A PHOTOCHEMICAL SYNTHESIS OF BENZ[*d*]INDENO[1,2-*b*]AZEPINES

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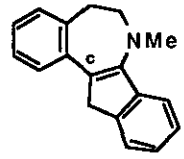
Abstract - A novel synthesis of benz[*d*]indeno[1,2-*b*]azepine (**10**) has been achieved by photochemical cyclization of the bromo enaminone (**8**). On the other hand, irradiation of enolates and enamides failed to give the cyclized azepines.

The benz[*d*]indeno[1,2-*b*]azepine system (**1**) constitutes the basic nucleus of the indenobenzazepine alkaloids isolated from *Fumaria* plants, which are probably biogenetically related to spirobenzylisoquinolines[1] and are important key intermediates for the total synthesis of rhoeadine- and protopine-type alkaloids.[2] Because of their structural relationship with 3-benzazepines, they are also of interest from a medicinal viewpoint.[3]

Our interest in these alkaloids[4] has led us to investigate their synthesis by a route in which the key step is the formation of bond **c** of the azepine ring by photochemically promoted cyclization of a suitable arylbromide. It is known that aryl halides can undergo efficient homolytic carbon-halogen bond fission on irradiation, and the aryl radical so formed is susceptible to nucleophilic attack; this mechanism gives the same overall transformation as nucleophilic aromatic substitution but does not rely on electron-deficient aromatic rings.[5]



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This paper is dedicated to Prof. Arnold Brossi on the occasion of his 65th birthday.

In this work we have investigated the photochemical cyclization of three different precursors (**6**, **7** and **8**), the nucleophilic components, a ketone enolate, an enamide and an enaminone, respectively.

RESULTS AND DISCUSSION

It is known that aryl halides react with enolates under irradiation in liquid ammonia by a radical chain mechanism initiated by transfer of an electron to the aryl halide.[6] The first intramolecular example of this photo-$S_{RN}1$ process was reported in an efficient ring closure constituting the key step in the synthesis of cephalotaxine.[7] The success of this reaction led us to initiate the present study using bromo ketones (**6**).

We initially attempted the intramolecular photoarylation of bromo amino ketone (**6b**), which was obtained by condensation of bromophenethylamine (**2b**) with indenone (**3**). Unfortunately **6b** was not soluble in liquid ammonia, so we used DMSO and KO^{t}Bu (7 eq.) to generate the ketone enolate. Upon external irradiation (Pyrex filter) of this solution with a 450W medium-pressure mercury arc for 4 h at room temperature, the solution turned faintly brown. After conventional work-up the main product was isolated as the indoline (**9**) in 42% yield. This compound arises from preferential formation of a five membered ring *via* nucleophilic attack by the nitrogen on the aryl ring, a result which has precedents in related systems.[8]

The above result led us to introduce *N*-protecting groups. The amide (**6c**) and urethane (**6d**) were prepared from amine (**6a**), but their photochemical irradiation gave an intractable mixture of products in both cases.

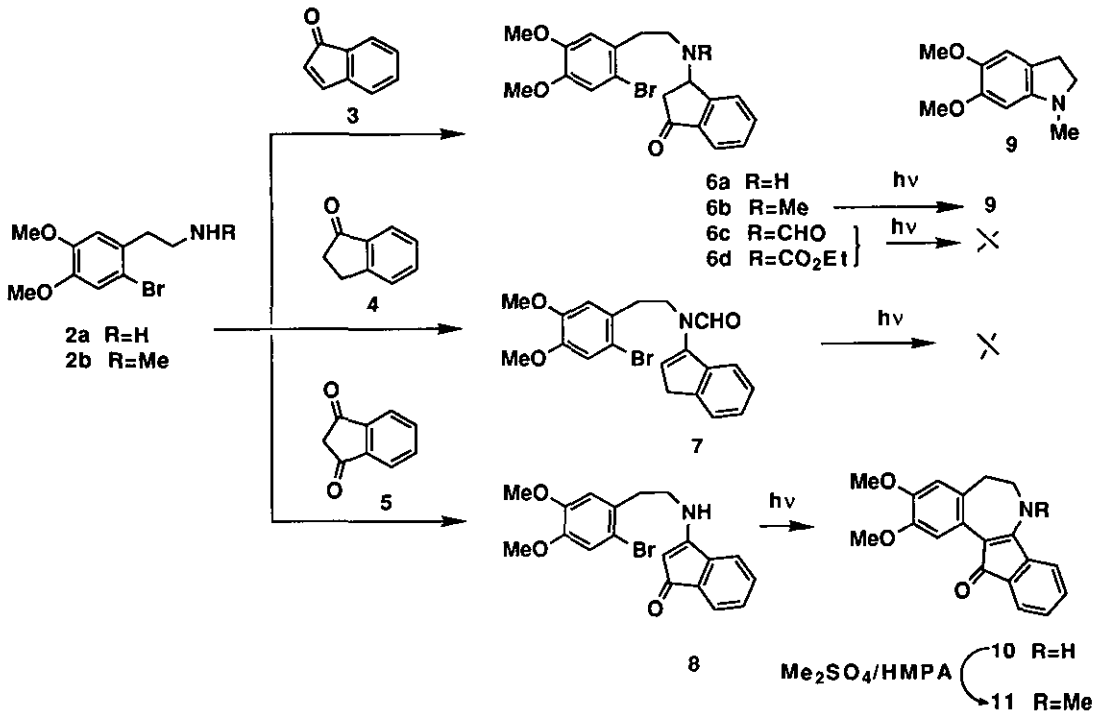
We then turned our attention to the photocyclization of the enamide system (**7**). The intramolecular photoarylation of enamides to give azaheterocycles has been extensively studied,[9] particularly in the field of benzazepine synthesis.[10] Yields are usually low. Formamide (**7**) was prepared by condensing the bromophenethylamine (**2a**) with indanone (**4**), followed by treatment of the crude imine with formic-acetic anhydride (75% overall yield). However, irradiation of **7** under Vycor- or Pyrex-filtered light in various solvents (dioxane, benzene, acetonitrile) in the presence of triethylamine led to an intractable mixture of unindentified products. By contrast, treatment of compound (**7**) with tributyltin hydride and AIBN in refluxing benzene afforded the corresponding indenobenzazepine in high yield.[4]

The next alternative considered as a candidate for photocyclization was an enaminone. The chemical behavior of enaminones differs significantly from that of both enamines and ketones; in particular, intramolecular photoarylation of enaminones has been reported to give good yields of cyclized products.[11]

We therefore prepared the known *N*-phenethylenaminone (**8**) by reaction of the 1,3-indandione (**5**) with bromophenethylamine (**2a**).[12] Upon irradiation of (**8**) in degassed *p*-dioxane containing triethylamine using a 450W medium-pressure mercury lamp at room temperature, the indenobenzazepine (**10**) was produced in 55 % yield. The presence of the azepine ring in (**10**) was confirmed by its nmr spectrum, which showed the

disappearance of the vinylic proton. In addition, one of two aromatic proton singlets (δ 6.59 and 8.09 ppm) was shifted considerably downfield, indicating that the C1 proton lies in close proximity to the carbonyl group in the cyclized product. Finally, the *N*-methyl derivative (**11**) was obtained in 90 % yield by reaction of the indenobenzazepine (**10**) with Me_2SO_4/HMPA.

In conclusion, we have shown that the indenobenzazepine system can be prepared in acceptable yield by photocyclization of the corresponding bromo enaminone precursor.



EXPERIMENTAL SECTION

Microanalyses were performed by Microanalysis Service of the University of Santiago de Compostela. Melting points were determined on a Kofler apparatus and are uncorrected. Mass spectra (ms) were obtained on a Hewlett-Packard HP-59970 spectrometer, and high resolution mass spectra (HRms) on a Kratos MS-50 spectrometer. Proton magnetic resonance and carbon-13 magnetic resonance spectra were recorded with a Bruker WM-250 spectrometer at 250 MHz (^{1}H nmr) and 62.83 MHz (^{13}C nmr) using $CDCl_3$ as solvent and TMS as internal standard. Infrared (ir) spectra were recorded with a Perkin Elmer 1420 spectrophotometer and ultraviolet (uv) spectra on a Hewlett Packard 8452 A spectrophotometer. Thin layer chromatography (tlc) was performed using Merck GF-254 type 60 silica gel and dichloromethane-methanol mixtures as eluant; the tlc

spots were visualized with UV light or iodine vapor. Column chromatography was carried out using Merck type 9385 silica gel. Solvents were purified by standard procedures.[13]

Photolysis experiments were performed using a 450W Hanovia medium-pressure mercury lamp at room temperature.

β-(2-Bromo-4,5-dimethoxyphenyl)ethylamine (2a)

To a stirred solution of homoveratrylamine hydrochloride (10 g, 45.97 mmol) in 50 ml of acetic acid kept at room temperature, 15 g of bromine (93.75 mmol) was added dropwise over 30 min and the mixture was stirred for 2 h. The reaction mixture was poured into water (100 ml), a saturated solution of sodium thiosulfate (25 ml) was added and the mixture was basified to pH > 10 with 20% sodium hydroxide solution and extracted with dichloromethane (3 x 50 ml). The organic extracts were dried over anhydrous sodium sulfate and concentrated *in vacuo* to give 11 g (92 %) of a pale yellow oil of **2a**.[14] ^{1}H Nmr ($CDCl_3$): δ 7.01 (s, 1H, Ar-H), 6.73 (s, 1H, Ar-H), 3.84 (s, 3H, -OCH_3), 3.83 (s, 3H, -OCH_3), 2.96-2.91 (m, 2H, -CH_2-), 2.83-2.77 (m, 2H, -CH_2-).

β-(2-Bromo-4,5-dimethoxyphenyl)-N-methylethylamine (2b)

β-(2-Bromo-4,5-dimethoxyphenyl)ethylamine (**2a**, 1.3 g, 5 mmol) was dissolved in dry toluene (25 ml) containing benzaldehyde (0.51 ml, 5 mmol). The resulting mixture was refluxed for 4 h with azeotropic removal of the water formed. Without any purification, the imine intermediate obtained was heated at 90 °C for 8 h with dimethyl sulfate (0.35 ml, 5 mmol). After cooling, the mixture was stirred at room temperature for 1 h with 10% hydrochloric acid solution (15 ml). The aqueous solution was washed with dichloromethane (2 x 25 ml), basified to pH>10 with 10% sodium hydroxide solution and extracted several times with dichloromethane. The organic layer was dried over anhydrous sodium sulfate and concentrated *in vacuo*, yielding 0.77 g (60 %) of pure **2b** as a white oil; mp (hydrochloride): 151-153 °C (EtOH-ethyl acetate-ether) (lit.,[15] 152-153 °C).

N-[β-(2-Bromo-4,5-dimethoxyphenyl)ethyl]-3-amino-1-indanone (6a)

A solution of 0.2 g (1.54 mmol) of indenone (**3**) (prepared by the published procedure[16]) and 0.8 g (3.08 mmol) of bromophenethylamine (**2a**) in 50 ml of CCl_4 was heated at 60 °C for 18 h with stirring. After evaporation of solvent, the residue was taken up in 20 ml of 1N hydrochloric acid solution. The aqueous solution was washed with ether, neutralized with saturated sodium bicarbonate solution and extracted several times with ether. Drying and concentration of the organic extracts gave a residue which was purified by column chromatography on silica gel (eluant: 98/2 dichloromethane/methanol), yielding 0.36 g (60%) of pure **6a** as a brown oil; ir (ν, cm^{-1}, film): 3680 (N-H), 1710 (C=O), ^{1}H Nmr ($CDCl_3$): δ 7.75-7.41 (m 4H, Ar-H), 7.00 (s, 1H, Ar-H), 6.75 (s, 1H, Ar-H), 4.50 (dd, 1H, J= 6.7 and 3.1 Hz, H-3), 3.85 (s, 3H,-OCH_3), 3.83 (s, 3H,-OCH_3), 3.03-2.88 (m,

5H, 2 x -CH_2- and H-2), 2.50 (dd, 1H, J= 8.7 and 3.1 Hz, H-2'); ^{13}C Nmr ($CDCl_3$): δ 204.5 (C=O), 155.8 (C), 148.6 (C), 148.4 (C), 136.9 (C), 134.9 (CH), 131.0 (C), 128.7(CH), 125.9 (CH), 123.4 (CH), 115.9 (CH), 114.3 (C), 113.6 (CH), 56.2 (CH), 56.1 (OCH_3), 56.0 (OCH_3), 47.2 (CH_2), 44.7 (CH_2), 36.5 (CH_2); ms (m/z, %): 310 (M^+-Br, 7), 231 (22), 229 (20), 215 (6), 213 (3), 180 (14), 160 (31), 131 (100), 107 (36), 105 (28). HRms Calcd for $C_{19}H_{20}NO_3$ (M^+-Br): 310.1443. Found: 310.1454

N-[β-(2-Bromo-4,5-dimethoxyphenyl)ethyl]-N-methyl-3-amino-1-indanone (6b)

The aminoindanone (**6b**) was obtained in 55% yield from amine (**2b**) using the above procedure; mp (hydrochloride): 169 °C (ether). Spectroscopic data for ***6b***: *ir* (ν, cm^{-1}, *film*): 1710 (C=O); uv (λ, EtOH, *nm*): 236, 287; ^{1}H Nmr ($CDCl_3$): δ 7.75-7 39 (m, 4H, Ar-H), 6.97 (s, 1H, Ar-H), 6.67 (s, 1H, Ar-H), 4.64 (t, 1H, J= 5.1 Hz, H-3), 3.85 (s, 3H, -OCH_3), 3.83 (s, 3H, -OCH_3), 2.89-2 82 (m, 2H, -CH_2-), 2.67 (m, 2H), 2.58-2.52 (m, 2H), 2.30 (s, 3H, -NCH_3); ^{13}C Nmr ($CDCl_3$): δ 204 5 (C=O), 155.1 (C), 148.4 (C), 148.2 (C), 137.5 (C), 134.7 (CH), 131.5 (C), 128.5 (CH), 126.6 (CH), 123.0 (CH), 115.6 (CH), 114.3 (C), 113.6 (CH), 62.2 (CH-N), 56.1 (OCH_3), 56.0 (OCH_3), 53.6 (CH_2), 37.8 (NCH_3), 36.0 (CH_2), 34.6 (CH_2); ms (m/z, %): 324 (M^+-Br, 9), 23 1(7), 229 (8), 175 (12), 174 (100), 131 (66). Anal. Calcd for $C_{20}H_{22}NO_3Br{\cdot}HCl$· C, 54.50; H, 5.26; N, 3.18. Found: C, 54.30; H, 5.15; N, 2.96.

N-[β-(2-Bromo-4,5-dimethoxyphenyl)ethyl]-N-formyl-3-amino-1-indanone (6c)

To a solution of aminoindanone (**6a**) (0.65 g, 1.66 mmol) in dry benzene (25 ml) cooled at 4 °C under argon, triethylamine (1 ml, 4 mmol) and an excess of freshly prepared[17] acetic-formic anhydride (3 ml, 20 mmol) was added and the mixture was stirred for 1 h at room temperature. The solvent was removed *in vacuo* and the remaining residue was dissolved in dichloromethane (20 ml) and washed with water (3 x 15 ml). After drying over anhydrous sodium sulfate and evaporation of solvent, 0.69 g (quantitative yield) of pure **6c** was obtained as a white solid; mp: 193 °C (ether-dichloromethane); ir(ν, cm^{-1}, KBr): 1720 (C=O), 1670 (C=O); uv (λ, EtOH, nm). 238, 288; ^{1}H Nmr ($CDCl_3$): δ 8.42 (s, 2/3H, -NCHO), 8.33 (s, 1/3H, -NCHO), 7.83-7.45 (m, 4H, Ar-H indan), 6.91 (s, 1/3H, Ar-H), 6.86 (s, 2/3H, Ar-H), 6 69 (s, 2/3H, Ar-H), 6.40 (s, 1/3H, Ar-H), 6.09 (dd, 1/3H, J= 8.0 and 3.3 Hz, H-3), 5.33- 5.29 (m, 2/3H, H-3), 3.81 (s, 3H, -OCH_3), 3 79 (s, 3H, -OCH_3), 3.29-2 62 (m, 6H, 3 x-CH_2-); ^{13}C Nmr ($CDCl_3$): δ 201.3 (C=O), 163.5 (CHO), 163.0 (CHO), 152.2 (C), 151.3 (C), 148.7 (C), 148.5 (C), 137.7 (C), 135.5 (CH), 135.2 (CH), 129.8 (CH), 129.6 (C), 129.3 (CH), 128.4 (C), 126.1 (CH), 125.9 (CH), 123.9 (CH), 123.7 (CH), 115.8 (CH), 115 5 (CH), 113.9 (C), 113.5 (CH), 113.2 (CH), 56.1 (OCH_3), 56.0 (OCH_3), 50.3 (CH), 45.0 (CH_2), 42.1(CH_2), 41 9(CH_2), 41.4(CH_2), 37.9(CH_2), 34.3(CH_2); ms (m/z, %): 419 (1), 417 (1), 244 (46), 242 (49), 231 (25), 229 (29), 131 (88). Anal. Calcd for $C_{20}H_{20}NO_4Br$: C, 57.43; H, 4.82; N, 3.35. Found: C, 57.16; H, 4.89; N, 3.28

N-[β-(2-Bromo-4,5-dimethoxyphenyl)ethyl]-N-ethoxycarbonyl-3-amino-1-indanone (6d)

To an ice-cold solution of aminoindanone (**6a**) (0.7 g, 1.8 mmol) in dry benzene (25 ml), triethylamine (1 ml, 4 mmol) and ethyl chloroformate (1 ml, 24 mmol) were added. The mixture was stirred at room temperature for 15 min. Then the solvent was removed *in vacuo* and the remaining oil was dissolved in dichloromethane (25 ml) and washed with water (3 x 25 ml). The organic layer was dried over anhydrous sodium sulfate and concentrated *in vacuo* to give an oil which was subjected to column chromatography (eluant: dichloromethane) to afford 0.65 g (78.3%) of pure **6d** as a white powder; mp: 118 °C (ether); ir (ν, cm^{-1}, KBr): 1720 (C=O), 1690 (C=O); uv (λ, EtOH, nm): 238, 288; ^{1}H Nmr ($CDCl_3$): δ 7.75-7.40 (m, 4H, Ar-H indan), 6.87 (s, 1/2 H, Ar-H), 6.85 (s, 1/2 H, Ar-H), 6.66 and 6.36 (br s, 1/2 H each one, Ar-H), 5.83 and 5.48 (m, 1/2 H each one, H-3), 4.20-4.06 (m, 2H, $-OCH_2-$), 3.77 (s, 3H, $-OCH_3$), 3.75 (s, 3H, $-OCH_3$), 3.48-2.54 (m, 6H, 3 x $-CH_2-$), 1.32-1.04 (m, 3H, $-CH_3$); ^{13}C Nmr ($CDCl_3$): δ 203.0 (C=O), 158.8 (C), 153.2 (C), 148.6 (C), 148.4 (C), 137 4 (C), 135.0 (CH), 130.0 (C), 129.0 (CH), 125.8 (CH), 123.3 (CH), 115.6 (CH), 114.0 (C), 113.3 (CH), 61.6 (OCH_2), 56.1 (OCH_3), 56.0 (OCH_3), 54.8 (CH), 42.0 (CH_2), 35.9 (CH_2), 14.3 (CH_3); ms (m/z, %): 463 (2), 461 (2), 382 (3), 232 (26), 231 (7), 229 (7), 132 (13), 131 (100), 102(75); HRms Calcd for $C_{22}H_{24}NO_5Br$: 461.0838. Found: 461.0830.

N-[β-(2-Bromo-4,5-dimethoxyphenyl)ethyl]-N-formyl-1-aminoindene (7)

Under argon, a mixture of 1 g (3.85 mmol) of bromophenethylamine (**2b**), 0.482 g (3.65 mmol) of indanone (**4**) and 0.025 g of *p*-TsOH dissolved in dry toluene (50 ml) was refluxed with stirring for 36 h, with azeotropic distillation to remove the water formed. After cooling to 4 °C, 3 ml (25 mmol) of dry triethylamine and an excess (3 ml, 20 mmol) of freshly prepared[17] acetic-formic anhydride were added. After stirring at room temperature for 4 h, the solvent was evaporated and the remaining oil was dissolved in dichloromethane (25 ml) and washed with 10% sodium bicarbonate solution. The organic layer was washed several times with brine (3 x 20 ml) and dried over anhydrous sodium sulfate, and the solvent was then evaporated to dryness. The residue was subjected to column chromatography (eluant: dichloromethane) to yield 1.5 g (75%) of pure **7** as a pale yellow solid; mp: 108-109 °C (ether); ir (ν, cm^{-1}, KBr): 1660 (C=O); uv (λ, EtOH, nm): 232, 282; ^{1}H Nmr ($CDCl_3$): δ 8.47 (s, 1H, CHO), 7.50-7.27 (m, 4H, Ar-H indan), 6.93 (s, 1H, Ar-H), 6.75 (s, 1H, Ar-H), 6.21 (t, 1H, J= 2.2 Hz, HC=C-), 4.07-4.01 (m, 2H,$-CH_2-$), 3.82 (s, 3H, $-OCH_3$), 3.79 (s, 3H, $-OCH_3$), 3.43 (d, 2H, J= 2.2 Hz, $-CH_2-$ indan), 3.04-2 98 (m, 2H, $-CH_2-$); ^{13}C Nmr ($CDCl_3$): δ 162 1 (CHO), 148.5 (C), 148 4 (C), 143.5 (C), 142.2(C), 140.5 (C), 129.7 (C), 126.6 (CH), 126.0 (CH), 125.3 (CH), 124.6 (CH), 119.0 (CH), 115.6 (CH), 114.3 (C), 113.6 (CH), 56.1 (OCH_3), 56.0 (OCH_3), 44.2 (CH_2), 36.1 (CH_2), 33.9 (CH_2); ms (m/z): 403 (1), 401 (1), 322 (48), 244 (39), 242 (39), 144 (41), 115 (100). Anal. Calcd for· $C_{20}H_{20}NO_3Br$: C, 59.64; H, 5.00; N, 3.48. Found: C, 60.04; H, 4.98; N, 3.59.

PHOTOCHEMICAL IRRADIATION

General procedure for photochemical irradiation of 6b, 6c and 6d

The photochemical experiments were done with a standard Pyrex immersion well assembly adjacent to the reaction vessel.

The photochemical irradiation procedure described below for **6b** was applied to **6b**, **6c** and **6d**.

To a solution of potassium *tert*-butoxide (0.097 g, 0.87 mmol) in anhydrous oxygen-free dimethyl sulfoxide (15 ml) under an argon atmosphere was added 0.05 g (0.124 mmol) of solid *N*-methylaminoindanone (**6b**). The reaction mixture was stirred, placed close to a Hanovia 450W medium-pressure mercury arc, and irradiated. After 30 min, when tlc examination indicated consumption of all starting material, the mixture was stirred with 20% sodium carbonate solution (20 ml) and the aqueous solution was extracted with dichloromethane (3 x 15 ml). The organic layer was washed several times with brine (3 x 10 ml) and dried over anhydrous sodium sulfate, and the solvent was evaporated to dryness. The residue was subjected to column chromatography (eluant: dichloromethane) yielding 0.010 g (42%) of 1-methyl-5,6-dimethoxy-2,3-dihydroindole (**9**) as a yellow oil.[18] ^{1}H Nmr ($CDCl_3$): δ 6.76 (s, 1H, Ar-H); 6.20 (s, 1H, Ar-H); 3.86 (s, 3H, -OCH_3); 3.81 (s, 3H,-OCH_3); 3.24 (t, 2H, J= 7.8 Hz, -CH_2-); 2.87 (t, 2H, J= 7.8 Hz, -CH_2-); 2.72 (s, 3H, -NCH_3); ms (m/z, %): 193 (M^+,7); 191 (34); 178 (14); 176 (26); 148 (31); 133 (66); 118 (25); 83 (91). HRms Calcd for $C_{11}H_{15}NO_2$: 193.1103. Found: 193.1086.

Upon irradiation of aminoindanones (**6c**) and (**6d**), a complex mixture of unidentified products was obtained.

Photochemical irradiation of enamide (7)

A solution of 0.030 g (0.075 mmol) of **7** in 12 ml of dry, oxygen-free *p*-dioxane containing 0.15 ml of freshly distilled triethylamine was purged with argon for 30 min and irradiated at room temperature under an argon atmosphere using a Vycor filter and a Hanovia 450W medium pressure mercury lamp. After 2 h, when tlc examination indicated consumption of all starting material, the mixture was washed with water and dried with anhydrous sodium sulfate. The solvent was removed in a rotary evaporator, and tlc examination of the residue showed an intractable mixture of products.

Photochemical irradiation of enaminone (8)

A solution of **8**[12] (0.050 g, 0.13 mmol) in 12 ml of dry, oxygen-free *p*-dioxane containing 0.125 ml of freshly distilled triethylamine was irradiated at room temperature under an argon atmosphere for 2 h with Vycor filtered-light from a Hanovia 450W medium-pressure lamp.

When tlc plate examination indicated consumption of most of the starting material, the crude product was filtered and concentrated *in vacuo*, giving a residue which was subjected to preparative tlc on silica gel (eluant: 10:90 methanol/dichloromethane). The cyclized product (**10**) (0.022 g, 55%) was obtained as a reddish

powder; mp: 230 °C (ether-dichloromethane); ir (ν, cm^{-1}, KBr) 3430 (NH), 1720(C=O); uv (λ, EtOH, nm). 226, 290, 334, 484; ^{1}H Nmr ($CDCl_3$): δ 8.09 (s, 1H, Ar-H), 7.51-7.07 (m, 4H, Ar-H indan), 6.59 (s, 1H, Ar-H), 5.93 (br s, 1H, N-H), 3.96 (s, 3H, $-OCH_3$), 3.87 (s, 3H, $-OCH_3$), 3.84-3.75 (m, 2H, $-CH_2$-N), 3.10-3.06 (m, 2H, Ar-CH_2-); ^{13}C Nmr ($CDCl_3$): δ 192.2 (C=O), 158.6 (C), 147.7 (C), 146 4 (C), 138.3 (C), 135.3 (C), 131.0 (CH), 130.4 (C), 130.2 (CH), 125.8 (C), 120.6 (CH), 115.5 (CH), 112.7 (CH), 111.7 (CH), 104.1 (C), 56.0 (OCH_3), 55.9 (OCH_3), 47.8 (CH_2), 37.3 (CH_2); ms (m/z, %): 308 (31), 307 (30), 292 (37), 288 (27), 264 (9), 209 (10), 149 (75), 84 (100); HRms Calcd for $C_{19}H_{17}NO_3$: 307.1208. Found: 307.1209

5,6,7,13-Tetrahydro-2,3-dimethoxy-7-methylbenz[d]indeno[1,2-b]azepin-13-one (11)

Sodium hydride (0.041 g, 1.37 mmol, 80% mineral oil dispersion) was added to a solution of the azepine (**10**) (0.084 g, 0.37 mmol) in HMPA (0.5 ml) and dry benzene (2 ml). The resulting solution was stirred at room temperature for 15 min, dimethyl sulfate (3 drops) was added, and stirring was continued at room temperature for 1 h. Aqueous NH_3 (28%, 1 ml) was added to the reaction mixture, which was further stirred at room temperature for 30 min before extraction with chloroform. The organic layer was washed with water, dried, and evaporated to dryness. The residue was subjected to preparative tlc on silica gel (eluant: 10:90 methanol/dichloromethane) to afford the *N*-methyl derivative (**11**) (0.079 g, 90%) as reddish purple prisms; mp: 176 °C (methanol); ir (ν, cm^{-1}, KBr): 1720 (C=O), uv (λ, EtOH, nm): 228, 294, 338, 352, 502; ^{1}H Nmr ($CDCl_3$): δ 7.83 (s, 1H, Ar-H), 7.44-7.22 (m, 4H, Ar-H indan), 6.50 (s, 1H, Ar-H), 3.90 (s, 3H, $-OCH_3$), 3.79 (s, 3H, $-OCH_3$), 3.70-3.66 (m, 2H, $-CH_2$-N), 3.38 (s, 3H, $-NCH_3$), 2.93- 2.89 (m, 2H, Ar-CH_2-); ^{13}C Nmr ($CDCl_3$): δ 191.8 (C=O), 163 3 (C), 147.7 (C), 146.7 (C), 139.3 (C), 136.3 (C), 131.8 (C), 131.5 (CH), 130.0(CH), 125.8 (C), 122.4 (CH), 120 9 (CH), 112.5 (CH), 111.7 (CH), 108.5 (C), 60.3 (CH_2), 56.2 (OCH_3), 56 1 (OCH_3), 43.1 (NCH_3), 34.8 (CH_2); ms (m/z, %): 321 (100), 307 (18), 306 (75), 263 (15), 248 (10). Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4 36. Found: C, 74.48, H, 6.06, N, 4.37.

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