Thermal Fragmentation of a 1,5,2-Oxathiazole 5-Oxide system *via* Two Parallel Pathways: Interception of a Vinyl Nitrene and of a Sulphene

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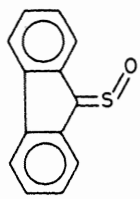
Heating of 1,5,2-oxathiazole 5-oxide (2) (obtained by cycloaddition of fluorene-9-thione *S*-oxide and benzonitrile oxide) in benzene resulted in the formation of the dispiro{fluorene-9,4'-[1,2]thiazole-5',9''-fluorene} 1',1'-dioxide (3) (84%). The formation of product (3) is explained by assuming thermal fragmentation of (2) *via* two parallel pathways, one involving the loss of benzonitrile to give fluorene-9-thione *S,S*-dioxide (5) and the other the elimination of sulphur dioxide to produce the vinyl nitrene (7). Cycloaddition of the sulphene (5) and the nitrene (7) then leads to the heterocycle (3). This mechanism is supported by the fact that the vinyl nitrene (7) could be trapped by reaction with 4,4'-dimethylthiobenzophenone, and the sulphene (5) by reaction with methanol. The alternative rationale for the formation of (3), *viz.* reaction of an azirine (4) with the sulphene (5), could be ruled out.

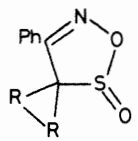
Cycloaddition reactions of sulphines [1] (thione *S*-oxides) with 1,3-dipoles, *e.g.* diazoalkanes,[2] nitrile imides,[3] nitrilium ylides,[4] and nitrile oxides,[5] represent a useful route to the synthesis of a variety of heterocyclic compounds. In some instances the cycloadducts of sulphines undergo cycloreversion or fragmentation reactions leading to compounds and/or reactive intermediates that are difficult to obtain otherwise.[1]

In a previous report [5] we reported that fluorenethione *S*-oxide (1) undergoes an efficient cycloaddition with benzonitrile oxide to give 1,5,2-oxathiazole 5-oxide (2) in high yield. This paper deals with the thermal fragmentation of this heterocyclic system *via* two parallel pathways leading to a vinyl nitrene and a sulphene, respectively, and also with the interception of these reactive species.

Heating of compound (2) in benzene at reflux temperature for 30 min afforded the new dispiro heterocycle (3) (84%), benzonitrile (25%), sulphur dioxide (24%), and some azirine (4) (10%). The structure of product (3) was deduced from its analytical and spectral properties (see Experimental section) and established unambiguously by *X*-ray analysis (see Figure 1).† Azirine (4) was compared with an authentically prepared sample.[6]

In order to explain the formation of products (3) and (4) we hypothesized that the cycloadduct (2) decomposes thermally by two parallel reaction pathways as depicted in Scheme 1. Loss of a molecule of benzonitrile from the heterocycle (2) leads to the formation of fluorene-9-thione *S,S*-dioxide (5) (path a). Such an extrusion of benzonitrile is comparable with the thermal behaviour of related heterocyclic systems.[3,7] The alternative cleavage of the cycloadduct (2) by path b involves initial breaking of the carbon–sulphur bond to give the zwitterionic intermediate (6). Such a hypothesis resembles the cleavage proposed for the cycloadduct of a phosphonium ylide and a nitrile oxide.[8] The zwitterion (6) then can either lose sulphur dioxide by an internal nucleophilic displacement to give the azirine (4) or by direct elimination to produce the vinyl nitrene (7). Cycloaddition of the sulphene (5) with the vinyl nitrene (7) then leads to the formation of the isolated heterocycle (3). A probable side reaction of the vinyl nitrene will be its ring closure [9] to the azirine (4).


(1)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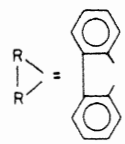

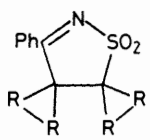
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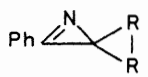

(4)

As a conceivable explanation for the formation of the product (3), reaction of the azirine (4) and the sulphene (5) can be envisaged. Therefore, the azirine (4) was treated in a separate experiment with fluorene-9-thione *S,S*-dioxide generated *in situ* from fluorene-9-sulphonyl chloride and triethylamine, with benzene as the solvent. However, the azirine was recovered unchanged. Hence, the alternative course of the reaction can be excluded.

In order to provide further evidence for the formation of both the sulphene (5) and the vinyl nitrene (7) the thermal fragmentation of the heterocycle (2) was performed in boiling methanol. On chromatography on silica gel the following products were isolated from the reaction mixture: methyl fluorene-9-sulphonate (8) (24%), 9-benzoyl-9-methoxyfluorene (9) (35%), ammonium fluorene-9-sulphonate (10) (30%), the azirine (4) (8%), and benzonitrile (44%). During the thermolysis sulphur dioxide was also liberated (20%). The structures of products (8)—(10) were assigned on the basis of their spectral and analytical properties. The sulphonate ester (8) is the result of addition of methanol to the sulphene (5) as expected from the well documented behaviour of sulphenes.[10,11] The formation of the methoxy ketone (9) can be rationalized by assuming reaction of the vinyl nitrene (7)

† Full details of this analysis will be published elsewhere. The authors are indebted to Drs. R. C. Haltiwanger and W. K. L. van Havere, Crystallography Laboratory, University of Nijmegen, for performing this *X*-ray analysis.

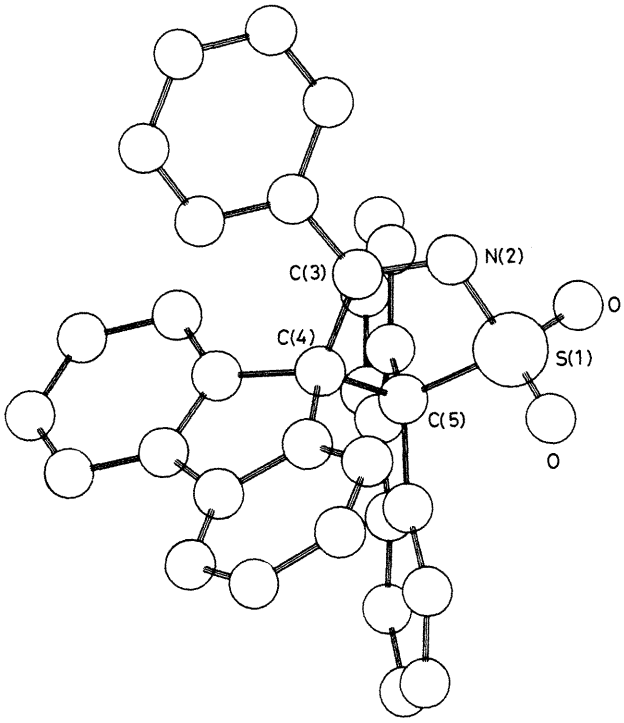


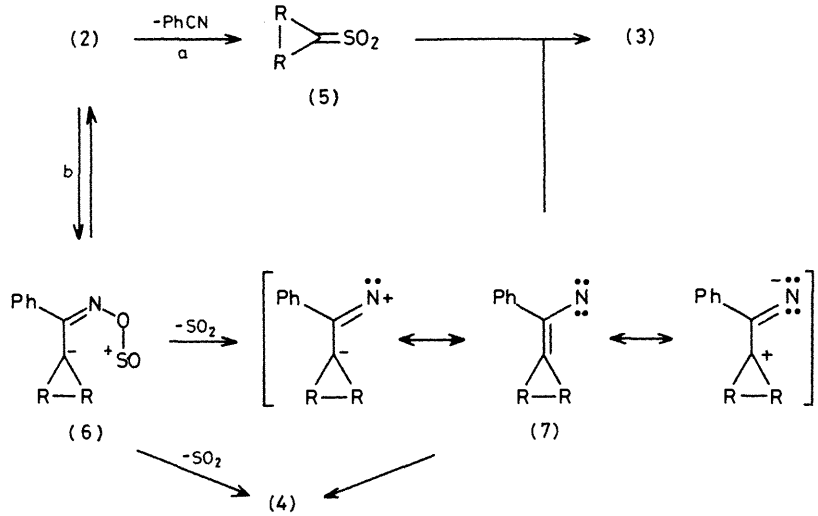
Figure 1. *Crystal data*: $a = 15.542(2)$ Å, $b = 10.116(2)$ Å, $c = 16.661$ Å, $\beta = 112.47(1)°$; $V = 2\,420$ Å^3; space group Pz_1/n; $Z = 4$, $D_c = 1.369$ g cm^{-3}. Data were measured on a CAD4 diffractometer and average to 3 153 independent points, of which 2 221 were observed [$I > 3\rho(I)$]. Full matrix anisotropic refinement converged with $R_w = \Sigma/w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o| = 0.042$, $w = 1.0/[\rho^2(F) + 0.0002\,F^2]$.

The proposed formation of a vinyl nitrene on thermolysis of compound (2) was supported by trapping the species with 4,4′-dimethylthiobenzophenone, thus showing it to be a 1,3-dipole. Reaction of equimolar amounts of the thione (12) and the heterocycle (2) in refluxing benzene for 30 min gave the two regioisomeric cycloadducts (13) and (14) in 6 and 5%, respectively. In addition, the azirine (4) (41%), benzonitrile (11%), the heterocycle (3) (16%), the thione (12) (25%), 4,4′-dimethylbenzophenone (19%), 4,4′-dimethylthiobenzophenone *S*-oxide (15) (19%), the spiro-thiirane (16) (29%), and sulphur (16%) were isolated by chromatography. Sulphur dioxide was liberated from the reaction mixture (63%).

The structures of the two regioisomeric cycloadducts (13) and (14) were mainly based on their mass spectra, which showed for both compounds the molecular ions and the fragments for ($M^+ - S$) and ($M^+ - PhCN$); for compound (14) the fragment at m/z 358 corresponding to the ion of 9-di-*p*-tolylmethylenefluorene was present. This fragment was not observed for the adduct (13).

The unexpected presence of the sulphine (15) can be explained by assuming oxidation of the thione (12) by the sulphur dioxide evolved during the thermolysis. This interesting suggestion was verified in an independent experiment. Indeed, treatment of the thione (12) with excess of sulphur dioxide in benzene for 1 h led to the formation of the sulphine (15) (19%) in addition to 4,4′-dimethylbenzophenone (34%). The starting thione was recovered in 44% yield. It should be noted that this mild oxidation of thiones represents a new synthesis of sulphines.

The identity of the thiirane (16) was ascertained by comparison with a sample, prepared by an independent route.[12] Its formation can be envisaged by means of the elimination of benzonitrile from either isomer (13) or (14). Alternatively, it may be speculated that the electrophilic carbon atom of the



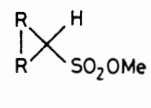
Scheme 1.

with methanol leading to the methoxy imine (11) which is then hydrolysed by the small amount of water present in methanol. The ammonium sulphonate (10) is a rather unexpected product; it probably arises from the addition of water (present in commercial methanol) to the sulphene (5) and subsequent salt formation with the ammonia mentioned above.

The ammonium salt (10) was also prepared independently from fluorene-9-sulphonyl chloride and ammonia in methanol solution.*

vinyl nitrene reacts with the thione sulphur to give a zwitterionic species which on further reaction eliminates benzonitrile to produce the isolated thiirane (16). The former possibility seems rather unlikely because the five-membered heterocycles (13) and (14) are stable in refluxing benzene or even toluene.

* In dry ether solution the same reaction leads to a quantitative yield of sulphonamide.



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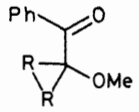

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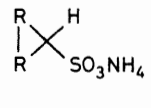

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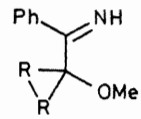

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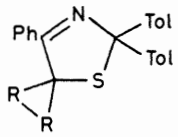

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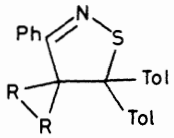

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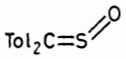

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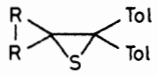
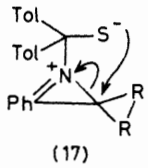


(16)

Tol = C_6H_4Me-4



(17)

It could be argued that the products (13) and (14) can also arise from the reaction of the azirine (4) and the thione (12). However, under the conditions mentioned above (refluxing benzene for 30 min) these species show no reaction.

At higher temperature (refluxing toluene) and prolonged reaction time (2 days), the azirine (4) and the thione (12) produced an adduct which was identified as the heterocycle (13) (71%). No trace of the regioisomer (14) nor of the thiirane (16) could be detected. This observation implies that this formation of (13) does not proceed *via* the intermediacy of the vinyl nitrene, because then both regioisomers and also compound (16) should have been obtained. Therefore, it is suggested that the azirine nitrogen reacts with the electrophilic thione carbon atom to give a zwitterionic species (17) which then undergoes a ring expansion reaction to produce the heterocycle (13). In accordance with other ring expansion reactions of azirinium ions this reaction is regiospecific, involving only the cleavage of the carbon–nitrogen single bond.[9,13]

In summary, the thermal reaction of the heterocyclic compound (2) produces simultaneously the sulphene (5) and the vinyl nitrene (7) which subsequently undergo a cycloaddition reaction to give the new heterocycle (3). It should be emphasized that these parallel fragmentation reactions leading to the reactive intermediates (5) and (7) must take place at almost equal rates, otherwise the production of (3) could not have occurred in such a high yield.

The reaction of sulphene with a vinyl nitrene represents a new example of a [2 + 4]-cycloaddition reaction of sulphenes. Till now such cycloadditions have been observed only with diazoalkanes [14] and *C,N*-diphenylnitrone.[15] It should also be noted that intermolecular cycloaddition reactions of vinyl nitrenes are rare, if known at all, while their intramolecular cyclizations have been observed frequently.[16]

Experimental

I.r. spectra were recorded with a Perkin-Elmer 257 grating spectrometer. ^{1}H N.m.r. spectra were run on a Varian EM 360L spectrometer using $SiMe_4$ as internal standard. ^{13}C N.m.r. spectra were run on a Varian XL-100 spectrometer. Mass spectra were recorded with a Jeol JMS D-100 spectrometer. All experiments were carried out under nitrogen. M.p.s and p.p.m. are uncorrected. 3′-Phenylspiro{fluorene-9,4′-[1,5,2]-oxathiazole} 5′-oxide (2) was prepared as described in ref. 5. Ether refers to diethyl ether.

Decomposition of Compound (2) *in Benzene.*—A solution of (2) (0.40 g, 1.21 mmol) in dry benzene (30 ml) was heated under reflux for 30 min and the SO_2 liberated was collected in 1M-NaOH. The reaction mixture was then concentrated under reduced pressure and the residue was washed with CS_2 (10 ml) giving *3′-phenyldispiro{fluorene-9,4′-[1,2]thiazole-5′,9″-fluorene} 1′,1′-dioxide* (3) (0.25 g, 83.6%), m.p. 309—310 °C (decomp.) (from benzene–n-pentane) (Found: C, 79.8; H, 4.3; N, 2.9; S, 6.7. $C_{33}H_{21}NO_2S$ requires C, 79.98; H, 4.27; N, 2.83; S, 6.47%); $\nu_{max.}$ (CCl_4) 1 170 and 1 350 cm^{-1} (SO_2); *m/z* 495 (M^+), 431 ($M^+ - SO_2$), 328 ($M^+ - PhCN - SO_2$), 267 (M^+ — fluorene=SO_2), 164 ($C_{13}H_8$), and 103 (PhCN).

The CS_2 solution was concentrated under reduced pressure and chromatographed on silica gel plates using benzene as eluant. The lower fraction (R_F 0.56) gave fluorenone (6.6 mg, 3%). The higher fraction (R_F 0.75) gave an oily product that after washing with cold methanol gave 3′-phenylspiro{fluorene-9,2′-[1]azirine} (4) (33.8 mg, 10.5%), m.p. 101—102 °C (lit.,[6] 103—104 °C); $\nu_{max.}$ (KBr) 1 745, 1 600, 1 445, 1 315, 1 290, 1 205, 1 175, 1 150, 1 120, 1 025, 1 000, 940, 925, 850, 780, 760, 750, 735, 680, 640, and 635 cm^{-1}. The strong band at 1 745 cm^{-1} is typical of the C=N group present in the azirine nucleus,[8] δ($CDCl_3$) 7—8.1 (m, ArH); *m/z* 267 (M^+), 190 (M^+ — Ph), 164 ($C_{13}H_8$) and 103 (PhCN); δ (^{13}C) ($CDCl_3$) 166.9 (C=N), 144.2, 140.8, 133.6, 129.9, 129.4, 127.8, 127.0, 122.9, 121.4, 120.2 (aromatic carbons), and 46.5 p.p.m. (C-9).

The methanolic solution, after concentration under reduced pressure, gave benzonitrile (31 mg, 25%) which was detected by g.l.c. The NaOH solution was neutralized with 1M-HCl and titrated with 0.1M-iodine solution.[17] The amount of SO_2 was calculated to be 0.29 mmol (24%).

Decomposition of Compound (2) *in Methanol.*—A solution of (2) (1.00 g, 3.02 mmol) in methanol (200 ml) was heated under reflux for 30 min and the SO_2 liberated was collected in 1M-NaOH. Chromatography of the reaction mixture on silica gel plates with benzene as eluant gave four fractions, *viz.* (from the top) an oily product that was washed with cold methanol giving the azirine (4) (63 mg, 7.9%) [the methanol solution after concentration under reduced pressure, gave benzonitrile (0.136 g, 43.9%)], *methyl fluorene-9-sulphonate* (8) (0.189 g, 24%), *9-benzoyl-9-methoxyfluorene* (9) (0.32 g, 35%), and *ammonium fluorene-9-sulphonate* (10) (0.26 g, 30%). The R_F values of (4), (8), (9), and (10) are 0.75, 0.46, 0.15, and 0.0, respectively.

Physical and spectral date of (8), (9), and (10) are as follows: compound (8), m.p. 98—99 °C (from methanol) (Found: C, 64.6; H, 4.7; S, 12.2. $C_{14}H_{12}O_3S$ requires C, 64.60; H, 4.65; S, 12.32%); $\nu_{max.}$ (CCl_4) 1 365, 1 180, and 1 140 cm^{-1} (SO_2–O); δ($CDCl_3$) 3.35 (3 H, s, Me), 5.23 (1 H, s), and 6.9—7.7 (8 H, m, ArH); δ (^{13}C) ($CDCl_3$) 141.1, 135.2, 129.8, 127.7, 126.9,

120.3 (aromatic carbons), 67.0 (OMe), and 58.0 p.p.m. (C-9); *m/z* 260 (M^+) and 165 ($M^+ - SO_3Me$).

Compound (9), m.p. 100—101 °C (from benzene–n-pentane) (Found: C, 83.8; H, 5.4. $C_{21}H_{16}O_2$ requires C, 83.98; H, 5.37%); $\nu_{max.}$ (CCl_4) 2 820, 1 685 (C=O), 1 445, and 1 105 cm^{-1}; δ($CDCl_3$) 2.75 (3 H, s, Me) and 6.5—7.4 (13 H, m, ArH); *m/z* 300 (M^+), 195 ($M^+ - PhCO$), 180 ($M^+ - PhCO - Me$), and 105 (PhCO).

Compound (10), m.p. >310 °C; $\nu_{max.}$ (KBr) 3 430—3 150 (NH_4^+), 1 445, 1 400, 1 200, 1 185, 1 145, and 1 040 cm^{-1}; δ(CD_3OD) 4.6 (4 H, s, NH_4^+), 4.92 (1 H, s), and 6.75—7.65 (8 H, m, ArH); δ(^{13}C) (D_2O) 139.3, 136.0, 126.9, 125.5, 124.3, 118.0 (aromatic carbons), and 64.5 (C-9); *m/z* (M^+ absent), 247 ($M^+ - O$) and 165 ($M^+ - SO_3NH_4$). Compound (10) was also characterized as the *S-benzylisothiouronium salt*, m.p. 190—191 °C (Found: C, 61.2; H, 4.9; N, 6.8; S, 15.3. $C_{21}H_{20}N_2O_3S_2$ requires C, 61.14; H, 4.89; N, 6.79; S, 15.55%). Product (10) was identical with that prepared according to the following procedure: a solution of fluorene-9-sulphonyl chloride [18] (0.10 g, 0.38 mmol) in methanol (25 ml) was dropped into a stirred solution of methanol (30 ml) through which dry ammonia had been bubbled for 2—3 min. After 1 h the reaction mixture was chromatographed on silica gel plates with benzene–ethyl acetate (1 : 1) as eluant, giving as the higher fraction g, 9′-bifluorenylidene (8 mg, 13%), as the middle fraction compound (8) (16 mg, 16%) and, as the lower fraction compound (10) (627 mg, 63%). The NaOH solution was neutralized with 1M-HCl and titrated with 0.1M-iodine solution.[17] SO_2 (0.9 mmol, 30%) was found.

Reaction of Compound (2) *with 4,4′-Dimethylthiobenzophenone*.—A solution of (2) (1.50 g, 4.53 mmol) and 4,4′-dimethylthiobenzophenone [19] (1.025 g, 4.53 mmol) in dry benzene (150 ml) was heated under reflux for 30 min and the SO_2 liberated was collected in 1M-NaOH. The reaction mixture was concentrated under reduced pressure and chromatographed on a silica gel column. Elution with light petroleum gave first sulphur (23 mg, 15.9% based on the thione) then unchanged 4,4′-dimethylthiobenzophenone (0.256 g, 25%) and finally 3′,3′-*di*-p-*tolylspiro*[*fluorene*-9,2′-*thiirane*] (16) (0.513 g, 29%), m.p. 193—194 °C (from ethanol) (Found: C, 86.2; H, 5.7; S, 8.2. $C_{28}H_{22}S$ requires C, 86.11; H, 5.68; S, 8.21%); δ($CDCl_3$) 2.15 (6 H, s, Me) and 5.9—7.6 (16 H, m, ArH); *m/z* 390 (M^+), 375 ($M^+ - Me$), 358 ($M^+ - S$), and 343 ($M^+ - S - Me$). The product (16) was identical with that prepared according to the general procedure for thiiranes: [12] a solution of di-*p*-tolyldiazomethane [20] (0.23 g, 1.02 mmol) in dry ether (20 ml) was added dropwise to a stirred solution of thiofluorenone [21] (0.20 g, 1.02 mmol) in dry ether (15 ml). The solution was then concentrated under reduced pressure and filtered giving a product identical in all respect with (16) (0.358 g, 88.6%).

Elution with benzene–light petroleum (1 : 1) gave 2′,2′-*di*-p-*tolyl*-4′-*phenylspiro*{*fluorene*-9,5′(2H)-[1,3]*thiazole*} (13) (0.133 g, 6%), m.p. 199—200 °C (from ethanol) (Found: C, 85.0; H, 5.6; N, 2.7; S, 6.5. $C_{35}H_{27}NS$ requires C, 85.15; H, 5.51; N, 2.84; S, 6.50%), δ($CDCl_3$) 2.3 (6 H, s, Me) and 6.7—7.5 (21 H, m, ArH); *m/z* 493 (M^+), 461 ($M^+ - S$), 390 ($M^+ - PhCN$), 375 ($M^+ - PhCN - Me$), 297 ($M^+ - Ctolyl_2 - 2H$), and 252 ($M^+ - Ph$ – fluorene).

Elution with benzene–light petroleum (2 : 1) gave 3′-*phenyl*-5′,5′-*di*-p-*tolylspiro*[*fluorene*-9,4′(5H)-[1,2]*thiazole*] (14) (0.112 g, 5%), m.p. 185—186 °C (from ethanol) (Found: C, 85.2; H, 5.5; N, 2.8; S, 6.4. $C_{35}H_{27}NS$ requires C, 85.15; H, 5.51; N, 2.84; S, 6.50%); δ($CDCl_3$) 2.2 (6 H, s, Me) and 6.9—7.9 (21 H, m, ArH); *m/z* 493 (M^+), 461 ($M^+ - S$), 390 ($M^+ - PhCN$), 375 ($M^+ - PhCN - Me$), 358 (fluorene=$Ctolyl_2$), 297 ($M^+ - Ctolyl_2 - 2H$), 267 ($M^+ - tolyl_2CS$), and 226 ($tolyl_2CS$).

Elution with benzene gave first an oily product that was washed with cold methanol giving the azirine (4) (0.489 g, 40.8%) [the methanolic solution after concentration under reduced pressure gave benzonitrile (50 mg, 11%) (detected by g.l.c.)], then 4,4′-dimethylbenzophenone (0.182 g, 19%) was eluted.

Elution with benzene–ether (1 : 1) gave first 4,4′-dimethylthiobenzophenone *S*-oxide [19] (15) (0.21 g, 19%) which was compared with an authentic sample. Finally, the heterocycle (3) (0.18 g, 16%) was eluted. The NaOH solution was neutralized with 1M-HCl and titrated with 0.1M-iodine solution.[17] SO_2 (2.85 mmol, 63%) was found. Both adducts (13) and (14) were separately heated in refluxing benzene. After 10 h they were recovered unchanged.

Reaction of 4,4′-Dimethylthiobenzophenone with Sulphur Dioxide.—Gaseous sulphur dioxide was bubbled for 1 h through a refluxing solution of 4,4′-dimethylthiobenzophenone [19] (0.159 g, 0.7 mmol) in dry benzene (10 ml). Chromatography of the reaction mixture on silica gel plates with benzene as eluant gave four fractions, *viz.* (from the top) sulphur (4.6 mg), unchanged 4,4′-dimethylthiobenzophenone (70 mg, 44%), 4,4′-dimethylbenzophenone (50 mg, 33.8%), and 4,4′-dimethylthiobenzophenone *S*-oxide [19] (15) (31 mg, 18.2%).

Reaction of Azirine (4) *with Thione* (12).—A solution of 4,4′-dimethylthiobenzophenone (12) (452 mg, 2 mmol) and 3′-phenylspiro[fluorene-9,2′-azirine] [6] (4) (529 mg, 2 mmol) in toluene (20 ml) was heated under reflux for 2 days under argon (until the blue colour of the thione had disappeared). After removal of the solvent under reduced pressure a green-yellow oil was obtained which was subjected to flash chromatography (silica gel, Merck 60H), using light petroleum (60—80 °C) containing 4% ethyl acetate as eluant (pressure 2 atm). The first fraction (50 mg) gave after crystallization from ethanol light red crystals (30 mg, 6%), m.p. 215—217 °C (decomp.); $\nu_{max.}$ (KBr) 1 585 cm^{-1}; δ($CDCl_3$) 2.33 (6 H, s) and 6.33—7.83 (br m, ArH); *m/z* 461.05 (M^+). (The structure of this material has not been established.) The second fraction gave a white solid (1.05 g) which after crystallization from ethanol containing a little ethyl acetate afforded 2′,2′-di-*p*-tolyl-4′-phenylspiro[fluorene-9,5′(2*H*)-[1,3]thiazole] (13) (700 mg, 71%), m.p. 202—204 °C.

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