Cycloaddition Reactions of Sulphines and Thiones with Azoalkenes

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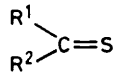
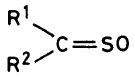
Fluorenethione *S*-oxide undergoes (2 + 4) cycloadditions with azoalkenes to yield 2*H*-1,2,3-thiadiazine 1-oxides together with a small amount of the regioisomeric 6*H*-1,3,4-thiadiazine 1-oxides. Fluorenethione, with azoalkenes, undergoes (2 + 4) regiospecific cycloaddition reactions leading to the formation of 6*H*-1,3,4-thiadiazine derivatives. Diarylsulphines and diarylthiones fail to react with azoalkenes.

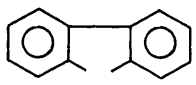
AZOALKENES are well known to undergo (4 + 2)-type cycloaddition reactions with a variety of carbon-carbon dienophiles [1-4] and heterodienophiles [5,6] leading to the formation of six-membered heterocyclic compounds.



(1)

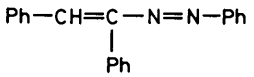


(2)

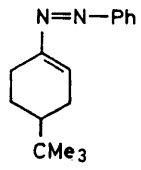
a; R^1, R^2 = 

b; $R^1 = R^2 = p$-MeC_6H_4

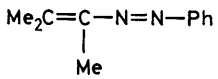
c; $R^1 = R^2 = p$-$NO_2C_6H_4$



(3)



(4)



(5)

Thiones and sulphines (thione *S*-oxides) represent an attractive class of heterodienophiles.[7] Many thiones [8-14] and a few particularly reactive sulphines [15,16] are, in fact, reported to undergo cycloaddition reactions with 1,3-dienes. We report here our results on the reactions of thiones (1a—c) and sulphines (2a—c) with azoalkenes (3)—(5).

RESULTS AND DISCUSSION

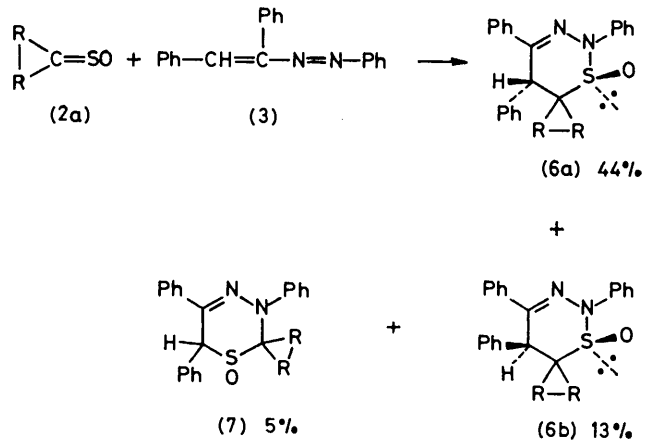
On reaction with (3) (mixture of *EE*- and *ZE*-isomers, see Experimental section) in benzene at room temperature, fluorenethione *S*-oxide (2a) gave, after one week, a mixture of the two diastereoisomers (6a) (44%) and (6b) (13%) together with a small amount of the regioisomer (7) (5%) in only one diastereoisomeric form (Scheme 1).

The structures of the products (6a), (6b), and (7) were assigned on the basis of the following evidence. Elemental analyses of the three compounds were correct for $C_{33}H_{24}N_2OS$ and mass spectra showed their molecular ions at *m/e* 496.

Mass spectra of both (6a) and (6b) showed the same fragmentation pattern with prominent peaks at *m/e* 357 (M^+ — PhNSO) and 139 (PhNSO), in agreement with the 1,2,3-thiadiazine structure. Their i.r. spectra displayed the same S=O absorption at 1 100 cm^{-1}, but in the n.m.r. spectra ($CDCl_3$) the H-5 signals exhibited different chemical shifts at δ 5.6 and 4.33, respectively, attributable to the different hydrogen stereochemistry of the two distereoisomers.

Compound (7) showed i.r. absorption of the S=O function at 1 080 cm^{-1} and its n.m.r. spectrum ($CDCl_3$) showed the H-6 signal at δ 5.44.

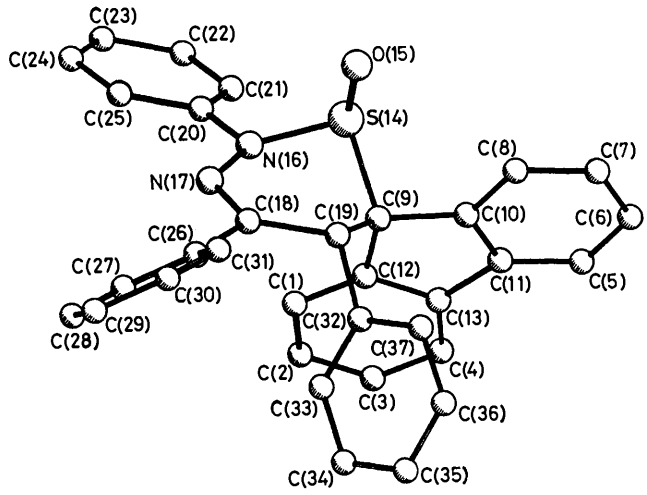
For final proof of the structures of (6a), (6b), and (7), an *X*-ray structural analysis was carried out on crystals



SCHEME 1

of (6a). Tables 1 and 2 list relevant bond lengths and angles, respectively; the molecule is shown in the Figure.

This analysis confirmed the proposed 1,2,3-thiadiazine structure and showed the oxygen *trans* to the C-5-phenyl. It is therefore reasonable that (6b) is the *cis*-isomer of



(6a), and (7) is one of the two possible 1,3,4-thiadiazine diastereoisomers.

The reaction of fluorenethione (1a) with phenylazostilbene (3) in benzene at room temperature, led, after 5 h, to the formation of (8) in very high yield (91%).

TABLE 1

Relevant interatomic bond lengths (Å) of compound (6a), with estimated standard deviations in parentheses; crystallographic numbering is shown in the Figure

	Molecule (A)	Molecule (B)
S(14)–O(15)	1.472(7)	1.481(7)
S(14)–C(9)	1.842(10)	1.844(10)
C(9)–C(19)	1.572(13)	1.555(13)
C(18)–C(19)	1.506(12)	1.515(13)
C(18)–N(17)	1.284(11)	1.280(11)
N(16)–N(17)	1.393(10)	1.404(10)
S(14)–N(16)	1.694(8)	1.684(8)

The structure of this adduct was established by oxidation with 1 mol equiv. of *m*-chloroperoxybenzoic acid (MCPBA), which gave the corresponding *S*-oxide, identical with adduct (7) (Scheme 2).*

Compound (7) in solution isomerizes into compounds (6a) and (6b).

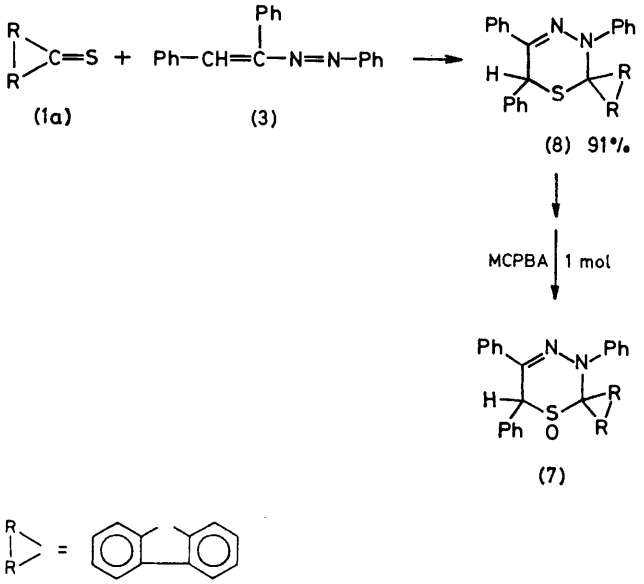
$$(7) \xrightarrow[1\text{ month}]{CDCl_3} \underset{53\%}{(6a)} + \underset{30\%}{(6b)} + \underset{17\%}{(7)}$$

TABLE 2

Relevant bond angles (°) for compound (6a) with estimated standard deviations in parentheses

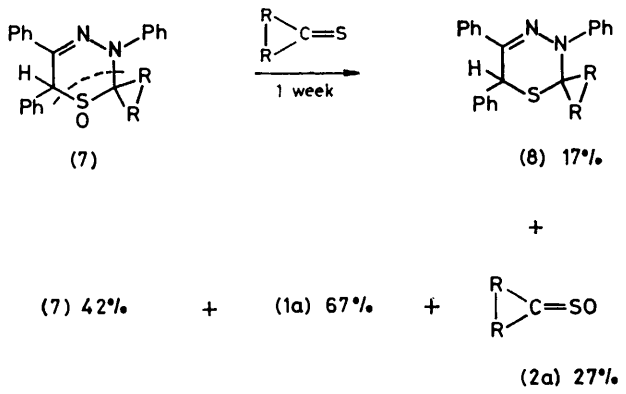
	Molecule (A)	Molecule (B)
N(16)–S(14)–O(15)	108.7(4)	109.6(4)
N(16)–S(14)–C(9)	93.9(4)	94.0(4)
O(15)–S(14)–C(9)	105.9(4)	105.6(4)
S(14)–C(9)–C(19)	106.7(6)	107.2(6)
S(14)–C(9)–C(12)	107.1(6)	105.3(6)
C(19)–C(9)–C(10)	114.4(7)	122.7(8)
C(9)–C(19)–C(18)	111.4(7)	112.6(7)
C(9)–C(19)–C(32)	113.4(7)	112.1(7)
C(18)–C(19)–C(32)	108.5(7)	109.3(7)
N(17)–C(18)–C(19)	128.3(8)	128.5(8)
N(17)–C(18)–C(26)	118.3(7)	118.4(7)
N(16)–N(17)–C(18)	120.4(8)	119.6(8)
S(14)–N(16)–N(17)	121.9(6)	121.5(6)
N(17)–N(16)–C(20)	119.8(6)	118.6(6)
S(14)–N(16)–C(20)	115.3(7)	114.2(7)

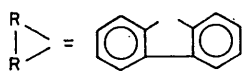
This isomerization probably takes place *via* a cycloreversion–recyclization process. Proof of such a mechanism is provided by the reaction of (7) with fluorene-



SCHEME 2

thione (1a) leading to the formation of sulphine (2a) which is expected for a cycloreversion, together with (8) arising from the recyclization of azoalkene with the new dipolarophile (fluorenethione) (Scheme 3).



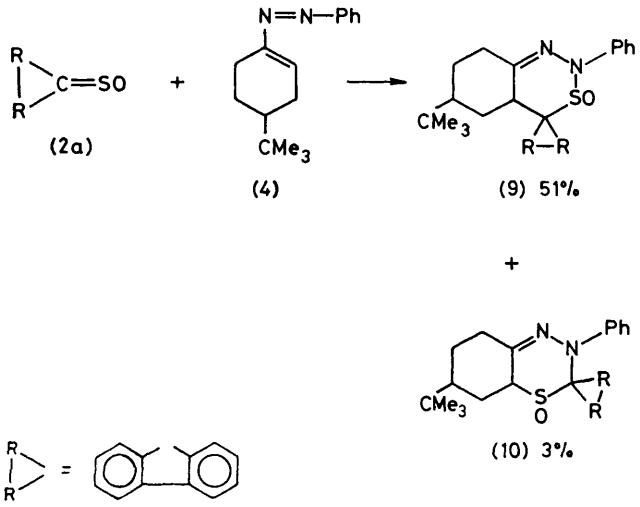


SCHEME 3

On reaction with azoalkene (4) in benzene at room temperature fluorenethione *S*-oxide (2a) gave, after one week, mainly the adduct (9) together with a small amount of the regioisomer (10) (Scheme 4).

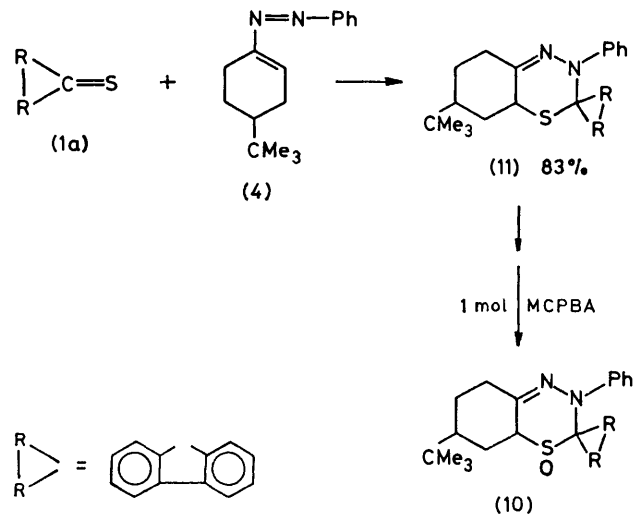
* One of the referees pointed out that the sulphinyl oxygen in (7) is almost certainly *trans*-oriented with respect to the adjacent phenyl group, owing to steric requirements for peroxyacid oxidation of sulphides to sulphoxides.

The structures of the products (9) and (10) were assigned on the basis of their analytical and spectral data by analogy with compounds (6a,b) and (7) (see Experimental section).



SCHEME 4

The reaction of fluorenethione (1a) with the same azoalkene (4) in benzene at room temperature for 5 h led to the formation of (11) in 83% yield. Oxidation of (11) with 1 mol of MCPBA gave the corresponding *S*-oxide, identical with the adduct (10).



SCHEME 5

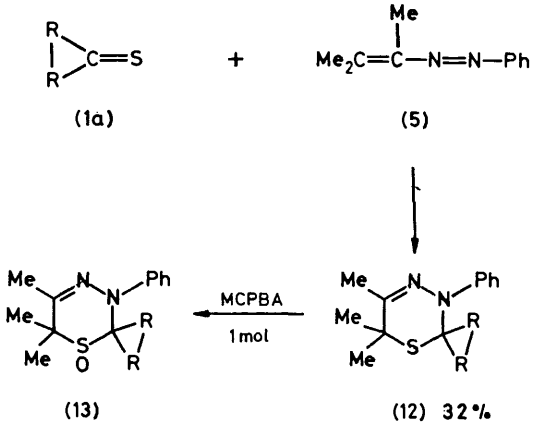
Compound (10), unlike (7), did not isomerize into compound (9). Fluorenethione *S*-oxide (2a) failed to react with the completely substituted azoalkene (5). Fluorenethione (1a), on the contrary, reacted with (5) in benzene at room temperature for 48 h giving the adduct (12) in 32% yield. Oxidation of (12) with 1 mol of MCPBA gave the corresponding *S*-oxide (13) (Scheme 6).

The structure of (13), and consequently that of (12), was assigned on the basis of its analytical and spectral data by analogy with compounds (7) and (10) (see Experimental section).

Both compounds (12) and (13) are rather unstable especially in solution, where they rapidly decompose to fluorenone and tars.

Thiones (1b,c) and sulphines (2b,c) failed to react with the azoalkenes (3)—(5).

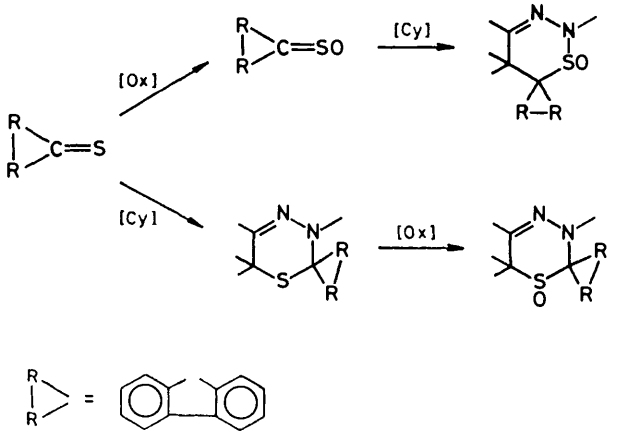
In conclusion, fluorenethione (1a) with the azoalkenes investigated, undergoes a (2 + 4) regiospecific cycloaddition reaction leading to the formation of 1,3,4-thiadiazine derivatives. Fluorenethione *S*-oxide (2a) with azoalkenes (3) and (4) undergoes a (2 + 4) cyclo-



SCHEME 6

addition reaction giving mainly 1,2,3-thiadiazine derivatives, *i.e.* the other regioisomer with respect to those obtained in the reaction with the thione.

This behaviour of fluorenethione (1a) and of its *S*-oxide



SCHEME 7

(2a) has already been observed in the 1,3-cycloaddition reactions with benzonitrile oxide,[17] and is rather unexpected, because the reactions of diarylthioketones and diarylsulphines with 1,3-dipoles [17,18] are regiospecific with the same orientation. Unfortunately we were not

able to obtain any adduct in the reaction of diarylthioketones and diarylsulphines with azoalkenes.

A salient preparative aspect of our experiments is the possibility of obtaining selectively the 1,2,3- and 1,3,4-thiadiazine systems from fluorenethione (1a) according to the order of sequence of MCPBA oxidation [Ox], and azoalkene–cycloaddition reactions [Cy] (Scheme 7).

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 grating spectrometer. ^{1}H N.m.r. spectra were run on a Varian XL-100 spectrometer ($SiMe_4$ as internal standard). Mass spectra were recorded with a JEOL JMS D100 spectrometer. All experiments were carried out under nitrogen and with dry solvents. Melting points are uncorrected.

Fluorenethione and fluorenethione *S*-oxide were prepared as described in refs. 19 and 20.

Phenylazoalkenes were prepared by published general procedures.[21-23]

Phenylazostilbene (3).—Phenylhydrazine (8.64 g, 8 mmol) was added to a solution of acetoxydeoxybenzoin (10 g, 3.9 mmol) in benzene (150 ml) and the mixture was allowed to stand at room temperature for 3 days. The orange solution was washed first with saturated aqueous Na_2CO_3 and then water, dried (Na_2SO_4), and evaporated under vacuum. The oily residue was chromatographed on a silica gel column with benzene–cyclohexane (1 : 4, v/v) as eluant. The product obtained (6.1 g, 55%) was a *ca.* 1 : 1 mixture of (*EE*)- and (*ZE*)-phenylazostilbenes. This mixture was directly used in our reactions with (1a—c) and (2a—c) owing to the observed interconversion of each isomer into the other one when dissolved in benzene, chloroform, or dichloromethane. Nevertheless the components of the mixture could be separated by several careful crystallizations from n-pentane.

(*ZE*)-Phenylazostilbene: orange needles m.p. 84—86 °C; $\lambda_{max.}$ (n-hexane) 234 (ε 13 888), 337 (29 978), 346 (31 164), and 447 nm (677) (Found: C, 83.4; H, 5.7; N, 9.8. $C_{20}H_{16}N_2$ requires C, 84.48; H, 5.67; N, 9.85%).

(*EE*)-Phenylazostilbene: deep red crystals, m.p. 72—73 °C; $\lambda_{max.}$ (n-hexane) 261 (ε 23 490), 354 (16 650), and 470 nm (559) (Found: C, 84.5; H, 5.6; N, 9.8. $C_{20}H_{16}N_2$ requires C, 84.48; H, 5.67; N, 9.85).

1-*Phenylazo*-4-*t*-*butylcyclohex*-1-*ene* (4).—Phenylhydrazine (8.64 g, 8 mmol) was added at room temperature to a stirred solution of t-butylcyclohexanone (9.32 g, 4 mmol) in benzene (150 ml). After 10 min the orange solution was washed first with saturated aqueous Na_2CO_3 then with water, dried (Na_2SO_4), and evaporated under vacuum. The residue was purified by chromatography on a silica gel column eluting with benzene–cyclohexane (1 : 1, v/v). A red-orange fraction was collected (6.0 g, 62%), m.p. 64—68 °C from methanol; $\lambda_{max.}$ (n-hexane) 305 nm (ε 23 442); δ ($CDCl_3$) 0.94 (9 H, s, Bu^t), 1.24—2.97 (7 H, m), 6.90—7.08 (1 H, m, vinylic H), and 7.3—7.9 (5 H, m, ArH) (Found: C, 78.4; H, 9.2; N, 12.0. $C_{16}H_{22}N_2$ requires C, 79.29; H, 9.15; N, 11.56)

2-*Methyl*-3-*phenylazobut*-2-*ene* (5).—3-Chloro-3-methylbutan-2-one (4.80 g, 4 mmol) was treated with phenylhydrazine (8.64 g, 8 mmol) in benzene (150 ml) with the same procedure used for the preparation of (4). A red oil (3.13 g, yield 45%) was collected by chromatography of the reaction mixture on a silica gel column eluting with benzene–cyclohexane (1 : 1, v/v); $\lambda_{max.}$ (n-hexane) 315 nm (ε 19 400); δ ($CDCl_3$) 1.84 (3 H, s, Me), 2.12 (3 H, s, Me), 2.36 (3 H, s, Me), and 7.1—8.2 (5 H, m, ArH) (Found: C, 76.2; H, 8.0; N, 15.8. $C_{11}H_{14}N_2$ requires C, 75.82; H, 8.10; N, 16.08%).

3′,6′-*Dihydro*-3′,5′,6′-*triphenylspiro*(*fluorene*-9,2′-[1,3,4]-*thiadiazine*) (8).—A solution of fluorenethione (0.345 g, 1.76 mmol) in benzene (15 ml) was added, at room temperature, to a stirred solution of phenylazostilbene (0.5 g, 1.76 mmol) in benzene (15 ml). After 5 h the reaction mixture was chromatographed on a silica gel column. Elution with benzene gave first brown tars (0.03 g), then the *adduct* (8) (0.77 g, 91%), m.p. 166—167 °C (from ethanol) (Found: C, 82.4; H, 5.1; N, 6.0; S, 6.5. $C_{33}H_{24}N_2S$ requires C, 82.47; H, 5.03; N, 5.83; S, 6.67%); δ ($CDCl_3$) 5.51 (1 H, s, H-6) and 6.7—7.9 (23 H, m, Ar-H); *m/e* 480 (M^+), 448 (M^+ — S), 284 (M^+ — fluorenethione), 196 (fluorenethione), and 178 (PhCCPh).

3′,6′-*Dihydro*-3′,5′,6′-*triphenylspiro*(*fluorene*-9,2′-[1,3,4]-*thiadiazine*) 1′-*Oxide* (7).—Adduct (8) (0.53 g, 1.1 mmol) in chloroform (25 ml) was treated with *m*-chloroperbenzoic acid (1.1 mmol) in chloroform (10 ml) for 12 h at 0 °C (until disappearance of the peracid). Usual work-up and subsequent chromatography on a silica gel column (eluant benzene) gave first brown tars (0.04 g), then fluorenone (0.06 g, 30.2%), and finally an oily product (0.4 g). This, after washing with ether, gave the *sulphoxide* (7) (0.25 g, 45.7%), m.p. 144—145 °C (from benzene–n-pentane at −15 °C) (Found: C, 79.3; H, 5.0; N, 5.5; S, 6.4. $C_{33}H_{24}N_2OS$ requires C, 79.81; H, 4.87; N, 5.64; S, 6.46%); $\nu_{max.}$ (CCl_4) 1 080 cm^{-1} (SO); δ ($CDCl_3$) 5.44 (1 H, s, H-6) and 6.8—8.0 (23 H, m, Ar-H); *m/e* 496 (M^+), 448 (M^+ — SO), 284 (M^+ — fluorenethione *S*-oxide), 212 (fluorenethione *S*-oxide), 196 (fluorenethione), and 178 (PhCCPh).

Reaction of Phenylazostilbene with Fluorenethione S-*Oxide*.—A solution of fluorenethione *S*-oxide (0.097 g, 0.46 mmol) in benzene (10 ml) was added, at room temperature, to a stirred solution of phenylazostilbene (0.13 g, 0.46 mmol) in benzene (15 ml). Stirring was continued for 1 week. Chromatography of the reaction mixture on silica gel plates (benzene eluant) gave four fractions; first brown tars (0.04 g); then a mixture of fluorenethione *S*-oxide and of cis-2′,5′-*dihydro*-2′,4′,5′-*triphenylspiro*(*fluorene*-9,6′-[1,2,3]-*thiadiazine*)1′-*oxide* (6b) (0.064 g); then the adduct trans-2′,5′-*dihydro*-2′,4′,5′-*triphenylspiro*(*fluorene*,9,6′-[1,2,3]-*thiadiazine*)1′-*oxide* (6a) (0.1 g, 44%); and finally the adduct (7) (0.011 g, 5%). The mixed fraction was chromatographed on silica gel plates with benzene–light petroleum (5 : 1, v/v) as eluant to give, as the faster-moving fraction, unreacted fluorenethione *S*-oxide (0.021 g, 21.6%), and as the slower-moving fraction the adduct (6b) (0.03 g, 13%). Physical and spectral data of (6a) and (6b): compound (6a) m.p. 194—195 °C (from ethanol) (Found: C, 79.8; H, 5.0; N, 5.7; S, 6.4. $C_{33}H_{24}N_2OS$ requires C, 79.81; H, 4.87; N, 5.64; S, 6.46%); $\nu_{max.}$ (CCl_4) 1 100 cm^{-1} (SO); δ ($CDCl_3$) 5.60 (1 H, s, H-5), 6.5—6.8 (5 H, m, Ar-H), 7.1—7.9 (17 H, m, Ar-H), and 8.15—8.35 (1 H, m, Ar-H); *m/e* 496 (M^+), 448 (M^+ — SO), 391 (M^+ — PhNN), 357 (M^+ — PhNSO), 284 (M^+ — fluorenethione *S*-oxide), 254 [9-(phenylmethylene)fluorene], 212 (fluorenethione *S*-oxide), 196 (fluorenethione), 179 (PhCHCPh), and 139 (PhNSO). Compound (6b), m.p. 199—200 °C (from ethanol) (Found: C, 79.2; H, 5.0; N, 5.5; S, 6.4. $C_{33}H_{24}N_2OS$ requires C, 79.81; H, 4.87; N, 5.64; S, 6.46%); $\nu_{max.}$ (CCl_4) 1 100 cm^{-1} (SO); δ ($CDCl_3$) 4.34 (1 H, s, H-5), 6.44—6.8 (2 H, m, Ar-H), and 6.9—8.0 (21 H, m, Ar-H); *m/e* 496 (M^+), 448 (M^+ — SO), 391 (M^+ — PhNN), 357 (M^+ —

PhNSO), 284 (M^+ — fluorenethione *S*-oxide), 254 [9-(phenylmethylene)fluorene], 212 (fluorenethione *S*-oxide), 196 (fluorenethione), 179 (PhCHCPh), and 139 (PhNSO).

Isomerization of (7).—A solution of (7) in $CDCl_3$ was allowed to stand at room temperature for 1 month. The n.m.r. spectrum recorded after this time showed the presence of unreacted (7) (17%), and (6a) (53%) and (6b) (30%). The ratio of the three isomers was determined by integrating the H-6 [for (7)] and H-5 [for (6a) and (6b)] signals, at δ 5.44, 5.60, and 4.34, respectively.

Reaction of (7) *with Fluorenethione.*—A solution of fluorenethione (0.024 g, 0.12 mmol) in chloroform (5 ml) was added at room temperature to a stirred solution of (7) (0.06 g, 0.12 mmol) in chloroform (5 ml). Stirring was continued for 1 week. Chromatography of the reaction mixture on silica gel plates with benzene as eluant gave six fractions (in order of decreasing R_F); unreacted fluorenethione (0.016 g, 67%), (8) (0.01 g, 17%), brown tars (0.01 g), fluorenethione *S*-oxide (0.007 g, 27.3%) which was compared with an authentic sample,[2] fluorenone * (0.005 g, 23%), and unreacted (7) (0.025 g, 42%).

2′,3′,5′,6′,7′,8′-Hexahydro-2′-phenyl-6′-t-butylspiro(fluorene-9,3′-[4,1,2]benzothiadiazine) (11).—A solution of fluorenethione (0.245 g, 1.25 mmol) in benzene (5 ml) was added at room temperature to a stirred solution of 1-phenylazo-4-t-butylcyclohex-1-ene (4) (0.3 g, 1.25 mmol) in benzene (5 ml). After 5 h the reaction mixture was chromatographed on a silica gel column. Elution with benzene gave first brown tars (0.04 g), then the *adduct* (11) (0.45 g, 82.9%) and finally fluorenone (0.02 g, 8.9%). Physical and spectral data of (11): m.p. 169—170 °C (from benzene–n-pentane) (Found: C, 79.6; H, 6.9; N, 6.4; S, 7.4. $C_{29}H_{30}N_2S$ requires C, 79.41; H, 6.89; N, 6.39; S, 7.31%), δ ($CDCl_3$) 0.90 (9 H, s, Bu^t), 1.1—3.05 (7 H, m), 3.64—4.0 (1 H, m), 6.5—7.5 (11 H, m, Ar-H), and 7.6—7.8 (2 H, m, Ar-H); *m/e* 438 (M^+) 379 ($M^+ - Bu^t - 2$ H), 255 (*N*-fluorenilideneaniline), 242 (M^+ — fluorenethione) and 196 (fluorenethione).

2′,3′,5′,6′,7′,8′-Hexahydro-2′-phenyl-6′-t-butylspiro(fluorene-9,3′-[4,1,2]benzothiadiazine) 4′-Oxide. (10).—Adduct (11) (0.145 g, 0.33 mmol) in ether (20 ml) was treated with *m*-chloroperbenzoic acid (0.33 mmol) in ether (5 ml) for 3 days at 0 °C (until disappearance of the peracid). Usual work-up and subsequent chromatography on silica gel plates with benzene as eluant gave, as the higher R_F fraction fluorenone (0.015 g, 25.2%) and as the lower R_F fraction the *sulphoxide* (10) (0.07g, 46.7%), m.p. 155—156 °C (from benzene–n-pentane) (Found: C, 76.3; H, 6.6; N, 6.1; S, 7.0. $C_{29}H_{30}N_2OS$ requires C, 76.61; H, 6.65; N, 6.16; S, 7.05%); $\nu_{max.}$ (CCl_4) 1 070 cm^{-1} (SO); δ ($CDCl_3$) 0.96 (9 H, s, Bu^t), 1.3—3.8 (8 H, m), and 6.6—7.9 (13 H, m, Ar-H); *m/e* 454 (M^+), 406 (M^+ — SO), 255 (*N*-fluorenilideneaniline), 242 (M^+ — fluorenethione *S*-oxide), 212 (fluorenthione *S*-oxide), and 196 (fluorenethione).

Reaction of 1-Phenylazo-4-t-butylcyclohex-1-ene with Fluorenethione S-Oxide.—A solution of fluorenethione *S*-oxide (0.785 g, 3.7 mmol) in benzene (15 ml) was added at room temperature to a stirred solution of 1-phenylazo-4-t-butylcyclohex-1-ene (4) (0.9 g, 3.7 mmol) in benzene (15 ml). After 1 week the reaction mixture was chromatographed on a silica gel column. Elution with benzene gave first brown tars (0.2 g) then unreacted fluorenethione *S*-oxide (0.3 g, 38.2%). Elution with methylene chloride gave first the adduct *4′,4a′,5′,6′,7′,8′-hexahydro-2′-phenyl-6′-t-butylspiro(fluorene-9,4′-[3,1,2]benzothiadiazine) 3′-oxide* (9) (0.86 g, 51%), then the adduct (10) (0.05 g, 3%). Physical and spectral data of (9): m.p. 196—197 °C (from ethanol) (Found: C, 76.8; H, 6.7; N, 6.3; S, 7.2. $C_{29}H_{30}N_2OS$ requires C, 76.61; H, 6.65; N, 6.16; S, 7.05%); $\nu_{max.}$ (CCl_4) 1 100 cm^{-1} (SO); δ ($CDCl_3$) 0.56 (9 H, s, Bu^t), 0.7—2.0 (5 H, m), 2.4—3.1 (2 H, m), 3.7—4.0 (1 H, m), 7.0—7.62 (10 H, m, Ar-H), and 7.7—7.9 (3 H, m, Ar-H); *m/e* 454 (M^+), 406 (M^+ — SO), 349 (M^+ — SO — Bu^t), 314 (M^+ — PhNSO — H), 242 (M^+ — fluorenethione *S*-oxide), 212 (fluorenethione *S*-oxide), and 196 (fluorenethione).

3′,6′-Dihydro-3′-phenyl-5′,6′,6′-trimethylspiro(fluorene-9,2′-[1,3,4]thiadiazine) (12).—A solution of fluorenethione (0.334 g, 1.7 mmol) in benzene (10 ml) was added, at room temperature, to a stirred solution of 2-methyl-3-phenylazo-but-2-ene (0.296 g, 1.7 mmol) in benzene (10 ml). After 48 h the reaction mixture was chromatographed on a silica gel column. Elution with benzene gave first brown tars (0.2 g), then fluorenone (0.12 g, 39.1%), and finally the *adduct* (12) (0.2 g, 31.8%), m.p. 120—121 °C (from benzene–n-pentane at −15 °C) (Found: C, 77.4; H, 6.0; N, 7.5; S, 8.5. $C_{24}H_{22}N_2S$ requires C, 77.80; H, 5.99; N, 7.56; S, 8.65%); δ ($CDCl_3$) 1.70 (6 H, s, Me), 2.27 (3 H, s, Me), 6.56—7.0 (5 H, m, Ar-H), and 7.1—7.8 (8 H, m, Ar-H); *m/e* 370 (M^+), 255 (*N*-fluorenilideneaniline), 196 (fluorenethione), 174 (M^+ — fluorenethione), and 132 (MeCNNPh).

3′,-6′Dihydro-3′-phenyl-5′,6′,6′-trimethylspiro(fluorene-9,2′-[1,3,4]thiadiazine) 1′-Oxide (13).—Adduct (12) (0.07 g, 0.19 mmol) in ether (10 ml) was treated with *m*-chloroperbenzoic acid (0.19 mmol) in ether (5 ml) for 6 days at 0 °C (until disappearance of the starting adduct). Usual work-up and subsequent chromatography on silica gel plates with benzene as eluant gave as the higher-R_F fraction fluorenone (0.005 g, 14.7%) and as the lower-R_F fraction the sulphoxide (13) (0.048 g, 65.8%), m.p. 127—128 °C (from benzene–n-pentene at −15 °C) (Found: C, 74.3; H, 5.8; N, 7.0; S, 8.2. $C_{24}H_{22}N_2OS$ requires C, 74.58; H, 5.74; N, 7.25; S, 8.30%); $\nu_{max.}$ (CCl_4) 1 075 cm^{-1} (SO); δ ($CDCl_3$) 1.60 (3 H, s, Me), 1.70 (3 H, s, Me), 2.28 (3 H, s, Me), 6.6—7.07 (5 H, m, Ar-H), and 7.13—7.8 (8 H, m, Ar-H); *m/e* 386 (M^+), 338 (M^+ — SO), 255 (*N*-fluorenilidineaniline), 212 (fluorenethione *S*-oxide), 196 (fluorenethione), and 174 (M^+ — fluorenethione *S*-oxide).

X-Ray Diffraction.—Single-crystal intensity data for derivative (6a) were collected by use of an automatic Philips PW 1100 diffractometer and Mo-K_α radiation (λ = 0.7107 Å). Of 4 998 independent reflections, 3 451 having $I > 2.5\sigma(I)$ were considered observed and used in the analysis.

Crystal data. $C_{33}H_{24}N_2OS$, M = 496.5. Triclinic, space group = $P\bar{1}$, a = 17.707, b = 13.375, c = 12.942 Å, α = 117.79, β = 87.11, γ = 106.55°; D_c = 1.21 g cm^{-3}, Z = 4.

The structure was solved by direct methods by use of the SHEL-X program system.[24] In the structure refinement only S and O atoms were treated anisotropically. The carbon atoms of the phenyl rings were refined as rigid groups. The final R was 0.095. Atomic co-ordinates and observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 23052 (27 pp.).†

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* Fluorenone can arise from the partial decomposition of both fluorenethione and its *S*-oxide.

† For details see *J. Chem. Soc., Perkin Trans. 1*, 1980, Index issue.

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