Novel Hexahydrofuro[3,4-*b*]-2(1*H*)-pyridones from 4-Aryl Substituted 5-Alkoxycarbonyl-6-methyl-3,4-dihydropyridones

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The title compounds **6** have been prepared in a one-step procedure from the corresponding 4-aryl substituted 5-alkoxycarbonyl-6-methyl-3,4-dihydropyridones **4** in good yields. Quantum chemical calculations reveal a non-planar molecule with a distorted dihydropyridone ring and two favoured conformations. The ^{13}C nmr data and theoretical calculations support a strong *push-pull* effect on the olefinic moiety.

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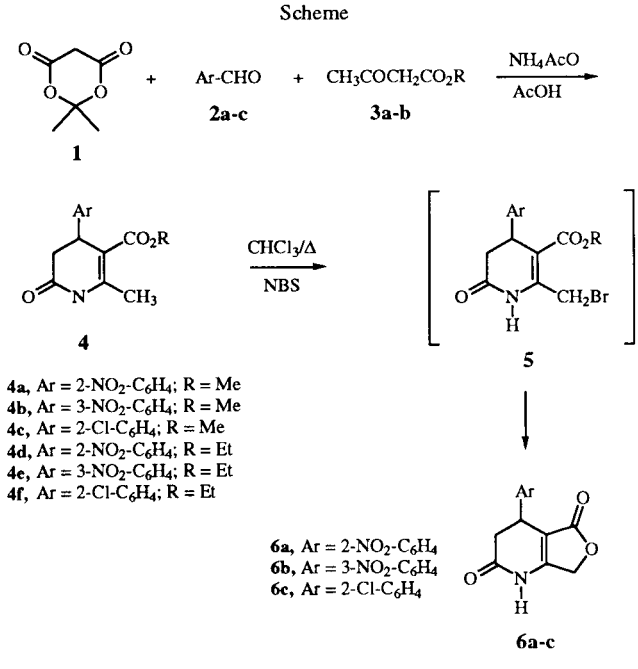
The research on the 1,4-dihydropyridine (1,4-DHP) systems is of current interest due to their exceptional properties as calcium antagonists [1]. Substitution on the 1,4-DHP ring has been widely studied [2] due to the dramatic effect that some substituents have on their biological activities. Thus, cyclohexanone and γ-lactone rings fused to the 1,4-DHP moiety result in a striking effect on the entry of calcium ions into the intracellular space (calcium agonist effect) [3] .

As for the lactone fused 1,4-DHP systems, most of the syntheses are based on the Hantzsch condensation of β-aminocrotonates and the appropriate aldehyde with protected 4-hydroxyacetoacetic esters and subsequent deprotection and lactonization [4]. The use of pyridinium bromide perbromide as the brominating reagent has allowed the direct conversion of methyl substituted *ortho*-alkoxycarbonyl 1,4-DHPs into the corresponding 1,4-DHP-fused monolactone [5]. Meldrum's acid has recently also been used as a second dicarbonyl component in a Hantzsch-like synthesis to obtain 3,4-dihydro-2(1*H*)-pyridones [6].

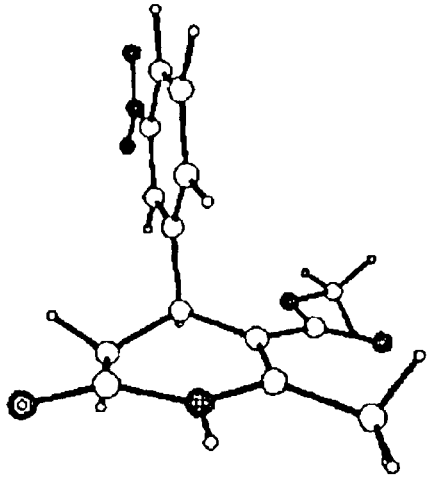
Very recently, we have described the synthesis and conformational study of tricyclic 1,4-DHP systems [7] and other acridine derivatives related to 1,4-DHPs [8]. In this paper we report an easy preparation of γ-lactone fused 1,4-DHPs **6** in a one-pot synthesis from the appropriate 3,4-dihydro-2(1*H*)-pyridone **4** and *N*-bromosuccinimide (NBS) as the brominating reagent. Semiempirical theoretical calculations on the novel bicyclic systems **6** are also presented.

Dihydropyridones **4** were prepared from the Meldrum's acid **1** by heterocyclization reaction with β-ketoester **3** and an aromatic aldehyde **2** in the presence of ammonium acetate by following the previously reported procedure [9]. We have, however, used acetic acid as solvent instead of ethanol resulting in a striking improvement on the yields (see Experimental). The presence of different alkoxy groups in ketoester **3** (methoxy or ethoxy) do not alter significantly the yields obtained.

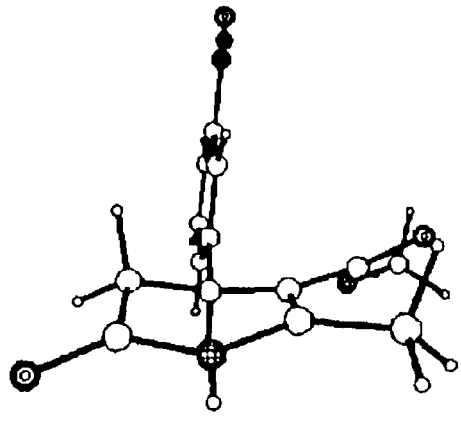
Scheme



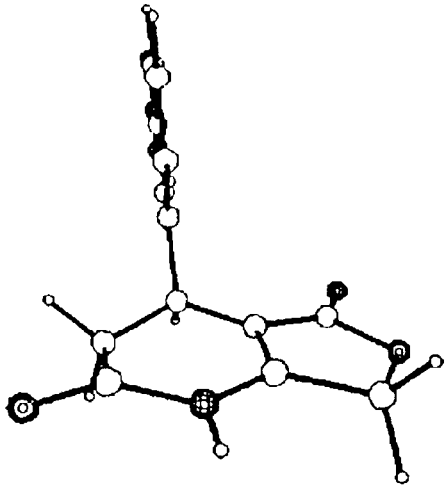
The ^1H nmr spectra of compounds **4** show the two protons on C-3 as a part of an ABX system which was confirmed by a doublet of doublets at δ 4.4-4.7 corresponding to the proton on C-4 due to the splitting by coupling with the protons on C-3 ($J_{3,4}$ = 1.9 Hz and $J_{3',4}$ = 8.3 Hz). This last coupling suggests a *trans*-diaxial configuration between the proton on C-4 and one of the protons on C-3. The ^{13}C nmr spectra of **4** show the signals for the olefinic carbons C-5 (δ ≈ 106) and C-6 (δ ≈ 147) at unusually low and high δ values respectively, thus indicating a strong *push-pull* effect due to the electronic behavior of the substituents.



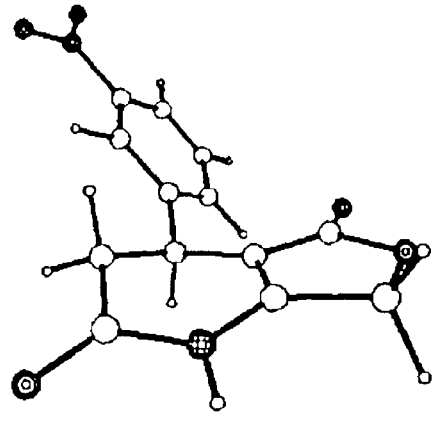
Compound **4c (A)**



Compound **4c (B)**



Compound **6c (A)**



Compound **6c (B)**

Figure. Geometry for the minimum energy conformations **A** and **B** for compounds **4c** and **6c**.

Furo[3,4-*b*]pyridones **6a-c** were obtained in moderate to good yields from dihydropyridones **4a-f** by reaction with NBS in refluxing chloroform for 10-14 hours. Lactonization could be accounted for by the allylic bromination at the methyl group to yield the non-isolable intermediate **5** followed by nucleophilic attack by bromide to the alkoxycarbonyl group in a similar way to the reported pyridinium bromide perbromide procedure for 1,4-DHPs [5]. Although the mechanism for the lactonization is not studied, some by-products resulting from polybromination in the alylic position [10] and the isolation of the bromomethylene intermediate [11], using pyridinium bromide perbromide as the brominating reagent, support the proposed structure for the non-isolated compound **5**.

The analytical and spectroscopic data are in good agreement with the proposed structure for compounds **6**. The ^{1}H nmr spectra show that the coupling between the protons on C-3 and C-4 atoms (J = 8.9 and J = 3.6 Hz) indicate that the fused γ-lactone ring modifies the geometry of the former dihydropyridone **4**.

Quantum chemical calculations using the AM1 method have been used to obtain the geometrical features of compounds **4** and **6**. Both compounds **4** and **6** are not planar, showing a twisted conformation for the dihydropyridone ring. The heats of formation indicate two energetically equally favoured conformations **A** and **B**. In conformation **A**, C-4 and C-3 carbon atoms are placed above and below from the molecular plane respectively. The position of these atoms (C-4 and C-3)

Table 1

Most Relevant Bond Distances and Dihedral Angles for Compounds **4** and **6** for Conformations **A**

	4a	**4b**	**4c**		**6a**	**6b**	**6c**
N1-C2	1.400	1.401	1.399	N1-C2	1.408	1.408	1.407
C2-C3	1.508	1.507	1.508	C2-C3	1.515	1.513	1.514
C3-C4	1.525	1.525	1.525	C3-C4	1.533	1.535	1.533
C4-C5	1.496	1.497	1.496	C4-C4a	1.477	1.477	1.476
C5-C6	1.374	1.374	1.374	C4a-C7a	1.375	1.375	1.375
C6-N1	1.389	1.388	1.389	C7a-N1	1.370	1.368	1.368
C2-N1-C6	122.4	122.4	122.4	C2-N1-C7a	119.0	119.2	119.2
C3-C4-C5	112.0	112.4	112.3	C3-C4-C4a	110.4	111.3	111.0
N1-C6-C5-C4	1.99	0.01	1.52	N1-C7a-C4aC4	1.20	-1.09	-0.34
C2-N1-C6-C5	10.41	9.58	10.07	C2-N1-C7a-C4a	5.10	5.73	5.39
C3-C4-C5-C6	-25.53	-22.52	-24.39	C3-C4-C4a-C7a	-18.79	-13.02	-14.94
C2'-C1'-C4-C5	-38.02	-47.35	-49.80	C2'-C1'-C4-C4a	-59.82	-54.08	-63.51
Ha3-C3-C4-H	-84.00	-85.75	-84.72	Ha3-C3-C4-H	-89.89	-98.38	-94.77
Hb3-C3-C4-H	34.17	31.81	33.63	Hb3-C3-C4-H	27.76	18.44	22.55
O-C-C5-C6	-6.02	-2.43	-3.64	O-C5-C4a-C7a	179.7	-179.5	-179.5

Table 2

Most Relevant Bond Distances and Dihedral Angles for Compounds **4** and **6** for Conformations **B**

	4a	**4b**	**4c**		**6a**	**6b**	**6c**
N1-C2	1.396	1.398	1.398	N1-C2	1.407	1.409	1.410
C2-C3	1.506	1.504	1.507	C2-C3	1.513	1.512	1.514
C3-C4	1.527	1.527	1.528	C3-C4	1.533	1.533	1.531
C4-C5	1.494	1.493	1.495	C4-C4a	1.477	1.474	1.482
C5-C6	1.372	1.376	1.374	C4a-C7a	1.376	1.378	1.380
C6-N1	1.390	1.385	1.389	C7a-N1	1.371	1.365	1.369
C2-N1-C6	122.4	122.7	122.3	C2-N1-C7a	119.2	119.5	118.6
C3-C4-C5	112.8	114.1	111.8	C3-C4-C4a	110.9	112.3	109.2
N1-C6-C5-C4	-2.00	-0.13	-3.28	N1-C7a-C4aC4	-3.10	-1.46	-2.30
C2-N1-C6-C5	-7.55	-4.77	-9.28	C2-N1-C7a-C4a	-4.19	13.57	-4.73
C3-C4-C5-C6	23.56	17.56	28.29	C3-C4-C4a-C7a	21.67	-13.02	-25.31
C2'-C1'-C4-C5	-57.32	-50.54	-57.52	C2'-C1'-C4-C4a	-55.78	-54.60	-57.24
Ha3-C3-C4-H	-159.5	-153.5	-164.3	Ha3-C3-C4-H	-157.5	-115.0	-167.7
Hb3-C3-C4-H	-41.38	-35.45	-45.83	Hb3-C3-C4-H	-39.67	-27.61	-48.26
O-C-C5-C6	-32.97	-22.73	-31.11	O-C5-C4a-C7a	178.2	177.1	176.9

is inverted in conformation **B** (see Figure). Interestingly, the phenyl group is in a pseudoaxial position in conformation **A** adopting a pseudoequatorial position in the conformation **B**.

The geometrical features are listed in Tables 1 and 2 showing the most relevant bond distances and dihedral angles for compounds **4** and **6** for the conformations **A** (Table 1) and **B** (Table 2).

The heats of formation and dipole moments are collected in Table 3. The calculated values indicate a higher dipolar moment in conformation **B** for compounds **4**, being higher for the conformation **A** in the furopyridones **6**.

Finally, the charge density values have also been calculated for the most relevant atoms and are shown in Tables 4 and 5 for the respective conformations **A** and **B**. These values confirm the electronic *push-pull* effect of the substituents on the olefinic double bond observed by ^{13}C nmr spectra.

In summary, we describe a novel synthesis of furo-[3,4-*b*]-2(1*H*)-pyridones from the corresponding 4-aryl substituted 5-alkoxycarbonyl-6-methyl-3,4-dihydropyridones by reaction with NBS as the brominating reagent. The compounds thus obtained have been studied by theoretical calculations and show a non-planar geometry with two favored conformations. The calculated charge density values obtained support the *push-pull* effect observed in the ^{13}C nmr spectra.

Table 3

Heats of Formation and Dipole Moments for the Favored Conformations **A** and **B** for Compounds **4** and **6**

	Heat of Formation (Kcal/mol)		Dipole Moment (Debye)	
Compound	A	B	A	B
4a	-95.94	-92.75	1.357	2.115
4b	-83.45	-79.51	4.460	4.729
4c	-86.85	-84.17	5.147	5.451
6a	-71.11	-70.64	3.359	2.000
6b	-58.01	-57.33	6.627	3.307
6c	-61.69	-60.54	7.716	5.816

Table 4

Charge Density Values for the Most Relevant Atoms in Compounds **4** and **6** for Conformation **A**

	4a	4b	4c		6a	6b	6c
N-1	-0.330	-0.333	-0.331	N-1	-0.309	-0.308	-0.307
C-2	0.311	0.307	0.308	C-2	0.310	0.309	0.309
C-3	-0.172	-0.171	-0.177	C-3	-0.172	-0.171	-0.177
C-4	-0.008	-0.012	-0.002	C-4	0.012	0.006	0.019
C-5	-0.249	-0.260	-0.257	C-4a	-0.259	-0.274	-0.272
C-6	0.140	0.147	0.146	C-7a	0.049.	0.057	0.057
O(COMe)	-0.382	-0.377	-0.377	O(C5)	-0.270	-0.268	-0.270
O(C2)	-0.331	-0.326	-0.325	O(C2)	-0.320	-0.316	-0.315

Table 5

Charge Density Values for the Most Relevants Atoms in Compounds **4** and **6** for Conformation **B**

	4a	4b	4c		6a	6b	6c
N-1	-0.326	-0.321	-0.328	N-1	-0.306	-0.298	-0.309
C-2	0.312	0.320	0.310	C-2	0.314	0.324	0.312
C-3	-0.180	-0.185	-0. 181	C-3	-0.178	-0.182	-0.181
C-4	-0.009	-0.004	-0.006	C-4	0.024	0.020	0.025
C-5	-0.235	-0.280	-0.255	C-4a	-0.256	-0.3044	-0.275
C-6	0.129	0.168	0.140	C-7a	0.050	0.083	0.060
O(COMe)	-0.370	-0.367	-0.368	O(C5)	-0.272	-0.279	-0.287
O(C2)	-0.337	-0.331	-0.326	O(C2)	-0.322	-0.318	-0.305

EXPERIMENTAL

Melting points were determined in capillary tubes in a Electrothermal C14500 apparatus and are uncorrected. The nmr spectra were recorded on a Bruker AC-250 F spectrometer. Chemical shifts are given as δ values against tetramethylsilane as internal standard. The ir spectra were measured with a Bruker IRS48 instrument as potassium bromide pellets. Microanalyses were performed by the Servicio de Microanálisis of Universidad Complutense de Madrid. The reactions were monitored by tlc performed on silica-gel plates (Merck $60F_{250}$) and using benzene:methanol (8:2) for compounds **4** and chloroform:acetone (8:2) for compounds **6** as the eluent. The geometry optimization was carried out with the semiempirical AM1 method by using the MOPAC molecular orbitals set. Previously the molecular geometry was optimized by using Allinger's Molecular Mechanics with PCMODEL program. Calculations were performed on a PC 486/33 computer.

Meldrum's acid, methyl acetoacetate, ethyl acetoacetate, ammonium acetate, *N*-bromosuccinimide, 2-chlorobenzaldehyde, 2-nitrobenzaldehyde and 3-nitrobenzaldehyde were obtained from commercial sources (Aldrich and Merck) and were used without further purification. Aromatic aldehydes were distilled before use.

4-Aryl-6-methyl-5-alcoxycarbonyl-3,4-dihydropyridones **4a-f**. General Procedure.

A mixture of an aromatic aldehyde (40 mmoles), the corresponding acetoacetate (methyl or ethyl) (40 mmoles), and ammonium acetate (42 mmoles) in acetic acid (40 ml) was refluxed for 10 hours and then poured into ice water. The solid that precipitated was collected by filtration. Further purification was accomplished by recrystallization from ethanol.

4-(2-Chlorophenyl)-6-methyl-5-methoxycarbonyl-3,4-dihydropyridone (**4a**).

This compound was obtained by following the above general procedure using methyl acetoacetate, in 60% yield, mp 198-200°; ir (potassium bromide): 3217 (NH), 1708 (CO, ester), 1685 (C=O), 1615 (C=C) cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 8.81 (s, 1H, NH), 7.38-7.03 (m, 4H, aryl), 4.69 (dd, 1H, H-4, J = 8.3 Hz, J = 1.9 Hz, X part of ABX), 3.60 (s, 3H, OCH_3), 2.90 (dd, 1H, H-3, J = 16.5 Hz, J = 8.3 Hz, A part of ABX), 2.72 (dd, 1H, H-3', J = 16.5 Hz, J = 1.9 Hz, B part of ABX), 2.45 (s, 3H, CH_3); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 171.0 (C2), 167.0 (COO), 147.9 (C6), 138.2, 133.3, 130.2, 128.3, 127.2, 124.1 (aryl), 105.7 (C5), 51.5 (OCH_3), 36.3 (C3), 34.9 (C4), 18.8 (CH_3).

Anal. Calcd. for $C_{14}H_{14}ClNO_3$ (279.72): C, 60.11; H, 5.04; N, 5.01. Found: C, 60.31; H, 5.17; N, 5.22.

6-Methyl-5-methoxycarbonyl-4-(2-nitrophenyl)-3,4-dihydropyridone (**4b**).

This compound was obtained by following the above general procedure using methyl acetoacetate, in 57% yield, mp 203-204° lit yield 26%, mp 205-207° [9].

6-Methyl-5-methoxycarbonyl-4-(3-nitrophenyl)-3,4-dihydropyridone (**4c**).

This compound was obtained by following the above general procedure using methyl acetoacetate, in 63% yield, mp 204-205° lit yield 24%, mp 206-207° [9].

5-Ethoxycarbonyl-6-methyl-4-(2-chlorophenyl)-3,4-dihydropyridone (**4d**).

This compound was obtained by following the above general procedure using ethyl acetoacetate, in 60% yield, mp 180-182°; ir (potassium bromide): 3226 (NH), 1693 (CO, ester), 1680 (C=O), 1629 (C=C) cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 8.74 (s, 1H, NH), 7.86-7.29 (m, 4H, aryl), 4.74 (dd, 1H, H-4, J = 8.3 Hz, J = 1.9 Hz, X part of ABX), 3.97 (q, 2H, CH_2-CH_3), 3.09 (dd, 1H, H-3, J = 16.5 Hz, J = 8.3 Hz, A part of ABX), 2.83 (dd, 1H, H-3', J = 16.5 Hz, J = 1.9 Hz, B part of ABX), 2.47 (s, 3H, CH_3), 1.03 (t, 3H, CH_2-CH_3); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 170.6 (C2), 166.0 (COO), 149.1 (C6), 147.7, 137.3, 133.3, 128.1, 127.9, 124.7 (aryl), 106.2 (C5), 60.3 (OCH_2), 37.1 (C3), 33.6 (C4), 18.8 (CH_3), 13.8 (CH_2-CH_3).

Anal. Calcd. for $C_{15}H_{16}ClNO_5$ (293.75): C, 61.33; H, 5.49; N, 4.77. Found: C, 61.41; H, 5.53; N, 4.85.

5-Ethoxycarbonyl-6-methyl-4-(2-nitrophenyl)-3,4-dihydropyridone (**4e**).

This compound was obtained by following the above general procedure using ethyl acetoacetate, in 60% yield, mp 200-202°; ir (potassium bromide): 3230 (NH), 1704 (CO, ester), 1697 (C=O), 1639 (C=C), 1525 and 1350 (NO_2) cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 8.92 (s, 1H, NH), 7.04-7.38 (m, 4H, aryl), 4.72 (dd, 1H, H-4, J = 8.3 Hz, J = 1.9 Hz, X part of ABX), 4.05 (q, 2H, CH_2-CH_3), 2.92 (dd, 1H, H-3, J = 16.5 Hz, J = 8.3 Hz, A part of ABX), 2.69 (dd, 1H, H-3', J = 16.5 Hz, J = 1.9 Hz, B part of ABX), 2.44 (s, 3H, CH_3), 1.10 (t, 3H, CH_2-CH_3); ^{13}C nmr (dimethyl sulfoxide-d_6):

δ 171.2 (C2), 166.5 (COO), 147.5 (C6), 138.7, 133.2, 130.1, 128.3, 127.2, 127.1 (aryl), 106.1 (C5), 60.2 (OCH_2), 36.4 (C3), 35.0 (C4), 18.7 (CH_3), 14.0 (CH_2CH_3); ms: m/z 304 (M^+)

Anal. Calcd. for $C_{15}H_{16}N_2O_5$ (304.3): C, 59.21; H, 5.30; N, 9.21. Found: C, 59.32; H, 5.41; N, 9.37.

5-Ethoxycarbonyl-6-methyl-4-(3-nitrophenyl)-3,4-dihydropyridone (**4f**).

This compound was obtained by following the above general procedure using ethyl acetoacetate, in 65% yield, mp 165-167°; ir (potassium bromide): 3220 (NH), 1697 (CO, ester), 1682 (C=O), 1631 (C=C), 1531 and 1349 (NO_2) cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 8.70 (s, 1H, NH), 8.01-7.35 (m, 4H, aryl), 4.37 (dd, 1H, H-4, J = 8.1 Hz, J = 1.8 Hz, X part of ABX), 4.13 (q, 2H, CH_2-CH_3), 3.02 (dd, 1H, H-3, J = 16.3 Hz, J = 8.1 Hz, A part of ABX), 2.70 (dd, 1H, H-3', J = 16.3 Hz, J = 1.8 Hz, B part of ABX), 2.44 (s, 3H, CH_3), 1.20 (t, 3H, CH_2-CH_3); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 170.6 (C2), 166.4 (COO), 148.5, 147.3, 144.4, 133.0, 129.8, 122.2, 121.4 (aryl), 106.1 (C5), 60.5 (OCH_2), 37.8 (C4), 37.7 (C3), 19.1 (CH_3), 14.2 (CH_2CH_3).

Anal. Calcd. for $C_{15}H_{16}N_2O_5$ (304.3): C, 59.21; H, 5.30; N, 9.21. Found: C, 59.35; H, 5.38; N, 9.32.

4-Aryl-5-oxo-1,2,3,4,5,7-hexahydrofuro[3,4-*b*]-2(1*H*)-pyridones (**6a-f**). General Procedure.

A solution of the corresponding 3,4-dihydro-2(1*H*)-pyridone **4** (5 mmoles), *N*-bromosuccinimide (0.89 g, 5 mmoles) in 10 ml of dry chloroform was refluxed for 12 hours. The reaction mixture was cooled and the solid that precipitated was collected by filtration. Further purification was accomplished by recrystallization from ethanol.

4-(2-Chlorophenyl)-5-oxo-1,2,3,4,5,7-hexahydrofuro[3,4-*b*]-2(1*H*)-pyridone (**6a**).

This compound was obtained by following the above general procedure, from **4a**, in 56% yield, from **4d**, in 60% yield, mp 218-219°; ir (potassium bromide): 3210 (NH), 1718 (CO, ester), 1680 (C=O), 1620 (C=C) cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 11.22 (s, 1H, NH), 7.92-7.57 (m, 4H, aryl), 5.37 (dd, 2H, OCH_2) 4.76 (dd, 1H H-4, J = 8.9 Hz, J = 3.8 Hz, X part of ABX), 3.59 (dd, 1H, H-3, J = 16.7 Hz, J = 8.9 Hz, A part of ABX), 2.87 (dd, 1H, H-3', J = 16.6 Hz, J = 3.7 Hz, B part of ABX); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 170.6 (C2), 169.0 (C5), 162.1 (C7a), 138.0, 132.2, 129.9, 129.0, 128.1, 127.7 (aryl), 99.9 (C4a), 65.5 (C7), 37.4 (C3), 30.8 (C4).

Anal. Calcd. for $C_{13}H_{10}ClNO_5$ (274.23): C, 59.22; H, 3.82; N, 5.31. Found: C, 59.32; H, 3.97; N, 5.40.

4-(2-Nitrophenyl)-5-oxo-1,2,3,4,5,7-hexahydrofuro[3,4-*b*]-2(1*H*)-pyridone (**6b**).

This compound was obtained by following the above general procedure, from **4b**, in 55% yield, from **4e**, in 60% yield, mp 214-215°; ir (potassium bromide): 3260 (NH), 1735 (CO, ester), 1715 (C=O), 1629 (C=C), 1530 and 1344 (NO_2) cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 11.27 (s, 1H, NH), 8.38-7.82 (m, 4H, aryl protons), 5.34 (dd, 2H, OCH_2), 4.85 (dd, 1H, H-4, J = 8.8 Hz, J = 3.8 Hz, X part of ABX), 3.64 (dd, 1H, H-3, J = 16.5 Hz, J = 8.8 Hz, A part of ABX), 3.03 (dd, 1H, H-3', J = 16.4 Hz, J = 3.7 Hz, B part of ABX); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 170.4 (C2), 168.0 (C5), 162.0 (C7a), 148.6, 135.1, 133.8, 129.1, 128.7, 124.4 (aryl), 99.8 (C4a), 65.5 (C7), 38.1 (C3), 29.6 (C4); ms: m/z 274 (M^+).

Anal. Calcd. for $C_{13}H_{10}N_2O_5$ (274.23): C, 56.94; H, 3.68, N, 10.22. Found: C, 56.99; H, 3.72; N, 10.31.

4-(3-Nitrophenyl)-5-oxo-1,2,3,4,5,7-hexahydrofuro[3,4-*b*]-2(1*H*)-pyridone (**6c**).

This compound was obtained by following the above general procedure, from **4c**, in 52% yield, from **4f**, in 58% yield, mp 234-235°; ir (potassium bromide): 3300 (NH), 1725 (CO, ester), 1700 (C=O), 1626 (C=C), 1540 and 1340 (NO_2) cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 10.86 (s, 1H, NH), 8.12-7.64 (m, 4H, aryl protons), 4.97 (dd, 2H, OCH_2) 4.25 (dd, 1H, H-4, J = 9.0 Hz, J = 3.6 Hz, X part of ABX), 3.15 (dd, 1H, H-3, J = 16.6 Hz, J = 8.9 Hz, A part of ABX), 2.67 (dd, 1H, H-3', J = 16.6 Hz, J = 3.6 Hz, B part of ABX); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 170.8 (C2), 169.3 (C5), 161.4 (C7a), 148.0, 143.9, 133.6, 130.3, 122.1, 121.6 (aryl), 100.5 (C4a), 65.5 (C7), 38.0 (C3), 33.1 (C4).

Anal. Calcd. for $C_{13}H_{10}N_2O_5$ (274.23): C, 56.94; H, 3.68; N, 10.22. Found: C, 57.01; H, 3.71; N, 10.33.

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