Benzannulation of Heteroaromatics by Photoreaction of Arenecarbothioamides with 2-Methoxyfuran[1]

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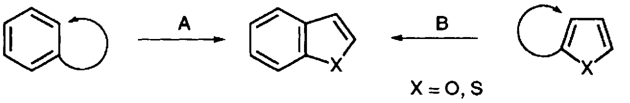
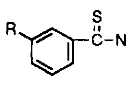
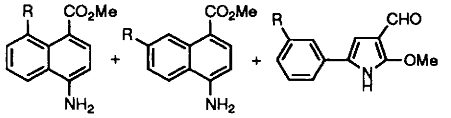
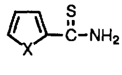
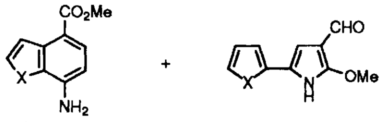
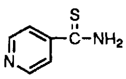
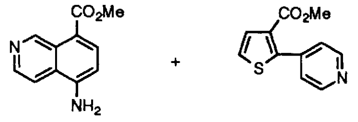
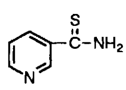
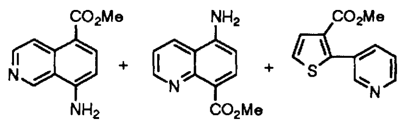
Irradiation of arenecarbothioamides **1** with 2-methoxyfuran **2** in benzene solution gives benzo-fused arene derivatives **3** in moderate yields.

The most often used method [Scheme 1, method (A)] for the syntheses of benzo-fused heteroaromatics is the intramolecular cyclization of a suitable substituted benzene.[2] However, little is known about the alternative method of benzannulation of substituted heterocycles [Scheme 1, method (B)].[3] Very recently, however, an efficient benzannulation of heteroaromatics was reported by Liebeskind and Wang,[4] providing a novel method for the synthesis of substituted benzoheterocycles by cross-coupling of heteroaryl stannanes with 4-chloro-2,3-substituted cyclobut-2-enones. During the course of our study on the photochemistry of arenecarbothioamide systems,[1,5–9] a photobenzannulation reaction was discovered. In this paper, we now report a photoreaction of arenecarbothioamides with 2-methoxyfuran, a facile synthesis of benzo-fused heteroaromatics and aromatics having both an amino and a carbonyl group on a benzene ring, by photobenzannulation reaction. Photoreactions of arenecarbothioamides **1** with 2 equivalents of 2-methoxyfuran **2** were carried out in benzene using a high pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere. The results are listed in Table 1.



Scheme 1

Table 1 Photoproducts of arenecarbothioamides **1** with 2-methoxyfuran **2**

Arenecarbothioamide	*t*/h	Photoproduct yield (%)
 **1a** R = H **1b** R = Me **1c** R = OMe	 20 20 10	 **3a** 62% — **4a** 13% **3b** 11% **3b′** 13% **4b** 8% **3c** 23% **3c′** 48% **4c** 11%
 **1d** X = O **1e** X = S	 20 20	 **3d** 41% **4d** 23% **3e** 34% **4e** 18%
 **1f**	 20	 **3f** 38% **5f** 25%
 **1g**	 20	 **3g** 34% **3g′** 11% **5g** 13%

Irradiation of thiobenzamide **1a** with **2** for 20 h gave the methyl 2-naphthoate derivative **3a** (62%) and a small amount of the pyrrole derivative[9] **4a** (13%). Further, the photoreaction of a series of heteroaromatic thioamides **1d–g** with **2** was performed. As expected, the corresponding benzo-fused heteroaromatics were obtained in moderate yields accompanied by small amounts of the biheteroaryl compounds **4** and **5**. It is noteworthy that the biheteroaryl compounds, otherwise inaccessible, are obtained by a novel reaction type in the photochemistry of thioamide systems, although the formation pathway is still uncertain.

To investigate the photobenzannulation reaction pathway, substituted benzenecarbothioamides **1b** and **c** were irradiated along with **2** in a similar manner to that described above. As a result, a pair of regioisomers of methyl 2-naphthoate (**3b** and **3b′** from **1b**, **3c** and **3c′** from **1c**) were obtained. Interestingly, the benzannulation reaction of **1c** proceeded more efficiently. From these experiments, the reaction seems to proceed in several steps involving initial thietane **6** formation between the thioamide and 2-methoxyfuran, leading to the phenylbutadiene **10**,[10] which subsequently cyclizes to the methyl 2-naphthoate derivative **3a** as shown in Scheme 2.

In conclusion, the new photobenzannulation of arenecarbothioamide with 2-methoxyfuran promises to have broad applications to the synthesis of various benzo-fused heteroaromatics involving polycyclic oxygen, nitrogen and sulfur heteroaromatics. In addition, it was shown that 2-methoxyfuran is a potentially useful building block in a photosynthesis of benzo-fused heteroaromatics. The detailed study of the benzannulation reaction pathway is in progress.

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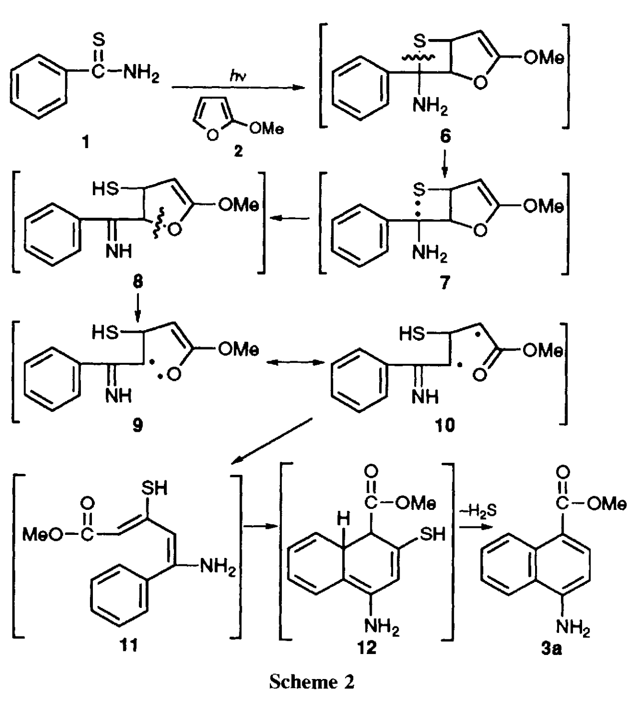

Scheme 2

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* All products showed reasonable analytical and spectral data.

References

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