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Studies on the Syntheses of Heterocyclic Compounds. DCXCII.[1a] A Novel Synthetic Route to Phthalideisoquinoline and Spirobenzylisoquinoline Type Alkaloids[1b]

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Permanganate oxidation of 12-chloro-5,6,7,7a-tetrahydro-2,3,9,10-tetramethoxy-7-methylindeno[2,1-*a*][3] benzazepine (**5**) in the presence of piperidine gave the diketospirobenzylisoquinoline (**11**) and the lactone (**15**), the latter of which was converted into *erythro*- and *threo*-phthalideisoquinoline (**16** and **17**). 2,3-Dihydro-7,8-dimethoxy-5-(2,3-dimethoxybenzoyl)-3-methyl-1H-3-benzazepine (**4**) was prepared from N-β-(3,4-dimethoxyphenethyl)-2,3-dimethoxyphenylacetamide (**26**) in four steps.

Keywords——phthalideisoquinoline type alkaloid; spirobenzylisoquinoline type alkaloid; permanganate oxidation; 12-chloro-5,6,7,7a-tetrahydro-2,3,9,10-tetramethoxy-7-methylindeno[2,1-*a*][3] benzazepine; 2,3-dihydro-7,8-dimethoxy-5-(2,3-dimethoxybenzoyl)-3-methyl-1H-3-benzazepine

The important role of the protoberberine alkaloids in the biogenesis of many isoquinoline alkaloids, such as the phthalideisoquinoline,[3] benzophenanthridine,[3] protopine,[3,4] spirobenzylisoquinoline[5,6] and rhoeadine type alkaloids,[7] is now well known. On the other hand, the indeno[2,1-*a*][3]benzazepines, which have been prepared from a spirobenzylisoquinoline[8] and a protoberberine precursor,[9] occupy an important position chemically and have already been converted into the rhoeadine[8,10] and spirobenzylisoquinoline alkaloids.[11] Here we wish to report a novel synthesis of the phthalideisoquinoline and spirobenzylisoquinoline type compounds from indeno[2,1-*a*][3]benzazepine.

Refluxing 2,3-dihydro-5-(3,4-dimethoxybenzoyl)-3-methyl-1H-3-benzazepine (3),[12] which was obtained by reaction of 3,4-dihydropapaveraldine methiodide (1) with diazomethane, with phosphoryl chloride in dry toluene gave 12-chloro-5,6,7,7a-tetrahydro-2,3,9,10-tetramethoxy-7-methylindeno[2,1-*a*][3]benzazepine (5)[13] in addition to a small amount of 5-formyl-2,3-di-

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hydro-4-(3,4-dimethoxyphenyl)-3-methyl-1H-3-benzazepine (**7**), the latter of which was synthesised in good yield by treatment of **3** with phosphorus pentoxide in boiling toluene. The structure of **7** was determined by spectral analysis. Further treatment of **7** with phosphoryl chloride in boiling toluene afforded only the 5-benzoylbenzazepine (**3**) as an isolated product.

The oxidation of the chloroindeno[2,1-*a*][3]azepine (**5**) with potassium permanganate in acetone in the presence of piperidine and acetic acid[14] at 0° for *ca.* 2 hr gave the diketospirobenzylisoquinoline (**11**), mp 244.5—245.5°, and the lactone (**15**), mp 195—196°. The mass spectrum [*m/e* 397 (M^+)] and microanalysis of the former compound (**11**) indicated the molecular formula to be $C_{22}H_{23}NO_6$ and infrared (IR) spectrum [$\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1730, 1688 (C=O)], ultraviolet (UV) spectrum [$\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 316 (4.16), 295 (4.06), and 258 (4.82)] and nuclear magnetic resonance (NMR) spectrum (δ in $CDCl_3$) [2.37 (3H, s, NMe), 2.92—3.10 (2H, m, $C\underline{H}_2CH_2N$), 3.23—3.42 (2H, m, $CH_2C\underline{H}_2N$), 3.50 and 3.83 (each 3H, each s, 2×OMe), 4.02 (6H, s, 2×OMe), 5.92 (1H, s, 1-H), 6.66 (1H, s, 4-H) and 7.41 (2H, s, 9- and 12-H)] were similar to those of compound (**12**) which had already been prepared.[15]

The latter compound (**15**) whose molecular formula, $C_{22}H_{23}NO_6$, was determined by mass spectrum [*m/e* 397 (M^+)] and microanalysis, was hydrogenated in the presence of Adams catalyst to afford an epimeric mixture of phthalideisoquinolines, **16** and **17**, in a ratio of 9:1, whose structures were determined, after separation by preparative thin-layer chromatography (TLC), on silica gel, to be the *erythro* compound (**16**) and *threo* compound (**17**), respectively, by comparison with the data reported by Shamma.[16] Reduction of **15** with sodium borohydride in methanol yielded only the *erythro* compound (**16**) but no *threo* compound (**17**) was obtained. The above results suggested that the oxidised product has structure **15**. The stereochemistry of **15** was tentatively assigned the Z-form, because of the presence of two *O*-methyl groups (δ 3.51 and 3.83) resonating at abnormally high field, which is similar to that of 1,2,9,10-tetramethoxyaporphine.[17] The above conversion of benzylisoquinoline to phthalideisoquinoline through indenobenzazepine serves as a third synthetic method for phthalideisoquinolines.

The mechanism for the formation of the diketospirobenzylisoquinoline (**11**) and the lactone (**15**) from the chloroindenobenzazepine (**5**) is considered to be as follows. The chloroindenobenzazepine (**5**) is oxidised to the keto alcohol (**8**), ring contraction of which, followed by hydroxylation and further oxidation of **10**, yields the diketospirobenzylisoquinoline (**11**) as shown by route a. Further oxidation of **8** affords the ring-opened ketocarboxylic acid (**13**), aziridine formation of which, followed by ring opening of the resulting **14** furnishes the lactone (**15**). Another possible product (**29**) was not obtained in the above reaction.

On the other hand, all the attempts to cyclise 2,3-dihydro-7,8-dimethoxy-5-(2,3-dimethoxybenzoyl)-3-methyl-1H-3-benzazepine (**4**) to **6** or its analogue gave an infructuous result. 2,3-Dimethoxybenzaldehyde (**18**) was converted into the amide (**26**)[18] by two modified classical methods, **18→19→20→21→26** and **18→22→23→24→25→26**. Details of the synthesis of the amide (**26**) are described in the experimental section. Bischler-Napieralski reaction of **26** with phosphoryl chloride afforded the 3,4-dihydroisoquinoline (**27**), oxidation of which by stirring in ethanol in the presence of iodine and sodium acetate, followed by treatment of the resulting benzoylisoquinoline (**28**) with methyl iodide, gave the methiodide (**2**). Ring expansion of **2** with diazomethane furnished the benzazepine (**4**).

Since reactions of **4** with phosphoryl chloride in several solvents yielded the starting material or a tarry product, the desired cyclized compound (**6**) could not be obtained. The methoxyl group at C_2-position on the benzoyl group must be easily cleaved under the condition of the cyclization.

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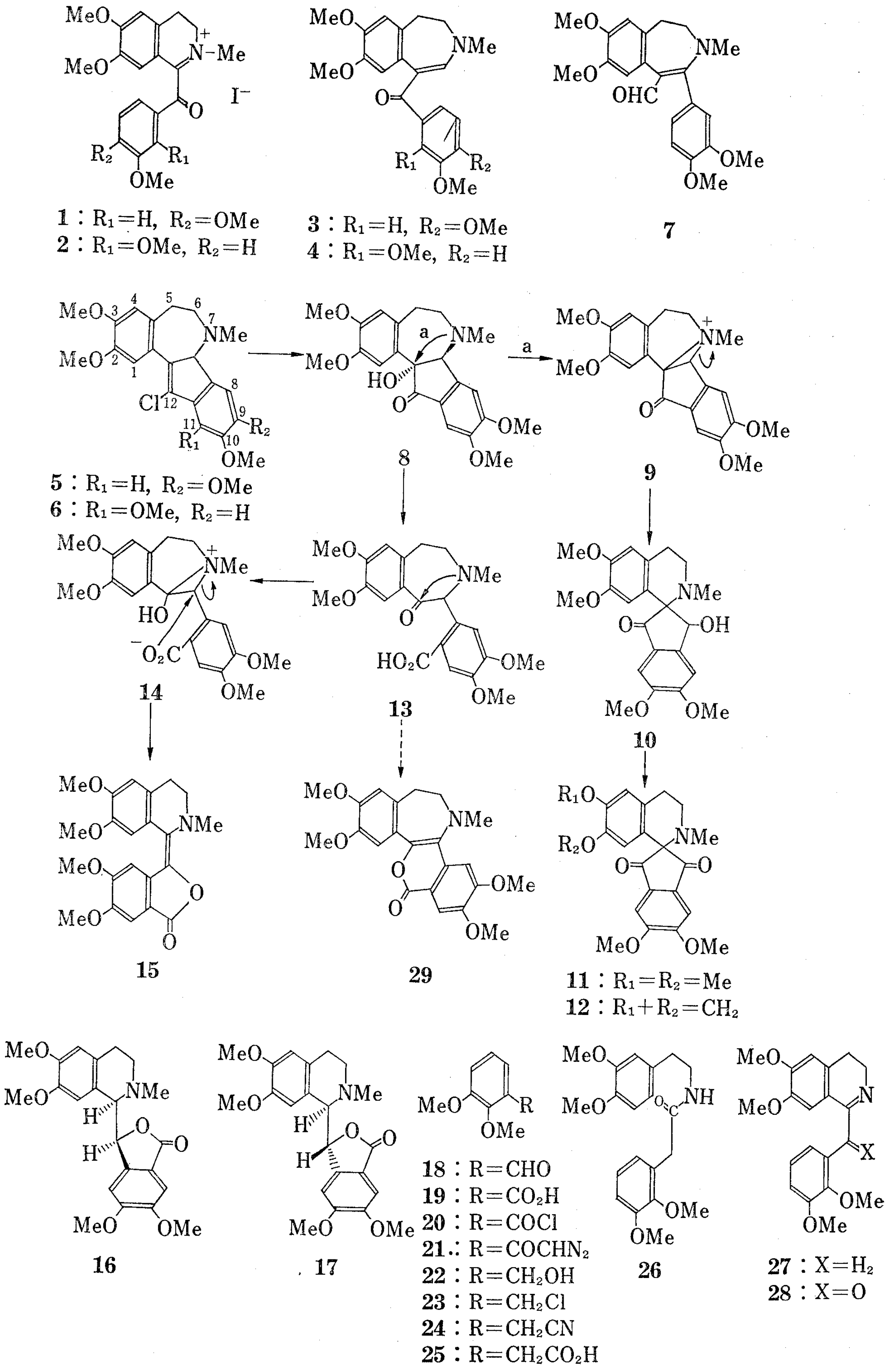

1 : R_1=H, R_2=OMe
2 : R_1=OMe, R_2=H

3 : R_1=H, R_2=OMe
4 : R_1=OMe, R_2=H

7

5 : R_1=H, R_2=OMe
6 : R_1=OMe, R_2=H

8

9

14

13

10

15

29

11 : R_1=R_2=Me
12 : R_1+R_2=CH_2

16

17

18 : R=CHO
19 : R=CO_2H
20 : R=COCl
21 : R=$COCHN_2$
22 : R=CH_2OH
23 : R=CH_2Cl
24 : R=CH_2CN
25 : R=CH_2CO_2H

26

27 : X=H_2
28 : X=O

Chart

Experimental[19]

5-Formyl-2,3-dihydro-4-(3,4-dimethoxyphenyl)-3-methyl-1H-3-benzazepine (7)——A mixture of the benzazepine (3)[12] (100 mg) and phosphorous pentoxide (3 g) in dry toluene (30 ml) was refluxed with stirring for 30 min and the excess of phosphorous pentoxide was decomposed by dropwise addition of water. The resulting mixture was then basified with concentrated ammonia and extracted with chloroform. The extract was washed with water, dried over $\mathrm{Na_2SO_4}$ and evaporated to leave a gum, which was purified by chromatography on silica gel (3 g). The chloroform–methanol (99: 1 v/v) eluate gave a yellow powder, which was recrystallised from methanol–ether to afford **7** (80 mg) as crystals, mp 185—186°, UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm: 350, 323^{sh}, 293^{sh}, 266 and 229, NMR ($\mathrm{CDCl_3}$) ppm: 2.63 (3H, s, NMe), 2.9—3.2 and 3.6—3.9 (each 2H, each m, $\mathrm{C\underline{H}_2{-}C\underline{H}_2{-}N}$), 3.86 (3H, s, OMe), 3.90 (9H, s, 3×OMe), 6.61, 6.84, 6.92, and 7.20 (each 1H, each s, 4×ArH) and 8.91 (1H, s, CHO), Mass Spectrum *m/e*: 383 ($\mathrm{M^+}$) and 354 ($\mathrm{M^+-CHO}$). *Anal.* Calcd. for $\mathrm{C_{22}H_{25}O_5N}$: C, 68.91; H, 6.57; N, 3.65. Found: C, 68.44; H, 6.47; N, 3.46.

Oxidation of 12-Chloro-5,6,7,7a-tetrahydro-2,3,9,10-tetramethoxy-7-methylindeno[2,1-*a*][3]benzazepine (5)——The indenobenzazepine (**5**) hydrochloride[13] (200 mg) was converted, by usual method, into the free base, which was dissolved in acetone (75 ml). To the above stirred solution, potassium permanganate (200 mg) and piperidine (200 mg) were added below 0°. After stirring for 110 min, acetic acid (5 drops) was added and the resulting mixture was further stirred for 20 min. After treatment with a mixture of diluted hydrochloric acid and sodium bisulphite, the mixture was basified with 10% aqueous sodium bicarbonate and extracted with chloroform. The extract was washed with water, dried over $\mathrm{Na_2SO_4}$ and evaporated to give a gum, which was purified by chromatography on silica gel. The benzene–methanol (99.5: 0.5 v/v) eluate gave a powder, recrystallisation of which from chloroform–methanol afforded the diketospirobenzylisoquinoline (**11**) (5 mg) as crystals, mp 244.5—245.5°, UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 316 (4.16), 295 (4.06), and 258 (4.82), IR $\nu_{\max}^{\mathrm{CHCl_3}}$ $\mathrm{cm^{-1}}$: 1730 and 1688 (2×C=O), NMR ($\mathrm{CDCl_3}$) ppm: 2.37 (3H, s, NMe), 2.92—3.10 (2H, m, $\mathrm{C\underline{H}_2CH_2N}$), 3.23—3.42 (2H, m, $\mathrm{CH_2C\underline{H}_2N}$), 3.50 (3H, s, OMe), 3.83 (3H, s, OMe), 4.02 (6H, s, 2×OMe), 5.92 (1H, s, 1-H), 6.66 (1H, s, 4-H), and 7.41 (2H, s, 9- and 12-H), Mass Spectrum *m/e*: 397 ($\mathrm{M^+}$), 382, 368, 354, and 338. *Anal.* Calcd for $\mathrm{C_{22}H_{23}NO_6}$: C, 66.49; H, 5.83; N, 3.52. Found: C, 66.57; H, 5.65; N, 3.76.

The benzene–methanol (98.5: 1.5 v/v) eluate gave a powder, which was recrystallised from chloroform–methanol to afford the lactone (**15**) (40 mg) as crystals, mp 195—196°, UV $\lambda_{\max}^{\mathrm{MeOH}}$ (log ε): 248 (4.08) and 308 nm (4.41), IR $\nu_{\max}^{\mathrm{CHCl_3}}$ $\mathrm{cm^{-1}}$ 1690 (C=O), NMR ($\mathrm{CDCl_3}$) ppm: 2.48 (3H, s, NMe), 3.51, 3.83, 4.03, and 4.05 (each 3H, each s, 4×OMe), 6.27, 6.61, 7.57, and 7.70 (each 1H, each s, 4×ArH), Mass Spectrum *m/e*: 397 ($\mathrm{M^+}$), 382, 368, 367, 352, 338, and 208. *Anal.* Calcd. for $\mathrm{C_{22}H_{23}O_6N \cdot H_2O}$: C, 63.60; H, 6.07; N, 3.37. Found: C, 63.56; H, 5.92; N, 3.20.

Reduction of the Lactone (**15**)——a) To a solution of the lactone (**15**) (35 mg) in methanol (100 ml), sodium borohydride (200 mg) was added in portions at room temperature under stirring. The mixture was stirred overnight at room temperature and then evaporated. Water was added to the above residue, which was then acidified with concentrated hydrochloric acid and allowed to stand overnight at room temperature. The resulting mixture was basified with diluted sodium hydroxide aqueous solution and extracted with chloroform. The extract was washed with water, dried over $\mathrm{Na_2SO_4}$ and evaporated to leave a gum,which was purified by preparative TLC on silica gel using benzene–acetone–methanol (5: 4: 0.8 v/v) to give, after recrystallisation from ethanol, the *erythro*-phthalideisoquinoline (**16**) (15 mg) as crystals, mp 166—167° (lit.,[16] mp 157—159°), UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 303 (3.80), 290 (4.00), 258 (4.05) and 222 (4.49), IR $\nu_{\max}^{\mathrm{CHCl_3}}$ $\mathrm{cm^{-1}}$: 1750 (C=O), NMR ($\mathrm{CDCl_3}$) ppm: 2.58 (3H, s, NMe), 3.73, 3.78, 3.86, 3.92 (each 3H, each s, 4×OMe), 6.18, 6.48, 6.62, and 7.25 (each 1H, each s, 4×ArH), Mass Spectrum *m/e*: 399 ($\mathrm{M^+}$) and 206. *Anal.* Calcd. for $\mathrm{C_{22}H_{25}O_6N \cdot 0.5H_2O}$: C, 64.96; H, 6.41; N, 3.42. Found: C, 64.91; H, 6.11; N, 3.45.

b) A mixture of the lactone (**15**) (35 mg) and platinum oxide (170 mg) in methanol (100 ml) was stirred for 16 hr under hydrogen atmosphere at room temperature until the absorption of hydrogen ceased. After filtration to remove the catalyst, the combined filtrate and washings were evaporated to give a gum, which was purified by preparative TLC on silica gel using benzene–acetone–methanol (5: 4: 0.8 v/v). The upper zone, on elution with 10% methanolic chloroform, gave the *threo*-phthalideisoquinoline (**17**) (2 mg) as crystals, mp 115—116° (from ethanol) (lit.,[16] mp 115—117°), IR $\nu_{\max}^{\mathrm{CHCl_3}}$ $\mathrm{cm^{-1}}$: 1750 (C=O), NMR ($\mathrm{CDCl_3}$) ppm: 2.70 (3H s, NMe), 3.73, 3.78, 3.83, and 3.91 (each 3H, each s, 4×OMe), 6.30, 6.62, 6.96, and 7.17 (each 1H, each s, 4×ArH), Mass Spectrum *m/e*: 399 ($\mathrm{M^+}$) and 206. The lower zone, on elution with 10% methanolic chloroform, afforded the *erythro*-phthalideisoquinoline (**16**) (18 mg), mp 166—167° (from ethanol), IR and NMR spectra of which were identical with those of the above product obtained by the method (a).

N-β-(3,4-Dimethoxyphenyl)-2,3-dimethoxyphenylacetamide (26)——2,3-Dimethoxybenzoic acid (19)[20] (5 g) was gently refluxed on a water bath with thionyl chloride (15 ml) for 0.5 hr. The excess reagent was

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19) All melting points are uncorrected. IR spectra were measured with a Hitachi 215 spectrometer, UV spectra with a Hitachi 124 spectrophotometer, NMR spectra with a JNM-PMX-60 spectrometer (solution in deuteriochloroform with tetramethylsilane as internal reference), and mass spectra with a Hitachi RMU-7 spectrometer.

20) G.A. Edwards, W.H. Perkin, Jr., and F.W. Stoyle, *J. Chem. Soc.*, **127**, 197 (1925).

removed under reduced pressure and the residue distilled *in vacuo* to get the acid chloride (**20**), bp 105° (6 mmHg) (lit.,[21] bp 142—143° (13 mmHg)). A solution of the above acid chloride in ether (15 ml) was added to an ethereal solution of diazomethane at 0°. Stirring was continued at 0—5° for 1 hr and overnight at room temperature. The ether was removed under reduced pressure (bath temperature 20—30°) and the residual gum was cooled in ice to get a yellow solid (**21**) which was used in the next step.

To the diazoketone in dioxane (80 ml), which was kept at 55—60° was added a solution of homoveratrylamine (4 g) in dioxane (20 ml). Then silver oxide [half the amount obtained by precipitation from silver nitrate (3 g) in water (67 ml) using 5% potassium hydroxide] was added in portions. The temperature was raised to 65—70° and the solution stirred for 2 hr. The remaining silver oxide was then added and the solution refluxed for 1 hr. Towards the end (5 min before stopping the reflux) a small amount of charcoal was added. The solution was filtered, washed with dioxane and the solvent removed under reduced pressure. The residue was dissolved in benzene and passed through a short column of alumina (50 g) to obtain the amide (**4**), which was recrystallised from benzene–hexane to give colourless needles (3.96 g), mp 130—131° (lit.,[18] mp 130—131°), IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 3400 (NH), 1647 cm^{-1} (C=O), NMR ($CDCl_3$) ppm: 2.66 (2H, t, $J=7$ Hz, $C\underline{H}_2CH_2N$), 3.35 (2H, t, $J=7$ Hz, $CH_2C\underline{H}_2N$), 3.75 (3H, s, OMe), 3.80 (3H, s, OMe), 3.81 (6H, s, 2×OMe), and 6.53—7.06 (5H, m, 5×ArH).

2,3-Dimethoxybenzyl Alcohol (**22**)——To an ice-cooled solution of 2,3-dimethoxybenzaldehyde (125 g) in methanol (500 ml) was added sodium borohydride (12.5 g) in small portions. The mixture was stirred for 2 hr at room temperature and then left overnight. The solvent was removed using a rotary evaporator. Water was added to the residue and the oily layer separated. The aqueous layer was extracted with chloroform. The combined extracts were washed with water, dried over Na_2SO_4 and evaporated to leave an oil (123 g) which solidified on cooling. This was recrystallised from ether–hexane to give colourless needles (116.25 g), mp 50—51° (lit.,[22] mp 50°), NMR ($CDCl_3$) ppm; 1.91 (1H, br s, OH), 3.8 (6H, s, 2×OMe), 4.53 (2H, s, CH_2), and 6.6—6.95 (3H, m, 3×ArH).

2,3-Dimethoxybenzyl Chloride (**23**)——A solution of thionyl chloride (52 ml) in ether (52 ml) was added dropwise to cooled solution of the above alcohol (110 g) in ether (500 ml) at 0—5°. The stirring was continued for 1.5 hr at 0°. The solution was worked up as usual to leave an oil (113 g) which was used in the next step.

2,3-Dimethoxybenzyl Cyanide (**24**)——To a stirred suspension of sodium cyanide (45 g) in dimethyl sulphoxide (150 ml) was added gradually a solution of 2,3-dimethoxybenzyl chloride (113 g) in dimethyl sulphoxide (150 ml) and the mixture was stirred for 24 hr at room temperature. It was worked up by pouring into a mixture of ice and water and then extracted with chloroform. The chloroform extract was washed with water, dried over Na_2SO_4 and evaporated to leave a ceam oil (105 g), IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 2250 (C≡N), NMR ($CDCl_3$) ppm: 3.56 (2H, s, CH_2), 3.8 and 3.83 (each 3H, each s, 2×OMe), and 6.83 (3H, m, ArH), which was used in the next step.

3,4-Dihydro-6,7-dimethoxy-1-(2,3-dimethoxybenzyl)isoquinoline (**27**)——The above cyanide (**24**) (105 g) in alcohol (700 ml) was hydrolysed with potassium hydroxide (110 g) in water (110 ml) as described by Tsatsas,[22] to afford 2,3-dimethoxyphenylacetic acid (**25**), whose condensation with amine gave N-β-(3,4-dimethoxyphenethyl)-2,3-dimethoxyphenylacetamide (**26**), mp 130—131°, according to Chakravarthi and Swaminathan.[23]

The above amide (**26**) (2 g) in toluene (10 ml) was gently refluxed with phosphoryl chloride (6 ml) for 2 hr. The excess solvent and reagent were distilled off under reduced pressure and the residue obtained used as such in the next step. A portion was dissolved in chloroform and washed with diluted sodium hydroxide solution and water, dried over Na_2SO_4 and evaporated to leave a gum, NMR ($CDCl_3$) ppm: 3.78 (3H, s, OMe), 3.83 (3H, s, OMe), 3.86 (6H, s, 2×OMe), 4.08 (2H, s, $ArCH_2$), 6.61 (1H, s, ArH), 6.80 (1H, s, ArH), 6.86 (2H, s, ArH) and 7.13 (1H, s, ArH).

3,4-Dihydro-6,7-dimethoxy-1-(2,3-dimethoxybenzoyl)isoquinoline (**28**)——The isoquinoline hydrochloride (**27**) (1.67 g) was stirred at room temperature with ethanol (40 ml) and sodium acetate (8 g), to a mixture of which was added dropwise a solution of iodine (2.4 g) in ethanol (80 ml). The solution was then stirred until a TLC check showed complete disappearance of the starting material. Sodium thiosulphate solution was added to decompose the excess iodine and the benzoylisoquinoline was precipitated as the picrate by addition of an aqueous solution of picric acid. The picrate (2.05 g) was then filtered and the free base recovered from the picrate either by passing a chloroform solution of the picrate through an alumina column or basification with dilute ammonia. A portion of the picrate (1.5 g) in chloroform was passed through alumina to give a gum (770 mg), trituration of which with ether gave a solid (320 mg). The solid obtained can be purified by silica gel chromatography, and crystallisation from chloroform-methanol gave crystals, mp 109—111°, IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1662 (C=O), NMR ($CDCl_3$) ppm: 2.75 (2H, t, $J=7$ Hz, CH_2), 3.66, 3.81, 3.86, 3.93 (each 3H, each s, 4×OMe), 6.75 (1H, s, ArH) and 7.03—7.45 (4H, m, 4×ArH). *Anal.* Calcd. for $C_{20}H_{21}O_5N$: C, 67.59; H, 5.96; N, 3.94. Found: C, 67.54; H, 6.30; N, 3.84.

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21) F. Mauthner, *J. Prakt. Chem.*, **112**, 60 (1926).
22) G. Tsatsas, *Ann. Pharm. Franc.*, **7**, 138 (1947).
23) S.N. Chakravarthi and N. Swaminathan, *J. Indian Chem. Soc.*, **11**, 107 (1934).

It was often more convenient to use the gum obtained directly in the next step and purify then.

3,4-Dihydro-6,7-dimethoxy-1-(2,3-dimethoxybenzoyl)-2-methylisoquinolinium Iodide (2)——The benzoylisoquinoline (882 mg) in benzene (6 ml) was refluxed with methyl iodide (2 ml) for 4 hr. The solid obtained was filtered off to give the methiodide (1.23 g) which was crystallised from methanol–ethyl acetate to give yellow crystals, mp 148—149°. *Anal.* Calcd. for $C_{21}H_{24}O_5NI \cdot 0.5H_2O$: C, 49.79; H, 5.17; N, 2.76. Found: C, 49.57; H, 5.20; N, 2.69.

2,3-Dihydro-7,8-dimethoxy-5-(2,3-dimethoxybenzoyl)-3-methyl-1H-3-benzazepine (4)——An excess of ethereal diazomethane was added to a solution of the methiodide (3 g) in methylene chloride (150 ml) at 0°. After standing for 2 hr, solvent was removed under reduced pressure to leave a gum (2.8 g) which was dissolved in benzene. Scratching then gave a crystalline solid (1.47 g) which was filtered and washed with ether. Recrystallization from methanol gave colorless crystals (0.93 g), mp 181—182°, NMR ($CDCl_3$) ppm: 2.93 (3H, s, NMe), 2.77—3.15 (2H, m, $C\underline{H}_2CH_2N$), 3.39—3.65 (2H, m, $CH_2C\underline{H}_2N$), 3.76, 3.79, 3.81 and 3.83 (each 3H, each s, 4 × OMe), 6.48 (1H, s, $>C=C\underline{H}-N$), 6.77—7.03 (3H, m, 3 × ArH) and 7.16 and 7.23 (each 1H, each s, 2 × ArH). *Anal.* Calcd. for $C_{22}H_{24}O_5N$: C, 68.91; H, 6.57; N, 3.65. Found: C, 68.63; H, 6.54; N, 3.60.

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