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Photoreaction of Arenecarbothioamides with 2-Vinylfuran Analogues. The Formation of Tetracyclic Indoles and 2,3-Diaryl-2-pyrrolin-5-ones[1)]

Kazuaki ODA,* Hisao TSUJITA, Masayuki SAKAI, and Minoru MACHIDA*

Faculty of Pharmaceutical Sciences, Health Sciences University of Hokkaido, Ishikari-Tobetsu, Hokkaido 061–0293, Japan. Received June 4, 1998; accepted July 3, 1998

Photoreaction of arenecarbothioamides (1) with 2-vinylfuran analogues (2, 6) in benzene solution gave tetracyclic indole systems (3, 8) *via* photogenerated diarylethylene intermediates. In the case of reaction of furan- or thiophenecarbothioamide (1c, 1d) with 2-furanacrylic acid (2-i), 2,3-diaryl-2-pyrrolin-5-ones (5c-i, 5d-i) were obtained.

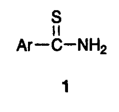
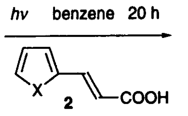
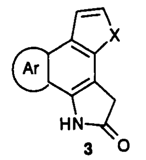
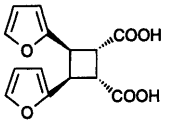
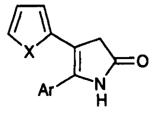
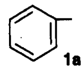
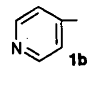
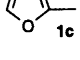
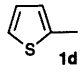
Key words photochemistry; arenecarbothioamide; 2-vinylfuran analogue; intermolecular photoreaction; tetracyclic indole; pyrrolin-5-one

Since indoles are found in biologically active natural products and play a key role in a variety of pharmaceuticals, their synthesis has received considerable attention.[2)] Although numerous synthetic routes to indole systems are known, little is known about facile synthetic routes to multicyclic indole systems such as benzo[*g*]furano[2,3-*e*]indole and benzo[*g*]thiopheno[2,3-*e*]indole. For the construction of multicyclic indole systems, Moskal and van Leusen reported synthetic methods based on thermal or photochemical electrocyclic ring closure of dialkenylpyrroles.[3,4)] Recently, the 1*H*-dibenz[*e*,*g*]indole skeleton was described as one of the candidates of choice for a potential DNA intercalative drug delivery vehicle.[5)]

In a previous paper,[6)] we reported the facile synthesis of a tetracyclic indole system through intermolecular photoreaction of benzenecarbothioamide with 2-vinylfuran analogues. As an extension of this synthetically useful reaction, the generality of conversion of 2-vinylfuran analogues and 5-membered heterocyclic arenecarbothioamides into a variety of multicyclic indole systems was examined. The present report is concerned with full details of further research on the photoreaction of arenecarbothioamides with 2-vinylfuran analogues.

In order to examine whether an exocyclic double bond in the furan can participate in this annulation, readily available 2-furanacrylic acid (**2**-i) was first selected as an olefin-conjugated furan. As a preliminary experiment, photolysis of benzenecarbothioamide (**1a**) with 2 eq of **2**-i was carried out in benzene using a high pressure mercury lamp through a Pyrex filter under a N_2 atmosphere. As a result, the tetracyclic compound (**3a**-i) was obtained in 20% yield, along with the photodimer (**4**) of **2**-i in 18% yield. To avoid the formation of **4**, the molar ratio of **1a** and **2**-i was varied. As expected, the yield of **3a**-i increased to 39% with the ratio of 2 : 1 (Table 1). Similarly, in the case of reaction of **1a** with thiopheneacrylic acid (**2**-ii), the tetracyclic compound (**3a**-ii) was obtained in 32% yield, accompanied by 2,3-diaryl-2-pyrrolin-5-one (**5a**-ii) in 6% yield. In the photoreaction of 4-pyridinecarbothioamide (**1b**) with furan- or thiopheneacrylic acid (**2**-i, **2**-ii), although irradiation for 30 h was required, tetracyclic indole (**3b**) and 2,3-diaryl-2-pyrrolin-5-one (**5b**) were obtained in 28—31% and 4—5% yields, respectively. In the photoreaction of 5-membered heterocyclic carbothioamides (**1c**, **d**) with furan- or thiopheneacrylic acid (**2**-i, **2**-

Table 1. Photoreaction of **1a**—**d** with **2**

 $Ar-\overset{\overset{S}{\|}}{C}-NH_2$ **1** Ar		mole ratio (1/2)	 **3**	 **4**	 **5**
 **1a**	**2**-i X=O	0.5	**3a**-i 20%	18%	—
		1	**3a**-i 28%	trace	—
		2	**3a**-i 39%	—	**5a**-i 2%
	2-ii X=S	2	**3a**-ii 32%	—	**5a**-ii 6%
 **1b**	**2**-i X=O	2[a)]	**3b**-i 31%	—	**5b**-i 5%
	2-ii X=S	2[a)]	**3b**-ii 28%	—	**5b**-ii 4%
 **1c**	**2**-i X=O	2	—	—	**5c**-i 25%
	2-ii X=S	2	—	—	**5c**-ii 31%
 **1d**	**2**-i X=O	2	—	—	**5d**-i 39%
	2-ii X=S	2	—	—	**5d**-ii 26%

a) Irradiation time: 30 h.

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* To whom correspondence should be addressed.

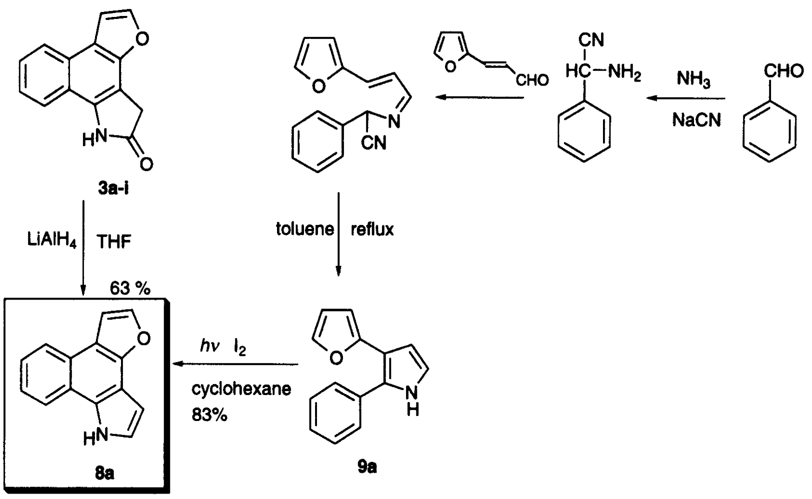
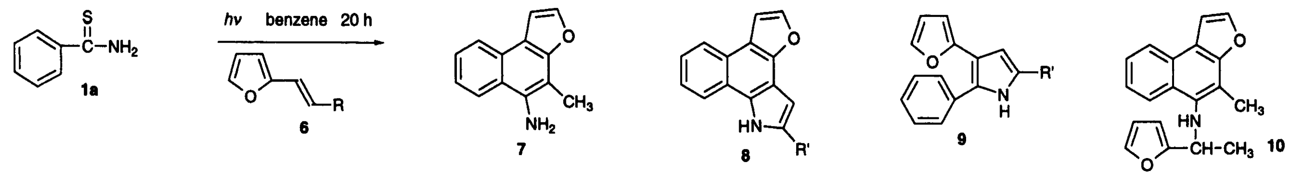


Chart 1

Table 2. Photoreaction of **1a** with **6a**—**f**



6	7	8	9	10
6a R=H	**7a** 39%			**10a**[a] 2%
6b R=CHO		**8b** 31% (R'=H)	**9b** 6% (R'=H)	
6c R=COCH$_3$		**8c** 27% (R'=CH$_3$)	**9c** 9% (R'=CH$_3$)	
6d R=CONH$_2$		—	—	
6e R=COOCH$_3$		—	—	
6f R=CN		—	—	

a) Stereochemistry is not determined.

ii), 2,3-diaryl-2-pyrrolin-5-ones (**5c**, **d**) were obtained as the sole product in moderate yield, and no tetracyclic compound (**3c**, **d**) was detected. Further, the conversion of **5** to tetracyclic compounds (**3**) was next examined. The 2,3-diaryl-2-pyrrolin-5-ones (**5a**, **b**), derived from 6-membered arenecarbothioamides, were easily transformed to tetracyclic compounds (**3a**, **b**) in good yield by photolysis in the presence of iodine. However, in the case of 2,3-diaryl-2-pyrrolin-5- ones (**5c**, **d**), derived from 5-membered arenecarbothioamides, tetracyclic compound was not isolated even after irradiation for 20 h under similar conditions and unchanged **5c**, **d** were recovered.

The structure of **3a**-i was assigned on the basis of elemental analysis and spectral data. In the IR spectrum, absorptions for an amino group and an amide carbonyl appeared at 3350 and 1700 cm^{-1}, respectively. The ^{1}H-NMR spectrum showed two singlets at 3.36 and 11.20 ppm assignable to a methylene group and an amide proton of a pyrrolin-5-one ring, respectively. In addition, the spectrum exhibited the presence of six aromatic protons at 7.49—8.27 ppm. The ^{13}C-NMR spectrum of **3a**-i also supported the presence of an amide carbonyl [176.8 ppm (s)] and the mass spectrum showed a molecular ion peak at M$^+$ 223, corresponding to the molecular weight of **3a**-i. To further confirm the structure, **3a**-i was treated with LiAlH$_4$ to give reduction product (**8a**). The structure of **8a** was established by comparison with a sample that was independently synthesized by the iodine-catalyzed photooxidation[7] of 2-phenyl-3-furanylpyrrole (**9a**).[8] The physical and spectral data of **8a** photochemically derived from **9a** were identical with those of the reduction product (**8a**) (Chart 1).

Structural assignments for the 2,3-diaryl-2-pyrrolin-5-ones (**5**) were also made on the basis of spectral data and elemental analyses. For example, the IR spectrum of **5a**-ii showed NH and amide carbonyl absorptions at 3150 and 1700 cm^{-1}, respectively, and the ^{1}H-NMR spectrum showed two signals at 3.58 and 10.18 ppm assignable to a methylene group and the NH of a pyrrolin-5-one ring. Furthermore, signals due to a monosubstituted benzene and a monosubstituted thiophene indicated a 2,3-diarylpyrrolin-5-one structure for **5a**-ii.

In order to identify photochemical substrates suitable for efficient formation of tetracyclic compounds, photoreaction of benzenecarbothioamide **1a** with other 2-vinylfuran analogues (**6**) was carried out (Table 2). At first, we chose a simple 2-vinylfuran (**6a**) as an olefin-conjugated furan. As a result, the tricyclic compound (**7a**) was obtained in 39% yield, accompanied by a small amount of the photoadduct (**10**) generated from **7** and **6a**. In the case of 3-(2-furanyl)acrolein (**6b**) and 2-furanylacetone (**6c**), the tetracyclic indoles, *i.e.* benzo[*g*]furano[2,3-*e*]indole derivatives, (**8b**, **c**) were obtained in 31 and 27% yields, along with diarylpyrroles (**9b**, **c**) in 6 and 9% yields, respectively. Also, the diarylpyrrole (**9b**) was easily transformed to **8b** in 85% yield by photolysis in the presence of iodine, but was not transformed in the absence of iodine. In the case of vinylfuran derivatives (**6d**—**f**),

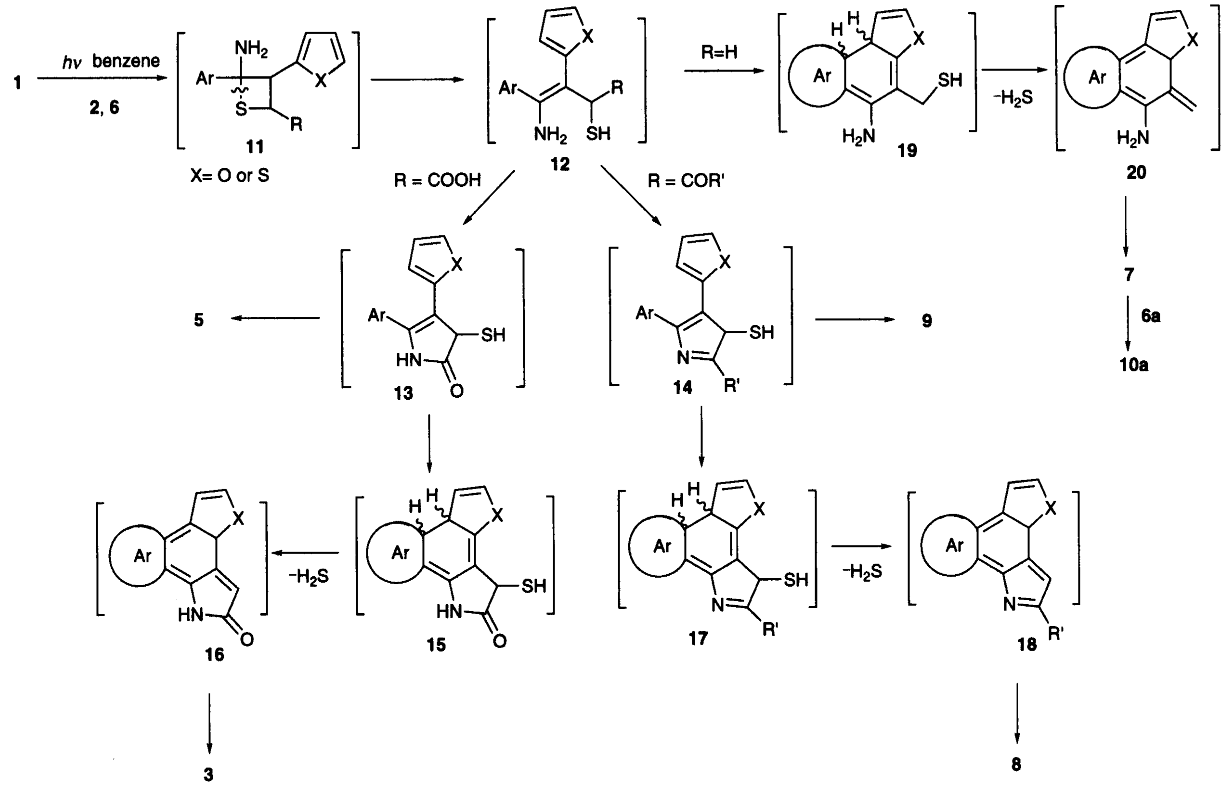


Chart 2

Table 3. Physical Data for Photoproducts (**3**, **5**, **7**—**10**)

Product	Appearance	mp (°C)	Recryszt. solvent	Formula	Analysis (%)					
					Calcd			Found		
					C	H	N	C	H	N
3a-i	Colorless needles	205 (dec.)	Ethyl acetate	$C_{14}H_9NO_2$	75.32	4.06	6.28	75.03	4.10	6.25
3a-ii	Colorless plates	275 (dec.)	Ethanol	$C_{14}H_9NOS$	70.27	3.79	5.85	70.02	3.86	5.72
3b-i	Colorless plates	151—153	Ethyl acetate	$C_{13}H_8N_2O_2$	69.64	3.60	12.49	69.41	3.43	12.30
3b-ii	Colorless plates	188—191	Ethyl acetate	$C_{13}H_8N_2OS$	64.98	3.36	11.66	65.19	3.22	11.72
5a-i	Colorless plates	203—205	*n*-Hexane–ethyl acetate	$C_{14}H_{11}NO_2$	74.65	4.92	6.22	74.51	4.89	6.46
5a-ii	Colorless plates	131—133	Ethyl acetate	$C_{14}H_{11}NOS$	69.68	4.56	5.80	69.88	4.81	5.59
5b-i	Colorless needles	149—151	Ethyl acetate	$C_{13}H_{10}N_2O_2$	69.02	4.46	12.38	68.85	4.23	12.18
5b-ii	Colorless oil			$C_{11}H_9NO_2S$	64.44	4.16	6.60	60.11	4.29	6.50
5c-i	Colorless needles	204—206	Ethanol	$C_{12}H_9NO_3$	66.97	4.22	6.51	66.86	4.26	6.39
5c-ii	Colorless needles	190—193	Ethanol	$C_{12}H_9NO_2S$	62.34	3.92	6.06	62.18	3.84	6.03
5d-i	Colorless needles	172 (dec.)	*n*-Hexane–ethyl acetate	$C_{12}H_9NO_2S$	62.32	3.92	6.06	62.31	3.90	6.01
5d-ii	Colorless needles	180 (dec.)	*n*-Hexane–ethyl acetate	$C_{12}H_9NOS_2$	58.27	3.66	5.66	58.13	3.78	5.50
7a	Colorless oil			$C_{13}H_{11}NO$	79.17	5.62	7.10	79.11	5.49	7.20
8b	Colorless needles	157—158	Benzene–*n*-hexane	$C_{14}H_9NO$	81.14	4.38	6.76	81.10	4.53	6.76
8c	Colorless plates	161—162	Benzene–*n*-hexane	$C_{15}H_{11}NO$	81.43	5.01	6.33	81.22	5.19	6.21
9b	Colorless oil			$C_{14}H_{11}NO$	80.36	5.30	6.69	80.33	5.41	6.59
9c	Colorless oil			$C_{15}H_{13}NO$	80.69	5.87	6.21	80.53	5.78	5.99
10a	Colorless oil			$C_{19}H_{17}NO_2$	78.32	5.88	4.81	78.33	6.01	4.63

no products were isolated even after irradiation for 20 h, and unchanged **1a** was quantitatively recovered, although the reasons for the photochemical inactivity of **6d**—**f** toward **1a** were not obvious.

The structure of **7a** was assigned on the basis of elemental analysis and spectral data. In the IR spectrum, an absorption for an amino group appeared at 3300 cm^{-1}. The ^{1}H-NMR spectrum showed two doublets at 6.62 and 7.61 ppm in the aromatic region, suggesting the presence of a 2,3-disubstituted furan moiety. In addition, the ^{1}H-NMR spectrum exhibited the presence of a methyl group at 1.22 ppm and four aromatic protons in the 7.49—8.30 ppm region. The ^{13}C-NMR spectrum also supported the structure of **7a**. The mass spectrum showed a molecular ion peak at M^{+} 197, corresponding to the molecular weight of **7a**.

From these results, together with those reported in the previous papers,1b,9—14) the reaction pathway for the formation of a tetracyclic indole system may be outlined as illustrated in Chart 2. The reaction seems to proceed in several steps involving initial thietane (**11**) formation between thiocarbonyl and the exocyclic double bond of the vinylfuran, leading to the key intermediate vicinal-diarylethylene (**12**),[15] which subsequently cyclized to give the 2,3-diaryl-2-pyrrolin-5-ones (**13**) or diarylpyrroles (**14**). However, no evidence is available at this time to suggest whether this step is a thermal or photochemical process. When the aryl group (Ar) is a six-membered ring, further cyclization proceeded to give tetracyclic compounds (**3**, **8**), in which **15** or **17** undergo a loss of hydrogen sulfide, since the conformation of the intermediate (**13** or **14**) is favorable for the photocyclization. However, in the case of an intermediate (**13** or **14**) having two five-membered heterocyclic rings on a pyrrolinone or a pyrrole ring, they ultimately led to **5** or **9**, and further cyclization through photoarylation did not proceed because of an unfavorable rigid conformation and/or their photoreversible property.[16]

In this study, the present photoreaction has been shown to provide a new and convenient single-step convergent annulation approach for the construction of a multicyclic indole system. Furthermore, the resulting system can be considered as potential modified intercalative templates that possess two or three hetero atoms in the coplanar aromatic rings, as described above.

It is worth noting that this formation of a tetracyclic indole system *via* photochemically generated vicinal-diarylethylene

Table 4. Spectral Data for Photoproducts (**3**, **5**, **7**—**10**)

Compd.	IR (cm^{-1}) (Nujol)	MS (*m/z*)	1H-NMR (CDCl$_3$) δ ppm	^{13}C-NMR (CDCl$_3$) δ ppm
3a-i[a]	3350 1700	223	3.36 (s, 2H, CH$_2$), 7.49 (m, 3H), 7.97 (m, 1H), 8.17 (m, 1H), 8.27 (m, 1H), 11.20 (br s, 1H, NH).	34.3 (t), 106.1 (d), 117.0 (s), 117.1 (s), 122.8 (d), 123.9 (d), 124.2 (d), 124.4 (d), 126.1 (s), 126.6 (s), 137.7 (s), 143.9 (d), 148.1 (s), 176.8 (s).
3a-ii[a]	3150 1700	239	3.83 (s, 2H, CH$_2$), 7.60 (m, 2H), 7.58 (d, 1H, J=5.4 Hz), 8.17 (t, 2H, J=5.4 Hz), 8.52 (d, 1H, J=7.8 Hz), 11.20 (br s, 1H, NH).	36.4 (t), 113.9 (s), 118.0 (s), 122.6 (d), 122.9 (d), 123.4 (d), 124.6 (d), 125.2 (d), 126.3 (d), 128.3 (s), 131.1 (s), 135.4 (s), 136.9 (s), 176.8 (s).
3b-i[a]	3250	224	3.35 (s, 2H), 7.58 (m, 1H), 8.19 (m, 1H), 8.33 (m, 1H), 8.45 (s, 1H), 8.50 (m, 1H), 11.20 (br s, 1H, NH).	32.8 (t), 115.3 (s), 119.9 (s), 122.9 (s), 123.4 (d), 124.8 (d), 128.9 (s), 137.7 (s), 143.9 (s), 145.2 (d), 146.3 (d), 148.1 (d), 176.1 (s).
3b-ii[a]	3250	240	3.41 (s, 2H), 7.45 (m, 1H), 8.10 (m, 1H), 8.21(m, 1H), 8.43 (s, 1H), 8.62 (m, 1H), 11.00 (br s, 1H, NH).	34.2 (t), 115.8 (s), 121.1 (s), 121.9 (d), 123.4 (d), 123.9 (d), 127.7 (s), 129.7 (s), 133.9 (s), 135.2 (d), 145.9 (d), 147.5 (s), 176.8 (s).
5a-i	3350 1700	225	3.40 (s, 2H, CH$_2$), 6.98 (m, 1H), 7.40 (m, 2H), 7.93 (m, 3H), 8.17 (m, 1H), 8.21 (m, 1H), 11.20 (br s, 1H, NH).	32.1 (t), 105.6 (d), 118.1 (d), 117.5 (s), 121.2 (d), 123.2 (d), 124.0 (d), 124.1 (d), 126.3 (d), 126.5 (s), 135.2 (s), 142.7 (d), 143.4 (s), 176.8 (s),
5a-ii	3150 1700	241	3.58 (s, 2H, CH$_2$), 7.20 (m, 2H), 7.58 (m, 1H), 7.63 (m,2H), 8.20 (m, 2H), 8.43 (m, 1H), 10.18 (br s, 1H, NH).	32.7 (t), 112.2 (s), 118.5 (d), 123.0 (d), 123.5 (d), 124.1 (d), 124.8 (d), 126.0 (d), 126.3 (d), 129.6 (s), 131.5 (d), 135.8 (s), 137.9 (s), 176.8 (s).
5b-i	3250	226	3.55 (s, 2H), 7.12 (1H, m), 7.58 (m, 2H), 8.19 (m, 1H), 8.33 (m, 1H), 8.45 (s, 1H), 8.50 (m, 1H), 11.20 (br s, 1H, NH).	32.8 (t), 117.1 (s), 118.9 (s), 122.9 (d), 123.0 (d), 127.1 (d), 129.9 (s), 135.4 (s), 143.0 (d), 146.2 (d), 146.3 (d), 149.8 (d), 175.1 (s).
5b-ii	3250	242	3.44 (s, 2H), 7.27 (m, 1H), 7.30 (m, 2H), 7.42 (m, 1H), 7.61 (m, 2H), 8.31 (s, 1H), 8.52 (m, 1H), 11.00 (br s, 1H, NH).	32.1 (t), 119.3 (s), 121.1 (s), 121.9 (d), 122.9 (d), 126.4 (d), 127.8 (s), 128.4 (d), 132.6 (d), 135.1 (d), 143.5 (d), 146.2 (s), 175.1 (s).
5c-i	3150 1700	215	3.39 (s, 2H), 6.41 (m, 1H), 6.54 (m, 1H), 6.59 (m, 1H), 6.92 (m, 1H), 7.52 (m, 1H), 7.74 (m, 1H), 10.10 (br s, 1H, NH).	39.1 (t), 103.1 (s), 107.5 (d), 111.1 (d), 112.0 (d), 112.1 (d), 125.4 (s), 141.9 (d), 144.1 (d), 145.0 (s), 149.1 (s), 175.9 (s).
5c-ii	3150 1700	231	3.58 (s, 2H), 6.65 (m, 1H), 6.91 (m, 1H), 7.02 (m, 1H), 7.17 (m, 1H), 7.40 (m, 1H), 7.85 (m, 1H), 10.18 (br s, 1H, NH).	41.4 (t), 107.4 (s), 111.0 (d), 111.8 (d), 124.6 (d), 125.5 (s), 125.6 (d), 127.0 (d), 136.5 (s), 143.8 (d), 144.4 (d), 175.5 (d).
5d-i	3150 1700	231	3.49 (s, 2H), 6.38 (m, 1H), 6.50 (m, 1H), 7.13 (m, 1H), 7.50 (m, 1H), 7.61 (m, 1H), 7.66 (m, 1H), 10.20 (br s, 1H, NH).	41.4 (t), 107.4 (s), 111.0 (d), 111.8 (d), 124.6 (d), 125.5 (d), 125.6 (d), 127.4 (d), 136.5 (s), 143.8 (d), 144.4 (s), 175.5 (s).
5d-ii	3450 1700	247	3.57 (s, 2H), 6.96 (m, 1H), 7.11 (m, 1H), 7.15 (m, 1H), 7.33 (m, 1H), 7.44 (m, 1H), 7.61 (m, 1H), 10.20 (1H, br s, NH).	42.0 (t), 109.9 (s), 124.8 (d), 125.5 (d), 127.0 (d), 127.5 (d), 127.7 (d), 128.6 (d), 129.8 (s), 131.0 (s), 136.3 (s), 176.7 (s).
7a	3300	197	1.22 (s, 3H), 6.62 (d, J=2.4 Hz, 1H), 7.61 (m, 1H), 7.49 (d, J=2.4 Hz, 1H), 7.49—8.30 (m, 3H), 8.20 (br s, 2H, NH$_2$).	21.0 (p), 109.3 (d), 110.9 (d), 113.1 (s), 118.2 (s), 127.2 (s), 127.4 (d), 127.7 (s), 128.0 (d), 133.8 (s), 138.0 (d), 13142.1 (s), 143.2 (d).
8b	3350	207	6.92 (1H, m), 7.24 (m, 1H), 7.51 (m, 2H), 7.71 (m, 1H), 8.00 (m, 1H), 8.17 (m, 1H), 8.94 (br s, 1H, NH).	100.7 (d), 106.4 (d), 113.4 (s), 116.2 (s), 120.2 (d), 120.3 (d), 122.5 (d), 124.4 (d), 124.5 (s), 124.7 (d), 125.4 (s), 130.4 (s), 142.1 (d), 148.0 (s).
8c	3200	209	6.21 (m 1H), 6.34 (m, 2H), 6.53 (m, 1H), 6.84 (m, 1H), 7.25—7.50 (m, 6H), 8.20 (br s, 1H, NH).	104.2 (d), 109.3 (d), 110.9 (d), 113.1 (s), 118.2 (d), 127.2 (s), 127.4 (d), 127.7 (d), 127.8 (s), 127.9 (d), 128.6 (d), 128.7 (d), 133.1 (s), 140.2 (d).
9b	3200	209	6.21 (m, 1H), 6.43 (m, 1H), 6.53 (m, 1H), 6.48 (m, 1H), 7.25—7.50 (m, 6H), 8.20 (br s, 1H, NH)	104.2 (d), 109.3 (d), 110.9 (d), 113.1 (s), 118.2 (d), 127.2 (s), 127.4 (d), 127.7 (d), 127.8 (s), 127.9 (d), 128.6 (d), 128.7 (d), 133.1 (s), 140.2 (d).
9c	3200	223	2.29 (s, 3H, CH$_3$), 6.18 (m, 2H), 6.32 (m, 1H), 7.23—7.36 (m, 6H), 7.85 (br s, 1H, NH).	12.8 (p), 104.0 (d), 107.1 (d), 110.8 (s), 112.5 (s), 126.9 (s), 127.2 (d), 127.5 (s), 128.2 (d), 128.4 (d), 128.8 (s), 129.1 (d), 133.3 (s), 140.1 (d), 151.2 (d).
10a	3400	291	1.62 (d, J=6.8 Hz, 3H), 2.32 (s, 3H, CH$_3$), 3.65 (br s, 1H, NH), 4.46 (q, J=6.8 Hz, 1H), 5.92 (m, 1H), 6.22 (m, 1H), 7.17—7.66 (m, 5H), 8.08 (m, 1H), 8.16 (m, 1H).	10.3 (q), 20.1 (q), 52.9 (d), 104.1 (d), 105.5 (d), 105.6 (d), 106.4 (d), 110.2 (d), 114.6 (s), 117.9 (s), 123.7 (d), 124.1 (d), 126.9 (s), 128.5 (s), 138.4 (s), 141.3 (d), 141.7 (d), 152.6 (s), 157.1 (s).

[a] NMR solvent: DMSO-d_6.

is the first example, although it is well known that vicinal-diarylethylene always plays a role as a useful photochemical substrate for annulation through photoarylation (photocyclization).[15]

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 JNM LA-300 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; q, quartet; m, multiplet. Mass spectra (MS) were obtained on a Shimadzu GC-MS 9100-MK 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 2-Vinylfuran Analogues (2, 6) and 2-(2-Phenyl- pyrrol-3-yl)furan (9b) Vinylfuran analogues (**2**, **6b**) were commercial products and other vinylfuran analogues (**6a**,[17] **6c**,[18] **6d**,[19] **6e**,[20] **6f**[21]) were prepared by the reported procedures. 2-(2-Phenyl-pyrrol-3-yl)furan (**9b**) was prepared from benzaldehyde according to the method of Tsuge *et al.*[8]

Irradiation of Arenecarbothioamides (1) with 2-Vinylfuran Analogues (2). General Procedure A solution of **1a** (5 mmol) and **2**-i (0.25 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 on a silica gel column (*n*-hexane–ethyl acetate, 5 : 1; v/v). The results are summarized in Tables 1, 2, 3 and 4.

Irradiation of 2,3-Diaryl-2-pyrrolin-5-one (5) or Diarylpyrrole (9) in the Presence of Iodine. General Procedure A mixture of **5a**-i (100 mg) and iodine (4 mg) in cyclohexane (150 ml) was irradiated for 1 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 on a silica gel column (*n*-hexane–ethyl acetate, 2 : 1; v/v). Yields were 85% (for **3a**-i from **5a**-i), 78% (for **3a**-ii from **5a**-ii), 75% (for **3b**-i from **5b**-i), 81% (for **3b**-ii from **5b**-ii), 83% (for **8b** from **9b**), and 81% (for **8c** from **9c**), respectively.

References and Notes

1) *a*) Dedicated to Dr. Yuichi Kanaoka, Professor Emeritus, Hokkaido University, on the occasion of his 70th birthday; *b*) Photochemistry of the Nitrogen-Thiocarbonyl Systems, Part 31, Part 30: Oda K., Sakai M., Machida M., *Chem. Pharm. Bull.*, **45**, 584—589 (1997).
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