Benzolactams. II. Synthesis of Tetrahydrobenz[*d*]indeno-[1,2-*b*]azepines and their 12-Oxo Derivatives

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Aromatic methoxy and/or methylenedioxy substituted 7-methyltetrahydrobenz[*d*]indeno[1,2-*b*]-azepines **7** and their 12-oxo derivatives **8** were efficiently synthesized by the general method consisting of two types of intramolecular dehydrative cyclizations, as follows. *N*-Methyl-*N*-β-phenethylacetamides **1** were cyanomethylated in the two-step process of chloromethylation and treatment of the resultant benzyl chlorides with sodium cyanide. The condensation of the benzyl cyanides **2** with the appropriate benzaldehydes, followed by reduction of the benzylidene function, gave α,β-diphenylpropionitriles **3**. Successively, hydrolysis to the amino acids **4** and the thermal cyclization converted **3** to the benzylbenzazepinones **5**, which were also prepared by benzylation of the benzazepinones **6** smoothly by heating of **5** with phosphoryl chloride to afford the title azepines **7**. Further, these tetracyclic enamines **7** underwent autoxidation to the corresponding 12-oxo derivatives **8**, on exposure to oxygen in the presence of Triton B.

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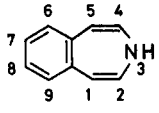
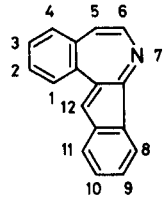
In 1925, von Brown and Reich reported the synthesis of 1,2,4,5-tetrahydro-3*H*-3-benzazepin-2-one (1). Since then, a number of procedures for the preparation of 3-benzazepines have been studied because of their possible pharmacological properties (2) and structural features characteristic of rhoeadine, isopavine and cephalotaxine



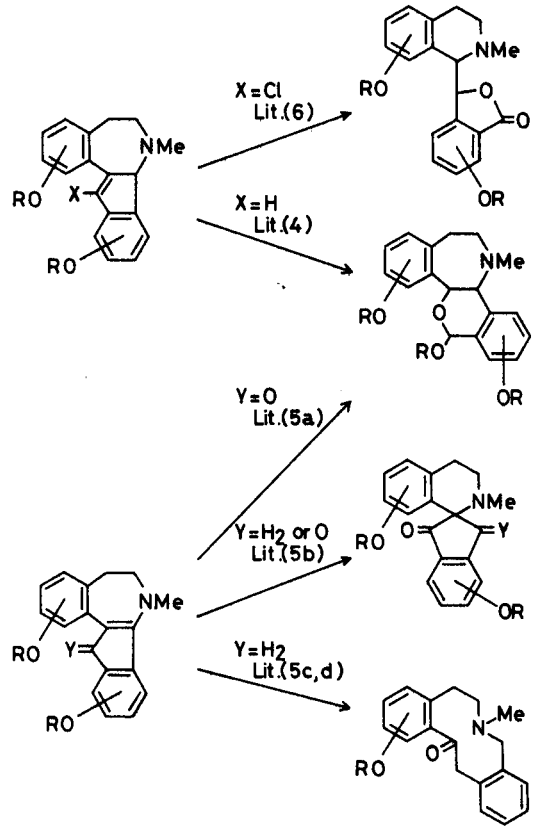
3H-3-benzazepine



benz[d]indeno[1,2-b]azepine

alkaloids (3). Benz[*d*]indeno[1,2-*b*]azepines, one of the 3-benzazepine families, have also received attention recently especially because of the important key-intermediates in the synthesis of isoquinoline alkaloids of rhoeadine (4,5a), spirobenzyl (5b), phthalide (6) and protopine (5c,d) types, as shown in Figure 1. Several methods have been known to give this type of tetracyclic compounds (4-11). However, most of them consist essentially of the transformation reactions of the natural or synthetic alkaloids (4,7-11), and the practical procedures in common routes have not been scrutinized (5,6). The context stimulated us to investigate possible routes to the construction of the benz[*d*]indeno[1,2-*b*]azepine ring system and we now wish to report a new and efficient method for the preparation of the title compounds **7a-d** as well as their 12-oxo derivatives **8a-d**.

Figure 1



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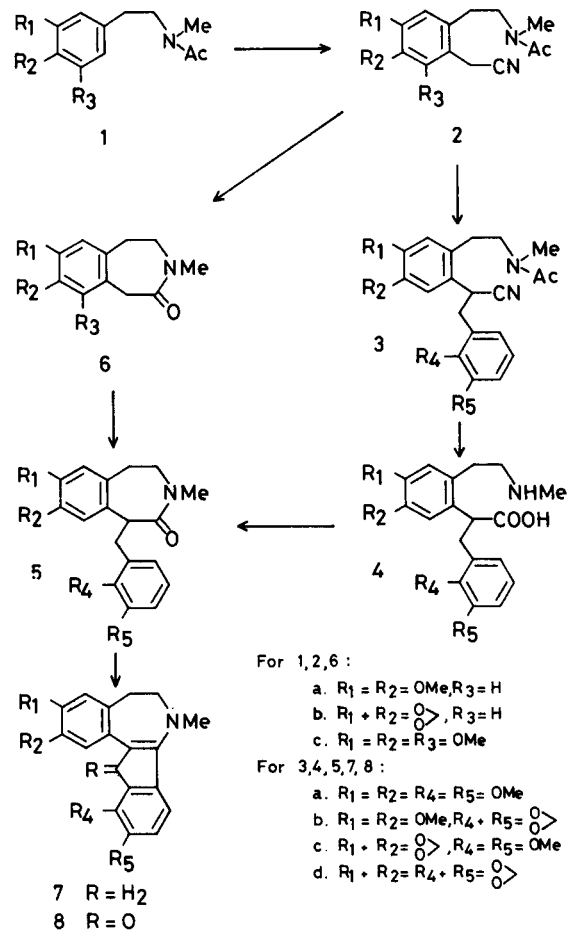
A brief statement of the preparation of **2a** and **3a** was previously made (5a), and a reinvestigation and extension of the method led to formation of aromatic alkoxy substituted 1-benzyl-3-methyl-1,2,4,5-tetrahydro-3*H*-3-benzazepin-2-ones (**5**), as follows. Acetamides **1** were almost quantitatively obtained by the interaction of the corresponding *N*-β-phenethylacetamides with methyl iodide and sodium hydride in a mixture of dimethylformamide and tetrahydrofuran (1:10 volume %) in accordance with Coggins and Benoiton's procedure (12). These amides, which crystallized on vacuum distillation, appear as a mixture of two rotamers at room temperature due to the tertiary amide group in a ratio of 1:1.2 in **1a**, 8:9 in **1b** and 1:1.5 in **1c**, respectively. Cyanomethylation of **1** was started by chloromethylation. Treatment of **1a** with formalin and hydrogen chloride at −15° (13) was carried out using a relatively longer reaction time (1.5 hours), compared with that of **1b** or **1c** (20 or 34 minutes). The oily chloromethyl derivatives produced, which were found to be neutral by ^{1}H nmr analysis contrary to Brossi's hydrochloride complex for analogous compounds (13b), were subsequently treated with sodium cyanide to give benzyl cyanides **2a,b,c** in 78, 59 and 52% yields, respectively. The condensation of the benzyl cyanides **2a,b** with 2,3-dimethoxy- or 2,3-methylenedioxybenzaldehyde, followed by the reduction of the resultant benzylidene function with 2% sodium amalgam (14), produced the α,β-diphenylpropionitriles **3a-d** (>80%). Hydrolysis of **3** in aqueous ethanol containing 10% sodium hydroxide and neutralization followed by drying gave the corresponding crude amino acids **4**. These were contaminated with inorganic salts and, without any purification or separation, were heated in xylene for 20 hours. This intramolecular dehydrative cyclization process gave the seven membered benzolactams **5a,b,c** in good yields (85,76 and 74%). On the other hand, similar treatment of **3d** even under longer treatment of its crude amino acid **4d** in boiling xylene gave rise to only 37% yield of **5d**. Later, we found that the intermediate, amino acid **4d**, m.p. 227-228°, was isolable in the pure state (96%) (15) and somehow less soluble in hot xylene than other amino acids **4a,b,c**. Consequently, the addition of a small amount of dimethylsulfoxide into boiling xylene led to the improved formaion of **5d** (87% from **3a**).

These lactams **5** were also obtained along the alternative scheme [**2**→**6**→**5**] partly analogous to the conversion of **3** to **5**. Hydrolysis of the cyano and acetamide functions of the compounds **2** and dehydrative cyclization between the resultant amino and carboxyl groups led to formation of benzazepinones **6a,b,c** (81, 88 and 85%). When the benzazepinone **6a** in dimethylformamide and tetrahydrofuran (1:10 volume %) was heated with 1.1 equivalents of benzyl bromide in the presence of sodium hydride at a gently boiling tetrahydrofuran temperature

Figure 2



(16), the smooth monobenzylation onto C_1 carbon proceeded to afford the known 1-benzyl-3-methyl-1,2,4,5-tetrahydro-3*H*-3-benzazepin-2-one **5e** (86%) (5d). In this reaction sequence, the interaction of **6a,b** with the appropriate 2,3-alkoxy-substituted benzyl bromides furnished alkoxybenzylbenzazepinones (84-87%) which were identical with **5a-d** as shown in Figure II.

Subsequently, these azepinones **5** were treated with phosphoryl chloride in refluxing dry toluene for 5 hours in a similar method to the previous transformation of **5e** to **7e** (5d), and underwent smooth cyclization to the desired enamines, tetrahydrobenz[*d*]indeno[1,2-*b*]azepines **7a-d**, including the known tetramethoxy or bismethylenedioxy derivative (**7a** or **7d**) (4,5a), in 83, 87, 78 and 61% yields, respectively. Further, when these tetracyclic enamines were dissolved in pyridine containing Triton B and exposed to molecular oxygen on the basis of the oxidation of indene to indenone (17), the mixture turned to a deep purple color immediately. Thus, the 12-oxo derivatives (**8a-d**) of **7** were formed as purplish red needles in yields of 79, 75, 76 and 74%, respectively (18).

EXPERIMENTAL

Melting points were determined on a Meltemp apparatus and are uncorrected. Boiling points are uncorrected. Infrared and ultraviolet spectra were recorded on Hitachi-Perkin Elmer Model 125 and Hitachi 124 spectrophotometers, respectively. The nmr spectra were run in deuteriochloroform solutions, unless otherwise stated, with tetramethylsilane as an internal reference at ambient temperature and registered on a 90 MHz Hitachi R-22 spectrometer. Mass spectra were obtained on a JEOL JMS-D300 instrument. Preparative thin layer chromatography was performed on Merck silica gel 60 PF-254 (Catalog No. 7749).

N-Methyl-*N*-(3,4-dimethoxyphenethyl)acetamide (**1a**).

To a stirred suspension of *N*-acetylhomoveratrylamine (40 g., 0.18 mole), m.p. 98.5-99.5° (lit. (19) m.p. 94-95°), and sodium hydride (8.6 g., 0.36 mole) (thoroughly washed 50% mineral oil with dry *n*-hexane) in dry dimethylformamide and tetrahydrofuran (1:10 volume %, 300 ml.) was gradually added methyl iodide (40 ml., 0.64 mole). The mixture was slowly heated to about 40°. After vigorous hydrogen evolution ceased, it was continuously stirred maintaining gently refluxing in an 80° oil bath for 10 hours. White precipitates of sodium chloride were removed by suction filtration and most of solvents were evaporated *in vacuo*. An oily residue was dissolved in chloroform, washed with dilute sodium thiosulfate solution and water, and dried over anhydrous sodium sulfate. After the solvent was removed in a rotary evaporator, the short pass distillation of an oily residue furnished pure **1a** (41.5 g., 98%), b.p. 153-156°/0.25 mm Hg. This oil crystallized later on standing at room temperature and melted at 38-44°; ir (chloroform): 1635 cm^{-1}; (nujol): 1640 cm^{-1}; nmr: δ 1.82, 2.02 (two s, 3H, N-$COCH_3$, 1:1.2), 2.6-3.0 (m, 2H, ArCH_2CH_2N), 2.86, 2.91 (two s, 3H, N-CH_3, 1.2:1), 3.3-3.7 (m, 2H, ArCH_2CH_2N), 3.82, 3.84 (two s, 6H, 2 × OCH_3, 1.2:1) and 6.6-6.8 (m, 3H, aromatic H's).

Anal. Calcd. for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90. Found: C, 65.99; H, 8.08; N, 5.89.

N-Methyl-*N*-(3,4-methylenedioxyphenethyl)acetamide (**1b**).

N-Acetylhomopiperonylamine (41.4 g., 0.2 mole), m.p. 102-103° (lit. (19) m.p. 105-106°), was treated with sodium hydride (9.6 g., 0.4 mole), methyl iodide (35.2 ml., 0.57 mole) in dry tetrahydrofuran (300 ml.) and dimethylformamide (30 ml.) under gentle refluxing for 10 hours. The mixture was worked up in the same manner as the reaction of dimethoxy derivative **1a** to **2a**. Distillation of the oily residue *in vacuo* yielded **1b** (42.2 g., 96%), b.p. 146-150°/0.3 mm Hg, which on standing crystallized, m.p. 66.5-68°; ir (neat); 1640 cm^{-1}; nmr: δ 1.91, 2.04 (two s, 3H, N-$COCH_3$, 8:9), 2.6-3.0 (m, 2H, ArCH_2CH_2N), 2.91, 2.96 (two s, 3H, N-CH_3, 9:8), 3.3-3.7 (m, 2H, ArCH_2CH_2N), 5.94, 5.96 (two s, 2H, OCH_2O, 8:9), 6.5-6.9 (m, 3H, aromatic H's).

Anal. Calcd. for $C_{12}H_{15}O_3N$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.23; H, 6.80; N, 6.44.

N-Methyl-*N*-(3,4,5-trimethoxyphenetyl)acetamide (**1c**).

N-Acetylmescaline (25.3 g., 0.1 mole), m.p. 87.5-89° (lit. (20) m.p. 93-94°) was treated with methyl iodide (25 ml., 0.4 mole) and sodium hydride (4.8 g., 0.2 mole) in the mixed solvents of dry dimethylformamide (17 ml.) and tetrahydrofuran (170 ml.). After gentle refluxing for 10 hours, the mixture was worked up as described for **b** or **c** series, and distillation of the crude product gave a pure **1c**, b.p. 161-163°/0.06 mm Hg (24.0 g., 90%). This all crystallized on standing at room temperature two days later, and melted at 61-64°; ir (neat): 1640 cm^{-1}; nmr: δ 1.90, 2.09 (two s, 3H, N-$COCH_3$, 1:1.5), 2.7-3.0 (m, 2H, ArCH_2CH_2N), 2.95 (broad s, 3H, N-CH_3), 3.4-3.8 (m, 2H, ArCH_2CH_2N), 3.86 (s, 3H, OCH_3), 3.88 (s, 3H, 2 × OCH_3) and 6.40, 6.48 (two s, 2H, aromatic H's).

Anal. Calcd. for $C_{14}H_{12}NO_4$: C, 62.90; H, 7.92; N, 5.24. Found: C, 62.73; H, 7.93; N, 5.16.

N-Methyl-*N*-(2-cyanomethyl-4,5-dimethoxyphenethyl)acetamide (**2a**).

A suspension of the aforementioned acetamide **1a** (40 g.), 37% formaldehyde solution (105 ml.) and chloroform (350 ml.) was stirred and cooled at −15°, and dry hydrogen chloride was introduced through the stirred suspension being kept at −20 to −15° for 100 minutes. After 30 minutes, a voluminous precipitate once appeared. This suspension gradually became homogenious and, after 80 minutes, the insoluble material again separated. The mixture was poured into ice-water (1 l.) and extracted with chloroform. The combined extracts were dried over anhydrous sodium sulfate, and removal of the solvent left a colorless oil (46 g.) of the crude chloromethyl derivative; nmr: δ 1.92, 2.12 (two s, 3H, N-$COCH_3$, 1:2), 2.6-3.0 (m, 2H, ArCH_2CH_2N), 2.98 (s, 3H, N-CH_3), 3.4-3.8 (m, 2H, ArCH_2CH_2N), 3.90 (s, 6H, 2 × OCH_3), 4.67, 4.74 (two s, 2H, Ar-CH_2, 1:2), 6.69, 6.84, 6.98 (three s, 2H, aromatic H's, 1:2:3).

This oil was dissolved in dimethylsulfoxide (400 ml.) and sodium cyanide (30 g) was added dropwise. The mixture, after being stirred for 1.5 hours, was poured into ice-water (1.2 l.) and extracted with chloroform (5 × 150 ml.). The chloroform extracts were combined, washed with saturated brine (5 × 300 ml.), and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a colorless oil (40.5 g.), which on crystallization from benzene-ether afforded white crystals of **2a** (36.5 g., 78%), m.p. 106-108°. Recrystallization from benzene gave an analytical sample, m.p. 108-109.5°; ir (chloroform): 1632 cm^{-1}; nmr: δ 1.89, 2.11 (two s, 3H, N-$COCH_3$, 1:3), 2.6-3.1 (m, 2H, ArCH_2CH_2N), 3.4-3.8 (m, 2H, ArCH_2CH_2N), 2.99, 3.01 (two s, 3H, N-CH_3, 1:3), 3.69, 3.85 (two s, 2H, ArCH_2CN, 1:3), 6.68, 6.81, 6.93, 6.95 (four s, 2H, aromatic H's, 1:3:1:3).

Anal. Calcd. for $C_{15}H_{20}N_2O_3$: C, 65.19; H, 7.30; N, 10.14. Found: C, 65.15; H, 7.29; N, 10.07.

This crystalline benzyl cyanide could be distilled to give an oily **2a**, b.p. 210°/0.3 mm Hg, which ir spectrum (neat) revealed peaks at 2270, 1645 cm^{-1}.

N-Methyl-*N*-(2-cyanomethyl-4,5-methylenedioxyphenethyl)acetamide (**2b**).

To a solution of the acetamide **1b** (10 g.) in chloroform (90 ml.) was added 37% formaldehyde solution (30 ml.). The mixture was cooled vigorously stirred, and dry hydrogen chloride was introduced at −15°. After about 10 minutes, a precipitate appeared, and in another 5 minutes the solids had dissolved. After an additional 5 minutes, the homogenious mixture was poured into ice-water (150 ml.) and extracted with chloroform (4 × 50 ml.). The combined extracts were dried and evaporated to leave a colorless oil (11.9 g.); nmr: δ 2.08 (broad s, 3H, N-$COCH_3$), 2.7-3.1 (m, 2H, ArCH_2CH_2N), 2.99 (s, 3H, N-CH_3), 3.4-3.7 (m, 2H, ArCH_2CH_2N), 4.66 (broad s, 2H, ArCH_2Cl), 5.99 (s, 2H, OCH_2O), 6.73 (broad s, 1H, Ar-H), 6.87 (s, 1H aromatic H).

This crude benzyl chloride was treated with sodium cyanide (7.5 g.) in dimethylsulfoxide (100 ml.) for 1.5 hours, as described for the dimethoxy derivative **2a**. The reaction mixture was poured into ice-water (300 ml.), and extracted with chloroform (5 × 10 ml.). The extracts were washed with saturated brine (5 × 75 ml.), dried and evaporated to dryness to give an oil (11.4 g.), which was crystallized from ethyl acetate-ether to yield **2b** (6.9 g., 59%), m.p. 87-89°. Recrystallization from the same solvents gave an analytical sample, m.p. 89-90.5° (b.p. 208-211°/0.2 mm Hg); ir (nujol): 2240, 1630 cm^{-1}; nmr: δ 1.92, 2.08 (two s, 3H, N-$COCH_3$, 1:2.6), 2.6-2.9 (m, 3H, ArCH_2CH_2N), 2.95, 2.29 (two s, 3H, N-CH_3, 1:2.7), 3.3-3.6 (m, 2H, ArCH_2CH_2N), 3.61, 3.79 (two s, 2H, ArCH_2CN, 1:3.1), 5.96, 5.97 (two s, 2H, OCH_2O, 2.7:1), 5.96, 5.97, 6.62, 6.69 (four s, 2H, aromatic H's, 1:2.7:1:2.7).

Anal. Calcd. for $C_{14}H_{16}O_3N_2$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.72; H, 6.14; N, 10.69.

N-Methyl-*N*-(2-cyanomethyl-3,4,5-trimethoxyphenethyl)acetamide (**2c**).

A mixture of the above acetamide **1c** (11.5 g.), chloroform (100 ml.) and 37% formaldehyde solution (33 ml.) was stirred and cooled to −20°. To this dry hydrogen chloride was introduced and, after 17 minutes, a precipitate appeared. For another 17 minutes, hydrogen chloride was continuously passed into the mixture kept below −15° and the cold mixture was poured into ice-water (170 g.). The chloroform extracts (4 × 55 ml.) were dried over anhydrous sodium sulfate and the solvent was evaporated in a rotary evaporator to leave an oil (15.7 g.) of the crude benzyl chloride **2c**. The nmr spectrum displayed broad peaks at 1.98, 2.12 (two s, 3H, N-$COCH_3$, 1:3), 2.7-3.2 (m, 2H, ArCH_2CH_2N), 3.01 (s, 3H, N-CH_3), 3.5-3.9 (m, 2H, ArCH_2CH_2N), 3.84 (s, 6H, 2 × OCH_3), 3.99 (s, 3H,

OCH_3), 4.77, 4.78 (two s, 2H, $ArCH_2Cl$, 3:1) and 6.44, 6.56 (two s, 1H, aromatic H).

This crude oil was dissolved in dimethylsulfoxide (115 ml.) and stirred with powdered sodium cyanide (7.6 g.) in a water bath for 1.5 hours. The mixture was treated with ice-water (340 g.) and extracted with chloroform (4 × 45 ml.). The combined extracts were washed with saturated sodium chloride solution (5 × 90 ml.). Drying over anhydrous sodium sulfate and evaporation of the solvent left an oily residue (16.5 g.), which on crystallization from ethyl acetate-ether afforded white crystals of **2c** (6.8 g., 52%), m.p. 77-78°. An analytical sample was recrystallized from benzene-ether, m.p. 77-78°; ir (nujol): 2250, 1640 cm^{-1}; nmr: δ 1.91, 2.12 (two s, 3H, $N\text{-}COCH_3$, 1:4), 2.7-3.1 (m, 2H, $ArCH_2CH_2N$), 2.95, 3.02 (two s, 3H, $N\text{-}CH_3$, 1:4), 3.4-4.1 (m, 4H, $ArCH_2CN$ and $ArCH_2CH_2N$), 3.88 (s, 6H, 2 × OCH_3), 4.02 (s, 3H, OCH_3), 6.45, 6.60 (s, 1H, aromatic H, 1:4).

Anal. Calcd. for $C_{16}H_{22}O_4N_2$: C, 62.72; H, 7.24; N, 9.14. Found: C, 62.82; H, 7.41; N, 8.86.

2-[-β-(*N*-Methyl-*N*-acetylamino)ethyl-4,5-dimethoxyphenyl]-3-(2,3-dimethoxyphenyl)propionitrile (**3a**).

To a stirred mixture of the benzyl cyanide **2a** (5.52 g., 0.02 mole) and 2,3-dimethoxybenzaldehyde (3.32 g., 0.02 mole) in 95% ethanol (20 ml.) in an ice-bath was added a sodium ethoxide solution [prepared from sodium metal (200 mg.) and absolute ethanol (4 ml.)]. The cooling bath was removed, and the solution was kept overnight at 30-35°. The mixture was then diluted with 95% ethanol (100 ml.). To this, 2% sodium amalgam (80 g.) (21) was added dropwise in the course of 1 hour. After stirring for another 4 hours, the ethanol layer was separated from mercury and distilled to leave an oil, which was shaken with water and chloroform. The chloroform extracts were dried and evaporated to afford an oily substance. Crystallization from benzene-ether yielded 7.45 g. (87%) of crystals, m.p. 113-115°, of **3a**. An analytical sample was prepared by recrystallization from the same solvents and melted at 114-115°; ir (nujol): 2260, 1650 cm^{-1}; nmr: δ 1.79, 2.07 (two s, 3H, $N\text{-}COCH_3$, 4.5:2), 2.6-3.1 (m, 2H, $ArCH_2CH_2N$), 2.88, 3.95 (two s, 3H, $N\text{-}CH_3$, 2:4.5), 3.13 (d, J = 8 Hz, 2H, $ArCH(CN)CH_2Ar$), 3.3-3.7 (m, 2H, $ArCH_2CH_2N$), 3.8-4.0 (12H, 4 × OCH_3), 4.49 (t, J = 8 Hz, 1H, $ArCH(CN)CH_2Ar$), 6.5-7.1 (m, 5H, aromatic H's).

Anal. Calcd. for $C_{24}H_{30}O_5N_2$: C, 67.58; H, 7.09; N, 6.57. Found: C, 67.48; H, 7.10; N, 6.48.

2-[2-β-(*N*-Methyl-*N*-acetylamino)ethyl-4,5-dimethoxyphenyl]-3-(2,3-methylenedioxyphenyl)propionitrile (**3b**).

The reaction of the benzyl cyanide **2a** (8.28 g., 0.03 mole) with 2,3-methylenedioxybenzaldehyde (4.5 g., 0.03 mole) furnished crystals (11.2 g., 82%), m.p. 85-88°, of **3b**. Recrystallization from 95% ethanol gave an analytically pure sample, m.p. 89-90°; ir (nujol): 2280, 1625 cm^{-1}; nmr: δ 1.90, 2.06 (two s, 3H, $N\text{-}COCH_3$, 1:3), 2.6-3.1 (m, 2H, $ArCH_2CH_2N$), 2.86, 2.95 (two s, 3H, $N\text{-}CH_3$, 3:1), 3.14 (d, J = 8 Hz, 2H, $ArCH(CN)CH_2Ar$), 3.3-3.7 (m, 2H, $ArCH_2CH_2N$), 3.97 (6H, 2 × OCH_3), 4.46 (t, J = 8 Hz, 1H, $ArCH(CN)CH_2Ar$), 5.92 (2H, OCH_2O), 6.5-7.0 (m, 5H, aromatic H's).

Anal. Calcd. for $C_{23}H_{26}O_5N_2$: C, 65.77; H, 7.07; N, 6.14. Found: C, 65.94; H, 7.08; N, 6.28.

2-[2-β-(*N*-Methyl-*N*-acetylamino)ethyl-4,5-methylenedioxyphenyl]-3-(2,3-dimethoxyphenyl)propionitrile (**3c**).

The reaction of the benzyl cyanide **2b** (1.3 g., 5 mmoles) with 2,3-dimethoxybenzaldehyde (0.84 g., 5 mmoles) using 50 mg. of sodium metal and 20 g. of 2% sodium amalgam gave crystalline product (1.88 g., 92%), m.p. 125-126°, which was recrystallized from benzene, to afford a sample of **3c** for analysis, m.p. 126-128°; ir (nujol) 2250, 1630 cm^{-1}; nmr: δ 1.96, 2.07 (two broad s, 3H, $N\text{-}COCH_3$, 2:5), 2.6-3.1 (m, 2H, $ArCH_2CH_2N$), 2.91, 2.94 (two broad s, 3H, $N\text{-}CH_3$), 3.11 (d, 2H, J = 8 Hz, $ArCH(CN)CH_2Ar$), 3.3-3.6 (m, 2H, $ArCH_2CH_2N$), 3.97 (s, 6H, 2 × OCH_3), 4.37 (t, J = 8 Hz, 1H, $ArCH(CN)CH_2Ar$), 5.98 (s, 2H, OCH_2O), 6.5-7.1 (m, 5H, aromatic H's).

Anal. Calcd. for $C_{23}H_{26}O_5N_2$: C, 67.30; H, 6.39; N, 6.83. Found: C, 67.35; H, 6.34; N, 7.82.

2-[2-β-(*N*-Methyl-*N*-acetylamino)ethyl-4,5-methylenedioxyphenyl]-3-(2,3-methylenedioxyphenyl)propionitrile (**3d**).

The reaction of the benzyl cyanide **2b** (1.3 g., 5 mmoles) with 2,3-methylenedioxybenzaldehyde (0.75 g., 5 mmoles) using 40 mg. of sodium metal and 20 g. of 2% sodium amalgam gave crystals (1.74 g., 89%), m.p. 143-145°, which on recrystallization from benzene furnished an analytical sample, m.p. 145-146°, of **3d**; ir (nujol): 2280, 1645 cm^{-1}; nmr: δ 2.00, 2.09 (two s, 3H, $N\text{-}COCH_3$, 1:4), 2.6-3.1 (m, 2H, $ArCH_2CH_2N$), 2.92, 2.97 (two s, 3H, $N\text{-}CH_3$), 3.12 (d, J = 8 Hz, 1H, $ArCH(CN)CH_2Ar$), 3.3-3.6 (m, 2H, $ArCH_2CH_2N$), 4.46 (t, J = 8 Hz, 1H, $ArCH(CN)CH_2Ar$), 5.95, 5.97 (two s, 4H, 2 × OCH_2O), 6.6-7.1 (m, 5H, aromatic H's).

Anal. Calcd. for $C_{22}H_{22}O_5N$: C, 66.99; H, 5.62; N, 7.10. Found: C, 66.84; H, 5.49; N, 7.04.

1-(2,3-Dimethoxybenzyl)-7,8-dimethoxy-3-methyl-1,2,4,5-tetrahydro-3*H*-3-benzazepin-2-one (**5a**).

A mixture of the nitrile **3a** (7.8 g.) and 50% ethanol (120 ml.) containing 10% sodium hydroxide was heated to reflux for 20 hours. After cooling, the mixture was brought to *p*H 11-10 by addition of concentrated hydrochloric acid, and insoluble material was filtered off through a thin layer of Celite powder under reduced pressure. A clear solution obtained was neutralized with dilute hydrochloric acid to *p*H 7.0. The solvents were removed in a rotary evaporator. The residue was dried in vacuum desicator over phosphorus pentoxide, and then was ground with a mortar pestle. The resultant powdered mixture was heated in xylene (160 ml.) under a Dean-Stark water separator for 20 hours. The xylene solution was separated from the inorganic precipitate by suction filtration, and evaporated to leave an oil, which was triturated with benzene to afford crystals (6.0 g., 85%), m.p. 147-149°, which on recrystallization from benzene afforded a sample of **5a** for analysis; m.p. 147-148°; ir (nujol): 1660 cm^{-1}; nmr: δ 2.96 (s, 3H, $N\text{-}CH_3$), 2.9-4.1 (m, 4H, C_4- and C_5-H_2), 2.49 (d, J = 7.5 Hz, 2H, benzyl H's), 3.77, 3.80 (two s, 6H, 2 × OCH_3), 3.86 (s, 6H, 2 × OCH_3), 4.54 (t, J = 7.5 Hz, 1H, C_1-H), 6.60, 6.68 (two s, 2H, C_1- and C_4-H), 6.7-7.0 (m, 3H, aromatic H's).

Anal. Calcd. for $C_{22}H_{27}O_5N$: C, 68.55; H, 7.06; N, 3.63. Found: C, 68.67; H, 7.03; N, 3.65.

1-(2,3-Methylenedioxybenzyl)-7,8-dimethoxy-3-methyl-1,2,4,5-tetrahydro-3*H*-3-benzazepin-2-one (**5b**).

In the same manner as described above, the nitrile **3b** (2.5 g.) was hydrolyzed in the alcoholic sodium hydroxide solution (40 ml.), and the resultant powdered precipitate was heated in boiling xylene (50 ml.) for 20 hours. The work-up afforded an oily material, which was purified by preparative thin layer chromatography (silica gel, 3% methanol-dichloromethane). A band with Rf 0.4 was extracted with a 1:2 mixture of methanol and dichloromethane. The solvents were evaporated to leave an oil, which was dissolved in dichloromethane, washed with water and dried over anhydrous sodium sulfate. Removal of the solvent *in vacuo* left an amorphous product, **5b** (2.11 g., 76%), which showed the following spectral data; ir (chloroform): 1640 cm^{-1}; nmr: δ 2.96 (s, 3H, $N\text{-}CH_3$), 3.0-4.2 (m, 6H, 3 × CH_2), 3.77, 3.84 (two s, 6H, 2 × OCH_3), 4.59 (t, J = 7.5 Hz, 1H, C_1-H), 5.89, 5.91 (ABq, J = 2 Hz, 2H, OCH_2O), 6.62, 6.68 (two s, 2H, C_1- and C_2-H), 6.6-6.9 (m, 3H, aromatic H's); m/e 369.1569 (Calcd. for $C_{21}H_{23}O_5N$: 369.1573).

Anal. Calcd. for $C_{21}H_{23}O_5N$: C, 68.28; H, 6.28; N, 3.79. Found: C, 68.21; H, 6.24; N, 3.54.

1-(2,3-Dimethoxybenzyl)-7,8-methylenedioxy-3-methyl-1,2,4,5-tetrahydro-3*H*-3-benzazepin-2-one (**5c**).

Similarly, the nitrile **3c** (2.96 g.) in the alcoholic sodium hydroxide solution (45 ml.) was hydrolyzed, and the resultant amino acid was dehydrated in boiling xylene (60 ml.). Crystals (1.90 g., 74%), m.p. 127-129°, of **5c** were obtained by trituration with benzene-ether. Recrystallization from the same solvents furnished an analytically pure sample, m.p. 127-129°; ir (nujol): 1658 cm^{-1}; nmr: δ 2.89 (s, 3H, $N\text{-}CH_3$),

2.9-4.2 (m, 6H, 3 × CH_2), 3.85, 3.87 (two s, 6H, 2 × OCH_3), 4.56 (t, J = 5 Hz, 1H, C_1-H), 5.92 (s, 2H, OCH_2O), 6.63, 6.81 (two s, 2H, C_1- and C_4-H's), 6.7-7.1 (m, 3H, aromatic H's).

Anal. Calcd. for $C_{21}H_{23}O_5N$: C, 68.28; H, 6.28; N, 3.79. Found: C, 68.34; H, 6.30; N, 3.83.

1-(2,3-Methylenedioxybenzyl)-7,8-methylenedioxy-3-methyl-1,2,4,5-tetrahydro-3*H*-3-benzazepin-2-one (**5d**).

The nitrile **3d** (3.5 g.) was heated in the alcoholic sodium hydroxide solution (50 ml.) and the resultant crude amino acid was heated in boiling xylene (70 ml.) for 3 days. The work-up and the purification by preparative thin layer chromatography as described for **5b** yielded the benzylbenzazepinone **5d** as an amorphous substance (1.45 g., 37%); ir 1640 cm^{-1}; nmr: δ 2.90 (s, 3H, N-CH_3), 2.85-4.1 (m, 6H, 3 × CH_2), 4.58 (t, J = 7.5 Hz, 1H, C_1-H), 5.91, 5.93 (two s, 4H, 2 × OCH_2O), 6.6-6.9 (m, 5H, aromatic H's); m/e 353.1314 (Calcd. for $C_{20}H_{19}O_5N$: 353.1262).

Anal. Calcd. for $C_{20}H_{19}O_5N$: C, 67.98; H, 5.42; N, 3.96. Found: C, 68.02; H, 5.42; N, 3.75.

2[2-β-(*N*-Methylamino)ethyl-4,5-methylenedioxyphenyl]-3-(2,3-methylenedioxyphenyl)propionic Acid (**4d**) and Its Cyclization in a Mixture of Dimethylsulfoxide and Xylene to **5d**.

The nitrile **3d** (2.7 g.) was heated in boiling 95% ethanol (45 ml.) containing 10% sodium hydroxide for 20 hours, and treated with hydrochloric acid in the same manner as described above. The resultant neutral solution, after removal of insoluble material, was concentrated to about 30 ml. and cooled. The precipitate which separated was collected, washed with aqueous ethanol and amounted to 2.44 g. (96%), m.p. 227-228°. These crystals were practically pure without further purification for the next reaction, and gave the following analytical data; ir (nujol): 3100-2100, 1630, 1600 (sh), 1565 cm^{-1}.

Anal. Calcd. for $C_{20}H_{21}O_6N$: C, 64.68; H, 5.70; N, 3.77. Found: C, 64.57; H, 5.72; N, 3.86.

A stirred suspension of the amino acid **4d** (2.30 g.) in xylene (50 ml.) and dimethylsulfoxide (2 ml.) was heated to reflux under a Dean-Stark trap for 4 days. The solution was evaporated *in vacuo* to leave an oil, which was subjected to preparative thin layer chromatography (silica gel, 3% methanol-dichloromethane) in the identical method with the above. The dichloromethane solution was dried over anhydrous sodium sulfate, and evaporated to dryness to afford an oily benzylbenzazepine **5a** (1.99 g., 91%).

7,8-Dimethoxy-3-methyl-1,2,4,5-tetrahydro-3*H*-3-benzazepin-2-one (**6a**).

The aforementioned nitrile **2a** (5 g.) was heated in 50% ethyl alcohol (75 ml.) containing 10% sodium hydroxide. After refluxing for 20 hours, the mixture was cooled and neutralized with dilute hydrochloric acid to *p*H 7.0. The insoluble material was removed by suction filtration through a thin layer of Celite powder. A clear solution obtained was evaporated in a rotary evaporator and then dried with phosphorus pentoxide in a vacuum desiccator. The dry precipitate was powdered with a mortar and pestle and heated in refluxing xylene (100 ml.) under a Dean-Stark trap for 24 hours. The solution was freed of inorganic precipitate and evaporated to leave an oil, which on crystallization from benzene-ether gave **6a** (3.45 g., 81%), m.p. 135-137°. Recrystallization from 95% ethanol afforded a pure sample, m.p. 137-138°; ir (nujol): 1650 cm^{-1}; nmr: δ 3.07 (s, 3H, N-CH_3), 3.0-3.2 (m, 2H, ArC$H_2$$CH_2$N), 3.65-3.75 (m, 2H, $ArCH_2CH_2N$), 3.88 (s, 2H, $ArCH_2CO$), 3.89 (s, 6H, 2 × OCH_3), 6.62, 6.65 (two s, 2H, aromatic H's).

Anal. Calcd. for $C_{13}H_{17}O_3N$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.24; H, 7.44; N, 6.05.

7,8-Methylenedioxy-3-methyl-1,2,4,5-tetrahydro-3*H*-3-benzazepin-2-one (**6b**).

The nitrile **2b** (5 g.) in 50% ethanol (75 ml.) containing 10% sodium hydroxide was heated to reflux for 22 hours. The alkaline solution was neutralized with dilute hydrochloric acid. The precipitates were removed by suction filtration. The filtrate was evaporated, and the residue was dried in a vacuum desiccator to be brought to constant weight. The resultant dry, white solid, after being powdered, was heated in xylene (100 ml.) under a Dean-Stark water separator for 20 hours. Xylene layer was evaporated to leave an oil, which was crystallized from 95% ethanol to give **6b** (3.7 g., 88%), m.p. 167-168°. Recrystallization from the same solvent afforded a sample for analysis, m.p. 167-168°; ir (nujol): 1640 cm^{-1}; nmr: δ 3.00 (s, 3H, N-CH_3), 2.9-3.2 (m, 2H, ArC$H_2$$CH_2$N), 3.5-3.8 (m, 2H, $ArCH_2CH_2N$), 3.80 (s, 2H, $ArCH_2CO$), 5.93 (s, 2H, OCH_2O), 6.62, 6.64 (two s, 2H, aromatic H's).

Anal. Calcd. for $C_{12}H_{13}O_3N$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.71; H, 5.92; N, 6.32.

7,8,9-Trimethoxy-3-methyl-1,2,4,5-tetrahydro-3*H*-3-benzazepin-2-one (**6c**).

The nitrile **2c** (3.2 g.) was hydrolyzed in 50% ethanol (48 ml.) containing 10% sodium hydroxide under refluxing for 22 hours. The same work-up as described for other lactams **6a,b** led to a powdered mixture of the crude amino acid and inorganic salts, which was heated in xylene (90 ml.) to reflux under a Dean-Stark trap for 20 hours. After cooling to room temperature, the organic layer was evaporated to leave a pale brown oil, which on crystallization from benzene-ether gave white crystals of **6c** (2.35 g., 85%), m.p. 120-122°. Recrystallization from 90% ethanol afforded an analytical sample, m.p. 120.5-121.5°; ir (nujol): 1650 cm^{-1}; nmr: δ 3.02 (s, 3H, N-CH_3), 2.9-3.2 (m, 2H, ArC$H_2$$CH_2$N), 3.5-4.0 (m, 4H, $ArCH_2CO$ and $ArCH_2CH_2N$), 3.86, 3.89 (two s, 9H, 3 × OCH_3) and 6.47 (s, 1H, aromatic H).

Anal. Calcd. for $C_{14}H_{19}O_4N$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.27; H, 7.18; N, 5.06.

Reactions of Benzazepinones **6a,b** with Benzyl Bromides.

To a stirred suspension of **6a** (235 mg., 1 mmole) and sodium hydride (48 mg., 2 mmoles) in dry dimethylformamide and tetrahydrofuran (1:10 volume %, 1 ml.) under a nitrogen atmosphere was added benzyl bromide (205 mg., 1.1 mmoles) in the above solvents (1 ml.). The mixture was heated at 80° in an oil bath for 4 hours, and then tetrahydrofuran was evaporated. The residue, after addition of ice-water (20 ml.), was extracted with chloroform (3 × 10 ml.). The extracts were washed with saturated brine (5 × 20 ml.), dried over anhydrous sodium sulfate and evaporated to leave an oil (330 mg.). Crystallization from benzene-ether afforded white crystals **5e** (280 mg., 86%), m.p. 141-142°, which spectral data were identical with those of 1-benzyl-7,8-dimethoxy-3-methyl-1,2,4,5-tetrahydro-3*H*-3-benzazepin-2-one (lit. (5d), m.p. 141°).

In the same manner, **6a** (235 mg., 1 mmole) was reacted with 2,3-dimethoxybenzyl bromide (254 mg., 1.1 mmoles). Crystallization of the crude product from benzene-ether afforded the alkoxybenzylbenzazepinone (325 mg., 84%), m.p. 146-148°, which was identical in all respects with the aforementioned benzylbenzazepinones **5a**.

The benzazepinone **6a** (235 mg., 1 mmole) and 2,3-methylenedioxybenzyl bromide (237 mg., 1.1 mmoles) gave an oily residue, which was purified by preparative thin layer chromatography (silica gel, 3% methanol-dichloromethane). Extraction of an Rf, 0.4 band with 1:2 methanol-dichloromethane, followed by evaporation of the solvents and washing the resultant oil in dichloromethane with water, led to an oil (340 mg., 87%), which spectral data were identical with those of **5b**.

The reaction of **6b** (219 mg., 1 mmole) with 2,3-dimethoxybenzyl bromide (254 mg., 1.1 mmoles) afforded crystalline material (322 mg., 87%), m.p. 125-127°, from benzene-ether. This spectral data was identical with those of the benzazepinone **5c**.

The benzazepinone **6b** (219 mg., 1 mmole) was benzylated with 2,3-methylenedioxybenzyl bromide (237 mg., 1.1 mmoles). Purification of an oily residue by the same procedure as described for **5d**, gave an oil (304 mg., 86%), which was identical in all respects with the compound **5d**.

Reaction of **5a-d** with Phosphoryl Chloride.

2,3,10,11-Tetramethoxy-7-methyl-5,6,7,12-tetrahydrobenz[*d*]indeno-[1,2-*b*]azepine (**7a**).

A stirred mixture of the benzylbenzazepinone **5a** (578 mg., 1.5 mmoles) and phosphoryl chloride (690 mg., 4.5 mmoles) in dry toluene (8

ml.) was heated to reflux under nitrogen for 5 hours. After cooling, the mixture was poured into ice-water, basified with dilute sodium hydroxide solution and extracted with dichloromethane. The extracts were combined, washed with saturated brine and dried over anhydrous sodium sulfate. Solvents were evaporated and the residue (640 mg.) was crystallized from 95% ethanol to give 305 mg. of **7a** m.p. 129-130°, in 83% yield. Recrystallization from the same solvent afforded a sample for analysis, m.p. 133-134° (lit (4 and 5a) m.p. 133-134°); ir (nujol): 1605, 1577, 1558 cm^{-1}; uv (ethanol): 262 (ϵ 11,800) and 342 (24,300) mμ; uv (ethanol-hydrogen chloride): 238 (ϵ 18,900) and 323 (22,000) mμ; nmr: δ 3.04 (s, 3H, N-CH_3), 2.9-3.1 (m, 2H, ArCH_2CH_2N), 3.15-3.25 (m, 2H, ArCH_2CH_2N), 3.87 (s, 2H, C_{12}-H), 3.93 (s, 6H, 2 × OCH_3), 3.40, 3.42 (two s, 6H, 2 × OCH_3), 6.74 (s, 1H, C_4-H), 6.94, 7.23 (ABq, J = 8 Hz, 2H, C_8- and C_9-H), 7.12 (s, 1H, C_1-H).

Anal. Calcd. for $C_{22}H_{25}O_4N$: C, 71.91; H, 6.86; N, 3.81. Found: C, 71.87; H, 6.82; N, 3.81.

2,3-Dimethoxy-10,11-methylenedioxy-7-methyl-5,6,7,12-tetrahydrobenz-[*d*]indeno[1,2-*b*]azepine (**7b**).

Similarly, **5b** (369 mg., 1 mmole) was treated with phosphoryl chloride (460 mg., 3 mmoles) as described above. Crude product (305 mg., 87%), m.p. 176-177°, was recrystallized from 95% ethanol to lead to a pure sample, m.p. 176-177°, of **7b**; ir (nujol): 1603, 1578, 1552 cm^{-1}; uv (ethanol): 266 (ϵ 8,500) and 340 (20,900) mμ; uv (ethanol-hydrogen chloride): 239 (ϵ 14,200), 316 (12,600) and 341 (15,000) mμ; nmr: δ 2.99 (s, 3H, N-CH_3), 2.9-3.1 (m, 2H, C_5-H_2), 3.1-3.35 (m, 2H, C_6-H), 3.73 (s, 2H, C_{12}-H), 3.90, 3.93 (two s, 6H, 2 × OCH_3), 6.00 (s, 2H, OCH_2O), 6.70 (s, 1H, C_4-H), 6.80, 7.01 (ABq, J = 8 Hz, 2H, C_8- and C_9-H), 7.03 (s, 1H, C_1-H).

Anal. Calcd. for $C_{21}H_{21}O_4N$: C, 71.78; H, 6.02; N, 3.99. Found: C, 71.85; H, 5.94; N, 3.74.

10,11-Dimethoxy-2,3-methylenedioxy-7-methyl-5,6,7,12-tetrahydrobenz-[*d*]indeno[1,2-*b*]azepine (**7c**).

Compound **7c** was obtained by interaction of **5c** (738 mg., 2 mmoles) with phosphoryl chloride (910 mg., 6 mmoles) in the same manner as the above, m.p. 174-175°; (550 mg., 78%). Recrystallization from 95% ethanol gave a pure sample, m.p. 177-178°; ir (nujol): 1612, 1562 (sh), 1555 cm^{-1}; uv (ethanol): 263 (ϵ 10,000) and 344 (21,900) mμ: uv (ethanol-hydrogen chloride): 241 (ϵ 15,400) and 322 (20,100) mμ; nmr: δ 3.00 (s, 3H, N-CH_3), 2.85-3.05 (m, 2H, C_5-H), 3.1-3.3 (m, 2H, C_6-H), 3.79 (s, 2H, C_{12}-H), 3.90, 3.98 (two s, 6H, 2 × OCH_3), 5.92 (s, 2H, OCH_2O), 6.64 (s, 1H, C_4-H), 6.87, 7.56 (ABq, J = 8 Hz, 2H, C_8- and C_9-H), 7.06 (s, 1H, C_1-H).

Anal. Calcd. for $C_{21}H_{21}O_4N$: C, 71.78; H, 6.02; N, 3.99. Found: C, 71.85; H, 5.94; N, 3.74.

2,3,10,11-Bismethylenedioxy-5,6,7,12-tetrahydro-7-methylbenz[*d*]-indeno[1,2-*b*]azepine (**7d**).

When **5d** (353 mg., 1 mmole) was treated with phosphoryl chloride (460 mg., 3 mmoles), **7d** (205 mg., 61%), m.p. 201-202°, was obtained. This crude enamine was recrystallized from 99% ethanol, m.p. 202-203° (lit (4) m.p. 220-222°); ir (nujol): 1608, 1560 cm^{-1}; uv (ethanol): 272 (ϵ 7,800) and 344 (18,500) mμ; uv (ethanol-hydrogen chloride): 247 (ϵ 12,600), 316 (10,700) and 342 (12,600) mμ; nmr: δ 2.99 (s, 3H, N-CH_3), 2.95-3.05 (m, 2H, C_5-H), 3.1-3.3 (m, 2H, C_6-H), 3.72 (s, 2H, C_{12}-H), 5.94, 6.00 (two s, 4H, 2 × OCH_2O), 6.66 (s, 1H, C_4-H), 6.80, 7.01 (ABq, J = 8 Hz, 2H, C_8- and C_9-H), 7.01 (s, 1H, C_1-H).

Anal. Calcd. for $C_{20}H_{17}O_4N$: C, 71.63; H, 5.11; N, 4.18. Found: C, 71.73; H, 5.22; N, 4.16.

Oxidation of the Enamines **7a-d**.

2,3,10,11-Tetramethoxy-7-methyl-5,6,7,12-tetrahydrobenz[*d*]indeno[1,2-*b*]-azepin-12-one (**8a**).

To a stirred solution of the enamine **7a** (2.75 g., m.p. 133-134°) in dry pyridine (60 ml.) was added dropwise 20% Triton B-pyridine solution (5 ml.), and then a stream of oxygen (30 ml./minute) was passed through a glass bubbler into the reaction mixture which was being kept at 20° with cooling bath for 40 minutes. The reaction was exothermic for the first 20 minutes. The solvent was removed in a rotary evaporator below 35° to leave a deep-purple oil, which was dissolved in chloroform, washed with dilute hydrochloric acid and water. After drying over anhydrous sodium sulfate, the chloroform was distilled in a rotary evaporator and the residue was recrystallized from 95% ethanol to give purplish red needles (2.25 g.) of **8a** m.p. 159-161° in 79% yield. The sample was recrystallized from the same solvent to afford an analytical sample, m.p. 161-162°, (lit (5a) m.p. 159-161°); ir (nujol): 1652 cm^{-1}; uv 225 sh (ϵ 19,800), 242 sh (18,300), 305 sh (26,900), 317 (32,200) and 500 (visible 2,200) mμ; nmr: δ 2.85-3.15 (m, 2H, C_5-H), 3.42 (s, 3H, N-CH_3), 3.6-3.9 (m, 2H, C_6-H), 3.88 (s, 6H, 2 × OCH_3), 3.98, 4.05 (two s, 6H, 2 × OCH_3), 6.59 (s, 1H, C_4-H), 6.72, 7.10 (ABq, J = 8 Hz, 2H, C_8- and C_9-H), 7.90 (s, 1H, C_1-H).

Anal. Calcd. for $C_{22}H_{25}O_5N$: C, 69.27; H, 6.08; N, 3.67. Found: C, 69.15; H, 6.17; N, 3.77.

2,3-Dimethoxy-10,11-methylenedioxy-7-methyl-5,6,7,12-tetrahydrobenz-[*d*]indeno[1,2-*b*]azepin-12-one (**8b**).

Compound **7b** (600 mg., m.p. 176-177°) in pyridine (16 ml.) was treated with 20% Triton B-pyridine solution (1 ml.) and oxygen, and purplish red crystals (466 mg.), m.p. 233-235°, of **8b** (75%) were obtained by crystallization from 95% ethanol. An analytical sample was recrystallized from the same solvent and melted at 235-236°; ir (nujol): 1650 cm^{-1}; uv (ethanol): 222 sh (ϵ 29,000), 311 sh (30,400), 322 (38,000) and 497 (visible, 2,300) mμ; nmr: δ 2.8-3.1 (m, 2H, C_5-H), 3.36 (s, 3H, N-CH_3), 3.6-3.8 (m, 2H, C_6-H), 3.80, 3.88 (two s, 6H, 2 × OCH_3), 6.05 (s, 2H, OCH_2O), 6.52 (s, 1H, C_4-H), 6.57, 6.86 (ABq, J = 8 Hz, 2H, C_8- and C_9-H), 7.89 (s, 1H, C_1-H).

Anal. Calcd. for $C_{21}H_{19}O_5N$: C, 69.03; H, 5.24; N, 3.83. Found: C, 68.94; H, 5.10; N, 3.73.

10,11-Dimethoxy-2,3-methylenedioxy-7-methyl-5,6,7,12-tetrahydrobenz-[*d*]indeno[1,2-*b*]azepin-12-one (**8c**).

Compound **8c** (315 mg.), m.p. 187-188°, was formed in 76% yield by the oxidation of **7c** (400 mg., m.p. 177-178°) in the presence of 20% Triton B-pyridine solution (0.6 ml.). Recrystallization from the same solvent, 95% ethanol, gave an analytically pure sample, m.p. 190-191° (lit. (11) m.p. 188-189°); ir (nujol): 1648 cm^{-1}; uv: 233 (ϵ 22,900), 302 sh (27,800), 319 (31,300) and 499 (visible, 2,600) mμ; nmr: δ 2.85-3.05 (m, 2H, C_5-H), 3.87, 4.04 (two s, 6H, 2 OCH_3), 5.92 (s, 2H, OCH_2O), 6.55 (m, 1H, C_4-H), 6.71, 7.10 (ABq, J = 8 Hz, 2H, C_8- and C_9-H), 7.65 (s, 1H, C_1-H).

Anal. Calcd. for $C_{21}H_{19}O_5N$: C, 69.03; H, 5.24; N, 3.83. Found: C, 69.08; H, 5.11; N, 3.70.

2,3,10,11-Bismethylenedioxy-7-methyl-5,6,7,12-tetrahydrobenz[*d*]indeno-[1,2-*b*]azepin-12-one (**8d**).

Compound **7d** (335 mg., m.p. 190-191°) was oxidized in a similar manner to afford crude crystals of **8d** (258 mg., 74%), m.p. 243-244°, which was recrystillized from 95% ethanol-benzene, m.p. 244-245°; ir (nujol): 1660 cm^{-1}; uv: 223 sh (ϵ 25,500), 304 sh (24,700), 324 (33,000) and 493 (visible, 2,200) m_m; nmr: δ 2.85-3.05 (m, 2H, C_5-H), 3.39 (s, 3H, N-CH_3), 3.15-3.35 (m, 2H, C_6-H), 5.91, 6.10 (two s, 4H, 2 × OCH_2O), 6.59 (s, 1H, C_4-H), 6.71, 7.10 (Abq, J = 8 Hz, 2H, C_8- and C_9-H), 7.90 (s, 1H, C_1-H).

Anal. Calcd. for $C_{20}H_{15}O_5N$: C, 68.76; H, 4.33; N, 4.01. Found: C, 68.53; H, 4.27; N, 3.94.

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