PHOTOREACTION OF PHTHALIMIDES POSSESSING AN ORTHO-METHYLPHENYL GROUP IN THEIR N-SIDE CHAIN. SYNTHESIS OF TETRACYCLIC NITROGEN HETEROCYCLES[1]

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Abstract — Upon irradiation phthalimides (5 and 8) possessing an o-methylphenyl group in their N-side chain gave mainly the tetracyclic ring systems (9 and 10). It was shown that the photocyclization occurs at ε- or ζ-position across the carbons of the benzene ring (B ring).

Photoreactions of phthalimides (1)[2] possessing a certain functional group or a hetero atom, such as olefin,[3] anilino,[4] and methylthio[5] in their N-side chain, have given rise to a variety of new heterocycles including large-sized ring systems. Among them, the phthalimide (2) possessing an o-methylphenyl group in its N-side chain effectively undergoes δ-hydrogen abstraction to give tetracyclic heterocycles, isoindoloindolone (3) (Chart 1).[6] Furthermore, in order to extend this type of the reaction to a general synthesis of tetracyclic compounds having various ring size, photoreactions of phthalimides possessing an o-methylphenyl group in the N-side chain were investigated. In the present paper we wish to report

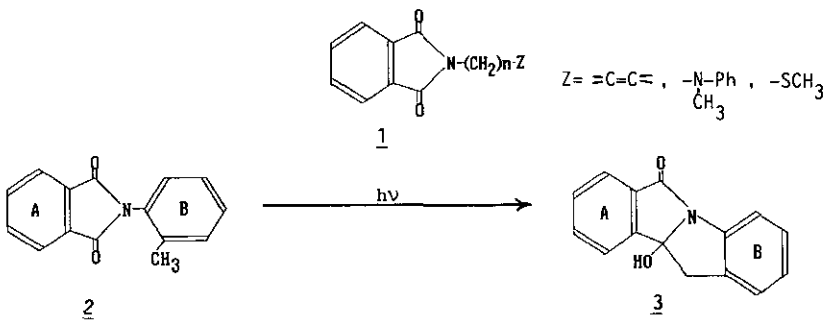
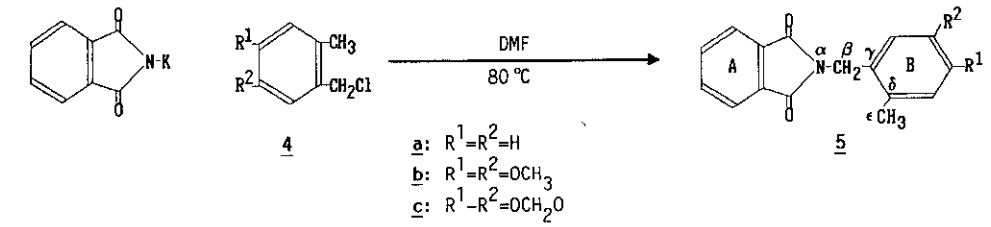


Chart 1

the photocyclization of two types of phthalimide derivatives (5 and 8).

A series of phthalimides (5 and 8) were prepared by the reactions shown in Chart 2. The phthalimide derivatives 5 were prepared from potassium phthalimide and the corresponding benzyl halide (4) in dimethylformamide at 80°C. Phthalimides 8 were prepared by fusing a mixture of the corresponding phenethylamine (7) and phthalic anhydride (6) at 150°C. Photolyses of 5a-c and 8a-d were carried out in acetone (or acetonitrile) solution using a 500 W (or 1 kW) high-pressure mercury lamp at room temperature for 0.5-7 h under a nitrogen atmosphere (Chart 3). The photolysis was monitered for the disappearance of the unchanged starting material on thin layer chromatography. These results are collected in Table I.



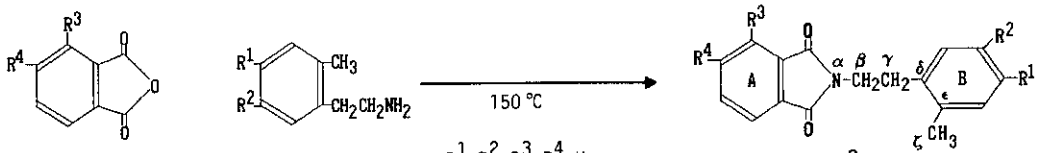


Chart 2

Table I. Photoreaction of N-(o-Methylbenzyl)phthalimides (5).

Substrate 5	Solvent	Time (h)	Product 9	Product phthalimide	Recovery of 5
a	CH_3CN	7	18	-	52
a	acetone	2.5	-	40	56
b	acetone	50(min)	52	-	28
c	acetone	0.5	25	-	20

Photolysis of 5a in acetonitrile for 7 h gave the cyclized product (9a) in 18% yield together with recovery of 5a (52%), but in acetone gave only simple phthalimide (40%) which is probably produced by Norrish type II fission. In the case of 5b which possesses two methoxy groups on the o-methylbenzyl moiety (B ring), the yield of tetracyclic compound (9b) increased up to 52%. Likewise, 5c which

possesses a methylenedioxy group on the B ring gave the cyclized product (9c) in 25% yield, and phthalimide was not obtained.

Structural assignments of tetracyclic compounds 9a-c were made on the basis of analytical and spectral data. For a typical example, the mass (ms) spectrum of 9a showed the molecular ion peak (m/z=251) consistent with the molecular weight of 5a. The infrared (ir) spectrum indicated the presence of a lactam and a hydroxy group at 1675 and 3210 cm^{-1}, respectively. In the proton magnetic resonance (^{1}H-nmr) spectrum of 9a, two characteristic AB quartets with the coupling constants of 16.5 and 17 Hz appeared at 2.88, 3.48 and 4.31, 4.98 ppm, respectively. The former peak indicated the presence of newly formed methylene protons by carbon-carbon bond formation of a carbonyl and an o-methyl group at the ε-position to the carbonyl group, while the latter showed the presence of methylene protons adjacent to a nitrogen atom. As expected, treatment of 9a in the presence of hydrochloric acid afforded the dehydration product (12) (Chart 3).

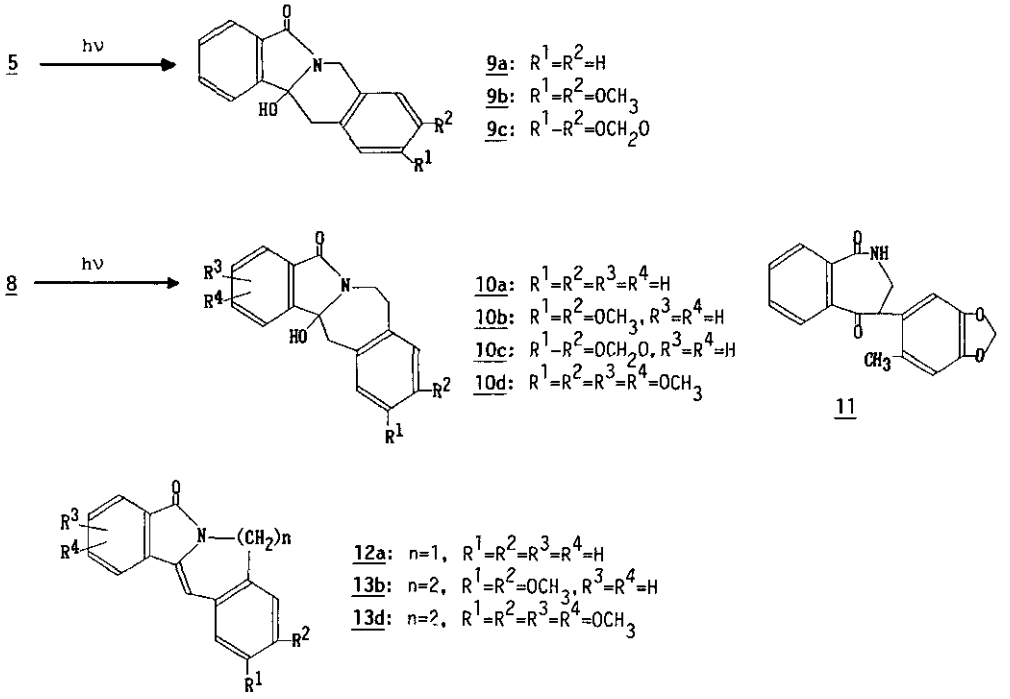


Chart 3

Further, in order to test whether the photocyclization can occur at the ζ-position across the carbon atoms of benzene ring or not, photolysis of 8 was carried out under the similar conditions as that of 5. The results are listed in Table II. From 8a, tetracyclic ring system (10a) including a skeleton of benzazepine (Schöpf-Schweickert amine VI)[7] was obtained in 5% yield after prolonged irradiation (7 h). As in the case of 5b, the presence of two methoxy groups on the o-methylbenzyl moiety (B ring

of 8b) seems favorable for the reaction, and 10b was obtained in 19-27% yields from 8b. Presumably the rate of hydrogen abstraction of the methyl group at the ζ-position is enhanced due to stabilization of the intermediate benzyl radical. Photolysis of 8c possessing a methylenedioxy group gave 10c and 11, through two competing pathways of ζ and γ abstraction, respectively. Structures of all products 10a-c and 11 were determined on the basis of analytical and spectral data. For a typical example, spectral data of 10a are as follows: ms: m/z=265 (M^+), ir: 1665 (amide), 3300 (OH) cm^{-1}, nmr: 2.7-3.5 (3H, m, N-C<u>H</u>C<u>H</u>$_2$), 3.05 and 3.50 (2H, AB q, C(OH)C<u>H</u>$_2$, J=15 Hz), 4.2-4.7 (1H, m, N-C$_7$H), 6.00 (1H, s, OH) ppm. That a new AB quartet and a singlet peak for 10a appeared at 3.05, 3.50 and 6.00 ppm, respectively, instead of a singlet at 2.40 ppm due to the methyl protons which was in 8a, indicated the C-C bond formation between a carbonyl group and a methyl group. Further, to confirm the structure chemically, 10b was treated with conc. hydrochloric acid. The resulting dehydration product was identified with 13b, whose structure had been established.[7] The formation of 11 can be explained on the basis of the general pattern of phthalimide photochemistry,[1a,8] and its spectral data were analogous to those of the benzazepine analogs obtained by the photoreaction of phthalimide systems.[1a,8]

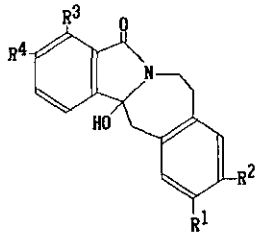
Table II. Photoreaction of N-[2-(o-Methylphenyl)ethyl]phthalimides (8a-d).

Substrate 8	Solvent	lamp (HP)	Time (h)	Product 10	Product 11	Recovery of 8
a	CH_3CN	500W	7	5	-	29
b	acetone	500W	2.5	19	-	41
b	acetone	1kW(Pyrex)	1.5	27	-	55
c	acetone	500W	35(min)	9	10	30
c	acetone	1kW(Pyrex)	45(min)	17	14	19
d	acetone	500W	10	24	-	8
d	acetone	1kW(Pyrex)	6	35	-	21

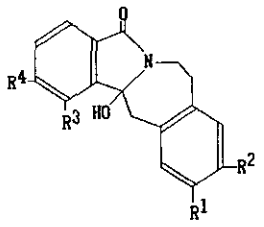
In view of synthetic application to isoindolobenzazepine alkaloids such as lennoxamine and chilelenamine,[9] photolysis of the aryl-substituted phthalimide (8d) was then examined. In spite of the earlier observation that phthalimides possessing an electron-donating substituent on the A ring resisted to the photoreaction,[6b] 8d which has two methoxy groups underwent the photocyclization to give 10d in 24% yield. When a 1 kW mercury lamp through a Pyrex filter was used to shorten the irradiation times, 10d and 13d were obtained in 23 and 12% yields, respectively, together with recovery of 8d (21%), of which the latter seems to arise from 10d during the column chromatography of the photolysates. Although two possible structures for 10d were inferred as shown in Chart 4 from spectral data, the structure was tentatively assigned as 10d-i on the analogy of ^{1}H-nmr data of isoindolobenzazepine derivatives,[9] in which one methoxy group showed a lower field shift due to the anisotropic effect of the carbonyl

group.

In conclusion, two methoxy substituents on the B ring promoted the photocyclization at relatively remote ε- or ζ-position, and these aryl-substituted phthalimides underwent cyclization even when the A ring has two methoxy groups. The substituents on the B ring may influence the stability of the intermediate benzyl radical, without substantial effects on the excited state of the carbonyl.[6b] Although the reason of the preferential reaction at ε- or ζ-position across the B ring is uncertain, the o-methyl group serves to construct the tetracyclic ring system. Thus, photocyclization of phthalimides possessing an o-methylphenyl group may provide a synthetic entry to tetracyclic ring systems related to berberine nor- and homoanalogs.[10]



10d-i



10d-ii

Chart 4

EXPERIMENTAL

All melting points were determined on a Yamato melting point apparatus (model MP-21) and are uncorrected. Ir spectra were recorded on a JASCO-A-102 or a Shimadzu IR-400 spectrometer. Nmr spectra were taken on a Hitachi R-40 and a JEOL FX-60 spectrometers. Chemical shifts are reported in ppm (δ) relative to TMS (0.0 ppm) as an internal standard. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were obtained on a Shimadzu-LKB 9000 gas chromatograph-mass spectrometer with a direct inlet system. Preparative irradiation were conducted by using a 500 W or a 1 kW high-pressure mercury lamp (Eikosha PIH-500, EHB-W-1000) at room temperature. Stirring of the reaction mixture was effected by the introduction of a stream of nitrogen at the bottom of outer jacket. Column chromatography was conducted using silica gel (Merck, Kieselgel 60, 70-230 mesh).

Preparation of o-Methylbenzyl Chloride Derivatives 4b,c.

4,5-Dimethoxy-2-methylbenzyl chloride (4b) was prepared from 3,4-dimethoxytoluene and chloromethyl methyl ether in acetic acid at room temperature. 4b: Yield 64%, colorless oil, bp 123-135°C/0.4 mmHg. Nmr ($CDCl_3$): 2.31 (3H, s, Me), 3.80 (6H, s, MeOx2), 4.50 (2H, s, $-CH_2Cl$), 6.60 (1H, s, aromatic H), 6.7 (1H, s, aromatic H). Similarly, 4,5-methylenedioxy-2-methylbenzyl chloride (4c) was prepared from 3,4-methylenedioxytoluene and chloromethyl methyl ether. 4c: Recrystallization from benzene-hexane gave colorless prisms of mp 60-61°C (yield 52%). Nmr ($CDCl_3$): 2.30 (3H, s, Me), 4.48 (2H, s, $-CH_2Cl$), 5.84 (2H, s, $-OCH_2O-$), 6.59 (1H, s, aromatic H), 6.71 (1H, s, aromatic H).

General Procedure for Preparation of N-(o-Methylbenzyl)phthalimide 5.

Phthalimide 5 was prepared from potassium phthalimide and o-methylbenzyl chloride 4 in dimethylformamide at 80°C in the usual manner.[3a] Compound 5a: Yield 86%, colorless needles, mp 152-153°C

(from EtOH). Ir (nujol): 1765, 1710 cm^{-1}. Ms: m/z 251 (M^+). Nmr ($CDCl_3$): 2.47 (3H, s, Me), 4.84 (2H, s, N-CH_2), 6.9-7.4 (4H, m, aromatic H), 7.5-7.9 (4H, m, aromatic H). Found: C, 76.41; H, 5.18; N, 5.37. Calc for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22; N, 5.57. 5b: 82%, colorless needles, mp 139.5 (EtOH). Ir (nujol): 1760, 1700 cm^{-1}. Ms: m/z 311 (M^+). Nmr ($CDCl_3$): 2.45 (3H, s, Me), 3.80 (6H, s, MeOx2), 4.75 (2H, s, N-CH_2), 6.60, 6.95 (1Hx2, sx2, aromatic H), 7.5-7.9 (4H, m, aromatic H). Found: C, 69.43; H, 5.42; N, 4.38. Calc for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50. 5c: 79%, colorless needles, mp 149-149.5°C (EtOH). Ir (nujol): 1765, 1700 cm^{-1}. Ms: m/z 265 (M^+). Nmr ($CDCl_3$): 2.40 (3H, s, Me), 4.72 (2H, s, N-CH_2), 5.81 (2H, s, -OCH_2O-), 6.60, 6.80 (1Hx2, sx2, aromatic H), 7.5-7.9 (4H, m, aromatic H). Found: C, 69.10; H, 4.44; N, 4.82. Calc for $C_{17}H_{13}NO_4$: C, 69.14; H, 4.44; N, 4.74.

Preparation of 3,4-Dimethoxyphthalic Anhydride (6).

6,7-Dimethoxyphthalide was prepared from 2,3-dimethoxybenzoic acid, conc. hydrochloric acid, and 37% formaldehyde according to the method of White and Bursey,[11] mp 95-97°C (lit.[11] mp 100.2-100.6°C). Then resulting phthalide was oxidized with potassium permanganate to 2,3-dimethoxybenzoic acid,[11] mp 170-173°C (lit.,[12] mp 177°C). Next, 3,4-dimethoxyphthalic acid was treated with acetyl chloride, and the product was recrystallized from benzene, mp 166-168°C (lit.,[12] mp 168°C).

General Procedure for Preparation of o-Methylbenzyl Cyanide Derivatives.

o-Methylbenzyl cyanide was prepared from o-methylbenzyl halide (4) and potassium cyanide in the presence of benzyltriethylammonium chloride in a mixture of benzene and water according to the modified method of Starks.[13] o-Methylbenzyl cyanide: Yield 91%, bp 125-134°C/16 mmHg (lit.,[14] bp 125°C/14 mmHg). Ir (nujol): 2250 cm^{-1}. 4,5-Dimethoxy-2-methylbenzyl cyanide: 83%, mp 88°C. Ir (nujol): 2220 cm^{-1}. Nmr ($CDCl_3$): 2.25 (3H, s, Me), 3.55 (2H, s, CH_2CN), 3.80 (6H, s, MeOx2), 6.63, 6.78 (1Hx2, sx2, aromatic H). 4,5-Methylenedioxy-2-methylbenzyl cyanide: 94%, mp 39-40°C. Ir (nujol): 2250 cm^{-1}. Nmr ($CDCl_3$): 2.23 (3H, s, Me), 3.53 (2H, s, CH_2CN), 5.88 (2H, s, -OCH_2O), 6.63, 6.76 (1Hx2, sx2, aromatic H).

General Procedure for Preparation of o-Methylphenethylamine Derivatives (7a-c).

The resulting cyanides were converted to the corresponding amines (7a-c) by reduction with sodium borohydride and trifluoroacetic acid according to the method of Umino et al.[15] Compound 7a: Yield 94%, oily product. Ir (neat): 3300 cm^{-1}. Nmr ($CDCl_3$): 1.13 (2H, s, NH_2 exchanged with D_2O), 2.26 (3H, s, Me), 2.5-3.0 (4H, m, $CH_2CH_2NH_2$), 7.02 (4H, s, aromatic H). Hydrogen chloride of 7a, mp 155-156°C. Found: C, 62.84; H, 8.26; N, 8.18. Calc for $C_9H_{14}NCl$: C, 62.96; H, 8.28; N, 8.16. 7b: 95%, oily product. Ir (neat): 3350 cm^{-1}. Nmr ($CDCl_3$): 1.20 (2H, s, NH_2 exchanged with D_2O), 2.23 (3H, s, Me), 2.5-3.3 (4H, m, $CH_2CH_2NH_2$), 3.80 (6H, s, MeOx2), 6.63 (2H, s, aromatic H). Hydrogen chloride of 7b, mp 182-183°C. Found: C, 57.02; H, 7.78; N, 6.07. Calc for $C_{11}H_{18}NO_2Cl$: C, 57.01; H, 7.83; N, 6.05. 7c: 90%, oily product. Ir (neat): 3300 cm^{-1}. Nmr ($CDCl_3$): 1.33 (2H, s, NH_2 exchanged with D_2O), 2.20 (3H, s, Me), 2.5-3.0 (4H, m, $CH_2CH_2NH_2$), 5.81 (2H, s, -OCH_2O-), 6.58 (2H, s, aromatic H). Hydrogen chloride of 7c, mp 183-184°C. Found: C, 55.41; H, 6.49; N, 6.46. Calc for $C_{10}H_{14}NO_2Cl$: C, 55.69; H, 6.54; N, 6.49.

General Procedure for Preparation of N-[2-(o-Methylphenyl)ethyl]phthalimides (8a-d).

The phthalimides 8a-d were obtained by fusing a mixture of the corresponding phenethylamine 7 and phthalic anhydride 6 at 150°C in the usual manner. Compound 8a: Yield, 72%, colorless plates (from EtOH), mp 96-96.5°C. Ir (nujol): 1765, 1700 cm^{-1}. Ms: m/z 265 (M^+). Nmr ($CDCl_3$): 2.40 (3H, s, Me), 2.8-4.0 (2H, m, NCH_2CH_2), 3.7-4.0 (2H, m, NCH_2CH_2), 7.03 (3H, s, aromatic H), 7.5-7.9 (3H, m, aromatic H). Found: C, 76.80; H, 5.53; N, 5.28. Calc for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. 8b: 78%, colorless plates (EtOH), mp 160-160.5°C. Ir (nujol): 1765, 1710 cm^{-1}. Ms: m/z 325 (M^+). Nmr ($CDCl_3$): 2.35 (3H, s, Me), 2.8-3.1 (2H, m, NCH_2CH_2), 3.7-4.0 (2H, m, NCH_2CH_2), 3.73 (3H, s, MeO), 3.82 (3H, s, MeO), 6.64 (2H, s, aromatic H), 7.5-7.9 (4H, m, aromatic H). Found: C, 70.07; H, 5.86; N, 4.56. Calc for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.31. 8c: 82%, colorless needles (EtOH), mp 169-169.5°C. Ir (nujol): 1770, 1710 cm^{-1}. Ms: m/z 309 (M^+). Nmr ($CDCl_3$): 2.29 (3H, s, Me), 2.8-3.2 (2H, m, NCH_2CH_2),

3.7-4.1 (2H, m, NCH_2CH_2), 5.80 (2H, s, $-OCH_2O-$), 6.58, 6.61 (1Hx2, sx2, aromatic H), 7.5-7.9 (4H, m, aromatic H). Found: C, 69.77; H, 4.81; N, 4.48. Calc for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. **8d**: 75%, colorless needles (EtOH), mp 153-153.5°C. Ir (nujol): 1760, 1705 cm^{-1}. Ms: m/z 385 (M^+). Nmr ($CDCl_3$) : 2.34 (3H, s, Me), 2.7-3.1 (2H, m, NCH_2CH_2), 3.6-4.1 (2H, m, NCH_2CH_2), 3.73 (3H, s, MeO), 3.80 (3H, s, MeO), 3.91 (3H, s, MeO), 4.10 (3H, s, MeO), 6.62 (2H, s, aromatic H), 7.04 and 7.46 (3H, AB q, J=8 Hz aromatic H). Found: C, 65.35; H, 5.92; N, 3.54. Calc for $C_{21}H_{23}NO_6$: C, 65.44; H, 6.02; N, 3.63.

General Procedure for Irradiation of Phthalimides (5 and 8).

A solution of the phthalimide (1 g) in acetone (500 ml) was irradiated at room temperature. After removal of the solvent in vacuo, the products were separated by column chromatography on silica gel, and purified by recrystallization.

Compound **9a**: Colorless needles (AcOEt), mp 170-171°C. Ir (nujol): 3210, 1675 cm^{-1}. Ms: 251 (M^+). Nmr (DMSO-d_6): 2.88 and 3.48 (2H, AB q, J=16.5 Hz, $C(OH)CH_2$), 4.07 (1H, s, OH), 4.31 and 4.98 (2H, AB q, J=17 Hz, NCH_2), 7.10-7.35 (4H, m, aromatic H), 7.35-7.85 (4H, m, aromatic H). Found: C, 76.63; H, 5.30; N, 5.60. Calc for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22; N, 5.57. **9b**: Colorless needles (dimethylformamide), mp 220-223°C (dec.). Ir (nujol): 3210, 1670 cm^{-1}. Ms: m/z 311 (M^+). Nmr (DMSO-d_6): 2.73 and 3.43 (2H, AB q, J=16 Hz, $C(OH)CH_2$), 3.78 (6H, s, MeOx2), 4.29 and 5.03 (2H, AB q, J=17 Hz, NCH_2), 4.97 (1H, s, OH), 6.80, 6.94 (1Hx2, sx2, aromatic H), 7.4-7.9 (4H, m, aromatic H). **9c**: Colorless needles (AcOEt), mp 160-164°C. Ir (nujol): 3250, 1670 cm^{-1}. Ms: m/z 295. Nmr (DMSO-d_6): 2.79 and 3.39 (2H, AB q, J=17 Hz, $C(OH)CH_2$), 4.35 and 5.07 (2H, AB q, J=17 Hz, NCH_2), 5.91 (2H, s, $-OCH_2O-$), 6.10 (1H, s, OH), 6.62, 6.67 (1Hx2, sx2, aromatic H), 7.3-7.9 (4H, m, aromatic H). Found: C, 68.96; H, 4.54; N, 4.66. Calc for $C_{17}H_{13}NO_4$: C, 69.14; H, 4.44; N, 4.74.

Compound **10a**: Colorless needles (benzene), mp 174-176°C. Ir (nujol): 3300, 1665 cm^{-1}. Ms: m/z 265 (M^+). Nmr (DMSO-d_6): 2.7-3.5 (3H, m, $N-CHCH_2$), 3.05 and 3.50 (2H, AB q, J=15 Hz, $C(OH)CH_2$), 4.2-4.7 (1H, m, N-CH), 6.00 (1H, s, OH), 7.07 (4H, s, aromatic H), 7.2-7.8 (4H, m, aromatic H). Found: C, 77.04; H, 5.59; N, 5.16. Calc for $C_{17}H_{15}NO_4$: C, 76.96; H, 5.70; N, 5.28. **10b**: Colorless needles (EtOH), mp 233.5-235°C. Ir (nujol): 3320, 1670 cm^{-1}. Ms: m/z 325 (M^+). Nmr (DMSO-d_6): 2.7-3.7 (5H, m), 3.73 (3H, s, MeO), 3.77 (3H, s, MeO), 4.1-4.5 (1H, m), 6.21 (1H, s, OH), 6.82, 6.84 (1Hx2, sx2, aromatic H), 7.4-8.0 (4H, m, aromatic H). Found: C, 69.90; H, 5.98; N, 4.29. Calc for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.31. **10c**: Colorless needles ($CHCl_3$), mp 180-182°C. Ir (nujol): 3300, 1670 cm^{-1}. Ms: m/z 309 (M^+). Nmr (DMSO-d_6): 2.7-3.6 (5H, m), 4.0-4.4 (1H, m), 5.90 (2H, s, $-OCH_2O-$), 6.18 (1H, s, OH), 6.65, 6.74 (1Hx2, sx2, aromatic H), 7.3-7.9 (4H, m, aromatic H). Found: C, 69.76; H, 4.72; N, 4.55. Calc for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. **10d**: Colorless needles (EtOH), mp 192-196°C. Ir (nujol): 3250, 1660 cm^{-1}. Ms: m/z 385 (M^+). Nmr ($CDCl_3$): 2.7-3.5 (5H, m), 3.74 (1H, s, OH), 3.85 (3Hx2, sx2, MeOx2), 3.93 (3H, s, MeO), 4.03 (3H, s, MeO), 3.6-4.5 (1H, m), 6.6-6.8 (2H, m, aromatic H), 6.87-7.13 (2H, AB q, J=8.7 Hz, aromatic H).

Compound **11**: Colorless needles (AcOEt), mp 236.5-237.5°C. Ir (nujol): 3170, 3050 cm^{-1}. Ms: m/z 309 (M^+). Nmr (DMSO-d_6): 2.26 (3H, s, Me), 3.3-3.7 (2H, m, NCH_2CH_2), 4.2-4.4 (2H, m, NCH_2CH_2), 5.90 (2H, s, $-OCH_2O-$), 6.39, 6.78 (1Hx2, sx2, aromatic H), 7.4-7.9 (4H, m, aromatic H), 8.3-8.6 (1H, m, NH). Found: C, 69.66; H, 4.76; N, 4.49. Calc for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53.

Dehydration of **9a**, **10b** and **10d**: General Procedure.

A solution of **10b** (50 mg) and one drop of conc. HCl in EtOH (5 ml) was stirred at room temperature for 30 min. After removal of the solvent, the residue was purified by recrystallization from EtOH quantitatively to give **13b** as yellow prisms, mp 189-190°C (lit.,[7] mp 195-196°C). Ir (nujol): 1695, 1650 cm^{-1}. Ms: m/z 307 (M^+). Nmr (DMSO-d_6): 3.0-3.2 (2H, m, NCH_2CH_2), 3.89 (6H, s, MeOx2), 4.0-4.2 (2H, m, NCH_2CH_2), 6.47 (1H, s, vinyl H), 6.63, 6.82 (1Hx2, sx2, aromatic H), 7.2-7.9 (4H, m, aromatic H).

Dehydration compound **12a** (from **9a**): Warmed at 70-80°C, and the product was purified by thin-layer chromatography (silica gel, $CHCl_3$). Yellow needles (AcOEt-hexane), mp 157-158°C. Ir (nujol): 1685, 1655 cm^{-1}. Ms: m/z 233 (M^+). Nmr ($CDCl_3$): 4.96 (2H, s, N-CH_2), 6.30 (1H, s, vinyl H), 7.07 (4H, s, aromatic H), 7.2-7.9 (4H, m, aromatic H). Found: C, 82.56; H, 4.72; N, 5.98. Calc for $C_{16}H_{11}NO$: C, 82.38; H, 4.75; H, 6.01. **13d** (from **10d**): Yellow prisms (EtOH), 194-196°C. Ir (nujol): 1685, 1630 cm^{-1}. Ms: 367 (M^+). Nmr (DMSO-d_6): 2.9-3.2 (2H, m, NCH_2CH_2), 3.8-4.1 (2H, m, N-CH_2CH_2), 3.83, 3.84, 3.95, 3.98 (3Hx4, sx4, MeOx4), 6.81 (1H, s, vinyl H), 6.94, 7.10 (1Hx2, sx2, aromatic H), 7.14 and 7.48 (2H, AB q, J=8.5 Hz, aromatic H). Found: C, 68.48; H, 5.66; N, 3.77. Calc for $C_{21}H_{21}NO_5$: C, 68.65; H, 5.76; N, 3.81.

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