Photochemistry of the nitrogen–thiocarbonyl systems. Part. 24.[1] Photoreactions of thiobenzamide with various substituted furans: regioselective β-benzoylation and transformation of furans to other aromatic compounds

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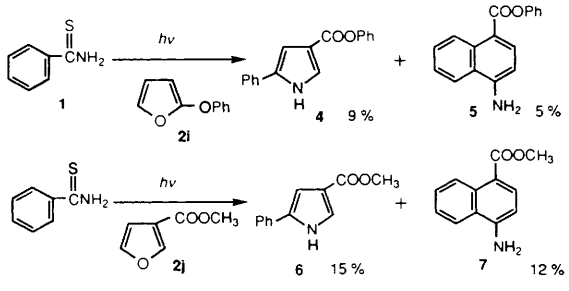
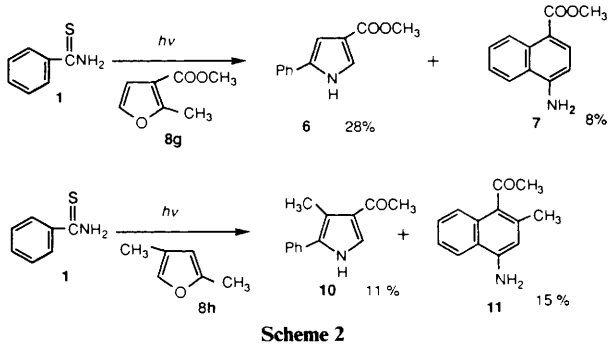
In the photoreaction of thiobenzamide **1** with the substituted furans **2** and **8**, β-benzoylation was the major reaction. With other furans, **2i**, **j** and **8g**, **h**, both transformation of furans to pyrroles and benzannulation occurred in preference to benzoylation.

Since furans have a key role in a variety of pharmaceuticals[2] and are found in many biologically active natural products,[3] their synthesis has received considerable attention.[3] Equally, furans and dihydrofurans[4] are useful synthetic intermediates, and serve as versatile building blocks in organic syntheses.[5] For example, the dihydrofuran (Paterno–Büchi product) obtained from furan-carbonyl photoaddition can be converted into a variety of functionalized systems with a high degree of stereochemical control.[6] However, we found that arenecarbothioamides undergo a Paterno–Büchi type reaction with various olefins, such as nonconjugated olefins,[7] styrene derivatives,[8] and furans,[9] to give a variety of aryl ketones. Among them, furans as an olefin analogue (Paterno–Büchi acceptor) showed interesting photochemical behaviour towards arenecarbothioamides, *e.g.*, regioselective formation of 3-aroylfuran,[9a,b] a facile conversion into arylpyrrole,[9c] and photobenzannulation of arenecarbothioamide with 2-methoxyfuran.[1] As an extension of this synthetically useful reaction, the generality of conversion of substituted furans into a variety of functionalized systems was examined. The present report is an account of our work on the intermolecular photoreaction of thiobenzamide with various mono- and di-substituted furans to investigate the distribution of products arising from the position and variation of substituent on a furan ring.

Photoreactions of thiobenzamide **1** with 2- or 3-monosubstituted furans **2** were carried out in benzene using Pyrex-filtered radiation from a high-pressure mercury lamp under a nitrogen atmosphere; the results are listed in Table 1 and Scheme 1. Irradiation of **1** with 2-phenylfuran **2b** (20 equiv.) for 10 h gave exclusively 3-benzoyl-5-phenylfuran **3b** in 59% yield. Similarly, with other monosubstituted furans **2c–h**, the corresponding 4-benzoyl-2 (or 3)-substituted furans **3c–h** were obtained in moderate yields. 2-Phenoxyfuran **2i** and methyl 3-furoate **2j** in such reactions gave the pyrrole derivatives **4** and **6**, respectively,

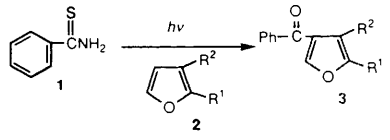


Scheme 1



Scheme 2

Table 1 Photoreactions of compound **1** with compound **2**



	R^1	R^2	Yield (%)
a	CH_3	H	67[9b]
b	Ph	H	59
c	CH_2OH	H	42
d	CHO	H	43
e	$COCH_3$	H	51
f	$COOCH_3$	H	61
g	H	CH_2OH	52
h	H	COOH	42*[,9b]

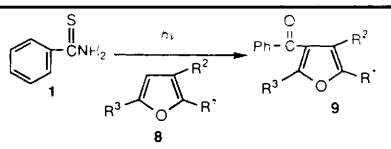
* Isolated as 3-benzoylfuran (α-cleavage product).

and the naphthalene derivatives **5** and **7** respectively, but none of benzoylated products (Scheme 1).

Next, irradiation of **1** with the disubstituted furan **8** was performed under conditions similar to those described above; the results are listed in Table 2. 2,5-Disubstituted **8a–d** and 1,2-disubstituted **8e**, **8f** furans gave the 3-benzoyl derivatives **9a–f** exclusively in moderate yields. However, methyl 2-methyl-3-furoate **8g** and 2,4-dimethylfuran **8h** gave both the pyrrole derivatives **6** and **10** respectively and the naphthalene derivatives **7** and **11** respectively, but no benzoylated products (Scheme 2).

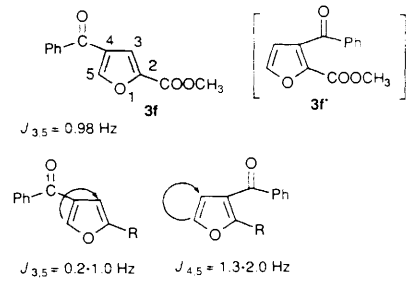
Structural assignments for the benzoylated products were made on the basis of the spectral results and elemental analyses. In the IR spectrum of **3f**, the carbonyl absorption appeared at 1735 and 1670 cm^{-1}. The ^{13}C NMR spectrum of **3f** also

Table 2 Photoreactions of compound **1** with compound **8**



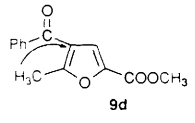
	R^1	R^2	R^3	Yield (%)
a	CH_3	H	CH_3	38[9b]
b	CH_3	H	CHO	20
c	CH_3	H	$COCH_3$	22
d	CH_3	H	$COOCH_3$	28
e	CH_3	CH_3	H	64
f	$COOCH_3$	CH_3	H	51

supported the presence of a carbonyl group [188.0 (s)] and an ester group [158.5 (s)], suggesting the presence of furan and phenyl rings. The benzoylated structure of **2f** was considered to be **3f** or **3f'** (see Scheme 3). The two regioisomers could be easily



Scheme 3

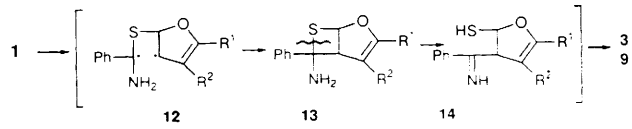
distinguished by ^1H NMR spectroscopy; that is, the small coupling constant of 0.98 Hz between two protons of the furan ring is indicative of **3f** because the *ortho* coupling constant ($J_{4,5}$ 1.3–2.0 Hz) between vicinal protons of furan ring is, in general, larger than that of *meta* position ($J_{3,5}$ 0.2–1.0). Further, to clarify the benzoylation site of products **9a–d**, the HMBC (^1H detected heteronuclear multiple bond connectivity) spectrum of **9d** was recorded (Scheme 4). Since the methyl proton signal at



Scheme 4 Selective HMBC correlation

2.65 ppm was correlated to the quaternary carbon at C-4 (122.1 ppm), clearly the benzoylation occurred at the β-position of the less hindered site (methyl) rather than that adjacent to the methoxycarbonyl on furan. Structural assignments for the pyrrole derivatives were also made on the basis of spectral results and elemental analyses. For example, in its IR spectrum compound **10** showed NH and CO absorption at 3150 and 1750 cm^{-1} whilst in its ^1H NMR spectrum it showed three singlet signals at 2.42, 2.44 and 6.99 ppm assignable to an acetyl group, a methyl group and a proton of the pyrrole ring, respectively. Further, signals due to a monosubstituted aromatic ring and the NH of a pyrrole ring (8.60 ppm) indicated a trisubstituted (acetyl, methyl and phenyl) pyrrole structure for **10**. The ^{13}C NMR spectrum also supported the presence of a carbonyl group [194.7 ppm (s)] and benzene and pyrrole rings. Similarly, structural assignments for the naphthalene derivatives **7** were made on the basis of spectral results and elemental analysis. In the IR spectrum of **7**, amino and ester carbonyl group absorption appeared at 3500–3400 and 1695 cm^{-1}, respectively, whilst in its ^1H NMR spectrum two triplets and two doublets (J 7.3 Hz) suggested the presence of an *ortho* disubstituted benzene skeleton. In addition, the spectrum exhibited a characteristic AB pattern at δ 7.07 and 7.73 (J 8.79 Hz), indicating the presence of two vicinal protons in a benzene ring. The presence of a 1,4-disubstituted naphthalene skeleton was also suggested by spectral evidence. Thus, the ^{13}C NMR spectrum of **7** supported the presence both of an ester carbonyl [169.3 ppm (s)] and a naphthalene skeleton, whilst the mass spectrum showed the molecular ion peak at M^+ 201, corresponding to the molecular weight of **7**.

The formation of regioselectively benzoylated products can be explained as illustrated in Scheme 5. Aryl ketones arise from



Scheme 5

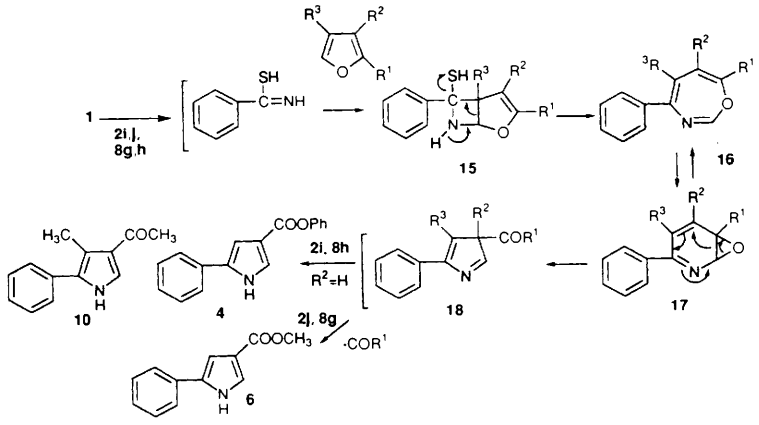
the initially formed thietane **13** followed by photochemical fission of the C–S bond of the thietane ring, and then by hydrolysis of the imine **14** generated during chromatographic work-up.[9a,b] The regioselectivity of thietane formation in the first step seems to reflect the steric effect of an α-substituent on an unsymmetrically substituted furan.

With respect to the formation of pyrrole derivatives, we have already proposed that the reaction would proceed in several steps involving initial [2 + 2] cycloaddition between the C=N double bond and furan, leading to the aryloxazepine **16**, which, subsequently, rearranges to the phenylpyrrole as shown in Scheme 6.[9c] Further, as an additional pathway the formation of **6** may be explained in terms of loss of a formyl group from the intermediate **18** which possesses geminal keto and ester substituents (β-keto ester unit) on the pyrrole ring.

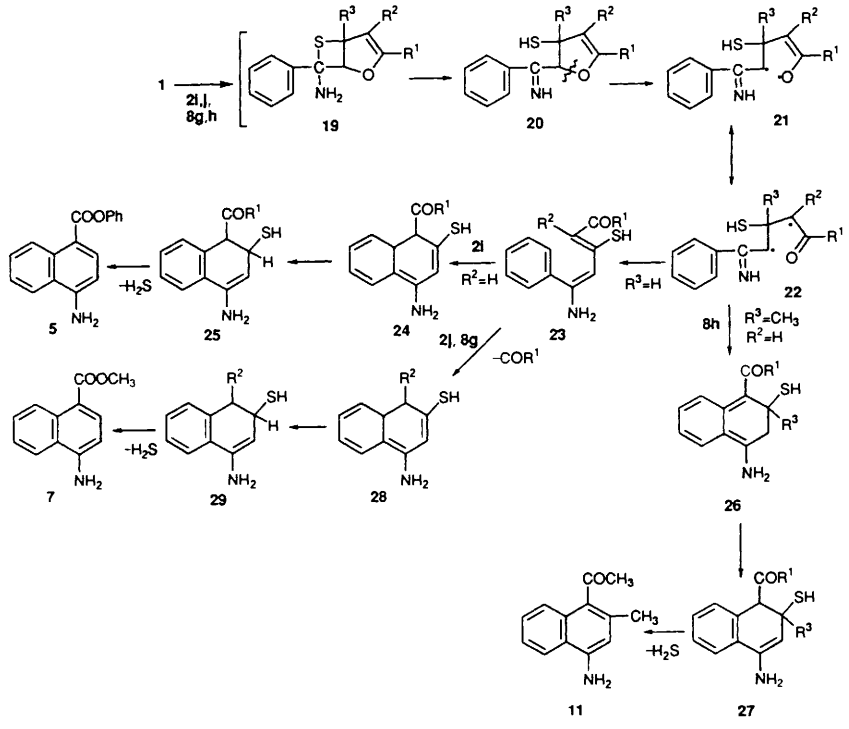
Regarding the benzannulation, plausible pathways might be tentatively explained by means of a biradical as outlined in Scheme 7.[1] The route to products is explained satisfactorily if a biradical intermediate such as **21**/**22** is involved. This would be formed by C–O bond fission. However, no evidence is available at this time to suggest if this step is thermal or photochemical. Analogously to the previously reported benzannulation with 2-methoxyfuran,[9c] the reaction with 2-phenoxyfuran seems also to proceed in several steps involving initial thietane **19** formation between the thioamide with furan, leading to the biradical intermediate **21** ⟷ **22**, which subsequently cyclizes to the naphthalene derivative **5** *via* a key phenylbutadiene intermediate **23**.[10] In the formation of the naphthalene **7** derived from **8g** (R^3=H), the intermediate **23** possessing a β-keto ester unit cyclizes to **28** which involves loss of a formyl group. However, in the case of **11** derived from **8h** (R^3=Me), cyclization of biradical intermediate **22** may occur to give **11** by elimination of hydrogen sulfide. Thus, involvement of deacylation (α-cleavage) seems to depend on the structure, which has whether a β-keto ester unit or not in the generated intermediate **23**.

Compared with initial addition of thiocarbonyl and that of carbonyl to an unsymmetrically substituted furan, the regioselectivity in thietane formation was higher than that found in oxetane formation. For example, photoaddition of benzaldehyde with 2-methylfuran **2a** (furan–carbonyl photoaddition) provides a 1.3:1 mixture of oxetane,[11] while photoaddition of thiobenzamide with 2-methylfuran **2a** afforded only **3a**. As a result, benzoylation occurred only at the β-position of the less hindered site on substituted furans.

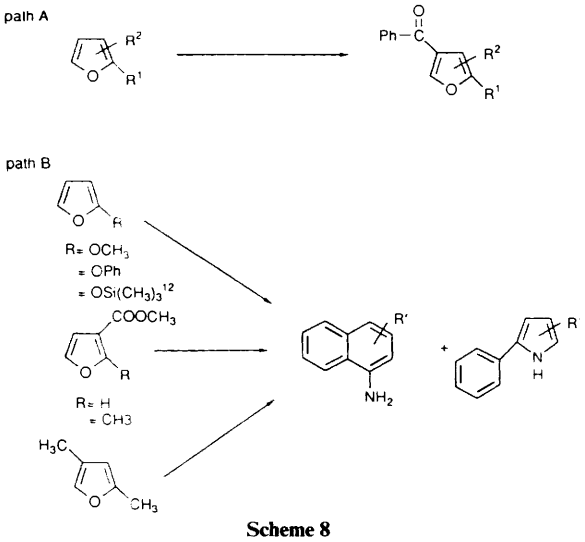
The above results, coupled with those reported in the previous papers,[1,9] suggest that in the photoreaction of thiobenzamide with a substituted furan, benzoylation is the



Scheme 6



Scheme 7



Scheme 8

main reaction (path A, Scheme 8). With certain furan derivatives,[12] however, both pyrrole formation and benzannulation occurred in preference to benzoylation (path B, Scheme 8). As has already been reported,[9c] arylpyrrole is formed only in methanol solution and not in benzene. However, in this experiment, the arylpyrrole formation occurs along with benzannulation even in benzene solution, as seen in the structural variation of the substrates employed, *e.g.* 2-alkoxyfuran **2i**, methyl 3-furoate derivatives **2j** and **8g** and 2,4-dimethylfuran **8h**. Nevertheless, it is difficult to predict the path a reaction will follow and to rationalize differences in photochemical behaviour between the substrates used. Thus, the distribution of photoproducts may be affected by the properties of, and the position of substituent(s) on, a particular furan.

It is noteworthy that these readily available furans are a potentially useful building block in a photosynthesis of benzo-fused aromatics, serving for benzannulation as three-carbon annulation units.

Experimental

All mps were determined on a Yamato mp apparatus (model MP-21) and are uncorrected. IR spectra were recorded on a

JASCO-A-102 spectrometer. NMR spectra were taken on a JEOL JNM EX-400 spectrometer. Chemical shifts are reported in ppm (δ) relative to TMS (0.0 ppm) as an internal standard. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra (MS) were obtained on a JEOL JMS-QH-100 gas chromatograph–mass spectrometer and high-resolution MS (HR-MS) spectra were recorded using a JEOL JMS-DX 303 mass spectrometer. Preparative irradiations were conducted by using a 1 kW high-pressure mercury lamp (Eikosha EHB-W-1000) through a Pyrex filter at room temperature. Stirring of the reaction mixture was effected by the introduction of a stream of nitrogen at the bottom of the outer jacket. Column chromatography was conducted using silica gel (Merck, Kieselgel 60, 70–230 mesh).

Irradiation of compound 1 with furan derivatives 2 and 8

General procedure. A solution containing compounds **1** (5 mmol) and **2b** (0.1 mol) in benzene (500 cm^3) under N_2 at room temperature was subjected for 10 h to radiation from a Pyrex-filtered 1 kW high-pressure mercury lamp. After this, the reaction mixture was evaporated under reduced pressure and the residue was chromatographed over silica gel.

Phenyl 5-phenyl-3-furyl ketone 3b. Mp 97–98 °C (Found: C, 82.1; H, 4.9. $C_{17}H_{12}O_2$ requires C, 82.24; H, 4.87%); ν_{max}(Nujol)/cm^{-1} 1640 (ketone); δ_H(400 MHz; $CDCl_3$) 7.11 (1 H, s), 7.30 (1 H, m), 7.45 (4 H, m), 7.58 (1 H, m), 7.70 (2 H, m), 7.87 (2 H, m) and 7.89 (1 H, s); δ_C(100 MHz; $CDCl_3$) 104.7 (d), 124.1 (d × 2), 128.2 (s), 128.3 (d), 128.5 (d × 2), 128.8 (d × 4), 129.6 (s), 132.4 (d), 138.7 (s), 147.6 (d), 155.5 (s) and 189.2 (s); *m*/*z* 248 (M^+).

Phenyl 5-hydroxymethyl-3-furyl ketone 3c. Mp 96–99 °C (Found: C, 71.3; H, 5.1. $C_{12}H_{10}O_3$ requires C, 71.28; H, 4.99%); ν_{max}(Nujol)/cm^{-1} 3600–3200 (OH) and 1640 (ketone); δ_H(400 MHz; $CDCl_3$) 3.22 (1 H, br s), 4.63 (2 H, s), 6.75 (1 H, s), 7.46 (2 H, m), 7.57 (1 H, m) and 7.81 (3 H, m); δ_C(100 MHz; $CDCl_3$) 57.0 (t), 107.7 (d), 126.0 (s), 128.5 (d × 2), 128.7 (d × 2), 132.5 (d), 138.4 (s), 148.4 (d), 159.5 (s) and 189.6 (s); *m*/*z* 202 (M^+).

Phenyl 5-formyl-3-furyl ketone 3d. Mp 110–111 °C (Found: C, 71.9; H, 4.1. $C_{12}H_8O_3$ requires C, 71.99; H, 4.03%); ν_{max}(Nujol)/cm^{-1} 1690 (aldehyde) and 1660 (ketone); δ_H(400 MHz; $CDCl_3$) 7.51 (2 H, m), 7.63 (2 H, m), 7.85 (2 H, m), 8.17 (1 H, s) and 9.75 (1 H, s); δ_C(100 MHz; $CDCl_3$) 120.1 (d), 128.0 (s), 128.8 (d × 4), 133.1 (d), 137.6 (s), 151.5 (d), 153.0 (s), 177.9 (d) and 187.8 (s); *m*/*z* 200 (M^+).

Phenyl 5-acetyl-3-furyl ketone 3e. Mp 117–118 °C (Found: C, 72.8; H, 4.7. $C_{13}H_{10}O_3$ requires C, 72.89; H, 4.71%); ν_{max}(Nujol)/cm^{-1} 1680 (ketone) and 1640 (ketone); δ_H(400 MHz; $CDCl_3$) 2.54 (3 H, s), 7.50–7.90 (6 H, m) and 8.07 (1 H, s); δ_C(100 MHz; $CDCl_3$) 26.1 (q), 116.6 (d), 127.8 (s), 128.7 (d × 2), 128.8 (d × 2), 133.0 (d), 137.7 (s), 150.3 (d), 153.0 (s), 186.5 (s) and 188.2 (s); *m*/*z* 214 (M^+).

Phenyl 5-methoxycarbonyl-3-furyl ketone 3f. Mp 111–113 °C (Found: C, 67.6; H, 4.5. $C_{13}H_{10}O_4$ requires C, 67.82; H, 4.38%); ν_{max}(Nujol) cm^{-1} 1735 (ester) and 1670 (ketone); δ_H(400 MHz; $CDCl_3$) 3.94 (3 H, s), 7.51 (2 H, m), 7.59 (1 H, d, *J* 0.98), 7.62 (1 H, m), 7.85 (2 H, m) and 8.05 (1 H, d, *J* 0.98); δ_C(100 MHz; $CDCl_3$) 52.3 (q), 117.4 (d), 127.6 (s), 128.7 (d × 2), 128.8 (d × 2), 132.9 (d), 137.8 (s), 145.4 (s), 150.3 (d), 158.5 (s) and 188.0 (s); *m*/*z* 230 (M^+).

Phenyl 4-hydroxymethyl-3-furyl ketone 3g. Mp 103–104 °C (Found: C, 71.1; H, 5.1. $C_{12}H_{10}O_3$ requires C, 71.28; H, 4.99%); ν_{max}(Nujol) cm^{-1} 3600–3200 (OH) and 1640 (ketone); δ_H(400 MHz; $CDCl_3$) 4.30 (1 H, t, *J* 6.84), 4.63 (2 H, d, *J* 6.84), 7.58–7.52 (3 H, m), 7.60 (1 H, m) and 7.82–7.84 (3 H, m); δ_C(100 MHz; $CDCl_3$) 55.2 (t), 125.6 (s), 125.9 (s), 128.7 (d × 2), 129.0 (d × 2), 132.9 (d), 138.7 (s), 141.8 (d), 151.2 (d) and 191.6 (s); *m*/*z* 202 (M^+).

Phenyl 5-phenyl-1*H*-pyrrole-3-carboxylate 4. Mp 158–160 °C (Found: C, 76.7; H, 5.0; N, 5.4. $C_{17}H_{13}NO_2$ requires C, 76.55; H, 4.98; N, 5.32%); ν_{max}(Nujol)/cm^{-1} 3355 (NH) and 1680 (ester); δ_H(400 MHz; [$^2H_6$]-DMSO) 7.30 (1 H, s), 7.19–7.27 (4 H, m), 7.37–7.45 (4 H, m), 7.72 (3 H, m) and 12.14 (1 H, br s); *m*/*z* 263 (M^+).

Phenyl 4-aminonaphthalene-1-carboxylate 5. Mp 129–130 °C (Found: C, 76.6; H, 5.0; N, 5.2. $C_{17}H_{13}NO_2$ requires C, 76.55; H, 4.98; N, 5.32%); ν_{max}(Nujol)/cm^{-1} 3400–3500 (NH_2) and 1700 (ester); δ_H(400 MHz; $CDCl_3$) 6.76 (2 H, br s), 7.09 (1 H, d, *J* 8.79), 7.22 (3 H, m), 7.42 (3 H, m), 7.54 (1 H, m), 7.74 (1 H, m), 7.83 (1 H, m) and 8.06 (1 H, d, *J* 8.79); δ_C(100 MHz; $CDCl_3$) 102.8 (s), 116.0 (d), 121.5 (d), 122.1 (d × 2), 122.9 (s), 125.4 (d), 125.7 (d), 126.6 (d), 128.6 (d), 128.8 (d), 129.4 (d × 2), 136.7 (s), 150.1 (s), 151.0 (s) and 167.6 (s); *m*/*z* 263 (M^+).

Methyl 5-phenylpyrrole-3-carboxylate 6. Mp 162–164 °C (Found: 201.0765. $C_{12}H_{11}NO_2$ requires 201.0767); ν_{max}(Nujol)/cm^{-1} 3350 (NH) and 1750 (ester); δ_H(400 MHz; [$^2H_6$]-DMSO) 3.84 (3 H, s), 6.90 (1 H, m), 7.25 (1 H, m), 7.37 (2 H, m), 7.47 (3 H, m) and 9.02 (1 H, br s); δ_C(100 MHz; [$^2H_6$]-DMSO) 51.2 (q), 106.6 (d), 117.6 (s), 124.1 (d × 2), 124.2 (d), 127.1 (d), 129.0 (d × 2), 131.7 (s), 133.1 (s) and 165.5 (s); *m*/*z* 201 (M^+).

Methyl 4-aminonaphthalene-1-carboxylate 7. Colourless oil (Found: 201.0769. $C_{12}H_{11}NO_2$ requires 201.0767); ν_{max}(Nujol)/cm^{-1} 3400–3500 (NH_2) and 1695 (ester); δ_H(400 MHz; $CDCl_3$) 3.91 (3 H, s), 6.82 (2 H, br s), 7.07 (1 H, d, *J* 8.79), 7.46 (1 H, t, *J* 7.3), 7.54 (1 H, t, *J* 7.3), 7.73 (1 H, d, *J* 8.79), 7.85 (1 H, d, *J* 7.3) and 7.87 (1 H, d, *J* 7.3); δ_C(100 MHz; $CDCl_3$) 51.5 (q), 104.1 (s), 115.9 (d), 121.5 (d), 123.1 (s), 125.2 (d), 126.5 (d), 128.4 (d), 128.5 (d), 136.4 (s), 148.9 (s) and 169.3 (s); *m*/*z* 201 (M^+).

Phenyl 2-formyl-5-methyl-3-furyl ketone 9b. Colourless oil (Found: 214.0603. $C_{13}H_{10}O_3$ requires 214.0576); ν_{max}(Nujol)/cm^{-1} 1720 (aldehyde) and 1680 (ketone); δ_H(400 MHz; $CDCl_3$) 2.68 (3 H, s), 7.40 (1 H, s), 7.52 (2 H, m), 7.78 (1 H, m), 7.81 (2 H, m) and 9.61 (1 H, s); δ_C(100 MHz; $CDCl_3$) 14.7 (q), 122.6 (d), 122.7 (s), 122.8 (d × 2), 129.0 (d × 2), 133.0 (d), 138.0 (s), 150.2 (s), 165.0 (s), 177.3 (d) and 189.9 (s); *m*/*z* 214 (M^+).

Phenyl 2-acetyl-5-methyl-3-furyl ketone 9c. Mp 84–85 °C (Found: C, 73.6; H, 5.5. $C_{14}H_{12}O_3$ requires C, 73.67; H, 5.30%); ν_{max}(Nujol) cm^{-1} 1660 (ketone); δ_H(400 MHz; $CDCl_3$) 2.48 (3 H, s), 2.65 (3 H, s), 7.33 (1 H, s), 7.51 (2 H, m), 7.61 (1 H, m) and 7.79 (2 H, m); δ_C(100 MHz; $CDCl_3$) 14.3 (q), 25.6 (q), 118.6 (d), 122.1 (s), 128.3 (d × 2), 128.7 (d × 2), 132.5 (d), 137.9 (s), 149.7 (s), 163.0 (s), 185.9 (s) and 189.8 (s); *m*/*z* 228 (M^+).

Phenyl 2-methoxycarbonyl-5-methyl-3-furyl ketone 9d. Colourless oil (Found: 244.0737. $C_{14}H_{12}O_4$ requires 244.0736); ν_{max}(Nujol) cm^{-1} 1720 (ester) and 1650 (ketone); δ_H(400 MHz; $CDCl_3$) 2.65 (3 H, s), 3.90 (3 H, s), 7.34 (2 H, m), 7.61 (2 H, m), 7.77 (1 H, m) and 7.80 (1 H, m); δ_C(100 MHz; $CDCl_3$) 14.6 (q), 52.1 (q), 119.5 (d), 122.1 (s), 128.3 (d), 128.6 (d × 2), 129.0 (d × 2), 138.2 (s), 141.9 (s), 158.8 (s), 163.2 (s) and 190.2 (s); *m*/*z* 244 (M^+).

Phenyl 4,5-dimethyl-3-furyl ketone 9e. Colourless oil (Found: 200.0810. $C_{13}H_{12}O_2$ requires 200.0783); ν_{max}(Nujol) cm^{-1} 1640 (ketone); δ_H(400 MHz; $CDCl_3$) 2.19 (3 H, s), 2.25 (3 H, s), 7.42–7.59 (4 H, m) and 7.79–7.81 (2 H, m); δ_C(100 MHz; $CDCl_3$) 9.2 (q), 11.2 (q), 115.0 (s), 126.1 (s), 128.4 (d × 2), 128.9 (d × 2), 132.1 (d), 139.6 (s), 147.6 (d), 149.9 (s) and 191.1 (s); *m*/*z* 200 (M^+).

Phenyl 5-methoxycarbonyl-4-methyl-3-furyl ketone 9f. Mp 129–130 °C (Found: C, 68.8; H, 5.05. $C_{14}H_{12}O_4$ requires C, 68.84; H, 4.95%); ν_{max}(Nujol) cm^{-1} 1715 (ester) and 1660 (ketone); δ_H(400 MHz; $CDCl_3$) 2.60 (3 H, s), 3.92 (3 H, s), 7.48–7.52 (2 H, m), 7.55 (1 H, m) and 7.81–7.82 (3 H, m); δ_C(100 MHz; $CDCl_3$) 10.4 (q), 51.9 (q), 127.0 (s), 128.7 (d × 2), 129.1 (d × 2), 131.4 (s), 132.9 (d), 138.8 (s), 141.9 (s), 150.2 (d), 159.6 (s) and 189.8 (s); *m*/*z* 244 (M^+).

Methyl 4-methyl-5-phenylpyrrol-3-yl ketone 10. Mp 161–162 °C (Found: C, 78.3; H, 6.8; N, 7.0. $C_{13}H_{13}NO$ requires C, 78.36; H, 6.58; N, 7.03%); ν_{max}(Nujol)/cm^{-1} 3150 (NH) and 1750 (ketone); δ_H(400 MHz; [$^2H_6$]–DMSO) 2.42 (3 H, s), 2.44 (3 H, s), 7.39 (1 H, m), 7.40–7.44 (5 H, m) and 8.60 (1 H, br s); δ_C(100 MHz; [$^2H_6$]DMSO) 11.6 (q), 28.0 (q), 117.1 (s), 124.8 (d), 125.5 (s), 127.2 (d), 127.5 (d × 2), 128.8 (d × 2), 130.9 (s), 132.4 (s) and 194.7 (s); *m/z* 199 (M^+).

Methyl 4-amino-2-methyl-1-naphthyl ketone 11. Mp 72–74 °C (Found: 199.0978. $C_{13}H_{13}NO$ requires 199.0959); ν_{max}(Nujol) cm^{-1} 3400–3500 (NH) and 1700 (ketone); δ_H(400 MHz; $CDCl_3$) 2.55 (3 H, s), 2.57 (3 H, s), 5.97 (2 H, br s), 6.99 (1 H, s), 7.39 (1 H, m), 7.47 (1 H, m), 7.63 (1 H, m), 7.79 (1 H, m); δ_C(100 MHz; $CDCl_3$) 23.1 (q), 33.0 (q), 119.0 (d), 121.4 (s), 122.3 (d), 124.8 (d), 127.7 (d), 128.0 (d), 128.5 (s), 132.9 (s), 134.9 (s), 143.8 (s) and 205.1 (s); *m/z* 199 (M^+).

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References

1 Part 23, K. Oda and M. Machida, *J. Chem. Soc., Chem. Commun.*, 1994, 1477.
2 K. Nakanishi, *Natural Products Chemistry*, Kodansha, Ltd, Tokyo, 1974.
3 F. M. Dean and M. V. Sargent, in *Comprehensive Heterocyclic Chemistry*, ed. C. W. Bird and G. W. Cheeseman, Pergamon Press, New York, 1984, vol. 4, part 3, p. 531.
4 A. R. Katritzky, J. Li and M. F. Gordeev, *J. Org. Chem.*, 1993, **58**, 3038.
5 F. M. Dean, in *Advances in Heterocyclic Chemistry*, ed. A. R. Katritzky, Academic Press, New York, 1982, vol. 30, p. 167; vol. 31, p. 237.
6 (*a*) S. L. Schreiber and K. Satake, *J. Am. Chem. Soc.*, 1984, **106**, 4186; (*b*) S. L. Schreiber, D. Desmaele and J. A. Porco, Jr., *Tetrahedron Lett.*, 1988, **28**, 6689.
7 (*a*) M. Machida, K. Oda and Y. Kanaoka, *Tetrahedron Lett.*, 1984, **25**, 409; (*b*) *Heterocycles*, 1990, **30**, 983.
8 K. Oda, M. Machida and Y. Kanaoka, *Synlett*, 1992, 603.
9 (*a*) M. Machida, K. Oda and Y. Kanaoka, *Tetrahedron Lett.*, 1989, **30**, 4421; (*b*) K. Oda and M. Machida, *Chem. Pharm. Bull.*, 1993, **41**, 1299; (*c*) *J. Chem. Soc., Chem. Commun.*, 1993, 437.
10 W. H. Laarhoven, in *Organic Photochemistry*, ed. A. Padwa, Marcel Dekker Inc., New York, 1989, vol. 10, p. 163.
11 G. Jones, in *Organic Photochemistry*, ed. A. Padwa, Marcel Dekker Inc., New York, 1981, vol. 5, p. 2.
12 K. Oda and M. Machida, unpublished results.

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