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# Spiro Heterocyclic Compounds. IV.[1] Synthesis of Spiro[oxindole-3,4′-(2′,3′-dihydro-4′*H*-pyran)] and Spiro[oxindole-3,4′-(1′,4′-dihydropyridine)] Compounds

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The Michael reaction of 3-(carboethoxy-cyano)methyleneoxindole (Ia) or 3-dicyanomethyleneoxindole (Ib) with active methyl groups, *e.g.*, acetophenone and acetone, afforded, the corresponding normal Michael adducts (IIa—c). The reduction of IIa with $NaBH_4$ gave the spiro[oxindole-3,4′-(2′,3′-dihydro-4′*H*-pyran)] compound (III), which on reaction with diazomethane afforded two methoxy derivatives (IVa, b) diastereomeric at C-2′ of the 2′,3′-dihydropyran ring. The reduction of IIb, c with $NaBH_4$ gave similar spiro compounds (V—VI), which gave similar diastereoisomers, Va, b and VIa, b, respectively.

Refluxing of IIc with $NH_2OH$ gave the spiro[oxindole-3,4′-(1′,4′-dihydropyridine)] compound (X). When the same reaction was carried out at 0°, compound (IX), the precursor of X, was obtained.

**Keywords**——spiro[oxindole-3,4′-(2′,3′-dihydro-4′*H*-pyran)]; spiro[oxindole-3,4′-(1′,4′-dihydropyridine)]; Michael reaction; active methyl group; 3-cyanomethyleneoxindole; spiro heterocyclic compound

In the preceding paper,[1] we reported the formation of spiro[oxindole-3,4′-(4′*H*-pyran)] compounds by the Michael reactions of 3-cyanomethyleneoxindoles with an active methylene group. As an extension of this study, we have attempted the synthesis of other heterocycles with a spiro system at C-3 of oxindole by analogous Michael reactions. Some of the results obtained are reported in this paper.

The reactions of 3-cyanomethyleneoxindoles (Ia,b)[3,4] with acetophenone in the presence of piperidine as a catalyst at room temperature for 10 days gave colorless products (IIa) and (IIb) in yields of 62 and 98%, respectively. In the reactions of Ia,b with acetone, only Ib gave a colorless product (IIc) in a short reaction time (40% yield). These products, IIa—c, were considered to be the normal Michael adducts, produced by carbanion attack of the active methyl group on C-3 of oxindole, on the basis of the appearance of methylene signals as an AB-quartet and methine protons in their proton magnetic resonance (PMR) spectra, and satisfactory elemental analysis data. These products were not enolized and directly converted into pyran derivatives, in contrast to the products of the Michael reactions reported previously.[1] Therefore, the following conversions were undertaken.

The reaction of IIa with $NaBH_4$ in MeOH at room temperature afforded a colorless product (III) in excellent yield. The infrared (IR) spectrum of III showed a weak peak at 2250 $cm^{-1}$ due to a non-conjugated CN group and two peaks of C=O groups at 1740 and 1720 $cm^{-1}$. The PMR spectrum of III exhibited a significant signal due to methylene-methine protons as a dull ABX-pattern and a singlet due to an isolated methine proton. These results indicated that III was a diastereomeric mixture of the lactone compound formed by intramolecular cyclization between the ester and the reduced OH groups, as shown by III′ in Chart 1.

When III was treated with diazomethane in THF at room temperature, the production of two diastereomers was suggested by the TLC result. The reaction product was subjected

1) Part III: K. Higashiyama and H. Otomasu, *Chem. Pharm. Bull.*, **28**, 648 (1980).
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3) M. Yokoyama, *J. Chem. Soc. Japan*, **57**, 251 (1936).
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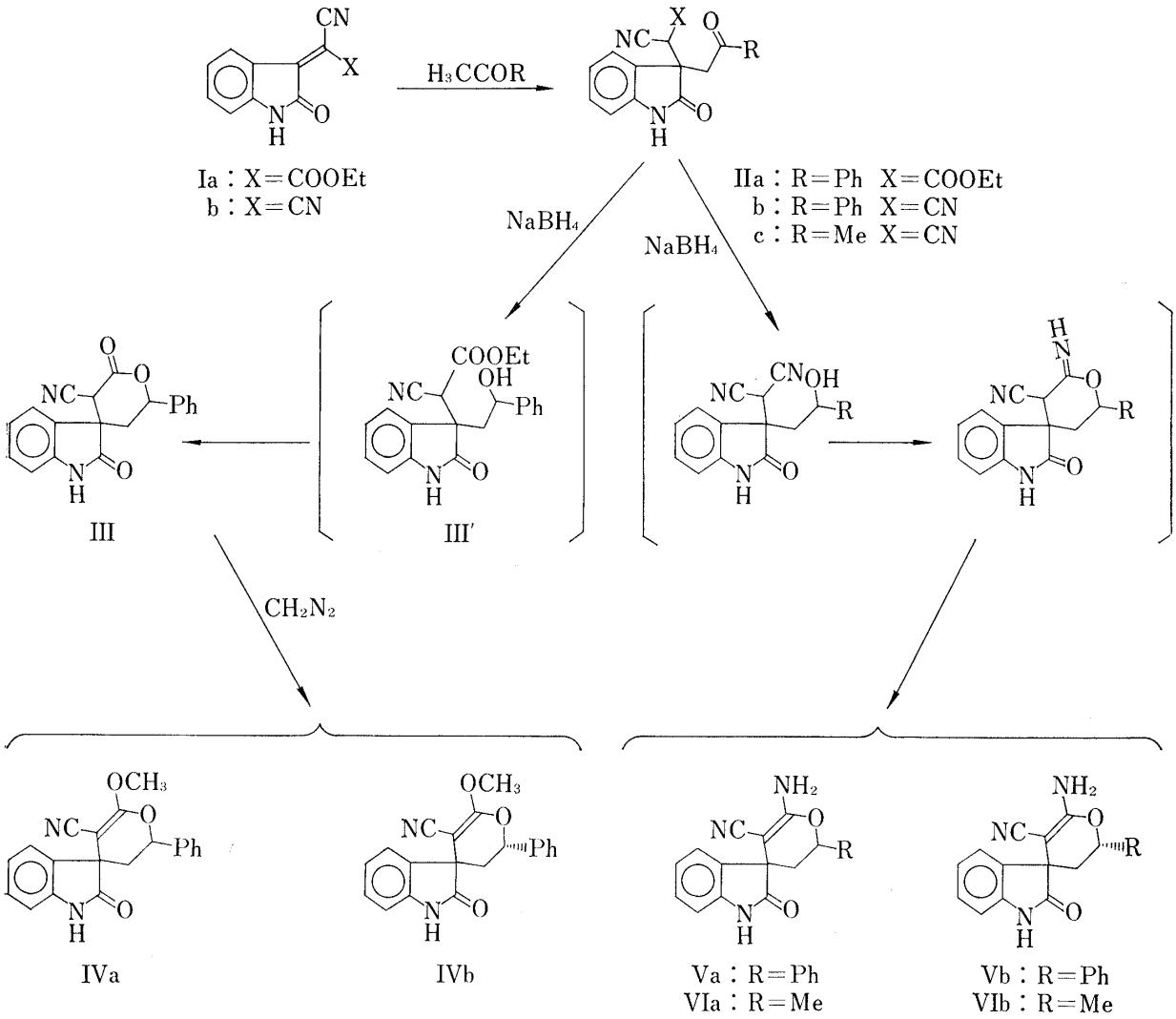


Chart 1

to column chromatography on silica gel, and the two diastereomers, IVa and IVb were obtained in a ratio of 3 : 1. IVa showed a conjugated CN group at 2200 $cm^{-1}$ in the IR spectrum and the PMR spectrum of IVa showed signals of methylene-methine protons as an ABX-pattern at $\delta$ 2.04, 2.53 and 5.46 ($J_{AB}$=14.0, $J_{AX}$=2.2 and $J_{BX}$=12.2 Hz) and methyl protons at $\delta$ 3.91. From the above results and the analytical data, the structure of IVa was deduced to be spiro[oxindole-3,4′-(5′-cyano-2′,3′-dihydro-6′-methoxy-2′-phenyl-4′*H*-pyran)]. Compound IVb is designated as the diastereomer having a different configuration at C-2′ of the dihydropyran ring, since it gave the same spectral (MS, IR, and PMR) and analytical data as IVa except for the proton signals of the ABX-pattern ($\delta$ 2.17, 2.23, and 6.11, $J_{AB}$=14.0, $J_{AX}$=5.4, and $J_{BX}$=7.8 Hz).

Analogously, in the reactions of IIb,c with $NaBH_4$, cycloaddition occurred between the CN and reduced OH groups to give the corresponding spiro dihydropyran compounds, V and VI, in good yields. The products V and VI thus obtained were mixtures of two diastereomers, as indicated by their PMR signals for the methylene-methine moiety and their TLC properties. Recrystallization from ethyl acetate permitted the separation of the diastereomers, Va,b and VIa,b in ratios of *ca.* 3 : 1. Their IR and PMR spectra were very similar to those of IVa,b, respectively, except for the absorptions due to the C-2′ and C-6′ substituents.

The a- and b-type configurations with respect to C-2′ of compounds IV—VI and typical PMR spectral patterns for instance, Va and Vb, are presented in Fig. 1. The a-type C-2′

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methine proton signal was centered at $\delta$ 5.55 as a pair of doublets (dd) coupling with the adjacent methylene protons. In contrast, the b-type C-2′ proton signal appeared as a dd shifted to lower field at $\delta$ 5.95. Since these results were best explained in terms of the magnetic aniso-

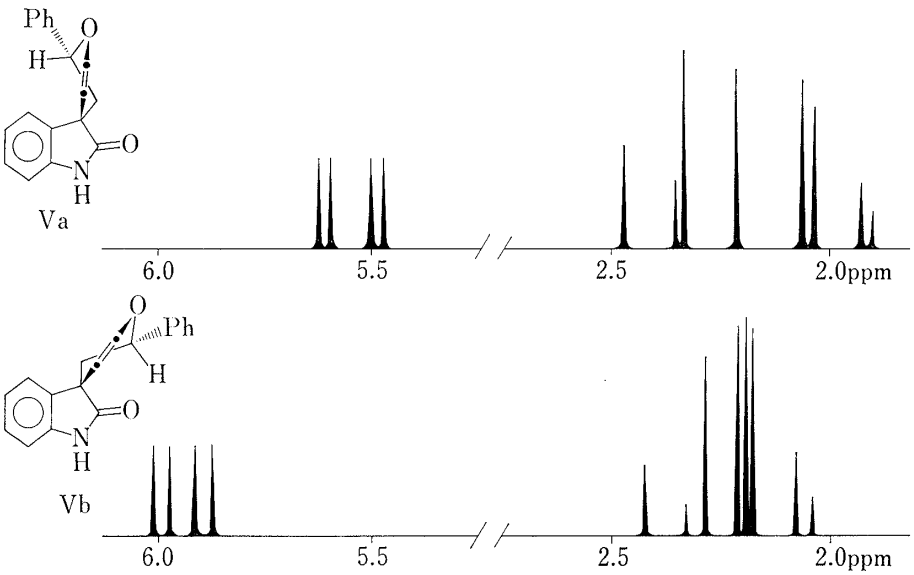


Fig. 1

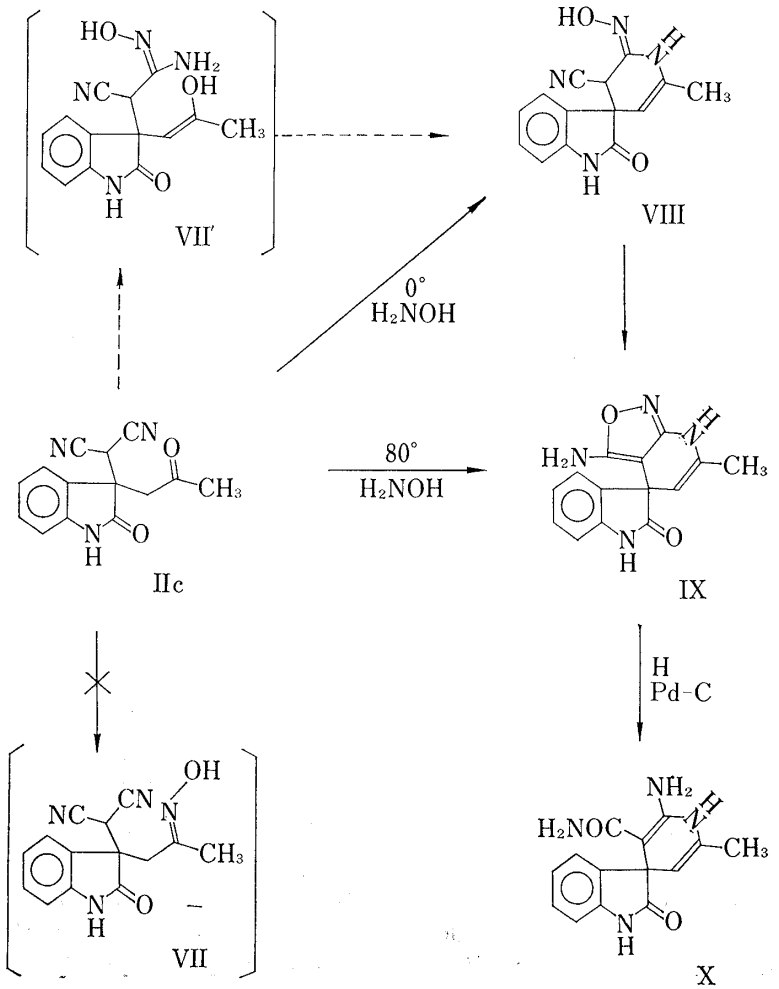


Chart 2

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tropy effect of the C=O bond, a- and b-type IV-VI were assigned as the stereostructures in which the C-2′ hydrogen of the dihydropyran ring is close to and distant from the C=O group of oxindole, respectively.

Next, a successful conversion of IIc into a pyridine derivative was achieved. Initially we expected that the oxime (VII) of IIc would be reduced to an amino compound, which would immediately undergo intramolecular cyclization to form a 1,4-dihydropyridine skeleton. However, the reaction was not straightforward, as illustrated in Chart 2.

Refluxing an MeOH solution of IIc with $NH_2OH$ gave a colorless product (IX), mp 208°, in 85% yield, whose spectral data indicated a more complicated structure than that of the expected oxime (VII). The IR spectrum of IX showed no band due to a CN group and showed bands due to an $NH_2$ and two NH groups. In the PMR spectrum, the presence of one $NH_2$ and two NH groups was clearly observed, together with a long-range coupling between the CH= and $CH_3$ protons. Based on these spectral data, IX was assumed to be a transformed product of the oxime (VII). In order to obtain the oxime (VII), the same reaction was carried out under mild conditions at 0° for 12 hr, and a colorless product (VIII) was obtained in 94% yield. This product was rather unstable, and changed into IX on direct heating or on recrystallization with heating. The PMR spectrum of VIII showed three singlets exchangeable with $D_2O$, and a singlet due to a methine proton, together with a long-range coupling of CH= and $CH_3$ protons. The IR spectrum showed a weak peak of non-conjugate CN on the higher frequency side and a sharp peak due to oxime C=N at 1660 $cm^{-1}$. The structures of the products (VIII) and (IX) can reasonably be rationalized by assuming the initial formation of an intermediate (VII′) involving hydroxylamine attack on one CN group of the starting compound (IIc). Namely, the spectral data of the product (VIII) are consistent with a spiro[oxindole-3,4′-(3′-cyano-1′,4′-dihydro-2′-hydroxyimino-6′-methylpyridine)] structure, assumed to be formed by intramolecular cyclization between the amino and enolic OH groups of the hydroxylamine adduct (VII′). The foregoing discussion supported the structure spiro[(1-amino-4,7-dihydro-5-methylisoxazolo[3,4-*b*]pyridine)-7,3′-oxindole] for the product (IX), this might be produced by cyclo-addition between HO–N= and another CN group of compound VIII.

Confirmation of the structure of IX was obtained by the following experiment. The catalytic hydrogenation of IX with one molar hydrogen uptake gave a colorless product (X) in good yield. The PMR spectrum of X showed two singlets (each of one proton) attributable to CONH and NH, two singlets due to $CONH_2$ and $NH_2$, which disappeared with $D_2O$, together with long-range coupling signals of CH= and $CH_3$ protons. The IR spectrum showed absorption bands at 3500—3150 $cm^{-1}$ due to the above $NH_2$ and NH grouping, and at 1700 and 1680 $cm^{-1}$ due to CONH and $CONH_2$ groups, respectively. It is known that the catalytic hydrogenation of 5-aminoisoxazoles results in ring-cleavage of the C-N bond, affording the aminocarboxamide compound.[5,6] Thus, the structure of X was assigned as spiro[oxindole-3,4′-(2′-amino-1′,4′-dihydro-6′-methylpyridine-3′-carboxamide)].

In spite of the purity of the compounds IX and X, their C, H, N, contents were low upon elemental analysis.[7] However, their molecular formulae were accurately determined by high resolution mass spectrometry.

## Experimental

All melting points are uncorrected. IR spectra were recorded with a Hitachi 215 spectrometer. Low and high resolution mass spectra were taken with Hitachi RMS-4 and JEOL D-300 machines, respectively, at 70 eV. NMR spectra were determined on a JEOL FX-100 spectrometer using tetramethylsilane as the internal standard. All concentration procedures were performed on rotary evaporators *in vacuo*.

Starting materials Ia, b were prepared by the known methods.[3,4]

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**3-(Carboethoxy-cyano)methyl-3-phenacyloxindole (IIa)**——A mixture of Ia (10.0 g), acetophenone (5.0 g) and 10 drops of piperidine in EtOH (70 ml) was stirred at room temperature for 6 days. After adding 10 more drops of piperidine, the reaction was continued under the same conditions for 4 days. The colorless solid that separated was filtered off, washed with 50% AcOH and recrystallized from MeOH to give pure IIa of mp 163°. Yield, 9.4 g (63%). IR $\nu_{max}^{Nujol}$ cm$^{-1}$: 2260 (CN), 1740, 1700 (C=O), 1720 (–NHCO-). MS *m/e*: 362 ($M^+$). PMR ($CDCl_3$) $\delta$: 1.03 (3H, t, $J$=7.1 Hz, $\underline{CH_3}CH_2$–), 4.03 (2H, q, $J$=7.1 Hz, $CH_3\underline{CH_2}$–), 3.71 and 4.19 (2H, ABq, $J$=17.6 Hz, $-CH_2-$), 4.40 (1H, s, –CH), 6.99—7.91 (9H, m, ArH), 8.39 (1H, s, –NH-CO–). *Anal.* Calcd for $C_{21}H_{18}N_2O_4$: C, 69.60; H, 5.00; N, 7.73. Found: C, 69.25; H, 5.09; N, 7.45.

**3-Dicyanomethyl-3-phenacyloxindole (IIb)**——This compound was obtained from Ib by a procedure similar to that used for the preparation of IIa. Colorless prisms, mp 183° (MeOH). Yield, 15.8 g (98%). IR $\nu_{max}^{Nujol}$ cm$^{-1}$: 2250 (CN), 1720 (–NHCO–), 1650 (C=O). MS *m/e*: 315 ($M^+$). PMR ($CDCl_3$) $\delta$: 3.81 and 4.30 (2H, ABq, $J$=17.9 Hz, $-CH_2-$), 5.60 (1H, s, –CH), 6.94—7.94 (9H, m, ArH), 11.6 (1H, s, –NHCO–). *Anal.* Calcd for $C_{19}H_{13}N_3O_2$: C, 72.32; H, 4.16; N, 13.33. Found: C, 72.44; H, 4.40; N, 13.00.

**3-Acetonyl-3-dicyanomethyloxindole (IIc)**——A solution of Ib (8.0 g) in acetone (50 ml) was treated with 5 drops of piperidine under stirring at 40° over 1 hr. After removal of the acetone, the residue was rinsed with $CH_2Cl_2$ and the insoluble solid was recrystallized from AcOEt to give colorless prisms of mp 196°. Yield, 4.26 g (41%). IR $\nu_{max}^{Nujol}$ cm$^{-1}$: 2260 (CN), 1730 (C=O), 1710 (–NHCO–). MS *m/e*: 253 ($M^+$). PMR ($d_6$-acetone) $\delta$: 2.12 (3H, s, $CH_3$), 3.38 and 3.67 (2H, ABq, $J$=18.0 Hz, $-CH_2-$), 5.09 (1H, s, –CH), 6.99—7.51 (4H, m, ArH), 9.96 (1H, s, –NHCO–). *Anal.* Calcd for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38; N, 16.59. Found: C, 66.61; H, 4.47; N, 16.48.

**Spiro[oxindole-3,4′-(5′-cyano-2′,3′-dihydro-2′-phenyl-4′*H*-pyran-6′-one)] (III)**——$NaBH_4$ (0.24 g) was added in small portions to a solution of IIa (1.0 g) in MeOH (20 ml) over a period of 30 min at room temperature under stirring. After stirring for a further 30 min, MeOH was evaporated off and the residue was dissolved in wather (20 ml). The solution was acidified with dil. HCl, and the separated solid was recrystallized from MeOH to give colorless prisms of mp 228°. Yield, 0.98 g (98%). IR $\nu_{max}^{Nujol}$ cm$^{-1}$: 2260 (CN), 1740 (C=O), 1720 (–NHCO–). MS *m/e*: 318 ($M^+$). *Anal.* Calcd for $C_{19}H_{14}N_2O_3$: C, 71.69; H, 4.43; N, 8.80. Found: C, 71.70; H, 4.42; N, 8.50. This product was indicated to be a stereoisomeric mixture from its PMR spectrum.

**Spiro[oxindole-3,4′-(5′-cyano-2′,3′-dihydro-6′-methoxy-2′-phenyl-4′*H*-pyran)] (IVa, b)**——An ether solution (100 ml) of diazomethane, prepared from 6.0 g of nitrosomethylurea, was added to a solution of III (2.0 g) in THF (60 ml) over a period of 20 min under ice-cooling and stirring. The reaction mixture was left to stand overnight at room temperature, the solvent was evaporated off and the residue was dissolved in $CH_2Cl_2$. The solution was applied to a silica gel column and eluted with $CH_2Cl_2$–MeOH–28%$NH_4OH$ (495: 5: 1). The first effluent fraction was recrystallized from ether to give 0.54 g (26%) of IVb as colorless needles of mp 225°. IR $\nu_{max}^{Nujol}$ cm$^{-1}$: 2200 (CN), 1700 (–NHCO–). MS *m/e*: 332 ($M^+$). PMR ($CDCl_3$) $\delta$: 2.17 (1H, dd, $J$=14.0 and 5.4 Hz, 5′-$CH_2$–), 2.23 (1H, dd, $J$=14.0 and 7.8 Hz, 5′-$CH_2$–), 3.92 (3H, s, $OCH_3$), 6.11 (1H, dd, $J$=5.4 and 7.8 Hz, 6′-CH), 6.96—7.40 (9H, m, ArH), 8.12 (1H, s, –NHCO–). *Anal.* Calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43. Found: C, 71.95; H, 4.96; N, 8.67.

The last effluent fraction gave 1.46 g (70%) of IVa as colorless needles of mp 207° ($CH_2Cl_2$). IR $\nu_{max}^{Nujol}$ cm$^{-1}$: 2200 (CN), 1720 (–NHCO–). MS *m/e*: 332 ($M^+$). PMR ($CDCl_3$) $\delta$: 2.40 (1H, dd, $J$=14.0 and 2.2 Hz, 5′-$CH_2$–), 2.53 (1H, dd, $J$=14.0 and 12.2 Hz, 5′-$CH_2$–), 3.91 (3H, s, $OCH_3$), 5.46 (1H, dd, $J$=2.2 and 12.2 Hz, 6′-CH), 6.92—7.45 (9H, m, ArH), 8.09 (1H, s, –NHCO–). *Anal.* Calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43. Found: C, 72.50; H, 4.92; N, 8.59.

**Spiro[oxindole-3,4′-(6′-amino-5′-cyano-2′,3′-dihydro-2′-phenyl-4′*H*-pyran)] (Va, b)**——$NaBH_4$ (0.24 g) was added to a solution of IIb (1.0 g) in MeOH (20 ml) in small portions over 30 min at room temperature under stirring. The reaction mixture was stirred for a further 30 min then the solvent was removed. The residue was dissolved in water, acidified with HCl and the colorless solid that separated was collected. Yield, 0.98 g (98%). Recrystallization from a mixture of MeOH and AcOEt (1: 1) gave 0.75 g (77%) of Va as colorless prisms of mp 249°. IR $\nu_{max}^{Nujol}$ cm$^{-1}$: 3400—3200 (NH, $NH_2$), 2160 (CN), 1700 (–NHCO–). MS *m/e*: 317 ($M^+$). PMR ($d_6$-acetone) $\delta$: 1.98 (1H, dd, $J$=13, 8 and 2.3 Hz, 5′-$CH_2$–), 2.33 (1H, dd, $J$=13.8 and 12.2 Hz, 5′-$CH_2$–), 5.55 (1H, dd, $J$=2.3 and 12.2 Hz, 6′-CH), 6.00 (2H, s, $NH_2$), 6.92—7.67 (9H, m, ArH), 9.51 (1H, s, –NHCO–). *Anal.* Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.83; H, 4.74; N, 12.78.

The mother liquor after the separation of Va was concentrated to dryness, giving a colorless residue. On recrystallization from MeOH, this gave 0.23 g (23%) of Vb as colorless prisms, mp 258°. IR $\nu_{max}^{Nujol}$ cm$^{-1}$: 3400—3200 (NH, $NH_2$), 2160 (CN), 1700 (–NHCO–). MS *m/e*: 317 ($M^+$). PMR ($d_6$-acetone) $\delta$: 2.17 (1H, dd, $J$=14.4 and 3.8 Hz, 5′-$CH_2$–), 2.29 (1H, dd, $J$=14.4 and 9.8 Hz, 5′-$CH_2$–), 5.95 (1H, dd, $J$=3.8 and 9.8 Hz, 6′-CH), 6.02 (2H, s, $NH_2$), 6.89—7.45 (9H, m, ArH), 9.45 (1H, s, –NHCO–). *Anal.* Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.70; H, 4.68; N, 13.04.

**Spiro[oxindole-3,4′-(6′-amino-5′-cyano-2′,3′-dihydro-2′-methyl-4′*H*-pyran)] (VIa, b)**——By treatment similar to that described above, a stereoisomeric mixture was obtained from IIc in quantitative yield. Recrystallization from AcOEt gave VIa as colorless prisms of mp 272°. Yield, 0.74 g (75%). IR $\nu_{max}^{Nujol}$ cm$^{-1}$: 3520—3300 (NH, $NH_2$), 2180 (CN), 1720 (–NHCO–). MS *m/e*: 255 ($M^+$). PMR ($d_6$-acetone) $\delta$: 1.40 (3H, d,

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$J$=6.2 Hz, $CH_3$), 1.80 (1H, dd, $J$=13.6 and 2.2 Hz, 5′-$CH_2$–), 1.99 (1H, dd, $J$=13.6 and 9.7 Hz, 5′-$CH_2$–), 4.62 (1H, m, 6′-CH), 5.84 (2H, s, $NH_2$), 6.89—7.42 (4H, m, ArH), 9.47 (1H, s, –NHCO–). *Anal.* Calcd for $C_{14}H_{13}N_3O_2$: C, 65.83; H, 5.13; N, 16.46. Found: C, 66.10; H, 5.51; N, 17.07.

The mother liquor after the separation of VIa was concentrated to dryness, and the residue was recrystallized from MeOH to give VIb as colorless prisms, mp 284°. Yield 0.25 g (25%). IR $\nu_{max}^{Nujol}$ $cm^{-1}$: 3450—3250 (NH, $NH_2$), 2180 (CN), 1710 (–NHCO–). MS *m/e*: 255 ($M^+$). PMR ($d_6$-acetone) $\delta$: 1.34 (3H, d, $J$=6.6, $CH_3$), 1.82 (1H, dd, $J$=13.1 and 9.8 Hz, 5′-$CH_2$–), 1.94 (1H, dd, $J$=13.1 and 3.7 Hz, 5′-$CH_2$–), 4.99 (1H, m, 6′-CH), 5.87 (2H, s, $NH_2$), 6.87—7.35 (4H, m, ArH), 9.35 (1H, s, –NHCO–). *Anal.* Calcd for $C_{14}H_{13}N_3O_2$: C, 65.83; H, 5.13; N, 16.46. Found: C, 65.61; H, 5.51; N, 16.14.

**Spiro[oxindole-3,4′-(3′-cyano-1′,4′-dihydro-2′-hydroxyimino-6′-methylpyridine)] (VIII)**——A solution of IIc (2.0 g), $NH_2OH \cdot HCl$ (0.55 g) and AcONa (0.65 g) in MeOH (50 ml) was left to stand overnight at 0°. The solvent was removed below 30°, then the residual solid was washed with water and dried. Yield, 1.8 g (85%). Recrystallization from MeOH gave colorless needles of mp 209°. IR $\nu_{max}^{Nujol}$ $cm^{-1}$: 2250 w (CN), 1700 (–NHCO–). MS *m/e*: 268 ($M^+$). PMR ($d_6$-DMSO) $\delta$: 1.84 (3H, s, $CH_3$), 4.12 (1H, s, =CH–), 4.74 (1H, s, 3′-CH), 6.82—7.33 (4H, m, ArH), 8.38 (1H, s, 1′-NH–), 10.32 (1H, s, 1-NHCO–), 10.52 (1H, s, HO–N=). This product was rather unstable and was transformed into IX on heating directly or in solution.

**Spiro[(1-amino-4,7-dihydro-5-methylisoxazolo[3,4-*b*]pyridine)-7,3′-oxindole] (IX)**——A solution of IIc (2.0 g), $NH_2OH \cdot HCl$ (0.55 g) and AcONa (0.65 g) in MeOH (40 ml) was refluxed for 3 hr. The solvent was removed, then the residual product was washed with water and dried. Yield, 2.0 g (94%). Recrystallization from MeOH gave colorless needles, mp 208°. IR $\nu_{max}^{Nujol}$ $cm^{-1}$: 3500—3100 (NH, $NH_2$), 1700 (–NHCO–). MS *m/e*: 268.0954 ($M^+$, $C_{14}H_{12}N_4O_2$ requires 268.0959). PMR ($d_6$-DMSO) $\delta$: 1.79 (3H, s, $CH_3$), 3.83 (1H, s, =CH–), 5.55 (2H, s, $NH_2$), 6.78—7.24 (4H, m, ArH), 8.59 (1H, s, 4-NH–), 10.18 (1H, s, 1′-NHCO–).

**Spiro[oxindole-3,4′-(2′-amino-1′,4′-dihydro-6′-methylpyridine-3′-carboxamide)] (X)**——A mixture of IX (2.0 g) and Pd-C (10%, 0.2 g) in MeOH (30 ml) was shaken in hydrogen at room temperature and atmospheric pressure. When the absorption of hydrogen ceased, the mixture was filtered and the filtrate was evaporated to dryness. The residue was recrystallized from MeOH to give colorless prisms of mp 202°. Yield, 1.9 g (94%). IR $\nu_{max}^{Nujol}$ $cm^{-1}$: 3500—3150 (NH, $NH_2$), 1700 (–NHCO–), 1680 ($CONH_2$). MS *m/e*: 270.1088 ($M^+$, $C_{14}H_{14}N_4O_2$ requires 270.1115). PMR ($d_6$-DMSO) $\delta$: 1.67 (3H, s, $CH_3$), 3.81 (1H, s, =CH–), 4.76 (2H, s, 2′-$NH_2$), 6.79—7.20 (4H, m, ArH), 7.25 (2H, s, 3′-$CONH_2$), 7.74 (1H, s, 1′-NH–), 10.32 (1H, s, 1-NHCO–).

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