

## Sulphines. Part IV.<sup>1</sup> Reactions of Aromatic Sulphines with Diazoalkanes

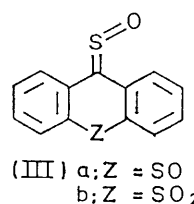
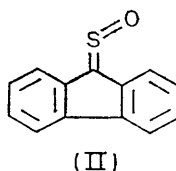
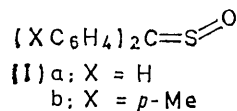
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The cycloaddition reactions of aromatic sulphines, such as thiobenzophenone *S*-oxide and thiofluorenone *S*-oxide, with 2-diazopropane lead to 1,3,4-thiadiazoline 1-oxides in high yields. Diazomethane reacts more sluggishly with sulphines: only with thiofluorenone *S*-oxide was a cycloadduct obtained. The structure of the cycloadducts has been proven by photochemical extrusion of sulphur monoxide from 2,2-dimethyl-5,5-di-(*p*-tolyl)-1,3,4-thiadiazoline 1-oxide. In solution the cycloadducts readily undergo a retro-cycloaddition. The adduct from thioxanthen-9-thione *SSS'*-trioxide and 2-diazopropane not only reverts to the starting sulphine, but also shows a reversed retro-cycloaddition reaction to give diazothioxanthen *SS*-dioxide and thioacetone *S*-oxide.

CYCLOADDITION reactions with heterocumulenes often provide an attractive method for the synthesis of heterocyclic compounds.<sup>2</sup> We report here the cycloaddition reaction of diazoalkanes with aromatic sulphines (thione *S*-oxides), which are now readily accessible by oxidation of thienes with peroxy-acids.<sup>3,4</sup>

Thiobenzophenone *S*-oxide (Ia), in a smooth reaction with 2-diazopropane, gave a 1:1 adduct in 90% yield, for which structure (IVa) is proposed. The i.r. spectrum displayed SO absorption at 1055 cm<sup>-1</sup> and an N=N band at 1560 cm<sup>-1</sup>, and the n.m.r. spectrum exhibited two non-equivalent methyl absorptions at δ 1.10 and 1.99 p.p.m. in addition to the aromatic multiplet. The sulphoxide (IVa) could be oxidized to the corresponding

sulphone (V), which showed, as expected, only one methyl signal in the n.m.r. spectrum (δ 1.57 p.p.m.).



The orientation of the cycloaddition was established unambiguously by the photolysis of the thiadiazoline

<sup>2</sup> H. Ulrich, 'Cycloaddition Reactions of Heterocumulenes,' Academic Press, New York, 1967.

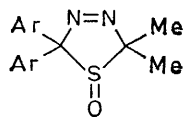
<sup>3</sup> B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1967, **86**, 577.

<sup>4</sup> B. F. Bonini, S. Ghersetti, G. Maccagnani, and G. Mazzanti, *Boll. sci. Fac. Chim. ind. Bologna*, 1969, **27**, 419.

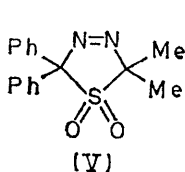
† Present address: Department of Organic Chemistry of the University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands.

<sup>1</sup> Part III, A. Battaglia, A. Dondoni, P. Giorgianni, G. Maccagnani, and G. Mazzanti, *J. Chem. Soc. (B)*, 1971, 1547; the present paper is also Part XV in the series 'Chemistry of Sulphines' by the Dutch group (Part XIV, *Rec. Trav. chim.*, accepted for publication).

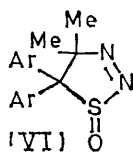
(IVb) [obtained from (Ib) and 2-diazopropane in 65% yield]. Irradiation \* in dichloromethane at  $-20^{\circ}$  gave the unsymmetrical azine (VII) and the symmetrical



(IV) a: Ar = Ph  
b: Ar = *p*-MeC<sub>6</sub>H<sub>4</sub>

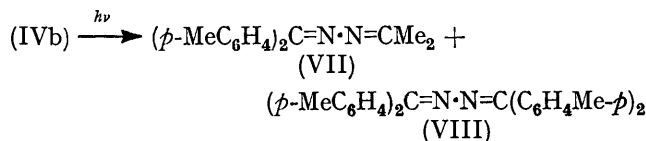


(V)



(VI)

azine (VIII), both identified by comparison (g.l.c. and n.m.r.) with authentic samples. The alternative adduct structure (VI) is thus ruled out, since it could not apparently yield the azine (VII). The symmetrical azine (VIII) arises from disproportionation of the unsymmetrical azine (VII). An independent experiment demonstrated the ease of this reaction.



Several unsuccessful attempts were made to extrude sulphur dioxide photochemically from the sulphone (V). However, chromatography of the sulphone (V) on neutral (grade I) alumina with dry light petroleum-ether (1 : 1) as eluant, gave a smooth elimination of sulphur dioxide to yield benzophenone isopropylidene hydrazone almost quantitatively.<sup>6</sup> This experiment independently substantiates the suggested direction of the cycloaddition. Until recently only two examples of S-oxides of 1,3,4-thiadiazoline had been reported.<sup>5,7,8</sup> The cycloaddition reactions of thiones<sup>9</sup> and sulphenes<sup>6,10</sup> with diazoalkanes in some cases give rise to the same heterocyclic system. A more general route<sup>5,7,8</sup> to these thiadiazolines, however, involves dehydrogenation of 1,3,4-thiadiazolidines.

Thiofluorenone S-oxide (II), the sulphoxide sulphine (IIIa) and the sulphone sulphine (IIIb) also react smoothly with 2-diazopropane to give the five-membered ring adducts (IXa), (IXa), and (IXb), respectively. The n.m.r. spectra of these three thiadiazoline S-oxides show

\* During the preparation of this manuscript it was reported<sup>5</sup> that photolysis of cyclohexanespiro-2'-1',3',4'-thiadiazoline-5'-spirocyclohexane 1'-oxide gave cyclohexanone azine in 54% yield. This result agrees well with our finding.

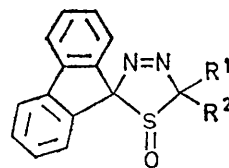
<sup>5</sup> D. H. R. Barton and B. J. Willis, *J.C.S. Perkin I*, 1972, 305.

<sup>6</sup> Cf. G. Hesse and E. Reichold, *Chem. Ber.*, 1957, **90**, 2101.

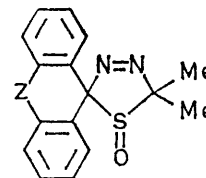
one aromatic proton resonance at higher field than the others, owing to the fact that in these spiro-cycloadducts the *peri*-proton of one of the aromatic rings is situated in the shielding zone of the sulphoxide group.

The reaction of the sulphine (II) and diazoethane gave the cycloadduct (IXb) in 50% yield. The n.m.r. spectrum indicated that only one of the possible pair of diastereoisomers had been isolated.

Diazomethane reacted more sluggishly with sulphines. In most cases a complex mixture of products was obtained. Only thiofluorenone S-oxide gave the desired 1 : 1 cycloadduct (IXc), in 50% yield. The n.m.r.



(IX) a: R<sup>1</sup> = R<sup>2</sup> = Me  
b: R<sup>1</sup> = H, R<sup>2</sup> = Me  
c: R<sup>1</sup> = R<sup>2</sup> = H



(X) a: Z = SO  
b: Z = SO<sub>2</sub>

spectrum of this adduct (IXc) clearly showed the AB quartet due to the methylene protons adjacent to the pyramidal sulphoxide group, indicating that no prototropic shift to the  $\Delta^2$ -isomer had taken place. As in the case of the other spiro-cycloadducts (IXa and b) and (Xa and b) this product (IXc) also showed a single aromatic proton absorbing at a higher field than the others.

The cycloadducts from sulphines and diazoalkanes are unstable; they slowly deteriorate on storage, some of them even below  $0^{\circ}$ . It is therefore essential that the reaction conditions for the cycloaddition are chosen such that the products crystallize from the reaction mixture.

Solutions of the adducts (IV), (IX), and (X) in chloroform often became purple-coloured, especially if gently warmed. The i.r. spectrum of such a solution displayed absorption at 2050–2070  $\text{cm}^{-1}$  characteristic of a diazo-function. These observations suggested a retro-cycloaddition reaction. This reaction was examined in more detail for adduct (Xb). In dichloromethane, in the presence of silica gel at room temperature, a smooth and clean reaction was observed and the aromatic diazo-sulphone (XI) (60%) and the sulphone sulphine (IIIb) (39%) were isolated. In the n.m.r. spectrum of a solution of adduct (Xb) in [<sup>2</sup>H]chloroform warmed at  $40^{\circ}$  for a few minutes, signals for the aromatic protons of the diazo-compound (XI)<sup>11</sup> and the sulphine (IIIb) were present. In the aliphatic region two quadruplets were

<sup>7</sup> R. M. Kellogg, S. Wassenaar, and J. Buter, *Tetrahedron Letters*, 1970, 4689.

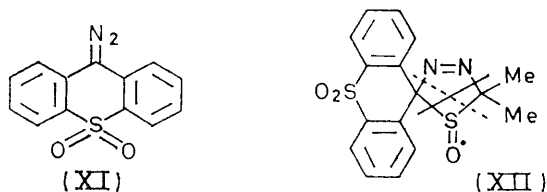
<sup>8</sup> D. H. R. Barton, E. H. Smith, and B. J. Willis, *Chem. Comm.*, 1970, 1226.

<sup>9</sup> A. P. Krapcho, D. R. Rao, M. P. Silvon, and B. Abegaz, *J. Org. Chem.*, 1971, **36**, 3885, and references cited therein.

<sup>10</sup> H. H. Inhoffen, R. Jonas, H. Krösche, and U. Eder, *Annalen*, 1966, **694**, 19.

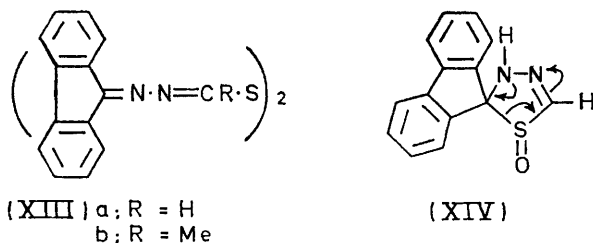
<sup>11</sup> F. Klages and K. Bott, *Chem. Ber.*, 1964, **97**, 735.

observed, at  $\delta$  2.08 and 2.33 p.p.m. ( $J$  ca. 1 Hz), attributed to the methyl protons of thioacetone *S*-oxide.\* These results indicate that ring scission has taken place in two different ways, *viz.* the retro-cycloaddition [dotted line in (XII)] and the reverse retro-reaction [(XII) solid line].



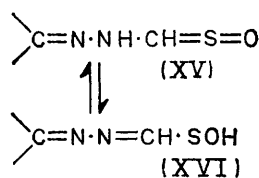
The cycloadduct (IXc) from thiofluorenone *S*-oxide and diazomethane, when passed through a column of silica gel, gave an orange-red product ( $C_{28}H_{18}N_4S_2$ ) to which structure (XIIIa) is tentatively assigned. Its i.r. spectrum displayed a C=N band at  $1621\text{ cm}^{-1}$  and its n.m.r. spectrum showed, besides the aromatic multiplet at  $\delta$  8.4–7.2, a singlet at  $\delta$  8.12 p.p.m. (=CH). The mass spectrum showed a weak molecular ion peak at  $m/e$  474 and a strong peak at  $m/e$  442 ( $M - S$ , indicative of the disulphide system<sup>13</sup>).

The formation of structure (XIIIa) can be envisaged, as involving a prototropic shift, most likely catalysed by the silica gel, in (IXc), leading to its  $\Delta^2$ -isomer (XIV). Subsequent ring opening gives the aminosulphine (XV), which is in tautomeric equilibrium<sup>14</sup> with the imino-sulphenic acid from (XVI). Disproportionation<sup>14</sup> of the latter then gives the disulphide (XIIIa). Oxidations of several thioamides and thiourethanes similarly give rise to disulphides *via* an intermediate aminosulphine.<sup>14</sup>



(XIII) a; R = H  
b; R = Me

(XIV)



Support for this reaction sequence is found in the fact that the cycloadduct (IXb) is converted into a

\* Thioacetone *S*-oxide,<sup>12</sup> produced in solution ( $CH_2Cl_2$ ) by dehydrohalogenation of 1-methylethanesulphonyl chloride with triethylamine, showed two methyl signals as quadruplets at  $\delta$  2.10 and 2.32 p.p.m., ( $J$  ca. 1 Hz). 2-Diazopropane which is also expected, decomposes rapidly in solution at  $40^\circ$ .

<sup>12</sup> Cf. W. A. Sheppard and J. Diekmann, *J. Amer. Chem. Soc.*, 1964, **86**, 1891 (the n.m.r. data were kindly supplied by Dr. W. A. Sheppard).

similar product, *viz.* (XIIIb), whereas (IXa), lacking protons at C-2 required for the prototropic shift, only shows retro-cycloaddition reactions.

## EXPERIMENTAL

I.r. spectra were taken on a Perkin-Elmer 225 or 257 spectrometer. N.m.r. spectra were taken on a Jeol PS 100 or C 60 HL spectrometer. Spectra of compounds (IVb), (IXc), (Xa), and (Xb) were analysed with a Varian A-60D spectrometer. Chemical shifts are reported in p.p.m. from internal tetramethylsilane. Mass spectra were determined on a Jeol MS-OISG double-focusing spectrometer.

Elemental analyses of the adducts (IV), (IX), and (X) and of the sulphone (V) were performed immediately after isolation or purification, owing to their instability. Even so certain analytical data are unsatisfactory.

**2,2-Dimethyl-5,5-diphenyl-1,3,4-thiadiazoline 1-Oxide (IVa).**—2-Diazopropane<sup>15</sup> in ethereal solution (1.1 equiv.) was added slowly to a stirred and cooled ( $-10^\circ$ ) solution of the sulphine (Ia) (1.5 g, 7.0 mmol) in ether (20 ml). After 24 h the white adduct (IVa) was filtered off, washed with dry ether, and recrystallized from dichloromethane-hexane (yield 1.79 g, 90%); m.p.  $93-94^\circ$  (Found: C, 68.4; H, 5.45; N, 9.7.  $C_{16}H_{16}N_2OS$  requires C, 67.55; H, 5.65; N, 9.85%); for i.r. and n.m.r. spectra see text.

Oxidation was performed as follows. A solution of monoperphthalic acid (3.5 mmol) in ether was added at  $0^\circ$  to the adduct (IVa) (0.5 g, 1.74 mmol) dissolved in chloroform (10 ml). After 10 h at  $5^\circ$  the oxidation was still not complete. Phthalic acid was filtered off, the filtrate was concentrated, and the residue chromatographed on silica. Elution with benzene afforded the sulphone (V), which was crystallised from dichloromethane-hexane (yield 0.20 g, 38%); m.p.  $94-95^\circ$  (Found: C, 63.1; H, 5.35; N, 9.2.  $C_{16}H_{16}N_2O_2S$  requires C, 63.95; H, 5.35; N, 9.3%),  $\nu_{max}$  ( $CCl_4$ ) 1130 and  $1325\text{ cm}^{-1}$  ( $SO_2$ );  $\delta$  ( $CCl_4$ ) 1.57 (6H, s, Me) and 7.2–7.7 (10H, m, ArH).

**Benzophenone Isopropylidenehydrazone from the Sulphone (V).**—A solution of the sulphone (V) (150 mg, 0.5 mmol) in anhydrous benzene (10 ml) was passed through a column of neutral grade I alumina. Elution with anhydrous light petroleum-ether (1 : 1) gave the azine (100 mg, 85%) as a low-melting solid (traces of solvent strongly depress the m.p.), identical (i.r. and n.m.r. spectra) with an authentic sample<sup>16</sup> (m.p.  $60^\circ$ ).

**2,2-Dimethyl-5,5-di-p-tolyl-1,3,4-thiadiazoline 1-Oxide (IVb).**—2-Diazopropane in ethereal solution (1 equiv.) was added to a cooled ( $-10^\circ$ ) solution of the sulphine (Ib)<sup>4</sup> (2.42 g, 10 mmol) in dichloromethane (10 ml) and ether (5 ml). The mixture was immediately decolorised. The solvents were removed *in vacuo* until crystallization occurred. The product was filtered off (1.75 g) and the mother liquor concentrated giving another 0.3 g of cycloadduct (yield 65%); m.p.  $84-85^\circ$  (decomp.) (Found: C, 68.9, 69.15; H, 6.45, 6.5; N, 9.0, 8.95; S, 10.1, 10.25.  $C_{18}H_{20}N_2OS$  requires C, 69.2; H, 6.45; N, 8.95; S, 10.25%),  $\nu_{max}$  (KBr) 1065 ( $S=O$ ) and  $1560\text{ cm}^{-1}$  ( $N=N$ );  $\delta$  ( $CDCl_3$ ) 1.10 (s, Me), 1.97

<sup>13</sup> J. H. Bowie, S.-O. Lawesson, J. O. Madsen, C. Nolde, G. Schroll, and D. H. Williams, *J. Chem. Soc. (B)*, 1966, 946.

<sup>14</sup> Cf. W. Walter and K.-D. Bode, *Annalen*, 1965, **681**, 64.

<sup>15</sup> S. D. Andrews, A. C. Day, and P. Raymond, *Org. Synth.*, 1970, **50**, 27; A. C. Day, P. Raymond, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. (C)*, 1966, 467.

<sup>16</sup> Th. Curtius and F. Rautemberg, *J. prakt. Chem.*, 1891, **44**, 192.

(s, Me), 2.33br (6H, s, tolyl Me), and 6.9—7.6 (8H, m, ArH). The i.r. spectrum of the product in carbon tetrachloride showed a diazo-absorption at 2050  $\text{cm}^{-1}$ , due to di-*p*-tolyl-diazomethane formed in the reverse retro-cycloaddition.

*Photolysis of the Adduct (IVb).*—A solution of the adduct (300 mg) in dichloromethane (120 ml) was irradiated (Hanau S81; quartz) for 4 h at  $-20^\circ$  (nitrogen atmosphere). Hydrogen sulphide was evolved (no explanation for its formation could be given). Removal of the solvent left an oily residue which was chromatographed on silica gel (35 g). Elution with carbon tetrachloride and with carbon tetrachloride-dichloromethane (85:15) gave unidentified sulphur-containing products; use of a 7:3 ratio gave *p,p'*-dimethylbenzophenone azine (VIII) (105 mg), m.p. 193—195° (from light petroleum) (lit.,<sup>17</sup> 190—191°), and use of a 1:1 ratio yielded *p,p'*-dimethylbenzophenone isopropylidenehydrazone (VII) (100 mg) identical (g.l.c., i.r. and n.m.r. spectra) with an authentic sample prepared<sup>18</sup> from acetone and *p,p'*-dimethylbenzophenone hydrazone.

*5',5'-Dimethylfluorene-9-spiro-2'-1',3',4'-thiadiazoline 1'-Oxide (IXa).*—A solution of 2-diazopropane (13 mmol) in ether was added gradually to a stirred and cooled ( $-10^\circ$ ) solution of thiofluorenone *S*-oxide (II)<sup>3</sup> (0.70 g, 3.3 mmol) in the minimum of dry ether. After 1 h the *cycloadduct* was filtered off and washed with cold ether and light petroleum (yield 0.7 g, 80%), m.p. 72° (decomp.) (Found: C, 67.3; H, 4.9; N, 9.55.  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{OS}$  requires C, 68.05; H, 5.0; N, 9.9%). The product was unstable; it could be stored for a few days only if kept below 0°;  $\nu_{\text{max}}$  (Nujol) 1050 (SO) and 1540 (N=N)  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{C}_6\text{D}_6$ ) 1.35 (s, Me), 1.80 (s, Me), 6.9—8.0 (7H, m, ArH), and 6.25 (1H, d, *J* 6.0 Hz, ArH).

*5'-Methylfluorene-9-spiro-2'-5'H-1',3',4'-thiadiazoline 1'-Oxide (IXb).*—This *adduct*, obtained like (IXa) from diazoethane<sup>19</sup> instead of 2-diazopropane and the *S*-oxide (II) (1.4 g) (yield 0.8 g, 45%), had m.p. 74—76° (decomp.) (Found: C, 68.9; H, 4.4; N, 8.3; S, 12.4.  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{OS}$  requires C, 67.15; H, 4.5; N, 10.45; S, 11.95%);  $\nu_{\text{max}}$  (Nujol) 1540 (N=N), 1065, and 1055 (S=O)  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{C}_6\text{D}_6$ ) 1.90 (3H, d, *J* 7.5 Hz, Me), 4.90 (1H, q, *J* 7.5 Hz,  $\text{CH}\cdot\text{CH}_3$ ), 6.10 (1H, d, *J* 7.5 Hz, ArH), and 6.6—8.0 (7H, m, ArH).

Chromatography of the adduct (IXb) (0.4 g) dissolved in benzene on silica (elution with benzene) gave *bis*-[1-(fluorene-9-ylidenehydrazone)ethyl] disulphide (XIIIb) (0.3 g), m.p. 168—169° (from ethanol) (Found: C, 71.05; H, 4.4; N, 10.95; S, 12.8.  $\text{C}_{30}\text{H}_{22}\text{N}_4\text{S}_2$  requires C, 71.7; H, 4.4; N, 11.15; S, 12.75%);  $\delta$  ( $\text{CDCl}_3$ ) 2.8 (6H, s, Me) and 7.0—8.5 (16H, m, ArH).

*Fluorene-9-spiro-2'-5'H-1',3',4'-thiadiazoline 1'-Oxide (IXc).*—A dry, freshly prepared solution of diazomethane (20 mmol) in ether was added gradually to a stirred and cooled ( $-5^\circ$ ) solution of the *S*-oxide (II) (1.0 g, 4.7 mmol) in ether (80 ml). After 1 h the *product* was filtered off and washed with ether and light petroleum (yield 0.6 g, 50%); m.p. 83—85° (decomp.) (Found: C, 66.35; H, 3.95; N, 10.6; S, 12.7.  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{OS}$  requires C, 66.1; H, 3.95; N, 11.0; S, 12.6%);  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ ) 1055 (S=O), 1545 (N=N), and 1445 ( $\text{CH}_2$ )  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 5.85 and 6.46 (2H, ABq, *J* 18.1 Hz,  $\text{CH}_2$ ), 7.0—8.0 (7H, m, ArH), and 6.4 (1H, d, *J* 7.4 Hz, ArH).

A solution of the product (IXc) in benzene was chromatographed on silica; elution with benzene gave an almost

quantitative yield of the orange-red *disulphide* (XIIIa), m.p. 174—175° (from benzene-light petroleum) (Found: C, 70.7; H, 3.9; N, 11.6; S, 13.7.  $\text{C}_{28}\text{H}_{18}\text{N}_4\text{S}_2$  requires C, 70.85; H, 3.8; N, 11.8; S, 13.5%);  $\delta$  ( $\text{CDCl}_3$ ) 8.4—7.2 (8H, m, ArH) and 8.12 (1H, s);  $\nu_{\text{max}}$  (Nujol) 1621, 1593, and 1532  $\text{cm}^{-1}$ ; *m/e* 474 ( $M^+$ , small), 442 (100%,  $M - S$ ), 355 ( $\text{C}_{26}\text{H}_{15}\text{N}_3^+$ ), and 328 ( $\text{C}_{26}\text{H}_{16}^+$ ).

*5',5'-Dimethylthioxanthene-9-spiro-2'-1',3',4'-thiadiazoline 1',10-Dioxide (Xa).*—The sulphine (IIIa)<sup>3</sup> (0.52 g, 2.0 mmol) dissolved in dichloromethane (5 ml) was treated with 1 equiv. of 2-diazopropane at  $-30^\circ$ . After stirring for 0.5 h, pentane-ether (1:1; 10 ml) was added. After 3 days the *product* (Xa) was collected (368 mg); the mother liquor slowly deposited another 78 mg (total yield 67%); m.p. 95° (decomp.) (Found: C, 57.75; 58.05; H, 4.3, 4.2; N, 8.45, 8.45; S, 19.4, 19.4.  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2\text{S}_2$  requires C, 58.15; H, 4.25; N, 8.5; S, 19.4%);  $\nu_{\text{max}}$  (KBr) 1030 and 1065 (S=O) and 1570  $\text{cm}^{-1}$  (N=N);  $\delta$  ( $\text{CDCl}_3$  at  $-30^\circ$ ) 1.50 (s, Me), 1.93 (s, Me), 6.69—6.94 (1H, m, ArH), 7.24—7.72 (5H, m, ArH), and 7.84—8.17 (2H, m, ArH).

At room temperature a solution of this adduct (Xa) turned purple rapidly, owing to a reverse retro-cycloaddition reaction.

*5',5'-Dimethylthioxanthene-9-spiro-2'-1',3',4'-thiadiazoline 1',10,10-Trioxide (Xb).*—A calculated amount of 2-diazopropane was added slowly to a solution of the sulphone sulphine (IIIb)<sup>3</sup> (2.76 g, 10.0 mmol) in chloroform (25 ml) chilled to 0°. The mixture was kept at  $-20^\circ$  for 4 days, then the white *precipitate* was collected and washed with a little pentane (yield 2.22 g, 65%); m.p. 99° (decomp.) (Found: C, 54.7; 54.55; H, 4.25, 4.0; N, 8.0, 8.0; S, 18.0, 18.1.  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_3\text{S}_2$  requires C, 55.45; H, 4.1; N, 8.1; S, 18.5%);  $\nu_{\text{max}}$  (KBr) 1075 (S=O), 1170br and 1310 ( $\text{SO}_2$ ), and 1572 (N=N)  $\text{cm}^{-1}$ . The formation of 9-diazothioxanthene 10,10-dioxide (XI) took place even during the preparation of a KBr pellet:  $\nu_{\text{max}}$  2070  $\text{cm}^{-1}$  (N=N);  $\delta$  ( $\text{CDCl}_3$  at 0°) 1.50 (s, Me), 1.92 (s, Me), 6.66—6.84 (1H, m, ArH), 7.18—7.80 (5H, m, ArH), and 8.05—8.40 (2H, m, ArH).

*Retro-cycloaddition Reaction of the Adduct (Xb).*—(a) A solution of the adduct (100 mg, 0.29 mmol) in dichloromethane (5 ml) containing silica gel for chromatography (2g; 60—120 mesh) was stirred at room temperature for 4 h. The mixture was then filtered and the silica gel was washed with dichloromethane and ether. Concentration of the filtrate gave a residue which was crystallized from dichloromethane-ether. Together with material from the mother liquor, a mixture (76 mg) of the sulphone sulphine (IIIb) and the diazo-compound (XI) was obtained in the ratio 6:9 (n.m.r.). Repeated fractional crystallization of the mixture eventually gave (IIIb) and (XI) separately. The same result could be achieved by chromatography on silica.

(b) The adduct (Xb) (50 mg) partially dissolved in benzene (1 ml) was heated for 30 min at 60°. The diazo-compound (XI) crystallized out and was filtered off (20 mg). The mother liquor was not worked up.

(c) A solution of the adduct (Xb) in [ $^2\text{H}$ ]chloroform was heated in an n.m.r. tube. No change of spectrum was observed at 0° and 10°; however, at 40° in a few min the spectrum had changed completely (see text).

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<sup>17</sup> H. Staudinger and J. Goldstein, *Ber.*, 1916, **49**, 1923.

<sup>18</sup> J. Elguero, R. Jacquier, and C. Marzin, *Bull. Soc. chim. France*, 1968, 713.

<sup>19</sup> Houben-Weyl, 'Methoden der Organischen Chemie,' IVth edn., vol. 10, p. 539.