Photocyclization Reactions. Part **8** [1]. Synthesis of 2-Quinolone, Quinoline and Coumarin Derivatives Using *Trans-Cis* Isomerization by Photoreaction

Takaaki Horaguchi* and Nobuyuki Hosokawa

Department of Chemistry, Faculty of Science, Niigata Univeristy, Ikarashi, Niigata 950-2181, Japan

Kiyoshi Tanemura and Tsuneo Suzuki

School of Dentistry at Niigata, The Nippon Dental University, Hamaura-cho 1-8, Niigata 951-8151, Japan

Received April 30, 2001

2-Quinolone **2**, quinoline **3**, coumarin (2*H*-1-benzopyran-2-one) **5**, and 2*H*-1-benzopyran hemiacetal **6** were synthesized by photocyclization reaction of *trans-o*-aminocinnamoyl derivatives *trans*-**1** and *trans-o*-hydroxycinnamoyl derivatives *trans*-**4**. The reaction proceeds through *trans-cis* isomerization followed by intramolecular cyclization.

J. Heterocyclic Chem., **39**, 61 (2002).

Introduction.

It is known that *cis-o*-hydroxycinnnamic acid (*o*-coumarinic acid) [2], its ester [3], and amide [4] undergo lactonization to give coumarin. *Cis*-2-hydroxychalcone also cyclizes to 2*H*-1-benzopyran hemiacetal [5]. Similarly, esters [6] and amides [7] of *trans-o*-hydroxycinnnamic acid are transformed to their *cis*-isomers on irradiation of ultraviolet light and cyclize to give coumarin. Irradiation of *trans-o*-hydroxychalcone affords 2*H*-1-benzopyran hemiacetal *via trans-cis* isomerization followed by intramolecular cyclization [8]. Thus, when the distance between the hydroxyl group and carbonyl group becomes close to each other in the *cis*-isomers, intramolecular cyclization occurs. This method allows for the syntheses of heterocyclic compounds. Irradiation is an useful method to convert *trans*-isomers to *cis*-isomers [9].

We planned to synthesize six-membered ring heterocyclic compounds **2**, **3**, **5**, and **6** through photoinduced *trans-cis* isomerization of *trans-o*-aminocinnnamoyl derivatives *trans*-**1** and *trans-o*-hydroxycinnnamoyl derivatives *trans*-**4**.

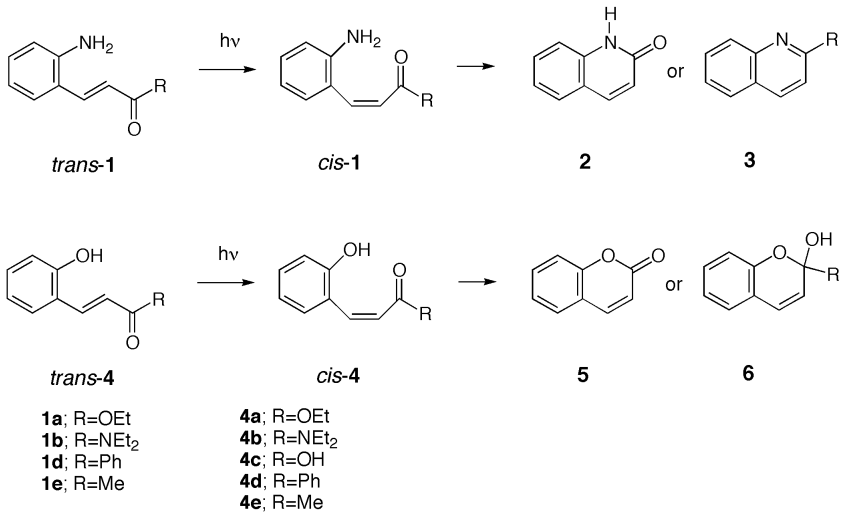
Results and Discussion.

Starting materials *trans*-**1a**, *trans*-**1b**, *trans*-**1d**, *trans*-**1e**, and *trans*-**4a** for photoreactions were prepared as shown in Scheme 2 (see Experimental). Compounds *trans*-**4b** [10], *trans*-**4d** [11], and *trans*-**4e** [12] were synthesized according to the literature. Compound *trans*-**4c** is commercially available.

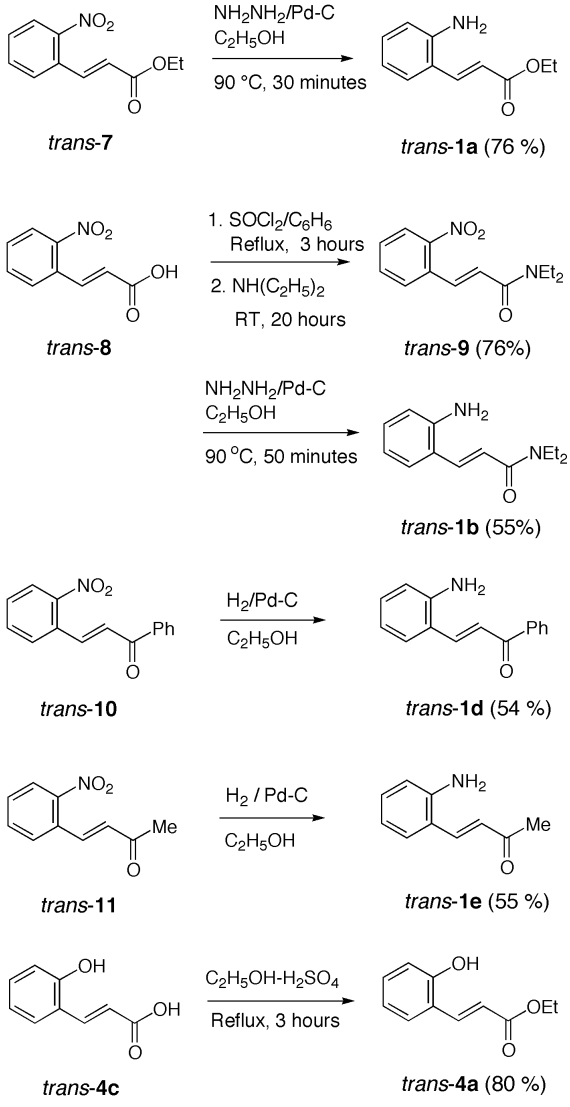
First, photoreactions of ethyl *trans-o*-aminocinnnamate *trans*-**1a** were examined in acetonitrile, benzene, and methanol using a 400W high-pressure mercury lamp (Riko UVL-400 HA) with a Pyrex filter (see Figure 1). The results are summarized in Table 1.

When *trans*-**1a** was irradiated in acetonitrile and monitored by hplc, the amount of *trans*-**1a** was found to decrease rapidly. After 10 minutes the reaction stopped and conversion did not change anymore even after 60 minutes irradiation (Entry 1, 2). The solution was evaporated and the residue was chromatographed on silica gel to give 2-quinolone **2** in excellent yield (Method A). Similarly, photoreactions of *trans*-**1a** in benzene or methanol gave almost

Scheme 1



Scheme 2



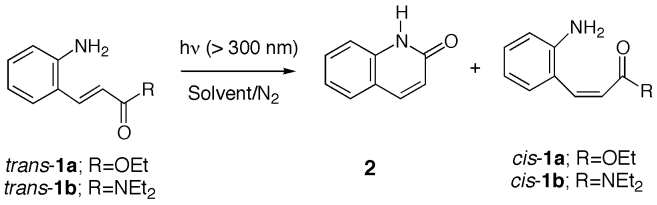


Figure 1

the same results though reaction time was longer in methanol (Entry 3-6). To examine the reaction progress, *trans*-**1a** was dissolved in deuterioacetonitrile and irradiated in an nmr tube (external irradiation) monitored by ^{1}H nmr (Method B, see Figure 2). The results are shown in Table 2.

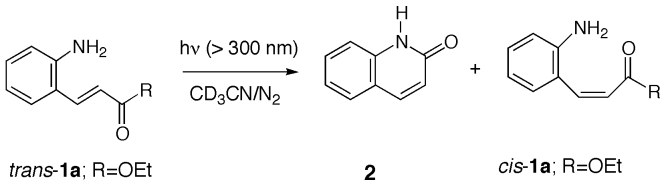


Figure 2

On irradiation of *trans*-**1a** the conversion increased gradually with reaction time. However, 2-quinolone was not detected even after 180 minutes irradiation. After warming (60 °C, 15 minutes) the reaction solution in an nmr tube, the ^{1}H nmr spectrum showed disappearance of *cis*-**1a** and formation of 2-quinoline. These results show that irradiation of *trans*-**1a** induces only *trans*-*cis* equilibrium and the following operation (heating during evaporation of the solution) gives intramolecular cyclization of *cis*-**1a** to 2-quinolone.

To accelerate cyclization of *cis*-**1a** to 2-quinolone, pyridine or acetic acid [7,2a] was added as a catalyst to the acetonitrile solution and then irradiation was carried out (Table 1, Entry 7-10). Addition of pyridine (1 ml) had no

Table 1

Photoreactions of ethyl *trans*-*o*-aminocinnamate *trans*-**1a** and *trans*-*N*,*N*-diethyl-*o*-aminocinnamamide *trans*-**1b** [a]

Entry	Starting material [b]	R	Solvent	Irradiation time (minutes)	Conversion (%)	Product **2**	yield [c] (%) *cis*-**1**
1	*trans*-**1a**	OEt	CH_3CN	10	45	88	0
2	*trans*-**1a**	OEt	CH_3CN	60	44	93	0
3	*trans*-**1a**	OEt	C_6H_6	10	46	90	0
4	*trans*-**1a**	OEt	C_6H_6	75	48	88	0
5	*trans*-**1a**	OEt	CH_3OH	10	29	84	0
6	*trans*-**1a**	OEt	CH_3OH	60	50	68	0
7	*trans*-**1a**	OEt	CH_3CN/P y [d]	20	38	76	0
8	*trans*-**1a**	OEt	CH_3CN/P y [d]	60	37	83	0
9	*trans*-**1a**	OEt	CH_3CN/HOAc [e]	60	100	7	0
10	*trans*-**1a**	OEt	CH_3CN/HOAc [f]	60	95	79	0
11	*trans*-**1b**	NEt_2	CH_3CN	60	67	0	100 [g]
12	*trans*-**1b**	NEt_2	C_6H_6	75	85	0	100 [g]
13	*trans*-**1b**	NEt_2	CH_3OH	90	71	0	100 [g]

Table 1 (continued)

[a] Method A for entry 1-13; [b] 2 Mmoles in 500 ml solvent; [c] Yield based on reacted starting material; [d] 1 Ml of pyridine in 500 ml of acetonitrile; [e] 1 Ml of acetic acid in 500 ml of acetonitrile; [f] 0.1 Ml of acetic acid in 500 ml of acetonitrile; [g] Isolation of *trans*-**1b** and *cis*-**1b** was difficult by chromatography and the *cis*-**1b** yield were determined from the ^{1}H nmr spectrum of the mixture.

Table 2

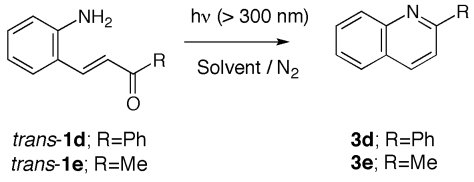
Photoreactions of ethyl *trans*-*o*-aminocinnamate *trans*-**1a** in a nmr tube [a]

Entry	Starting material	R	Solvent	Irradiation time (minutes)	Conversion [b] (%)	Product [b] (%) yield **2**	*cis*-**1a**
1	*trans*-**1a**	OEt	CD_3CN	20	13	0	100
2	*trans*-**1a**	OEt	CD_3CN	60	28	0	100
3	*trans*-**1a**	OEt	CD_3CN	180	38	0	100

[a] Method B for entry 1-3. [b] Conversion and product yield were determined from the ^{1}H nmr spectrum of the mixture.

effect on cyclization of *cis*-**1a** to 2-quinolone (Entry 7-8). In contrast, addition of acetic acid (0.1 ml) accelerated cyclization of *cis*-**1a** to 2-quinolone (Entry 10). However, excess of acetic acid (1 ml) induced decomposition (Entry 9). When *trans*-*o*-aminocinnamamide was irradiated in acetonitrile, benzene, or methanol only a mixture of *trans*-**1b** and *cis*-**1b** isomers was obtained (Entry 11-13). In this case, cyclization of *cis*-**1b** to 2-quinolone did not occur during the isolation procedure. Isolation of *trans*-**1b** and *cis*-**1b** was difficult by chromatography and the ratio was determined by the ^{1}H nmr spectrum of the mixture.

Photoreactions of *trans*-*o*-aminochalcone and *trans*-*o*-aminobenzalacetone were examined (see Figure 3). The results are summarized in Table 3.



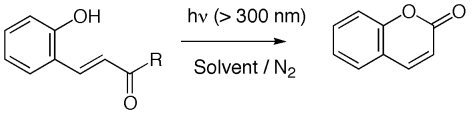
trans-**1d**; R=Ph
trans-**1e**; R=Me

3d; R=Ph
3e; R=Me

Figure 3

When *trans*-**1d** was irradiated in acetonitrile, the conversion was complete within 25 minutes to give 2-phenylquinoline in 88% yield (Entry 1). Similarly, on irradiation of *trans*-**1d** in benzene and methanol, complete conversion gave **3d** in good yield (Entry 2-4). When *trans*-*o*-aminobenzalacetone was irradiated in acetonitrile, benzene, and methanol, 2-methylquinoline was produced smoothly (Entry 5-8). Photoreactions of *trans*-**1d** and **1e** in methanol took a longer reaction time than that in acetonitrile or benzene. The results show that the cyclization of *cis*-**1d** and *cis*-**1e** to quinolines **3d** and **3e** is fast and completed within minutes.

Photoreactions of *trans*-*o*-hydroxycinnamic acid and its derivatives were examined (see Figure 4). The results are summarized in Table 4.



trans-**4a**; R=OEt
trans-**4b**; R=NEt_2
trans-**4c**; R=OH

5

Figure 4

When ethyl *trans*-*o*-hydroxycinnamate was irradiated in acetonitrile for 15 minutes (69% conversion), coumarin **5** (94% based on percent conversion) was produced (Entry 1). Further irradiation (180 minutes) did not change the conversion nor the product yield of **5** (Entry 2). The results show that photoequilibrium between *trans*-**4a** and *cis*-**4a** was attained during the irradiation, and *cis*-**4a** was converted to coumarin during isolation procedure. Irradiation of *trans*-**4a** in benzene and methanol afforded similar

Table 3

Photoreactions of *trans*-*o*-aminochalcone *trans*-**1d** and *trans*-*o*-aminobenzalacetone *trans*-**1e** [a]

Entry	Starting material [b]	R	Solvent	Irradiation time (minutes)	Conversion (%)	Product	Yield [c] (%)
1	*trans*-**1d**	Ph	CH_3CN	25	100	**3d**	88
2	*trans*-**1d**	Ph	C_6H_6	20	100	**3d**	69
3	*trans*-**1d**	Ph	CH_3OH	30	27	**3d**	79
4	*trans*-**1d**	Ph	CH_3OH	140	100	**3d**	87
5	*trans*-**1e**	Me	CH_3CN	15	100	**3e**	71
6	*trans*-**1e**	Me	C_6H_6	22	100	**3e**	74
7	*trans*-**1e**	Me	CH_3OH	20	33	**3e**	59
8	*trans*-**1e**	Me	CH_3OH	75	100	**3e**	62

[a] Method A for entry 1-8. [b] 2 Mmoles in 500 ml solvent. [c] Yield based on reacted starting material.

Table 4

Photoreactions of ethyl *trans*-*o*-hydroxycinnamate *trans*-**4a** and *trans*-*N*,*N*-diethyl-*o*-hydroxycinnamamide *trans*-**4b** and *trans*-*o*-hydroxycinnnamic acid *trans*-**4c** [a]

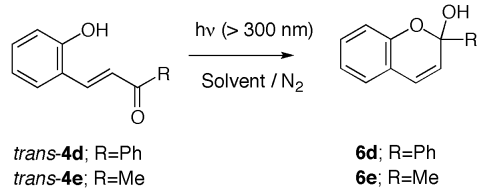
Entry	Starting Material [b]	R	Solvent	Irradiation time (minutes)	Conversion (%)	Product **5**	yield [c] (%) *cis*-**4**
1	*trans*-**4a**	OEt	CH_3CN	15	69	94	0
2	*trans*-**4a**	OEt	CH_3CN	180	74	93	0
3	*trans*-**4a**	OEt	C_6H_6	16	68	95	0
4	*trans*-**4a**	OEt	C_6H_6	60	81	95	0
5	*trans*-**4a**	OEt	CH_3OH	15	65	92	0
6	*trans*-**4a**	OEt	CH_3OH	60	68	94	0
7	*trans*-**4b**	NEt_2	CH_3CN	60	67	68	25 [d]
8	*trans*-**4b**	NEt_2	CH_3CN	180	62	40	53 [d]
9	*trans*-**4b**	NEt_2	CH_3OH	15	97	47	44 [d]
10	*trans*-**4b**	NEt_2	CH_3OH	180	96	49	41 [d]
11	*trans*-**4c**	OH	CH_3CN	20	71	95 [e]	5 [e]
12	*trans*-**4c**	OH	CH_3CN	60	72	93 [e]	7 [e]
13	*trans*-**4c**	OH	CH_3OH	20	69	100 [e]	0 [e]
14	*trans*-**4c**	OH	CH_3OH	60	69	100 [e]	0 [e]

[a] Method A for entry 1-10, Method C for entry 11-14; [b] 2 Mmoles in 500 ml solvent; [c] Yield based on reacted starting material; [d] Isolation of *cis*-**4** and *trans*-**4** was difficult by chromatography and the *cis*-**4** yield and conversion were determined from the ^{1}H nmr spectrum of the mixture; [e] Yield was determined from the ^{1}H nmr spectrum of the product mixture which was obtained by evaporation of the reaction solution.

results (Entry 3-6). Irradiation of *trans*-*N*,*N*-diethyl-*o*-hydroxycinnamamide in acetonitrile gave coumarin **5** and *cis*-**4b** (Entry 7-8). In this case, a considerable amount of *cis*-**4b** was obtained, indicating slow cyclization reaction between the hydroxyl group and the amide group. However, when *trans*-**4b** was irradiated in methanol, conversion was near 100% (Entry 9-10). Benzene was not studied as a solvent because of poor solubility of *trans*-**4b**. Irradiation of *trans*-*o*-hydroxycinnamic acid in acetonitrile or methanol afforded mainly coumarin **5** (Entry 11-14). In this case, conversion and yield were determined from the ^{1}H nmr spectrum of the product mixture which was obtained after evaporation of the reaction solution (Method C). Method C was used to avoid changing the product ratio of the photoreaction by chromatography.

Finally, photoreactions of *trans*-*o*-hydroxychalcone and *trans*-*o*-hydroxybenzalacetone were examined using ^{1}H nmr (see Figure 5). The results are summarized in Table 5.

Compound *trans*-**4d** dissolved in deuterioacetonitrile in a nmr tube was irradiated by high-pressure mercury lamp (external irradiation). After 90 minutes irradiation, conversion was 100%. The ^{1}H nmr spectrum showed production



trans-**4d**; R=Ph
trans-**4e**; R=Me

6d; R=Ph
6e; R=Me

Figure 5

of 2*H*-1-benzopyran hemiacetal **6d** [8c]. Cyclization of *trans*-*o*-hydroxychalcone to 2*H*-1-benzopyran hemiacetal on irradiation is well-known [8]. Similarly, irradiation of *trans*-*o*-hydroxybenzalacetone *trans*-**4e** gave 2*H*-1-benzopyran hemiacetal **6e** from the ^{1}H nmr spectrum.

General mechanisms of photocyclization reactions on *trans*-*o*-aminocinnamoyl compounds *trans*-**1** and *trans*-*o*-hydroxycinnamoyl compounds *trans*-**4** are shown in Scheme 3.

Irradiation of *trans*-**1** induces an equilibrium mixture of *trans*-**1** and *cis*-**1**. In the case of R=OEt, cyclization of *cis*-**1** occurrs thermally during concentration to give 2-quinolone **2** through **12**. However, in the case of

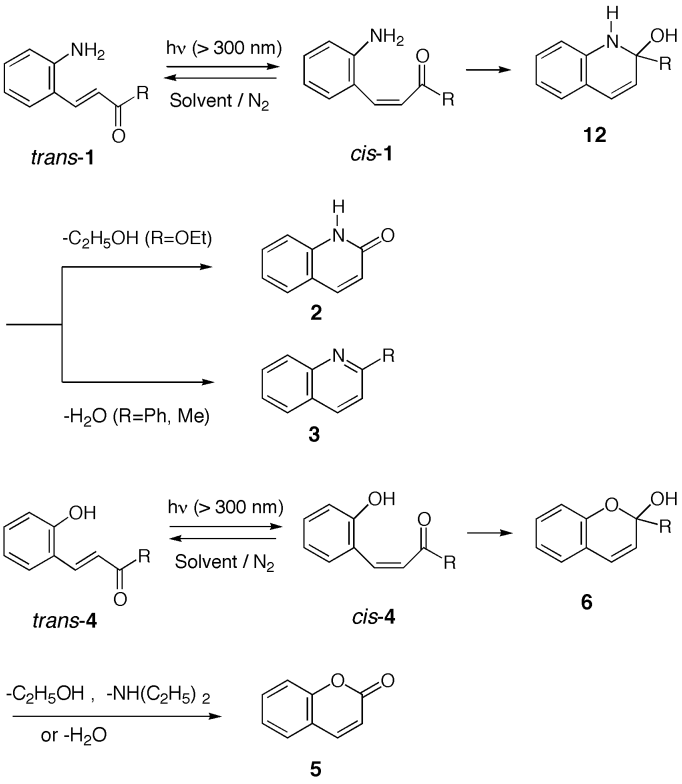
Table 5

Photoreactions of *trans*-*o*-hydroxychalcone *trans*-**4d** and *trans*-*o*-hydroxybenzalacetone *trans*-**4e** in a nmr tube [a]

Entry	Starting Material	R	Solvent	Irradiation time (minutes)	Conversion	Product [b] (%)	Yield [b] (%)
1	*trans*-**4d**	Ph	CD_3CN	90	100	**6d**	100
2	*trans*-**4e**	Me	CD_3CN	90	100	**6e**	100

[a] Method B for entry 1-2. [b] Conversion and product yield were determined from the ^{1}H nmr specrum of the mixture.

Scheme 3



R=NEt_2, cyclization does not occur because of low reactivity of the amide group. In contrast, when R is Ph or Me, cyclization of *cis*-**1** occurrs spontaneously during irradiation to give quinolines **3**, consistent with the reactivity of amines with ketones.

Similarly, irradiation of *trans-o*-hydroxycinnamoyl derivatives produces *trans-cis* equilibrium between *trans*-**4** and *cis*-**4**. When R is OEt, NEt_2, or OH, elimination of ethanol, diethylamine or water from **6** affords coumarin **5**. In the case of R=Ph and Me, 2*H*-1-benzopyran hemiacetals **6** are produced because further reaction is not possible.

In conclusion, photoinduced *trans-cis* isomerization followed by intramolecular cyclization is a useful synthetic method for six-membered heterocyclic compounds which contain a nitrogen or oxygen atom.

EXPERIMENTAL

The melting points are uncorrected. Column chromatography was performed on silica gel (Wakogel C-200). Unless otherwise stated, anhydrous sodium sulfate was employed as the drying agent. Ether refers to diethyl ether. The ir spectra were determined on a Hitachi Model 270-30 IR spectrometer. The ^1H and ^{13}C nmr spectra were determined at 500 MHz and 125 MHz on a Varian Unity plus-500W NMR spectrometer, using tetramethylsilane as the internal standard.

Synthesis of *trans*-**4b**, *trans*-**4d**, and *trans*-**4e**.

Trans-o-hydroxycinnamamide [10], *trans-o*-hydroxychalcone [11], and *trans-o*-hydroxybenzalacetone [12] were prepared according to literature.

Ethyl *trans-o*-Aminocinnamate.

Ethyl *trans-o*-nitrocinnamate (1.00 g, 4.52 mmol) [13] and hydrazine monohaydrate (0.44 ml, 9.06 mmol) were dissolved in ethanol (100 ml). After 7% palladium-charcoal (0.10 g) was added, the solution was refluxed for 30 minutes. After removal of the palladium-charcoal by filtration, the ethanol was evaporated. The residue was extracted with ether. The extract was washed with water, dried, and evaporated. The residue was chromatographed and eluted with benzene-ether (9:1) to give *trans*-**1a** (0.66 g, 76%) as pale yellow crystals, mp 74-75 °C from benzene-hexane; ir (potassium bromide): 3472 (NH_2), 3380 (NH_2), 1690 cm^{-1} ($CO_2CH_2CH_3$); ^1H nmr (deuteriochloroform): δ 1.33 (t, J=7.0 Hz, 3H, CH_2CH_3), 3.46 (broad s, 2H, NH_2), 4.26 (q, J=7.0 Hz, 2H, CH_2CH_3), 6.36 (d, J=16.0 Hz, 1H, CH=C*H*CO), 6.73 (d, J=8.0 Hz, 1H, Ar-H), 6.80 (dd, J=8.0 and 8.0 Hz, 1H, Ar-H), 7.17 (dd, J=8.0 and 8.0 Hz, Ar-H), 7.39 (d, J=8.0 Hz, 1H, Ar-H), 7.83 (d, J=16.0 Hz, 1H, C*H*=CHO); ^{13}C nmr (deuteriochloroform): δ 14.2 (q), 60.3 (t), 116.6 (d), 117.9 (d), 118.7 (d), 119.7 (s), 127.9 (d), 131.1 (d), 140.0 (d), 145.6 (s), 167.2 (s).

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.09, H, 6.85, N, 7.33. Found: C, 69.24; H, 6.83; N, 7.20.

trans-N,N-Diethyl-*o*-nitrocinnamamide.

A mixture of *trans-o*-nitrocinnamic acid (5.00 g, 25.9 mmol), thionyl chloride (20 ml), and benzene (10 ml) was refluxed for 2.5 hours. The benzene and unreacted thionyl chloride were removed by distillation under reduced pressure. The residue was dissolved in diethylamine (40 ml) and allowed to stand for 20 hours at room temperature. The solution was extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene-ethyl acetate (1:1) to give *trans*-**9** (4.89 g, 76%) as pale yellow crystals, mp 56-57 °C from hexane-benzene-ether; ir (potassium bromide): 1662 cm^{-1} ($CON(CH_2CH_3)_2$); ^1H nmr (deuteriochloroform): δ 1.21 (broad s, 3H, CH_2CH_3), 1.26 (broad s, 3H, CH_2CH_3), 3.49 (broad s, 4H, CH_2CH_3 and CH_2CH_3), 6.71 (d, J=15.0 Hz, 1H, CH=C*H*CO), 7.51 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.61-7.64 (m, 2H, Ar-H_2), 8.00 (d, J=15.0 Hz, 1H, C*H*=CHCO), 8.01 (d, J=7.5 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 13.1 (q), 15.0 (q), 41.0 (t), 42.4 (t), 123.5 (d), 124.7 (d), 129.3 (d), 129.5 (d), 131.8 (s), 133.2 (d), 137.2 (d), 148.3 (s), 164.8 (s).

Anal. Calcd. for $C_{13}H_{16}N_2O_3$: C, 62.89; H, 6.50; N, 11.28. Found: C, 62.81; H, 6.65; N, 11.35.

trans-N,N-Diethyl-*o*-aminocinnamamide.

trans-N,N-Diethyl-*o*-nitrocinnamamide (1.00 g, 4.03 mmol) and hydrazine monohydrate (0.45 ml, 9.27 mmol) were dissolved in ethanol (30 ml). After 7% palladium-charcoal (0.05 g) was added, the solution was refluxed for 1 hour. During reflux, hydrazine monohydrate (0.35 ml, 7.21 mmol) and 7% palladium-charcoal (0.05 g) were added to complete the reaction. After removal of the palladium-charcoal by filtration, the ethanol was evaporated. The residue was extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene-acetone (1:1) to give *trans*-**1b** (0.49 g, 55%) as pale yellow crystals, mp 64-66 °C from

ether-hexane; ir (potassium bromide): 3320 (NH_2), 3216 (NH_2), 1642 cm^{-1} ($CON(CH_2CH_3)_2$); ^1H nmr (deuteriochloroform): δ 1.19 (t, J=7.0 Hz, 3H, $CON(CH_2CH_3)_2$), 1.26 (t, J=7.0 Hz, 3H, $CON(CH_2CH_3)_2$), 3.1-4.3 (broad s, 2H, NH_2), 3.46-3.50 (m, 4H, $CON(CH_2CH_3)_2$ and $CON(CH_2CH_3)_2$), 6.72-6.78 (m, 3H, Ar-H_2 and CH=C*H*CO), 7.15 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.37 (d, J=7.5 Hz, 1H, Ar-H), 7.85 (d, J=15.5 Hz, 1H, C*H*=CHCON); ^{13}C nmr (deuteriochloroform): δ 13.6 (q), 15.5 (q), 41.3 (t), 42.5 (t), 117.0 (d), 117.9 (d), 118.2 (d), 121.0 (s), 128.1 (d), 130.9 (d), 138.1 (d), 148.0 (s), 165.9 (s).

Anal. Calcd. for $C_{13}H_{18}N_2O$: C, 71.53; H, 8.31; N, 12.83. Found: C, 71.48; H, 8.30; N, 12.71.

trans-*o*-Aminochalcone.

trans-*o*-Nitrochalcone (2.00 g, 7.90 mmol) [14] in ethanol (100 ml) was catalytically hydrogenated at 0 °C in the presence of 7% palladium-charcoal (1.00 g) until 600 ml (3 equivalents) of hydrogen was absorbed. During the reduction the reaction flask was covered with aluminum foil to protect from the side reaction by light. After removal of the catalyst by filtration, the ethanol was evaporated. The residue was chromatographed and eluted with benzene-ether (8:2) to give *trans*-**1d** (0.95 g, 54%) as yellow crystals, mp 114-116 °C (lit. [14] mp 115 °C) from ethanol-water; ir (potassium bromide) : 3232 (NH_2), 1658 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 4.08 (broad s, 2H, NH_2), 6.73 (d, J=7.5 Hz, 1H, Ar-H), 6.80 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.21 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.48-7.54 (m, 4H, Ar-H_3 and CH=C*H*CO), 7.58 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 8.00 (d, J=15.5 Hz, 1H, C*H*=CHCO), 8.03 (d, J=7.5 Hz, 2H, Ar-H_2); ^{13}C nmr (deuteriochloroform): δ 116.8 (d), 118.8 (d), 120.1 (s), 121.6 (d), 128.0 (d), 128.4 (d), 128.5 (d), 131.6 (d), 132.7 (d), 138.2 (s), 140.1 (d), 146.3 (s), 190.2 (s).

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.74; H, 6.09; N, 6.36.

trans-*o*-Aminobenzalacetone.

trans-*o*-Nitrobenzalacetone (1.00 g, 5.23 mmol) [15] in ethanol (100 ml) was catalytically hydrogenated at 0 °C in the presence of 7% palladium-charcoal (0.50 g) until 450 ml (3 equivalents) of hydrogen was absorbed. During the reduction the reaction flask was covered with aluminum foil to protect from the side reaction by light. After removal of the catalyst by filtration, the ethanol was evaporated. The residue was chromatographed and eluted with benzene-ether (8:2) to give *trans*-**1e** (0.47 g, 55%) as yellow crystals, mp 48-50 °C from ether-hexane; ir (potassium bromide): 3452 (NH_2), 3352 (NH_2), 1668 cm^{-1} (C=O);); ^1H nmr (deuteriochloroform): δ 2.37 (s, 3H, CH_3), 3.97 (broad s, 2H, NH_2), 6.68 (d, J=16.0 Hz, 1H, CH=C*H*CO), 6.71 (d, J=7.5 Hz, 1H, Ar-H), 6.79 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.19 (dd, 7.5 and 7.5 Hz, 1H, Ar-H), 7.40 (d, J=7.5 Hz, 1H, Ar-H), 7.68 (d, J=16.0 Hz, 1H, C*H*=CHCO); ^{13}C nmr (deuteriochloroform): δ 28.0 (q), 116.8 (d), 119.0 (d), 119.8 (s), 126.7 (d), 128.1 (d), 131.5 (d), 138.6 (d), 145.9 (s), 198.2 (s).

Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.62; H, 6.81; N, 8.76.

Ethyl *trans*-*o*-Hydroxycinnamate.

A mixture of *trans*-*o*-hydroxycinnamic acid (5.00 g, 30.5 mmol), ethanol (50 ml), and concentrated sulfuric acid (1.0 ml) was refluxed for 3 hours. The solution was poured into water (200 ml) and extracted with ether. The extract was washed, dried, and evaporated. The residue was chromatographed and eluted with benzene-ether (9:1) to give *trans*-**4a** (4.68 g, 80 %) as colorless crystals, mp 86-87 °C from ether-hexane; ir (potassium bromide): 3420 (OH), 1685 cm^{-1} (CO_2); ^1H nmr (deuteriochloroform): δ 1.35 (t, J=7.0 Hz, 3H, CH_2CH_3), 4.29 (q, J=7.0 Hz, 2H, CH_2CH_3), 6.63 (d, J=16.5 Hz, 1H, CH=C*H*O), 6.73 (s, 1H, OH), 6.85 (d, J=7.5 Hz, 1H, Ar-H), 6.91 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.23 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.47 (d, J=7.5 Hz, 1H, Ar-H), 8.04 (d, J=16.5 Hz, 1H, C*H*=CHCO); ^{13}C nmr (deuteriochloroform): δ 14.2 (q), 60.9 (t), 116.4 (d), 117.8 (d), 120.3 (d), 121.5 (s), 129.1 (d), 131.5 (d), 141.3 (d), 155.9 (s), 169.1 (s).

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.56; H, 6.40.

General Procedure for Photocyclization Reactions of *trans*-**1** and *trans*-**4**.

Method A.

In acetonitrile, benzene, or methanol solvent (500 ml), 2.00 mmol of the starting materials **1**, or **4** were dissolved. In some case, pyridine or acetic acid was added. The solution was deoxygenated by bubbling nitrogen gas for 1 hour and then irradiated with high-pressure mercury lamp (Riko UVL-400HA, Pyrex filter) while monitoring by high performance liquid chromatography (hplc). The irradiation was stopped when reaction did not proceed. After irradiation, the solvent was evaporated under reduced pressure below 40 °C. The residue was chromatographed and eluted with solvent to give products.

Method B.

Starting materials *trans*-**1a**, *trans*-**4d**, or *trans*-**4e** (0.05 mmol) was dissolved in deuterioacetonitrile (2 ml) in an nmr tube. The solution was deoxygenated by bubbling nitrogen gas for 1 hour and then irradiated (external irradiation) with high-pressure mercury lamp (Riko UVL-400HA, Pyrex filter) while monitoring with ^1H nmr spectra. Conversion and product yield were determined from the ^1H nmr spectra.

Method C.

In acetonitrile, benzene, or methanol solvent (500 ml), 2.00 mmol of the starting materials **1** or **4** were dissolved. The solution was deoxygenated by bubbling nitrogen gas for 1 hour and then irradiated with high-pressure mercury lamp (Riko UVL-400HA, Pyrex filter) while monitoring by high performance liquid chromatography (hplc). The irradiation was stopped when the reaction did not proceed. After irradiation the solvent was evaporated under reduced pressure below 40 °C. The residue was dissolved in deuteriochloroform and the products and product yield were determined from the ^1H nmr spectra. This method was used to prevent change of the product ratio by chromatography.

2-Quinolone.

^1H and ^{13}C nmr spectra of **2** were identical with those of a commercially available sample. Recrystallization gave colorless crystals from benzene, mp 198-200 °C (Commercially available sample, mp 198-201 °C); ir (potassium bromide): 3000 (broad, NH), 1656 cm^{-1} (CONH); ^1H nmr (deuteriochloroform): δ 6.73 (d, J=10.0 Hz, 1H, CH=C*H*CO), 7.23 (dd, J=8.0 and 8.0 Hz, 1H, Ar-H), 7.46 (d, J=8.0 Hz, 1H, Ar-H), 7.52 (dd, J=8.0 and 8.0 Hz, 1H, Ar-H), 7.57 (d, J=8.0 Hz, 1H, Ar-H), 7.82 (d, J=10.0 Hz, 1H, C*H*=CHCO), 12.55 (broad s, 1H, NH); ^{13}C nmr (deuteriochloro-

form): δ 116.3 (d), 119.9 (s), 121.3 (d), 122.7 (d), 127.7 (d), 130.7 (d), 138.5 (s), 141.1 (d), 164.8 (s).

2-Phenylquinoline.

^{1}H and ^{13}C nmr spectra of **3d** were identical with those of a commercially available sample. Recrystallization gave colorless crystals from ether, mp 84-85 °C (Commercially available sample, mp 84-85 °C); ^{1}H nmr (deuteriochloroform): δ 7.49 (dd, J=8.5 and 8.5 Hz, 1H, Ar-H), 7.54-7.57 (m, 3H, Ar-H$_3$), 7.75 (dd, J=8.5 and 8.5 Hz, 1H, Ar-H), 7.86 (d, J=8.5 Hz, 1H, Ar-H), 7.90 (d, J=8.5 Hz, 1H, Ar-H), 8.18-8.21 (m, 3H, Ar-H$_3$), 8.25 (d, J=8.5 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 119.0 (d), 126.3 (d), 127.2 (s), 127.4 (d), 127.6 (d), 128.8 (d), 129.3 (d), 129.7 (d), 136.8 (d), 139.6 (s), 148.2 (s), 157.3 (s).

2-Methylquinoline.

^{1}H and ^{13}C nmr spectra of **3e** were identical with those of a commercially available sample. Colorless oil; ^{1}H nmr (deuteriochloroform): δ 2.75 (s, 3H, CH$_3$), 7.27 (d, J=6.0 Hz, 1H, Ar-H), 7.48 (dd, J=6.0 and 6.0 Hz, 1H, Ar-H), 7.68 (dd, J=6.0 and 6.0 Hz, 1H, Ar-H), 7.76 (d, J=6.0 Hz, 1H, Ar-H), 8.03 (d, J=6.0 Hz, 1H, Ar-H), 8.03 (d, J=6.0 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 25.3 (q), 122.0 (d), 125.7 (d), 126.5 (s), 127.5 (d), 128.5 (d), 129.5 (d), 136.3 (d), 147.8 (s), 158.9 (s).

Coumarin.

^{1}H and ^{13}C nmr spectra of **5** were identical with those of a commercially available sample. Recrystallization gave colorless crystals from ethanol, mp 69-72 °C (Comercially available sample, mp 68-72 °C), ir (potassium bromide): 1706 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 6.44 (d, J=9.5 Hz, 1H, CH=C*H*CO), 7.30 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.35 (d, J=7.5 Hz, 1H, Ar-H), 7.50 (d, J=7.5 Hz, 1H, Ar-H), 7.53 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.72 (d, J=9.5 Hz, 1H, C*H*=CHCO); ^{13}C nmr (deuteriochloroform): δ 116.7 (d), 116.9 (d), 118.8 (s), 124.4 (d), 127.9 (d), 131.8 (d), 143.4 (d), 154.1 (s), 160.8 (s).

2-Phenyl-2*H*-1-benzopyran-2-ol.

The ^{1}H nmr spectrum of **6d** was identical with that of literature [8c]. ^{1}H nmr (deuterioacetonitrile): δ 5.23 (broad s, 1H, OH), 5.87 (d, J=10.5 Hz, 1H, CH=C*H*C-OH), 6.72 (d, J=10.5 Hz, 1H, C*H*=CH-OH), 6.96 (d, J=8.0 Hz, 1H, Ar-H), 7.00 (dd, J=8.0 and 8.0 Hz, 1H, Ar-H), 7.24-7.28 (m, 2H, Ar-H$_2$), 7.35-7.60 (m, 3H, Ar-H$_3$), 7.61 (d, J=8.0 Hz, 2H, Ar-H$_2$).

2-Methyl-2*H*-1-benzopyran-2-ol.

^{1}H nmr (deuterioacetonitrile): δ 1.64 (s, 3H, CH$_3$), 4.52 (broad s, 1H, OH), 5.86 (d, J=10.0 Hz, 1H, CH=C*H*-C-OH), 6.62 (d, J=10.0 Hz, 1H, C*H*=CH-C-OH), 6.86 (d, J=8.0 Hz, 1H, Ar-H), 6.94 (dd, J=8.0 and 8.0 Hz, 1H, Ar-H), 7.18 (d, J=8.0 Hz, 1H, Ar-H), 7.20 (dd, J=8.0 and 8.0 Hz, 1H, Ar-H).

Acknowledgement.

We thank Mr. Yoshiaki Matsuda for the elemental analyses.

REFERENCES AND NOTES

[1] Part 7, E. M. Sharshira and T. Horaguchi, *J. Heterocyclic Chem*., **34**, 1837 (1997).

[2a] R. Hershfield and G. L. Schmir, *J. Am. Chem. Soc*., **95**, 7359 (1973); [b] R. Hershfield and G. L. Schmir, *J. Am. Chem. Soc*., **95**, 8032 (1973).

[3] R. A. McClelland, R. Somani, and A. J. Kresge, *Can. J. Chem*., **57**, 2260 (1979).

[4] B. Bang, H. Zhang, and W. Wang, *Bioorg. Med. Chem. Lett*., **6**, 945 (1996).

[5a] R. A. McClelland and S. Gedge, *J. Am. Chem. Soc*., **102**, 5838 (1980); [b] D. B. Devine and R. A. McClelland, *J. Org. Chem*., **50**, 5656 (1985); [c] F. Pina, M. J. Melo, M. Maestri, R. Ballardini, and V. Balzami, *J. Am. Chem. Soc*., **119**, 5556 (1997): [d] F. Pina, M. Maestri, and V. Balzami, *J. Chem. Soc., Chem. Commun.*, 107 (1999).

[6a] R. S. Mali, S. N. Yeola, and B. K. Kulkarmi, *Indian J. Chem.*, **22B**, 352 (1983); [b] A. D. Turner, S. V. Pizzo, G. W. Rozakis, and N. A. Porter, *J. Am. Chem. Soc*., **109**, 1274 (1987); [c] A. D. Turner, S. V. Pizzo, G. Rozakis, and N. A. Porter, *J. Am. Chem. Soc*., **110**, 244 (1988); [d] N. A. Porter and J. D. Bruhnke, *Photochem. Photobiol*., **51**, 37 (1990); [e] P. M. Koenigs, B. C. Faust, and N. A. Porter, *J. Am. Chem. Soc*., **115**, 9371 (1993); [f] D. N. Nicolaides, K. C. Fylaktakidou, K. E. Litinas, and S. G. Adamopoulos, *J. Heterocyclic Chem*., **35**, 91 (1998).

[7] B. Wang and A. Zheng, *Chem. Pharm. Bull*., **45**, 715 (1997).

[8a] D. Dewar and R. G. Sutherland, *J. Chem. Soc., Chem. Commun*., 272 (1970); [b] R. Matsushima and M. Suzuki, *Bull. Chem. Soc. Jpn*., **65**, 39 (1992); [c] H. Horiuchi, A. Yokawa, T. Okutsu, and H. Hiratsuka, *Bull. Chem. Soc. Jpn*., **72**, 2429 (1999); [d] H. Horiuchi, H. Shirase, T. Okutsu, R. Matsushima, and H. Hiratsuka, *Chemistry Lett.*, 96 (2000).

[9] V. R. Gopal, A. M. Reddy, and V. J. Rao, *J. Org. Chem*., **60**, 7966 (1995).

[10] D. Papa, E. Schwenk, F. Villani, and E. Klingsberg, *J. Am. Chem. Soc*., **72**, 3885 (1950).

[11] H. Bablich and S. V. Kostanecki, *Ber. Dtsch. Chem. Ges*., **29**, 233 (1896); [b] C. Harries and G. Busse, *Ber. Dtsch. Chem. Ges*., **29**, 375 (1896).

[12a] C. D. Harries, *Ber. Dtsch. Chem. Ges*., **24**, 3180 (1891); [b] M. Winter, *Helv. Chim. Acta*, **44**, 2110 (1961).

[13] D. Sicker, A. Rabe, A. Zakrzewski, and G. Mann, *J. Prak. Chem*., **329**, 1063 (1987).

[14] W. Davey and J. R. Gwilt, *J. Chem. Soc*., 1008 (1957).

[15] J. H. Burckhalter and S. H. Johnson, Jr., *J. Am. Chem. Soc*., **73**, 4835 (1951).