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Synthesis and Photocyclization of 2-Aroyl-3-methylcyclohex-2-enones

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Preparation and photocyclization of a number of 2-aroyl-3-methylcyclohex-2-enones have been investigated. Irradiation of these systems resulted in a photo-enolization followed by a pericyclic reaction to give 3,4-dihydroanthracen-1(2H)-ones.

Keywords——preparation of 2-aroyl-3-methylcyclohex-2-enones; photocyclization; photo-enol; peri-cyclic reaction; nonoxidative intramolecular cyclization; formation of 9-hydroxy-3,4-dihydroanthracen-1(2H)-ones

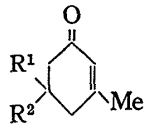
In connection with our studies on the photochemistry of 3-substituted cyclohex-2-enones,[1,2] we briefly reported[3] a cyclization of 2-(*o*-methoxyaroyl)-3,5,5-trimethylcyclohex-2-enones (**2a**—**c**), which undergo photo-enolization followed by cyclization and eventual elimination of methanol to give 9-hydroxy-3,4-dihydroanthracen-1(2H)-ones (**14a**—**c**) or of hydrogen to give 9-hydroxy-8-methoxy-3,4-dihydroanthracen-1(2H)-ones (**15a**—**c**). We have now examined the general preparation of 2-aroyl-3-methylcyclohex-2-enones and their photochemical behavior. The present paper describes these results including full details of the previous work.[3]

Results and Discussion

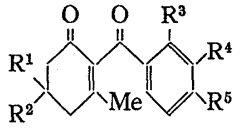
Preparation of 2-Aroyl-3-methylcyclohex-2-enones (2a—g)

Direct introduction of an aroyl group into the α-position of 3-methylcyclohex-2-enones (**1**) seems to be a simple route to 2-aroyl-3-methylcyclohex-2-enones (**2**). Although a direct method for the synthesis of **2** using sodium *tert*-amyloxide as a base was reported with isophorone (**1a**) (method A),[3,4] the yields and generality for other enones (**1b**, **c**) were quite poor. Thus, the reaction of 3,5-dimethylcyclohex-2-enone (**1b**) and *o*-methoxybenzoyl chloride under these conditions gave a considerable amount of the same enone dimer (**3**) that was obtained by House[5] in the reaction of **1b** with aqueous sodium hydroxide, accompanied by the desired enone (**2d**). Therefore, we examined the preparation of **2** by various methods including method A.

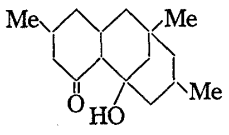
As mentioned above, the yields of **2** by method A were generally poor and quite variable according to the reaction conditions. After many runs, the best yields were obtained by addition of an equimolar amount of aroyl chloride to the anion generated from the enone (**1b** or **1c**) and a 0.3—3 N benzene solution of sodium *tert*-amyloxide under ice-cooling followed by stirring at room temperature for an appropriate time under argon. It was reported that coupling of lithium dialkylcuprate to β-acetoxy-[6] or β-alkoxycyclohex-2-enones[7] derived from cyclohexane-1,3-dione gave 3-alkylcyclohex-2-enone. This procedure, however, could not be applied to 2-aroyl-substituted analogs for the synthesis of **2**. Thus, both methylation and acetylation of 2-benzoylcyclohexane-1,3-dione (**4**) using diazomethane and acetic anhydride-pyridine failed to afford the corresponding β-methoxy- (**5**) and β-acetoxycyclohex-2-enones (**6**), respectively. All other attempts to introduce an aroyl group into the α-position of 2-phenylsulfenyl-(**7**)[8,9] and 2-phenylsulfinyl-3-methylcyclohexanones (**8**)[9] leading to **2** failed. Other approaches were therefore investigated.



1a: $R^1=R^2=Me$
1b: $R^1=Me$, $R^2=H$
1c: $R^1=R^2=H$



2a: $R^1=R^2=Me$, $R^3=OMe$, $R^4=R^5=H$
2b: $R^1=R^2=Me$, $R^3=R^4=OMe$, $R^5=H$
2c: $R^1=R^2=Me$, $R^3=R^5=OMe$, $R^4=H$
2d: $R^1=Me$, $R^2=R^4=R^5=H$, $R^3=OMe$
2e: $R^1=R^2=R^4=R^5=H$, $R^3=OMe$
2f: $R^1=R^2=Me$, $R^3=R^4=R^5=H$
2g: $R^1=R^2=R^3=R^4=R^5=H$



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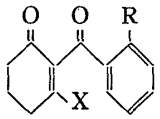
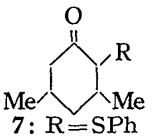
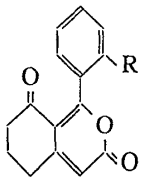


4a: X=OH, R=H
4b: X=OH, R=OMe
5: X=OMe, R=H
6: X=OAc, R=H
9a: X=Cl, R=H
9b: X=Cl, R=OMe



7: R=SPh
8: R=SOPh



10a: R=H
10b: R=OMe

We examined the reaction of 2-benzoyl-3-chlorocyclohex-2-enones (**9a, b**) with some carbanions, since the 2-acetyl analog is known to react site-specifically with amino compounds at the C-3 position.[10] Although reaction of **9** (obtained by the chlorination of **4** with oxalyl chloride) with methyl lithium or methyl magnesium chloride failed to give a satisfactory result, reaction of **9** with sodium di-*tert*-butylmalonate followed by thermal decarboxylation gave a moderate yield of the desired enone (**2**) accompanied by a small amount of the lactone (**10**) (method B).

In recent years there have been many reports[11] on the cuprous ion-catalyzed conjugated addition of lithium dialkylcuprates to α,β-unsaturated ketones to produce metal enolates, which can be trapped under nonequilibrating conditions with electrophiles. Reactions of this type permit the introduction of substituents into both the α- and β-positions of α,β-unsaturated ketones in a one-pot operation. Conjugate addition of lithium dimethylcuprate to cyclohex-2-enone (**11**) followed by aroylation was highly site-selective, producing a single ketone, 2-aroyl-3-methylcyclohexanone (**12**),[12] in a considerable yield. The stereochemistry of the newly introduced methyl and aroly groups was assigned as *trans* on the basis of the coupling constant ($J_{2,3}=11$ Hz) in the nuclear magnetic resonance (NMR) spectrum. Introduction of a phenylseleno group into the α-position of **12** was readily achieved by the standard procedure,[13] giving the compound (**13**). Treatment of **13** under oxidative elimination conditions, using *m*-chloroperbenzoic acid (*m*-CPBA) in methylene chloride at room temperature, gave the desired enone (**2**) in a fair yield (method C). An attempt at oxidative elimination using the sulfenyl group[14] instead of the phenylseleno group was unsuccessful. In conclusion, method A is recommended for the preparation of **2** on a large scale, although it is still not easy to control the reaction conditions and both methods B and C are useful on an experimental scale, although inefficient for preparative purposes.

Photocyclization of 2-Aroyl-3-methylcyclohex-2-enones (2a—f)

Photolysis of 2-aroyl-3-methylcyclohex-2-enones (**2a—f**) was examined. Irradiation of a 0.4% degassed ether solution of **2f** with a 350W high-pressure mercury lamp in a sealed quartz vessel for 40 hr afforded 3,3-dimethyl-9-hydroxy-3,4-dihydroanthracen-1(2H)-one (**14a**) in a moderate yield. When 2-(*o*-methoxybenzoyl)-3,5,5-trimethylcyclohex-2-enone (**2a**) in ether or methanol was irradiated similarly, cyclization with simultaneous elimination of the *ortho* methoxy group took place to give **14a** and a small amount of another naphthol, 3,3-

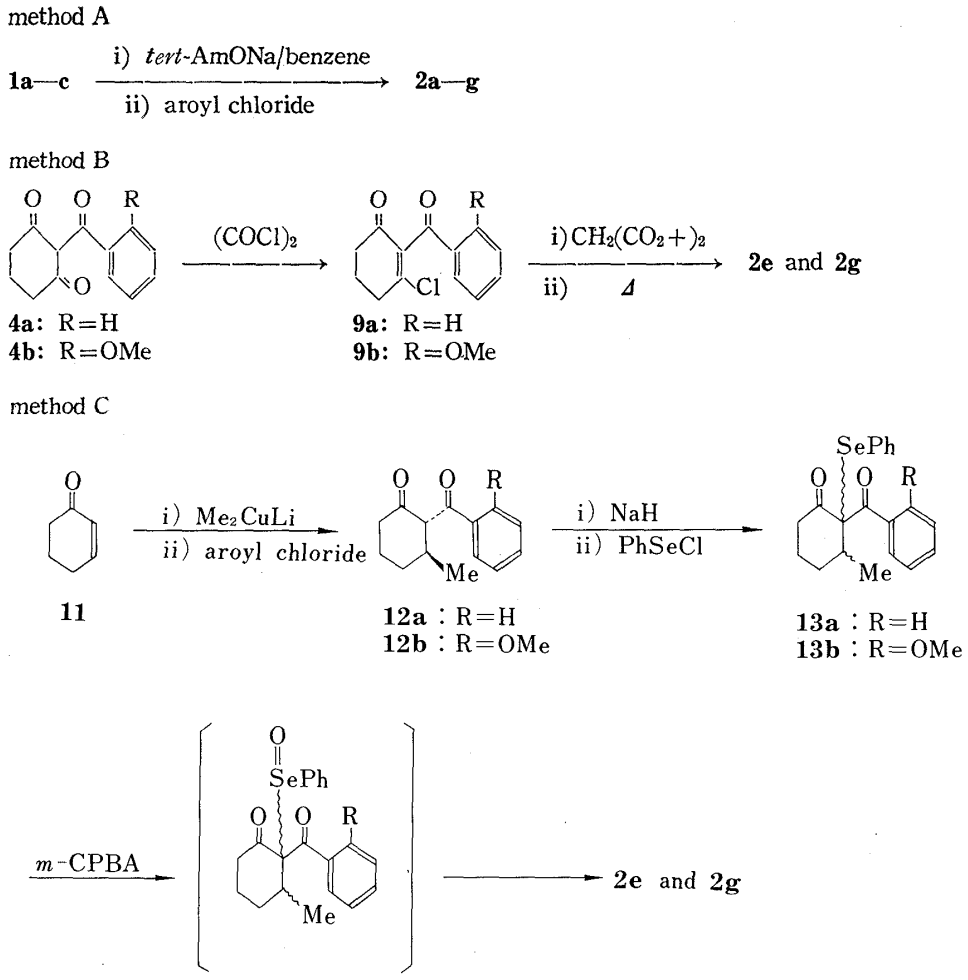


Chart 1

dimethyl-9-hydroxy-8-methoxy-3,4-dihydroanthracen-1(2H)-one (**15a**). This demethoxycyclization was also observed with other 2-(*o*-methoxyaroyl)-3,5,5-trimethylcyclohex-2-enones (**2b**—**e**) which gave the corresponding compounds (**14b**—**e**) together with small amounts of the compounds (**15b**—**e**). Irradiation of **2a** with oxygen bubbling through the ether solution or in the presence of iodine in the ether solution decreased the yield of the cyclization products and gave many by-products (as judged by TLC). Addition of BF_3 to the solution was found to favor the photo-cyclization. The results are summarized in Table I.

The formation of the naphthols (**14** and **15**) could be explained by the mechanism shown in Chart 2. Presumably, photo-enolization[15] to the enol species [*e.g.*, (iv) and (v)] does occur in this instance and is followed by a rapid non-oxidative cyclization (hexatriene-to-cyclohexadiene type, whether thermal or photochemical), which is aided by reformation of the benzene ring. The unstable cyclized intermediate [(vi) or (vii)] undergoes either rapid loss of methanol[16] to give the naphtol (**14**) or of hydrogen to give the naphthol (**15**), respectively. That the cyclization process is rapid was demonstrated by the failure to trap the intermediate enol species (iv or v) with an active dienophile such as dimethylacetylene dicarboxylate or N-phenylmaleimide, the naphthols (**14** and **15**) still being formed in considerable yields. An analogous type of photo-cyclization through photo-enolization was reported in an aromatic compound, 2-methylbenzophenone.[17] However, the yield of the anthracenone produced was only 1% on flushing the previously irradiated solution with oxygen. The cyclization of the photo-enol (v) derived from **2** might occur more rapidly than that of 2-methylbenzophenone because the loss of the resonance stabilization of enolization in **2** is less than in 2-

methylbenzophenone and/or because the enol (v) has a long life-time owing to the stabilization by intramolecular hydrogen bonding. The latter possibility is strongly supported by the results of photolysis of **2** in the presence of boron trifluoride: the photo-enol (v) might be stabilized by coordination between the electron-deficient boron atom and the oxygen atom of the C-1 carbonyl, *e.g.*, (viii).

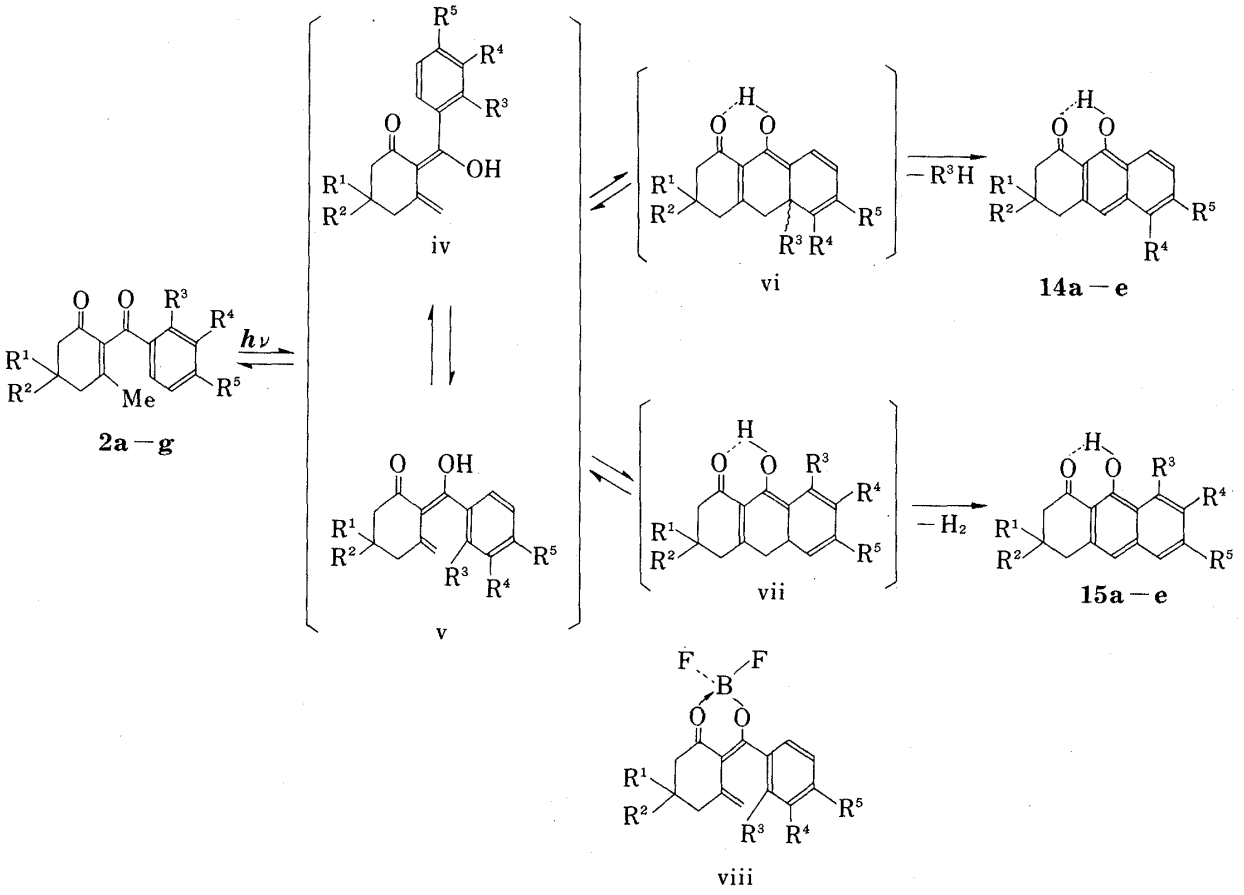


Chart 2

TABLE I. Reaction Conditions and Yields of Products

	Starting enones (2a—f)					Reaction conditions[a]	% yields of products		
	R¹	R²	R³	R⁴	R⁵		14	15	2 (recovered)
2a	Me	Me	OMe	H	H	in MeOH, 40h	(**14a**) 11	(**15a**) —	(**2a**) 66
						in Et_2O, 40h	22	10	58
						in Et_2O, O_2, 40h	17	—	22
						in Et_2O, I_2, 40h	16	—	77
						in Et_2O, BF_3–Et_2O, 40h	18	8	25
						in Et_2O, BF_3–Et_2O, 20h	38	16	26
2b	Me	Me	OMe	OMe	H	in Et_2O, 40h	(**14b**) 35	(**15b**)[b]	(**2b**) 35
						in Et_2O, BF_3–Et_2O, 20h	23	[b]	66
2c	Me	Me	OMe	H	OMe	in Et_2O, 40h	(**14c**) 15	(**15c**)[b]	(**2c**) 47
						in Et_2O, BF_3–Et_2O, 20h	26	6	66
2d	Me	H	OMe	H	H	in Et_2O, 40h	(**14d**) 19	(**15d**) 7	(**2d**) 39
						in Et_2O, BF_3–Et_2O, 20h	32	10	34
2e	H	H	OMe	H	H	in Et_2O, 40h	(**14e**) 12	(**15e**) 4	(**2e**) 78
						in Et_2O, BF_3–Et_2O, 20h	36	8	32
2f	Me	Me	H	H	H	in Et_2O, 40h	(**14a**) 30		(**2f**) 36
						in Et_2O, BF_3–Et_2O, 20h	34		46

a) Photolysis was performed in a quartz vessel with a 350w high-pressure mercury lamp.
b) The yield was less than 2%.

Experimental

All melting and boiling points are uncorrected. Infrared (IR) absorption spectra were recorded on a Shimadzu IR-27G spectrometer, and NMR spectra on a Hitachi R-20A or a Hitachi R-600 spectrometer (with tetramethylsilane as an internal standard). Ultraviolet (UV) absorption spectra were recorded on a Hitachi 124 spectrometer. Mass spectra (MS) were obtained with a Hitachi RMU-6M instrument, and high resolution MS with a JMS D-300 instrument with a direct inlet system. Column chromatography was carried out on Merck Silica-gel 60.

Starting Enones (1a—c)——3,5,5-Trimethylcyclohex-2-enone (**1a**) is commercially available. Other enones, 3,5-dimethyl- (**1b**) and 3-methylcyclohex-2-enones (**1c**) were prepared by the reported methods; (**1b**): bp 65—70°/14 mmHg (lit. 84—86°/9 mmHg[18]), 45% yield, (**1c**): bp 78—79°/18 mmHg (lit. 76—78°/14 mmHg[19]), 56% yield.

General Procedure (Method A) for 2-Aroyl-3-methylcyclohex-2-enones (2a—g)——The enone (**1**) was added to a stirred 0.3—3 N benzene solution of *tert*-AmONa (prepared from sodium and *tert*-AmOH in benzene), cooled in ice. The mixture was stirred at room temperature for 1 hr and cooled at 0°, then aroyl chloride was added in portions during a few minutes. After the reaction mixture had been stirred at room temperature for 1 hr, it was acidified with 10% hydrochloric acid. Ether (or chloroform in the case of **2c**) was added to the mixture, and the organic layer was washed with brine and dried ($MgSO_4$). Concentration of the extract by evaporation *in vacuo* gave a residue, which was crystallized from isopropanol or, in some cases, purified by column chromatography on silica gel to give the corresponding 2-aroyl-3-methylcyclohex-2-enone (**2**). Molar ratio, yield, melting point (recrystallization solvent), and analytical and spectral data are given below.

2-(2-Methoxybenzoyl)-3,5,5-trimethylcyclohex-2-enone (2a)——This was prepared from 3 N *tert*-AmONa (27 ml, 80 mmol), **1a** (12 g, 80 mmol), and 2-methoxybenzoyl chloride (6.9 g, 40 mmol) in 19% yield (5.4 g). Recrystallization from isopropanol gave **2a**, mp 122—123°. *Anal.* Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.92; H, 7.29 IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665 and 1645. NMR ($CDCl_3$) δ: 7.82 (1H, dd, J=2.5 and 8 Hz, ArH), 7.38 (1H, ddd, J=2.5, 8, and 8 Hz, ArH), 7.03 (1H, ddd, J=2.5, 8, and 8 Hz, ArH), 6.91 (1H, dd, J=2.5 and 8 Hz, ArH), 3.75 (3H, s, OMe), 2.25 (4H, s, $CH_2\times2$), 1.84 (3H, s, Me), and 1.08 (6H, s, Me×2); UV λ_{max}^{EtOH} nm (log ε): 314 (3.60) and 249 (4.12). MS *m/e* 272 (M^+).

2-(2,3-Dimethoxybenzoyl)-3,5,5-trimethylcyclohex-2-enone (2b)——This was prepared from 1.8 N *tert*-AmONa (5.5 ml, 10 mmol), **1a** (1.38 g, 10 mmol), and 2,3-dimethoxybenzoyl chloride (1 g, 5 mmol) in 11% yield (350 mg). Recrystallization from isopropanol gave **2b**, mp 106—107°. *Anal.* Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.57; H, 7.44. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1670 and 1650. NMR ($CDCl_3$) δ: 7.50—7.0 (3H, m, ArH), 3.82 (3H, s, OMe), 3.71 (3H, s, OMe), 2.28 (4H, s, $CH_2\times2$), 1.86 (3H, s, Me), and 1.07 (6H, s, Me×2). UV λ_{max}^{EtOH} nm (log ε): 314 (2.95) and 251 (3.75). MS *m/e* 302 (M^+).

2-(2,4-Dimethoxybenzoyl)-3,5,5-trimethylcyclohex-2-enone (2c)——This was prepared from 1.7 N *tert*-AmONa (16 ml, 27 mmol), **1a** (3.5 g, 25 mmol), and 2,4-dimethoxybenzoyl chloride (2.6 g, 13 mmol) in 24% yield. Recrystallization from isopropanol gave **2c**, mp 115—116°. *Anal.* Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.59; H, 7.35. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665 and 1640. NMR ($CDCl_3$) δ: 7.92 (1H, d, J=9.5 Hz, ArH), 6.58 (1H, dd, J=2.5 and 9.5 Hz, ArH), 6.25 (1H, d, J=2.5 Hz, ArH), 3.88 (3H, s, OMe), 3.80 (3H, s, OMe), 2.31 (4H, s, $CH_2\times2$), 1.89 (3H, s, Me), and 1.13 (6H, s, Me×2). UV λ_{max}^{EtOH} nm (log ε): 313 (4.08), 276 (4.07), and 231 (4.39). MS *m/e* 302 (M^+).

3,5-Dimethyl-2-(2-methoxybenzoyl)cyclohex-2-enone (2d)——This was prepared from 0.3 N *tert*-AmONa (34 ml, 10 mmol), **1b** (1.74 g, 10 mmol), and 2-methoxybenzoyl chloride (1.7 g, 10 mmol) in 42% yield (1.1 g). Recrystallization from isopropanol gave **2d**, mp 102—103°. *Anal.* Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.46; H, 7.07. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680 and 1650. NMR ($CDCl_3$) δ: 7.94—6.70 (4H, m, ArH), 3.78 (3H, s, OMe), 2.65—2.0 (5H, m, CH_2CHCH_2), 1.87 (3H, s, Me), and 1.12 (3H, d, J=4.0 Hz, Me). UV λ_{max}^{EtOH} nm (log ε): 315 (3.50), 248 (4.01), and 212 (4.22).

2-(2-Methoxybenzoyl)-3-methylcyclohex-2-enone (2e)——This was prepared from 0.8 N *tert*-AmONa (23 ml, 18 mmol), **1c** (2.3 g, 20 mmol), and 2-methoxybenzoyl chloride (3.4 g, 20 mmol) in 39% yield. Recrystallization from isopropanol gave **2e**, mp 74—74.5°. *Anal.* Calcd for $C_{15}H_{16}O_3$: C, 73.35; H, 6.60. Found: C, 73.31; H, 6.61. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1670 and 1650. NMR ($CDCl_3$) δ: 7.98—6.73 (4H, m, ArH), 3.78 (3H, s, OMe), 2.75—1.90 (6H, m, $CH_2\times3$), and 1.90 (3H, s, Me). UV λ_{max}^{EtOH} nm (log ε): 315 (3.60), 248 (4.11), and 212 (4.21). MS *m/e* 244 (M^+). This sample was identical with that obtained by method B.

2-Benzoyl-3,5,5-trimethylcyclohex-2-enone (2f)——This was prepared from 1.7 N *tert*-AmONa (55 ml, 94 mmol), **1a** (12.9 g, 93 mmol), and benzoyl chloride (6.5 g, 50 mmol) in 16% yield (3.5 g). Recrystallization from isopropanol gave **2f**, mp 102—103°. *Anal.* Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.14; H, 7.49. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1675 and 1650. NMR ($CDCl_3$) δ: 7.90—7.35 (5H, m, ArH), 2.30 (4H, s, $CH_2\times2$), 1.80 (3H, s, Me), and 1.20 (6H, s, Me×2). UV λ_{max}^{EtOH} nm (log ε): 246 (4.16). MS *m/e* 242 (M^+).

2-Benzoyl-3-methylcyclohex-2-enone (2g)——This was prepared from 1.4 N *tert*-AmONa (4 ml, 5.6 mmol), **1c** (0.62 g, 5.6 mmol), and benzoyl chloride (0.79 g, 5.6 mmol) in 18% yield. Recrystallization from isopropanol gave **2g**, mp 66.5—67°. *Anal.* Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.01; H, 6.38.

IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1670 and 1650. NMR ($CDCl_3$) δ: 7.87—7.32 (5H, m, ArH), 2.52—1.95 (6H, m, $CH_2\times3$), and 1.84 (3H, s, Me). UV λ_{max}^{EtOH} nm (log ε): 245 (3.68). MS *m/e* 214 (M^+). This sample was identical with that obtained by method B.

2-Benzoylcyclohexane-1,3-dione (4a)——Benzoyl chloride (9 g, 64 mmol) was added to a stirred solution of cyclohexane-1,3-dione (7.3 g, 65 mmol) and pyridine (5 g, 64 mmol) in chloroform (150 ml). The mixture was stirred at room temperature for 4 hr and poured into cold water. The organic layer was washed with dilute hydrochloric acid, sat. aqueous $NaHCO_3$, and brine, dried (Na_2SO_4), and concentrated *in vacuo* to give the crude 3-benzoyloxycyclohex-2-enone as a syrup. The crude enol ester was added to a stirred solution of anhydrous $AlCl_3$ (15 g, 120 mmol) in dichloroethane (160 ml). The mixture was stirred at room temperature for 17 hr and then poured into cold 10% hydrochloric acid. The organic phase was separated and the aqueous phase was extracted with dichloroethane. The combined organic phase was washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was dissolved in the minimum quantity of ether and the solution was treated with 1 N NaOH. The aqueous layer was acidified with conc. hydrochloric acid and extracted with ether. The ethereal solution was dried (Na_2SO_4) and concentrated *in vacuo* to give a residue, which was recrystallized from hexane to give a 49% yield (6.7 g) of **4a**, mp 53—54° (lit. 55—58°[20]).

2-(2-Methoxybenzoyl)cyclohexane-1,3-dione (4b)——2-Methoxybenzoyl chloride (19.0 g, 111 mmol) was added to a stirred solution of cyclohexane-1,3-dione (11.3 g, 101 mmol) and pyridine (8.0 g, 101 mmol) in chloroform (200 ml). The mixture was stirred at room temperature for 15 hr and poured into cold water. The organic layer was washed with dilute hydrochloric acid, sat. aqueous $NaHCO_3$, and brine, and then dried ($MgSO_4$). The solvent was removed *in vacuo* to leave a syrup, which was distilled to give a 46% yield (11.5 g) of 3-(2-methoxybenzoyloxy)cyclohex-2-enone, bp 178—180°/4 mmHg. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1755 and 1680. NMR ($CDCl_3$) δ: 7.95—6.80 (4H, m, ArH), 5.95 (1H, s, CH=), 3.88 (3H, s, OMe), and 2.85—1.90 (6H, m, $CH_2\times3$). The enol ester failed to give 2-(2-methoxybenzoyl)cyclohexane-1,3-dione (**4b**) under the conditions described for the preparation of **4a** from the corresponding enol ester. Photo-Fries rearrangement[2] of the enol ester gave **4b**. A solution of the enol ester (282 mg, 1.15 mmol) in degassed benzene (25 ml) was irradiated with a 350 W high-pressure mercury lamp in a Pyrex vessel for 80 hr. After concentration of the reaction mixture *in vacuo*, the residue was dissolved in dilute aqueous NaOH (15 ml). The aqueous layer was washed with ether, acidified with aqueous 10% HCl, and extracted with ether (10 ml×3). The extract was washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (benzene: ethyl acetate=4: 1 as the eluting solvent) to give a 16% yield (45 mg) of **4b**. Recrystallization from *n*-hexane gave an analytical sample, mp 100—101°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725 and 1665. NMR ($CDCl_3$) δ: 16.99 (1H, s, OH), 7.60—6.70 (4H, m, ArH), 3.72 (3H, s, OMe), and 2.90—1.85 (6H, m, $CH_2\times3$). Exact MS calcd. for $C_{14}H_{14}O_4$: 246.0893. Found: 246.0900.

3,5-Dimethyl-2-phenylsulfenylcyclohexanone (7)——A solution of *n*-BuLi (1.6 N, 10 ml, 16 mmol) was added dropwise under argon to a stirred solution of diisopropylamine (1.9 g, 18 mmol) in THF (10 ml) cooled at −78°. The mixture was stirred for 0.5 hr, then a solution of 3,5-dimethylcyclohexanone (2.0 g, 16 mmol) in THF (5 ml) was added, and the whole was stirred for 1 hr under the same conditions. Next, a solution of diphenyldisulfide (3.3 g, 15 mmol) in THF (5 ml) was added, and the mixture was stirred at room temperature overnight. After cooling in an ice bath, the reaction mixture was partitioned between 1 N hydrochloric acid and chloroform. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (benzene: hexane=1: 1 as the eluting solvent) to give a 56% yield (2.07 g) of **7** as a mixture of *cis*- and *trans*-isomers (*cis*/*trans*=1/3); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1700. NMR ($CDCl_3$) δ: 7.50—7.14 (5H, m, ArH), 3.52 (3/4H, d, J=7 Hz, C_2H *trans*), 3.40 (1/4H, d, J=11 Hz, C_2H *cis*), 3.0—1.30 (6H, m, $CH_2\times2$ and $CH\times2$), 1.17 (3/4H, d, J=7 Hz, C_5Me *cis*), and 0.78 (9/4H, d, J=7 Hz, C_5Me *trans*). Exact MS calcd. for $C_{14}H_{18}OS$: 234.1075. Found: 234.1074. This mixture was used for the next reaction without separation of the isomers.

3,5-Dimethyl-2-phenylsulfinylcyclohexanone (8)——A solution of $NaIO_4$ (280 mg, 1.4 mmol) in water (5 ml) was added dropwise to a stirred solution of the sulfide (**7**) (300 mg, 1.3 mmol) in methanol (10 ml), cooled in an ice bath. The reaction mixture was stirred at room temperature for 3 hr, and then chloroform was added. The organic layer was washed with sat. aqueous $NaHCO_3$, and brine, and dried ($MgSO_4$). Removal of the solvent *in vacuo* followed by preparative TLC on silica gel (benzene as the developing solvent) gave the *trans*-isomer ($\mathbf{8}_{trans}$) and *cis*-isomer ($\mathbf{8}_{cis}$) in 49% and 43% yields, respectively. $\mathbf{8}_{trans}$: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1695 and 1650. NMR ($CDCl_3$) δ: 7.80—7.30 (5H, m, ArH), 3.37 (1H, d, J=10.5 Hz, C_2H), 2.60—1.30 (6H, m, $CH_2\times2$ and $CH\times2$), 1.29 (3H, d, J=6 Hz, C_3Me), and 0.98 (3H, d, J=6.5 Hz, C_5Me). $\mathbf{8}_{cis}$: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1695 and 1640. NMR ($CDCl_3$) δ: 7.47 (5H, s, ArH), 3.04 (1H, d, J=5 Hz, C_2H), 2.60—1.70 (6H, m, $CH_2\times2$ and $CH\times2$), 1.56 (3H, d, J=6.5 Hz, C_3Me), and 1.08 (3H, d, J=5 Hz, C_5Me). Spectroscopic data were fully consistent with the proposed structures, but satisfactory analytical data could not be obtained.

2-Benzoyl-3-chlorocyclohex-2-enone (9a)——Oxalyl chloride (3.8 ml, 45 mmol) was added dropwise to 2-benzoylcyclohexane-1,3-dione (**4a**) (4.8 g, 22 mmol) at 0°. After the reaction mixture had been stirred at 0° for 3 hr, excess oxalyl chloride was removed *in vacuo*. The residual syrup was distilled under reduced pressure to give a 76% yield (3.9 g) of **9a**, bp 185—195°/0.15 mmHg (bath temperature). *Anal.* Calcd for $C_{13}H_{11}ClO_2$: C, 66.52; H, 4.73. Found: C, 66.64; H, 4.64. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1675 and 1640. NMR ($CDCl_3$) δ: 7.95—7.25 (5H, m, ArH) and 3.05—2.10 (6H, m, $CH_2\times3$).

3-Chloro-2-(2-methoxybenzoyl)cyclohex-2-enone (9b)——This was prepared from oxalyl chloride (0.1 ml, 1.2 mmol) and **4b** (58 mg, 0.24 mmol) by the method described for the preparation of **9a**. Distillation of the syrup under reduced pressure gave a 97% yield (60 mg) of **9b**. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1675 and 1650. NMR ($CDCl_3$) δ: 8.15—6.80 (4H, m, ArH), 3.82 (3H, s, OMe), and 3.15—1.85 (6H, m, $CH_2\times3$). Exact MS calcd for $C_{14}H_{13}ClO_3$: 264.0554. Found: 264.0554.

General Procedure (Method B) for the Enones (2e and 2g) from 2-Benzoyl-3-chlorocyclohex-2-enones (9a and 9b)——A solution of di-*tert*-butyl malonate in benzene was added dropwise at room temperature to a stirred solution of sodium hydride in dry benzene. The mixture was stirred for 15 min, then a solution of 2-benzoyl 3-chlorocyclohex-2-enone in dry benzene was added, and the whole was warmed at 60° for 2.5 hr. After cool ing in an ice bath, the reaction mixture was quenched with water. The aqueous layer was acidified with 10% hydrochloric acid and extracted with ether. The combined organic layer was washed with brine, dried ($MgSO_4$), and concentrated *in vacuo* to give a residue. The residue was dissolved in benzene and *p*-TsOH was added to the solution. The mixture was heated under reflux for 10 hr. After cooling, the mixture was washed with water, sat. aqueous $NaHCO_3$, and brine, and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residual syrup was distilled under reduced pressure to give **2**. From the distilled residue, the lactone (**10**) was obtained by repeated recrystallization.

Conversion of 9a into 2g and the Lactone (10a)——A solution of 2-benzoyl-3-chlorocyclohex-2-enone (**9a**) (4.0 g, 17 mmol) in benzene (60 ml) was added to a suspension of NaH (1.65 g, 34 mmol) and di-*tert*-butyl-malonate (7.4 g, 34 mmol) in benzene (90 ml). The reaction mixture was heated at 60° for 2.5 hr, then cooled to 0°, and quenched with water (20 ml). The separated aqueous layer was acidified with aqueous 10% hydrochloric acid and extracted with ether (50 ml). The combined organic layer was washed with brine, dried ($MgSO_4$), and concentrated *in vacuo* to give 3-(di-*tert*-butyloxycarbonyl)methylcyclohex-2-enone as a crude solid, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740, 1720, 1675, and 1660. NMR ($CDCl_3$) δ: 7.95—7.20 (5H, m, ArH), 4.11 (1H, s, CH), 2.90—1.85 (6H, m, $CH_2\times3$), and 1.49 (18H, s, Me×6). The crude ester was used for the next decarboxylation without purification. A solution of the ester and *p*-TsOH (500 mg) in benzene (50 ml) was heated under reflux for 10 hr, and then water (10 ml) was added to the mixture. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*. Distillation of the residual syrup under reduced pressure gave a 33% yield (1.21 g, overall yield from **9a**) of **2g**, bp 160—200°/0.1 mmHg (bath temperature), which was identical with the authentic specimen obtained by method A. Repeated recrystallization of the distilled residue from benzene–pet-ether gave a 20% yield (0.81 g, overall yield from **9a**) of **10a**, mp 171—173.5°. *Anal.* Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.69; H, 4.95. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740 and 1685. NMR ($CDCl_3$) δ: 7.45 (5H, s, ArH), 6.08 (1H, t, J=1.5 Hz, CH=), and 3.00—1.90 (6H, m, $CH_2\times3$). MS *m/e* 240 (M^+).

Conversion of 9b into 2e——Treatment of a suspension of NaH (21 mg, 0.45 mmol) and di-*tert*-butyl-malonate (100 mg, 0.45 mmol) in benzene (5 ml) with 3-chloro-2-(2-methoxybenzoyl)cyclohex-2-enone (**9b**) (60 mg, 0.23 mmol) in benzene (3 ml) was carried out under conditions similar to those described for the conversion of **9a** into **2g**. The residue was purified by preparative TLC on silica gel using benzene–ethyl acetate (4: 1) as the developing solvent to give a 15% yield (8 mg, overall yield from **9b**) of **2e**, mp 71—73°. This compound was identical with the authentic specimen obtained by method A.

2-Benzoyl-3-methylcyclohexanone (12a)——A solution of **1c** (480 mg, 5 mmol) in dry ether (5 ml) was added dropwise, with stirring under argon, to a chilled solution of lithium dimethylcuprate[21] prepared from methyl lithium (12.8 ml of 0.78 M ether solution, 10 mmol) and cuprous iodide (950 mg, 5 mmol) in dry ether (10 ml). The mixture was stirred at room temperature for 0.5 hr, then cooled to −78°. A solution of benzoyl chloride (1.05 g, 7.5 mmol) in dry ether (5 ml) and dry HMPA (6 ml) was then added, and the mixture was stirred at room temperature for 2 hr. After cooling in an ice bath, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The combined extract was washed with sat. aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (chloroform as the eluting solvent) to give a 60% yield (580 mg) of **12a**. Recrystallization from light petroleum gave a pure *trans*-isomer (**12a**$_{trans}$), mp 64—65° (lit. 65—66.5°[12]). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1700 and 1670. NMR ($CDCl_3$) δ: 7.8—7.6 (2H, m, ArH), 7.5—7.2 (3H, m, ArH), 3.90 (1H, d, J=10 Hz, COCHCO), 2.7—1.1 (7H, m, $CH_2\times3$ and CH), and 0.95 (3H, d, J=7 Hz, Me).

2-(2-Methoxybenzoyl)-3-methylcyclohexanone (12b)——Compound **1c** (1.2 g, 12 mmol) was treated with dimethyl cuprate (20 mmol) and 2-methoxybenzoyl chloride (2.5 g, 13 mmol) in ether–HMPA by the procedure described for **12a**. The crude **12b** was purified by column chromatography on silica gel (chloroform as the eluting solvent) to give a 48% yield (1.18 g) of pure *trans*-isomer (**12b**$_{trans}$), mp 72—73°. *Anal.* Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.30; H, 7.37. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1705 and 1670. NMR ($CDCl_3$) δ: 7.80—6.80 (4H, m, ArH), 4.18 (1H, d, J=11 Hz, COCHCO), 3.87 (3H, s, OMe), 2.75—1.27 (7H, m, $CH_2\times3$ and CH), and 1.01 (3H, d, J=6.5 Hz, Me). MS *m/e* 246 (M^+).

2-Benzoyl-3-methyl-2-phenylselenylcyclohexanone (13a)——A solution of **12a** (195 mg, 0.94 mmol) in dry THF (1 ml) was added to a stirred suspension of NaH (60%, 78 mg, 2 mmol) in dry THF (2 ml) under argon. The mixture was stirred at room temperature for 0.5 hr, then a solution of PhSeCl (194 mg, 1 mmol) in THF (1 ml) was added, and the whole was stirred overnight under the same conditions. The mixture was partitioned between 1 N hydrochloric acid and a pentane–light petroleum (1: 1) solution. The organic

layer was washed with sat. aqueous $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated *in vacuo* to give a residue, which was subjected to column chromatography on silica gel (chloroform: *n*-pentane=1: 1 as the eluting solvent) to give a 58% yield (215 mg) of **13a** as a mixture of *cis*- and *trans*-isomers, mp 95—96°. *Anal.* Calcd for $C_{20}H_{20}O_2Se$: C, 64.69; H, 5.43. Found: C, 64.80; H, 5.39. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1700 and 1660. NMR ($CDCl_3$) δ: 8.20—7.18 (10H, m, ArH), 2.50—1.60 (7H, m, $CH_2\times3$ and CH), and 1.26 (3H, dd, J=5 and 6 Hz, Me).

2-(2-Methoxybenzoyl)-3-methyl-2-phenylselenylcyclohexanone (13b)——According to the procedure described for **13a**, **12b** (738 mg, 3 mmol) was treated with NaH (60%, 125 mg, 3.2 mmol) and PhSeCl (689 mg, 3.6 mmol) in THF (7 ml). The crude **13b** was purified by column chromatography on silica gel (chloroform as the eluting solvent) to give a 60% yield (720 mg) of **13b** as a mixture of *cis*- and *trans*-isomers. Recrystallization from ether–pet·ether gave a pure sample, mp 109—110.5°. *Anal.* Calcd for $C_{21}H_{22}O_3Se$: C, 62.84; H, 5.53. Found: C, 62.87; H, 5.52. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690 and 1670. NMR ($CDCl_3$) δ: 8.05—6.80 (9H, m, ArH), 3.74 (3H, s, OMe), 2.60—1.42 (7H, m, $CH_2\times3$ and CH), and 1.10 (3H, dd, J=7 and 8 Hz, Me).

General Procedure (Method C) for 2-Aroyl-3-methylcyclohex-2-enones (2e and 2g)——A solution of a slight excess of *m*-CPBA in CH_2Cl_2 was added dropwise to a cooled and stirred solution of the selenide (**13**) in CH_2Cl_2. The reaction mixture was allowed to stand at room temperature. After removal of the resulting crystals by filtration, the filtrate was washed with sat. aqueous Na_2SO_3, sat. aqueous $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated *in vacuo* to give a residue, which was subjected to column chromatography on silica gel (chloroform as the eluting solvent) to give the corresponding 2-aroyl-3-methylcyclohex-2-enone (**2**). **2e**: This was prepared from **13b** (700 mg, 1.7 mmol) and *m*-CPBA (741 mg, 3.4 mmol) in CH_2Cl_2. Purification by column chromatography gave a 58% yield (230 mg) of **2e**, mp 65—67°. **2g**: This was prepared from **13a** (500 mg, 1.3 mmol) and *m*-CPBA (520 mg, 2.4 mmol) in CH_2Cl_2. Purification by column chromatography gave a 73% yield (250 mg) of **2g**, mp 145—147°. These enones were identical with the corresponding authentic specimens obtained by method A.

General Procedure for the Photocyclization of 2-Aroyl-3-methylcyclohex-2-enones (2) to 3,4-Dihydroanthracen-1(2H)-ones (14 and 15)——A solution of **2** in degassed ether was irradiated with a 350 W high-pressure mercury lamp in a sealed quartz vessel for 40 hr. Removal of the solvent *in vacuo* followed by preparative TLC on silica gel (benzene: ethyl acetate=10: 1 or chloroform as the developing solvent) gave the 3,4-dihydroanthracen-1(2H)-ones, **14** and **15**. Irradiation of **2** with oxygen bubbling through the ether solution and in the presence of iodine or boron trifluoride in the ether solution was also performed. The reaction conditions and yields of the products are listed in Table I. Molar ratios, melting points (recrystallization solvents), analytical and spectral data are given below.

Photocyclization of 2a into 14a and 15a——14a: Recrystallization from light petroleum gave an analytical sample, mp 97—98°. *Anal.* Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.93; H, 6.67. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1620. NMR ($CDCl_3$) δ: 14.05 (1H, s, OH), 8.45—7.20 (4H, m, ArH), 6.97 (1H, s, ArH), 2.76 (2H, s, CH_2), 2.47 (2H, s, CH_2,) and 1.03 (6H, s, Me×2). UV λ_{max}^{EtOH} nm (log ε): 297 (3.57), 286 (3.54), 267 (4.20), and 259 (4.18). MS *m/e* 240 (M^+). **15a**: Recrystallization from light petroleum gave an analytical sample, mp 149—150°. Exact MS calcd. for $C_{17}H_{18}O_3$: 270.1256. Found: 270.1259. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1625. NMR ($CDCl_3$) δ: 15.10 (1H, s, OH), 7.62—6.92 (4H, m, ArH), 3.99 (3H, s, OMe), 2.78 (2H, s, CH_2), 2.52 (2H, s, CH_2), and 1.03 (6H, s, Me×2).

Photocyclization of 2b into 14b and 15b——14b: Recrystallization from light petroleum gave an analytical sample, mp 153—154°. Exact MS calcd. for $C_{17}H_{18}O_3$: 270.1253. Found: 270.1246. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1615. NMR ($CDCl_3$) δ: 13.90 (1H, s, OH), 7.94 (1H, dd, J=1 and 4.5 Hz, ArH), 7.42 (1H, s, ArH), 7.38 (1H, d, J=4.3 Hz, ArH), 6.92 (1H, dd, J=1 and 4.5 Hz, ArH), 3.98 (3H, s, OMe), 2.88 (2H, s, CH_2), 2.55 (2H, s, CH_2), and 1.07 (6H, s, Me×2). **15b**: Spectroscopic data were consistent with the proposed structure, but satisfactory analytical data could not be obtained. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1620, 1595, and 1565; NMR ($CDCl_3$) δ: 14.88 (1H, s, OH), 3.97 (6H, s, OMe×2), and other signals assignable to the indicated structure.

Photocyclization of 2c into 14c——14c: Recrystallization from light petroleum gave an analytical sample, mp 159—160°. *Anal.* Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.57; H, 6.80. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1625. NMR ($CDCl_3$) δ: 14.15 (1H, s, OMe), 8.34 (1H, d, J=9 Hz, ArH), 7.80 (1H, s, ArH), 7.11 (1H, dd, J=2.5 and 9 Hz, ArH), 6.97 (1H, s, ArH), 3.94 (3H, s, OMe), 2.82 (2H, s, CH_2), 2.54 (2H, s, CH_2), and 1.08 (6H, s, Me×2). MS *m/e* 270 (M^+).

Photocyclization of 2d into 14d and 15d——14d: Recrystallization from light petroleum gave an analytical sample, mp 93—93.5°. *Anal.* Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.24; H, 5.79. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1620. NMR ($CDCl_3$) δ: 13.26 (1H, s, OH), 8.43—6.94 (5H, m, ArH), 3.23—2.22 (5H, m, $CH_2\times2$ and CH), and 1.15 (3H, d, J=6 Hz, Me); UV λ_{max}^{EtOH} nm (log ε): 376 (3.53), 296 (3.75), 286 (3.72), 267 (4.32), and 258 (4.34). MS *m/e* 226 (M^+). **15d**: Recrystallization from light petroleum gave an analytical sample, mp 169—170°. *Anal.* Calcd for $C_{16}H_{16}O_3$: C, 79.62; H, 6.24. Found: C, 79.24; H, 5.99. Exact MS Calcd for $C_{16}H_{16}O_3$: 256.1098. Found: 256.1093. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1620. NMR ($CDCl_3$) δ: 14.18 (1H, s, OH), 7.46—6.81 (4H, m, ArH), 4.00 (3H, s, OMe), 3.11—2.05 (5H, m, $CH_2\times2$ and CH), and 1.23 (3H, d, J=6 Hz, Me).

Photocyclization of 2e to 14e and 15e——14e: Recrystallization from light petroleum gave an analytical sample, mp 93.5—94°. *Anal.* Calcd for $C_{14}H_{22}O_2$: C, 79.22; H, 5.70. Found: C, 79.15; H, 5.50. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1625. NMR ($CDCl_3$) δ: 13.22 (1H, s, OH), 8.40—6.94 (5H, m, ArH), 3.02 (2H, t, J=3.5 Hz, CH_2),

2.75 (2H, t, J=3.5 Hz, CH_2), and 2.12 (2H, q, J=3.5 Hz, CH_2). MS *m/e* 212 (M^+). **15e**: Recrystallization from light petroleum gave an analytical sample, mp 153—154°. Exact MS calcd. for $C_{15}H_{14}O_3$: 242.0941. Found: 242.0941. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1620. NMR ($CDCl_3$) δ: 14.22 (1H, s, OH), 7.62—6.65 (4H, m, ArH), 2.98 (2H, t, J=3.5 Hz, CH_2), 2.74 (2H, t, J=3.5 Hz, CH_2), and 2.08 (2H, t, J=3.5 Hz, CH_2).

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