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

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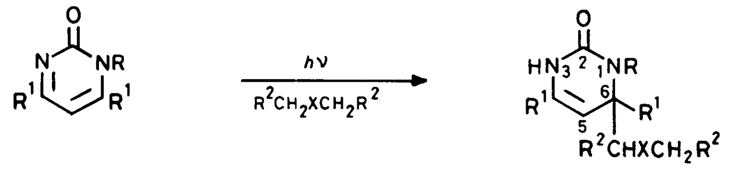
Irradiation of 1-alkyl-4,6-diarylpyrimidin-2(1*H*)-ones (**1a**—**c**) in the presence of hydrogen donors such as acyclic or cyclic ethers (**2a**—**d**), sulphides (**2e**—**g**), and xanthene (**2h**) gave the C–C bonded 1:1 adducts (**3**)—(**16**) of (**1**) and (**2**), *via* intermolecular hydrogen 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.[1] 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.[2] Intramolecular hydrogen abstraction by the nitrogen of CO–N=C and CO–C=N– chromophores was reported by Koch *et al.*,[2a,c] Knappe *et al.*,[2b,f] Toshima *et al.*,[2d] and Izawa *et al.*[2e] Toshima and his co-workers also reported intermolecular hydrogen abstraction by acylimines.[2h–j] During the course of our studies dealing with the photochemical reactivities of cyclic conjugated nitrogen-carbonyl systems such as pyrimidinones[3] and pyrazinones,[4] intramolecular hydrogen abstraction by pyrimidin-2-ones was observed.[2g] Upon irradiation, 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 γ-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).[5]

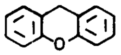
Results and Discussion

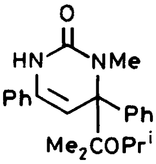
Irradiation of a solution of 1-methyl-4,6-diphenylpyrimidin-2(1*H*)-one (**1a**) in benzene or methanol with a high-pressure mercury lamp through a Pyrex filter under argon at room temperature, gave no photoproducts, starting pyrimidin-



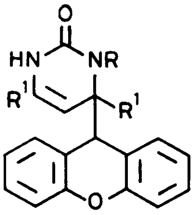
(**1**) (**2**) (**3**),(**5**)-(**9**),(**11**),(**13**)-(**15**),(**17**)

	R	R^1
a;	Me	Ph
b;	Me	*p*-Tol
c;	Pr	Ph
d;	Ph	Me

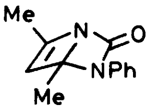
	R^2	X
a;	Me	O
b;	Pr^{i}OPr^i	
c;	-(CH$_2$)$_2$-	O
d;	-CH$_2$OCH$_2$-	O
e;	Me	S
f;	-(CH$_2$)$_2$-	S
g;	-(CH$_2$)$_3$-	S
h;		



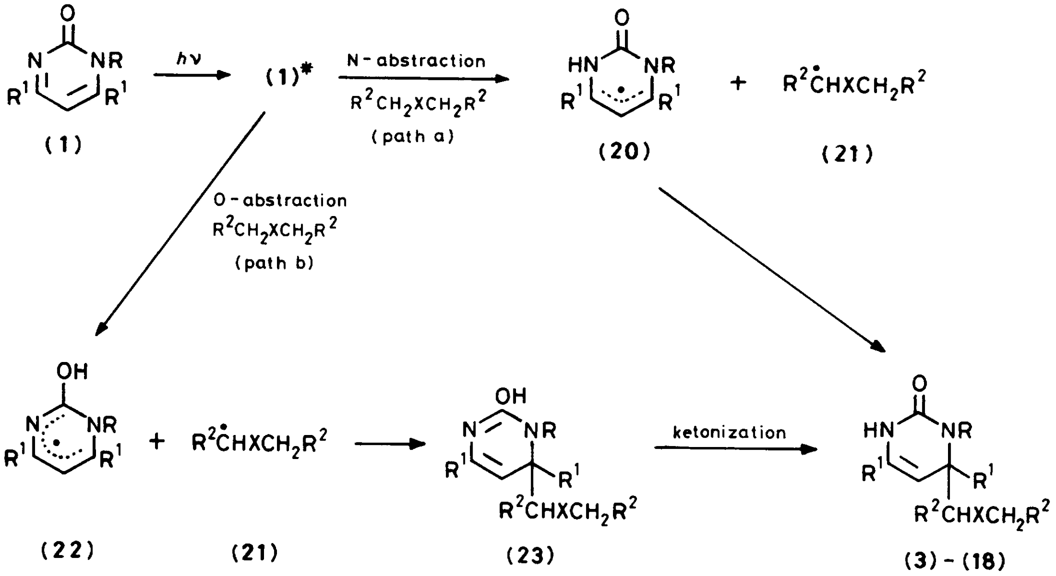
(**4**)



(**10**), (**12**), (**16**), (**18**)



(**19**)



Scheme.

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

Compd.	R	R^1	R^2	X	Yield (%)[a]
(**3**)	Me	Ph	Me	O	56
(**4**)	Me	Ph	Me$_2$COPr^i		43
(**5**)	Me	Ph	–(CH$_2$)$_2$–	O	51
(**6**)	Me	Ph	–CH$_2$–O–CH$_2$–	O	65[b]
(**7**)	Me	Ph	Me	S	45
(**8**)	Me	Ph	–(CH$_2$)$_2$–	S	21, 19[c]
(**9**)	Me	Ph	–(CH$_2$)$_3$–	S	14[d]
(**10**)	Me	Ph	Xanthenyl		93
(**11**)	Me	*p*-Tol	Me	S	24
(**12**)	Me	*p*-Tol	Xanthenyl		78
(**13**)	Pr	Ph	Me	O	42
(**14**)	Pr	Ph	–(CH$_2$)$_2$–	O	92[e]
(**15**)	Pr	Ph	Me	S	69
(**16**)	Pr	Ph	Xanthenyl		77
(**17**)	Ph	Me	–(CH$_2$)$_2$–	O	6 *19* (45%)
(**18**)	Ph	Me	Xanthenyl		22 *19* (37%)

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

Table 2. Yield of the 1:1 adduct (**10**) by photoreaction (366 nm)[a] of (**1a**)[b] in the presence of xanthene (**2h**)

		Yield (%)[c]	
Solvent	Additive	(**10**)	Recovered (**1a**)
Benzene		80	18
Acetone		77	22
Benzene	*trans*-Stilbene[d]	<2	81

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

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 δ 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.[6] 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 xanthene (**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 (**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$_2$ stretching) and *ca.* 1 645—1 700 cm^{1} (two CO stretching bands); no C=N absortion was observed. The ^{1}H N.m.r. spectra of the 1:1 adducts (**3**)—(**10**) showed a signal at *ca.* δ 4.85—5.24 with a coupling constant of 2.0—2.5 Hz (C-5 olefinic H) and the ^{13}C n.m.r. spectra a signal at δ$_C$ 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 xanthene (**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 xanthene (**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 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,[7] 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,[2g] 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 photoproducts, 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.[2g] 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 micromelting point apparatus (MP-J3). U.v. spectra were determined with a JASCO UVIDEC-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 $CDCl_3$ as solvent and $SiMe_4$ as internal standard, and mass spectra were recorded on a Hitachi M-80 spectrometer. A HALōs (Eikosha 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,[8,9] and 1-phenyl-4,6-dimethylpyrimidin-2(1*H*)-one (**1d**) was prepared according to the method of Nováček.[8] The properties of compounds (**1a**—**c**) are listed below.

1-*Methyl*-4,6-*diphenylpyrimidin*-2(1H)-*one* (**1a**), m.p. 184—185 °C (Found: C, 77.95; H, 5.3; N, 10.75. $C_{17}H_{14}N_2O$ requires C, 77.85; H, 5.4; N, 10.75%); $\lambda_{max.}$(EtOH) 271 (ε 15 800) and 333 nm (12 300); $\nu_{max.}$(KBr) 1 645, 1 600, 1 595, 770, 705, and 690 cm^{-1}; δ_H 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(1H)-*one* (**1b**), m.p. 189—190 °C (Found: C, 78.3; H, 6.1; N, 9.6. $C_{19}H_{18}N_2O$ requires C, 78.6; H, 6.25; N, 9.65%); $\lambda_{max.}$(EtOH) 274 (ε 17 000) and 334 nm (13 600); $\nu_{max.}$(KBr) 1 665, 1 645, 1 495, 810, and 790 cm^{-1}; δ_H 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(1H)-*one* (**1c**), m.p. 170—171 °C (Found: C, 78.45; H, 6.25; N, 9.65. $C_{19}H_{18}N_2O$ requires C, 78.6; H, 6.25; N, 9.65%); $\nu_{max.}$(KBr) 1 660, 1 645, 1 600, 780, and 705 cm^{-1}; δ_H 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(1H)-*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. $C_{21}H_{24}N_2O_2$ requires C, 74.95; H, 7.2; N, 8.3%); $\lambda_{max.}$(EtOH) 268 (ε 4 500); $\nu_{max.}$(KBr) 3 230, 1 680, 1 660, 1 105, 760, and 700 cm^{-1}; δ_H 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_C 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^+ + 1).

The 1:1 adduct (**4**), m.p. 73 °C (decomp.) (Found: C, 75.55; H, 7.6; N, 7.6. $C_{23}H_{28}N_2O_2$ requires C, 75.8; H, 7.75; N, 7.7%); $\nu_{max.}$(KBr) 3 250, 1 670, 1 650, 1 155, 765, 700, and 685 cm^{-1}; δ_H 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_C 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. $C_{21}H_{22}N_2O_2$ requires C, 75.4; H, 6.65; N, 8.35%); $\nu_{max.}$(KBr) 3 220, 1 700, 1 675, 1 075, 755, and 700 cm^{-1}; δ_H 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_C 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. $C_{21}H_{22}N_2O_3$ requires C, 72.0; H, 6.3; N, 8.0%]; $\nu_{max.}$(KBr) (for a mixture) 3 220, 1 690, 1 660, 1 125, 760, and 700 cm^{-1}; δ_H(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_H[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. $C_{21}H_{24}N_2OS$ requires C, 71.55; H, 6.85; N, 7.95%); $\lambda_{max.}$(EtOH) 267 nm (ε 3 300); $\nu_{max.}$(KBr) 3 250, 1 680, 1 660, 775, 765, and 705 cm^{-1}; δ_H 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. $C_{21}H_{22}N_2OS$ requires C, 71.95; H, 6.3; N, 8.0%); $\nu_{max.}$(KBr) 3 240, 1 675, 1 660sh, 775, 755, and 700 cm^{-1}; δ_H 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_C 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. $C_{21}H_{22}N_2OS$ requires C, 71.95; H, 6.3; N, 8.0%); $\nu_{max.}$(KBr) 3 220, 1 675, 1 665, 760, 700, and 685 cm^{-1}; δ_H 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_C 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. $C_{22}H_{24}N_2OS$ requires C, 72.5; H, 6.65; N, 7.7%]; $\nu_{max.}$(for a mixture) 3 230, 1 680, 1 660, 765, and 705 cm^{-1}; δ_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); δ_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. $C_{30}H_{24}N_2O_2$ requires C, 81.05; H, 5.45; N, 6.3%); $\nu_{max.}$(KBr) 3 220, 1 675, 1 655, 765, 750, and 700 cm^{-1}; δ_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); δ_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. $C_{23}H_{28}N_2OS$ requires C, 72.6; H, 7.4; N, 7.35%); $\nu_{max.}$(KBr) 3 220, 1 680, 1 660, and 815 cm^{-1}; δ_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); δ_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. $C_{32}H_{28}N_2O_2$ requires C, 81.3; H, 5.95; N, 5.9%); $\nu_{max.}$(KBr) 3 200, 1 665, 1 645, 805, and 745 cm^{-1}; δ_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. $C_{23}H_{28}N_2O_2$ requires C, 75.8; H, 7.75; N, 7.7%); $\nu_{max.}$(KBr) 3 240, 1 665, 1 650sh, 765, and 700 cm^{-1}; δ_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. $C_{23}H_{26}N_2O_2$ requires C, 76.2; H, 7.25; N, 7.7%]; $\nu_{max.}$(for a mixture) 3 210, 1 665, 1 645sh, 1 075, 750, and 695 cm^{-1}; δ_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); δ_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. $C_{23}H_{28}N_2OS$ requires C, 72.6; H, 7.4; N, 7.35%); $\nu_{max.}$(KBr) 3 239, 1 665, 1 655sh, 780, 755, and 700 cm^{-1}; δ_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); δ_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. $C_{32}H_{28}N_2O_2$ requires C, 81.3; H, 5.95; N, 5.9%); $\nu_{max.}$(KBr) 3 210, 1 675, 1 650, 765, 745, and 695 cm^{-1}; δ_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. $C_{16}H_{20}N_2O$ requires C, 70.55; H, 7.4; N, 10.3%); $\nu_{max.}$(KBr) 3 220, 1 655, 760, and 700 cm^{-1}; δ_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); δ_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. $C_{25}H_{22}N_2O_2$ requires C, 78.5; H, 5.8; N, 7.3%); $\nu_{max.}$(KBr) 3 220, 1 695, 1 660, 765, 750, and 700 cm^{-1}; δ_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); δ_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).

References

1 A. Padwa, *Chem. Rev.*, 1977, **77**, 37; A. C. Pratt, *Chem. Soc. Rev.*, 1977, **6**, 63.

2 For intramolecular hydrogen abstraction by the C=N double bond of a keto imine system see: (*a*) T. H. Koch, R. J. Sluski, and R. H. Moseley, *J. Am. Chem. Soc.*, 1973, **95**, 3957; (*b*) M. Gladys and W. R. Knappe, *Chem. Ber.*, 1974, **107**, 3658; (*c*) T. H. Koch, J. A. Olesen, and J. DeNiro, *J. Org. Chem.*, 1975, **40**, 14; (*d*) M. Saeki, N. Toshima, and H. Hirai, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 476; (*e*) Y. Izawa, K. Yokoi, and H. Tomioka, *Chem. Lett.*, 1981, 1473; (*f*) V. J. Ram, W. R. Knappe, and W. Pfleiderer, *Liebigs Ann. Chem.*, 1982, 762; (*g*) T. Nishio, S. Kameyama, and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1147; for intermolecular hydrogen abstraction by the C=N double bond of a keto imine system see: (*h*) N. Toshima, S. Asao, K. Takeda, and H. Hirai, *Tetrahedron Lett.*, 1970, 5123; (*i*) M. Saeki, N. Toshima, and H. Hirai, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 476; (*j*) S. Asao, N. Toshima, and H. Hirai, *ibid.*, 1975, **48**, 2068.

3 (*a*) T. Nishio, A. Kato, Y. Omote, and C. Kashima, *Tetrahedron Lett.*, 1978, 1543; T. Nishio, A. Kato, C. Kashima, and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, 1980, 607; (*b*) T. Nishio, K. Katahira, A. Kato, C. Kashima, and Y. Omote, *Tetrahedron Lett.*, 1979, 4211; T. Nishio, K. Katahira, and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, 1981, 943; T. Nishio and Y. Omote, *ibid.*, 1984, 239.

4 T. Nishio, N. Nakajima, and Y. Omote, *Tetrahedron Lett.*, 1981, **22**, 753; T. Nishio, N. Nakajima, M. Kondo, Y. Omote, and M. Kaftory, *J. Chem. Soc., Perkin Trans. 1*, 1984, 391; T. Nishio, M. Kondo, and Y. Omote, *ibid.*, 1985, 2497; T. Nishio, T. Nishiyama, and Y. Omote, *Tetrahedron Lett.*, 1986, **27**, 5637.

5 For a preliminary communication, see: T. Nishio, K. Katahira, and Y. Omote, *Chem. Lett.*, 1982, 1675.

6 L. M. Jackman and S. Sternhell, 'Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon Press, Oxford, 2nd edn., 1969, p. 338.

7 P. H. Mazzocchi and M. Boven, *J. Org. Chem.*, 1976, **41**, 1279.

8 A. Nováček, *Collect. Czech. Chem. Commun.*, 1968, **33**, 3919.

9 T. Nishio and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1773.

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