Spirocyclization of 1-(*o*-Aminophenyl)cycloalkanols and 1-(2'-Amino-3'-pyridinyl)cycloalkanols

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A one-step synthesis of spiro[cycloalkane-1,4'-2*H*-3',1-benzoxazin]-2'-ones and spiro[cycloalkane-1,4'-1*H*-pyrido[2',3'-*d*][1',3']oxazin]-2'-ones, obtained in good yield from the corresponding 1-(*o*-aminophenyl) and 1-(2'-amino-3'-pyridinyl)cycloalkanols is described using ethyl carbonate in presence of *n*-butyllithium.

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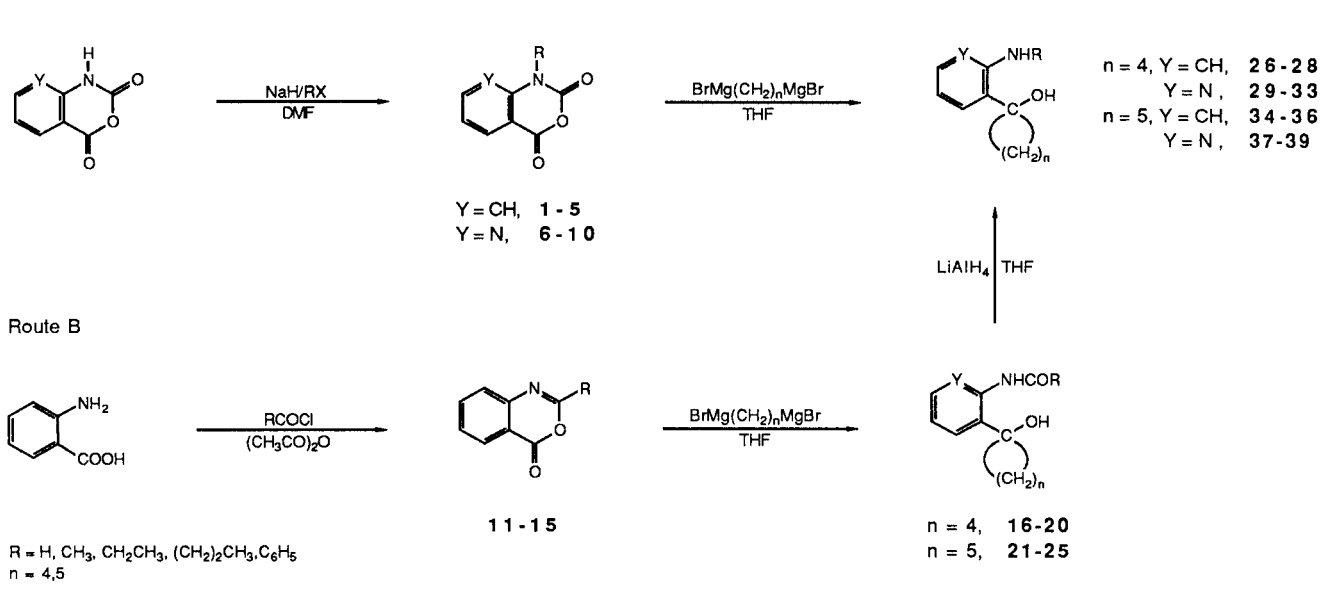
We have previously reported the synthesis of five- and six-membered 1-(*o*-aminophenyl)- and 1-(2'-amino-3'-pyridinyl)cycloalkanols based on the reactions of α,ω-bis-(bromomagnesio)alkanes with isatoic and azaisatoic anhydrides [1]. In spite of the great advantage of using isatoic anhydrides and their aza-homologues for their general regioselectivity toward nucleophilic attack [2], this method of formation of aminoalcohols appears rather limited for some particular substrates. For instances, yields of the cyclization process remain relatively low in the cases of isatoic **1**, *N*-benzylisatoic **5**, azaisatoic **6** and *N*-benzylisatoic **10** anhydrides, even in presence of an excess of the Grignard reagent. More recently, in order to improve these results, we elaborated a new procedure based on the complete reaction of organodimagnesium compounds with 2-substituted-4*H*-3,1-benzoxazin-4-ones prepared from anthranilic acid [3,4]. The amidoalcohols obtained are then treated with lithium aluminium hydride to afford the desired aminocyclic compounds.

To compare both methods, we examined the two alternative routes (A and B) which are illustrated in Scheme 1. Experiments revealed in fact that route B is more efficient than route A, leading selectively to the expected aminocycloalkanols with better yields, without any detectable amount of byproducts. 1-(*o*-Aminophenyl) and 1-(2'-amino-3'-pyridinyl)cycloalkanols are precursors of spirocycloalkanebenzoxazinones and spirocycloalkanepyridooxazinones derivatives and analogous substances are important on account of their herbicidal and pharmacological properties [5-8].

The synthesis of brofoxine and other substituted benzoxazinones has previously been developed involving the use of reactions with phosgene or thiophosgene [9-14]. However, in contrast to available information relating to 4-alkyl benzoxazin-2-ones [15-16], the preparations of spiro[cycloalkane-1,4'-2*H*-3',1'-benzoxazin]-2'-ones, spiro-[cycloalkane-1,4'-1*H*-pyrido[2',3'-*d*][1',3']oxazin]-2'-ones and their *N*-alkylated homologue series, could not be carried out. Thus, it seemed imperative to undertake a study of these types of reactions in order to explore this new method of spirocyclization.

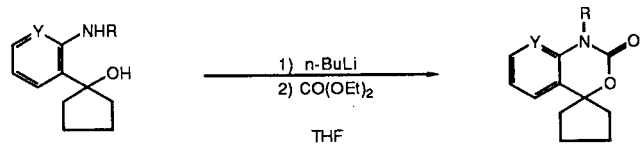
Scheme 1



In the present communication, we propose an efficient route for the preparation of spirobenzoxazinones from aminocycloalkanols, using a cheaper and less toxic reagent than phosgene. This method consists in the utilization of diethyl carbonate in presence of dilithium salts of the aminoalcohols. In order to test the feasibility of this heterocyclization, we tried various 1-(*o*-aminophenyl)cyclopentanols **26-28**, the treatment of these compounds with 2 equivalents of *n*-butyllithium in tetrahydrofuran, followed by the addition of diethyl carbonate, gave, after hydrolysis, the corresponding spiro[cyclopentane-1,4'-2*H*-3',1'-benzoxazin]-2'-ones **40-42**. An excess of *n*-butyllithium was also used in the reaction of aminocyclopentanol **28** but the reaction proceeded less efficiently because of the presence of the benzyl group, and, extensive purification by chromatography was necessary to obtain a pure compound (*i.e.* **42**).

These encouraging results have led to the application of this methodology to the preparation 1-(2'-amino-3'-pyridinyl)cyclopentanols **29-33** (Scheme 2). Condensation of dilithium salts with diethyl carbonate provided, after

Scheme 2

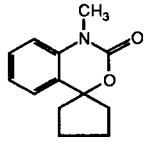
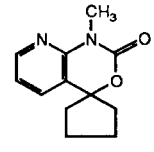
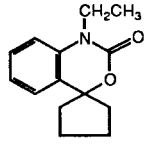
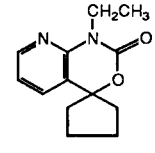
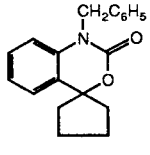
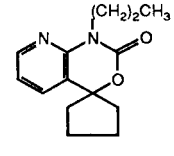
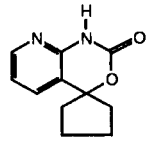
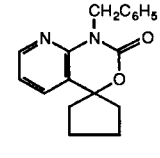


26: R = CH_3, Y = CH
27: R = CH_2CH_3, Y = CH
28: R = $CH_2C_6H_5$, Y = CH
29: R = H, Y = N
30: R = CH_3, Y = N
31: R = CH_2CH_3, Y = N
32: R = $(CH_2)_2CH_3$, Y = N
33: R = $CH_2C_6H_5$, Y = N

40-47

TABLE 1

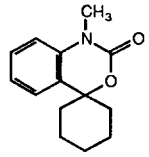
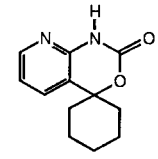
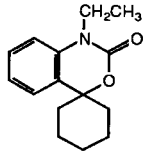
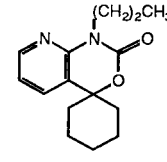
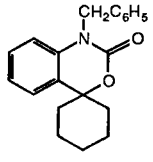
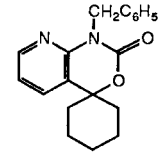
Spiro[cyclopentane-1,4'-2*H*-3',1'-Benzoxazin]-2'-ones and Spiro[cyclopentane-1,4'-1*H*-Pyrido[2',3'-*d*][1',3']oxazin]-2'-ones

Aminocyclopentanols	Product	Yield [1] (%)	Aminocyclopentanols	Product	Yield [1] (%)
26	 **40**	65	**30**	 **44**	45
27	 **41**	73	**31**	 **45**	55
28	 **42**	52	**32**	 **46**	51
29	 **43**	51	**33**	 **47**	53

[1] Yields were determined from isolated products.

TABLE 2

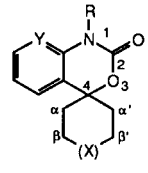
Spiro[cyclohexane-1,4'-2*H*-3',1'-Benzoxazin]-2'-ones and Spiro[cyclohexane-1,4'-1*H*-Pyrido[2',3'-*d*][1',3']oxazin]-2'-ones

Aminocyclohexanols	Product	Yield [1] (%)	Aminocyclohexanols	Product	Yield [1] (%)
34	 48	75	37	 51	47
35	 49	82	38	 52	55
36	 50	48	39	 53	51

[1] Yields were determined from isolated products.

Table 3

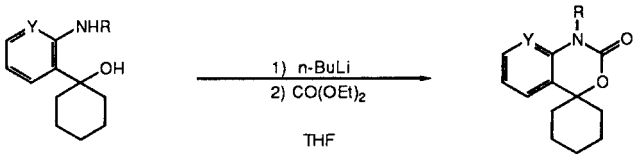
^{13}C NMR Comparative Data for Spirobenzoxazinones and Spiropyridoxazinones



	Compound	δ (Carbon) [a] 2	4	α	α'	β	β'	X	R
40	(R = CH_3; y = CH)	152.56	90.58	31.24	31.24	23.71	23.17	-	38.78
48	(R = CH_3; y = CH)	152.34	81.15	31.24	31.24	25.17	25.17	20.49	35.49
41	(R = C_2H_5; y = CH)	151.98	90.37	38.99	38.49	28.28	28.28	-	40.61-12.37
49	(R = C_2H_5; y = CH)	151.61	80.78	35.49	35.49	25.17	25.17	20.93	38.85-12.27
42	(R = $CH_2C_6H_5$; y = CH)	156.33	84.66	38.78	38.78	23.27	23.27	-	48.22
50	(R = $CH_2C_6H_5$; y = CH)	156.02	82.49	39.37	39.37	24.02	24.02	23.20	48.95
43	(R = H ; y = N)	151.46	91.60	39.80	39.80	23.78	23.78	-	-
51	(R = H ; y = N)	152.73	82.68	35.68	35.68	25.68	25.68	21.80	-
44	(R = CH_3 ; y = N)	152.41	89.63	37.46	37.46	23.78	23.78	-	39.37
45	(R = C_2H_5; y = N)	152.70	89.70	37.79 [b]	37.79 [b]	23.66	23.66	-	39.19 [b]-12.96
46	(R = C_3H_7; y = N)	157.90	83.38	38.41	38.41	23.12	23.12	-	45.58
52	(R = C_3H_7; y = N)	157.34	75.51	35.99	35.99	25.83 [c]	28.83 [c]	21.95	43.42-22.98 [c]-11.85
47	(R = $CH_2C_6H_5$; y = N)	157.44	83.27	38.41	38.41	23.05	23.05	-	45.58
53	(R = $CH_2C_6H_5$; y = N)	156.95	73.83	35.99	35.99	25.75	25.75	21.88	45.51

[a] Chemical Shifts are in δ (parts per million from TMS). Solutions were 0.75 mole/l in deuteriochloroform. [b-c] Assignments could be interchanged.

Scheme 3



34: R = CH_3, Y = CH
35: R = CH_2CH_3, Y = CH
36: R = $CH_2C_6H_5$, Y = CH
37: R = H, Y = N
38: R = $(CH_2)_2CH_3$, Y = N
39: R = $CH_2C_6H_5$, Y = N

48-53

hydrolysis, the desired spiro[cyclopentane-1,4'-1*H*-pyrido-[2',3'-*d*][1',3']oxazin]-2'-ones **43-47** with satisfactory yields in spite of the high reactivity of pyridine towards *n*-butyllithium [17] (Table 1).

In order to demonstrate the versatility of this method, we extended the heterocyclization to the 1-(*o*-aminophenyl)cyclohexanols **34-36** and 1-(2'-amino-3'-pyridinyl)-cyclohexanols **37-39** (Scheme 3). Under the same experimental conditions, the corresponding spiro[cyclohexanone-1,4'-2*H*-3',1'-benzoxazin]-2'-ones **48,49** have been obtained in very good yield. Cyclization of compounds **36-39** into spirobenzoxazinones **50-53** gave similar results with those obtained in the case of five-membered spirocompounds (Table 2). Compounds **50-53** have been purified by column chromatography. The ^1H, ^{13}C nmr and mass spectra of all synthetized compounds **40-53** unambiguously confirm all structural assignments. The ^{13}C nmr data also provided the following correlations: The spiro carbon chemical shifts are characteristic of the ring size (namely, 83-91 ppm for a cyclopentane spiro carbon and 73-82 ppm for a cyclohexane spiro carbon) and are found to be general. The spiro carbon chemical shift values of spiropyridoxazinones **43-47** and **51-53** are lower than those of spirobenzoxazinones **40-42** and **48-50** (Table 3). Similarly, the δ values of α, β and γ carbon atoms showed a significant difference between the two series.

EXPERIMENTAL

Melting points were determined in capillary tubes with a Thomas-Hoover apparatus and are uncorrected. Analytical thin-layer chromatography was performed on Woelm Silica Gel 60F 254 plates (0.25 mm). Purification and separation of products were achieved by column chromatography, eluting with ethyl acetate-petroleum ether (5 to 20% gradient). Infrared spectra were obtained on a Beckman IR-4250 spectrophotometer. The ^1H nmr spectra were determined on a Bruker HX-90 or a Varian XL-200 spectrometer in deuteriochloroform solution and are reported in δ units downfield from tetramethylsilane. The ^{13}C nmr spectra were determined on a Bruker WP-80 or on a Varian XL-200 in deuteriochloroform by using tetramethylsilane as internal standard. Mass spectra were obtained with a Hewlett-Packard 5995 A GC/MS.

Preparation of Spiro[cycloalkane-1,4'-2*H*-3',1'-Benzoxazin]-2'-ones and Spiro[cycloalkane-1,4'-1*H*-Pyrido[2',3'-*d*][1',3']oxazin]-2'-ones **40-53**.

The 1-(*o*-Aminophenyl)cycloalkanols **26-39** (11 mmoles), obtained from isatoic and azaisatoic anhydrides **1-10** [1] or from 4*H*-3,1-benzoxazin-4-ones **11-15**, in anhydrous tetrahydrofuran (50 ml) were cooled to 0° with an ice bath under an atmosphere of nitrogen and then, 11 mmoles of *n*-butyllithium (1.55 *M* in hexane) was added dropwise to the solution and stirred for 30 minutes at the same temperature and for an additional 3 hours at room temperature. After, the diethyl carbonate (22 mmoles) was added dropwise to the mixture and was stirred 3 hours more. After hydrolysis with ammonium chloride, the organic layer was separated, the aqueous layer was extracted with ether and the combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the resulting residue was separated by column chromatography, eluting with petroleum ether (40-60°)-ethyl acetate (9:1-5:1).

N-Methylspiro[cyclopentane-1,4'-2*H*-3',1'-benzoxazin]-2'-one (**40**).

This compound was obtained in 65% yield (1.55 g), mp 82-83°, recrystallized from hexane-ethyl acetate; ^1H nmr: δ 1.5-2.6 (m, 8H), 3.4 (s, 3H), 6.7-7.6 (m, 4H) ppm; ^{13}C nmr: δ 152.56, 128.85, 127.71, 127.41, 123.14, 122.28, 113.19, 90.59, 38.78, 31.24, 23.71 ppm; ir (Nujol): 1710 cm^{-1}; ms: m/z 217 (M^+, 10%), 173 (m^+-CO_2, 5%), 130 (100%).

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.80; H, 6.90; N, 6.44. Found: C, 71.80; H, 6.91; N, 6.33.

N-Ethylspiro[cyclopentane-1,4'-2*H*-3',1'-benzoxazin]-2'-one (**41**).

This compound was obtained in 73% yield (1.85 g); ^1H nmr: δ 1.28 (t, 3H), 1.50-2.50 (m, 8H), 3.95 (q, 2H), 6.8-7.5 (m, 4H) ppm; ^{13}C nmr: δ 151.98, 136.61, 128.78, 127.90, 123.15, 122.90, 113.34, 90.37, 40.61, 38.99, 28.78, 12.37 ppm; ir (Nujol): 1710 cm^{-1}; ms: m/z 231 (m^+, 12%), 187 (m^+CO_2, 1%), 144 (100%).

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.73; H, 7.35; N, 6.05. Found: C, 72.46; H, 7.81; N, 6.31.

N-Benzylspiro[cyclopentane-1,4'-2*H*-3',1'-benzoxazin]-2'-one (**42**).

This compound was obtained in 52% yield (1.39 g), mp 40°, recrystallized from petroleum ether-ethyl acetate; ^1H nmr: δ 1.5-2.8 (m, 8H), 4.5-5.2 (s, 2H), 6.6-7.6 (m, 9H) ppm; ^{13}C nmr: 156.33, 140.88, 140.12, 129.44, 128.78 (d), 127.54, 127.09, 125.27, 116.27, 111.95, 84.66, 48.22, 38.78, 23.27 ppm; ir (Nujol): 1710 cm^{-1}; ms: m/z 293 (M^+, 7%), 158.15 (79%), 91 (100%).

Anal. Calcd. for $C_{19}H_{19}NO_2$: C, 77.82; H, 6.48; N, 4.78. Found: C, 77.74; H, 7.00; N, 4.71.

Spiro[cyclopentane-1,4'-1*H*-pyrido[2',3'-*d*][1',3']oxazin]-2'-one (**43**).

This compound was obtained in 51% yield (1.09 g), mp 205°, recrystallized from petroleum ether-ethyl acetate; ^1H nmr: δ 1.78-2.39 (m, 8H), 5.40-5.50 (s, 1H), 7.02-7.05 (dd, 1H), 7.25-7.49 (dd, 1H), 8.32-8.37 (dd, 1H) ppm; ^{13}C nmr: δ 151.46, 149.12, 147.80, 131.85, 120.29, 118.90, 91.60, 39.80, 23.78 ppm; ir (Nujol): 1740 cm^{-1}; ms: m/z 204 (m^+, 30%), 160 (m^+-CO_2, 100%).

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.71; H, 5.88; N, 13.73. Found: C, 64.53; H, 6.10; N, 13.44.

N-Methylspiro[cyclopentane-1,4'-1*H*-pyrido[2',3'-*d*][1',3']-2'-one (**44**).

This compound was obtained in 45% yield (1.08 g); ^1H nmr: δ 1.4-3.0 (m, 8H), 3.6 (s, 3H), 6.8-7.3 (dd, 1H), 7.3-7.6 (dd, 1H), 8.2-8.5 (dd, 1H) ppm; ^{13}C nmr: δ 152.41, 149.63, 147.66, 130.98, 122.19, 118.54, 89.63, 39.37, 37.46, 23.78 ppm; ir (Nujol): 1725 cm^{-1}; ms: m/z 218 (m^+, 29%), 174 (m^+-CO_2, 20%), 146 (100%).

Anal. Calcd. for $C_{12}H_{14}N_2O_2$: C, 66.06; H, 6.42; N, 12.84. Found: C, 66.23; H, 6.61; N, 12.60.

N-Ethylspiro[cyclopentane-1,4'-1*H*-pyrido[2',3'-*d*][1',3']oxazin]-2'-one (**45**).

This compound was obtained in 55% yield (1.40 g); ^1H nmr: δ 1.25-1.34 (t, 3H), 1.81-2.30 (m, 8H), 4.13-4.22 (q, 2H), 6.96-7.02 (dd, 1H), 7.41-7.44 (dd, 1H), 8.27-8.30 (dd, 1H) ppm; ^{13}C nmr: δ 152.70, 149.50, 147.44, 130.41, 122.00, 118.33, 89.70, 39.19, 37.79, 23.66, 12.96 ppm; ir (Nujol): 1715 cm^{-1}; ms: m/z 232 (m^+, 27%), 188 (m^+-CO_2, 10%), 173 (100%).

Anal. Calcd. for $C_{13}H_{16}N_2O_2$: C, 67.24; H, 6.90; N, 12.07. Found: C, 67.14; H, 6.95; N, 11.90.

N-Propylspiro[cyclopentane-1,4'-1*H*-pyrido[2',3'-*d*][1',3']oxazin]-2'-one (**46**).

This compound was obtained in 89% yield (1.38 g), recrystallized from petroleum ether-ethyl acetate; ^{1}H nmr: δ 0.50-1.00 (t, 3H), 1.00-2.50 (m, 10H), 2.9-3.5 (t, 3H), 6.10-6.40 (dd, 1H), 6.40-7.30 (dd, 1H), 7.70-8.00 (dd, 1H) ppm; ^{13}C nmr: δ 157.90, 146.85, 131.99, 130.22, 123.58, 110.99, 83.34, 43.39, 38.41, 23.12 (d), 11.78 ppm; ir (Nujol): 1725 cm^{-1}; ms: m/z 246 (m$^+$ 10%), 202 (m$^+$-CO_2, 5%), 173 (100%).

Anal. Calcd. for $C_{14}H_{18}N_2O_2$: C, 68.29; H, 7.32; N, 11.38. Found: C, 68.19; H, 7.12; N, 11.42.

N-Benzylspiro[cyclopentane-1,4'-1*H*-pyrido[2',3'-*d*][1',3']oxazin]-2'-one (**47**).

This compound was obtained in 53% yield (1.71 g); ^{1}H nmr: δ 1.70-2.09 (m, 8H), 4.64 (s, 2H), 6.44-6.51 (dd, 1H), 7.22-7.37 (m, 6H), 7.97-8.01 (dd, 1H) ppm; ^{13}C nmr: δ 157.46, 146.78, 140.49, 132.07, 128.56, 127.76, 126.88, 126.51, 123.80, 111.66, 83.27, 45.58, 38.41, 23.05 ppm; ir (Nujol): 1700 cm^{-1}; ms: m/z 294 (m$^+$, 7%), 250 (m$^+$-CO_2, 17%), 91 (100%).

Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.97; H, 6.12; N, 9.52. Found: C, 73.80; H, 5.98; N, 9.30.

N-Methylspiro[cyclohexane-1,4'-2*H*-3',1'-benzoxazin]-2'-one (**48**).

This compound was obtained in 75% yield (1.91 g), mp 104-105°, recrystallized from petroleum ether-ethyl acetate; ^{1}H nmr: δ 1.2-2.4 (m, 10H), 3.38 (s, 3H), 6.7-7.5 (m, 4H) ppm; ^{13}C nmr: δ 152.34, 137.27, 129.43, 128.78, 123.22, 123.07, 113.27, 81.15, 35.49, 31.24, 25.17, 20.99 ppm; ir (Nujol): 1690 cm^{-1}; ms: m/z 232 (m$^+$, 16%), 187 (m$^+$-CO_2, 13%), 130 (100%).

Anal. Calcd. for $C_{14}H_{12}NO_2$: C, 72.64; H, 7.35; N, 6.05. Found: C, 72.45; H, 7.33; N, 5.89.

N-Ethylspiro[cyclohexane-1,4'-2*H*-3',1'-benzoxazin]-2'-one (**49**).

This compound was obtained in 82% yield (2.26 g), mp 60°, recrystallized from petroleum ether-ethyl acetate; ^{1}H nmr: δ 1.30 (t, 3H), 1.5-2.4 (m, 10H), 3.98 (q, 2H), 6.8-7.6 (m, 4H) ppm; ^{13}C nmr: δ 151.61, 136.02, 129.02, 128.63, 123.29, 122.93, 113.34, 80.78, 38.85, 35.49, 25.17, 20.93, 12.29 ppm; ir (Nujol): 1710 cm^{-1}; ms: m/z 245 (m$^+$, 10%), 202 (m$^+$-CO_2, 29%), 172 (100%).

Anal. Calcd. for $C_{15}H_{19}NO_2$: C, 73.46; H, 7.75; N, 5.71. Found: C, 73.53; H, 7.99; N, 5.78.

N-Benzylspiro[cyclohexane-1,4'-2*H*-3',1'-benzoxazin]-2'-one (**50**).

This compound was obtained in 48% yield (1.62 g), mp 110-114°, recrystallized from petroleum ether-ethyl acetate; ^{1}H nmr: δ 1.3-2.6 (m, 10H), 4.9-5.3 (s, 2H), 6.5-7.9 (m, 9H) ppm; ^{13}C nmr: δ 156.02, 141.80, 141.30, 130.46, 128.93, 127.90 (d), 127.46, 124.80, 114.51, 82.49, 48.95, 39.37, 24.02, 23.20 ppm; ir (Nujol): 1700 cm^{-1}; ms: m/z 307 (m$^+$, 17%), 172 (87%), 91 (100%).

Anal. Calcd. for $C_{20}H_{21}NO_2$: C, 78.18; H, 6.84; N, 4.56. Found: C, 77.74; H, 7.07; N, 4.31.

Spiro[cyclohexane-1,4'-1*H*-pyrido[2',3'-*d*][1',3']-2'-one (**51**).

This compound was obtained in 47% yield (1.12 g), mp 150-154°, recrystallized from petroleum ether-benzene; ^{1}H nmr: δ 1.64-2.17 (m, 10H), 5.50-5.22 (s, 1H), 6.54-6.62 (dd, 1H), 7.26-7.38 (dd, 1H), 7.91-7.94 (dd, 1H) ppm; ^{13}C nmr: δ 152.73, 146.71, 137.63, 133.24, 123.27, 122.30, 82.68, 35.68, 25.68, 21.80 ppm; ir (Nujol): 1720 cm^{-1}; ms: m/z 218 (m$^+$, 45%), 174 (m$^+$-CO_2, 100%).

Anal. Calcd. for $C_{12}H_{14}N_2O_2$: C, 66.06; H, 6.42; N, 12.84. Found: C, 65.99; H, 6.77; N, 12.89.

N-Propylspiro[cyclohexane-1,4'-1*H*-pyrido[2',3'-*d*][1',3']oxazin]-2'-one (**52**).

This compound was obtained in 55% yield (1.57 g); ^{1}H nmr: δ 0.5-1.2 (t, 3H), 1.25-2.50 (m, 12H), 3.2-3.5 (t, 2H), 6.2-6.6 (dd, 1H), 7.0-7.4 (dd, 1H), 7.8-8.1 (dd, 1H) ppm; ^{13}C nmr: δ 157.34, 141.63, 132.39, 130.27, 125.41, 111.14, 75.51, 43.32, 25.83, 22.98, 21.95, 11.85 ppm; ir (Nujol): 1720 cm^{-1}; ms: m/z 260 (m$^+$, 10%), 216 (m$^+$-CO_2, 6%).

Anal. Calcd. for $C_{15}H_{20}N_2O_2$: C, 69.25; H, 7.69; N, 10.77. Found: C, 69.60; H, 7.50; N, 10.55.

N-Benzylspiro[cyclohexane-1,4'-1*H*-pyrido[2',3'-*d*][1',3']oxazin]-2'-one (**53**).

This compound was obtained in 51% yield (1.73 g); ^{1}H nmr: δ 0.8-2.4 (m, 10H), 4.65 (s, 2H), 6.3-6.6 (dd, 1H), 7.2-7.6 (m, 6H), 7.8-8.2 (dd, 1H) ppm; ^{13}C nmr: δ 156.95, 146.63, 140.78, 132.51, 128.56, 127.68, 126.80, 126.51, 125.17, 111.88, 73.83, 45.51, 35.99, 25.75, 21.88 ppm; ir (Nujol): 1730 cm^{-1}; ms: m/z 308 (m$^+$, 10%), 264 (m$^+$-CO_2, 6%), 91 (100%).

Anal. Calcd. for $C_{19}H_{20}N_2O_2$: C, 74.03; H, 6.49; N, 9.09. Found: C, 74.47; H, 6.89; N, 6.66.

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