Chemical Behaviour of *N*-(2-Hydroxybenzyl)anthranilic Acids in the Presence of Acyclic Anhydrides

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The synthesis of 11-acyl-11,12-dihydrodibenz[*b*,*f*][1,5]oxazocin-6-ones **9-13** is reported by reaction of *N*-(2-hydroxybenzyl)anthranilic acids **1** with acetic, isobutyric, 2-ethylbutyric anhydrides. The structures of the obtained 6,8,6 products are proved with the use of ir, mass spectrometry, ^1H and ^{13}C nmr spectra, homo- and heteronuclear two-dimensional nmr experiments. The formation of **9-13** is discussed in relation to the obtainment of 12*H*-quino[2,1-*b*][1,3]benzoxazin-5-ones **2-8** and 6a,12-dihydro[3,1]benzoxazino[2,1-*b*][1,3]-benzoxazin-5-ones **14-19** from the same starting products **1** with suitable anhydrides under controlled reaction conditions.

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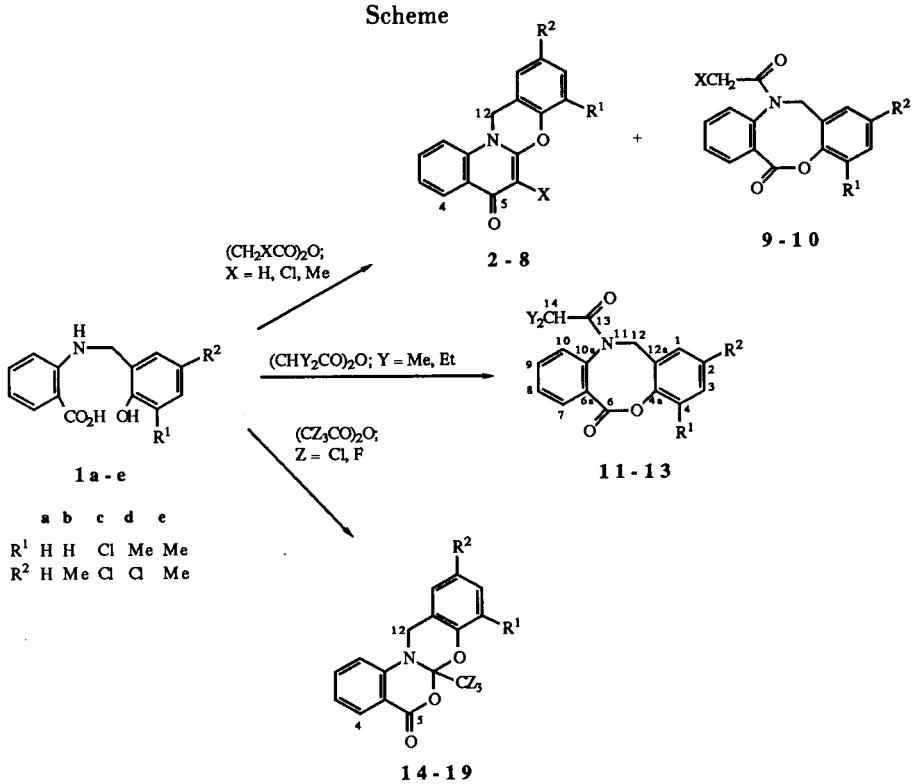
The *N*-(2-hydroxybenzyl)anthranilic acids **1** [1] were shown to be useful starting products to synthesize fused heteropolycyclic derivatives [2]. Previously we reported the obtainment of the 6,6,6,6 systems **14-19** and **2-8** by reacting Mannich products **1a,b,d,e** with suitable acyclic symmetric anhydrides, trifluoroacetic [2a] and acetic, chloroacetic, propionic anhydrides [2b] respectively. Now we recognize the relevance of giving a conclusive comprehensive view on the chemical behaviour of Mannich products **1** in the presence of anhydrides, reporting the following new results, which mainly concern the synthesis of dibenz-[*b*,*f*][1,5]oxazocines. Some representative derivatives [3] of this 6,8,6 system - together with their differently fused [*b*,*g*] [4] and [*c*,*f*] [3a,5] isomers - are reported chiefly in the patent literature, useful as analgesic, antidepressant, anti-inflammatory drugs, hypotensive agents, and sedatives [3a,b,d,4a,c,5a].

When the starting products **1b** and **1c** were reacted at

Scheme



	a	b	c	d	e
R^1	H	H	Cl	Me	Me
R^2	H	Me	Cl	Cl	Me

	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
R^1	H	H	H	H	Me	Me	Me	Cl	Me	H	H	Cl	H	H	Cl	Me	Me	Me
R^2	H	H	Me	Me	Me	Cl	Cl	Cl	Me	Me	Me	Cl	H	Me	Cl	Cl	Cl	Me
X	H	Cl	H	Me	H	H	Cl	H	H	--	--	--	-	--	--	--	--	--
Y	-	--	--	--	--	--	--	--	--	Me	Et	Me	-	--	--	--	--	--
Z	-	--	--	--	--	--	--	--	--	--	--	--	F	F	F	Cl	F	F

130° for 2 hours with an excess of isobutyric or 2-ethylbutyric anhydride [$(CHY_2CO)_2O$, Y = Me or Et, see Scheme], the 11-acyl-11,12-dihydrodibenz[*b,f*][1,5]oxazocin-6-ones **11-13** were obtained in almost quantitative yields. Also the 11-acetyl-2,4-dichloro-11,12-dihydrodibenz[*b,f*][1,5]oxazocin-6-one (**9**) was the only reaction product which we could obtain by treating **1c** with acetic anhydride [$(CH_2XCO)_2O$, X = H, see Scheme] but, when the starting product was the *N*-(3,5-dimethyl-2-hydroxybenzyl)anthranilic acid (**1e**), the synthesis of the 11-acetylderivative **10** required mild and well controlled reaction conditions, and this 6,8,6 product **10** was obtained always in low yield, together with the 6,6,6,6 derivative **6** (see Experimental).

A tentative rationalization of these experimental results firstly explains the only isolation of benzoxazinobenzoxazinones **14-19** by reaction of **1** with trichloro- and trifluoroacetic anhydrides [$(CZ_3CO)_2O$, Z = Cl or F, see Scheme] on the basis of high electrophilic properties of the carbonyl carbon atom of $NCOCCl_3$ or $NCOCF_3$ moiety of the openchain acyl derivative of **1**, which easily undergoes cyclization to 1,3-benzoxazine system, followed by the formation of the fused 3,1-benzoxazinone ring [2a]. Failing these marked electrophilic properties, as occurs in the reactions of **1** with anhydrides as isobutyric or 2-ethylbutyric, the intramolecular esterification to 6,8,6 systems **11-13** appears to be the preferred reaction course. Only $(CH_2XCO)_2O$ - as acetic, chloroacetic, propionic anhydrides - can afford the quinobenzoxazinones **2-8** [2b] in the reaction under study; the minor electrophilic properties of the acyl carbon atom, which would not favour the oxazine ring formation, appears counterbalanced by the obtainment of the fused 4-quinolone system, highly stabilized by mesomerism [2b]. So the 6,6,6,6 systems **2-8** are formed when the compounds **1a,b,d,e** react with an excess of $(CH_2XCO)_2O$ at 140-170° for 2 hours, and only milder reaction conditions enable $N\text{-}COCH_2X$ substituted 6,8,6 products to be isolated in low yields, together with **2-8**. In the reaction of *N*-(3,5-dichloro-2-hydroxybenzyl)anthranilic acid (**1c**) with acetic anhydride, the only formation of the 6,8,6 product **9** can be ascribed to the favourable influence of the halogeno-substitution to the intramolecular esterification, owing to the chlorine effect onto the reactivity of phenolic oxygen atom.

Table I

^{1}H NMR Spectroscopic Data of the 11-Acyl-11,12-dihydrodibenz[*b,f*][1,5]oxazocin-6-ones **9-13** (δ, ppm; J, Hz)

	11	**13**		**9**	**10**	**12**	
	$CDCl_3$/500 MHz	$(CD_3)_2SO$/500 MHz	$CDCl_3$/60 MHz	$CDCl_3$/60 MHz	$CDCl_3$/60 MHz	$(CD_3)_2SO$/200 MHz	$CDCl_3$/60 MHz
-CH*Me*$_2$	0.98, d 1.03, d J_{vic} 6.5	0.91, d 1.00, d J_{vic} 6.5	1.04, d J_{vic} 6.5				
Ar Me	2.16, s				2.14, br s	2.16, s	2.17, s
-*CH*Me$_2$	2.20, m	2.11, m	2.23, m				
2 x -CH$_2$*Me*						0.67, t 0.77, t J_{vic} 6.5	0.7-2.2, m -CHEt$_2$
-CH(CH$_2$)$_2$						1.2-1.8, m	
-COMe				1.81, s	1.80, s		
H$_2$-12	4.27, d 5.46, d J_{gem} -13.8	4.51, d 5.40, d J_{gem} -15.0	4.27, d 5.44, d J_{gem} -14.0	4.30, d 5.45, d J_{gem} -14.0	4.23, d 5.34, d J_{gem} -14.0	4.42, d 5.33, d J_{gem} -15.0	4.29, d 5.37, d J_{gem} -14.5
H-1	6.84, d $J_{1,3}$ 1.5	7.48, d $J_{1,3}$ 2.0	6.9-7.6, m	6.9-7.5, m	6.5-7.4, m	7.0-7.6, m	6.8-7.4, m ArH
H-3	6.92, dd $J_{3,4}$ 8.1	7.71, d					
H-4	6.86 d						
H-7	7.34, dd $J_{7,8}$ 7.5 $J_{7,9}$ 1.5	7.58, dd $J_{7,8}$ 8.0 $J_{7,9}$ 1.5					
H-8	7.28, dt $J_{8,9}$ 7.5 $J_{8,10}$ 0.8	7.52, dt $J_{8,9}$ 8.0 $J_{8,10}$ 0.5					
H-9	7.36, dt $J_{9,10}$ 8.0	7.65, dt $J_{9,10}$ 8.0					
H-10	7.03, dd	7.46, dd					

The structure of the compounds **9-13** was elucidated by ir, mass spectrometry, nmr (Tables I and II) spectral work, mainly by performing homo- and heteronuclear two-dimensional nmr experiments of the 11,12-dihydro-11-isobutanoyl-2-methyldibenz[*b*,*f*][1,5]oxazocin-6-one (**11**) in deuteriochloroform solution at 500 and 126 MHz for proton and carbon resonances respectively. The attribution of the high field resonances in the ^{1}H nmr spectrum of **11** is straightforward, but its aromatic portion deserves special comments. An accurate consideration of vicinal and long-range couplings allows the identification of H-1, H-3, and H-4 resonances at 6.84, 6.92, and 6.86 ppm respectively, owing to their multiplicities and $J_{para} < J_{meta}$. For the four protons of the other benzene ring, the sequence of multiplicity is d (7.03), t (7.28), d (7.34), and t (7.36 ppm) with all these lines further split by long-range couplings: noteworthy the ^{1}H-homonuclear correlation (COSY) spectrum [6a] of **11** shows an important interaction between 7.03 doublet and 7.36 triplet so the attribution of only one absorption allows to immediately assign the remaining three aromatic resonances. We suggest the reported attributions (Table I) on the basis of $J_{7,9} > J_{8,10}$, as verified in the related quinobenzoxazines **2-8** [2b]. Moreover the COSY experiment of **11** shows a slight interaction between 2-Me and the hydrogens of the same benzene ring, thus confirming the above attributions. The assignment of ^{13}C nmr spectrum of **11** relies upon evaluation of information from the two-dimensional ^{1}H-^{13}C shift correlation experiment [6b], a part from the quaternary carbons, whose attribution is suggested taking as model compounds methyl anthranilate [7], 6a,12-dihydro[3,1]benzoxazino[2,1-*b*][1,3]benzoxazin-5-ones [2a], and 12*H*-quino[2,1-*b*][1,3]benzoxazin-5-ones [2b]. All the other attributions reported in Tables I and II arise by analogy from the aforesaid considerations.

The aromatic ^{1}H nmr patterns of quinobenzoxazinones **2-8** and benzoxazinobenzoxazinones **14-19** are extended towards low fields (6.7-8.5 and 6.5-8.2 ppm respectively) and the most deshielded multiplet was attributed to H-4

Table II

^{13}C Chemical Shift Data (δ, ppm) for the 11-Acyl-11,12-dihydrodibenz[b,f][1,5]oxazocin-6-ones **11-13**

	11 $CDCl_3$/126 MHz	**12** $(CD_3)_2SO$/50 MHz	**13** $(CD_3)_2SO$/126 MHz
C-1	131.53	131.57	129.91
C-2	136.73	136.29	132.90
C-3	130.24	130.23	130.15
C-4	121.85	121.92	130.72
C-4a	149.68	149.20	145.96
C-6	168.37	167.83	166.64
C-6a	128.02	128.14	127.63
C-7	127.87	127.96	126.92
C-8	129.17	129.42	129.33
C-9	132.17	132.53	133.74
C-10	128.45	129.42	129.33
C-10a	136.88	136.29	133.74
C-12	50.20	49.27	48.94
C-12a	132.58	131.97	131.30
C-13	177.31	174.41	175.73
C-14	32.40	45.66	31.70
Ar*Me*	20.61	20.10	
-CH*Me*$_2$	19.63 19.65		19.19 19.42
-CH(*C*H$_2$)$_2$		24.21 24.61	
2 x -CH$_2$*Me*		11.47 11.70	

[2b]. Instead the corresponding aromatic resonances of the dibenzoxazocinones **9-13** are concentrated in the range 6.5-7.7 ppm, because the boat conformation of the eight-membered ring prevents the aromatic proton near the endocyclic carbonyl group (H-7 in **9-13**, H-4 in **2-8** and **14-19**) from being severely deshielded, as it is in the tetracyclic compounds **2-8** and **14-19**.

The ir data concerning the stretching of carbonyl groups are in line with the structures of the acyldibenzoxazocinones **9-13**. The ester carbonyl frequency is raised on going from **10-12** (1755-1760 cm^{-1}) to the 2,4-dichlorodibenzoxazocinones **9** and **13** (1780-1787 cm^{-1}): this behaviour is imputable to the electron withdrawing halogen substituents which reduce the tendency for the carbonyl oxygen to draw electrons from the other oxygen and thus weaken the C=O bond. As regards the amide C=O stretching, the carbonyl frequency weakly raises changing from isobutanoyl and 2-ethylbutanoyl derivatives **11-13** (1660-1665 cm^{-1}) to the acetylderivatives **9,10** (1675-1677 cm^{-1}), in accordance with the order of the inductive effect of alkyl groups.

The wide effectiveness of the reported synthetic route [2a] to 6a,12-dihydro[3,1]benzoxazino[2,1-*b*][1,3]benzoxazin-5-ones is strengthened by the obtainment of the new tetracyclic derivatives **16** and **17**. Noteworthy the H_2-12 nmr absorption - which appears as broad singlet in the range 4.67-4.53 ppm for the 6a-trifluoromethyl derivatives **14-16,18,19** - is resolved in a typical AB quartet (δ_A 4.84, δ_B 4.60 ppm; J_{AB} = −14.0 Hz) for the 10-chloro-6a,12-dihydro-8-methyl-6a-trichloromethyl[3,1]benzoxazino[2,1-*b*]-[1,3]benzoxazin-5-one (**17**).

EXPERIMENTAL

Elemental analyses were performed on a Carlo Erba Model 1106 instrument. All melting points are uncorrected. The ir spectra were run on a Perkin-Elmer 682 instrument. The nmr spectra were recorded on Bruker AM-500, 200, or Varian EM-360A instruments as solutions in hexadeuterioacetone, DMSO-d_6, or deuteriochloroform, and using TMS as the internal standard. Mass spectra were obtained on a Varian MAT CH7 (70 eV) spectrometer. Column chromatography was performed on Merck silica gel type 60 (70-230 mesh, 0.063-0.200 mm). Petroleum ether refers to the fraction bp 30-60°. The syntheses and characterizations of compounds **1a,b,d,e** and **2-8,14,15,18,19** are reported in [1] and [2] respectively.

N-(3,5-Dichloro-2-hydroxybenzyl)anthranilic Acid (**1c**).

It was obtained from 2,4-dichlorophenol, anthranilic acid, and paraformaldehyde following the general procedure reported in [1]. During the purification of the crude reaction mixture by column chromatography (petroleum ether-diethyl ether 7:3 v/v as eluent) some fractions were obtained which showed characteristic ^1H nmr absorptions, in hexadeuterioacetone at 60 MHz, of **1c** (singlet at 4.44 ppm) and its precursor [1] 1-(3',5'-dichloro-2'-hydroxybenzyl)-1,2-dihydro-3,1-benzoxazin-4-one (two singlets at 4.65 and 5.26 ppm) in variable mutual ratios. All these fractions were combined, and subjected to completion of benzoxazinone hydrolysis by treatment with an excess (almost 10:1 molar ratio) of 2.5 *N* aqueous sodium hydroxide at 60° for 30 minutes. The solution was then neutralized with 10% hydrochloric acid, and white crystals of **1c** separated (65% yield), mp 148-150°; ^1H nmr (hexadeuterioacetone): 60 MHz, δ 4.44 (s, 2H, CH_2), 6.3-8.0 (m, 6H, ArH).

Anal. Calcd. for $C_{14}H_{11}Cl_2NO_3$: C, 53.87; H, 3.55; N, 4.49. Found: C, 53.81; H, 3.50; N, 4.52.

11-Acetyl-2,4-dichloro-11,12-dihydrodibenz[*b*,*f*][1,5]oxazocin-6-one (**9**).

The starting product **1c** (5 mmoles) was suspended in anhydrous benzene (20 ml), acetic anhydride (12.5 mmoles) was added, and the reaction mixture warmed at reflux for 4 hours. After cooling at room temperature, water (10 ml) was added, and the mixture neutralized by solid sodium bicarbonate. The organic phase was dried (anhydrous sodium sulfate), and the residue, after having removed the solvent, was column chromatographed eluting with petroleum ether-chloroform (1:1 v/v) to give the title product **9** (50% yield), mp 144-146°; ir (nujol): 1787 (ester C=O), 1677 (amide C=O) cm^{-1}.

Anal. Calcd. for $C_{16}H_{11}Cl_2NO_3$: C, 57.17; H, 3.30; N, 14.17. Found: C, 57.11; H, 3.40; N, 4.09.

11-Acetyl-11,12-dihydro-2,4-dimethyldibenz[*b*,*f*][1,5]oxazocin-6-one (**10**).

The starting product **1e** [1] (1.85 mmoles) was suspended in anhydrous benzene (20 ml), acetic anhydride (4.6 mmoles) was added, and the reaction mixture kept at room temperature under stirring: **1e** was slowly dissolved. After 24 hours, water (10 ml) was added, and the mixture neutralized by solid sodium bicarbonate. The organic phase was dried, evaporated under vacuum, and the residue was column chromatographed eluting with petroleum ether-chloroform (1:1 v/v). This chromatographic separation afforded, besides the title compound **10**, comparable amounts of unreacted **1e**, and 8,10-dimethyl-12*H*-quino[2,1-*b*][1,3]benzoxazin-5-one (**6**) [2b]. The title compound **10** was further purified by preparative tlc on Merck silica gel 60 PF_{254} plates (2 mm thickness) using chloroform as eluent (18% yield), mp 174-176°; ir (chloroform): 1760 (ester C=O), 1675 (amide C=O) cm^{-1}.

Anal. Calcd. for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.21; H, 5.91; N, 4.73.

11,12-Dihydro-11-isobutanoyl-2-methyldibenz[*b*,*f*][1,5]oxazocin-6-one (**11**).

The Mannich product **1b** [1] (5 mmoles) was dissolved by warming in isobutyric anhydride (50 mmoles), and the mixture was stirred at 130° for 2 hours. Small amounts of **11**, separated by cooling, were collected by filtration, but the most **11** was obtained by column chromatography of the crude reaction mixture: the unreacted anhydride was eluted with petroleum ether-diethyl ether (8:2 v/v) while the title compound **11** was obtained (total yield >90%) with an 1:1 v/v eluent mixture of the same solvents, mp 215-217°; ir (nujol): 1760 (ester C=O) and 1660 (amide C=O) cm^{-1}; ms: m/z (% relative intensity) 309 (47, M^+), 266 (73), 189 (37), 146 (32), 120 (30), 119 (100), 90 (43), 89 (27), 43 (36).

Anal. Calcd. for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.71; H, 6.21; N, 4.59.

11,12-Dihydro-11(2'-ethylbutanoyl)-2-methyldibenz[*b*,*f*][1,5]oxazocin-6-one (**12**).

It was obtained (yield >90%) from **1b** [1] and 2-ethylbutyric anhydride (following the above-mentioned procedure of synthesis and isolation of **11**), mp 159-161°; ir (nujol): 1755 (ester C=O), 1665 (amide C=O) cm^{-1}.

Anal. Calcd. for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.49; H, 6.91; N, 4.14.

2,4-Dichloro-11,12-dihydro-11-isobutanoyldibenz[*b*,*f*][1,5]-oxazocin-6-one (**13**).

It was prepared from **1c** as above reported for **11**. The total yield in the title compound **13** exceeds 85%, mp 206-208°; ir (nujol): 1780 (ester C=O), 1660 (amide C=O) cm^{-1}.

Anal. Calcd. for $C_{18}H_{15}Cl_2NO_3$: C, 59.36; H, 4.15; N, 3.85. Found: C, 59.41; H, 4.09; N, 3.84.

8,10-Dichloro-6a,12-dihydro-6a-trifluoromethyl[3,1]benzoxazino[2,1-*b*][1,3]benzoxazin-5-one (**16**).

It was prepared (80% yield) by reaction of **1c** with trifluoroacetic anhydride according to [2a], mp 197-199°; ^1H nmr (deuteriochloroform): 60 MHz, δ 4.67 (br s, 2H, CH_2), 6.9-8.2 (m, 6H, ArH); ir (nujol): 1768 (C=O) cm^{-1}; ms: m/z (% relative intensity) 389 (20, M^+), 322 (3), 320 (5), 178 (20), 177 (7), 176 (100), 175 (12), 174 (75), 148 (25), 146 (57), 139 (12).

Anal. Calcd. for $C_{16}H_8Cl_2F_3NO_3$: C, 49.26; H, 2.07; N, 3.59. Found: C, 49.19; H, 2.11; N, 3.61.

10-Chloro-6a,12-dihydro-8-methyl-6a-trichloromethyl[3,1]benzoxazino[2,1-*b*][1,3]benzoxazin-5-one (**17**).

It was obtained (85% yield) by reacting **1d** with an excess of trichloroacetic anhydride in analogy with the general procedure reported in [2a], mp 164-165°; ^1H nmr (deuteriochloroform): 60 MHz, δ 2.33 (s, 3H, CH_3), 4.60 and 4.84 (AB q, 2H, $J_{gem} = -14.0$ Hz, CH_2), 6.8-8.0 (m, 6H, ArH); ir (nujol): 1760 (C=O) cm^{-1}; ms: m/z (% relative intensity) 417 (2, M^+), 386 (3), 385 (2), 384 (5), 383 (3), 382 (5), 340 (5), 339 (2), 338 (5), 336 (2), 334 (3), 314 (4), 305 (5), 304 (9), 303 (20), 302 (60), 301 (12), 300 (100), 265 (10), 228 (11), 202 (11), 200 (12), 156 (40), 155 (25), 154 (60), 146 (70), 126 (40).

Anal. Calcd. for $C_{17}H_{11}Cl_4NO_3$: C, 48.72; H, 2.64; N, 3.34. Found: C, 48.59; H, 2.80; N, 3.29.

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