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Intermolecular Photoaddition Reaction of Arenecarbothioamides to 2-Methoxy- and 2-Trimethylsiloxyfurans. Facile Synthesis of Arene-Fused Aminobenzoates by Novel Photoinduced Benzannulation[1)]

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Irradiation of arenecarbothioamides with 2-methoxyfuran in benzene solution gave arene-fused aminobenzoates in moderate yields accompanied by small amounts of arylpyrroles or arylthiophenes. In the case of 2-trimethylsiloxyfuran, arenecarbothioamides gave arene-fused aminobenzoates in good yields as sole products. It was demonstrated that certain furan derivatives are potentially useful as building blocks in photoinduced benzannulation.

Key words photobenzannulation; arenecarbothioamide; arene-fused aminobenzoate; 2-methoxyfuran; 2-trimethylsiloxyfuran

Although the photochemistry of thiocarbonyl compounds has been extensively studied,[2)] few reports have dealt with the photochemical properties of thioamides: namely, thiobenzanilides[3)] and 4-thiouracils[4)] have been the subjects of most reports, and little work has been presented on the photoreactions of arenecarbothioamides. During the course of our systematic studies on the photochemistry of nitrogen–thiocarbonyl systems, we found that arenecarbothioamides undergo the Paterno–Büchi type reaction with various olefins, such as nonconjugated olefins,[5)] styrene derivatives,[6)] and furans,[7)] to give a variety of photoproducts.

Recently, we reported a new type of benzannulation reaction using intermolecular photoreaction of arenecarbothioamide with 2-methoxyfuran to produce various arene-fused compounds having a methyl *p*-aminobenzoate moiety.[8)] Further, we have searched for photochemical substrates that would serve as efficient carbon sources for benzannulation. Here we present a full account of our work on the photoinduced benzannulation of heteroaromatics and aromatics, including the formation of arylpyrroles or arylthiophenes (Chart 1).

Photoreactions of arenecarbothioamides (**1**) with 2-methoxyfuran (**2**) were carried out in benzene using a high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere. Irradiation of benzthioamide (**1a**) with 3 eq of **2** for 20 h gave a methyl 2-naphthoate derivative (**3a**, 62%) and a small amount of α-arylpyrrole (**4a**, 13%). Next, the photoreaction of a series of heteroaromatic thioamides (**5a**—**d**) with **2** was performed. As expected, the corresponding arene-fused methyl *p*-aminobenzoates (**6a**—**d**) were obtained in moderate yields, accompanied by small amounts of α-arylpyrroles (**7a, b**) or α-arylthiophenes (**8c, d**) (Table 1, Chart 2).

Structural assignments for the benzannulated products were made on the basis of the spectral data and elemental analyses. In the IR spectrum of benzofuran (**6a**), absorptions of an amino and an ester carbonyl group appeared at 3400 and 1710 cm^{-1}, respectively. The ^{1}H-NMR spectrum of **6a** showed two singlets at δ 6.66 and 7.59, suggesting the presence of a 2,3-disubstituted furan moiety. In addition, the spectrum exhibited a characteristic AB pattern at δ 6.82 and 7.71 with the coupling constant $J = 8.8$ Hz, which indicated the presence of two vicinal protons in benzene. The presence of a 1,4-disubstituted benzofuran was suggested. Further, the ^{13}C-NMR spectrum of **6a** also supported the presence of an ester carbonyl [169.0 ppm (s)] and benzofuran, and the mass spectrum showed the molecular ion peak at M$^+$ 191, corresponding to the molecular weight of **6a**.

Structural assignments for the α-arylpyrroles (**7a, b**) were also made on the basis of spectral data and elemental analyses. For example, the IR spectrum of **7a** showed NH and CO absorptions at 3350 and 1750 cm^{-1}, respectively, while the ^{1}H-NMR spectrum showed three signals at 3.84, 5.75 and 10.10 ppm assignable to a methoxyl group, a proton of the pyrrole ring and an aldehyde group, respectively. Further, the signals due to a monosubstituted furan ring and NH of a pyrrole ring (9.06 ppm) indicated a trisubstituted (formyl, methoxy and furyl) pyrrole structure for **7a**.

Similarly, structural assignments for the α-arylthiophenes (**8c, d**) were made on the basis of spectral data and elemental analysis. In the IR spectrum of **8c**, an absorption due to an ester carbonyl group appeared at 1720 cm^{-1}. In the ^{1}H-NMR spectrum two multiplets at δ 7.41 (2H) and 8.65 (2H) suggest the presence of 4-substituted pyridine. In addition, the spectrum exhibited a characteristic

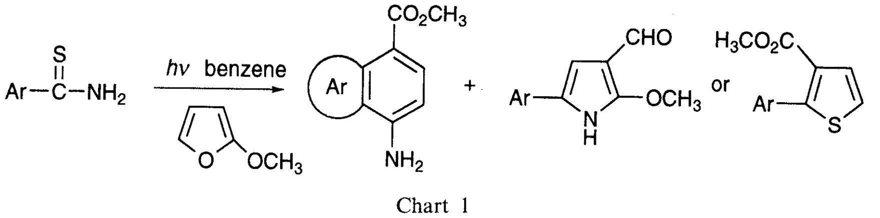

Chart 1

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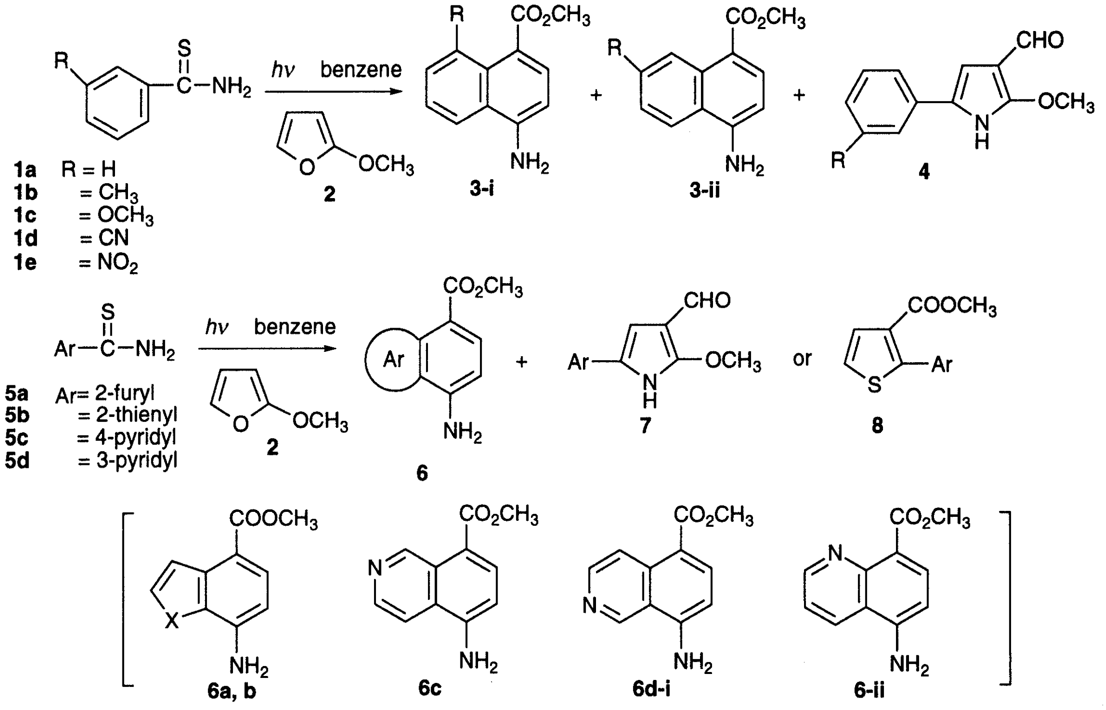

Chart 2

Table 1. Photoreactions of Arenecarbothioamides (**1**, **5**) with 2-Methoxyfuran (**2**)

Arenecarbothioamide	Photoproducts yield			
	Arene-fused methyl *p*-aminobenzoates		Pyrroles	Thiophenes
1a R = H	**3a** 62%		**4a** 13%	
1b R = Me	**3b-i** 11%$^{a)}$	**3b-ii** 13%$^{a)}$		
1c R = OCH_3	**3c-i** 23%	**3c-ii** 48%	**4c** 11%	
1d R = CN	**3d-i** 18%$^{a)}$	**3d-ii** 45%$^{a)}$	**4d** 9%	
1e R = NO_2	—	—	—	
5a X = O	**6a** 41%		**7a** 23%	
5b X = S	**6b** 34%		**7b** 18%	
5c	**6c** 38%			**8c** 25%
5d	**6d-i** 34%	**6d-ii** 11%		**8d** 13%

a) A mixture of two regioisomers as judged from the ^{1}H-NMR spectra.

AB pattern at δ 7.36 and 7.55 ($J = 5.4$ Hz), which indicated the presence of the two vicinal protons on a 1,2-disubstituted thiophene ring. The ^{13}C-NMR spectrum of **8c** also supported the presence of an ester carbonyl [163.3 (s)], pyridine and thiophene rings. The mass spectrum showed the molecular ion peak at M^+ 219, corresponding to the molecular weight of **8c**.

Further, in order to see whether a correlation exists between the position of ring closure and the nature of the substituent in the photoreaction, 3-substituted benzenecarbothioamides (**1b**—**e**) were irradiated along with **2** in a similar manner to that described above. In the photoreaction of 3-substituted benzenecarbothioamides (**1b**—**d**), 7-substituted methyl 4-amino-1-naphthoates (**3-ii**) were obtained in preference to 8-substituted methyl 4-amino-1-naphthoates (**3-i**), accompanied by small amounts of α-arylpyrroles (**4b**—**d**). But in the case of 3-nitrobenzenecarbothioamide (**1e**), no products were isolated even after irradiation for 20 h, and unchanged **1e** was recovered in 91% yield.

This result indicated that cycloaddition of a C = S or C = N double bond to the C = C bond of furan in the initial step was not influenced by the electronic properties of the substituent, although it is not clear why the nitro compound is inert toward photoreaction with furan. However, the annulation (ring closure) on a phenyl ring occurred mainly at the less hindered *ortho* position of thiocarbonyl. Such regioselective ring closure at the less hindered position has been reported in the photochemical transformation of 1,4-diphenyl-1,3-butadiene to naphthalene derivatives.9) Therefore, the formation of **3** may be explained by assuming a benzannulation pathway *via* the phenylbutadiene intermediate (**13**)10) (Chart 3). That is to say, the photoreaction of arenecarbothioamide with 2-methoxyfuran seems to proceed in several steps, involving initial thietane (**9**) formation between the thiocarbonyl and furan leading to the biradical intermediate (**11**↔**12**), followed by generation of the phenylbutadiene key intermediate (**13**), which subsequently cyclizes to the naphthalene derivative (**3**). No evidence is available at this time to suggest whether these steps are thermal or photochemical in nature.

In a previous paper,7d) we proposed a reaction pathway for the formation of α-arylpyrrole in the photoreaction of benzenecarbothioamide with 2-phenoxyfuran, by analogy with the known thermal rearrangement from oxazepine to pyrrole ring.11) As for the formation of α-arylpyrroles (**4a**—**d**, **7a**, **b**), this experiment also indicated that reaction would proceed in several steps involving initial [2 + 2] cycloaddition between the C = N double bond and furan,7d) leading to the aryloxazepine (**19**), which would subsequently rearrange to phenylpyrrole (**4a**) as shown in Chart 4. In the case of the arylpyrrole from 2-phenoxyfuran, cycloaddition of the C = N double bond in **17** toward the unsubstituted C = C double bond in furan

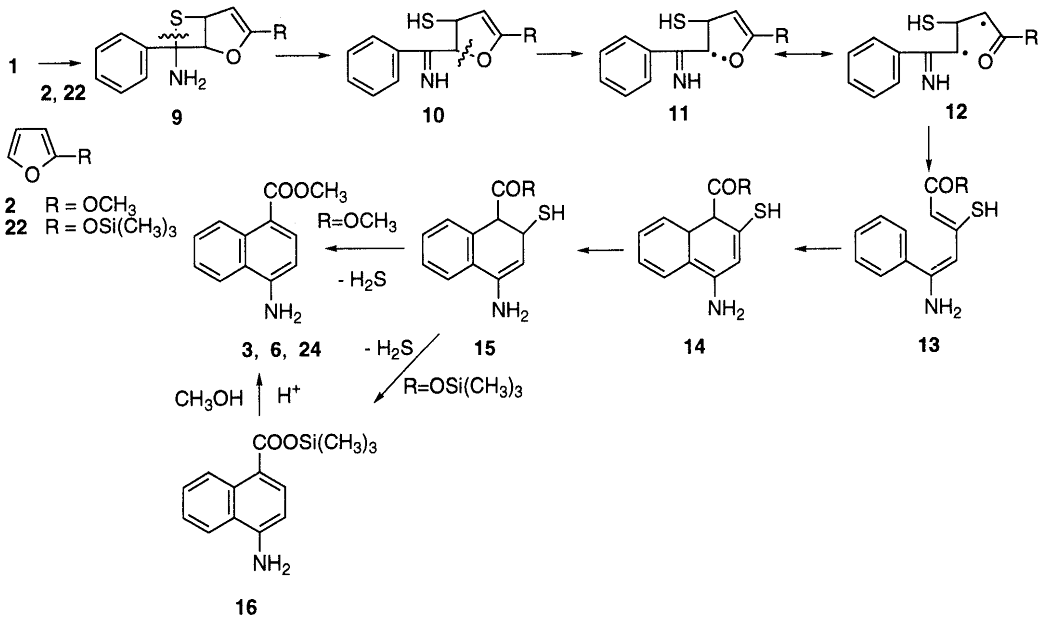

Chart 3

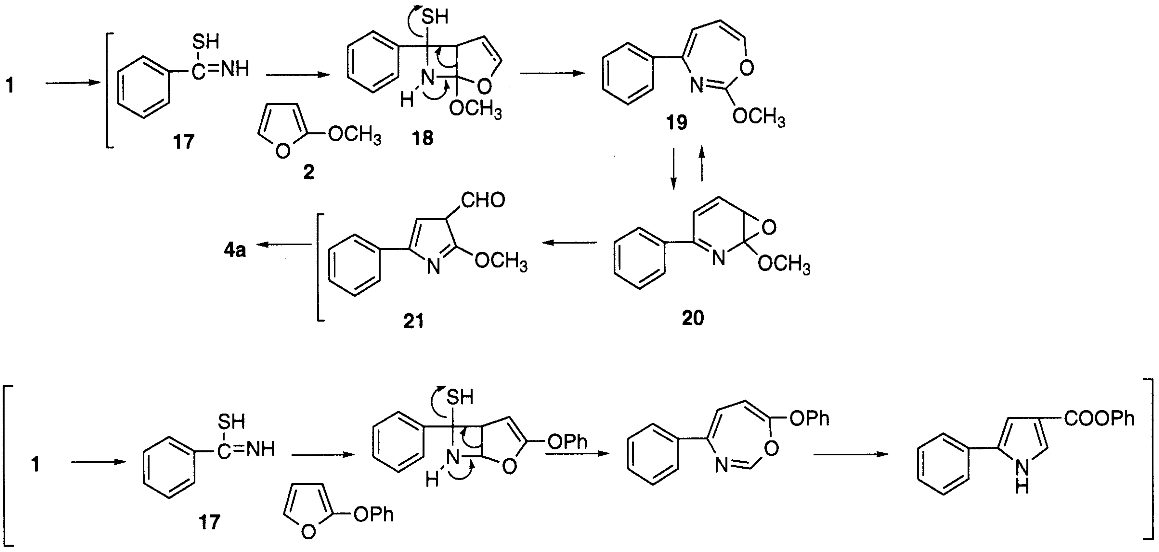

Chart 4

was observed.$^{7d)}$ However, in this study, it was thought that cycloaddition occurred between the C=N double bond in **17** and the substituted C=C double bond in furan, although such addition to substituted double bond carbons is unprecedented. Further work on this is needed. The pathway of formation of the α-arylthiophenes (**8c, d**) also remains unclear.

Next, in order to investigate the photochemical substrates that serve as efficient carbon sources for benzannulation, we chose 2-trimethylsiloxyfuran (**22**) as a 2-furan ether analogue. Irradiation of **1a** with 5 eq of **22** was performed under conditions similar to those described above. Since photoproducts from **22** were labile during silica gel column chromatography, they were treated with methanol in the presence of an acid catalyst and isolated as the methyl esters. In the case of **1a**, methyl 4-amino-1-naphthoate **3a** was obtained in 71% yield as the sole product. Similarly, in the photoreaction of heteroaromatic thioamides **5a**—**d** with **22**, the corresponding arene-fused methyl *p*-aminobenzoates (**6a**—**d**) were obtained in good yields (59—66%) (Table 2).

Table 2. Photoreactions of Arenecarbothioamides (**1**, **5**, **23**) with 2-Trimethylsiloxyfuran (**22**)

Arenecarbothioamide	Photoproducts yield Arene-fused methyl *p*-aminobenzoates
1a	**3a** 71%
5a	**6a** 62%
5b	**6b** 59%
5c	**6c** 65%
5d	**6d-i** 51% **6d-ii** 15%
23a	**24a** 69%
23b	**24b** 64%
23c	**24c** 53%

Further, in order to develop this photoreaction, photobenzannulations of 1- and 2-naphthalenecarbothioamide (**23a, b**), and 2-benzofurancarbothioamide (**23c**) were

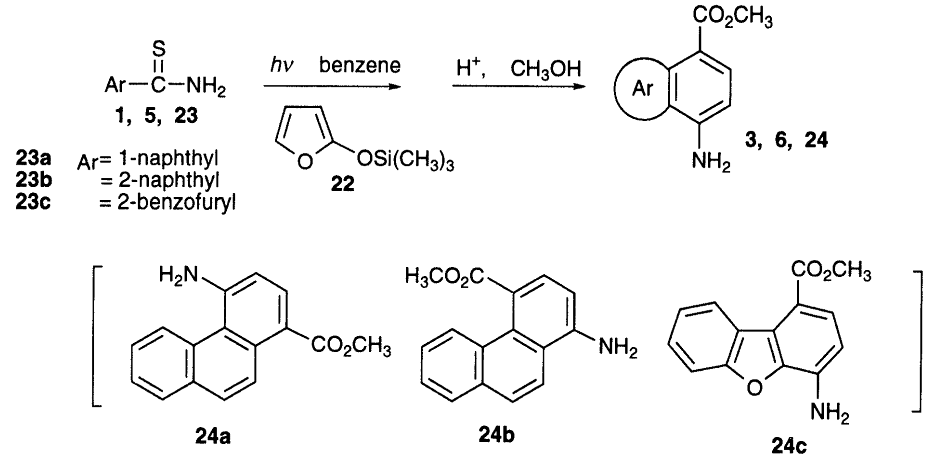

Chart 5

Table 3. Physical Data for Photoproducts (**3**, **4**, **6**, **7**, **8**, **11**)

Product	Appearance	mp (°C)	Recryst. solvent	Formula	Analysis (%)					
					Calcd			Found		
					C	H	N	C	H	N
3a	Colorless oil[7d]									
3b	Inseparable mixture			$C_{13}H_{13}NO_2$	72.53	6.09	6.51	72.71	6.22	6.58
3c-i	Colorless plates	98—99.5	*n*-Hexane–ethyl acetate	$C_{13}H_{13}NO_3$	67.51	5.67	6.06	67.37	5.55	6.13
3c-ii	Colorless plates	101—102	*n*-Hexane–ethyl acetate	$C_{13}H_{13}NO_3$	67.51	5.67	6.06	67.55	5.39	6.24
3d	Inseparable mixture			$C_{13}H_{10}N_2O_2$	69.02	4.46	12.38	69.11	4.22	12.41
4a	Colorless plates	105—107.5	Ethyl acetate	$C_{12}H_{11}NO_2$	71.61	5.51	6.96	71.50	5.38	7.02
4b	Colorless plates	113—114	Ethyl acetate	$C_{13}H_{13}NO_2$	72.53	6.09	6.51	72.58	6.30	6.73
4c	Colorless plates	131—133	Ethyl acetate	$C_{13}H_{13}NO_3$	67.51	5.67	6.06	67.69	5.43	6.29
4d	Colorless plates	89—92	Ethyl acetate	$C_{13}H_{10}N_2O_2$	69.02	4.46	12.38	68.89	4.50	12.17
6a	Colorless plates	132—134	*n*-Hexane–ethyl acetate	$C_{10}H_9NO_3$	62.81	4.75	7.33	62.59	4.81	7.50
6b	Colorless plates	55—56	*n*-Hexane–ethyl acetate	$C_{10}H_9NO_2S$	57.96	4.38	6.76	57.85	4.51	6.66
6c	Colorless plates	151—153	*n*-Hexane–ethyl acetate	$C_{11}H_{10}N_2O_2$	65.32	4.99	13.86	65.41	5.13	13.77
6d-i	Colorless plates	188—191	*n*-Hexane–ethyl acetate	$C_{11}H_{10}N_2O_2$	65.32	4.99	13.86	65.19	5.02	13.72
6d-ii	Colorless plates	203—205	*n*-Hexane–ethyl acetate	$C_{11}H_{10}N_2O_2$	65.32	4.99	13.86	65.11	4.89	13.66
7a	Colorless plates	131—133	Ethyl acetate	$C_{10}H_9NO_3$	62.81	4.75	7.33	62.88	4.81	7.50
7b	Colorless plates	149—151	Ethyl acetate	$C_{10}H_9NO_2S$	57.96	4.38	6.76	57.85	4.23	6.70
8c	Colorless oil			$C_{11}H_9NO_2S$	60.26	4.14	6.39	60.11	4.29	6.50
8d	Colorless plates	43—45	*n*-Hexane–ethyl acetate	$C_{11}H_9NO_2S$	60.26	4.14	6.39	60.39	3.98	6.39
24a	Colorless plates	111—112.5	Ethyl acetate	$C_{16}H_{13}NO_2$	76.47	5.22	5.58	76.66	5.10	5.43
24b	Colorless plates	108—109	Ethyl acetate	$C_{16}H_{13}NO_2$	76.47	5.22	5.58	76.33	5.41	5.29
24c	Colorless plates	129—130.5	Ethyl acetate	$C_{14}H_{11}NO_3$	69.69	4.60	5.81	69.53	4.78	5.99

carried out. As expected, the corresponding tricyclic arene-fused methyl *p*-aminobenzoates (**24a**—**c**) were obtained in good yields (Table 2).

With respect to the benzannulation with 2-trimethylsiloxyfuran, a possible pathway is outlined in Chart 2, based on the analogy with 2-methoxyfuran. As for the formation of the tricyclic compound **24b**, although annulation at the 1- and 3-position on the naphthalene ring (anthracene and phenanthrene derivatives) was predicted, only phenanthrene was regioselectively obtained. Such regioselective formation was also reported in the photocyclization of 1-(2-naphthyl)-4-phenyl-1,3-butadiene, for which preferred formation at the 1-position was predicted by means of simple Hückel molecular orbital theory.[12]

The above results, coupled with those reported in the previous papers,[7b,d] indicated that in the photoreaction of benzenecarbothioamide with 2-furan ether analogues, benzannulation is the main reaction process. In particular, 2-trimethylsiloxyfuran is a potentially useful building block for photosynthesis of arene-fused methyl *p*-aminobenzoate, serving as a three-carbon annulation unit for benzannulation without the formation of pyrroles as by-products. The advantages of this method are the ready availability of the starting materials and the simplicity of the reaction. This photoreaction may also be applied for the synthesis of polyaromatic systems, including heteroaromatics, by structural variation of the arenecarbothioamide.

In conclusion, we have developed a new photochemical benzannulation reaction in the thioamide system that promises to have broad application to the synthesis of various benzo-fused heteroaromatics.

Experimental

All melting points were determined on a Yamato melting point apparatus (model MP-21) and are uncorrected. IR spectra were recorded on a JASCO A-102 spectrometer. NMR spectra were taken on JEOL

Table 4. Spectral Data for Photoproducts (**3**, **4**, **6**, **7**, **8**, **24**)

Compd.	IR (cm^{-1}) (Nujol)	MS (*m/z*)	^{1}H-NMR (CDCl$_3$) δ ppm	^{13}C-NMR (CDCl$_3$) δ ppm
3c-i	3400 1740	231	3.91 (3H, s), 3.92 (3H, s), 6.73 (2H, br s), 6.88 (1H, d, *J*=8.8 Hz), 7.34 (1H, m), 7.42 (1H, m), 7.49 (1H, d), 7.85 (1H, d, *J*=8.8 Hz)	51.5 (q), 55.6 (q), 104.7 (s), 106.7 (d), 109.7 (d), 113.5 (d), 124.2 (s), 125.3 (d), 125.9 (d), 128.3 (s), 148.6 (s), 155.8 (s), 169.4 (s)
3c-ii	3400 1740	231	3.91 (3H, s), 3.92 (3H, s), 6.63 (2H, 7.01 (1H, d, *J*=8.8 Hz), 7.13 (1H, d, *J*=2.4 Hz), 7.21 (1H, dd, *J*=2.4, 8.8 Hz), 7.65 (1H, d, *J*=8.8 Hz), 7.74 (1H, d, *J*=8.8 Hz)	51.5 (q), 55.4 (q), 101.4 (d), 104.8 (s), 116.0 (d), 120.0 (d), 124.1 (s), 124.2 (d), 130.0 (d), 131.5 (s), 147.8 (s), 157.5 (s), 169.5 (s)
4a	3400 1700	201	3.81 (3H, s), 5.70 (1H, d, *J*=2.0 Hz), 7.46 (5H, m), 9.67 (1H, s), 11.8 (1H, s)	57.3 (q), 81.5 (d), 120.4 (s), 128.0 (d), 128.6 (d × 2), 128.7 (d × 2), 130.1 (s), 134.7 (s), 150.2 (s), 184.7 (d)
4b	3400 1700	215	2.15 (3H, s), 3.78 (3H, s), 5.80 (1H, d, *J*=2.0 Hz), 7.43 (5H, m), 9.67 (1H, s), 11.8 (1H, s)	20.1 (q), 58.1 (q), 81.0 (d), 120.6 (s), 128.5 (d), 128.6 (d), 128.7 (d), 130.5 (d), 131.3 (s), 135.5 (s), 150.9 (s), 183.1 (d)
4c	3400 1710	231	3.75 (3H, s), 3.78 (3H, s), 5.80 (1H, d, *J*=2.0 Hz), 7.43 (5H, m), 9.67 (1H, s), 11.8 (1H, s)	55.6 (q), 60.2 (q), 81.9 (d), 121.3 (s), 128.5 (d), 128.6 (d), 128.9 (d), 131.3 (s), 133.8 (d), 135.5 (s), 150.9 (s), 183.1 (d)
4d	3400 2220 1700	226	3.77 (3H, s), 5.72 (1H, d, *J*=2.0 Hz), 7.40 (4H, m), 9.65 (1H, s), 11.2 (1H, s)	55.5 (q), 81.0 (d), 115.2 (s), 120.6 (s), 127.9 (d), 128.7 (d), 131.3 (s), 132.5 (d), 135.5 (s), 138.9 (s), 139.0 (d), 183.5 (d)
6a	3400 1710	191	3.86 (3H, s), 6.09 (2H, br s), 6.66 (1H, s), 6.82 (1H, d, *J*=8.8 Hz), 7.59 (1H, s), 7.71 (1H, d, *J*=8.8 Hz)	51.4 (q), 106.1 (s), 107.6 (d), 108.4, 125.4 (d), 131.0 (s), 137.5 (s), 143.6, 146.5 (d), 169.0 (s)
6b	3350 1720	207	3.89 (3H, s), 6.12 (2H, br s), 7.15 (1H, d, *J*=8.3 Hz), 7.29 (1H, d, *J*=5.4 Hz), 7.51 (1H, d, *J*=5.4 Hz), 7.87 (1H, d, *J*=8.3 Hz)	51.6 (s), 105.2 (s), 112.3 (d), 125.3 (d), 126.8 (s), 127.0 (d), 128.3 (d), 143.9 (s), 146.0 (s), 169.1 (s)
6c	3400 1720	202	3.93 (3H, s), 6.99 (1H, d, *J*=8.8 Hz), 7.12 (2H, br s), 7.52 (1H, d, *J*=5.9 Hz), 8.06 (1H, d, *J*=8.8 Hz), 8.56 (1H, d, *J*=5.9 Hz), 9.37 (1H, s)	51.8 (q), 105.2 (s), 113.8 (d), 118.6 (s), 120.8 (d), 131.7 (d), 139.7 (s), 145.7 (d), 146.5 (d), 149.7 (s), 168.7 (s)
6d-i	3400 1700	202	3.94 (3H, s), 6.82 (2H, br s), 7.19 (1H, d, *J*=8.8 Hz), 7.65 (1H, d, *J*=6.4 Hz), 7.99 (1H, d, *J*=8.8 Hz), 8.56 (1H, d, *J*=6.4 Hz), 9.15 (1H, s)	51.9 (q), 106.8 (s), 114.4 (d), 114.5 (d), 126.5 (s), 128.2 (d), 130.8 (s), 143.0 (d), 147.5 (s), 152.7 (d), 168.8 (s)
6d-ii	3400 1700	202	3.93 (3H, s), 6.85 (2H, br s), 7.33 (1H, d, *J*=8.8 Hz), 7.38 (1H, m), 8.10 (1H, d, *J*=8.8 Hz), 8.24 (1H, m), 8.93 (1H, m)	51.7 (s), 104.6 (s), 117.3 (d), 118.2 (s), 119.9 (d), 130.2 (d), 130.6 (d), 148.9 (s), 151.3 (s), 152.1 (d), 168.9 (s)
7a	3350 1750	191	3.84 (3H, s), 5.75 (1H, d, *J*=2.2 Hz), 6.49 (1H, dd, *J*=1.5, 3.4 Hz), 6.82 (1H, d, *J*=3.4 Hz), 7.45 (1H, d, *J*=1.5 Hz), 9.06 (1H, s), 10.10 (1H, s)	58.0 (q), 82.7 (d), 108.8 (d), 112.3 (d), 120.9 (s), 124.0 (s), 142.7 (d), 145.8 (s), 150.1 (s), 185.8 (d)
7b	3400 1700	207	3.84 (3H, s), 5.78 (1H, d, *J*=3.0 Hz), 7.11 (1H, m), 7.21 (1H, m), 7.36 (1H, m), 8.64 (1H, br s), 9.94 (1H, s)	57.7 (q), 81.9 (d), 121.9 (s), 126.6 (d), 126.8 (d), 128.0 (d), 131.4 (s), 150.0 (s), 185.7 (d)
8c	1720	219	3.77 (3H, s), 7.36 (1H, d, *J*=5.4 Hz), 7.41 (2H, m), 7.55 (1H, d, *J*=5.4 Hz), 8.65 (2H, m)	51.8 (q), 124.3 (d × 2), 125.6 (d), 129.1 (s), 130.4 (d), 141.3 (s), 147.2 (s), 149.5 (d × 2), 163.3 (s)
8d	1720	219	3.75 (3H, s), 7.34 (2H, m), 7.57 (1H, d, *J*=5.4 Hz), 7.85 (1H, m), 8.62 (1H, m), 8.71 (1H, m)	51.7 (q), 122.7 (d), 125.1 (d), 128.9 (s), 129.6 (s), 130.3 (d), 137.2 (d), 146.8 (s), 149.5 (d), 150.0 (d), 163.3 (s)
24a	3350 1700	251	3.97 (3H, s), 7.11 (2H, br s), 7.13 (1H, d, *J*=8.8 Hz), 7.59 (3H, m), 7.75 (1H, d, *J*=8.8 Hz), 7.91 (1H, d, *J*=7.8 Hz), 8.05 (1H, d, *J*=8.8 Hz), 9.20 (1H, d, *J*=8.8 Hz)	57.4 (q), 106.3 (d), 110.8 (s), 118.8 (d), 120.9 (d), 124.5 (d), 126.3 (d), 127.0 (d), 127.5 (d), 127.8 (d), 128.8 (d), 131.0 (s), 132.8 (s), 135.0 (s), 148.8 (s), 169.3 (s)
24b	3300 1720	251	3.94 (3H, s), 6.74 (2H, br s), 7.65 (2H, m), 7.72 (1H, d, *J*=9.3 Hz), 7.80 (1H, d, *J*=9.3 Hz), 7.89 (1H, m), 8.05 (1H, d, *J*=8.8 Hz), 8.08 (1H, d, *J*=8.8 Hz), 8.64 (1H, m)	51.6 (q), 106.2 (s), 110.8 (d), 119.1 (d), 120.3 (s), 123.9 (d), 126.2 (d), 126.8 (d), 127.5 (d), 127.9 (d), 128.4 (d), 130.1 (s), 132.8 (s), 134.3 (s), 148.8 (s), 169.2 (s)
24c	3400 1720	241	3.92 (3H, s), 6.72 (2H, br s), 7.19 (1H, d, *J*=8.8 Hz), 7.34 (1H, m), 7.47 (1H, m), 7.56 (1H, d, *J*=8.3 Hz), 7.84 (1H, d, *J*=8.8 Hz), 7.91 (1H, d, *J*=7.8 Hz)	51.6 (q), 107.5 (d), 108.7 (s), 111.9 (d), 121.5 (d), 123.0 (d), 124.5 (s), 125.5 (d), 127.4 (s), 127.8 (d), 137.6 (s), 144.3 (s), 156.7 (s), 168.7 (s)

JNM FX-90Q and JEOL JNM EX-400 spectrometers. Chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) (0.0 ppm) as an internal standard. The abbreviations used are as follows: s, singlet; d, doublet; dd, doublet of doublets; q, quartet; m, multiplet. Mass spectra were obtained on a JEOL JMS-QH-100 gas chromatograph–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).

Preparation of Arenecarbothioamides (1) Arenecarbothioamides (**1a**, **5c**, **5d**) were commercial products and other thioamides (**1b**—**d**, **5a**, **b**,[13] **23a**, **b**,[14,15] and **23c**[16]) were prepared by the reported procedures.

Irradiation of Arenecarbothioamides (1) with 2-Methoxyfuran (2) General Procedure: A solution of **1** (5 mmol) and **2** (15 mmol) in benzene (200 ml) was irradiated for 20 h with a 1 kW high-pressure mercury lamp through a Pyrex filter under N_2 at room temperature. After removal of the solvent *in vacuo*, the residue was chromatographed over a silica gel column (*n*-hexane–ethyl acetate, 5 : 1; v/v). The results are summarized in Tables 1—4.

Irradiation of Arenecarbothioamides (1) with 2-Trimethylsiloxyfuran (22) General Procedure: A solution of **1** (6 mmol) and **22** (30 mmol) in benzene (200 ml) was irradiated for 5 h with a 1 kW high-pressure mercury lamp through a Pyrex filter under N_2 at room temperature. Removal of the solvent gave a residue, which was dissolved in methanol (50 ml) and concentrated hydrochloric acid (0.5 ml). The reaction mixture was refluxed for 2 h. After the reaction, the solvent was removed *in vacuo* and the residue was chromatographed over a silica gel column (*n*-hexane–ethyl acetate, 5 : 1; v/v). The results are listed in Tables 1—4.

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References

1) Photochemistry of the Nitrogen–Thiocarbonyl Systems. 30. Part 29: Oda K., Sakai M., Tsujita H., Machida M., *Synth. Commun.*, in press.
2) de Mayo P., *Accounts Chem. Res.*, **9**, 52—59 (1976).
3) de Mayo P., Sydnes L. K., Wenska, G., *J. Org. Chem.*, **45**, 1549—1554 (1980).
4) Fourrey J. L., Jouin P., Moron J., *Tetrahedron Lett.*, **1974**, 3005—3006.
5) *a*) Machida M., Oda K., Kanaoka Y., *Tetrahedron Lett.*, **25**, 409—410 (1984); *b*) Oda K., Machida M., Kanaoka Y., *Heterocycles*, **30**, 983—991 (1990).
6) *a*) Oda K., Machida M., Kanaoka Y., *Synlett.*, **1992**, 603—604; *b*) Oda K., Tsujita H., Sakai M., Machida M., *Heterocycles*, **42**, 121—124 (1996).
7) *a*) Oda K., Machida M., *Tetrahedron Lett.*, **30**, 4421—4422 (1989); *b*) *Idem*, *J. Chem. Soc., Chem. Commun.*, **1993**, 437—438; *c*) *Idem*, *Chem. Pharm. Bull.*, **41**, 1299—1301 (1993); *d*) Oda K., Tsujita H., Ohno K., Machida M., *J. Chem. Soc., Perkin Trans. 1*, **1995**, 2931—2935.
8) Oda K., Machida M., *J. Chem. Soc., Chem. Commun.*, **1994**, 1477—1478.
9) Leznoff C. C., Hayward R. J., *Can. J. Chem.*, **48**, 1842—1849 (1970).
10) Laarhoven W. H., "Organic Photochemistry," Vol. 10, ed. by Padwa A., Marcel Dekker Inc, New York, 1981, pp. 163—308.
11) Spence G. G., Taylor E. C., Buchardt O., *Chem. Rev.*, **70**, 231—265 (1970).
12) Hayward R. J., Hopkinson A. C., Leznoff C. C., *Tetrahedron*, **28**, 439—447 (1972).
13) Papadopoulos E. P., *J. Org. Chem.*, **39**, 2540—2542 (1974).
14) Badger G. M., Kowanko N., *J. Chem. Soc.*, **1957**, 1652—1657.
15) Tanaka S., *J. Am. Chem. Soc.*, **73**, 872 (1951).
16) Pan F., Wang T.-C., *J. Chinese Chem. Soc. (Taiwan) Ser. II*, **8**, 220—228 (1961).