

Novel Synthesis of Di-imines by the Transformation of 1-Aryl-4,6-disubstituted Pyrimidin-2(1H)-ones

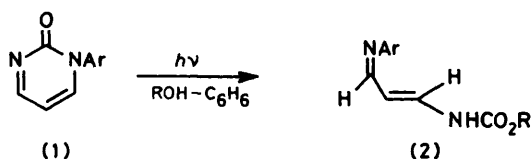
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The di-imines (4), which are versatile starting materials for the synthesis of heterocycles, are obtained in fair yields when the 1-aryl-4,6-disubstituted pyrimidin-2(1H)-ones (3) are treated with alkoxide, both photochemically and thermally. The di-imines (4) thus obtained, when treated with carbon disulphide, give the 1,3-thiazine-2-thiones (8) and/or the 1-arylpyrimidine-2(1H)-thiones (9).

THE di-imine compounds (4) may be considered as 1-azabutadiene derivatives and used as intermediates in the synthesis of various heterocycles that contain one or two nitrogen atoms in the ring, such as the pyridines,¹ pyrimidines,² and pyrazoles.³ It has been reported that the di-imines (4) can be prepared by the reaction of Schiff bases with saturated nitriles in the presence of aluminium trichloride as a catalyst.⁴ We report herein a new method for the synthesis of the di-imines (4) by the transformation of 1-aryl-4,6-disubstituted pyrimidin-2(1H)-ones (3).

RESULTS AND DISCUSSION

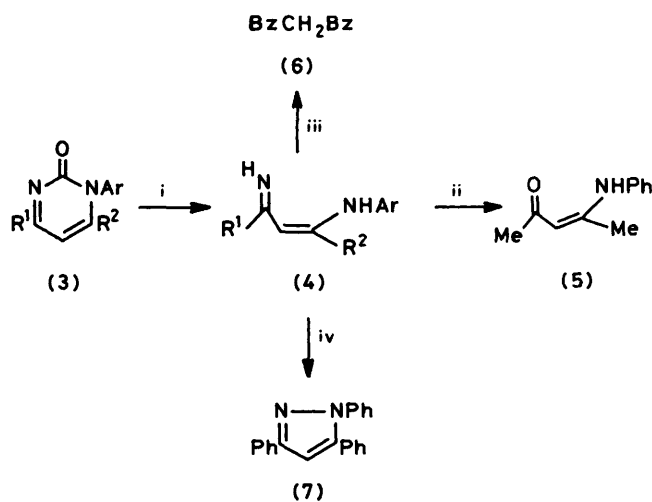
Transformation of 1-Aryl-4,6-disubstituted Pyrimidin-2(1H)-ones (3) to the Di-imines (4).—We reported previously the photochemical ring-opening of 1-arylpyrimidin-2(1H)-ones (1) to 1-alkoxycarbonylamino-3-arylaminoprop-1-enes (2).⁵ In order to elucidate the mech-



anism of formation of compounds (2), we investigated the photochemical reactions of the 1-arylpyrimidin-2(1H)-ones (1) and (3) in the presence of alkoxide. Irradiation of 1-phenylpyrimidin-2(1H)-one (1; Ar = Ph) in methanol-benzene (1 : 20) in the presence of sodium methoxide gave an intractable mixture. However, a solution of the pyrimidin-2(1H)-one (3a) in methanol-benzene (1 : 20) in the presence of sodium methoxide was irradiated with a high-pressure mercury lamp at room temperature for 12 h and then purified by a silica gel column chromatography to give the di-imine (4a) in 86% yield. On the other hand, irradiation of compound (3a) in methanol in the absence of sodium methoxide gave 3,4,6-triphenyl-2-oxo-1,3-diazabicyclo[2.2.0]hex-5-ene.⁶ The di-imine (4a) was also obtained in 76% yield when the arylpyrimidin-2(1H)-one (3a) was refluxed † in methanol-benzene (1 : 20) in the presence of sodium methoxide for 10 h. The structure of di-imine (4a) was confirmed on

† When compound (3a) was treated with sodium methoxide in methanol-benzene (1 : 20) at room temperature, no products were obtained and compound (3a) was recovered quantitatively.

the basis of physical properties and elemental analysis (see Experimental section). As expected, the di-imine (4a), when treated with hydrochloric acid in ethanol, gave dibenzoylmethane (6) in nearly quantitative yield. Furthermore, treatment of the di-imine (4a) with thionyl chloride in pyridine at 90 °C for 3 h³ gave 1,3,5-triphenylpyrazole (7) in 91% yield (Scheme 1).



	Ar	R ¹	R ²
a;	Ph	Ph	Ph
b;	C ₆ H ₄ Me- <i>p</i>	Ph	Ph
c;	C ₆ H ₄ Me- <i>m</i>	Ph	Ph
d;	C ₆ H ₃ OMe- <i>p</i>	Ph	Ph
e;	Ph	C ₆ H ₄ Me- <i>p</i>	C ₆ H ₄ Me- <i>p</i>
f;	Ph	Ph	C ₆ H ₄ Me- <i>p</i>
g;	Ph	Ph	Me
h;	Ph	Me	Me

SCHEME 1 i, *hν* or heat, alkoxide; ii, silica gel [(3h) only]; iii, HCl-EtOH [(4a) only]; iv, 90 °C, SOCl₂-C₅H₅N [(4a) only]

The di-imine (4a) was also obtained in fair yields by the treatment of the pyrimidin-2(1H)-one (3a) with sodium ethoxide or potassium *t*-butoxide. Similarly, the other 1-aryl-4,6-disubstituted pyrimidin-2(1H)-ones (3b)—(3g) were treated with alkoxide to afford the di-imines (4b)—(4g). In case of the pyrimidin-2(1H)-one (3h), 4-anilinopent-3-en-2-one (5) was obtained *via* hydrolysis of the imine functional group of the di-imine (4h), presumably formed initially from the reaction of compound (3h) with alkoxide. The results are summarized in Table 1.

Reaction of Di-imines (4) with Carbon Disulphide.—The versatility of di-imines (4) in the synthesis of various heterocycles that contain nitrogen atoms has been reported.⁷ We examined the reaction of the di-imine (4) with carbon disulphide* and found that the 1,3-thiazine-2-thiones (8) and/or 1-arylpurimidine-2(1H)-thiones (9)

TABLE 1

The di-imines (4) obtained from the 1-aryl-4,6-disubstituted pyrimidin-2(1H)-ones (3)

Compd.	Conditions	Alkoxide	Solvent	Yield of (4) (%) ^a
(3a)	<i>hν</i> , 12 h	NaOMe	MeOH-C ₆ H ₆	86
	reflux, 10 h	NaOMe	MeOH-C ₆ H ₆	76
	<i>hν</i> , 12 h	NaOEt	EtOH-C ₆ H ₆	75
(3b)	reflux, 5 h	KOBu ^t	C ₆ H ₆	71
	<i>hν</i> , 12 h	NaOMe	MeOH-C ₆ H ₆	80
	reflux, 5 h	KOBu ^t	C ₆ H ₆	57
(3c)	<i>hν</i> , 12 h	NaOMe	MeOH-C ₆ H ₆	81
(3d)	<i>hν</i> , 10 h	NaOMe	MeOH-C ₆ H ₆	70
	reflux, 5 h	KOBu ^t	C ₆ H ₆	65
(3e)	<i>hν</i> , 12 h	NaOMe	MeOH-C ₆ H ₆	56
(3f)	<i>hν</i> , 12 h	NaOMe	MeOH-C ₆ H ₆	63
(3g)	<i>hν</i> , 12 h	NaOMe	MeOH-C ₆ H ₆	40
	reflux, 5 h	KOBu ^t	C ₆ H ₆	10
(3h)	<i>hν</i> , 15 h	NaOMe	MeOH-C ₆ H ₆	43 ^b

^a Isolated yield. ^b The yield of 4-anilino-pent-3-en-2-one (5).

were formed. A solution of the di-imine (4a) in carbon disulphide was heated at 70 °C for 5 h to give the 1,3-thiazine-2-thione (8a) and pyrimidine-2(1H)-thione (9a) in 31% and trace yields, respectively. The structure of the 1,3-thiazine-2-thione (8a) was confirmed by spectroscopic data and elemental analyses. Similarly, other di-imines [(4b), (4d), (4g), and (4i)] reacted with carbon disulphide to give the 1,3-thiazine-2-thiones (8a) and (8i) and the pyrimidine-2(1H)-thiones (9d), (9g), and (9i) (see Table 2).

TABLE 2

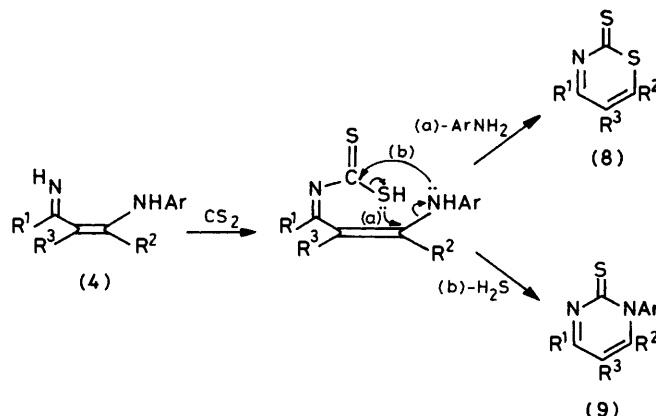
1,3-Thiazine-2-thiones (8) and 1-arylpurimidine-2(1H)-thiones (9) obtained from the di-imines (4) and carbon disulphide

Compound	Yield (%)	
	(8)	(9)
(4a)	31	trace
(4b)	38	trace
(4d)	30	36
(4g)	trace	24
(4i) ^a	36	64

^a The di-imine (4i) was independently prepared according to a method described previously (ref. 4).

The formation of 1,3-thiazine-2-thiones (8) and pyrimidine-1(2H)-thiones (9) can be explained easily by two alternative reaction paths, (a) and (b) (see Scheme 2). In all cases, the formation of aniline derivatives was detected by gas chromatography.

* Burluenga and his co-workers have reported that di-imines, prepared by the reaction of Schiff bases with saturated nitriles in the presence of aluminium trichloride,⁴ reacted with carbon disulphide to afford pyrimidine-2(1H)-thiones in high yields.⁸ In the experimental conditions described herein, 1,3-thiazine-2-thiones (8), in addition to pyrimidine-2(1H)-thiones, were obtained.



SCHEME 2 For compounds (4a), (4b), (4d), (4g), and (4i). [R³ = H for (4a), (4b), (4d), and (4g); compound (4i), prepared using a method described in ref. 4, has Ar = R¹ = R² = Ph, R³ = Me]

EXPERIMENTAL

Starting Materials.—The pyrimidin-2(1H)-ones (3a)—(3g) were prepared by a modification of a method described previously^{9,10} and compound (3h) was prepared as described in reference 10. The properties of, and data for, compounds (3a)—(3h) are listed below.

1,4,6-Triphenylpyrimidin-2(1H)-one (3a) had m.p. 247.5—249 °C; λ (EtOH) 208 (ϵ 3.61 \times 10⁴), 277 (1.97 \times 10⁴), and 340 nm (1.28 \times 10⁴); ν (KBr) 1 670 cm⁻¹; δ (CDCl₃) 6.93 (1 H, s), 7.1—7.7 (13 H, m), and 8.15—8.35 (2 H, m) (Found: C, 81.2; H, 4.85; N, 8.65. C₂₂H₁₆N₂O requires C, 81.45; H, 4.95; N, 8.45%).

4,6-Diphenyl-1-p-tolylpyrimidin-2(1H)-one (3b) had m.p. 245—246.5 °C; λ (EtOH) 207 (ϵ 3.79 \times 10⁴), 277 (1.84 \times 10⁴), and 340 nm (1.25 \times 10⁴); ν (KBr) 1 650 cm⁻¹; δ (CDCl₃) 2.27 (3 H, s), 6.89 (1 H, s), 7.05—7.70 (12 H, m), and 8.15—8.35 (2 H, m) (Found: C, 81.5; H, 5.2; N, 8.3. C₂₃H₁₈N₂O requires C, 81.65; H, 5.35; N, 8.3%).

4,6-Diphenyl-1-m-tolylpyrimidin-2(1H)-one (3c) had m.p. 206—207 °C; ν (KBr) 1 675 cm⁻¹; δ (CDCl₃) 2.26 (3 H, s), 6.87 (1 H, s), 6.9—7.3 (10 H, m), 7.43—7.57 (2 H, m), and 8.15—8.20 (2 H, m) (Found: C, 81.35; H, 5.15; N, 8.35. C₂₃H₁₈N₂O requires C, 81.65; H, 5.35; N, 8.3%).

1-p-Methoxyphenyl-4,6-diphenylpyrimidin-2(1H)-one (3d) had m.p. 283—284 °C; λ (EtOH) 207 (ϵ 3.82 \times 10⁴), 227sh (2.20 \times 10⁴), 277 (2.01 \times 10⁴), and 339 nm (1.30 \times 10⁴); ν (KBr) 1 655 cm⁻¹; δ (CDCl₃) 3.77 (3 H, s), 6.80—7.65 (13 H, m), and 8.15—8.35 (2 H, m) (Found: C, 77.75; H, 5.0; N, 8.1. C₂₃H₁₆N₂O₂ requires C, 77.95; H, 5.1; N, 7.9%).

1-Phenyl-4,6-di-p-tolylpyrimidin-2(1H)-one (3e) had m.p. 205—206 °C; ν (KBr) 1 670 cm⁻¹; δ (CDCl₃) 2.28 (3 H, s), 2.43 (3 H, s), 6.85 (1 H, s), 7.00—7.25 (11 H, m), and 8.11 (2 H, d, *J* 8.3 Hz) (Found: C, 81.45; H, 5.65; N, 7.9. C₂₄H₂₀N₂O requires C, 81.8; H, 5.7; N, 7.9%).

1,4-Diphenyl-6-p-tolylpyrimidin-2(1H)-one (3f) had m.p. 173 °C (decomp.); ν (KBr) 1 665 cm⁻¹; δ (CDCl₃-CD₃OD) 2.30 (3 H, s), 6.94 (1 H, s), 7.00—7.58 (12 H, m), and 8.10—8.20 (2 H, m) (Found: C, 81.35; H, 5.35; N, 8.35. C₂₃H₁₈N₂O requires C, 81.65; H, 5.35; N, 8.3%).

6-Methyl-1,4-diphenylpyrimidin-2(1H)-one (3g) had m.p. 271—272 °C; ν (KBr) 1 645 cm⁻¹; δ (CDCl₃) 2.07 (3 H, d, *J* 0.7 Hz), 6.77 (1 H, d, *J* 0.7 Hz), 7.20—7.55 (8 H, m), and 8.10—8.20 (2 H, m) (Found: C, 77.7; H, 5.4; N, 10.85. C₁₇H₁₂N₂O requires C, 77.85; H, 5.35; N, 10.65%).

4,6-Dimethyl-1-phenylpyrimidin-2(1H)-one (3 h) had m.p. 243—244 °C (lit.,¹⁰ m.p. 245—246 °C; $\lambda(\text{EtOH})$ 210 (ϵ 2.23 \times 10⁴) and 304 nm (9.5 \times 10³); $\nu(\text{KBr})$ 1 650 cm⁻¹; $\delta(\text{CDCl}_3)$ 1.97 (3 H, d, J 0.7 Hz), 2.40 (3 H, s), 6.20 (1 H, d, J 0.7 Hz), 7.14—7.31 (2 H, m), and 7.40—7.57 (3 H, m).

General Procedure for the Photochemical Reactions of the Pyrimidin-2(1H)-ones (3) in the Presence of Alkoxide.—A solution of the pyrimidin-2(1H)-one (3) (200 mg) in benzene (40 ml) in the presence of alkoxide [prepared from sodium (1 mol equiv.) and alcohol (2 ml)] was irradiated with a high-pressure mercury lamp for 10—15 h under argon at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene-ethyl acetate (10 : 1) to give the di-imine (4) [Note: Compound (3h) gave the product (5)]. The data for compounds (4a)—(4g) and (5) are given below.

General Procedure for Thermal Reactions of the Pyrimidin-2(1H)-ones (3) in the Presence of Alkoxide.—A solution of the pyrimidin-2(1H)-one (3) (200 mg) and alkoxide (1 mol equiv.) in benzene (40 ml) was refluxed under argon for 5—10 h. After removal of the solvent, the residue was chromatographed on a silica gel column. Elution with benzene-ethyl acetate (10 : 1) yielded the di-imine (4).

3-Anilino-1,3-diphenylprop-2-enimine (4a) had m.p. 129.5—130.5 °C (from chloroform-hexane); $\lambda(\text{EtOH})$ 205 (ϵ 3.34 \times 10⁴), 238 (1.82 \times 10⁴), and 363 nm (1.75 \times 10⁴); $\nu(\text{KBr})$ 3 455, 1 615, and 1 600 cm⁻¹; $\delta(\text{CDCl}_3)$ 5.39 (1 H, s) and 6.67—7.66 (17 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 96.3 (d), 156.6 (s), and 168.0 p.p.m. (s), in addition to aromatic carbon peaks (Found: C, 84.4; H, 6.05; N, 9.5. C₂₁H₁₈N₂ requires C, 84.55; H, 6.05; N, 9.4%).

1,3-Diphenyl-3-p-toluidinoprop-2-enimine (4b) had m.p. 164—165 °C (from chloroform-hexane); $\lambda(\text{EtOH})$ 207 (ϵ 2.90 \times 10⁴), 239 (1.85 \times 10⁴), and 365 nm (1.65 \times 10⁴); $\nu(\text{KBr})$ 3 455, 1 620, and 1 600 cm⁻¹; $\delta(\text{CDCl}_3)$ 2.22 (3 H, s), 5.38 (1 H, s), 6.62 (2 H, d, J 7.8 Hz), 6.90 (2 H, d, J 7.8 Hz), and 7.13—7.66 (12 H, m) (Found: C, 84.35; H, 6.4; N, 8.95. C₂₂H₂₀N₂ requires C, 84.6; H, 6.45; N, 8.95%).

1,3-Diphenyl-3-m-toluidinoprop-2-enimine (4c) had m.p. 86—87 °C (from chloroform-hexane); $\nu(\text{KBr})$ 3 450, 1 615, and 1 575 cm⁻¹; $\delta(\text{CDCl}_3)$ 2.20 (3 H, s), 5.38 (1 H, s), and 6.42—7.66 (16 H, m) (Found: C, 84.45; H, 6.45; N, 8.7. C₂₂H₂₀N₂ requires C, 84.6; H, 6.45; N, 8.95%).

3-p-Anisidino-1,3-diphenylprop-2-enimine (4d) had m.p. 134.5—135 °C (from chloroform-hexane); $\lambda(\text{EtOH})$ 206 (ϵ 3.01 \times 10⁴), 238 (1.85 \times 10⁴), and 369 nm (1.55 \times 10⁴); $\nu(\text{KBr})$ 3 460, 1 610, and 1 600 cm⁻¹; $\delta(\text{CDCl}_3)$ 3.70 (3 H, s), 5.37 (1 H, s), 6.65 (4 H, s), and 7.21—7.66 (12 H, m) (Found: C, 80.4; H, 6.1; N, 8.65. C₂₂H₂₀N₂O requires C, 80.45; H, 6.15; N, 8.55%).

3-Anilino-1,3-di-p-tolylprop-2-enimine (4e) had m.p. 127—128 °C (from chloroform-hexane); $\lambda(\text{EtOH})$ 206 (ϵ 3.96 \times 10⁴), 244 (1.85 \times 10⁴), and 363 nm (1.89 \times 10⁴); $\nu(\text{KBr})$ 3 455, 1 615, and 1 595 cm⁻¹; $\delta(\text{CDCl}_3)$ 2.27 (3 H, s), 2.38 (3 H, s), 5.38 (1 H, s), 6.68—7.20 (13 H, m), and 7.51 (2 H, d, J 8.3 Hz) (Found: C, 84.55; H, 6.7; N, 8.5. C₂₃H₂₂N₂ requires C, 84.6; H, 6.8; N, 8.6%).

3-Anilino-1-phenyl-3-p-tolylprop-2-enimine (4f) had m.p. 124.5—125.5 °C (from chloroform-hexane); $\lambda(\text{EtOH})$ 205 (ϵ 3.56 \times 10⁴), 236 (1.82 \times 10⁴), and 360 nm (1.71 \times 10⁴); $\nu(\text{KBr})$ 3 470, 1 610, and 1 520 cm⁻¹; $\delta(\text{CDCl}_3)$ 2.26 (3 H, s), 5.39 (1 H, s), and 6.69—7.66 (16 H, m) (Found: C, 84.55; H, 6.45; N, 8.9. C₂₂H₂₀N₂ requires C, 84.6; H, 6.45; N, 8.95%).

3-Anilino-1-phenylbut-2-enimine (4g) had m.p. 82.5—83.5 °C (from chloroform-hexane); $\lambda(\text{EtOH})$ 204 (ϵ 3.36 \times 10⁴), 229 (1.78 \times 10⁴), and 339 nm (1.89 \times 10⁴); $\nu(\text{KBr})$ 3 450, 1 615, and 1 590 cm⁻¹; $\delta(\text{CDCl}_3)$ 1.95 (3 H, s), 5.16 (1 H, s), and 6.79—7.63 (12 H, m) (Found: C, 81.2; H, 6.8; N, 11.55. C₁₆H₁₆N₂ requires C, 81.3; H, 6.8; N, 11.85%).

4-Anilinopent-3-en-2-one (5) had m.p. 101.5—103 °C (lit.,¹¹ m.p. 103 °C); $\nu(\text{KBr})$ 1 660 and 1 565 cm⁻¹; $\delta(\text{CDCl}_3)$ 1.99 (3 H, s), 2.10 (3 H, s), 5.19 (1 H, s), 7.05—7.43 (5 H, m), and 12.47br (1 H, s).

Reaction of the Di-imine (4a) with Hydrochloric Acid.—A solution of the di-imine (4a) (100 mg) and hydrochloric acid (1 ml) in ethanol (10 ml) was refluxed for 1 h. The reaction mixture was poured into water and extracted with dichloromethane. The extract was washed with aqueous sodium hydrogencarbonate, water, and then dried (anhydrous MgSO₄). After removal of the solvent, the residue was recrystallized from benzene-hexane to yield dibenzoyl-methane (6) in quantitative yield.

Reaction of the Di-imine (4a) with Thionyl Chloride in Pyridine.—To a solution of the di-imine (4a) (100 mg) in pyridine (5 ml) was added thionyl chloride (50 mg) at 0 °C (ice-bath). The mixture was stirred while being warmed to room temperature and then heated at 90 °C for 8 h. The reaction mixture was poured into ice-water and extracted with dichloromethane. The extract was washed with aqueous sodium hydrogencarbonate, water, and then dried (anhydrous MgSO₄). After removal of the solvent, the residue was recrystallized from hexane to yield 1,3,5-tripyrzole (7) (91% yield), m.p. 139 °C (lit.,³ m.p. 138—139 °C); $\nu(\text{BKr})$ 1 595, 1 560, 1 505, 1 485, 1 320, 1 310, 1 125, 765, 710, and 690 cm⁻¹; $\delta(\text{CDCl}_3)$ 6.96 (1 H, s), 7.16—7.58 (13 H, m), and 8.09—8.19 (2 H, m).

Reaction of the Di-imines (4a), (4b), (4d), (4g), and (4i) with Carbon Disulphide.*—A solution of the di-imine (4) (100 mg) in carbon disulphide (5 ml) in a sealed tube was heated at 70 °C for 5—10 h. After the carbon disulphide had been evaporated off under reduced pressure, the residual oil was chromatographed with benzene-ethyl acetate (10 : 1) to give the 1,3-thiazine-2(1H)-thione (8) and/or pyrimidine-2(1H)-thione (9). Data for compounds (8a), (8i), (9d), (9g), and (9i) are given below.

4,6-Diphenyl-1,3-thiazine-2-thione (8a) had m.p. 152—153 °C (from chloroform-hexane); $\lambda(\text{EtOH})$ 205 (ϵ 2.67 \times 10⁴), 242 (1.51 \times 10⁴), 321 (3.51 \times 10⁴), and 479 nm (5.1 \times 10³); $\nu(\text{KBr})$ 1 580, 1 560, 1 455, 1 240, 1 060, 760, and 690 cm⁻¹; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.40—7.75 (9 H, m) and 8.15—8.30 (2 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 111.4 (d), 136.7 (s), 164.3 (s), and 168.3 p.p.m. (s), in addition to aromatic carbon peaks (Found: C, 68.0; H, 3.9; N, 4.95. C₁₆H₁₁NS₂ requires C, 68.3; H, 3.95; N, 5.0%).

5-Methyl-4,6-diphenyl-1,3-thiazine-2-thione (8i) had m.p. 134—135 °C (from chloroform-hexane); $\lambda(\text{EtOH})$ 206 (ϵ 2.93 \times 10⁴), 234 (1.60 \times 10⁴), 315 (2.61 \times 10⁴), and 459 nm (4.9 \times 10³); $\nu(\text{KBr})$ 1 595, 1 545, 1 445, 1 250, 1 045, 755, and 690 cm⁻¹; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.10 (3 H, s), 7.41—7.51 (8 H, m), and 7.68—7.78 (2 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 19.0 (q), 122.2 (s), 138.2 (s), 163.8 (s), and 169.1 p.p.m. (s), in addition to aromatic carbon peaks (Found C, 69.15; H, 4.4; N, 4.7. C₁₇H₁₃NS₂ requires C, 69.1; H, 4.45; N, 4.75%).

1-p-Methoxyphenyl-4,6-diphenylpyrimidine-2(1H)-thione (9d) had m.p. 245 °C (decomp.) (from chloroform-hexane);

* The di-imine (4i) was independently prepared according to a method described previously (ref. 4).

$\lambda(\text{EtOH})$ 209 (ϵ 3.38×10^4), 298 (4.44×10^4), and 409 nm (4.0×10^3); $\nu(\text{KBr})$ 1 605, 1 590, 1 570, 1 510, 1 355, and 1 240 cm^{-1} ; $\delta(\text{CDCl}_3)$ 3.74 (3 H, s), 6.66—7.54 (13 H, m), and 8.18—8.28 (2 H, m) (Found: C, 74.65; H, 4.85; N, 7.45. $\text{C}_{23}\text{H}_{18}\text{N}_2\text{OS}$ requires C, 74.6; H, 4.85; N, 7.55%).

6-Methyl-1,4-diphenylpyrimidine-2(1H)-thione (9g) had m.p. 210—211 °C (decomp.) (from chloroform-hexane); $\nu(\text{KBr})$ 1 605, 1 590, 1 515, 1 350, and 1 240 cm^{-1} ; $\delta(\text{CDCl}_3)$ 2.12 (3 H, d, J 0.6 Hz), 7.10 (1 H, d, J 0.6 Hz), 7.19—7.30 (2 H, m), 7.42—7.64 (6 H, m), and 8.14—8.24 (2 H, m) (Found: C, 73.1; H, 5.0; N, 10.0. $\text{C}_{17}\text{H}_{14}\text{N}_2\text{S}$ requires C, 73.35; H, 5.0; N, 10.05%).

5-Methyl-1,4,6-triphenylpyrimidine-2(1H)-thione (9i) had m.p. 297—298 °C (lit.,⁸ m.p. 298—299 °C); $\nu(\text{KBr})$ 1 605, 1 580, 1 570, 1 500, 1 355, and 1 240 cm^{-1} ; δ_{H} (CDCl_3) 1.89 (3 H, s), 6.99—7.30 (11 H, m), 7.43—7.50 (2 H, m), and 7.67—7.78 (2 H, m); δ_{C} (CDCl_3) 16.9 (q), 116.2 (s), 158.9 (s), 169.1 (s), and 182.2 p.p.m. (s), in addition to aromatic carbon peaks.

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