

## Photochemistry of Pyrimidin-2(1*H*)-ones: Intermolecular Hydrogen Abstraction by an Imino Group Nitrogen

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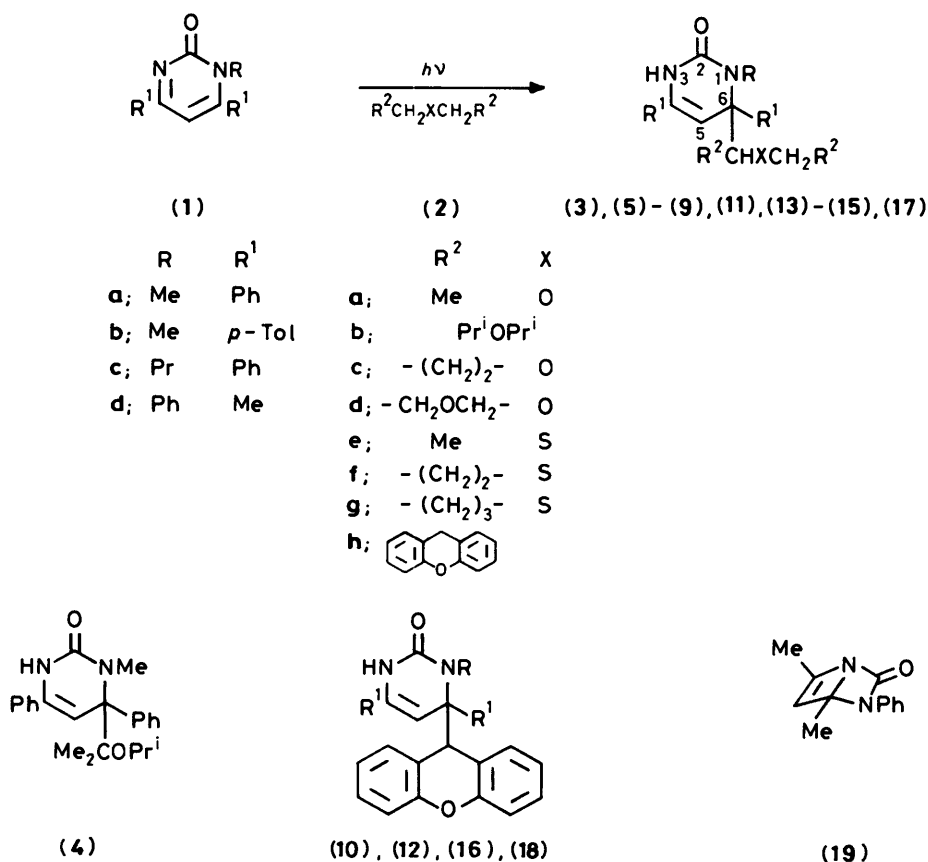
Irradiation of 1-alkyl-4,6-diarylpyrimidin-2(1*H*)-ones (**1a—c**) in the presence of hydrogen donors such as acyclic or cyclic ethers (**2a—d**), sulphides (**2e—g**), and xanthene (**2h**) gave the C—C bonded 1:1 adducts (**3**)—(**16**) of (**1**) and (**2**), *via* intermolecular hydrogen atom abstraction of the excited imino nitrogen of the starting pyrimidin-2(1*H*)-one (**1**). In contrast, irradiation of 1-aryl-4,6-dialkylpyrimidin-2(1*H*)-one (**1d**) in the presence of hydrogen donors gave, predominantly, the electrocyclization product (**19**) in addition to the 1:1 adducts (**17**)—(**18**).

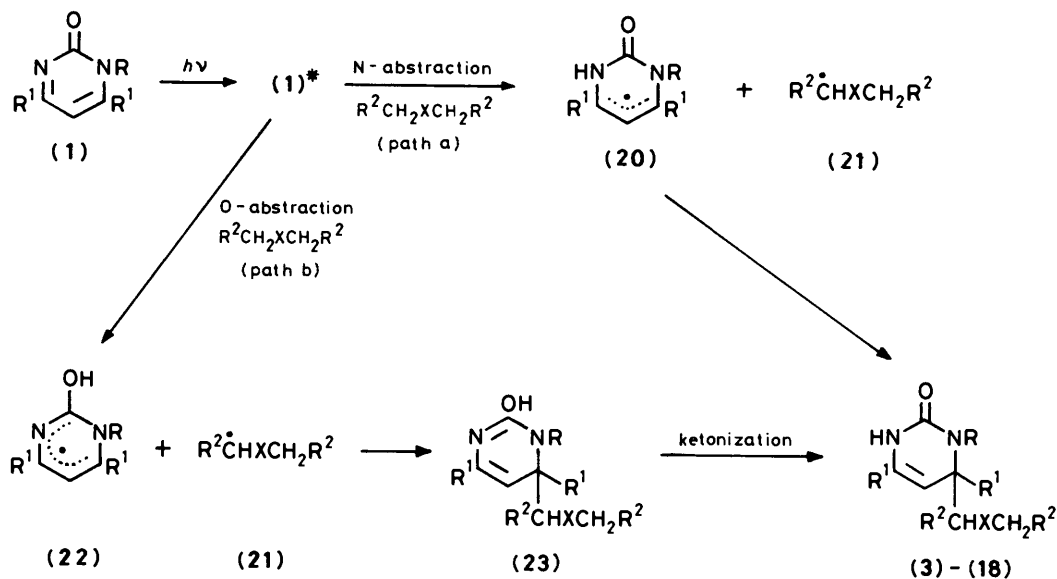
It is well documented that the excited states of imines have little tendency to undergo hydrogen abstraction.<sup>1</sup> The reason generally invoked is the poorer reactivity of the carbon–nitrogen double bond as a result of rapid radiationless decay processes which result from twisting around the carbon–nitrogen double bond. However, several reactions analogous to the hydrogen abstraction of the carbonyl group have been reported.<sup>2</sup> Intramolecular hydrogen abstraction by the nitrogen of CO–N=C and CO–C=N– chromophores was reported by Koch *et al.*,<sup>2a,c</sup> Knappe *et al.*,<sup>2b,f</sup> Toshima *et al.*,<sup>2d</sup> and Izawa *et al.*<sup>2e</sup> Toshima and his co-workers also reported intermolecular hydrogen abstraction by acylimines.<sup>2h–j</sup> During the course of our studies dealing with the photochemical reactivities of cyclic conjugated nitrogen-carbonyl systems such as pyrimidinones<sup>3</sup> and pyrazinones,<sup>4</sup> intramolecular hydrogen abstraction by pyrimidin-2-ones was observed.<sup>2g</sup> Upon irradi-

ation, 1-aryl-4-propyl- or 1-aryl-4-(3-ethoxypropyl)-6-methylpyrimidin-2(1*H*)-ones gave the photoelimination products, 1-aryl-4,6-dimethylpyrimidin-2(1*H*)-ones, *via* intramolecular  $\gamma$ -hydrogen atom abstraction by the excited imino nitrogen of the starting pyrimidine-2(1*H*)-one. Here we describe the photochemical addition of 1-alkyl-4,6-diarylpyrimidin-2(1*H*)-ones (**1a—c**) to aliphatic ethers (**2a—d**), sulphides (**2e—g**), and xanthene (**2h**) which proceeded by hydrogen atom abstraction by the imino nitrogen of (**1**).<sup>5</sup>

### Results and Discussion

Irradiation of a solution of 1-methyl-4,6-diphenylpyrimidin-2(1*H*)-one (**1a**) in benzene or methanol with a high-pressure mercury lamp through a Pyrex filter under argon at room temperature, gave no photoproducts, starting pyrimidin-



**Table 1.** Yield of photoproducts (3)—(19)

Compd.	R	R <sup>1</sup>	R <sup>2</sup>	X	Yield (%) <sup>a</sup>
(3)	Me	Ph	Me	O	56
(4)	Me	Ph	Me <sub>2</sub> COPr <sup>t</sup>		43
(5)	Me	Ph	-(CH <sub>2</sub> ) <sub>2</sub> -	O	51
(6)	Me	Ph	-CH <sub>2</sub> -O-CH <sub>2</sub> -	O	65 <sup>b</sup>
(7)	Me	Ph	Me	S	45
(8)	Me	Ph	-(CH <sub>2</sub> ) <sub>2</sub> -	S	21, 19 <sup>c</sup>
(9)	Me	Ph	-(CH <sub>2</sub> ) <sub>3</sub> -	S	14 <sup>d</sup>
(10)	Me	Ph	Xanthenyl		93
(11)	Me	<i>p</i> -Tol	Me	S	24
(12)	Me	<i>p</i> -Tol	Xanthenyl		78
(13)	Pr	Ph	Me	O	42
(14)	Pr	Ph	-(CH <sub>2</sub> ) <sub>2</sub> -	O	92 <sup>e</sup>
(15)	Pr	Ph	Me	S	69
(16)	Pr	Ph	Xanthenyl		77
(17)	Ph	Me	-(CH <sub>2</sub> ) <sub>2</sub> -	O	6 19 (45%)
(18)	Ph	Me	Xanthenyl		22 19 (37%)

<sup>a</sup> Isolated yield. <sup>b</sup> Mixture of two stereoisomers (ratio 63:37). <sup>c</sup> Another stereoisomer. <sup>d</sup> Mixture of two stereoisomers (ratio 66:34). <sup>e</sup> Mixture of two stereoisomers (ratio 67:33).

2(1*H*)-one (**1a**) being recovered quantitatively. In contrast, irradiation of the pyrimidin-2(1*H*)-one (**1a**) in diethyl ether-benzene under the same conditions gave the C-C bonded 1:1 adduct (**3**) of (**1a**) and diethyl ether (**2a**) in 56% yield. The following analytical and spectroscopic data indicated that the photoproduct (**3**) was a 1:1 adduct. Thus it showed olefinic, amino, and methine protons at  $\delta$  4.92 (1 H, d, *J* 2.0 Hz), 5.72 (1 H, br s), and 3.72 (1 H, q, *J* 6.4 Hz), respectively. The addition site of ether in the C-C bonded 1:1 adduct (**3**) was assigned to the 6-position since the n.m.r. spectrum of (**3**) showed long-range coupling (*J* 2.0 Hz) between the amino proton and the C-5 olefinic proton.<sup>6</sup> Furthermore, when the amino proton signal was irradiated, the olefinic proton signal, which appeared as doublet, collapsed to a singlet. In a similar manner, irradiation of the pyrimidin-2(1*H*)-one (**1a**) in benzene in the presence of hydrogen donors such as aliphatic ethers (**2b**–**d**), sulphides (**2e**–**g**), and xanthen (**2h**) under similar conditions to those described above gave the C-C bonded 1:1 adducts (**4**)–(**10**) in 14–65% yield. In the reaction of (**1a**) with tetrahydrothiophene

**Table 2.** Yield of the 1:1 adduct (**10**) by photoreaction (366 nm)<sup>a</sup> of (**1a**)<sup>b</sup> in the presence of xanthen (**2h**)

Solvent	Additive	Yield (%) <sup>c</sup>	
		( <b>10</b> )	Recovered ( <b>1a</b> )
Benzene		80	18
Acetone		77	22
Benzene	<i>trans</i> -Stilbene <sup>d</sup>	<2	81

<sup>a</sup> A Pyrex glass filter and a methanol solution of naphthalene (5 g l<sup>-1</sup>) were used to isolate the 366 nm region. Irradiation time, 3 h. <sup>b</sup> U.v. spectrum of (**1a**) showed an end absorption until 380 nm ( $\epsilon$  2 100 at 366 nm). <sup>c</sup> Isolated yield. <sup>d</sup> U.v. spectrum of *trans*-stilbene shows no absorption at 366 nm.

(**2f**), two stereoisomeric 1:1 adducts (**9**) and (**9'**), were isolated. Compound (**1a**) with dioxane (**2d**) and pentamethylene sulphide (**2g**) gave a mixture of two stereoisomeric photoproducts, (**6**) and (**9**). The structure of these photoproducts which were not separated was elucidated on the basis of spectroscopic properties and elemental analyses (see Experimental section). Characteristically the 1:1 adducts absorbed at *ca.* 3 220–3 250 (NH<sub>2</sub> stretching) and *ca.* 1 645–1 700 cm<sup>-1</sup> (two CO stretching bands); no C=N absorption was observed. The <sup>1</sup>H n.m.r. spectra of the 1:1 adducts (**3**)–(**10**) showed a signal at *ca.*  $\delta$  4.85–5.24 with a coupling constant of 2.0–2.5 Hz (C-5 olefinic H) and the <sup>13</sup>C n.m.r. spectra a signal at  $\delta_c$  61.8–66.0 p.p.m. (C-6). Irradiation of 1-alkyl-4,6-diarylpyrimidin-2(1*H*)-ones (**1b**, **c**) in the presence of the hydrogen donors (**2**) also yielded the C-C bonded 1:1 adducts (**11**)–(**16**) in moderate to high yields. In contrast, irradiation of 1-aryl-4,6-dialkylpyrimidin-2(1*H*)-one (**1d**) in tetrahydrofuran (**2c**) or in the presence of xanthen (**2h**) gave the 1,3-diazabicyclo[2.2.0]hex-5-ene (**19**) as the major product together with the C-C bonded 1:1-adducts (**17**) and (**18**). When a solution of the pyrimidin-2(1*H*)-one (**1a**) and xanthen (**2h**) in benzene was irradiated at 366 nm in the presence of *trans*-stilbene as a triplet quencher, formation of the 1:1 adduct (**10**) was almost completely quenched. Irradiation of (**1a**) and (**2h**) in both acetone and benzene at 366 nm gave the 1:1 adduct (**10**) in similar yield (see Table 2). These results suggest that the 1:1 adducts are formed *via* an excited triplet

state of the pyrimidin-2(1*H*)-one (**1**) and a mechanism for the reaction is shown in the Scheme. In this, the excited pyrimidin-2(1*H*)-one (**1**) abstracts a hydrogen atom from the hydrogen donor either with the imino group nitrogen (N-abstraction: path a) or the ureide group carbonyl oxygen (O-abstraction: path b) to yield radicals (**20**) or (**22**) and (**21**). Subsequent recombination of the radicals thus formed would give the C—C bonded 1:1 adducts (**3**)—(**18**). Although it is reported that the hydrogen abstraction process in amides is quite inefficient,<sup>7</sup> we studied the photochemical reactions of 4,6-diphenyl-1-propylpyrimidin-2(1*H*)-one (**1c**) and 4,6-dimethyl-1-propylpyrimidin-2(1*H*)-one,<sup>29</sup> in order to probe the possibility of a hydrogen abstraction reaction of the ureide carbonyl oxygen. Irradiation of the pyrimidin-2(1*H*)-one (**1c**) in benzene gave no photo-products, starting material being quantitatively recovered. Irradiation of 4,6-dimethyl-1-propylpyrimidin-2(1*H*)-one in benzene gave the 1,3-diazabicyclo[2.2.0]hex-5-ene as the sole product, no photoelimination products derived from a hydrogen abstraction process by the ureide carbonyl oxygen being produced.<sup>29</sup> These results suggest that the C—C bonded 1:1 adducts (**3**)—(**18**) arise *via* intermolecular hydrogen abstraction by the imino group nitrogen of (**1**) followed by recombination of the radicals (**20**) and (**21**) thus formed (path a).

## Experimental

M.p.s are uncorrected and measured with a Yanaco micro-melting point apparatus (MP-J3). U.v. spectra were determined with a JASCO UVIDECS-505 spectrophotometer, i.r. spectra were recorded on a Hitachi 260-30 spectrophotometer, n.m.r. spectra were run on a JEOL FX-100 spectrometer (100 MHz) using CDCl<sub>3</sub> as solvent and SiMe<sub>4</sub> as internal standard, and mass spectra were recorded on a Hitachi M-80 spectrometer. A HALōs (Eikossa EHP-300 W) high-pressure mercury lamp was used as an irradiation source.

**Starting Materials.**—1-Alkyl-4,6-diarylpyrimidin-2(1*H*)-ones (**1a**—**c**) were prepared by a modification of the method described in the literature,<sup>8,9</sup> and 1-phenyl-4,6-dimethylpyrimidin-2(1*H*)-one (**1d**) was prepared according to the method of Nováček.<sup>8</sup> The properties of compounds (**1a**—**c**) are listed below.

1-Methyl-4,6-diphenylpyrimidin-2(1*H*)-one (**1a**), m.p. 184—185 °C (Found: C, 77.95; H, 5.3; N, 10.75. C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O requires C, 77.85; H, 5.4; N, 10.75%); λ<sub>max</sub>(EtOH) 271 (ε 15 800) and 333 nm (12 300); ν<sub>max</sub>(KBr) 1 645, 1 600, 1 595, 770, 705, and 690 cm<sup>-1</sup>; δ<sub>H</sub> 3.45 (3 H, s), 6.73 (1 H, s), 7.30—7.70 (8 H, m), and 8.00—8.20 (2 H, m).

1-Methyl-4,6-di-*p*-tolylpyrimidin-2(1*H*)-one (**1b**), m.p. 189—190 °C (Found: C, 78.3; H, 6.1; N, 9.6. C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O requires C, 78.6; H, 6.25; N, 9.65%); λ<sub>max</sub>(EtOH) 274 (ε 17 000) and 334 nm (13 600); ν<sub>max</sub>(KBr) 1 665, 1 645, 1 495, 810, and 790 cm<sup>-1</sup>; δ<sub>H</sub> 2.41 (3 H, s), 2.46 (3 H, m), 3.47 (3 H, s), 6.70 (1 H, s), 7.22—7.33 (6 H, m), and 8.03 (2 H, d, *J* 8.2 Hz).

4,6-Diphenyl-1-propylpyrimidin-2(1*H*)-one (**1c**), m.p. 170—171 °C (Found: C, 78.45; H, 6.25; N, 9.65. C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O requires C, 78.6; H, 6.25; N, 9.65%); ν<sub>max</sub>(KBr) 1 660, 1 645, 1 600, 780, and 705 cm<sup>-1</sup>; δ<sub>H</sub> 0.75 (3 H, t), 1.59—1.81 (2 H, m), 3.88 (2 H, t), 6.67 (1 H, s), 7.34—7.58 (8 H, m), and 8.04—8.16 (2 H, m).

**General Procedure for the Photochemical Reactions of the Pyrimidin-2(1*H*)-ones (**1a**—**d**) in the Presence of the Hydrogen Donors (**2a**—**h**).**—A solution of the pyrimidin-2(1*H*)-one (**1**) (200 mg) in a hydrogen-donating solvent [THF (**2c**) or dioxane (**2d**)] (70 ml), or in ether (**2a**, **b**)—benzene (20—50 ml), or in benzene (70 ml) in the presence of a hydrogen donor [*ca.* 1 ml for (**2e**, **f**) and 2 molar equiv. for (**2h**)] was irradiated in a Pyrex vessel with a high-pressure mercury lamp (300 W) under argon

for 15 h at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene-ethyl acetate (9:1—1:1) as eluant to give the C—C bonded 1:1 adducts (**3**)—(**18**).

The 1:1 adduct (**3**), m.p. 134.5—135.5 °C (Found: C, 75.05; H, 7.2; N, 8.3. C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub> requires C, 74.95; H, 7.2; N, 8.3%); λ<sub>max</sub>(EtOH) 268 (ε 4 500); ν<sub>max</sub>(KBr) 3 230, 1 680, 1 660, 1 105, 760, and 700 cm<sup>-1</sup>; δ<sub>H</sub> 0.86 (3 H, t, *J* 7.3 Hz), 1.30 (3 H, d, *J* 6.4 Hz), 2.85 (3 H, s), 2.75—3.52 (1 H, m), 3.22—3.53 (1 H, m), 3.72 (1 H, q, *J* 6.4 Hz), 4.92 (1 H, d, *J* 2.0 Hz), 5.72 (1 H, br s), and 7.18—7.48 (10 H, m); δ<sub>C</sub> 15.2 (q), 15.6 (q), 32.3 (q), 63.6 (s), 65.3 (t), 105.6 (d), 125.6 (d), 128.3 (d), 128.5 (d), 135.6 (s), 140.2 (s), 146.4 (s), and 155.4 (s); *m/z* (c.i.) 337 (*M*<sup>+</sup> + 1).

The 1:1 adduct (**4**), m.p. 73 °C (decomp.) (Found: C, 75.55; H, 7.6; N, 7.6. C<sub>23</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub> requires C, 75.8; H, 7.75; N, 7.7%); ν<sub>max</sub>(KBr) 3 250, 1 670, 1 650, 1 155, 765, 700, and 685 cm<sup>-1</sup>; δ<sub>H</sub> 0.92 (3 H, d, *J* 6.8 Hz), 0.96 (3 H, s), 1.13 (3 H, d, *J* 6.8 Hz), 1.26 (3 H, s), 2.77 (3 H, s), 3.60—3.85 (1 H, m), 5.23 (1 H, d, *J* 2.0 Hz), 6.30 (1 H, br s), and 7.23—7.58 (10 H, m); δ<sub>C</sub> 21.1 (q), 22.5 (q), 24.5 (q), 25.0 (q), 32.3 (q), 63.9 (d), 64.7 (s), 79.7 (s), 105.1 (d), 126.7 (d), 127.0 (d), 127.7 (d), 128.4 (d), 128.6 (d), 135.9 (s), 141.0 (s), 144.6 (s), and 155.3 (s).

The 1:1 adduct (**5**), m.p. 208—210 °C (Found: C, 75.1; H, 6.6; N, 8.3. C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> requires C, 75.4; H, 6.65; N, 8.35%); ν<sub>max</sub>(KBr) 3 220, 1 700, 1 675, 1 075, 755, and 700 cm<sup>-1</sup>; δ<sub>H</sub> 1.55—2.15 (4 H, m), 2.87 (3 H, s), 3.75—4.02 (2 H, m), 4.31 (1 H, t, *J* 6.8 Hz), 4.92 (1 H, d, *J* 2.4 Hz), 5.61 (1 H, br s), and 7.17—7.52 (10 H, m); δ<sub>C</sub> 25.8 (t), 27.5 (t), 32.3 (q), 62.1 (s), 69.5 (t), 84.7 (d), 105.4 (d), 125.1 (d), 127.0 (d), 128.4 (d), 128.5 (d), 136.3 (s), 140.1 (s), 145.7 (s), and 155.3 (s).

The 1:1 adduct of (**1a**) and dioxane (**2d**) was a mixture of two incompletely separated stereoisomers (**6**) and (**6'**), the structures of which were elucidated on the basis of their n.m.r. spectra; m.p. (for a mixture) 188—189 °C [Found (for a mixture): C, 71.9; H, 6.1; N, 8.1. C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub> requires C, 72.0; H, 6.3; N, 8.0%]; ν<sub>max</sub>(KBr) (for a mixture) 3 220, 1 690, 1 660, 1 125, 760, and 700 cm<sup>-1</sup>; δ<sub>H</sub> (for **6**) 2.85 (3 H, s), 3.36—4.05 (7 H, m), 4.85 (1 H, d, *J* 2.4 Hz), 5.97 (1 H, br s), and 7.14—7.54 (10 H, m); δ<sub>H</sub> [for (**6'**)] 2.82 (3 H, s), 3.36—4.05 (7 H, m), 5.26 (1 H, d, *J* 2.4 Hz), 6.63 (1 H, br s), and 7.14—7.54 (10 H, m).

The 1:1 adduct (**7**), m.p. 182—183 °C (Found: C, 71.45; H, 6.8; N, 7.95. C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>OS requires C, 71.55; H, 6.85; N, 7.95%); λ<sub>max</sub>(EtOH) 267 nm (ε 3 300); ν<sub>max</sub>(KBr) 3 250, 1 680, 1 660, 775, 765, and 705 cm<sup>-1</sup>; δ<sub>H</sub> 1.17 (3 H, t, *J* 7.3 Hz), 1.24 (3 H, d, *J* 6.8 Hz), 2.39 (2 H, q, *J* 7.3 Hz), 2.85 (3 H, s), 3.19 (1 H, q, *J* 6.8 Hz), 5.24 (1 H, d, *J* 2.5 Hz), 6.20 (1 H, br s), and 7.26—7.53 (10 H, m).

The 1:1 adduct (**8**), m.p. 116—118 °C (Found: C, 72.25; H, 6.45; N, 7.75. C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>OS requires C, 71.95; H, 6.3; N, 8.0%); ν<sub>max</sub>(KBr) 3 240, 1 675, 1 660sh, 775, 755, and 700 cm<sup>-1</sup>; δ<sub>H</sub> 1.89—2.30 (4 H, s), 2.73—2.92 (2 H, m), 2.89 (3 H, s), 4.11 (1 H, br t), 4.92 (1 H, d, *J* 2.4 Hz), 5.97 (1 H, br s), and 7.13—7.46 (10 H, m); δ<sub>C</sub> 31.4 (t), 32.2 (q), 32.3 (t), 33.0 (t), 59.9 (d), 61.8 (s), 107.0 (d), 124.6 (d), 127.0 (d), 128.2 (d), 128.5 (d), 135.2 (s), 139.6 (s), 146.8 (s), and 155.1 (s).

The 1:1 adduct (**8'**), m.p. 125—127 °C (Found: C, 72.25; H, 6.55; N, 7.8. C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>OS requires C, 71.95; H, 6.3; N, 8.0%); ν<sub>max</sub>(KBr) 3 220, 1 675, 1 665, 760, 700, and 685 cm<sup>-1</sup>; δ<sub>H</sub> 1.63—2.20 (4 H, m), 2.63—2.84 (2 H, m), 2.87 (3 H, s), 4.11 (1 H, br t), 5.20 (1 H, d, *J* 2.0 Hz), 6.80 (1 H, br s), and 7.14—7.58 (10 H, m); δ<sub>C</sub> 31.6 (t), 32.2 (q), 33.0 (t), 60.4 (d), 62.5 (s), 105.7 (d), 125.3 (d), 127.1 (d), 128.2 (d), 128.4 (d), 140.8 (s), 144.1 (s), 145.8 (s), and 155.5 (s).

The 1:1 adduct of (**1a**) and thiane (**2g**) was a mixture of two stereoisomers (**9**) and (**9'**) which could not be completely separated; m.p. (for a mixture) 162—164 °C [Found (for a mixture): C, 72.75; H, 6.7; N, 7.65. C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>OS requires C, 72.5; H, 6.65; N, 7.7%]; ν<sub>max</sub>(for a mixture) 3 230, 1 680, 1 660,

765, and 705  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ [for (9)] 1.38—2.13 (6 H, m), 2.52—2.62 (2 H, m), 2.85 (3 H, s), 3.03—3.26 (1 H, m), 5.20 (1 H, d,  $J$  2.0 Hz), 5.94 (1 H, br s), and 7.14—7.60 (10 H, m);  $\delta_{\text{H}}$ [for (9')] 1.38—2.13 (6 H, m), 2.52—2.62 (2 H, m), 2.86 (3 H, s), 3.05—3.26 (1 H, m), 4.95 (1 H, d,  $J$  2.4 Hz), 5.76 (1 H, br s), and 7.16—7.60 (10 H, m).

The 1:1 adduct (10), m.p. 146—147 °C (Found: C, 81.25; H, 5.4; N, 6.3.  $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_2$  requires C, 81.05; H, 5.45; N, 6.3%);  $\nu_{\text{max}}$ (KBr) 3 220, 1 675, 1 655, 765, 750, and 700  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  2.40 (3 H, s), 4.40 (1 H, s), 5.07 (1 H, d,  $J$  2.4 Hz), 6.05 (1 H, br s), 6.82—6.91 (4 H, m), and 7.05—7.38 (14 H, m);  $\delta_{\text{C}}$  31.8 (q), 53.3 (d), 66.0 (s), 103.8 (d), 116.1 (d), 116.4 (d), 120.1 (d), 120.6 (d), 121.8 (d), 122.7 (d), 125.7 (d), 127.2 (d), 128.0 (d), 128.3 (d), 128.4 (d), 130.7 (d), 135.7 (s), 141.0 (s), 143.3 (s), 153.5 (s), and 154.8 (s).

The 1:1 adduct (11), m.p. 87—88 °C (Found: C, 72.4; H, 7.4; N, 7.3.  $\text{C}_{23}\text{H}_{28}\text{N}_2\text{OS}$  requires C, 72.6; H, 7.4; N, 7.35%);  $\nu_{\text{max}}$ (KBr) 3 220, 1 680, 1 660, and 815  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  0.98 (t, 3 H,  $J$  7.3 Hz), 1.40 (3 H, d,  $J$  6.8 Hz), 1.71—2.02 (2 H, m), 2.34 (6 H, s), 2.85 (3 H, s), 3.28 (1 H, q,  $J$  6.8 Hz), 4.98 (1 H, d,  $J$  2.5 Hz), 5.86 (1 H, br s), and 7.12—7.34 (8 H, m);  $\delta_{\text{C}}$  14.7 (q), 18.0 (q), 21.0 (q), 21.2 (q), 26.0 (t), 32.2 (q), 50.5 (d), 63.0 (s), 106.6 (d), 124.8 (d), 128.1 (d), 128.9 (d), 129.1 (d), 132.5 (s), 136.6 (s), 138.4 (s), 139.8 (s), 143.2 (s), and 155.2 (s).

The 1:1 adduct (12), m.p. 151.5—152.5 °C (Found: C, 81.0; H, 5.9; N, 5.95.  $\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_2$  requires C, 81.3; H, 5.95; N, 5.9%);  $\nu_{\text{max}}$ (KBr) 3 200, 1 665, 1 645, 805, and 745  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  2.35 (6 H, s), 2.36 (3 H, s), 4.35 (1 H, s), 5.03 (1 H, d,  $J$  2.5 Hz), 5.33 (1 H, br s), and 6.64—7.25 (16 H, m).

The 1:1 adduct (13), m.p. 109.5—110 °C (Found: C, 75.5; H, 7.7; N, 7.6.  $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_2$  requires C, 75.8; H, 7.75; N, 7.7%);  $\nu_{\text{max}}$ (KBr) 3 240, 1 665, 1 650sh, 765, and 700  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  0.44 (3 H, t,  $J$  6.8 Hz), 0.87 (3 H, t,  $J$  6.3 Hz), 1.00—1.20 (2 H, m), 1.29 (3 H, d,  $J$  6.1 Hz), 2.67—3.67 (3 H, m), 3.73 (2 H, q,  $J$  6.3 Hz), 4.94 (1 H, d,  $J$  2.2 Hz), 5.74 (1 H, br s), and 7.17—7.50 (10 H, m).

The 1:1 adduct (14) of (1c) and THF (2b) was a mixture of two stereoisomers, (14) and (14'), m.p. (for a mixture) 148—149.5 °C [Found (for a mixture): C, 76.3; H, 7.3; N, 7.5.  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_2$  requires C, 76.2; H, 7.25; N, 7.7%];  $\nu_{\text{max}}$ (for a mixture) 3 210, 1 665, 1 645sh, 1 075, 750, and 695  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$ [for (14)] 0.47 (3 H, t), 1.03—1.31 (2 H, m), 1.6—2.1 (4 H, m), 2.98—3.32 (1 H, m), 3.48—3.96 (3 H, m), 4.2—4.4 (1 H, m), 4.96 (1 H, d,  $J$  2.4 Hz), 5.71 (1 H, br s), and 7.22—7.58 (10 H, m);  $\delta_{\text{H}}$ [for (14')] 0.43 (3 H, t), 1.03—1.31 (2 H, m), 1.6—2.1 (4 H, m), 2.98—3.32 (1 H, m), 3.48—3.96 (3 H, m), 4.2—4.4 (1 H, m), 5.15 (1 H, d,  $J$  2.0 Hz), 6.24 (1 H, br s), and 7.22—7.58 (10 H, m).

The 1:1 adduct (15), m.p. 167.5—168.5 °C (Found: C, 72.6; H, 7.4; N, 7.2.  $\text{C}_{23}\text{H}_{28}\text{N}_2\text{OS}$  requires C, 72.6; H, 7.4; N, 7.35%);  $\nu_{\text{max}}$ (KBr) 3 239, 1 665, 1 655sh, 780, 755, and 700  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  0.41 (3 H, t,  $J$  7.3 Hz), 0.88—1.26 (2 H, m), 1.14 (3 H, t,  $J$  6.8 Hz), 1.29 (3 H, d,  $J$  6.8 Hz), 2.31 (2 H, q,  $J$  6.8 Hz), 2.99—3.27 (2 H, m), 3.55—3.84 (1 H, m), 5.31 (1 H, d,  $J$  2.0 Hz), 6.84 (1 H, br s), and 7.21—7.55 (10 H, m);  $\delta_{\text{C}}$  10.5 (q), 14.7 (q), 17.4 (q), 22.4 (t), 26.1 (t), 44.9 (t), 50.8 (d), 62.6 (s), 107.7 (d), 125.7 (d), 127.0 (d), 128.1 (d), 128.4 (d), 135.6 (s), 140.7 (s), 145.2 (s), and 155.6 (s);  $m/z$  (c.i.) 381 ( $M^+ + 1$ ).

The 1:1 adduct (16), m.p. 150—150.5 °C (Found: C, 81.1; H, 5.95; N, 5.9.  $\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_2$  requires C, 81.3; H, 5.95; N, 5.9%);

$\nu_{\text{max}}$ (KBr) 3 210, 1 675, 1 650, 765, 745, and 695  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  0.42 (3 H, t), 0.68—1.02 (2 H, m), 2.71—3.31 (2 H, m), 4.37 (1 H, s), 5.03 (1 H, d,  $J$  2.4 Hz), 5.67 (1 H, br s), and 6.67—7.67 (18 H, m).

The 1:1 adduct (17), m.p. 151—152 °C (Found: C, 70.35; H, 7.35; N, 10.65.  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}$  requires C, 70.55; H, 7.4; N, 10.3%);  $\nu_{\text{max}}$ (KBr) 3 220, 1 655, 760, and 700  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  1.29 (3 H, s), 1.78 (3 H, d,  $J$  1.0 Hz), 1.64—2.20 (4 H, m), 3.61—3.94 (3 H, m), 4.46 (1 H, br s), 6.81 (1 H, br s), and 7.12—7.44 (5 H, m);  $\delta_{\text{C}}$  18.3 (q), 26.3 (t), 27.0 (q), 27.4 (t), 64.0 (s), 69.0 (t), 84.0 (d), 99.0 (d), 127.7 (d), 130.8 (d), 131.7 (d), 138.0 (s), 154.2 (s), and 155.4 (s);  $m/z$  (c.i.) 273 ( $M^+ + 1$ ).

The 1:1 adduct (18), m.p. 124—125 °C (Found: C, 78.15; H, 5.8; N, 7.2.  $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_2$  requires C, 78.5; H, 5.8; N, 7.3%);  $\nu_{\text{max}}$ (KBr) 3 220, 1 695, 1 660, 765, 750, and 700  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  1.21 (3 H, m), 1.38 (3 H, d,  $J$  1.5 Hz), 3.84 (1 H, s), 4.43 (1 H, q,  $J$  1.5 Hz), 5.33 (1 H, br s), 6.76—6.85 (m, 2 H), and 7.02—7.38 (11 H, m);  $\delta_{\text{C}}$  19.9 (q), 26.7 (q), 52.6 (d), 59.6 (s), 102.3 (d), 116.4 (d), 121.6 (d), 122.6 (d), 122.9 (d), 127.6 (d), 128.2 (d), 128.5 (d), 129.7 (d), 130.6 (d), 130.9 (d), 134.6 (s), 137.8 (s), 153.4 (s), and 153.5 (s).

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