}C N.m.r. chemical shifts [a] in [^{2}H$_6$]dimethyl sulphoxide for compounds (1)—(4)

Compound	δ_{C_a}	$\delta_{C_{b-e}}$	δ_{C_f}	$\delta_{C_{Me}}$
(1)	102.2	(87.2—85.2)	92.1	−14.80
(2)	100.3	(94.4—87.6)	94.5	−40.9
(3)	99.8	(94.0—87.3)	100.4	−44.0
(4)	102.8	(96.9—87.5)	106.1	−49.1

[a] In p.p.m. from [^{2}H$_6$]dimethyl sulphoxide. Parentheses indicate tentative assignments.

The most interesting set of shifts are those associated with C$_a$ and C$_f$. In fact according to the most widely used electronegativity scales and referring to the ^{13}C n.m.r. resonances of the parent PhXMe$_3$ (X = C,[6] Si,[7] or Sn [8]), the chemical shifts of C$_a$ of the heterocyclic compounds should experience, if any, an upfield shift on going from the Si to the Sn derivative. The observed trend does not fulfil this expectation since the C$_a$ and C$_f$ resonances for (4) are deshielded by *ca.* 2.5 and 11.5 p.p.m. respectively relative to the silicon derivative (see Table 1). Ring strain in the heterocyclic framework and concomitant changes in hybridization provide a satisfactory explanation of this trend. The reflection in the ^{13}C n.m.r. spectra of the strain in compounds (1)—(4) is explained by a straightforward extension of Streitwieser's original argument [9] for fused rings where the strain is associated with decreased internal angles. In the strained systems (3) and (4) the increased internal angles would, according to Streitwieser's hypothesis, increase the *s*-character and therefore the electronegativity in the atomic orbitals used to construct the fused ring. Such an effect would of course decrease the electron density on C$_f$ and to a minor extent on C$_a$, which are sites of strain, in accord with the data in Table 1. A similar influence of conformational effects, such as bond angle variation, in strained systems on the ^{13}C resonances, has been shown by recent ^{13}C n.m.r. data of aromatic hydrocarbons, showing that the deshielding effect of the fused aryl ring is greater at the fused carbon of indane [10] (144 p.p.m.) and acenaphthene [11] (145 p.p.m.) than at the corresponding position of tetralin (137 p.p.m.) and 1,8-dimethylnaphthalene (134 p.p.m.) respectively, which are relatively free of ring strain.

To check the effects of changing X on the availability of the sulphur lone pair, we thought it of interest to investigate the changes in oxidation rate of cyclic sulphides to the corresponding sulphoxides with perbenzoic acid (PBA), since variation in reaction rates in these systems should arise as a result of changes in (i) angle strain, (ii) heterocyclic ring geometry, and also (iii) the electronic effect exerted by the (Me)$_2$X groups.

Compounds (1)—(4) undergo smooth oxidation and the relevant second-order rate constants (k_2) are listed in Table 2. As expected for oxidation, the variation in rates within the compounds studied is not very large but the observed trend is undoubtedly significant. With respect to the unfused analogue diphenyl sulphide, 9,9-dimethylthioxanthen (1) is in fact less reactive, the relative rate being *ca.* 0.4. Moreover on varying X from C to Sn, the oxidation rate steadily increases. The observed trend in reactivity is not correlated in a simple manner with the angle strain of the heterocyclic ring in agreement with previous results for oxidation of cyclic sulphides [12] and sulphoxides [13] having different ring sizes and strain. In fact the oxidation of the above system involves only minor changes in geometry on going from the reactant to the transition state, so no significant effects of ring size and strain on rates would be expected. On the other hand the increased reactivity along Group IVB cannot be ascribed to the inductive effect (+*I*) of the XMe$_2$ substituent, since this has been proved [14] to change little from silicon to tin, and also because of the large distance between this group and the reaction centre.

TABLE 2

Second-order rate constants (k_2) for the oxidation of sulphides (1)—(4) and diphenyl sulphide with perbenzoic acid at 25° in carbon tetrachloride

Compound	10 k_2/l mol^{-1} s^{-1}
Diphenyl sulphide	9.2
(1)	3.1
(2)	5.8
(3)	6.3
(4)	9.3

An attractive explanation for the slight but significant trend in reactivity is related to the geometrical differences of these compounds and to the consequent variation of the sulphur–ring conjugation. To test the importance of the geometrical variation the u.v. photoelectron spectra of (1)—(4) were obtained.

Photoelectron Spectra.—The Figure shows the photoelectron (He^{I}) spectra of (1)—(4) together with those of analogues of (2) in which the sulphur atom has been

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[6] J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, London, 1972, p. 97.

[7] G. Maciel and J. J. Notterstad, *J. Chem. Phys.*, 1965, 2427.

[8] D. Dodrell, M. L. Bullpitt, C. J. Moore, C. W. Fong, W. Kitching, W. Adcock, and B. D. Gupta, *Tetrahedron Letters*, 1973, 665.

[9] A. Streitwieser, jun., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, 1968, **90**, 1357.

[10] H. L. Retcofsky and R. A. Friedel, 'Spectrometry of Fuels,' Plenum Press, New York, 1970, p. 90.

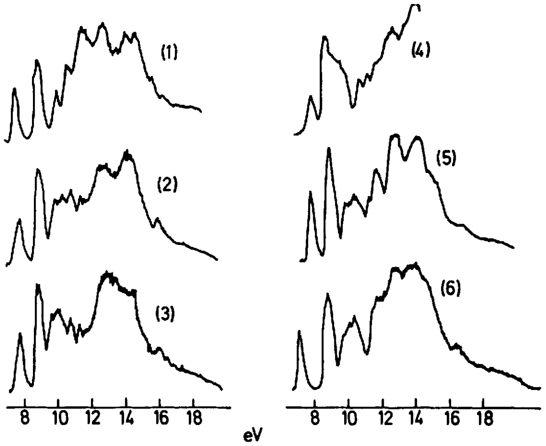
[11] D. H. Hunter and J. B. Stothers, *Canad. J. Chem.*, 1973, **51**, 2884.

[12] A. Cerniani, G. Modena, and P. E. Todesco, *Gazzetta*, 1960, **90**, 382.

[13] R. Curci, F. Di Furia, A. Levi, and G. Scorrano, *J.C.S. Perkin II*, 1975, 408.

[14] W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1970, **92**, 7476; C. J. Attridge, *Organometallic Chem. Rev. A*, 1970, **5**, 323, and references therein.

replaced by oxygen (5) or by an NMe group (6). Table 3 lists the corresponding ionisation energy (IE) values lower than *ca.* 10.5 eV together with those of diphenyl sulphide (DPS) for comparison. In the latter compound the first and the third bands have been previously assigned [15,16] to the antibonding (π_7) and bonding (π_3) combination respectively of the sulphur lone pair with the two π_8 orbitals of the rings (the 'symmetric' component of the benzene e_{1g} orbitals). Given that compounds (1)—(4) have the same number * of π-MOs as DPS and are formed by the same group orbitals, it is reasonable to assume that in the present compounds too π_7 and π_3 will have prevailing sulphur and ring character respectively. The IE value of π_7 increases with the atomic number of X. This trend will be discussed below.



Photoelectron (He^I) spectra of compounds (1)—(6)

TABLE 3

Ionization energy values (eV) of diphenyl sulphide (DPS) and compounds (1)—(6)

Compound	π_7	π_6, π_5, π_4		π_3	X–C	F.w.h.m. (π_7)
DPS [a]	7.88	9.20	9.5	10.11		
(1)	7.60	8.83 [b]	9.04	10.19	10.75	0.36
(2)	7.81	9.01	9.2 [b]	10.0	10.4	0.51
(3)	7.83	8.91	9.05 [b]	9.84	10.2	0.48
(4)	7.98	8.85			9.6	0.50
(5)	7.92	9.06	9.2 [b]	10.2	10.5	0.35
(6)	7.17	8.83		9.85 10.2	10.2 10.5	0.33

[a] Taken from ref. 15. [b] Shoulder. [c] F.w.h.m. = full width at half-maximum.

On the same basis, it is possible to assign the second band (formed by several overlapping bands) to the ionization of the two MOs formed by the interaction of the 'antisymmetric' component of the benzene e_{1g} orbitals (π_a^+ and π_a^-, *i.e.* π_6 and π_5) and to the non-bonding combination of the sulphur lone pair and the ring π_8 orbitals (π_4). The low IE peak (or shoulder) of this composite band has the energy trend [8.83 (1), 9.01 (2), 8.91 (3), and 8.85 (4) eV] expected for the π_a^+ orbital. In fact, π_a^+ can interact with the orbitals of the XMe_2 group *via* $(p\text{–}d)_\pi$ and hyperconjugative effects: the trend found parallels that of the HOMO in the $PhXMe_3$ series [17] [8.75 (C), 9.1 (Si), 8.98 (Ge), and 8.83 (Sn) eV].

In the low IE region of the spectra a broad band is also present centred at 10.75 (1), 10.4 (2), 10.2 (3), and *ca.* 9.6 (4) eV. The decrease of the IE value along the series suggests, in accord with the expected bond weakening, that the ionization involves MOs mainly localized on the X atom. It is likely that this band corresponds to ionization of the MOs mainly localized on the X–C bonds given that its IE value along the series parallels those of the degenerate X–C orbitals of t_2 symmetry of the corresponding tetramethyl derivatives: [18,19] 10.9 (C), 10.6 (Si), 10.2 (Ge), and 9.7 (Sn) eV.

From the above assignment it follows that π_3 should correspond to the third band in the spectra of (1)—(3) [the corresponding band in (4) is not resolved].

The first IE value increases on going from (1) to (4) in contrast with the trends observed in several other series such as $PhXMe_3$,[17,20] $PhCH_2XMe_3$,[17,20,21] $MeSXMe_3$,[22] $S(XMe_3)_2$,[22,23] $PhSXMe_3$,[23] and $p\text{-}Me_3XC_6H_4SMe$ [24] where the IE values decrease on going from the silicon to the tin derivatives and those of the carbon and tin compounds are often similar. This observation indicates that the trend of the IE values in (1)—(4) is mainly governed by variation of the conjugation between the sulphur lone pair and the benzene rings. Molecular models show in fact that on going from (1) to (4), the dihedral angle between the two benzene rings decreases and that the sulphur atom (as well as X) steadily goes out of the plane formed by the four substituted ring carbons, in the direction opposite to the rings. The consequent reduction of sulphur–ring conjugation should influence the nature of the HOMO, increasing its sulphur

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* Apart from those mainly localized on the XMe_2 group.

[15] F. P. Colonna, G. Distefano, G. Reichenbach, and S. Santini, *Z. Naturforsch.*, 1975, **30a**, 1213.

[16] S. Pignataro, unpublished results.

[17] G. Distefano, S. Pignataro, A. Ricci, F. P. Colonna, and D. Pietropaolo, *Ann. Chim.* (*Italy*), 1974, **64**, 153.

[18] A. E. Jonas, G. J. Schweitzer, F. A. Grimm, and T. A. Carlson, *J. Electron Spectroscopy*, 1972–1973, **1**, 29.

[19] S. Evans, J. C. Green, P. J. Joachim, A. F. Orchad, D. W. Turner, and J. P. Maier, *J.C.S. Faraday II*, 1972, 905.

[20] P. K. Bischof, M. J. S. Dewar, D. W. Goodman, and T. B. Jones, *J. Organometallic Chem.*, 1974, **82**, 89.

[21] A. Scheweig and U. Weidner, *J. Organometallic Chem.*, 1967, **67**, C4.

[22] G. Distefano, A. Ricci, F. P. Colonna, D. Pietropaolo, and S. Pignataro, *J. Organometallic Chem.*, 1974, **78**, 93.

[23] G. Distefano, A. Ricci, R. Danieli, A. Foffani, G. Innorta, and S. Torroni, *J. Organometallic Chem.*, 1974, **65**, 205.

[24] F. P. Colonna, R. Danieli, G. Distefano, and A. Ricci, *J.C.S. Perkin II*, 1976, 306.

lone pair character. An indirect proof of the increasing departure from planarity on going from (1) to (4) is given by the shape of the first band: its full width at half-maximum is smallest for (1), with its relative intensity (with respect to the rest of the spectrum and in particular to the other π bands) and the slope at the onset decreasing in the order (1) > (2) > (3) > (4). It has been suggested recently for related compounds [25] and polynuclear aromatics [26] that these trends are related to the increasing departure from planarity of the molecules in the ground state (while the corresponding molecular ions would be more planar).

It is also possible to speculate that a through-space interaction between the sulphur lone pair and the MOs mainly localized on the XMe$_2$ group * could contribute to the observed trends in the features of the first band. This possibility is supported by the fact that the first band in the spectra of compounds (5) and (6) [whose heteroatoms have less diffuse *p* orbitals or, as in (5), the HOMO has little oxygen character] resembles that in the spectrum of (1) (see Figure) where no $(n\text{-}d)_\pi$ bonding is possible and where σ^*_{X-C} orbitals have very high energy.

The oxidation rate and the IE value give two independent measurements of the tendency of sulphur to donate its electrons and, at first sight, their increase within the group IV series would indicate opposite trends. However, this discrepancy is not substantial since [29] (i) no simple relationship can be predicted between these two observables [*e.g.* the increase of the localization of the ' sulphur lone pair ' on sulphur from (1)—(4) favours the oxidation reaction despite the increase of the IE value] and (iii) in the oxidation process other MOs with sulphur character are involved and some of these appear from IE measurements, to be destabilized on going towards (4) (*e.g.* π_4 and π_3, see Table 3).

The conclusions from oxidation and photoelectron studies are therefore consistent and indicate that variations in geometry are the main factors responsible for both reaction rates and spectroscopic properties of these molecules.

EXPERIMENTAL

All reactions were carried out under dry, oxygen-free nitrogen. ^{1}H N.m.r. spectra were recorded using a JEOL C-60 instrument. Low temperature experiments were performed in Freon-22 as solvent with a PS-100 spectrometer. Proton-decoupled natural-abundance ^{13}C n.m.r. spectra were determined using the pulsed Fourier transform method on a JEOL JNM PS-100 spectrometer operating at 25.15 MHz. Samples were examined in 50% (w/w) solutions in [^{2}H$_6$]dimethyl sulphoxide at probe temperature.

Photoelectron spectra were recorded on a Perkin-Elmer PS 18 spectrometer and calibrated against Ar and Xe lines. The estimated error in the IE values is ±0.05 or ±0.1 eV depending upon the number of decimals quoted.

Materials.—Reagent grade carbon tetrachloride purified according to standard procedures [30] was used for the kinetic experiments. Perbenzoic acid was crystallized from light petroleum.

9,9-*Dimethylthioxanthen* (1).—This was prepared by a different procedure from that previously reported.[4] To 9,9-dichlorothioxanthen (10 g, 37.6 mmol) obtained [31] by chlorination of thioxanthone [32] in dry ether (50 ml) at 0 °C, was added over 1 h, the Grignard reagent formed by reaction of methyl iodide (21.3 g, 150 mmol) with magnesium turnings (3.6 g, 150 mmol). After the addition, the mixture was refluxed for 1 h, cooled, and hydrolysed with 5% aqueous hydrochloric acid. The ethereal layer was dried (Na$_2$SO$_4$), the ether removed, and the residual red oil was chromatographed over silica eluting with ligroin (b.p. 75—110°). Distillation of the yellow oil under high vacuum, b.p. 160° at 0.3 mmHg, gave a white solid which was crystallized from ethanol to give 9,9-dimethylthioxanthen (1) (2 g, 25%), m.p. 25° (lit.,[4] 25°).

The Noltes procedure [2] was used with slight modifications for the synthesis of 10,10-dimethylphenothia-silin (2), -germin (3), and -stannin (4).

10,10-*Dimethylphenothiasilin* (2).—A solution of bis-(2-bromophenyl) sulphide [33] (10 g, 30 mmol) in dry ether (50 ml) was added dropwise to a well stirred solution of butyl-lithium (60 mmol) in hexane (80 ml), cooled to 0°. After the addition the mixture was refluxed for 4 h. The resulting solution of (bis-2-lithiophenyl) sulphide was added dropwise under a dry nitrogen stream to a solution of dichloro(dimethyl)silane (3.9 g, 30 mmol) in dry ether (300 ml) at −5°, with vigorous stirring.

The mixture was refluxed for 1 h and then hydrolysed. The ethereal layer was dried (Na$_2$SO$_4$) and evaporated and the yellow oil chromatographed on alumina eluting with light petroleum (b.p. 40—70°). The oil thus obtained, when crystallized from ethanol gave 10,10-*dimethylphenothiasilin* (2) (5 g, 70%), m.p. 50—52° (Found: C, 69.05; H, 5.7; S, 13.2. $C_{14}H_{14}SSi$ requires C, 69.35; H, 5.8; S, 13.2%), δ (CCl$_4$) 6.9—7.6 (8 H, m, ArH) and 0.47 (6 H, s, CH$_3$).

10,10-*Dimethylphenothiagermin* (3).—This *compound* was obtained as a white solid, m.p. 68—70°, in 75% yield employing the procedure detailed for (2) (Found: C, 58.35; H, 5.0; S, 11.45. $C_{14}H_{14}GeS$ requires C, 58.6; H, 4.9; S, 11.15%), δ (CCl$_4$) 6.9—7.6 (8 H, m, ArH) and 0.58 (6 H, s, CH$_3$).

10,10-*Dimethylphenothiastannin* (4).—This was obtained in 70% yield using the procedure previously outlined. Physical and analytical properties of this compound corresponded well to those previously reported.[2]

10,10-Dimethylphenoxasilin (5) was prepared according to the literature.[1] N-*Methyl*-10,10-*dimethylphenazasiline* (6) was synthesized from 2,2′,4,4′-tetrabromo-*N*-methyldiphenylamine and dichloro(dimethyl)silane according to the Wassermann procedure [3] (Found: C, 74.95; H, 7.15; N,

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* Both *d* orbitals of X and/or the σ^* orbitals of the X–C bonds can participate in this charge transfer interaction.[27,28]

[25] H. J. Haink and J. R. Huber, *Chem. Ber.*, 1975, **108**, 1118.

[26] R. Boschi, E. Clar, and W. Schmidt, *J. Chem. Phys.*, 1974, **60**, 4406.

[27] D. P. Mollère and R. Hoffmann, *J. Amer. Chem. Soc.*, 1975, **97**, 3680.

[28] C. G. Pitt, *J. Organometallic Chem.*, 1973, **61**, 49.

[29] M. Yanez, O. Mo', and J. I. Fernandez-Alonzo, *Tetrahedron*, 1975, **31**, 245 and references therein.

[30] A. Weissberger, ' Technique of Organic Chemistry,' Interscience, New York, vol. 17, 1967.

[31] M. M. Hafez, N. Latif, and I. F. Zeid, *J. Org. Chem.*, 1961, **26**, 3988.

[32] M. Gomberg and E. C. Britton, *J. Amer. Chem. Soc.*, 1921, **43**, 1945.

[33] R. A. Wiley and J. H. Collins, *J. Medicin. Chem.*, 1969, **12**, 146.

TABLE 4

^{1}H N.m.r.[a] and analytical data for products of oxidation of sulphides (1)—(4) with PBA

Compound	Chemical shift δ [b]		M.p.[c]	Found (%)			Required (%)		
	ArH	XMe	(°C)	C	H	S	C	H	S
9,9-Dimethylthioxanthen 10-oxide [d]	8.10—7.00	1.28, 1.90	120	74.4	5.8	13.1	74.3	5.8	13.2
10,10-Dimethylphenothiasilin 9-oxide	8.01—7.13	0.70, 0.40	92	65.0	5.4	12.5	65.1	5.4	12.4
10,10-Dimethylphenothiagermin 9-oxide	8.37—7.18	0.82, 0.58	95	55.4	4.6	10.4	55.4	4.6	10.6
10,10-Dimethylphenothiastannin 9-oxide	7.05—7.88	0.75, 0.47	107	48.3	4.1	9.0	48.1	4.0	9.2

[a] In CCl_4 solution. [b] Downfield from Me_4Si. [c] Uncorrected. [d] See ref. 4.

5.75. $C_{15}H_{17}NSi$ requires C, 75.25; H, 7.15; N, 5.85%), m.p. 100°.

Oxidation Products.—These were obtained by oxidation of the parent sulphides with the stoicheiometric amount of *m*-chloroperbenzoic acid in carbon tetrachloride at 0°. After washing with 10% aqueous sodium hydrogen carbonate, the organic layer was dried (Na_2SO_4). Evaporation of carbon tetrachloride and crystallization of the residual heavy oil with light petroleum ether, gave the corresponding sulphoxides. The physical, analytical properties, and yields of these products are given in Table 4.

Rate Measurements.—Stock solutions of PBA were prepared by weighing and standardized by titration using the arsenic oxide–iodide method.[34] The kinetic measurements were carried out in a thermostatted 1 cm quartz cell, by adding to sulphide solution (2 ml, 4—8 × 10^{-5}M), PBA solution (1 ml), an excess of sulphide over PBA being used in all cases. The reactions were followed by observing the change in optical density at 270 nm with a Perkin-Elmer 402 spectrometer. The quantitative nature of the reaction was demonstrated by superimposition of the t_∞ spectrum with that of the corresponding sulphoxide. Second-order rate constants calculated in the usual way were averaged between two or more independent runs.

[6/426 *Received, 2nd March,* 1976]

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[34] S. Siggia, ' Quantitative Organic Analysis via Functional Groups,' Wiley, New York, 1967, p. 286.