to a powder. The mixture was charged to a 100 mL, round-bottom flask equipped with a Dean-Stark trap and condenser. The mixture was refluxed for 1 h, and the acetone byproduct was removed periodically through the Dean-Stark trap. The reaction product was then cooled, and the mixture was filtered to remove particles of caustic. After the solvent was stripped, a quantitative yield of 3-aminophenylacetylene (1.4 g) of greater than 98% purity as analyzed by gas chromatography was obtained: $n^{20}D$, 1.6186; NMR (CCl_4, Me_4Si) δ 3.0 (s, 1, C≡CH), 3.6 (s, 2, NH_2, exchanges with D_2O), and 6.3–7.2 (m, 4, ring).

Hydrogenation of (3-Nitrophenyl)acetylene Using a Homogeneous Catalyst. One gram of (3-nitrophenyl)acetylene in 130 mL of isopropyl alcohol–benzene (1/1) was hydrogenated in the Parr shaker in the presence of 0.15 g of dichlorotris(triphenylphosphine)-ruthenium(II) and one drop of triethylamine. After reacting for 16 h (25 °C, 50 psig H_2), the amber solution was analyzed by GLC. The products formed were identified as 3-nitrostyrene (94%) and 3-nitroethylbenzene (6%) at 42% substrate conversion.

Registry No.—2-Methyl-4-(3-nitrophenyl)-3-butyn-2-ol, 33432-52-9; ruthenium oxide, 12036-10-1; 2-methyl-4-(3-aminophenyl)-3-butyn-2-ol, 69088-96-6; acetone, 67-64-1; alumina, 1344-28-1; ruthenium chloride, 10049-08-8.

References and Notes

(1) N. Bilow, A. L. Landis, and L. J. Miller, U.S. Patent 3 845 018 (1974).
(2) R. F. Kovar and F. E. Arnold, U.S. Patent 3 975 444 (1976).
(3) A. Burawoy and J. P. Critchley, *Tetrahedron*, 340 (1959).
(4) P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals", Academic Press, New York, 1976, p 178.
(5) K. K. Kuzembaev, K. A. Zhubanov, and D. V. Sokol'skii, *Dokl. Vses. Konf. Khim. Atsetilena, 4th*, **3**, 235 (1972); *Chem. Abstr.*, **79**, 77771r (1963).
(6) K. A. Zhubanov, D. V. Sokol'skii, E. P. Mazin, and N. G. Krupenya, *Zh. Prikl. Khim. (Leningrad)*, **47**, 1885 (1974); *Chem. Abstr.*, **81**, 151684z (1974).
(7) G. F. Hennion and S. O. Barrett, *J. Am. Chem. Soc.*, **79**, 2146 (1957).
(8) C. Grob and E. Jenny, U.S. Patent 3 118 946 (1964).
(9) D. V. Sokol'skii, G. N. Sharifkanova, and N. F. Noskova, *Dokl. Akad. Nauk SSSR*, **194**, 599 (1970).
(10) Nitrobenzene and *p*-nitrotoluene were routinely used by us to test the activity of ruthenium catalysts.
(11) L. Fieser and M. Fieser, "Advanced Organic Chemistry", Reinhold, New York, 1961, p 235.
(12) E. T. Sabourin and C. M. Selwitz, U.S. Patent Application 840 553 (1978).
(13) D. Evans, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Nature (London)*, **208**, 1203 (1965).

Exploitation of Intramolecular Photochemical Arylation of N-Substituted Enaminones. Efficient, General Synthesis of Heterocyclic Compounds

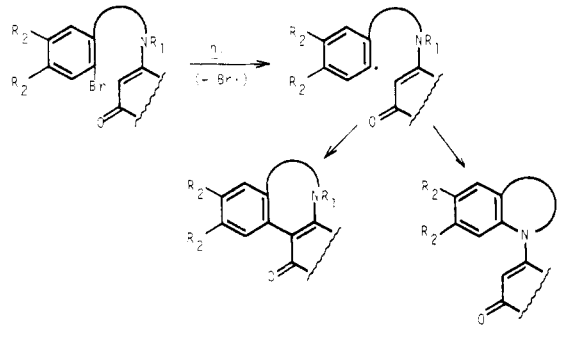
Hideo Iida, Yoshifumi Yuasa, and Chihiro Kibayashi*

Tokyo College of Pharmacy, Horinouchi, Hachioji, Tokyo 192-03, Japan

Received October 17, 1978

A general and facile photochemical method for the introduction of aryl groups into the enaminone system and its use in preparing heterocyclic compounds of varying ring sizes have been developed. Upon the photolysis of the *N*-phenyl (**3a, 3b,** and **5**), *N*-benzyl (**3c** and **7**), and *N*-phenethyl (**3d** and **9**) enaminones, intramolecular C-arylation proceeds to give the carbazoles (**4a, 4b,** and **6**), the phenanthridines (**9** and **10**), and the benzazepines (**12** and **13**), respectively. On the other hand, upon the photolysis of the *N*-phenethyl enaminone **15**, N-arylation occurs to give the indoline **18**. When the *N*-phenylpropyl enaminone **3e** is photolyzed, the benzazocine **22** and the tetrahydroquinoline **23** are obtained via competing process between C–C and C–N coupling, respectively. The applicability of this method to the synthesis of the naturally derived compound **28**, which is related to the lycorine alkaloids, is demonstrated.

Conjugated enamines such as enaminones are of current interest because of their unique characteristics different from those of both enamines and ketones with respect to physical properties and chemical behavior. The enaminone system, N—C=C—C=O, consists of three conjugated functional groups, i.e., amino, double bond, and carbonyl, and thus possesses five reaction sites. Despite the rather abundant literature on alkylation and acylation at these reaction sites, there appear to have been remarkably few reports of arylation, although such a process would be potentially useful.[1] We would like to report a photochemical method for the direct introduction of aryl groups into the enaminone system which provides a new, general synthesis of heterocyclic compounds with a variety of ring sizes. The reaction proceeds by a homolytic mechanism involving aryl radicals.



The required halo enaminones **3a–e** for photolysis were readily prepared by condensation of cyclic β-diketones **1** with appropriate primary amines **2** in fair to excellent yields (Table I). The structures of these products were determined by their analytical and spectral data (Table II).

Initial studies of photolysis of the halo enaminones so obtained were conducted with the *N*-phenyl derivatives **3a** and **3b** in dioxane–acetonitrile to afford the carbazoles **4a** and **4b** in 80 and 86% yield, respectively. Similar photolysis of the tertiary enaminone **5**, prepared by selective N-alkylation[2] with ethyl iodide and sodium hydride in toluene, gave the carbazole **6** in 64% yield.

The *N*-benzyl enaminone **3c** was next irradiated in dioxane–acetonitrile to give the phenanthridone **9** in 25% yield. When the tertiary enaminone **7**, prepared from **3c** by similar treatment with ethyl iodide described above for the preparation of **5**, was irradiated in dioxane, the diketo phenan-

0022-3263/79/1944-1236$01.00/0

Table I. Preparation of N-Substituted 3-Aminocyclohex-2-en-1-ones by Condensation of β-Diketones with Primary Amines

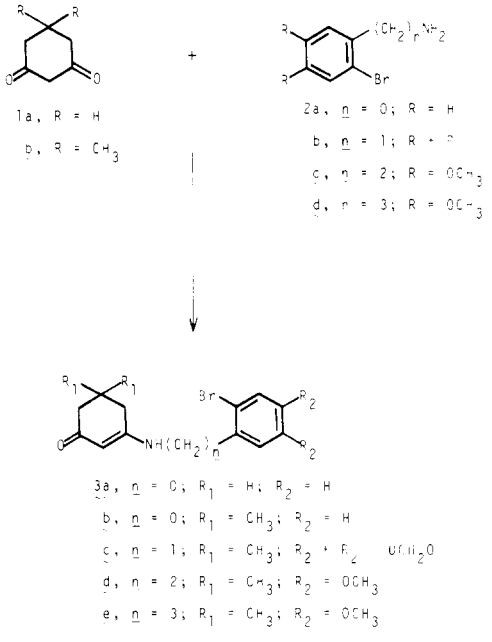
compd[a,d]	β-diketone[e]	primary amine[f]	method[b]	mp, °C	recrystn solvent	yield,[c] %
3a	**1a**	**2a**	A	167–168	acetone–hexane	80
3b	**1b**	**2a**	A	156–158	acetone–hexane	86
3c	**1b**	**2b**	B	223–224	ethanol	83
3d	**1b**	**2c**	B	167–168	acetone–hexane	81
3e	**1b**	**2d**	B	109–111	benzene–hexane	79

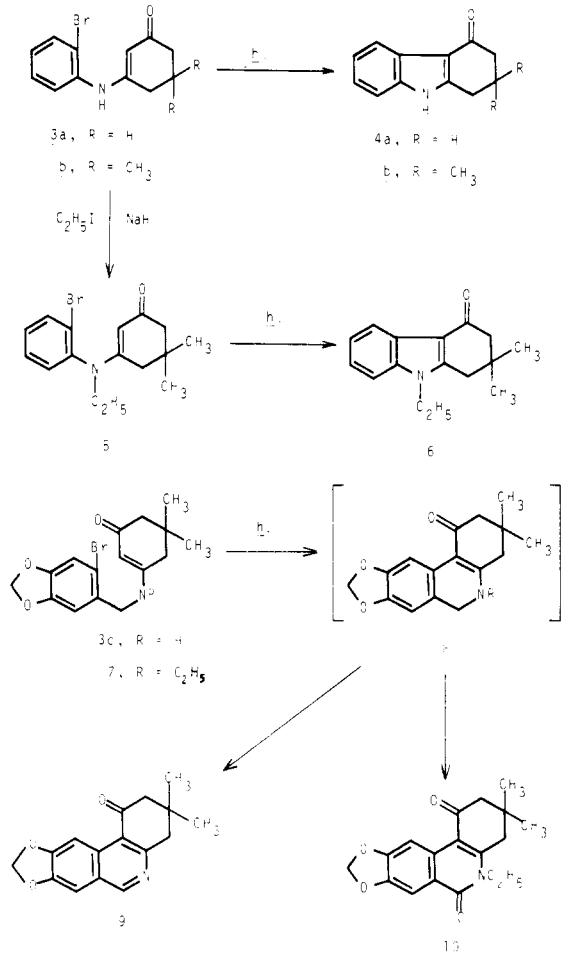
[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all compounds. [b] See Experimental Section. [c] Based on isolated yields after purification by recrystallization. [d] Registry no.: **3a,** 68890-19-7; **3b,** 68890-20-0; **3c,** 67496-30-4; **3d,** 68890-29-9; **3e,** 69089-11-8. [e] Registry no.: **1a,** 504-02-9; **1b,** 126-81-8. [f] Registry no.: **2a,** 615-36-1; **2b,** 67496-29-1; **2c,** 63375-81-5; **2d,** 69089-12-9.

Table II. IR and NMR Spectral Data for N-Substituted 3-Aminocyclohex-2-en-1-ones

	IR,[a] cm^{-1}			NMR,[b] δ			
compd	NH	C=O	C=C	vinylic H[c]	NH[d]	aromatic H	other
3a	3380	1620	1570	5.36	6.46	6.96–7.61 (m, 4 H)	1.86–2.92 (m, 6 H)
3b	3380	1620	1580	5.36	5.26	6.92–7.16 (m, 4 H)	1.17 (s, 6 H), 2.20 and 2.36 (each s, 2 H)
3c	3410	1605	1580	4.69	7.33	6.76 (s, 1 H, 6′-H), 7.06 (s, 1 H, 3′-H)	1.03 (s, 6 H), 2.00 and 2.26 (each s, 2 H), 4.15 (d, 2 H, J = 6 Hz), 6.00 (s, 2 H)
3d	3410	1610	1580	5.13	4.66	6.63 (s, 1 H, 6′-H), 6.96 (s, 1 H, 3′-H)	1.06 (s, 6 H), 2.15 (s, 4 H), 3.83 (s, 6 H)
3e	3400	1600	1575	5.09	4.92	6.66 (s, 1 H, 6′-H), 6.96 (s, 1 H, 3′-H)	1.06 (s, 6 H), 2.15 (s, 4 H), 3.84 (s, 6 H)

[a] All measurements in $CHCl_3$. [b] All measurements in $CDCl_3$ except for **3c** in $CDCl_3$–Me_2SO-d_6. [c] All signals appeared as singlets. [d] All signals appeared as broad singlets and disappeared by addition of D_2O.

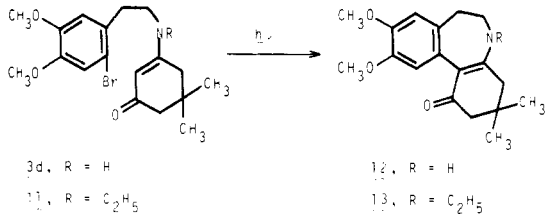




thridine **10** was obtained in lower yield (9.2%) as a main product along with the unchanged starting material and a mixture of unidentified photolysates. Both the cyclization products **9** and **10** may have arisen via oxidative aromatization of an initially formed intermediate **8**.

When photolysis was carried out on the *N*-phenethyl enaminone **3d**, intramolecular C-arylation proceeded more smoothly to give the benzazepine **12** in 91% yield. Similar photolysis of **11**, derived from **3d** via N-alkylation with ethyl iodide and sodium hydride, provided nearly quantitative yield of the benzazepine **13**.

In an anticipation of obtaining the benzazepine **19**, which can serve as a synthetic precursor of the alkaloid family of cephalotaxine **20**, the bromo enaminone **15** was prepared by reaction of cyclopentane-1,3-dione[3] with the phenethylamine **14** in the manner previously described for the preparation of **3**. On irradiation of **15**, however, photoreaction proceeded in a different fashion from that on the photolysis of the cyclo-

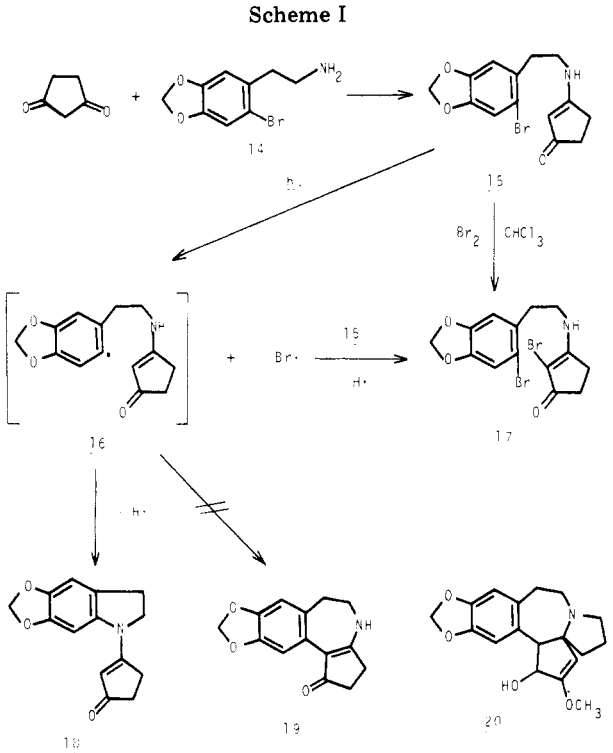


hexenone analogue **3d**; the initially formed aryl radical **16** cyclized via C–N coupling rather than C–C coupling, giving rise to the indoline **18**. On the other hand, the bromo radical generated from **15** was trapped by the starting enaminone **15** to give the dibromide **17** (Scheme I). To verify structure **17**, a sample of **17** was alternatively synthesized by treatment of **15** with bromine in chloroform and was directly compared with the photoproduct.

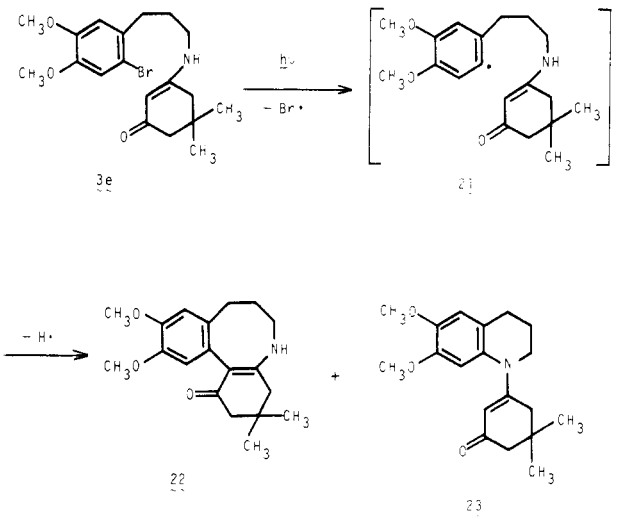
When the *N*-phenylpropyl enaminone **3e** was used as the substrate for photolysis, after free radical formation **3e** → **21**, arylation reaction occurred in competition between the α carbon and the nitrogen leading to the benzazocine **22** (37%) and the tetrahydroquinoline **23** (33%), respectively (Scheme II).[4]

An efficient method for the preparation of heterocyclic compounds via photochemical cyclization of the halo enaminones was thus established and we then considered the application of this procedure to the synthesis of a naturally derived compound related to the lycorine alkaloids. In search for a convenient synthesis of the required enaminones, the imino enol ether **24**,[5] which was prepared by the Birch reduction of 6-methoxyindoline according to our procedure previously reported, was allowed to react with the benzyl chloride **25a** in boiling toluene to give the desired enaminone **26a** (55%) along with a minor yield (3%) of the *C*-benzyl enaminone **27a**. Similar reaction of **24** with the benzyl chloride **25b** gave **26b** (50%) and **27b** (4%). Irradiation of the bromo enaminone **26a** in dioxane afforded the keto lactam **28** in 19% yield along with the photoreduction product **29** in 28% yield. Similarly, irradiation of the iodo enaminone **26b** gave **28** and **29** in 20 and 31% yield, respectively. Compound **28** is a degradation product derived from lycorine[6] or caranine[7] and has been converted into α-anhydrodihydrocaranine (**30**) and γ-lycorane (**31**) in our laboratory[5] as shown in Scheme III.

Scheme I



Scheme II



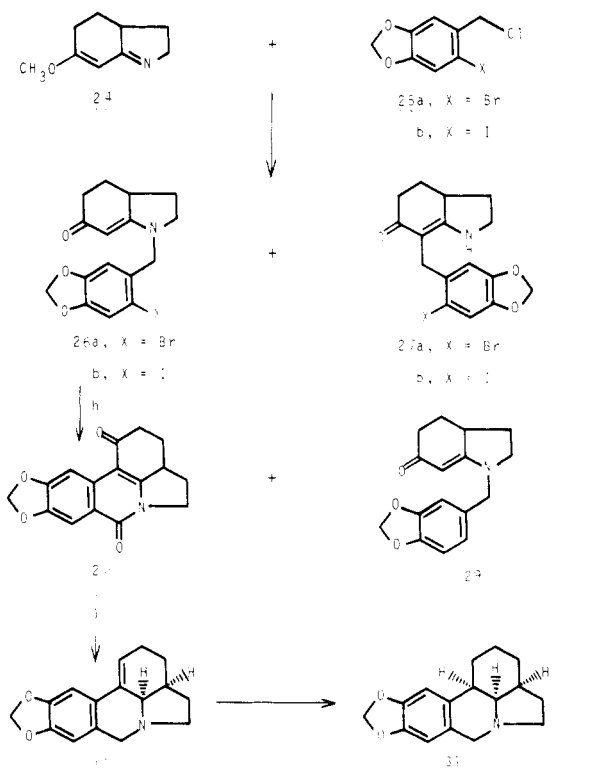
Experimental Section

Melting points were determined on a Yanagimoto micro apparatus and are uncorrected. IR spectra were taken on a Hitachi 215 grating spectrophotometer. NMR spectra were obtained from Varian T-60 and JOEL JNM-PS-100 spectrometers in $CDCl_3$ unless otherwise stated with $(CH_3)_4Si$ as internal standard. Mass spectra were determined using a Hitachi KMU-7L double-focusing spectrometer at 70 eV.

Photolysis experiments were performed in a Pyrex immersion well apparatus using a 100-W Ushio high-pressure mercury lamp.

General Procedure for the Preparation of N-Substituted 3-Aminocyclohex-2-en-1-ones (3a–e). Method A. A mixture of 14 mmol of cyclic β-diketone **1** and 14 mmol of *o*-bromoaniline was heated at 120–130 °C under nitrogen for 1 h. After cooling, the resulting yellow solid was crushed to a powder, washed with ether, then recrystallized from an appropriate solvent (Table I).

Scheme III



Method B. A mixture of 13 mmol of dimedone (**1b**) and 13 mmol of primary amine **2** in 50 mL of benzene was heated under reflux using a Dean-Stark trap for azeotropic removal of water for 2 h, and the solution was allowed to stand at room temperature for several hours. The crystals of the product were collected by filtration, washed with ether, and recrystallized from an appropriate solvent (Table I).

Photolysis of 3-(2-Bromoanilino)cyclohex-2-en-1-one (3a). A solution of 700 mg (2.6 mmol) of **3a** in 80 mL of dioxane–acetonitrile (30:10) containing 2 mL of triethylamine was irradiated for 70 h, at which time no starting material remained (TLC). After rotary evaporation of the solution, the residue was chromatographed on a silica gel column with chloroform to give the crystalline product. Further purification of this by recrystallization from chloroform–hexane gave 390 mg (80%) of 2,3-dihydrocarbazol-4(1*H*)-one (**4a**) as white prisms: mp 227–228 °C (lit.[8] mp 223 °C); IR ($CHCl_3$) 3430, 1635 cm^{-1}; NMR ($CDCl_3$–Me_2SO-d_6) δ 2.08–3.06 (m, 6 H, $CH_2CH_2CH_2$), 7.00–7.40 (m, 4 H, aromatic H), 8.05 (br s, 1 H, NH); MS *m/e* (rel intensity) 186 (M^+ + 1, 13), 185 (M^+, 84), 157 (100), 129 (70).

Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.46; H, 5.98; N, 7.12.

Photolysis of 3-(2-Bromoanilino)-5,5-dimethylcyclohex-2-en-1-one (3b). A solution of 500 mg (1.7 mmol) of **3a** in 80 mL of dioxane–acetonitrile (20:10) containing 2 mL of triethylamine was irradiated in the same manner as described above. Chromatography on a silica gel column and recrystallization from chloroform–hexane gave 310 mg (86%) of 2,3-dihydro-2,2-dimethylcarbazol-4(1*H*)-one (**4b**) as white prisms: mp 209–211 °C (lit.[9] mp 200–201.5 °C); IR ($CHCl_3$) 3430, 1630 cm^{-1}; NMR ($CDCl_3$) δ 1.13 (s, 6 H, 2 CH_3), 2.45 and 2.80 (each s, 2 H, CH_2), 7.13–7.32 (m, 4 H, aromatic H), 8.20 (s, 1 H, NH); MS *m/e* (rel intensity) 214 (M^+ + 1, 11), 213 (M^+, 65), 157 (100), 129 (53).

Anal. Calcd for $C_{14}H_{25}NO$: C, 78.84; H, 7.09; N, 6.56. Found: C, 78.55; H, 7.04; N, 6.11.

3-(2-Bromo-*N*-ethylanilino)-5,5-dimethylcyclohex-2-en-1-one (5). A mixture of 0.25 g (5.2 mmol) of NaH (50% dispersion in mineral oil) and 1.50 g (5.1 mmol) of **3b** in 80 mL of dry toluene was refluxed with stirring for 1 h and the mixture was allowed to cool to room temperature. To this 0.80 g (5.1 mmol) of ethyl iodide was added and the mixture was refluxed for 1 h. After quenching by addition of ice–water, the layers were separated. The aqueous layer was extracted with chloroform, and the combined extracts and organic layer were washed with water and dried ($MgSO_4$). The crude oil obtained on removal of the solvent by rotary evaporation was chromatographed on a silica gel column with chloroform to give 1.35 g (82%) of **5** as an oil: IR ($CHCl_3$) 1600 (C=O), 1545 cm^{-1} (C=C); NMR δ 1.02 (s, 6 H, 2 CH_3), 1.17 (t, 3 H, *J* = 7 Hz, NCH_2CH_3), 1.92 (br s, 2 H, 4-CH_2), 2.15 (s, 2 H, 6-CH_2), 3.55 (q, 2 H, *J* = 7 Hz, NCH_2CH_3), 5.30 (s, 1 H, vinylic H), 7.06–7.78 (m, 4 H, aromatic H); MS *m/e* (rel intensity) 323 (M^+ + 2, 35), 321 (M^+, 34), 306 (13), 293 (24), 242 (M^+ − Br, 100), 214 (25), 186 (26).

Exact mass, Calcd for $C_{16}H_{20}{}^{79}BrNO$: 321.0729. Found: 321.0747.

Photolysis of 3-(2-Bromo-*N*-ethylanilino)-5,5-dimethylcyclohex-2-en-1-one (5). A solution of 1.00 g (3.1 mmol) of **5** in 70 mL of dioxane–acetonitrile (20:10) containing 1 mL of triethylamine was irradiated for 46 h. Removal of the solvent by rotary evaporation and chromatography on a silica gel column with chloroform gave 480 mg (64%) of 9-ethyl-2,3-dihydro-2,2-dimethylcarbazol-4(1*H*)-one (**6**) as white prisms: mp 93–95 °C (from ether–hexane); IR ($CHCl_3$) 1630 (C=O), 1610 cm^{-1} (C=C); NMR δ 1.17 (s, 6 H, 2 CH_3), 1.36 (t, 3 H, *J* = 7 Hz, NCH_2CH_3), 2.40 and 2.73 (each s, 2 H, CH_2), 4.11 (q, 2 H, *J* = 7 Hz, NCH_2CH_3), 7.21–7.31 (m, 3 H, aromatic H), 8.20–8.33 (m, 1 H, aromatic H); MS *m/e* (rel intensity) 241 (M^+, 100), 185 (79), 157 (74), 129 (19).

Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.93; N, 5.80. Found: C, 79.73; H, 7.94; N, 5.82.

Photolysis of 3-(2-Bromo-4,5-methylenedioxybenzylamino)-5,5-dimethylcyclohex-2-en-1-one (3c). A solution of 1.20 g (3.7 mmol) of **3c** in 100 mL of dioxane–acetonitrile (10:10) containing 2 mL of triethylamine was irradiated for 120 h. Removal of the solvent by rotary evaporation and chromatography on a silica gel column with chloroform gave a solid which was recrystallized from acetone–hexane to give 230 mg (26%) of 3,4-dihydro-3,3-dimethyl-8,9-methylenedioxy-1(2*H*)-phenanthridone (**9**) as white prisms: mp 175–177 °C; IR ($CHCl_3$) 1660 cm^{-1} (C=O); NMR δ 1.13 (s, 6 H, 2 CH_3), 2.58 and 3.16 (each s, 2 H, CH_2), 6.05 (s, 2 H, OCH_2O), 7.06 (s, 1 H, 7-H), 8.73 (s, 1 H, 6-H), 8.86 (s, 1 H, 10-H); MS *m/e* (rel intensity) 270 (M^+ + 1, 19), 269 (M^+, 100), 213 (84), 185 (48).

Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.38; H, 5.54; N, 5.17.

3-[(2-Bromo-4,5-methylenedioxybenzyl)-*N*-ethylamino]-5,5-dimethylcyclohex-2-en-1-one (7). Reaction of 1.90 g (5.4 mmol) of **3c** with 0.50 g (1.0 mmol) of NaH (50% dispersion in mineral oil) and 0.85 g (5.4 mmol) of ethyl iodide was conducted in the same manner as in the preparation of **5** from **3b**. After usual workup, the crude product was recrystallized from acetone–ether to give 1.65 g (80%) of **7** as white prisms: mp 167–169 °C; IR ($CHCl_3$) 1610 (C=O), 1555 cm^{-1} (C=C); NMR δ 1.00 (s, 6 H, 2 CH_3), 1.10 (t, 3 H, *J* = 6 Hz, NCH_2CH_3), 2.07 and 2.20 (each s, 2 H, CH_2), 3.24 (q, 2 H, *J* = 6 Hz, NCH_2CH_3), 4.26 (s, 2 H, $PhCH_2$), 5.07 (s, 1 H, vinylic H), 5.84 (s, 2 H, OCH_2O), 6.35 (s, 1 H, 6′-H), 6.89 (s, 1 H, 3′-H); MS *m/e* (rel intensity) 381 (M^+ + 2, 5), 379 (M^+, 5), 300 (M^+ − Br, 100), 27 (37), 213 (49).

Anal. Calcd for $C_{16}H_{22}BrNO_3$: C, 56.85; H, 5.83; N, 3.68. Found: C, 56.91; H, 5.82; N, 3.50.

Photolysis of 3-[(2-Bromo-4,5-methylenedioxybenzyl)-*N*-ethylamino]-5,5-dimethylcyclohex-2-en-1-one (7). A solution of 330 mg (0.87 mmol) of **7** in 100 mL of dioxane containing 1 mL of triethylamine was irradiated for 160 h. After removal of the solvent by rotary evaporation, the residue was chromatographed on a silica gel column with chloroform. The major component included in the first fractions was further purified by preparative TLC on Merck precoated silica gel plates (chloroform), affording 25 mg (9.2%) of 5-ethyl-3,4-dihydro-3,3-dimethyl-8,9-methylenedioxy-2*H*-phenanthridine-1,6-dione (**9**) as pale yellow prisms: mp 212–214 °C (from acetone–hexane); IR ($CHCl_3$) 1715 and 1635 cm^{-1} (C=O); NMR δ 1.11 (s, 6 H, 2 CH_3), 1.24 (t, 3 H, *J* = 6 Hz, NCH_2CH_3), 2.82 and 2.44 (each s, 2 H, CH_2), 5.99 (s, 2 H, OCH_2O), 7.68 (s, 1 H, 7-H), 8.71 (s, 1 H, 10-H); MS *m/e* (rel intensity) 314 (M^+ + 1, 23), 313 (M^+, 74), 298 (100), 284 (69), 229 (87), 201 (68).

Exact mass. Calcd for $C_{18}H_{19}NO_4$: 313.1314. Found: 313.1312.

Further fractions obtained by above column chromatography gave the starting material unchanged (45 mg, 14%) and a mixture of unidentified products.

Photolysis of 3-[2-(2-Bromo-4,5-dimethoxyphenyl)ethylamino]-5,5-dimethylcyclohex-2-en-1-one (3d). A solution of 900 mg (2.4 mmol) of **3d** in 100 mL of dioxane–acetonitrile (50:10) containing 2 mL of triethylamine was irradiated for 125 h. After removal of the solvent, chromatography on a silica gel column with chloroform and recrystallization from chloroform–hexane gave 645 mg (91%) of 3,4,6,7-tetrahydro-3,3-dimethyl-9,10-dimethoxydibenz[*b,d*]azepin-1(2*H*,5*H*)-one (**12**) as white needles: mp 229–230 °C; IR ($CHCl_3$) 3420 (NH), 1615 (C=O), 1575 cm^{-1} (C=C); NMR δ 1.10 (s, 6 H, 2 CCH_3), 2.64 (br s, 4 H, 2 CH_2), 2.73–2.92 (m, 2 H, $PhCH_2$), 3.43–3.67 (m, 2 H, NCH_2), 3.83 (s, 6 H, 2 OCH_3), 4.83 (br s, 1 H, NH), 6.12 (s, 1 H, 8-H), 7.08 (s, 1 H, 11-H); MS *m/e* (rel intensity) 301 (M^+, 100), 286 (80), 255 (23), 217 (25).

Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.60; H, 7.83; N, 4.39.

3-[2-(2-Bromo-4,5-dimethoxyphenyl)-*N*-ethylethylamino]-5,5-dimethylcyclohex-2-en-1-one (11). Reaction of 760 mg (2.0 mmol) of **3d** with 70 mg (2.9 mmol) of NaH (50% dispersion in mineral oil) and 315 mg (2.0 mmol) of ethyl iodide was conducted in the same manner as in the preparation of **5** from **3b**, except that the reaction mixture was heated at 100 °C for 2 h. The product obtained by usual workup was then chromatographed on a silica gel column with chloroform to give 605 mg (74%) of **11** as an oil: IR ($CHCl_3$) 1610 (C=O), 1560 cm^{-1} (C=C); NMR δ 1.01 (s, 6 H, 2 CCH_3), 1.11 (t, 3 H, *J* = 7 Hz, NCH_2CH_3), 2.08 (s, 2 H, 6-CH_2), 2.18 (s, 1 H, 4-CH_2), 2.74–3.53 (m, 6 H, NCH_2CH_3 and CH_2CH_2), 3.82 (s, 6 H, 2 OCH_3), 5.17 (s, 1 H, vinylic H), 6.59 (s, 1 H, 6′-H), 6.91 (s, 1 H, 3′-H); MS *m/e* (rel intensity) 411 (M^+ + 2, 2), 409 (M^+, 2), 330 (M^+ − Br, 100), 242 (24).

Exact mass. Calcd for $C_{20}H_{28}{}^{79}BrNO_3$: 409.1252. Found: 409.1205.

Photolysis of 3-[2-(2-Bromo-4,5-dimethoxyphenyl)-*N*-ethylethylamino]-5,5-dimethylcyclohex-2-en-1-one (11). A solution of 200 mg (0.49 mmol) of **11** in 150 mL of acetonitrile containing 0.5 mL of triethylamine was irradiated for 44 h. Rotary evaporation of the solvent and chromatography on a silica gel column with chloroform gave 150 mg (93%) of 5-ethyl-3,4,5,6-tetrahydro-3,3-dimethyl-9,10-dimethoxydibenz[*b,d*]azepin-1(2*H*)-one (**13**) as an oil: NMR δ 1.15 (s, 6 H, 2 CCH_3), 1.16 (t, 3 H, *J* = 7 Hz, NCH_2CH_3), 2.35 (s, 2 H, 4-CH_2), 2.45 (s, 2 H, 2-CH_2), 2.73–2.89 (m, 2 H, $PhCH_2$), 3.25 (q, 2 H, *J* = 7 Hz, NCH_2CH_3), 3.56–3.73 (m, 2 H, NCH_2CH_2), 3.85 (s, 6 H, 2 OCH_3), 6.53 (s, 1 H, 8-H), 6.91 (s, 1 H, 11-H); MS *m/e* (rel intensity) 330 (M^+ + 1, 31), 329 (M^+, 100), 328 (M^+ − 1, 19), 314 (37), 286 (25), 143 (16).

Exact mass. Calcd for $C_{20}H_{27}NO_3$: 329.1991. Found: 329.1996.

3-[2-(2-Bromo-4,5-methylenedioxyphenyl)ethylamino]cyclopent-2-en-1-one (15). A mixture of 200 mg (2.0 mmol) of cyclopentane-1,3-dione and 500 mg (2.0 mmol) of 2-(2-bromo-4,5-meth-

ylenedioxyphenyl)ethylamine (**14**) in 20 mL of benzene was refluxed with azeotropic removal of water using a Dean-Stark trap for 4 h. The solution was allowed to stand at room temperature for several hours. The crystalline product was collected and recrystallized from ethanol to give 570 mg (86%) of **15** as white needles: mp 208–209 °C; IR ($CHCl_3$) 3400 (NH), 1650 (C=O), 1580 cm^{-1} (C=C); NMR ($CDCl_3$–Me_2SO-d_6) δ 2.23–3.34 (m, 8 H, 4 CH_2), 4.96 (s, 1 H, vinylic H), 5.92 (s, 2 H, OCH_2O), 6.69 (s, 1 H, 6′-H), 6.94 (s, 1 H, 3′-H); MS *m/e* (rel intensity) 325 (M^+ + 2, 2), 324 (M^+ + 1, 2), 323 (M^+, 2), 322 (M^+ − 1, 2), 244 (M^+ − Br, 100), 213 (17), 110 (100).

Anal. Calcd for $C_{14}H_{14}BrNO_3$: C, 51.87; H, 4.35; N, 4.32. Found: C, 52.16; H, 4.32; N. 4.44.

Photolysis of 3-[2-(2-Bromo-4,5-methylenedioxyphenyl)-ethylamino]cyclopent-2-en-1-one (15). A solution of 700 mg (2.2 mmol) of **15** in 300 mL of acetonitrile containing 1 mL of triethylamine was irradiated for 10 days. After removal of the solvent, the residue was chromatographed on a silica gel column. First elution gave 35 mg (4.0%) of 2-bromo-3-[2-(2-bromo-4,5-methylenedioxyphenyl)ethylamino]cyclopent-2-en-1-one (**17**). This sample (mp 194–196 °C dec) was identical with that prepared by bromination of **15** (vide infra).

Second elution gave 150 mg (29%) of 2,3-dihydro-5,6-methylenedioxy-1-(3-oxycyclopent-1-en-1-yl)indole (**18**) as white prisms: mp 243–246 °C dec (from chloroform–hexane); IR ($CHCl_3$) 1650 (C=O), 1545 cm^{-1} (C=C); NMR δ 2.44 (t, 2 H, J = 6 Hz, 5′-H_2), 2.98 (t, 2 H, J = 6 Hz, 4′-H_2), 3.10 (t, 2 H, J = 6 Hz, 3-H_2), 3.92 (t, 2 H, J = 6 Hz, 2-H_2), 5.20 (s, 1 H, vinylic H), 5.86 (s, 2 H, OCH_2O), 6.61 (s, 1 H, 4-H), 6.72 (s, 1 H, 7-H); MS *m/e* (rel intensity) 244 (M^+ + 1, 15), 243 (M^+, 100), 242 (M^+ − 1, 30), 214 (10).

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.03; H, 5.36; N, 5.83.

Further elution gave 280 mg (40%) of the starting material recovered.

Bromination of 3-[2-(2-Bromo-4,5-methylenedioxyphenyl)-ethylamino]cyclopent-2-en-1-one (15). To a stirred solution of 450 mg (1.39 mmol) of **15** in 10 mL of chloroform was added dropwise a solution of 230 mg (1.44 mmol) of bromine in 5 mL of chloroform upon cooling. The mixture was stirred at room temperature for 2 h, washed with 5% K_2CO_3 and water, and dried ($MgSO_4$). After removal of the solvent, the residue was chromatographed on a silica gel column with chloroform to give a solid which was recrystallized from chloroform–hexane to give 185 mg (33%) of 2-bromo-3-[2-(2-bromo-4,5-methylenedioxyphenyl)ethylamino]cyclopent-2-en-1-one (**17**): mp 194–196 °C dec (from chloroform–acetone–hexane); IR ($CHCl_3$) 3360 (NH), 1675 (C=O), 1590 cm^{-1} (C=C); NMR δ 5.88 (s, 2 H, OCH_2O), 6.58 (s, 1 H, 6′-H), 6.96 (s, 1 H, 3′-H); MS *m/e* (rel intensity) 405 (M^+ + 4, 4), 403 (M^+ + 2, 9), 401 (M^+, 5), 322 (M^+ − Br, 9), 243 (M^+ − 2 Br, 41), 213 (35), 188 (100).

Anal. Calcd for $C_{14}H_{13}Br_2NO_3$: C, 41.72; H, 3.25; N, 3.47. Found: C, 42.06; H, 3.36; N, 3.41.

Photolysis of 3-[3-(2-Bromo-4,5-dimethoxyphenyl)propylamino]-5,5-dimethylcyclohex-2-en-1-one (3e). A solution of 300 mg (0.71 mmol) of **3e** in 100 mL of acetonitrile containing 1 mL of triethylamine was irradiated for 10 days. After removal of the solvent, the residue was chromatographed on a silica gel column with chloroform. The first fractions contained 80 mg (33%) of 2,3-dihydro-6,7-dimethoxy-1-(5,5-dimethyl-3-oxocyclohex-1-en-1-yl)quinoline (**23**) as pale yellow prisms: mp 118–120 °C (from acetone–hexane); IR ($CHCl_3$) 1605 (C=O), 1545 cm^{-1} (C=C); NMR δ 1.00 (s, 6 H, 2 CCH_3), 1.84 (t, 2 H, J = 6 Hz, $PhCH_2CH_2$), 2.13 (s, 2 H, 6′-H_2), 2.31 (s, 2 H, 4′-H_2), 2.53 (t, 2 H, J = 6 Hz, $PhCH_2$), 3.46 (t, 2 H, J = 6 Hz, NCH_2), 3.42 and 3.44 (each s, 3 H, OCH_3), 5.43 (s, 1 H, vinylic H), 6.45 (s, 1 H, 5-H), 6.54 (s, 1 H, 8-H); MS *m/e* (rel intensity) 316 (M^+ + 1, 12), 315 (M^+, 33), 293 (24), 233 (22), 215 (48), 165 (100).

Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.35; H, 7.99; N, 4.44. Found: C, 72.06; H, 8.16; N, 4.53.

The second fractions contained 90 mg (37%) of 3,4,5,6,7,8-hexahydro-10,11-dimethoxy-3,3-dimethyldibenz[*b*,*d*]azocin-1(2*H*)-one (**22**) as white prisms: mp 231–233 °C (from chloroform); IR ($CHCl_3$) 3420 (NH), 1605 (C=O), 1575 cm^{-1} (C=C); NMR δ 1.12 (s, 6 H, 2 CCH_3), 2.28 (br s, 4 H, 2-CH_2 and 4-CH_2), 3.84 (s, 6 H, 2 OCH_3), 6.49 (s, 1 H, 9-H), 6.74 (s, 1 H, 12-H); MS *m/e* (rel intensity) 316 (M^+ + 1, 44), 315 (M^+, 100), 300 (35), 286 (23), 259 (17), 244 (17), 216 (15), 143 (35).

Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.35; H, 7.99; N, 4.44. Found: C, 72.60; H, 7.97; N, 4.38.

1-(2-Bromo-4,5-methylenedioxybenzyl)-1,2,3,3a,4,5-hexahydro-6*H*-indol-6-one (26a). A mixture of 1.51 g (10 mmol) of **24** and 2.50 g (10 mmol) of **25a** in 60 mL of dry toluene was refluxed for 10 h. After removal of the solvent by rotary evaporation, the residue was carefully chromatographed on a silica gel column with chloroform. First elution gave 90 mg (3%) of 7-(2-bromo-4,5-methylenedioxybenzyl)-1,2,3,3a,4,5-hexahydro-6*H*-indol-6-one (**27a**) as white needles: mp 201–202 °C (from benzene–hexane); IR ($CHCl_3$) 3380 (NH), 1625 (C=O), 1570 cm^{-1} (C=C); NMR δ 3.59 (d, 2 H, J = 2 Hz, $PhCH_2$), 5.23 (br s, 1 H, NH), 5.81 (s, 2 H, OCH_2O), 6.70 (s, 1 H, 6′-H), 6.81 (s, 1 H, 3′-H); MS *m/e* (rel intensity) 351 (M^+ + 2, 2), 349 (M^+, 2), 270 (M^+ − Br, 100), 213 (54), 135 (32).

Anal. Calcd for $C_{16}H_{16}BrNO_3$: C, 54.87; H, 4.60; N, 3.99. Found: C, 54.80; H, 4.57; N, 4.05.

Continued elution gave 1.93 g (55%) of **26a** as white needles: mp 157–158 °C (from chloroform–hexane); IR ($CHCl_3$) 1605 (C=O), 1580 cm^{-1} (C=C); NMR δ 4.40 (s, 2 H, $PhCH_2$), 5.10 (s, 1 H, vinylic H), 5.98 (s, 2 H, OCH_2O), 6.59 (s, 1 H, 6′-H), 7.02 (s, 1 H, 3′-H); MS *m/e* (rel intensity) 351 (M^+ + 2, 9), 349 (M^+, 10), 270 (M^+ − Br, 100), 242 (47), 213 (68).

Anal. Calcd for $C_{16}H_{16}BrNO_3$: C, 54.87; H, 4.60; N, 3.99. Found: C, 54.66; H, 4.52; N, 3.82.

1-(Iodo-4,5-methylenedioxybenzyl)-1,2,3,3a,4,5-hexahydro-6*H*-indol-6-one (26b). Reaction of **24** (1.51 g, 1.0 mmol) with **25b** (2.97 g, 1.0 mmol) was conducted in the same manner as described above. Workup and column chromatography (silica gel, chloroform) gave 7-(2-iodo-4,5-methylenedioxybenzyl)-1,2,3,3a,4,5-hexahydro-6*H*-indol-6-one (**27b**, 0.15 g, 4%) as the first component: mp 209–211 °C (from chloroform–hexane); IR ($CHCl_3$) 3370 (NH), 1620 (C=O), 1575 cm^{-1} (C=C); NMR δ 3.52 (d, 2 H, J = 2 Hz, $PhCH_2$), 5.10 (br s, 1 H, NH), 5.86 (s, 2 H, OCH_2O), 6.66 (s, 1 H, 6′-H), 7.13 (s, 1 H, 3′-H); MS *m/e* (rel intensity) 399 (M^+ + 2, 1), 397 (M^+, 1), 270 (M^+ − I, 100), 212 (31), 135 (48).

Anal. Calcd for $C_{16}H_{16}INO_3$: C, 48.38; H, 4.06; N, 3.52. Found: C, 48.43; H, 4.05; N, 3.57.

The major product **26b** (2.00 g, 50%) was then obtained as the second component: mp 173–174 °C (from chloroform–hexane); IR ($CHCl_3$) 1605 (C=O), 1580 cm^{-1} (C=C); NMR δ 4.39 (s, 2 H, $PhCH_2$), 5.09 (s, 1 H, vinylic H), 5.96 (s, 2 H, OCH_2O), 6.86 (s, 1 H, 6-H), 7.26 (s, 1 H, 3′-H); MS *m/e* (rel intensity) 397 (M^+, 2), 270 (M^+ − I, 100), 261 (48), 135 (63).

Anal. Calcd for $C_{16}H_{16}INO_3$: C, 48.42; H, 4.06; N, 3.28. Found: C, 48.38; H, 4.06; N, 3.52.

Photolysis of 1-(2-Bromo-4,5-methylenedioxybenzyl)-1,2,3,3a,4,5-hexahydro-6*H*-indol-6-one (26a). A solution of 500 mg (1.43 mmol) of **26a** in 150 mL of dioxane containing 1 mL of triethylamine was irradiated for 125 h. Removal of the solvent by rotary evaporation followed by column chromatography on silica gel with chloroform–benzene (50:50) gave two fractions. The component included in the first fraction was further purified by preparative TLC on Merck precoated silica gel plates [solvent system: chloroform–methanol (20:1)] to yield 77 mg (19%) of 3,3a,4,5-tetrahydro-9,10-methylenedioxypyrrolo[3,2,1-*de*]phenanthridine-1,7(2*H*)-dione (**28**) as white plates: mp 252–253 °C (from chloroform–hexane) (lit. mp 249–250 °C,[6] 251.5–253 °C,[7] 252–253 °C[5]). The IR and NMR spectra of this product were identical with those of an authentic sample.[5]

The second fraction contained 110 mg (28%) of 1-(3,4-methylenedioxybenzyl)-1,2,3,3a,4,5-hexahydro-6*H*-indol-6-one (**29**) as white prisms: mp 148–149 °C (from chloroform–hexane); IR ($CHCl_3$) 1610 (C=O), 1575 cm^{-1} (C=C); NMR δ 4.25 (s, 2 H, $PhCH_2$), 5.18 (s, 1 H, vinylic H), 5.98 (s, 2 H, OCH_2O), 6.63–6.70 (m, 3 H, aromatic H); MS *m/e* (rel intensity) 271 (M^+, 100), 243 (24), 215 (14), 135 (60).

Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.31; N, 5.16. Found: C, 70.84; H, 6.28; N, 4.97.

Photolysis of 1-(2-Iodo-4,5-methylenedioxybenzyl)-1,2,3,3a,4,5-hexahydro-6*H*-indol-6-one (26b). A solution of 500 mg (1.27 mmol) of **26b** in 150 mL of dioxane containing 1 mL of triethylamine was irradiated for 160 h. Essentially analogous workup as described above furnished 70 mg (20%) of **28** and 105 mg (31%) of **29**.

Registry No.—**4a**, 15128-52-6; **4b**, 40429-04-7; **5**, 69083-41-6; **6**, 69083-42-7; **7**, 67496-31-5; **9**, 67496-33-7; **10**, 69089-13-0; **11**, 68890-31-3; **12**, 69083-43-8; **13**, 69083-44-9; **14**, 63375-82-6; **15**, 69089-14-1; **17**, 69089-15-2; **18**, 69089-16-3; **22**, 69120-33-8; **23**, 69089-17-4; **24**, 59601-27-3; **25a**, 64603-67-4; **25b**, 65673-83-8; **26a**, 65673-79-2; **26b**, 65673-80-5; **27a**, 68890-37-9; **27b**, 68890-38-0; **28**, 69089-18-5; **29**, 65673-77-0; cyclopentane-1,3-dione, 3859-41-4.

References and Notes

(1) For reviews, see (a) T. Nishio, C. Kajima, and Y. Omote, *J. Synth. Org. Chem. Jpn.*, **34**, 526 (1976); (b) J. B. Greenhill, *Chem. Soc. Rev.*, **6**, 277 (1977).

(2) On electrophilic alkylation of primary or secondary enaminones, they are capable of leading to a wide variety of products such as N-, O-, and C-alkylated derivatives including those produced by α-, α'-, and γ-alkylation. The reaction conditions which determine where alkylation takes place may

be associated with the nature of the enaminone and the selection of the alkylating agent, the basic catalyst, and the solvent.

(3) F. Merényi and M. Nilson, *Org. Synth.*, **52**, 1 (1972).

(4) As to some of the variations in photochemical behavior observed in the present work (e.g., C–C vs. C–N coupling), a reviewer has suggested the possibility that they are due to solvent effects. In our experiments, all the photochemical reactions have been conducted in the presence of an excess of triethylamine, and, except in the case of **7**, **26a**, and **26b**, acetonitrile has been used as such or with dioxane as the solvent. The selection of the solvent has depended on the solubility of the substrates. Thus these photolyses should be regarded to have been conducted essentially in the same solvent system. Although a solvent effect has not been ruled out, we feel that the differences in the course of the cyclizations are due to structural differences in the substrates and not variations in solvent composition.

(5) H. Iida, S. Aoyagi, and C. Kibayashi, *J. Chem. Soc.*, 2502 (1975).

(6) K. Takeda and K. Kotera, *Chem. Pharm. Bull.*, **5**, 234 (1957).

(7) E. W. Warnhoff and W. C. Wildman, *J. Am. Chem. Soc.*, **79**, 2192 (1957).

(8) G. R. Clemo and D. G. I. Felton, *J. Chem. Soc.*, 700 (1951).

(9) R. F. Borch and R. G. Newell, *J. Org. Chem.*, **38**, 2729 (1973).

Structures and Chromotropic Properties of 1,4-Bis(4,5-diphenylimidazol-2-yl)benzene Derivatives

Yoshiko Sakaino

Department of Chemistry, Faculty of Education, Gunma University, Maebashi 371, Japan

Hiroshi Kakisawa* and Takenori Kusumi

Department of Chemistry, University of Tsukuba, Ibaraki 300-31, Japan

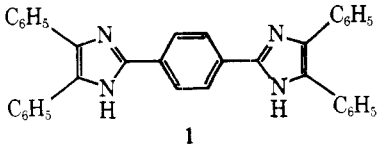
Koko Maeda

Department of Chemistry, Ochanomizu University, Otsuka, Tokyo 113, Japan

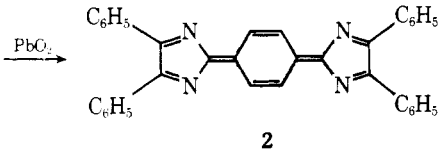
Received July 11, 1978

Three new imidazolyl derivatives (**5**–**7**) were prepared by ferricyanide oxidation of 1,4-bis(4,5-diphenylimidazol-2-yl)benzene (**1**). Base-catalyzed addition of ethanol to 3,6-bis(4,5-diphenyl-2*H*-imidazol-2-idene)-1,4-cyclohexadiene also afforded the compound **5**. The structure of diethoxy compound (**6**) was assigned 1,4-bis[4,4′-diethoxy-4,5-diphenyl-2(4*H*)-imidazolyl]benzene. The compound **7** was determined to be a dimer of the 4-ethoxyimidazolyl radical **10** produced by oxidation of **5**. Irradiation of **5** with UV light results in the formation of the starting quinonoid compound **2**, as indicated by its deep blue color. Diethoxy compound **6** was not affected by the light. Dimeric compound **7** shows chromotropism caused by radical dissociation of the dimer during irradiation, heating, or grinding.

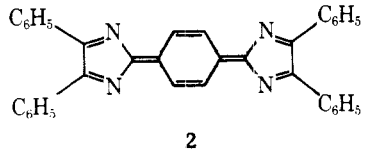
Zimmermann and co-workers prepared 3,6-bis(4,5-diphenylimidazol-2-yden)-1,4-cyclohexadiene (**2**) by bromine oxidation of the sodium salt of 1,4-bis(4,5-diphenylimidazoly-2-yl)benzene (**1**).[1] We also obtained the same quinonoid compound **2** by lead dioxide oxidation of **1** or ferricyanide oxidation of the potassium salt of **1** and reported that the



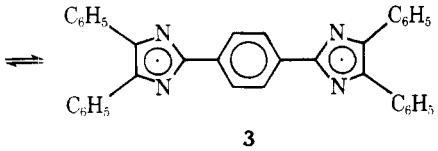
1



2



2



3

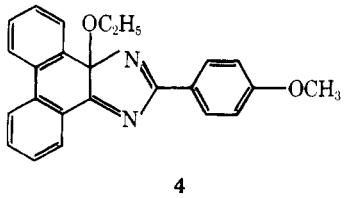
quinonoid compound **2** isomerizes on heating to a biradical (**3**), which reverses to the original quinone (**2**) on cooling.[2]

Whereas ferricyanide oxidation of bis(imidazolyl)benzene **1** in dioxane had afforded the quinonoid compound **2** as sole product, the same oxidation in an ethanolic potassium hydroxide solution gave a complex mixture, from which three new compounds were obtained. These compounds showed remarkable photo- and thermochromisms. We wish to report the results of structural and chromotropic studies on these compounds.

Results and Discussion

When an aqueous potassium ferricyanide solution was added to bis(imidazolyl)benzene **1** in an ethanolic potassium hydroxide solution at 5 °C, a purple color appeared at first, and a pale yellow precipitate gradually separated. The precipitate showed many spots on TLC, and three new compounds, **5**, **6**, and **7**, were isolated in a pure state. Although this reaction afforded **5** and **7** as the major products besides a minor amount of **6**, the same reaction carried out in an oxygen atmosphere yielded compound **6** as a main product.

Elemental analysis and the mass spectrum (*m/e* 558) of compound **5** gave the molecular formula $C_{34}H_{30}N_4O$, indicating the incorporation of one ethoxy group into compound **2**. The NMR spectrum of **5** exhibited a triplet at 1.22 (J = 7 Hz) for the methyl protons and a multiplet (XY part of A_3XY spectrum) centered at 3.45 ppm for the methylene protons.



4

0022-3263/79/1944-1241$01.00/0