Photoreaction of Thiobenzamide with Furans in Methanol.[1] Facile Construction of the Arylpyrrole Ring System

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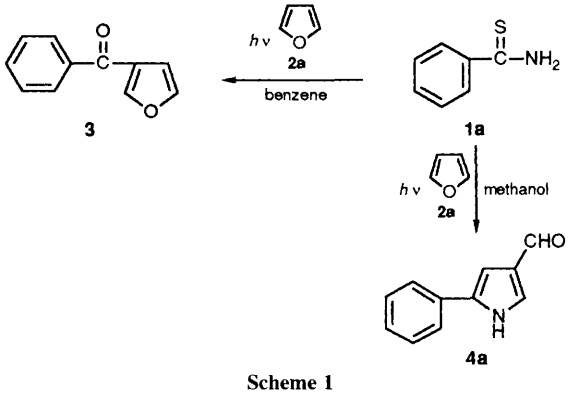
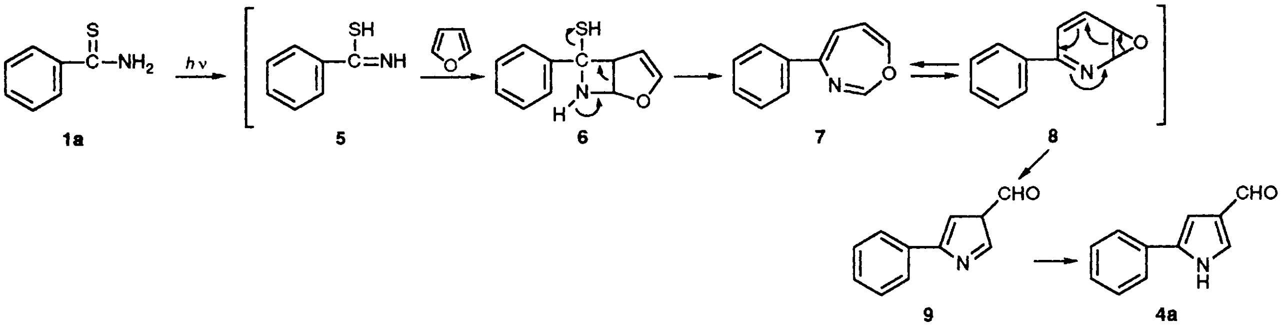
Irradiation of arenecarbothioamides **1** with furans **2** in methanol solution gives 2-arylpyrrole-4-carbaldehydes **4** in good yields.

The pyrrole ring is an important structural unit in many biologically active compounds. These compounds have been found in microorganisms, plants, and higher organisms, and some of them have antibiotic properties.[2] For example, pyrronitrin[3] and pyroluteorin[4] which have arylpyrrole nuclei were isolated from *Pseudomonas pyrrocinia* and *P. aeruginosa*, respectively, and their analogues have been synthesized because of their antibiotic activity. Although the construction of the pyrrole ring system has been achieved in a variety of ways,[5] photochemical synthesis of arylpyrroles still remains scarce. During the course of our study on the photochemistry of the arenecarbothioamide systems,[6] a construction of the pyrrole ring was found. In this paper we report the facile synthesis of arylpyrroles by photoreaction of arenecarbothioamides with furans in methanol.

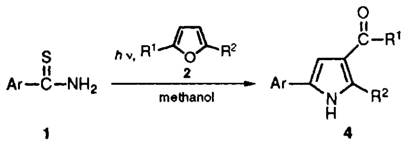


Scheme 1



Scheme 2

Table 1 Photoproducts of arenecarbothioamides with furans in methanol



Arenecarbothioamide	Furan	Irradiation time/h	Product[a] Yield (%)
1a; Ar = phenyl	**2a**; $R^1 = R^2 = H$	2	**4a**[b] 82
1a; Ar = phenyl	**2b**; $R^1 = Me, R^2 = H$	2	**4b** 73
1a; Ar = phenyl	**2c**; $R^1 = R^2 = Me$	2	**4c** 78
1b; Ar = 3-pyridyl	**2a**; $R^1 = R^2 = H$	4	**4d** 61
1c; Ar = 2-thienyl	**2a**; $R^1 = R^2 = H$	4	**4e** 65
1d; Ar = 2-furyl	**2a**; $R^1 = R^2 = H$	4	**4f** 68

[a] All products showed reasonable analytical and spectral data. [b] Ref. 7.

As has already been reported, irradiation of a benzene solution of thiobenzamide **1a** and furan **2a** (20 equiv.) resulted in the formation of 3-benzoylfuran **3** in 72% yield.[6] On the other hand, irradiation†[7] of the methanol solution of the same substrates afforded an alternative photoproduct **4a** (Scheme 1). Similarly, with a series of heteroaromatic thioamides **1b–d**, the corresponding 2-arylpyrrole-4-carbaldehydes were obtained in moderate yields. The results are listed in Table 1.

To find a clue on the reaction pathway, thiobenzamide was irradiated along with methyl-substituted furan **2b** or **2c** in a similar manner as described above. In the case of **2b**, the methyl substituent was transformed into the methyl of an acetyl group at the 4-position of pyrrole, while in the case of **2c**, methyl substituents were introduced as the methyl of the acetyl group at the 4-position and the methyl substitute at the 2-position on the pyrrole ring.

From these experiments, this reaction seems to proceed in several steps involving initial [2 + 2] cycloaddition between the C=N double bond and furan, leading to aryloxazepine **7**,[8] which subsequently is rearranged to phenylpyrrole **4a** as shown in Scheme 2. The present photoreaction would provide a convenient one step synthesis of arylpyrroles, and is of both mechanistic and synthetic interest.

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† A solution of **1a** (5 mmol) and **2a** (0.1 mol) in methanol (500 ml) was irradiated for 2 h with a 1 kW high-pressure mercury lamp through a Pyrex filter under N_2 at room temperature. Compound **4a**: m.p. 136.5–137 °C (lit.[7] m.p. 137 °C).

References

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