# Thiophene S,N-Ylides: A New Versatile Class of Sulphimides[†,1]

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Tetrachlorothiophene reacts with methyl, ethyl, and phenyl azidoformates and with toluene-*p*-sulphonyl azide at 130—150 °C to give stable thiophene S,N-ylides. 2,5-Dichloro- and 2,5-dibromo-thiophene and tetrabromothiophene yield products derived by nitrene attack at the α-position. The S,N-ylides undergo ready photolysis to liberate the parent nitrene, and react with a wide variety of electron-rich dienophiles as 4π-components to give tetrachlorodihydrobenzenes with extrusion of a thionitroso compound. With dienes the ylides react either as 2π- or 4π-systems. Thus with anthracene a dihydrothiophene analogue of triptycene is generated, efficiently aromatised and de-ylidated with zinc in methanol. With dimethyl acetylenedicarboxylate the ylides yield a thiazocine by a novel ring expansion. Oxidation of the ylide system with 3-chloroperbenzoic acid gives the corresponding ylide S-oxide. Tetrachlorothiophene also reacts efficiently with diazoalkanes under rhodium acetate catalysis to give thiophene S,C-ylides, which undergo cycloaddition with nucleophilic alkenes much more slowly than their nitrogen analogues.


In 1964 Hafner and Kaiser showed that thiophene and its simple homologues were converted into pyrroles by the action of ethyl azidoformate[2] (Scheme 1). This reaction has been
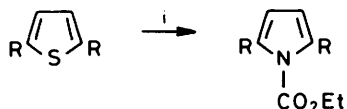
Scheme 1. *Reagents and conditions:* i, N_3CO_2Et, heat

interpreted either as a 1,4-nitrene cycloaddition with concomitant extrusion of sulphur[2] or as an electrophilic substitution of the thiophene α-position by the nitrene, followed by rearrangement.[3]

More recently, Porter and co-workers demonstrated that thiophenes react with carbenes, derived from diazomalonates, with rhodium acetate catalysis to give remarkably stable thiophene S,C-ylides [*e.g.* (1)].[4]


(1)   (2)   (3)
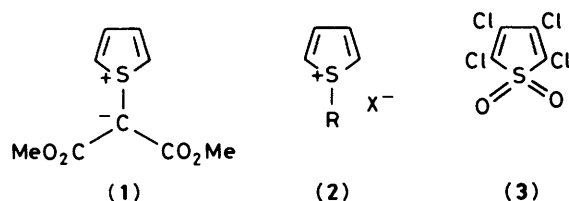
The only other known isolable systems in which a thiophene bears an S-substituent are the alkylthiophenium salts (2)[5] and the mono-[6] and di-oxides typified by the tetrachloro derivative (3).[7] We herein describe the synthesis and the versatile reactivity of a series of thiophene S,N-ylides.

The Synthesis of Thiophene S,N-*Ylides.*—Nitrenes, despite their ready ability to undergo C–H insertion reactions, tend to eschew such insertions at halogen-bearing carbons, making solvents such as dichloromethane or 1,1,2,2-tetrachloroethane[8] effective for solution chemistry. We argued that halogenothio-

phenes may thus direct attack away from the thiophene carbons and allow the formation of S-substituted products.

When 2,5-dichloro- or 2,5-dibromo-thiophene (4a or b) was heated at 145 °C with phenyl azidoformate, two products (5) and (6) were isolated (Scheme 2).
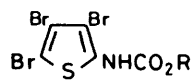

(4)

(5) a : 10%
    b : 15%

(6) a : 13%
    b : 15%

(7)

a : X = Cl
b : X = Br

(6)
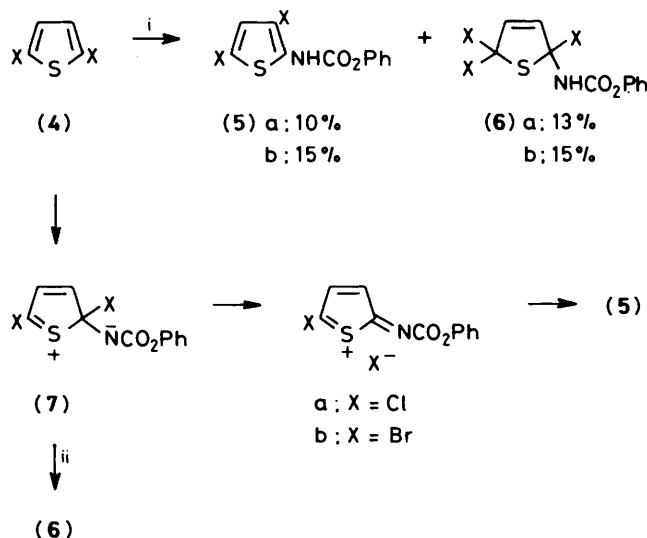
Scheme 2. *Reagents:* i, PhOCON₃; ii, X⁻

These products are clearly derived from the intermediate (7), itself the result of an electrophilic substitution, by attack of the halide anion either at C-3 or -5 of the thiophene ring. The structure of product (5b) was put beyond doubt by an unambiguous synthesis.

When a solution of tetrabromothiophene in tetrachloroethane was similarly treated with phenyl azidoformate, the principal product (82%) was benzoxazolone by intramolecular nitrene attack,[9] together with a small amount (1%) of phenyl *N*-(tribromo-2-thienyl)carbamate (8a). Ethyl azidoformate in a similar manner gave the corresponding carbamate (8b) (1%) together with ethyl hydrazinedicarboxylate (9) (1%), probably a triplet-nitrene-derived product.
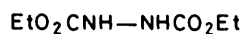
The halogenophobicity of nitrenes is clearly in evidence as

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† This work constitutes part of the thesis of G. van Vuuren for the M.Sc. degree of the University of South Africa.
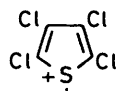
(8)

a; R = Ph
b; R = Et

$EtO_2CNH—NHCO_2Et$

(9)

(10)

R

a: CO_2Me
b: CO_2Et
c: CO_2Ph
d: $S(=O)_2C_6H_4Me$ - p

$RN^- —\overset{+}{S}Me_2$

(11)

a: R = $C_6H_4NO_2$-m
b: R = $C_6H_4NO_2$ - p
c: R = $S(=O)_2Me$
d: R = COPh

(12)

$Ph_2\overset{+}{S}—\overset{-}{N}S(=O)_2C_6H_4Me$ - p

(13)

well as the 'bromine effect' whereby brominated systems tend to increase yields of singlet-nitrene-reaction products.[8,10] If phenyl azidoformate is decomposed in tetrachloroethane solution, benzoxazolone is obtained in 65% yield.

In contrast to the above results a clean reaction occurs when azidoformates or tosyl azide are decomposed in tetrachlorothiophene solution, giving thiophene S,N-ylides (10a—d) in 16, 49, 23, and 24% yield respectively. The carbonyl azides were decomposed at 130 °C. Phenyl azidoformate gave, in addition to the ylide, benzoxazolone (48%) while the reaction with tosyl azide needed to be conducted at 150 °C and only attained 50% conversion because of undesirable darkening of the reaction mixture. Attempts to generate the N-cyano ylide (10; R = CN) by decomposition of cyanogen azide[11] in tetrachlorothiophene at 65 °C were without success, as were reactions of chloramine-T with tetrachlorothiophene, the classical approach to sulphonyl sulphimides.[12]

Structure of the Thiophene S,N-*Ylides.*—The structure of the ylides (10) was evident from their ^{13}C n.m.r. spectra which showed only two thiophene carbons [*e.g.* (10b) δ_C 130.8 and 132.7 p.p.m.] and were corroborated by X-ray crystallographic data.* The X-ray data were particularly revealing, showing, as expected, a pyramidal sulphur geometry but surprisingly short S–N bond lengths [(10b) 1.595; (10d) 1.589 Å] in comparison with those of known sulphimides [*e.g.* (11a) 1.622;[13a] (11b) 1.644;[13] (11c) 1.633;[14] (11d) 1.659;[15] (12) 1.629;[16] (13) 1.628 Å[17]]. Unlike the thiophene S,C-ylides[4,18] [*e.g.* (1)] the S,N-ylides would appear to have a significant S,N-double-bond character. The S,C-ylides have been proposed to possess considerable aromatic character and little ylidic mesomerism, while the S,N-ylides were conjectured to have antiaromatic properties more like the thiophene S,S-dioxides.[18] These features were further borne out in the widely different reactivity of the two systems.
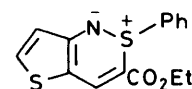
Reactivity of the Thiophene S,N-*Ylides*

(a) *Reactions involving* S–N *cleavage.*—The S–N bond in the ylides (10) is readily cleaved, despite the thermal stability of these compounds. Thus hydrogenolysis of the ylide (10b) with Raney nickel and hydrogen gave tetrachlorothiophene (61%) and ethyl carbamate (68% yield). Photolysis of the same azide
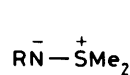
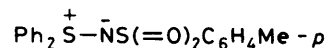in cyclohexane solution proceeded rapidly and efficiently with a medium-pressure mercury lamp to generate tetrachlorothiophene (85%) and ethyl cyclohexylcarbamate (82%), clearly a singlet-nitrene-derived product. This reaction is in marked contrast to the more difficult photolysis of ethyl azidoformate, which requires quartz equipment and low-wavelength light.[19] Furthermore the phenoxycarbonyl ylide (10c) yielded benzoxazolone (46%) on similar photolysis while the sulphonyl ylide gave N-cyclohexyltoluene-p-sulphonamide (24%), again a difficult reaction commencing with the azide.[20] Toluene-p-sulphonyl azide yields the same insertion product in 58% yield on thermolysis.†

(b) *Cycloadditions of Thiophene* S,N-*Ylides.*—(i) *The ylides as* 4π-*components.* Raasch[7] has recently shown that tetrachlorothiophene dioxide (3) is a powerful diene in [4 + 2]reactions with dienophiles, especially with electron-rich species. The reaction (Scheme 3) involves a concomitant extrusion of
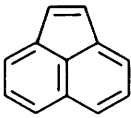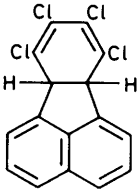
(3)
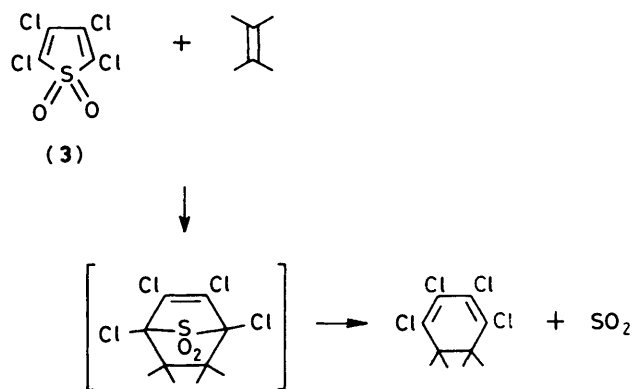
Scheme 3.
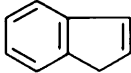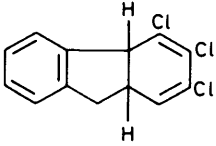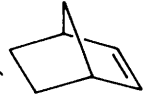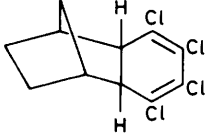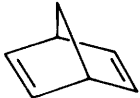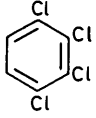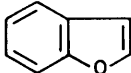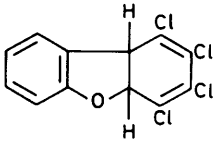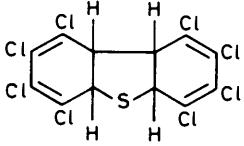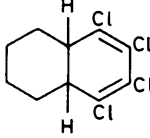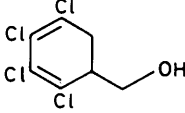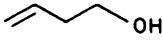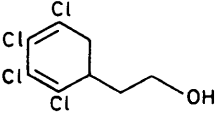
sulphur dioxide to give a tetrachlorodihydrobenzene. Attempts to involve the thiophene S,C-ylides [*e.g.* (1)] in such reactions (*vide infra*) indicated their aromaticity and general lack of reactivity in cycloadditions.[4,18] However, as already noted, the greater diene character of the S,N-ylides should show itself in cycloaddition reactivity.

When the ethoxycarbonyl ylide (10b) was stirred in dichloromethane solution with acenaphthylene at ambient temperature (for 10 min) a rapid reaction ensued with loss of the yellow colour and precipitation of the adduct (14) in 98% yield

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* Full details will be published elsewhere.

† M. F. Sloan, D. S. Breslow, and W. B. Renfrew, *Tetrahedron Lett.*, 1964, 2905; however, other workers[21] report only 17% yield of the insertion product and 40% of toluene-p-sulphonamide.

Table 1. Cycloadditions of the S,N-ylides (10) with alkenes

Ylide	Alkene	Conditions Temp. (°C)	Time	Product		Yield (%)
(10b—d)		20	10 min		(14)	98
(10b)		20	24 h		(15)	69
(10c)		20	48 h		(16)	83
(10b)		20	24 h		(17)	92
(10b)		20	72 h		(18)	60
(10b)		80	96 h		(19)	17
(10b—d)		80	3 h		(20)	93—35
(10b)		80	96 h	—		—
(10c)		80	3 h	—		—
(10b)		20	12 h		(21)	91
(10b)		20	12 h		(22)	92

(Table 1). A range of alkenes was examined and gave adducts as indicated in Table 1. Several points of interest emerge from these results. (I) Planar compounds react most effectively, indicating that a considerable steric problem exists in the cycloaddition transition state. Thus, even thiophene, a most reluctant diene, behaves as a bis-dienophile, while 2,3-dimethylbut-2-ene is unreactive. (II) Norbornadiene * gives tetrachlorobenzene (17) by a retro-Diels–Alder reaction of the initial adduct, liberating cyclopentadiene. (III) Although hex-1-ene reacts rather slowly with the ylide (10b), allyl alcohol and but-3-en-1-ol react rapidly even at room temperature and within 20—30 min at 80 °C to give the adducts (21) and (22) respectively. This remarkable difference in reactivity would appear to be due to an unprecedented hydrogen-bonding assistance as indicated in structure (23a). Alternatively, the involvement of a sulphurane (23b) may be envisaged. This effect is currently under study. (IV)
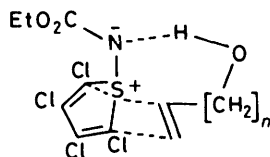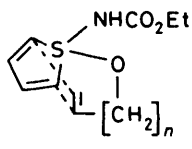
The S,N-ylides are, in some cases, as reactive as tetrachloro-thiophene dioxide (3), though much more sensitive to steric hindrance. (V) Whereas the dioxide (3) loses sulphur dioxide by extrusion to yield adducts, the S,N-ylides, by analogy, should eliminate a thionitroso compound (R–N=S). The trapping of these tacit intermediates is discussed in the following paper. (VI) As a basis for comparison we also prepared a series of S,C-ylides based on tetrachlorothiophene. Unlike the ylides prepared by Porter's group,[4] tetrachlorothiophene reacts with a range of diazo compounds under rhodium acetate catalysis to give the ylides (24). The ylide (24a) cycloadds to alkenes, albeit much more slowly than the nitrogen analogues (10). Thus with acenaphthylene, the aromatised adduct (25) is produced (some minor amounts of trichloro and tetrachloro derivatives are also present) in 97% yield after 7 h heating at 80 °C, while norbornene† with the same ylide gave the adduct (16) in 43% yield after 64 h at 80 °C.

type of reaction for electron-deficient thiones.[22] Albeit, attempts to trap the thione were unsuccessful.

The formation of the fluoranthene (25) deserves comment since a proton shift prior to loss of chlorine apparently occurs. When the dihydrotetrachlorofluoranthene (14) was heated in acetonitrile a very slow elimination did indeed occur to give compound (25), as indicated by t.l.c. The addition of sulphur had no effect. The location of the halogens is at present uncertain as is the mode of dehalogenation.

(ii) *The ylides as 2π-components.* The S,N-ylides (10) react as dienophiles with suitable dienes, again in a [4 + 2] manner. Thus, with anthracene and 9,10-dimethylanthracene, the adducts (26a) and (26b) were obtained in 65 and 72% yield respectively after heating under reflux in benzene solution for 68 h and 24 h respectively, while the S,C-ylide (24a) reacted similarly to give adduct (26c) (56% after 96 h at 80 °C).

(23a)   (23b)
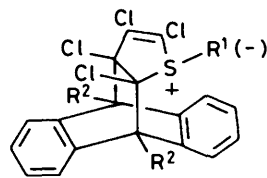
(26)

	R¹	R²
a :	NCO₂Et	H
b :	NCO₂Et	Me
c :	C(CO₂Me)₂	Me

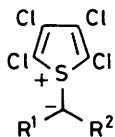The structure of these adducts was fully supported by spectroscopic and analytical data and in the case of (26c), by X-ray crystallography.‡ Furthermore, the adducts (26a and b) proved to be efficient intermediates for triptycene-analogue formation, since the action of zinc dust in hot methanol rapidly dechlorinated and de-ylidated them to give the corresponding triptycene analogues (27) in essentially quantitative yield. Only one other example of such a thiophene isostere of the triptycene system has been previously reported.[23] This route allows thiophene to be used as a ready dienophile, a previously untenable prospect.[24]

(24)   (25)

a : R¹ = R² = CO₂Me
b : R¹ = Ac , R² = CO₂Et

(27)

a : R = H
b : R = Me

In each case a second product, tetramethyl ethylenetetra-carboxylate [(MeO₂C)₂C=C(CO₂Me)₂], was also isolated in essentially quantitative yield. This product is evidently derived from dimethyl thioxomalonate [S=C(CO₂Me)₂] in a known
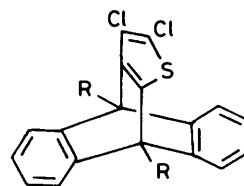
Raasch[7] showed that tetrachlorothiophene dioxide (3) underwent cycloaddition with cyclopentadiene to give both [4 + 2] adducts (28a) (25%) and (29) (44%).

Cyclopentadiene reacted with the S,N-ylide (10b) even at −78 °C to give the adduct (28b) in 20% yield, as well as several other products. Cyclohexadiene, on the other hand, behaved

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* Throughout this paper, norbornadiene is used to denote bicyclo[2.2.1]hepta-2,5-diene.
† Throughout this paper, norbornene is used to denote bi-cyclo[3.2.1]hept-2-ene.

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‡ Full details will be published elsewhere.

(28)
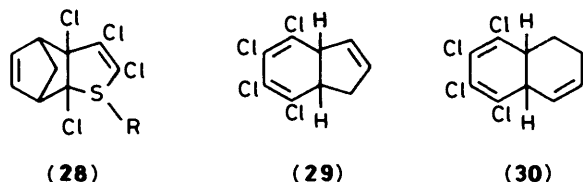
a : R = O$_2$ (sulphone)
b : R = NCO$_2$Et (ylide)

(29) (30)

Scheme 5.

solely as a dienophile with the ylide (10b) and after 2 h at 80 °C gave the adduct (30) in 85% yield. 2,3-Dimethylbutadiene reacted efficiently with the ylide (10b) both as a diene and as a dienophile (Scheme 4) to give the rearranged adduct (32) (40%)
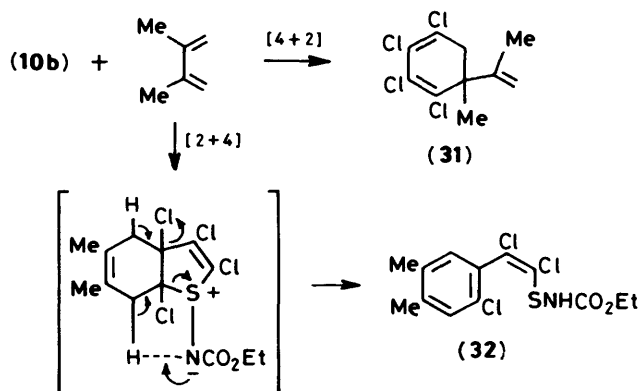
Scheme 4.

and the expected product (31) (59%). The rearrangement is favoured both by loss of the dipolar function and by subsequent aromatisation of the intermediate.

In accord with Raasch's observations on a thiophene dioxide,[25] 2,5-dimethylfuran behaved solely as a dienophile on reaction with the ylide (10b) to give the rearranged adduct (33) in 95% yield after 9 h at 80 °C.

(33)
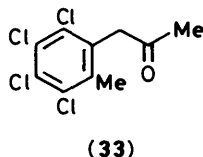
(iii) *The ylide as a 6π-component.* The S,N-ylide reacted only very slowly with electron-deficient dienophiles. With dimethyl acetylenedicarboxylate, for example, after 96 h at 60 °C the ylide was consumed and two products, amongst others, were isolated. The first (4%), dimethyl tetrachlorophthalate, was clearly derived by the Diels–Alder interaction with extrusion of the hetero-bridge. However, the second product (10%), a stable, crystalline 1 : 1 adduct of the two substrates, would appear to be the novel 1,2-thiazocine (34) reasonably derived by [6 + 2]-cycloaddition as depicted in Scheme 5, though not necessarily in a concerted reaction.

In support of the structure, as well as the expected elemental, i.r., [1]H n.m.r., and mass spectral data, the [13]C n.m.r. spectrum reveals, apart from the ester alkyl groups, solely unsaturated signals, thus ruling out bicyclic alternatives. Apart from the
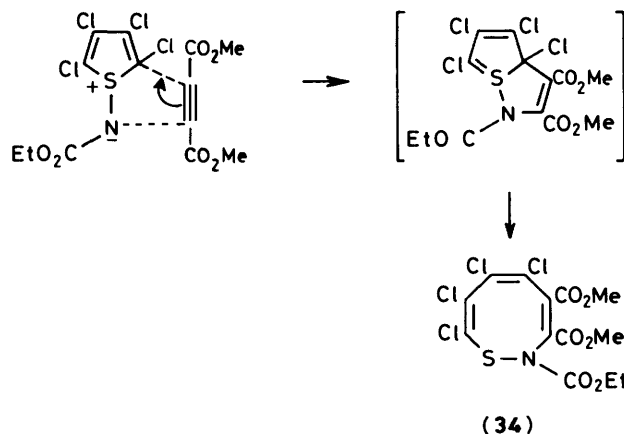
hexahydro S,S-dioxide derivatives[26] this is the first example of this ring system. The possibility of other such [6 + 2]cyclo-additions is under investigation.

(c) *Oxidation of the Thiophene S,N-Ylides.*—When the ethoxycarbonyl ylide (10b) was treated with 3-chloroperbenzoic acid (MCPBA) in hot 1,2-dichloroethane, the ylide was rapidly consumed and a product containing one extra oxygen atom was produced in 84% yield. This less polar and low melting compound (m.p. 59—60 °C) proved to be the S-oxide (35) for

(35)
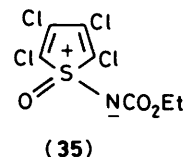
the following reasons. (a) Analytical and [1]H n.m.r. data were in accord with the proposed structure (35). (b) The [13]C n.m.r. spectrum revealed only two thiophene carbon resonances (δ_C 128.2 and 132.75 p.p.m.) at positions not significantly different from the shifts of the parent ylide (10b) (δ_C 131.1 and 131.4 p.p.m.) and tetrachlorothiophene dioxide (3) (δ_C 127.2 and 131.1 p.p.m.). (c) The mass spectrum shows a molecular ion and losses of OEt, CO$_2$Et, and NCO$_2$Et, together with a base peak for tetrachlorofuran. This base peak is also characteristic of the mass spectrum of tetrachlorothiophene dioxide, in accord with the proposed structure. (d) The i.r. spectrum contains carbonyl and C–O–C absorptions at 1 660 and 1 240 cm^{-1} respectively as in the parent ylide (10b). However, in addition, strong absorptions at 1 190 and 1 270 cm^{-1}, supportive of a sulphoximine function, are evident only in the oxidised ylide. N,S-Dimethyl-S-phenyl sulphoximide,[27] for example, absorbs at 1 145 and 1 235 cm^{-1}. (e) The oxide undergoes a rapid cycloaddition with acenaphthylene [though not as fast as with the parent ylide (10b)] at room temperature to give the same adduct (14) as the ylide (10b) together with the formation of a stable distillable intermediate, identical (i.r., [1]H n.m.r.) with the known sulphinylamine EtO$_2$CNSO.[28] This intermediate is unchanged after being kept in chloroform solution for 1 week, but rapidly reacts with added 2,3-dimethylbutadiene to give the known[28] thiazine oxide (36). This thiazine, like its sulphonyl counterpart (37) but unlike the deoxy analogue (38) shows non-equivalent geminal protons for the CH$_2$ adjacent to the S–O group. These data rule out alternative N–O derivatives of the ylide.

3·17   3·50 (J 16·5 Hz)

(36)

3·20   3·82 (J 16 Hz)

(37)

3·25

4·12

(38)
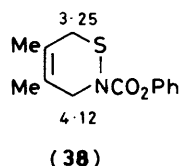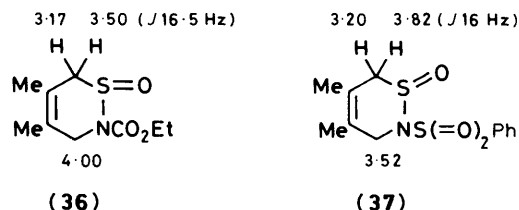
A similar oxidation on the sulphonyl ylide (10d) was ineffective, while oxidation of the S,C-ylide rapidly gave only tetrachlorothiophene. The sulphoximide (35) is the first such derivative in the thiophene series and only the second known type of thiophene with a tetraco-ordinate sulphur, the other example being the dioxide (3).

In conclusion, thiophene S,N-ylides would appear to show diene rather than aromatic properties and compare more with thiophene mono- and di-oxides rather than with the more aromatic S,C-ylides. Their ready synthesis and various modes of cycloaddition suggest that they are novel and useful intermediates. The concomitant extrusion of thionitroso compounds during their reactions as 4π-components in cycloadditions, a unique route to these inaccessible systems, will be dealt with in the following paper.

Experimental

M.p.s were recorded on a Reichert Kofler hot-stage apparatus and are uncorrected. I.r. spectra were obtained on a Perkin-Elmer 257 spectrophotometer as liquid films or Nujol mulls. Mass spectra were produced using a Varian M.A.T. 188 instrument, ^{1}H n.m.r. spectra on a Varian EM 390 (90 MHz) or Bruker WM 500 (500 MHz) spectrometer for deuterio-chloroform solution, referenced to internal tetramethylsilane, and ^{13}C n.m.r. spectra on a Varian CFT 20 (20 MHz) or Bruker WM 500 (125 MHz) instrument, also for deuterio-chloroform solutions. Photolyses were conducted in a Hanovia immersion photochemical reactor (125 W) with a medium-pressure mercury lamp. Silica gel (Merck Kieselgel 60) was used for column chromatography. T.l.c. was conducted using Merck Kieselgel 60F-254 plates while preparative layer chromatography (p.l.c.) employed Merck Kieselgel 60F-254, 200 × 200 × 2 mm plates. Light pertroleum refers to the fraction b.p. 60—80 °C. Mass spectra of halogeno compounds only indicate the major peak of the bunches of isotopic peaks. The following compounds were made by literature methods: methyl azidoformate,[29] ethyl azidoformate,[30] phenyl azidoformate,[31] toluene-p-sulphonyl azide,[32] 2,5-dichlorothiophene (4a),[33] 2,5-dibromothiophene (4b),[34] 2,3,5-tribromothiophene,[34] 2,3,4,5-tetrabromothiophene,[35] tetrachlorothiophene,[36] and 9,10-dimethylanthracene.[37]

Decomposition of the Azides in Substituted Thiophenes

(a) *Decomposition of Phenyl Azidoformate in 2,5-Dibromothiophene* (4b).—Phenyl azidoformate (5.82 g, 0.04 mol) was added dropwise to 2,5-dibromothiophene (4b) (44 ml, 0.39 mol) at 145 °C over a period of 10 min. The solution was stirred until no more nitrogen came off (∼ 20 min), and then cooled and the

excess of 2,5-dibromothiophene was distilled off under vacuum. The solution was chromatographed on silica, first with light petroleum and then with light petroleum–chloroform (40:60) to give *phenyl* N-(3,5-*dibromo-2-thienyl*)*carbamate* (5b) (1.95 g, 15%) recrystallised from ethyl acetate–light petroleum, m.p. 106—107 °C (Found: C, 34.75; H, 1.7; Br, 44.5; N, 3.75; S, 8.85. $C_{11}H_7Br_2NO_2S$ requires C, 35.04; H, 1.87; Br, 42.38; N, 3.72; S, 8.50%); $v_{max.}$ 3 380 (NH) and 1 735 cm^{-1} (C=O); m/z 375 (M^+), 281 (M^+ − PhOH), 253 (281 − CO), 174 (253 − Br), and 94 (PhOH); δ_H 6.68 (1 H, s) and 6.90—7.40 (5 H, m, Ph); δ_C 151.14 (C=O), 150.26 (C–O), 134.73 (C-1), 129.53, 126.23, and 121.22 (Ph), 128.49 (C-4), 105.23 (C-5), and 93.31 p.p.m. (C-3).

Eluting with chloroform yielded *phenyl* N-(2,5,5-*tribromo-2,5-dihydro-2-thienyl*)*carbamate* (6b) (2.40 g, 15%), m.p. 144—145 °C (from ethyl acetate–light petroleum) (Found: C, 28.7; H, 1.55; Br, 54.3; N, 2.9; S, 7.5. $C_{11}H_8Br_3NO_2S$ requires C, 28.85; H, 1.76; Br, 52.34; N, 3.06; S, 7.00%); $v_{max.}$ 3 260 (NH) and 1 720 cm^{-1} (C=O); m/z 455 (M^+), 361 (M^+ − PhOH), 282 (361 − Br), 240 (282 − NCO), 161 (240 − Br), and 94 (PhOH); δ_H 6.70 (1 H, d), 7.00—7.35 (5 H, m, Ph), 7.44 (1 H, d, J 10.5 Hz), and 8.35 (1 H, br, NH).

Alternative synthesis of phenyl N-(3,5-*dibromo-2-thienyl*)-*carbamate* (5b). n-Butyl-lithium (39 ml of a 1.6M solution) was added dropwise to a solution of 2,3,5-tribromothiophene (20.0 g, 0.06 mol) and dry diethyl ether (80 ml) under nitrogen at −70 °C. After addition the solution was added to an excess of solid carbon dioxide. Water was then added, followed by dropwise addition of conc. hydrochloric acid. The solid was filtered off and recrystallised from aqueous ethanol to give 3,5-dibromothiophene-2-carboxylic acid (11.0 g, 62%), m.p. 180—188 °C (lit.,[35] 180—188 °C).

Thionyl chloride (18 ml) was then added to a solution of 3,5-dibromothiophene-2-carboxylic acid (11.0 g, 0.04 mol) in benzene (50 ml) and the mixture was refluxed for 2 h, cooled, and filtered. The filtrate was distilled to give 3,5-dibromo-thiophene-2-carbonyl chloride (9.1 g, 77%), m.p. 62—63 °C; b.p. 126—128 °C at 0.1 mmHg (lit.,[38] b.p. 126—128 °C at 0.1 mmHg).

A solution of 3,5-dibromothiophene-2-carbonyl chloride (9.0 g, 0.03 mol) in acetone (55 ml) was added dropwise to an ice-cooled solution of sodium azide (3.0 g, 0.05 mol) in water (45 ml). It was stirred for 1 h with continued cooling and was then filtered, and the solid was washed with water. It was then dried (P$_2$O$_5$) to give 2-(azidocarbonyl)-3,5-dibromothiophene (8.0 g, 87%), m.p. 88—89 °C; $v_{max.}$ 2 160 (N$_3$) and 1 690 cm^{-1} (C=O).

A solution of 2-(azidocarbonyl)-3,5-dibromothiophene (2.0 g, 0.01 mol) in dry benzene (20 ml) was refluxed for 2.5 h to give the 3,5-dibromo-2-thienyl isocyanate, $v_{max.}$ 2 240 cm^{-1} (NCO). A solution of phenol (1.0 g, 0.01 mol) in dry benzene (5 ml) was added to this solution and the mixture was stirred for 1 h. The solution was washed with 10% aqueous sodium hydroxide and the product was extracted with diethyl ether, the extract was dried over magnesium sulphate, and the solvent was evaporated off. The product was recrystallised from ethyl acetate–light petroleum to give phenyl N-(3,5-dibromo-2-thienyl)carbamate (5b) (1.0 g, 41%), m.p. 106—107 °C, identical with that prepared above (mixed m.p., i.r., ^{1}H n.m.r.).

(b) *Decomposition of Phenyl Azidoformate in 2,5-Dichloro-thiophene* (4a).—The same method and quantities were used as with 2,5-dibromothiophene. Phenyl N-(3,5-dichloro-2-thienyl)-carbamate (5a) was obtained (10%), m.p. 69—70 °C; $v_{max.}$ 3 240 (NH) and 1 720 cm^{-1} (C=O); m/z 287 (M^+), 193 (M^+ − PhOH), 165 (193 − CO), 130 (165 − Cl), and 94 (PhOH, base peak); δ_H 5.20 (1 H, br, NH), 6.85 (1 H, s), and 7.05—7.60 (5 H, m, Ph).

Phenyl   N-(2,5,5-trichloro-2,5-dihydro-2-thienyl)carbamate

(6a) was also isolated (13%), m.p. 134—137 °C; $v_{max.}$ 3 250 (NH), 3 020 (C=C–H), and 1 730 cm^{-1} (C=O); m/z 323 (M^+), 229 (M^+ – PhOH), 194 (229 – Cl), 153 (194 – NCO), and 94 (PhOH, base peak); δ_H 6.25 (1 H, br, NH), 6.72 (d) and 7.02 (d, J 10.5 Hz, 2 H, 3- and 4-H), and 7.10—7.60 (5 H, m, Ph).

(c) *Decomposition of Phenyl Azidoformate in 2,3,4,5-Tetra-bromothiophene.*—Phenyl azidoformate (5.0 g, 0.03 mol) was added dropwise to a solution of tetrabromothiophene (42.0 g, 0.11 mol) in 1,1,2,2-tetrachloroethane (80 ml) at 145 °C. The solution was stirred at 145 °C for 40 min, when the solvent was distilled off and the residue was chromatographed on silica, and eluted with light petroleum to remove unchanged tetrabromothiophene. Further elution with light petroleum–chloroform (1:1) yielded *phenyl* N-(3,4,5-*tribromo-2-thienyl*)*carbamate* (8a) (0.09 g, 1%), m.p. 159—160 °C (Found: C, 29.0; H, 1.2; Br, 56.75; N, 3.0; S, 6.7. C$_{11}$H$_6$Br$_3$NO$_2$S requires C, 28.98; H, 1.33; Br, 52.57; N, 3.07; S, 7.03%); $v_{max.}$ 3 320 (NH) and 1 675 cm^{-1} (C=O); m/z 453 (M^+), 332 (M^+ – CO$_2$Ph), 252 (332 – HBr), and 173 (252 – Br); δ_H 7.17—7.58 (5 H, m, Ph) and 7.65 (NH). Elution with chloroform yielded benzoxazol-2-one (3.4 g, 82%), which recrystallised from light petroleum (b.p. 100—120 °C), m.p. 140—141 °C (lit.,[39] 139—140 °C); $v_{max.}$ 3 200 (NH) and 1 720br cm^{-1} (C=O).

(d) *Decomposition of Phenyl Azidoformate in 1,1,2,2-Tetra-chloroethane.*—Phenyl azidoformate (5.0 g, 0.03 mol) was added dropwise to 1,1,2,2-tetrachloroethane (50 ml) at 145 °C. The solution was stirred at 145 °C for 40 min. The excess of tetrachloroethane was distilled off under reduced pressure and the residue was chromatographed on silica. Elution with chloroform gave benzoxazol-2-one (2.67 g, 64%).

(e) *Decomposition of Ethyl Azidoformate in Tetrabromo-thiophene.*—Ethyl azidoformate (4.4 g, 0.04 mol) was added dropwise to a solution of tetrabromothiophene (32 g, 0.08 mol) and 1,1,2,2-tetrachloroethane (25 ml) at 130 °C. The solution was stirred at 130 °C for 50 min. The solution was then cooled, water was added, and the mixture was extracted with chloroform. The chloroform layer was dried over magnesium sulphate, filtered, and the solvent was evaporated off. The residue was chromatographed on silica with light petroleum as eluant to give recovered tetrabromothiophene. Elution with light petroleum–chloroform (2:3) then gave *ethyl* N-(3,4,5-*tribromo-2-thienyl*)*carbamate* (8b) (0.18 g, 1.1%) which was recrystallised from ethyl acetate–light petroleum, m.p. 257—259 °C (Found: C, 41.1; H, 6.9; N, 16.0. C$_6$H$_{12}$N$_2$O$_4$ requires C, 40.91; H, 6.89; N, 15.90%); $v_{max.}$ 3 390 (NH) and 1 690 cm^{-1} (C=O); m/z 405 (M^+), 360 (M^+ – OEt), 332 (360 – CO), and 174 (360 – 2Br); δ_H 1.35 (3 H, t, Me), 4.30 (2 H, q, CH$_2$), and 6.10 (1 H, br, NH); δ_C 153.59 (C=O), 133.46 (C-2), 114.62 (C-4), 109.35 (C-5), 108.51 (C-3), 62.24 (CH$_2$), and 14.43 p.p.m. (Me). Eluting with chloroform gave diethyl hydrazinedicarboxylate (9) (0.09 g, 1%), m.p. 131—132 °C (lit.,[40] m.p. 134—135 °C); $v_{max.}$ 3 410 (NH), 1 720 (C=O), and 1 220 cm^{-1} (C–O); m/z 176 (M^+), 131 (176 – OEt), 103 (131 – CO), and 45 (OEt, base peak); δ_H 1.30 (3 H, t, Me), 4.25 (2 H, q, CH$_2$), and 6.65 (2 H, br, NH).

(f) *Decomposition of Phenyl Azidoformate in Tetrachloro-thiophene.*—Phenyl azidoformate (5.82 g, 0.04 mol) was added dropwise to tetrachlorothiophene (85 g, 0.38 mol) at 145 °C and the mixture was stirred for 40 min at 145 °C. Excess of tetrachlorothiophene was distilled off under reduced pressure and the residue was chromatographed on silica with light petroleum as eluant to separate the remaining tetrachloro-thiophene. Elution with light petroleum–chloroform (2:3) then yielded N-*phenoxycarbonyl*-(2,3,4,5-*tetrachloro-1-thio-phenio*)*amide* (10c) (2.91 g, 23%), R_F (CHCl$_3$) 0.49; m.p. 131—

132 °C (recrystallised from ethanol or ethyl acetate–light petroleum) (Found: C, 37.0; H, 1.4; Cl, 43.0; N, 4.0; S, 9.0. C$_{11}$H$_4$Cl$_4$NO$_2$S requires C, 37.01; H, 1.41; Cl, 39.72; N, 3.92; 8.98%); $v_{max.}$ 1 670 cm^{-1} (C=O); m/z 355 (M^+), 262 (M^+ – OPh), 220 (tetrachlorothiophene, base peak), 185 (220 – Cl), 150 (185 – Cl), and 94 (PhOH); δ_H 7.00—7.55 (5 H, m); δ_C 160.2 (C=O), 151.8 (C–O), 130.8 and 132.7 (α-and β-carbons in tetrachlorothiophene ring), 121.1, 125.5, and 129.2 p.p.m. (phenyl ring). Further elution with chloroform yielded benz-oxazol-2-one (2.30 g, 48%).

(g) *Decomposition of Ethyl Azidoformate in Tetrachloro-thiophene.*—Ethyl azidoformate (4.5 g, 0.02 mol) was added dropwise to tetrachlorothiophene (85 g, 0.39 mol) at 130 °C. After 40 min the excess of tetrachlorothiophene was distilled off under reduced pressure and the residue was cooled and crystallised twice from light petroleum to give N-*ethoxy-carbonyl*-(2,3,4,5-*tetrachloro-1-thiophenio*)*amide* (10b) as white crystals (5.9 g, 49%), m.p. 118—120 °C (Found: C, 27.5; H, 1.65; Cl, 46.0; N, 4.7; S, 10.5. C$_7$H$_5$Cl$_4$NO$_2$S requires C, 27.20; H, 1.63; Cl, 45.89; N, 4.53; S, 10.38%); $v_{max.}$ 1 660 cm^{-1} (C=O); m/z 262 (M^+ – OEt), 220 (262 – NCO), 185 (220 – Cl), and 115 (185 – 2Cl); δ_H 1.25 (3 H, t, Me) and 4.15 (2 H, q, CH$_2$); δ_C 160 (C=O), 131.4 and 131.1 (α- and β-thiophenic carbons), 62.5 (CH$_2$), and 13.7 p.p.m. (Me).

(h) *Decomposition of Methyl Azidoformate in Tetrachloro-thiophene.*—In a similar manner to that described in (f) above, methyl azidoformate (5.0 g) was decomposed at 136 °C in tetrachlorothiophene (80 g). Work-up as above and chromat-ography of the residue on silica with light petroleum–chloroform (30:70) as eluant gave N-*methoxycarbonyl*-(2,3,4,5-*tetrachloro-1-thiophenio*)*amide* (10a) (2.31 g, 16%) as white crystals from ethyl acetate–light petroleum, m.p. 134—135 °C (Found: C, 24.5; H, 0.8; Cl, 48.8; N, 4.7; S, 10.9. C$_6$H$_3$Cl$_4$NO$_2$S requires C, 24.43; H, 1.03; Cl, 48.09; N, 4.75; S, 10.87%); $v_{max.}$ 1 630 cm^{-1} (C=O); m/z 293 (M^+), 262 (M^+ – OMe), 220 (262 – NCO), 185 (220 – Cl), and 150 (185 – Cl); δ_H 3.62 (s, Me); δ_C 161.8 (C=O), 131.9 and 131.1 (α- and β-thiophenic carbons), and 53.8 p.p.m. (Me).

(i) *Decomposition of Toluene-p-sulphonyl Azide in Tetrachloro-thiophene.*—The decomposition was conducted under the same conditions as for the ethyl and phenyl azidoformates, but at a temperature of 150 °C. The rate of the reaction was slow and the reaction was stopped after 45 min, when half of the amount of nitrogen had been evolved. The residue was chromatographed on silica, and elution with light petroleum–chloroform (30:70) yielded 2,3,4,5-*tetrachloro-1-thiophenio*-N-(p-*tolylsulphonyl*)-*amide* (10d) (24%), m.p. 173—174 °C (from ethanol) (Found: C, 33.6; H, 1.8; Cl, 35.9; N, 3.6; S, 16.0. C$_{11}$H$_7$Cl$_4$NO$_2$S requires C, 33.78; H, 1.80; Cl, 36.26; N, 3.58; S, 16.40%); $v_{max.}$ 1 300 and 1 135 cm^{-1} (SO$_2$); m/z 234 (M^+ OSO$_2$C$_6$H$_6$Me-*p*), 220 (tetrachlorothiophene), 185 (220 – Cl), 150 (185 – Cl), 115 (150 – Cl), and 91 (C$_7$H$_7$); δ_H 2.45 (3 H, s, Me) and 7.88 (d) and 7.30 (d, J 7.5 Hz, together 4 H, ArH); δ_C 143.80 (SO$_2$C), 138.53 (C–Me), 132.91 and 131.93 (α- and β-carbons of thiophene ring), 129.58 and 127.29 (4 phenyl carbons), and 21.65 p.p.m. (Me).

Reaction of Diazo Compounds with Tetrachlorothiophene and Rhodium Acetate

(a) *Bis*(*methoxycarbonyl*)-(2,3,4,5-*tetrachlorothiophenio*)-*methylide* (24a).—Dimethyl diazomalonate[41] (1.6 g, 0.01 mol) was added dropwise to a mixture of tetrakis(acetato)di-rhodium(II) (5 mg) and tetrachlorothiophene (10 ml, 0.08 mol) at room temperature. The solution was stirred at room temperature and the reaction was followed by i.r. spectroscopy

(disappearance of the diazo band, 24 h). The solution was then chromatographed on silica with light petroleum as eluant to separate the excess of tetrachlorothiophene. Elution with chloroform then gave the *title* S,C-*ylide,* which recrystallised from acetonitrile (2.6 g, 75%), m.p. 182—183 °C (Found: C, 30.4; H, 1.3; Cl, 40.1; S, 9.0. $C_9H_6Cl_4O_4S$ requires C, 30.71; H, 1.72; Cl, 40.29; S, 9.11%); $v_{max.}$ 1 655 cm^{-1} (C=O); m/z 351 (M^+), 292 (M^+ − CO_2Me), 221 (292 − CCO_2Me), and 59 (CO_2Me, base peak); δ_H 3.70 (s) and 3.80 (s) (2 × Me); δ_C 165.37 and 163.86 (2 × C=O) (2 × C=O), 131.50 and 127.55 (α- and β-carbons of thiophene ring), 51.98 and 51.74 (2 × Me), and 50.52 p.p.m. (C$^-$).

(b) C-*Acetyl*-C-*ethoxycarbonyl*-(2,3,4,5-*tetrachloro*-1-*thio-phenio*)*methylide* (**24b**).—Ethyl diazoacetoacetate[42] (1.6, 0.01 mol) was added dropwise to tetrakis(acetato)dirhodium(II) (5 mg) and tetrachlorothiophene (10 ml, 0.08 mol) at room temperature. The solution was stirred at room temperature for 3 days. It was then chromatographed on silica and elution with dichloromethane yielded the *title ylide* as a yellow oil (2.9 g, 83%), $v_{max.}$ 1 710 and 1 600 cm^{-1} (C=O); m/z 347 (M^+), 304 (M^+ − COMe), and 221 (tetrachlorothiophene); δ_H 1.35 (3 H, t, Me), 2.42 (3 H, s, Me), and 4.32 (2 H, q, CH_2); δ_C 163.34 and 160.0 (2 × CO), 138.07 and 135.27 (α-carbons of thiophene ring), 123.45 and 121.54 (β-carbons of thiophene ring), 106.32 (C$^-$), 61.81 (*CH$_2$*Me), 21.67 (*COMe*), and 13.76 (CH$_2$*Me*); m/z 347.894 501 (M^+). $C_{10}H_8Cl_4O_3S$ requires M, 347.894 824.

Reactions of the S,N-*Ylides* (**10**) *and* S,C-*Ylides* (**24**)

(a) *Reactions involving* S,N-*Bond Cleavage.*—(i) *Hydrogen-olysis of* N-*ethoxycarbonyl*-(2,3,4,5-*tetrachloro*-1-*thiophenio*)*amide* (**10b**). A mixture of the title ylide (0.10 g, 3.2 × 10^{-4} mol) and Raney nickel in tetrahydrofuran (10 ml) was hydrogenated (13 ml of H$_2$ was adsorbed in 4 h) and filtered, and the residue obtained on work-up was chromatographed on silica with light petroleum as eluant to afford tetrachlorothiophene (0.05 g, 61%). Elution with chloroform then gave ethyl carbamate (0.02 g, 68%), m.p. 49—50 °C (lit.,[43] 49—50 °C); $v_{max.}$ 3 480 and 3 320 (NH$_2$), and 1 700 cm^{-1} (C=O); δ_H 1.22 (3 H, t, Me), 4.12 (2 H, q, CH$_2$), and 4.75 (2 H, br, NH$_2$).

(ii) *Photolysis of* N-*ethoxycarbonyl*-(2,3,4,5-*tetrachloro*-1-*thiophenio*)*amide* (**10b**) *in cyclohexane solution.* The title ylide (0.50 g, 1.6 × 10^{-3} mol) in cyclohexane (200 ml) was photolysed for 1 h. The excess of cyclohexane was distilled off and the residue was chromatographed on silica and eluted with light petroleum to give tetrachlorothiophene (0.31 g, 85%). Elution with chloroform then yielded cyclohexyl carbamate (1.23 g, 81%), m.p. 56—57 °C (lit.,[44] 57 °C); $v_{max.}$ 3 300 (NH) and 1 670 cm^{-1} (C=O); m/z 171 (M^+) and 81 (M^+ − NHCO$_2$Et); δ_H 1.15—2.10 (9 H, m, cyclohexyl), 1.25 (3 H, t, Me), and 4.20 (2 H, q, C*H$_2$*Me).

(iii) *Photolysis of* N-*phenoxycarbonyl*-(2,3,4,5-*tetrachloro*-1-*thiophenio*)*amide* (**10c**). The ylide (0.20 g, 5.6 × 10^{-4} mol) in dichloromethane (200 ml) was photolysed for 2 h. The solvent was evaporated off and the residue was chromatographed on silica, with light petroleum as eluant, to yield tetrachloro-thiophene (0.06 g, 48%). Elution with chloroform then yielded benzoxazol-2-one (0.04 g, 46%).

(b) *Cycloaddition Reactions.*—*General method for the inter-action of the ylides* (**10**) *with various dienophiles.* The ylide (**10**) and the dienophile (equimolar amounts) were dissolved in the minimum amount of solvent (chloroform, dichloromethane, or benzene) and the solution was stirred at the required temperature. The reaction was monitored by t.l.c. Details of these experiments are recorded in Table 1.

In the case of thiophene, cyclohexene, hex-1-ene, allyl alcohol,

and but-3-en-1-ol the dienophile was used as solvent. After completion of the reaction the solvent and any excess of dienophile were removed under reduced pressure and the products were purified either by crystallisation or by elution through a silica column. The properties of the adducts are recorded in Table 2.

Reaction of 2,3,4,5-*Tetrachloro*-1-*thiophenio Ylide* (**24a**) *with Dienophiles.*—(i) *Reaction with norbornene.* The ylide (0.35 g, 0.01 mol) and norbornene (1.00 g) were heated in acetonitrile (2.5 ml) under reflux for 64 h; the disappearance of the ylide was monitored by t.l.c. (chloroform). Removal of the solvent and chromatography of the residue on silica gel yielded, on elution with light petroleum, an oil (0.24 g). This oil was separated (p.l.c.; light petroleum as developer) to yield (in order of decreasing R_F) tetrachlorothiophene (0.04 g, 18%, R_F 0.9) and the norbornene adduct (**16**) (0.12 g, 43%, R_F 0.7). Further elution with chloroform gave tetramethyl ethylenetetracarb-oxylate (0.14 g, 108%) as white needles from ethyl acetate–light petroleum, m.p. 120—120.5 °C (lit.,[45] 121 °C).

(ii) The ylide (0.35 g, 0.01 mol) and acenaphthylene (0.40 g, 0.026 mmol) were heated in acetonitrile (1 ml) under reflux for 7 h during which time a white solid precipitated. The cooled solution was filtered and the residue was washed repeatedly with light petroleum to give a dichlorofluoranthene (**25**) (0.33 g, 97%) which recrystallised from toluene as white rods, m.p. 355—357 °C (Found: C, 68.7; H, 3.5. $C_{16}H_8Cl_2$ requires C, 70.88; H, 2.97%. $C_{16}H_6Cl_4$ requires C, 56.52; H, 1.78%. $C_{16}H_7Cl_3$ requires C, 62.89; H, 2.31%). From the above filtrate, after evaporation of the solvent and chromatography on silica gel, was obtained (by elution with light petroleum) a trace of tetrachlorothiophene, while elution with chloroform gave tetramethyl ethylenetetracarboxylate (0.12 g, 92%), m.p. 120—120.5 °C.

Reaction of the Ylides (**10**) *and* (**24**) *with Dienes.*—(i) 9,10-*Dimethylanthracene.* The ylide (**10b**) (0.50 g, 1.6 × 10^{-3} mol) and 9,10-dimethylanthracene (0.50 g, 2.4 × 10^{-3} mol) were dissolved in hot benzene (2 ml) and the solution was refluxed for 2.5 days. The solution was cooled and the benzene was distilled off. The residue was chromatographed on silica and elution with dichloromethane yielded the *cycloadduct of* 9,10-*dimethyl-anthracene,* (**26b**), which was recrystallised from ethanol (0.60 g, 72%); R_F (CHCl$_3$) 0.48; m.p. 195—196 °C (Found: C, 53.9; H, 3.5; Cl, 26.15; N, 2.9; S, 6.7. $C_{23}H_{19}Cl_4NO_2S$ requires C, 53.61; H, 3.72, Cl, 27.52; N, 2.72; S, 6.22%); $v_{max.}$ 1 640 (C=O) and 1 240 cm^{-1} (C–O); m/z 478 (M^+ − Cl), 408 (478 − 2Cl), and 206 (9,10-dimethylanthracene); δ_H 1.25 (3 H, t, Me), 2.35 (s, 2 × Ar-*Me*), 2.42 (s), 4.15 (2 H, q, CH$_2$), and 7.25—7.70 (8 H, m, ArH); δ_C 164.07 (C=O), 140.53, 140.40, 139.77, 139.17, and 138.19 (C-4a, -9a, -10a, -8a, and α-unsaturated carbon of thiophene ring), 128.67, 127.81, 127.44, 125.06, 124.42, 123.43, and 123.25 (C-1—8 and β-unsaturated carbon of thiophene ring), 105.23 and 87.05 (α- and β-saturated carbon of thiophene ring bonded to anthracene ring), 62.38 (CH$_2$), 53.61 and 51.39 (C-9 and -10), 16.14 and 15.80 (2 × Me of anthracene ring), and 14.35 p.p.m. (CH$_2$*Me*).

The *bis*(*methoxycarbonyl*)-(2,3,4,5-*tetrachloro*-1-*thiophenio*)-*methylide cycloadduct of* 9,10-*dimethylanthracene,* compound (**26c**), was prepared by the same method (56%) and re-crystallised from ethanol, m.p. 234—237 °C (Found: C, 53.8; H, 3.4; Cl, 25.5; S, 5.75. $C_{25}H_{20}Cl_4O_4S$ requires C, 53.78; H, 3.61; Cl, 25.40; S, 5.74%); $v_{max.}$ 1 650 cm^{-1} (C=O); m/z 556 (M^+), 206 (9,10-dimethylanthracene), and 59 (CO$_2$Me); δ_H 2.30 (s, 2 × Me), 2.45 (s), 3.55 (s, 2 × OMe), 3.82 (s), and 7.30—7.80 (8 H, m, ArH); δ_C 167.39 and 163.92 (2 × CO), 140.71, 140.03, 139.66, 138.01, and 136.50 (C-4a, -10a, -8a, -9a, and α-unsaturated carbon of thiophene ring), 128.65, 127.99, 127.52,

Table 2. Properties of the cycloadducts (14)—(25)

Compound (Formula)	Solvent	M.p. (°C) (lit. m.p.)	Found (%) (Required) C	H	m/z	$\nu_{max.}$/cm^{-1}	^{1}H n.m.r. (δ_H)	^{13}C n.m.r. (δ_C/p.p.m.)
(14)	MeOH	173—174 (173—174)			340 (M^+), 305 ($M^+ - $Cl), 270 (305 $-$ Cl), 235 (270 $-$ Cl), 200 (235 $-$ Cl)	1 600	7.45—7.90 (6 H, m, ArH), 4.88 (2 H, s, CH)	
(15)	MeOH	95—96 (96—97)			304 (M^+), 269 ($M^+ - $Cl), 234 (269 $-$ Cl), 199 (234 $-$ Cl), 164 (199 $-$ Cl), 166 (indene)	1 610, 1 455, 1 380	7.20—7.65 (4 H, m, ArH), 4.32 (1 H, d, 4a-H), 3.42—3.82 (1 H, m, J 9 Hz, 9a-H), 3.33 (2 H, m, CH$_2$)	
(16) (C$_{11}$H$_{10}$Cl$_4$)	MeOH	101—102	47.07 (46.52)	3.59 (3.55)	282 (M^+), 247 ($M^+ - $Cl), 214 (C$_6H_2Cl_4$)	1 600, 1 450	2.88 (2 H, m, 4a- and 8a-H), 2.75 (2 H, m, 9-H$_2$), 1.15—1.80 (6 H, m, 2 × CH$_2$ and 8- and 5-H)	131.6 (C-6 and -7), 123.1 (C-5 and -8), 52.1 (C-1 and -4), 45.2 (C-4a and -8a), 34.5 (C-9), 28.9 (C-2 and -3)
(17)	EtOH	44—45			216, 214 (M^+)	3 060, 1 610	7.30 (2 H, s)	
(18) (C$_{11}$H$_6$Cl$_4$O)	MeOH	137—138	46.56 (46.80)	1.99 (1.96)	306 (M^+), 236 ($M^+ - $2Cl), 166 ($M^+ - $4Cl)	1 600, 1 450, 1 370	6.83—7.68 (4 H, m, C$_6$H$_4$), 5.47 (1 H, d, J 12 Hz, 4a-H), 4.48 (1 H, d, 9b-H)	
(19)	EtOH–light petroleum	216—217 (216.5—217)			426 (M^+), 425 ($M^+ - $Cl), 390 (425 $-$ Cl), 250 (390 $-$ 4Cl)	1 590	4.40 (4 H, m)	
(20)	MeOH	87—88 (88—89)			270 (M^+), 165 ($M^+ - $3Cl)	1 590, 1 430	2.88 (2 H, m, CH), 1.35—2.10 (8 H, m, CH$_2$)	
(21)	oil				272 (M^+), 215 ($M^+ - $ C$_4$H$_9$), 180 (215 $-$ Cl), 145 (180 $-$ Cl), 109 (145 $-$ HCl), 74 (109 $-$ Cl), 57 (C$_4$H$_9$) *271.9692 (271.9693)*	1 605	3.02 (1 H, dd, J 18 and 9 Hz, CH), 2.8—2.4 (2 H, m, ring CH$_2$), 1.8—1.0 [6 H, m, (CH$_2$)$_3$], 0.82 (3 H, t, Me)	129.5, 128.5, 125.9, 123.3 (C-1—4), 60.9 (CH$_2$OH), 44.5 (CH), 33.9 (CH$_2$)
(22)	oil				230 (M^+), 195 ($M^+ - $Cl), 125 (195 $-$ 2Cl), 90 (125 $-$ Cl), 73 (90 $-$ OH)	3 320br	3.70 (2 H, d, CH$_2$), 3.65 (1 H, s, OH), 2.87 (2 H, d, CH$_2$), 2.65—3.30 (1 H, m, CH)	133.4, 128.0, 124.4, 123.5 (C-1—4), 59.4 (CH$_2$OH), 39.0 (CH), 33.1 (CH$_2$CH$_2$OH)
(25) (C$_{16}$H$_8$Cl$_2$)[a]	PhMe	355—357 (decomp.)	68.88 (70.88)	3.48 (2.97)			7.3—8.2 (m)[b]	

[a] Contains small amount C$_{16}$H$_7$Cl$_3$ and C$_{16}$H$_6$Cl$_4$ by m.s. (CD$_3$)$_2$SO and CDCl$_3$ used as solvent.

125.05, 124.52, 124.05, 123.42, and 122.87 (C-1—8 and β-unsaturated carbon of thiophene ring), 104.29 and 86.52 (α- and β-carbon of thiophene ring bonded to anthracene ring), 59.08 (C⁻), 53.64 and 52.41 (C-9 and -10), 51.76 and 51.07 (2 × OMe), and 16.02 and 15.90 p.p.m. (2 × Me).

(ii) *Anthracene.* In a similar manner, but with anthracene instead of 9,10-dimethylanthracene, the ylide (10b) gave the *adduct* (26a) (65%) as white rhombic crystals from methanol, m.p. 208—209 °C (Found: C, 51.7; H, 2.9; N, 2.9. $C_{21}H_{15}Cl_4$-NO_2S requires C, 51.77; H, 3.10; N, 2.88%); $v_{max.}$ 1 640 cm⁻¹ (C=O); δ_H 1.27 (3 H, t, Me), 4.15 (2 H, q, CH_2), 4.88 and 4.92 (2 H, s, 2 × CH), and 7.20—7.65 (8 H, m, ArH).

Reduction of the adducts (26a) *and* (26b). The adduct (26b) (0.236 g, 0.46 mmol), zinc dust (0.20 g, 0.003 g-atom), and zinc chloride (0.05 g, 0.37 mmol) were heated under reflux in methanol (15 ml). The mixture was evaporated to dryness, a little chloroform was added, and the mixture was poured onto a column of silica gel. Elution with dichloromethane yielded 2,3-*dichloro-9,10-dimethyl-4,9-dihydro-4,9[1',2']benzenonaphtho-*[2,3-b]*thiophene* (27b) (0.167 g, 100%) as white rhombic crystals from methanol, m.p. 218—218.5 °C (Found: C, 66.9; H, 3.9. $C_{20}H_{14}Cl_2S$ requires C, 67.23; H, 3.95%); δ_H 2.52 and 2.23 (6 H, each s, Me) and 7.5—6.8 (8 H, m, ArH); m/z 356 (M^+), 321 ($M^+ - $ Cl), 306 (321 — Me), 285 (321 — HCl), 277 (321 — CS), 271 (306 — Cl), 242 (277 — Cl), 153, 136, and 113.

In a similar manner reduction of the adduct (26a) gave 2,3-*dichloro-4,9-dihydro-4,9[1',2']benzenonaphtho[2,3-b]thiophene* (27a) (98%) as white rhombic crystals from methanol, m.p. 214 °C (Found: C, 65.4; H, 2.9. $C_{18}H_{10}Cl_2S$ requires C, 65.65; H, 3.06%); δ_H 5.41 and 5.52 (2 H, s, 2 × CH), 6.9—7.2 (4 H, m, ArH), and 7.3—7.6 (4 H, m, ArH); m/z 328 (M^+), 293 ($M^+ - $ Cl), 258 (293 — Cl), 213 (258 — CHS), and 129.

(iii) *Cyclopentadiene.* The ylide (10b) (0.50 g, 0.0016 mol) and freshly distilled cyclopentadiene (~1 ml) were stirred in dichloromethane at −78 °C for 30 min, and the solution was kept at ambient temperature overnight. Removal of the solvent and elution of the residue through a silica column with light petroleum–chloroform (1 : 4) gave an oil which was further purified by p.l.c. (chloroform as developer) to give the *ylide adduct* (28b) (0.12 g, 20%) as crystals from ethyl acetate–light petroleum, m.p. 122—123 °C (Found: C, 38.4; H, 2.8; N, 3.8; S, 8.8; Cl, 37.4. $C_{12}H_{11}Cl_4NO_2S$ requires C, 38.4; H, 3.0; N, 3.7; S, 8.55; Cl, 37.08%); $v_{max.}$ 1 680 cm⁻¹ (CO); δ_H 1.25 (3 H, t, Me), 2.15—2.75 (2 H, m, 2 × CH), 3.50 (2 H, m, CH_2), 4.15 (2 H, t, OCH_2), and 6.33 and 6.55 (2 H, m, 2 × =CH); δ_C 163.3 (CO), 138.7 and 126.2 (thiophene C=C), 138.6 and 134.8 (CH=CH), 96.4 and 85.7 (2 × CCl), 57.0 and 55.8 (2 × CH), 62.4 (OCH_2), 49.0 (CH_2), and 14.3 p.p.m. (Me); m/z 373 (M^+) 338 ($M^+ - $ Cl), 328 ($M^+ - $ OEt), 286 (328 — NCO), 251 (286 — Cl), and 66 (C_5H_6).

(iv) *Cyclohexa-1,3-diene.* The ylide (10b) (0.50 g, 0.0016 mol) and cyclohexadiene (1 ml) were heated together under reflux for 2 h and the cooled material was separated on two p.l.c. plates developed with dichloromethane. The uppermost band (R_F 0.8) was removed and yielded oil (0.376 g) which was distilled in a Kugelrohr still (140 °C; 0.1 mmHg) to give 1,2,3,4-*tetrachloro-4a,5,6,8a-tetrahydronaphthalene* (30) (0.370 g, 85%) (Found: C, 44.2; H, 2.8. $C_{10}H_8Cl_4$ requires C, 44.49; H, 2.98%); δ_H 1.5—2.3 (4 H, m, 2 × CH_2), 2.8—3.1 (1 H, m, CH), 3.3—3.6 (1 H, m, CH), and 5.5—6.2 (2 H, m, CH=CH); m/z 268 (M^+), 233 ($M^+ - $ Cl), 198 (233 — Cl), 163 (198 — Cl), 121, 105, and 77.

(v) 2,3-*Dimethylbutadiene.* The ylide (10b) (0.50 g, 0.0016 mol) and 2,3-dimethylbutadiene (2 ml) were heated together under reflux for 1.5 h, after which the excess of diene reagent was evaporated off and the oily residue was chromatographed on silica gel, with dichloromethane as eluant, to give first 1,2,3,4-*tetrachloro-5-isopropenyl-5-methylcyclohexa-1,3-diene* (31) (0.30 g, 61%) as an oil, b.p. (Kugelrohr) 100 °C/0.15 mmHg (Found:

C, 44.0; H, 3.7; Cl, 51.2. $C_{10}H_{10}Cl_4$ requires C, 44.16; H, 3.71; Cl, 52.13%); δ_H 1.38 and 1.79 (together 6 H, 2 × s, 2 × Me), 2.64 and 2.96 (2 H, d, J 18 Hz, CH_2), 4.84 (1 H, s, =CH), and 4.94 (1 H, br s, =CH); δ_C 144.2 (s, C=CH_2), 137.1, 128.4, 125.9, and 123.5 (each s, C-1, -2, -3, and -4), 113.3 (t, =CH_2), 48.1 (s, C-5), 44.2 (t, CH_2), and 24.7 and 19.4 (each q, 2 × Me); the second product from the column was *ethyl N-[(α,β,2-trichloro-4,5-dimethyl-styryl)thio]carbamate* (32) (0.26 g, 46%) as a thick oil, δ_H 1.26 and 1.28 (3 H, t, CH_2Me), 2.25 (6 H, s, 2 × CMe), 4.25 and 4.27 (2 H, q, CH_2), 6.1 and 6.4 (1 H, br s, NH), and 7.19 and 7.22 (2 H, s, ArH) (the pairs of peaks for NH and Et groups are due to rotamers); δ_C 153.3 (C=O), 140.6, 135.9, 132.1, and 130.3 (Arom Cs and C=C), 63.2 (t, CH_2), and 19.7, 19.2, and 14.5 p.p.m. (each q, 3 × Me); m/z 353 (M^+), 318 ($M^+ - $ Cl), 245 (318 — CO_2Et), 230 (318 — $NHCO_2Et$), 210 (245 — Cl), 195 (230 — Cl); m/z (M^+) 352.9811. $C_{13}H_{14}^{35}Cl_3NO_2S$ requires M, 352.9811.

(vi) 2,5-*Dimethylfuran.* The ylide (10b) (0.50 g, 0.0016 mol) and 2,5-dimethylfuran (2 ml) were heated under reflux for 9 h and the dark solution was then evaporated. The residue was chromatographed on silica with chloroform as eluant to give 2,3,4,5-*tetrachloro-6-methylphenylacetone* (33) (0.44 g, 95%) which recrystallised from methanol as white needles, m.p. 128—129 °C (lit.,[25] 128—129 °C).

Reaction of the Ylide (10b) *with Dimethyl Acetylene-dicarboxylate.*—The ylide (10b) (0.50 g, 1.6 × 10⁻³ mol) was dissolved in dimethylacetylenedicarboxylate (0.23 g, 1.6 × 10⁻³ mol) and benzene (2 ml). The solution was stirred at 80 °C for 3 days. The benzene was distilled off and the residue was chromatographed on silica and eluted with chloroform to yield a yellow oil. This oil was further purified by p.l.c. with dichloromethane as developer. The band at R_F 0.52 yielded 5,6,7,8-*tetrachloro-2-ethoxycarbonyl-3,4-bis(methoxycarbonyl)-2H-1,2-thiazocine* (34) (0.07 g, 10%) as a white crystalline solid which recrystallised from ethyl acetate–light petroleum as yellow crystals, m.p. 110—111 °C (Found: C, 34.5; H, 2.5; N, 3.3; Cl, 30.5; S, 7.3. $C_{13}H_{11}Cl_4NO_6S$ requires C, 34.61; H, 2.46; N, 3.11; Cl, 31.44; S, 7.11%); $v_{max.}$ 1 710 br cm⁻¹ (COs); δ_H 1.40 (3 H, t, CH_2Me), 3.85 (3 H, s, OMe), 3.90 (3 H, s, OMe), and 4.40 (2 H, q, CH_2); m/z 449 (M^+), 414 ($M^+ - $ 2Cl), 344 ($M^+ - $ 3Cl), and 309 ($M^+ - $ 4Cl); δ_C 165.3, 159.3, 157.7, 153.4, 128.45, 127.2, 124.85, 124.3 (COs and ring Cs), 63.5 (CH_2), 54.8 and 53.8 (2 × OMe), and 14.2 p.p.m. (Me).

(c) *Oxidation of the Ylides. General Method.*—A solution of the ylide (0.50 g) in 1,2-dichloroethane (5 ml) was treated with a slight excess of MCPBA; the mixture was subjected to reflux and the reaction was followed by t.l.c. (silica) with dichloromethane as eluant. The hot solution was added to a column of silica (prepacked in dichloromethane) and elution with dichloromethane gave the products indicated. From the ethoxycarbonylamidoylide (10b) was obtained N-(*ethoxy-carbonyl*)-(*2,3,4,5-tetrachloro-1-thiophenio*)*amide S-oxide* (35) (84%) as pale yellow rhombs from pentane, m.p. 58—59 °C (Found: C, 25.7; H, 1.5; N, 4.25. $C_7H_5Cl_4NO_3S$ requires C, 25.9; H, 1.55; N, 4.3%); $v_{max.}$ 1 660 (CO), 1 270 and 1 190 (O–S–N), and 1 240 cm⁻¹ (OC–O); m/z 325 (M^+), 280 ($M^+ - $ OEt), 254 ($M^+ - CO_2Et$), 236 ($M^+ - $ NCOOEt), and 206 (C_4Cl_4O); δ_H 1.31 (t, Me) and 4.23 (q, CH_2); δ_C 154.8 (CO), 132.75 and 128.2 (thiophenic Cs), 63.4 (CH_2), and 14.1 p.p.m. (Me).

Under the same conditions the sulphonyl ylide (10d) was unchanged. The carbon ylide (24a) gave tetrachlorothiophene (79%) after only 5 min heating.

Reaction of the Sulphoximide (35) *with Alkenes.*—(i) A mixture of the sulphoximide (35) (0.19 g, 0.58 mmol) and acenaphthylene (0.09 g, 0.59 mmol) in dichloromethane (5 ml) was kept for 1 h and then solvent was removed. Distillation of

the residue in a Kugelrohr apparatus at 55 °C/ 20 mmHg gave ethyl sulphinylcarbamate (0.07 g, 89%) as an oil, identical (i.r. ^{1}H n.m.r.) with a sample prepared by Levchenko's excellent method.[28] The crystalline residue from the distillation was the dihydrofluoranthene (14), (0.19 g, 96%).

(ii) The above experiment was repeated with the added presence of 2,3-dimethylbutadiene (0.5 ml, 0.0061 mol), when a similar work-up gave, on distillation, the thiazine oxide (36) (0.11 g, 89%), b.p. 140 °C/0.5 mmHg, identical with a sample prepared by Levchenko's method[28] [$v_{max.}$ 1 700 (CO), 1 300, 1 270, 1 240, and 1 080 cm^{-1}; δ_H 1.28 (t, CH$_2Me$), 1.78 (s, 2 × Me), 3.17 (d, J 1.65 (Hz, SCH), 3.50 (1 H, br d, J 16.5 Hz, SCH), 4.00 (2 H, br s, CH$_2$), and 4.25 (q, OCH$_2$)].

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