An Unambiguous Synthesis of Pyrazoles by Sulphur Extrusion from 1,2,6-Thiadiazines

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Di-imines (1) react with thionyl chloride and sulphur monochloride and dichloride giving different 1,2,6-thiadiazine S-oxides (3) and 1,2,6-thiadiazines (4), respectively. These last two compounds lead, by heating, to pyrazoles (6) *via* thermal extrusion of sulphur oxide or sulphur. On the other hand, 1,2,6-thiadiazine S-dioxides (5), which can be obtained by oxidation of (3) or (4), do not undergo the extrusion of sulphur dioxide.

1-AZABUTADIENE derivatives (1) are versatile starting materials for the synthesis of different types of six-membered-ring heterocycles containing one or two nitrogen atoms.[1] In a recent paper[2] we discussed thoroughly the two general reaction mechanisms operating in the heterocyclation of these systems, namely electrocyclic reactions and condensation processes [Scheme 1, paths (a) and (b), respectively].

dicarboxylic acid esters, or heterocumulenes respectively, can be understood in terms of the electrocyclic reaction path (a). However, the reaction of di-imines (1) with carbonyl compounds,[5] ethyl chloroformate, or carbon disulphide,[1] proceed through a condensation process (b).

From these results it seems probable that di-imines (1) might be suitable precursors for six-membered heterocycles containing the N–Z–N (Z = heteroatom) group
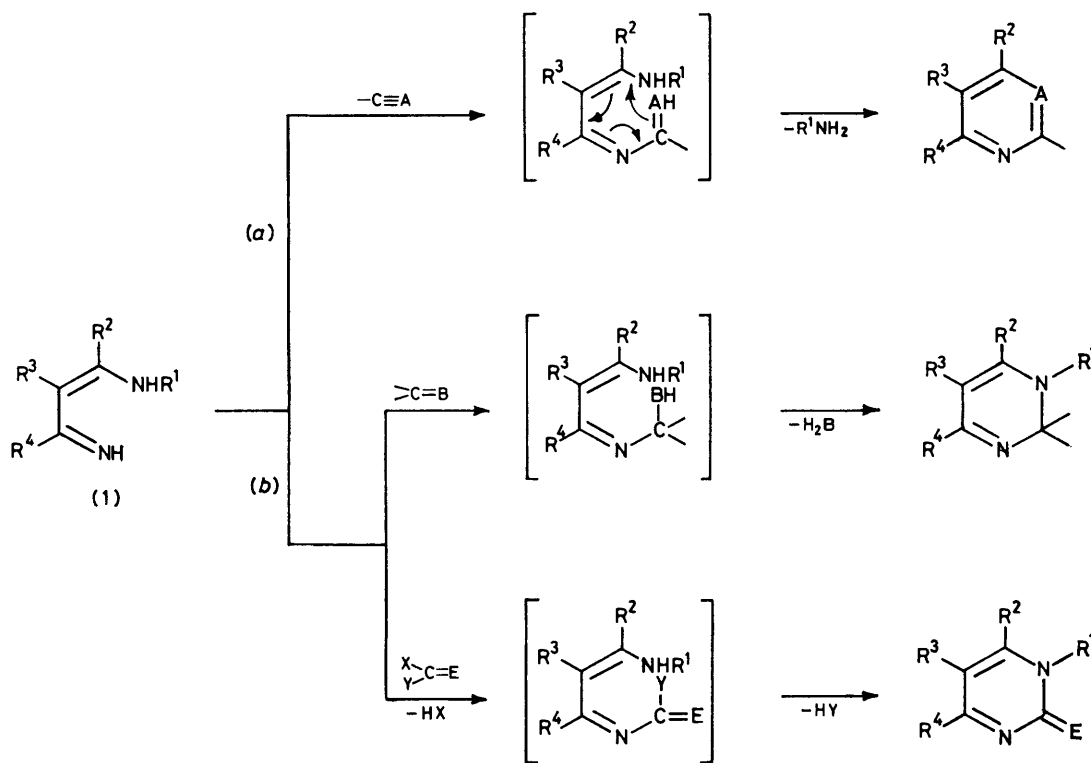
SCHEME 1

Different types of heterocycles are obtained depending on the structure of the intermediate compounds. These intermediates have been isolated in some instances.[2,†] Thus, the synthesis of pyrimidines,[3] pyridines,[4] and pyrimidones and thiopyrimidones,[2] obtained by reacting compounds (1) with saturated nitriles, acetylene-

† In the reaction of (1) with ethyl chloroformate, the products of mono-condensation of the imine N–H in (1) and the ester, with loss of 1 mol of HCl, were isolated.

in the ring.[6] In this paper, we describe our results on the reactions of (1) with different sulphur-containing reagents. We also report a new synthesis of N-substituted pyrazoles.

RESULTS AND DISCUSSION

Synthesis of Thiadiazine Derivatives.—Here we discuss the reaction of di-imines (1) with thionyl chloride, sulphur monochloride and dichloride, and sulphuryl

TABLE 1

Synthesis of 1,2,6-thiadiazine S-oxides (3), 1,2,6-thiadiazines (4), 1,2,6-thiadiazine S-dioxides (5), and pyrazoles (6)

| | | | | | (3) | | (4) [a] | (5) | | (6) | |
Product	R¹	R²	R³	R⁴	Yield (%)	m.p. (°C)	Yield [b] (%)	Yield [c] (%)	m.p. (°C)	Yield [d] (%)	m.p. (°C)
a	Ph	Ph	Me	Ph	80	133—135	75	70	192—194	86	122—124
b	Ph	Ph	Me	p-tolyl	82	148—149	78			88	168—170
c	p-Tolyl	Ph	Me	Ph	78	150—152	76			84	114—116
d	p-Tolyl	Ph	Me	p-tolyl	79	161—162	77	73	246—248	86	144—146
e	Cyclohexyl	Ph	Me	Ph	85	146—147	74			85	96—98
f	Cyclohexyl	Ph	Me	p-tolyl	84	160—161	73			84	147—149
g	Ph	p-chlorophenyl	Me	p-tolyl	80	156—158	77	75	199—201	87	165—167
h	Ph	Ph	H	Ph	86	153—154	75			93	138—139
i	o-Tolyl	Ph	Me	Ph	78	136—138	80			90	115—117
j	p-Tolyl	Ph	H	cyclohexyl	84	122—124	78	72	120—122	94	163—165
k	Ph	Ph	H	p-tolyl	77	156—157		71	260—262		
l	p-Tolyl	Ph	H	p-tolyl	87	184—185				90	173—175

[a] Compounds (4) were oils. [b] Obtained from sulphur dichloride. [c] Obtained from (3). [d] Obtained by Method A (see Experimental section).

chloride. Thionyl chloride is one of the most common reagents used in the synthesis of heterocycles containing sulphur *via* condensation reactions.[7] Di-imines (1) react with thionyl chloride (2) (Z = SO) at room temperature in pyridine or benzene–triethylamine giving rise to different 1,2,6-thiadiazine S-oxides (3) (Z = SO) in high yields (Table 1). The formation of (3) can be explained by a simple condensation reaction (Scheme 2).
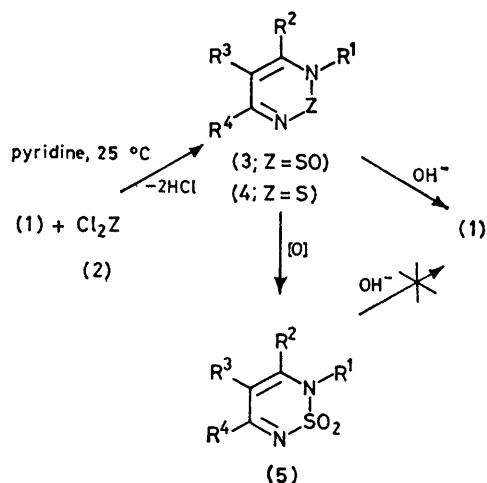
SCHEME 2

Compounds (3) display in the i.r. spectra a clear absorption at *ca.* 1 150 cm⁻¹ which is assigned to the SO stretching vibration. The M^+ — SO peak is the base in the mass spectra of compounds (3). The parent peak shows a very low intensity. From both features we conclude that these compounds have a strong tendency to expel sulphur oxide. When (3) is treated with 6N potassium hydroxide at 60 °C, the starting di-imines (1) are regenerated quantitatively.

Sulphur dichloride and monochloride S_xCl_2 (x = 1 or 2) have been known since the late nineteenth century and employed as valuable synthetic reagents for a wide range of purposes.[8] Accordingly, the di-imines (1) were allowed to react with both sulphur chlorides under similar conditions to those used in the reactions with thionyl chloride, leading in both instances to 1,2,6-

thiadiazines (4) (Z = S) (Table 1). Di-imines (1) are regenerated on alkaline hydrolysis of compounds (4).

On the other hand, treatment of compounds (1) with sulphuryl chloride (Z = SO₂) gives rise only to chlorinated di-imines and not to 1,2,6-thiadiazines S-dioxides (5). The structure of these chlorinated compounds will be reported elsewhere.[9] However, heterocycles (5) are obtained in high yields from oxidation with *m*-chloroperbenzoic acid of both compounds (3) and (4) (Table 1). Their i.r. spectra display two clear absorptions at 1 130 and 1 300 cm⁻¹, which are assigned to the stretching vibrations of the SO₂ group. The M^+ and M^+ — SO₂ peaks in the mass spectra are of approximately equal intensity. Treatment of (5) with potassium hydroxide does not regenerate the starting di-imines (1).

Synthesis of Pyrazoles.—Both the hydrolysis and the mass spectra of compounds (3) and (4) clearly show the ability of these heterocycles in eliminating sulphur monoxide or sulphur, respectively. On this basis, we examined the effect of heating on thiadiazines and found that pyrazoles (6) are obtained in high yields when compounds (3) or (4) are heated at 90 °C in toluene (Table 1). Additionally *in situ* reaction of di-imines (1) with sulphur derivatives (2) (Z = SO, S, or S₂) in pyridine at 90 °C leads directly to the pyrazoles (6). Their structure has been confirmed in some cases (R¹ = R⁴), by an alternative synthesis using 1,3-dicarbonyl compounds and phenylhydrazine as starting materials.[10]

The formation of pyrazoles (6) can be explained in terms of N–N bond formation following the extrusion of SO or S (Scheme 3). The most widespread methods for the synthesis of pyrazoles are those involving the formation of 1,5 and 2,3 bonds, *e.g.* reactions of dicarbonyl compounds with monosubstituted hydrazines, or of 1,3 and 3,4 bonds, *e.g.* dipolar additions of diazoalkanes to acetylenic systems.[11] All these methods lead to mixtures of regioisomers when asymmetrical dicarbonyl compounds or acetylenes are used. However, the method described here is regioselective and the ring-closure step occurs with the formation of a 1,2 bond. Thus this pathway is a novel and general approach to the synthesis of N-substituted pyrazoles.

The thermal extrusion of small stable molecules, such as CO, CO_2, COS, N_2, RCN, and SO_n, from cyclic compounds is a process commonly used in organic synthesis.[12] The extrusion of sulphur,[13] sulphur oxide,[14] or sulphur dioxide[15] allows C–C and, in some instances, C–N[16] bond formation. However, to our knowledge,
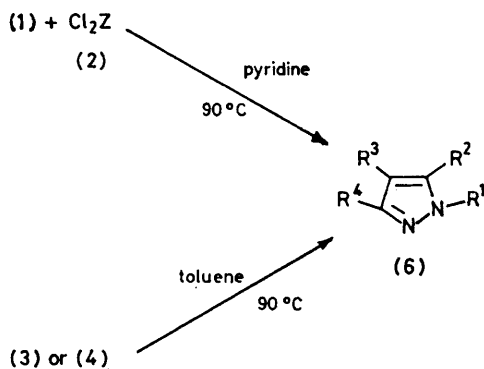
SCHEME 3

this is the first example of N–N bond formation via extrusion of sulphur oxide or sulphur. Although the formation of pyrazoles from (3) or (4) takes place under mild conditions, the extrusion of sulphur dioxide from heterocycles (5) does not occur even when these compounds are heated, in the presence of copper powder,[16] up to 200 °C in ethylene glycol as solvent. The different thermal behaviour of compounds (3) and (4) compared with (5) corresponds to the behaviour on potassium
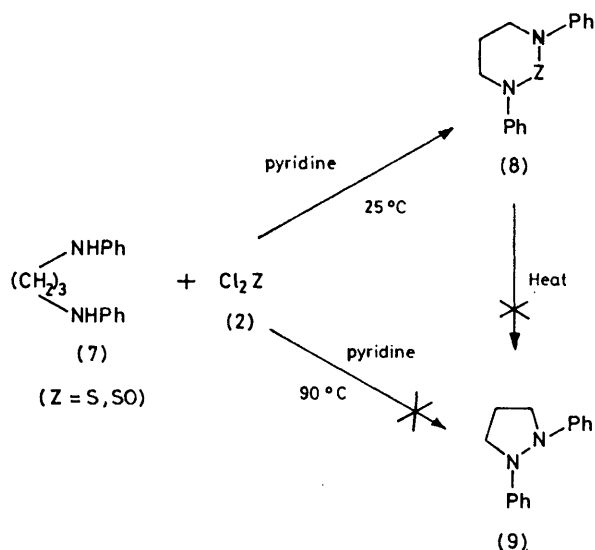
SCHEME 4

hydroxide hydrolysis, and also with the different relative intensities found for the M^+ and $M^+ - SO_x$ ($x = 0, 1$, or 2) peaks in the mass spectra.

The mild conditions under which the extrusion takes place contrasts with the fact that heterocycles (8), obtained by reacting 1,3-diamines (7) and thionyl chloride or sulphur dichloride, cannot be transformed

into compounds (9) by sulphur oxide or sulphur extrusion, respectively. This extrusion does not take place at temperatures up to 200 °C even in presence of phosphine derivatives, which normally promote this type of reactions in other cases[17] (Scheme 4). These facts suggest that the formation of pyrazoles is a concerted reaction.

EXPERIMENTAL

M.p.s are uncorrected. I.r. spectra were recorded on a Pye–Unicam SP-1000 instrument. ^{1}H N.m.r. spectra were recorded on a Varian EM-390 spectrometer in deuteriochloroform, with tetramethylsilane as an internal lock. Mass spectra were taken on a Hewlett Packard 5930 A spectrometer. Microanalyses were performed on a Perkin-Elmer Model 240. Di-imines (1)[18] and diamine (7)[19] were obtained according to literature procedures. Sulphur chlorides were purified as previously reported.[8]

1,2,6-Thiadiazine S-Oxides (3). *General Procedure.*— Thionyl chloride (12 mmol) was added to a solution of di-imine (1) (10 mmol) in pyridine (50 ml) at 0 °C and the mixture was allowed to warm to room temperature. After 2 h stirring the solution was poured into ice-cooled 4N H_2SO_4 (200 ml). The resulting mixture was extracted with ether and tetrahydrofuran, and the organic layer dried over anhydrous sodium sulphate, filtered, and evaporated. The residue was purified by recrystallization from hot hexane. Data for the products are given in Table 2.

1,2,6-Thiadiazines (4). *General Procedure.*—Sulphur monochloride or dichloride (12 mmol) was added to a solution of di-imine (1) (10 mmol) in pyridine (50 ml) at 0 °C and the mixture was allowed to warm to room temperature. After 2 h stirring the solution was poured into ice-cooled 4N H_2SO_4 (200 ml). The resulting mixture was extracted with ether and tetrahydrofuran, and the organic layer dried over anhydrous sodium sulphate, filtered, and evaporated. The residue was purified by column chromatography [silica; benzene–ether (1 : 1)]. Data for the products are given in Table 2.

1,2,6-Thiadiazine S-Dioxides (5). *General Procedure.*— m-Chloroperbenzoic acid (30 mmol) was added to a solution of (3) (15 mmol) or (4) (7.5 mmol) in chloroform at 0 °C and the mixture was allowed to warm at room temperature. After 3 h of stirring the solution was poured into 5% NaHCO₃. The resulting mixture was extracted with ether, and the organic layer dried over anhydrous sodium sulphate, filtered, and evaporated. The residue was purified by recrystallization from hot hexane–tetrahydrofuran. Data for the products are given in Table 2.

Preparation of Pyrazoles (6).—*Method A.* A solution of (3) (10 mmol) or (4) (10 mmol) in toluene (60 ml) was heated at 90 °C for 8h; evaporation of solvent *in vacuo* then gave the heterocycles (6). Compounds (6) were purified by recrystallization from hot hexane.

Method B. A mixture of the di-imine (1) (10 mmol) and Cl_2SO or Cl_2S_x ($x = 1$ or 2) (2) (12 mmol) in pyridine (50 ml) was heating at 90 °C for 8h, and then slowly poured into ice-cooled 4N H_2SO_4 (200 ml). The resulting mixture was extracted with ether, and the organic layer dried over anhydrous sodium sulphate, filtered, and evaporated. The residue was purified by recrystallization from hot hexane. Data for the products are given in Table 3.

Treatment of 1,2,6-Thiadiazine S-Oxides (3a—l) *with* 6N

TABLE 2

Physical data of compounds (3), (4), and (5)

Compound	Formula	Molecular weight	Analysis Found (Calc.)			$\nu_{max.}$(Nujol)/cm^{-1}	^{1}H N.m.r. (δ from SiMe$_4$)
			C	H	N		
(3a) [a]	C$_{22}$H$_{18}$N$_2$OS	(358.46)	73.6 (73.71)	5.1 (5.06)	7.7 (7.81)	1 130 (SO)	2.0 (3 H, s, Me), 7.0—7.9 (15 H, m, aromatic)
(3b)	C$_{23}$H$_{20}$N$_2$OS	(372.48)	74.5 (74.16)	5.6 (5.41)	7.5 (7.52)	1 120 (SO)	2.0 (3 H, s, Me), 2.4 (3 H, s, Me), 6.9—7.9 (14 H, m, aromatic)
(3c)	C$_{23}$H$_{20}$N$_2$OS	(372.48)	74.4 (74.16)	5.5 (5.41)	7.4 (7.52)	1 140 (SO)	2.1 (3 H, s, Me), 2.3 (3 H, s, Me), 6.9—8.0 (14 H, m, aromatic)
(3d)	C$_{24}$H$_{22}$N$_2$OS	(386.51)	74.7 (74.58)	5.6 (5.74)	7.15 (7.25)	1 120 (SO)	1.9 (3 H, s, Me), 2.2 (3 H, s, Me), 2.4 (3 H, s, Me), 6.8—7.8 (13 H, m, aromatic)
(3e) [b]	C$_{22}$H$_{24}$N$_2$OS	(364.50)	72.3 (72.49)	6.55 (6.64)	7.5 (7.68)	1 120 (SO)	0.9—2.2 (10 H, m, 5 CH$_2$), 1.8 (3 H, s, Me), 3.2—3.6 (1 H, m, N–CH), 7.0—7.9 (10 H, m, aromatic)
(3f)	C$_{23}$H$_{26}$N$_2$OS	(378.53)	73.1 (72.98)	6.85 (6.92)	7.25 (7.40)	1 120 (SO)	0.9—2.3 (10 H, m, 5 CH$_2$), 1.8 (3 H, s, Me), 2.4 (3 H, s, Me), 3.2—3.6 (1 H, m, N–CH), 7.0—7.8 (9 H, m, aromatic)
(3g)	C$_{23}$H$_{19}$ClN$_2$OS	(407.29)	68.05 (67.83)	4.9 (4.79)	6.7 (6.88)	1 130 (SO)	2.0 (3 H, s, Me), 2.4 (3 H, s, Me), 7.0—7.8 (13 H, m, aromatic)
(3h)	C$_{21}$H$_{16}$N$_2$OS	(344.43)	73.2 (73.23)	4.75 (4.68)	8.0 (8.13)	1 130 (SO)	7.0 (1 H, s, =CH), 7.1—8.3 (15 H, m, aromatic)
(3i)	C$_{23}$H$_{20}$N$_2$OS	(372.48)	74.3 (74.16)	5.25 (5.41)	7.6 (7.52)	1 130 (SO)	1.9 (3 H, s, Me), 2.1 (3 H, s, Me), 6.9—7.9 (14 H, m, aromatic)
(3j)	C$_{22}$H$_{24}$N$_2$OS	(364.50)	72.7 (72.49)	6.7 (6.64)	7.6 (7.68)	1 130 (SO)	1.0—2.0 (10 H, m, 5 CH$_2$), 2.1 (3 H, s, Me), 2.3—2.7 (1 H, m, CH), 6.3 (1 H, s, =CH), 6.8—7.6 (9 H, m, aromatic)
(3k)	C$_{22}$H$_{18}$N$_2$OS	(358.46)	73.85 (73.71)	5.2 (5.06)	7.7 (7.81)	1 135 (SO)	2.3 (3 H, s, Me), 6.9 (1 H, s, =CH), 7.0—8.2 (14 H, m, aromatic)
(3l)	C$_{23}$H$_{20}$N$_2$OS	(372.48)	74.0 (74.16)	5.5 (5.41)	7.35 (7.52)	1 130 (SO)	2.2 (3 H, s, Me), 2.4 (3 H, s, Me), 6.9 (1 H, s, =CH), 7.0—8.0 (13 H, m, aromatic)
(4a)	C$_{22}$H$_{18}$N$_2$S	(342.46)	77.4 (77.16)	5.1 (5.30)	8.3 (8.18)		2.0 (3 H, s, Me), 6.6—7.9 (15 H, m, aromatic)
(4b)	C$_{23}$H$_{20}$N$_2$S	(356.48)	77.8 (77.49)	5.4 (5.65)	7.6 (7.86)		2.0 (3 H, s, Me), 2.4 (3 H, s, Me), 6.5—7.8 (14 H, m, aromatic)
(4c)	C$_{23}$H$_{20}$N$_2$S	(356.48)	77.65 (77.49)	5.8 (5.65)	7.8 (7.86)		2.0 (3 H, s, Me), 2.4 (3 H, s, Me), 6.5—8.0 (14 H, m, aromatic)
(4d)	C$_{24}$H$_{22}$N$_2$S	(370.54)	77.5 (77.80)	6.1 (5.98)	7.6 (7.56)		2.0 (3 H, s, Me), 2.2 (3 H, s, Me), 2.4 (3 H, s, Me), 6.5—7.8 (13 H, m, aromatic)
(4e)	C$_{22}$H$_{24}$N$_2$S	(348.50)	75.6 (75.82)	7.0 (6.94)	8.15 (8.04)		0.8—1.8 (10 H, m, 5 CH$_2$), 1.9 (3 H, s, Me), 3.1—3.4 (1 H, m, N–CH), 7.0—8.0 (10 H, m, aromatic)
(4f)	C$_{23}$H$_{26}$N$_2$S	(362.53)	76.4 (76.20)	7.4 (7.23)	7.5 (7.73)		0.8—1.8 (10 H, m, 5 CH$_2$), 1.9 (3 H, s, Me), 2.4 (3 H, s, Me), 2.9—3.2 (1 H, m, N–CH), 7.1—7.8 (9 H, m, aromatic)
(4g)	C$_{23}$H$_{19}$ClN$_2$S	(390.93)	70.8 (70.66)	5.1 (4.90)	6.95 (7.17)		2.0 (3 H, s, Me), 2.1 (3 H, s, Me), 6.5—7.9 (13 H, m, aromatic)
(4h)	C$_{21}$H$_{16}$N$_2$S	(328.43)	77.0 (76.80)	4.65 (4.91)	8.4 (8.53)		6.4—7.7 (16 H, m, =CH and 15 H aromatic)
(4i)	C$_{23}$H$_{20}$N$_2$S	(356.48)	77.6 (77.49)	5.5 (5.65)	7.7 (7.86)		2.0 (3 H, s, Me), 2.15 (3 H, s, Me), 6.3—7.9 (14 H, m, aromatic)
(4j)	C$_{22}$H$_{24}$N$_2$S	(348.50)	76.0 (75.82)	6.8 (6.94)	8.2 (8.04)		0.8—1.8 (10 H, m, 5 CH$_2$), 2.4 (3 H, s, Me), 2.9—3.2 (1 H, m, CH), 7.3—8.5 (10 H, m, =CH and 9 H aromatic)
(5a) [c]	C$_{22}$H$_{18}$N$_2$O$_2$S	(374.45)	70.7 (70.57)	4.75 (4.84)	7.5 (7.48)	1 190, 1 315 (SO$_2$)	1.9 (3 H, s, Me), 7.2—8.3 (15 H, m, aromatic)
(5d)	C$_{24}$H$_{22}$N$_2$O$_2$S	(402.51)	71.75 (71.62)	5.6 (5.51)	6.95 (6.96)	1 180, 1 345 (SO$_2$)	1.9 (3 H, s, Me), 2.2 (3 H, s, Me), 2.4 (3 H, s, Me), 6.9—7.7 (13 H, m, aromatic)
(5g)	C$_{23}$H$_{19}$ClN$_2$O$_2$S	(422.93)	65.5 (65.32)	4.3 (4.53)	6.7 (6.62)	1 170, 1 330 (SO$_2$)	1.9 (3 H, s, Me), 2.4 (3 H, s, Me), 7.1—7.8 (13 H, m, aromatic)
(5j)	C$_{22}$H$_{24}$N$_2$O$_2$S	(380.50)	69.5 (69.44)	6.2 (6.36)	7.1 (7.36)	1 175, 1 335 (SO$_2$)	1.0—2.1 (10 H, m, 5 CH$_2$), 2.2 (3 H, s, Me), 2.35—2.9 (1 H, m, CH), 6.3 (1 H, s, =CH), 6.9—8.0 (9 H, m, aromatic)
(5k)	C$_{22}$H$_{18}$N$_2$O$_2$S	(374.45)	70.8 (70.57)	4.65 (4.84)	7.3 (7.48)	1 180, 1 340 (SO$_2$)	2.4 (3 H, s, Me), 6.8 (1 H, s, =CH), 7.0—8.1 (14 H, m, aromatic)

[a] m/e 358 (M^+).   [b] m/e 364 (M^+).   [c] m/e 374 (M^+).

Potassium Hydroxide.—A solution of (3) (10 mmol) in tetrahydrofuran (50 ml) was treated with 6N KOH (50 ml) and heated at 60 °C for 1 h. The resulting solution was extracted with ether, dried, and evaporated to give in all cases almost quantitative yields of the corresponding di-imine (1).

Treatment of 1,2,6-Thiadiazines (4a—j) *with 6N Potassium*

Hydroxide.—A solution of (4) (10 mmol) in tetrahydrofuran (50 ml) was treated with 6N KOH (50 ml) and heated at 60 °C for 24 h. The resulting solution was then acidified with ice-cooled 4N H$_2$SO$_4$ (200 ml), extracted with ether, and evaporated to give in all cases *ca.* 2.5 mmol of starting material (4a—j). The acid layer was treated with ice-cooled concentrated KOH solution until basic, extracted with

TABLE 3

Physical data of compounds (6)

Compound	Formula	Molecular weight	Found (Calc.) (%) C	H	N	^{1}H N.m.r. (δ from SiMe$_4$)
(6a)	C$_{22}$H$_{18}$N$_2$	310.91	85.3 (85.13)	5.4 (5.84)	9.2 (9.02)	2.2 (3 H, s, Me), 6.9—8.0 (15 H, m, aromatic)
(6b) ^{a}	C$_{23}$H$_{20}$N$_2$	324.42	85.0 (85.15)	6.5 (6.21)	8.4 (8.63)	2.2 (3 H, s, Me), 2.4 (3 H, s, Me), 6.9—7.8 (14 H, m, aromatic)
(6c)	C$_{23}$H$_{20}$N$_2$	324.42	85.4 (85.15)	6.0 (6.21)	8.5 (8.63)	2.1 (3 H, s, Me), 2.3 (3 H, s, Me), 6.9—7.9 (14 H, m, aromatic)
(6d)	C$_{24}$H$_{22}$N$_2$	338.45	85.0 (85.17)	6.8 (6.55)	8.15 (8.28)	2.2 (3 H, s, Me), 2.3 (3 H, s, Me), 2.4 (3 H, s, Me), 6.7—7.9 (13 H, m, aromatic)
(6e)	C$_{22}$H$_{24}$N$_2$	316.44	83.8 (83.50)	7.5 (7.64)	8.65 (8.85)	1.0—2.0 (10 H, m, 5 CH$_2$), 2.1 (3 H, s, Me), 3.7—4.1 (1 H, m, N–CH), 7.0—7.8 (10 H, aromatic)
(6f)	C$_{23}$H$_{26}$N$_2$	330.32	83.8 (83.63)	7.6 (7.93)	8.5 (8.48)	1.0—2.0 (10 H, m, 5 CH$_2$), 2.1 (3 H, s, Me), 2.35 (3 H, s, Me), 3.7—4.1 (1 H, m, N–CH), 7.1—7.7 (9 H, m, aromatic)
(6g)	C$_{23}$H$_{19}$ClN$_2$	358.87	77.15 (76.98)	5.2 (5.34)	7.65 (7.81)	2.2 (3 H, s, Me), 2.4 (3 H, s, Me), 7.0—7.8 (13 H, m, aromatic)
(6h)	C$_{21}$H$_{16}$N$_2$	296.37	85.0 (85.11)	5.6 (5.44)	9.3 (9.45)	6.8 (1 H, s, =CH), 7.0—7.8 (15 H, m, aromatic)
(6i)	C$_{23}$H$_{20}$N$_2$	324.42	85.4 (85.15)	5.9 (6.21)	8.8 (8.63)	2.2 (3 H, s, Me), 2.3 (3 H, s, Me), 6.9—7.9 (14 H, m, aromatic)
(6j)	C$_{22}$H$_{24}$N$_2$	316.44	83.7 (83.50)	7.4 (7.64)	8.7 (8.85)	0.9—2.1 (10 H, m, 5 CH$_2$), 2.2 (3 H, s, Me), 2.3—2.7 (1 H, m, CH), 6.3 (1 H, s, =CH), 6.7—7.5 (9 H, m, aromatic)
(6l)	C$_{23}$H$_{20}$N$_2$	324.42	85.3 (85.15)	6.3 (6.21)	8.35 (8.63)	2.2 (3 H, s, Me), 2.4 (3 H, s, Me), 6.8—8.2 (14 H, m, =CH and 13 H aromatic)

^{a} m/e 324 (M^+).

ether, and evaporated to give in all cases ca. 7.5 mmol of the corresponding di-imine (1).

3,4-Dihydro-2,6-diphenyl-1,2,6-thiadiazine S-Oxide (8).— To a solution of (7) (2.26 g, 10 mmol) in pyridine (50 ml), thionyl chloride (1.43 g, 12 mmol) was added at 0 °C, and the mixture allowed to warm to room temperature. The solution was stirred for 2 h and then treated with ice-cooled 4N H$_2$SO$_4$ (200 ml), extracted with ether, dried, and evaporated in vacuo. The residue (2.1 g, 80%) was purified by recrystallization from hot hexane: m.p. 112—114 °C; i.r. (Nujol) 1 100 [ν(SO)] cm^{-1}; δ 1.65—2.6 (2 H, m, CH$_2$), 3.1—3.4 (2 H, m, 2 × CH$_{ax}$H–N), 4.0—4.4 (2 H, m, 2 × CH$_{eq}$H–N), and 6.95—7.6 (10 H, m, aromatic) (Found: C, 66.3; H, 6.05; N, 10.1. C$_{15}$H$_{16}$N$_2$OS requires C, 66.15; H, 5.92; N, 10.28%).

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