Reaction of Ketenes with *N,N*-Disubstituted α-Aminomethyleneketones. XVII. Synthesis of 2*H*-[1]Benzothiepino[5,4-*b*]pyran Derivatives

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1,4-Cycloaddition of dichloroketene to a number of *N,N*-disubstituted (*E*)-4-aminomethylene-3,4-dihydro-[1]benzothiepin-5(2*H*)-ones gave in excellent yield *N,N*-disubstituted 4-amino-3,3-dichloro-3,4,5,6-tetrahydro-2*H*-[1]benzothiepino[5,4-*b*]pyran-2-ones III, which are derivatives of the 2*H*-[1]benzothiepino[5,4-*b*]pyran system. Dehydrochlorination of III with DBN afforded *N,N*-disubstituted 4-amino-3-chloro-5,6-dihydro-2*H*-[1]-benzothiepino[5,4-*b*]pyran-2-ones, generally in excellent yield.

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In a previous paper [1] we described the synthesis of a new heterocyclic system containing the 1-benzoxepin moiety condensed with the 2*H*-pyran ring, namely 2*H*-pyrano[3,2-*d*][1]benzoxepin.

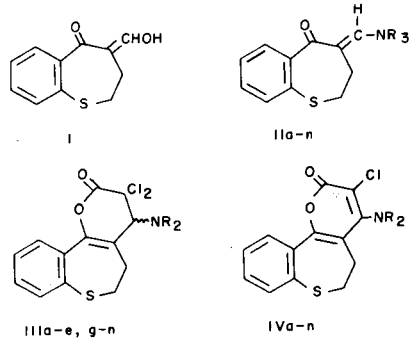
In pursuing our work on heterocyclic systems derived from 2*H*-pyran and incorporating potential pharmacologically active molecules, we have now chosen 1-benzothiepin moiety, the thioisoster of 1-benzoxepin, to build up derivatives of 2*H*-[1]benzothiepino[5,4-*b*]pyran, an heterocyclic system of which only two derivatives are known [2].

1-Benzothiepin was already condensed with other interesting heterocyclic rings such as thiophene [2], pyrazole [2-4], isoxazole [5], indole and thiochroman [6], pyrimidine [2,4], quinoline and dihydrothiazepine [2].

The starting enaminones IIa-n (Table I), necessary for the polar 1,4-cycloaddition of dichloroketene, were prepared in excellent yield from 3,4-dihydro-4-hydroxymethylene[1]benzothiepin-5(2*H*)-one I and secondary amines, following a previously described procedure [7]. They are probably *E* isomers, at least as can be seen from the upfield shifts of C-2 (δ 0.2-0.5) and C-3 (δ 0.3-0.6) protons caused by the phenyl group(s) in compounds IIm,n in comparison with IIa-l (Table II).

The reaction of II with dichloroacetyl chloride and triethylamine (dichloroketene prepared *in situ*) occurred readily both in the case of aliphatic and aromatic *N*-substitution to give in excellent yields *N,N*-disubstituted 4-amino-3,3-dichloro-3,4,5,6-tetrahydro-2*H*-[1]benzothiepino[5,4-*b*]pyran-2-ones IIIa-e,h,i,m,n (Table III), whose structure was confirmed by ir and nmr spectral data (Table IV).

Also enaminones IIg,l gave the corresponding cycloadducts, but they were too unstable to be purified and characterized, therefore they were used in the dehydrochlorination step without further purification Enaminone IIf afforded directly, albeit in low yield, the dehydrochlorinated compound IVf.



I IIa-n IIIa-e, g-n IVa-n

	NR_2
a	$N(CH_3)_2$
b	$N(C_2H_5)_2$
c	$N[CH(CH_3)_2]_2$
d	$N(CH_3)CH_2C_6H_5$
e	$N(CH_3)CH_2CH_2C_6H_5$
f	$N(CH_3)CH_2CH_2N(CH_3)_2$
g	1-Pyrrolidinyl
h	1-Piperidinyl
i	4-Morpholinyl
l	1-(4-Methylpiperazinyl)
m	$N(CH_3)C_6H_5$
n	$N(C_6H_5)_2$

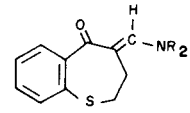
All these adducts were dehydrochlorinated with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in refluxing toluene to give *N,N*-disubstituted 4-amino-3-chloro-5,6-dihydro-2*H*-[1]benzothiepino[5,4-*b*]pyran-2-ones IVa-e, g-n (Tables V and VI), generally in excellent yields.

EXPERIMENTAL

The uv spectra were measured in 95% ethanol with a Hitachi-Perkin-Elmer Model EPS-3T spectrophotometer. The ir spectra were taken in chloroform on a Perkin-Elmer Model 398 spectrophotometer; the nmr spectra were recorded in deuteriochloroform on a Perkin-Elmer Model R-600 instrument (60 MHz, TMS as internal standard, J in Hz). Melting points were determined with a Mettler FP1 apparatus.

Table I

N,N-Disubstituted (*E*)-4-Aminomethylene-3,4-dihydro-[1]benzothiepin-5(2*H*)-ones IIa-n [a]



Formula Number	NR_2	Yield %	Mp °C	Molecular Formula	Analyses % Calcd./Found C	H	N
IIa	$N(CH_3)_2$	96	143 [b]	$C_{13}H_{15}NOS$	66.92	6.48	6.00
					67.03	6.53	5.87
IIb	$N(C_2H_5)_2$	87	116 [c]	$C_{15}H_{19}NOS$	68.93	7.33	5.36
					69.08	7.37	5.29
IIc	$N[CH(CH_3)_2]_2$	72	155 [c]	$C_{17}H_{23}NOS$	70.55	8.01	4.84
					70.41	8.02	4.99
IId	$N(CH_3)CH_2C_6H_5$	97	150 [b]	$C_{19}H_{19}NOS$	73.75	6.19	4.53
					73.50	6.07	4.41
IIe	$N(CH_3)CH_2CH_2C_6H_5$	93	78 [c]	$C_{20}H_{21}NOS$	74.27	6.54	4.33
					74.16	6.59	4.39
IIf	$N(CH_3)CH_2CH_2N(CH_3)_2$	98	98 [c]	$C_{16}H_{22}N_2OS$	66.17	7.63	9.64
					66.08	7.58	9.57
IIg	1-Pyrrolidinyl	99	146 [b]	$C_{15}H_{17}NOS$	69.46	6.61	5.40
					69.66	6.59	5.36
IIh	1-Piperidinyl	96	134 [c]	$C_{16}H_{19}NOS$	70.29	7.00	5.12
					70.55	7.14	5.24
IIi	4-Morpholinyl	94	171 [b,d]	$C_{15}H_{17}NO_2S$	65.43	6.22	5.09
					65.18	6.21	5.32
II l	1-(4-Methylpiperazinyl)	96	132 [c]	$C_{16}H_{20}N_2OS$	66.63	6.99	9.71
					66.41	6.97	9.65
IIm	$N(CH_3)C_6H_5$	90	143 [b]	$C_{18}H_{17}NOS$	73.19	5.80	4.74
					73.31	5.75	4.77
IIn	$N(C_6H_5)_2$	88	158 [b]	$C_{23}H_{19}NOS$	77.28	5.36	3.92
					77.03	5.39	3.89

[a] Compounds IIa-l were prepared according to the general procedure a) and compounds IIm-n according to the general procedure b) previously described [7]. [b] From ethyl acetate. [c] From anhydrous diethyl ether. [d] Ref [10] mp 166-167°.

Table II

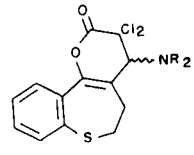
UV, IR and NMR Spectral Data of Compounds IIa-n

Compound	UV, λ max nm (log ε)	IR, cm^{-1} C=O	C=C	NMR, δ
IIa	248 (4.065)	1643	1534	2.60 (t, J = 6, CH_2-3), 3.00 (t, J = 6, CH_2-2), 3.14 [s, $(CH_3)_2N$],
	350 (4.24)			7.44 (mc, 4 H ar), 7.89 (s, =CHN)
IIb	247.5 (4.09)	1637	1524	1.25 (t, J = 7.2, 2 CH_3), 2.55 (t, J = 6, CH_2-3), 3.01 (t, J = 6, CH_2-2),
	351 (4.26)			3.37 (q, J = 7.2, 2 CH_2N), 7.45 (mc, 4 H ar), 7.95 (s, =CHN)
IIc	248 (3.99)	1631	1512	1.27 (d, J = 6.6, 4 CH_3), 2.57 (t, J = 6, CH_2-3), 3.01 (t, J = 6, CH_2-2),
	355 (4.21)			3.90 (h, J = 6.6, 2 CHN), 7.42 (mc, 4 H ar), 8.13 (near s, =CHN)
IId	248 (4.015)	1642	1528	2.57 (t, J = 6, CH_2-3), 2.95 (t, J = 6, CH_2-2), 3.07 (s, CH_3N),
	350 (4.20)			4.50 (s, CH_2N), 7.35 (s, C_6H_5), 7.44 (mc, 4 H ar), 8.12 (s, =CHN)
IIe	248 (4.02)	1642	1532	2.58 (t, J = 6, CH_2-3), 2.95 (mc, CH_2-2 + CH_2Ph), 3.07 (s, CH_3N),
	353 (4.18)			3.54 (t, J = 7.2, CH_2N), 7.1-7.8 (m, C_6H_5 + 4 H ar), 7.89 (s, =CHN)
IIf	247 (3.71)	1640	1528	2.26 [s, $(CH_3)_2N$], 2.62 (mc, CH_2-3 + CH_2N), 3.00 (t, J = 6, CH_2-2),
	348 (3.82)			3.15 (s, CH_3N), 3.41 (t, J = 7.2, CH_2N), 7.44 (mc, 4 H ar), 7.90 (near s, =CHN)

IIg	248.5 (3.955) 355 (4.225)	1638	1523	1.93 (mc, 2 CH_2 pyr), 2.59 (t, J = 6, CH_2-3), 3.00 (t, J = 6, CH_2-2), 3.58 (mc, 2 CH_2N), 7.45 (mc, 4 H ar), 8.11 (s, =CHN)
IIh	247.5 (3.97) 353 (4.135)	1640	1525	1.66 (mc, 3 CH_2 pip), 2.58 (t, J = 6, CH_2-3), 3.02 (t, J = 6, CH_2-2), 3.47 (mc, 2 CH_2N), 7.43 (mc, 4 H ar), 7.88 (near s, =CHN)
IIi	249 (3.97) 298 (3.77) 350.5 (3.985)	1644	1533	2.60 (t, J = 6, CH_2-3), 3.00 (t, J = 6, CH_2-2), 3.58 (mc, 2 CH_2N), 3.70 (mc, 2 CH_2O), 7.46 (mc, 4 H ar), 7.79 (s, =CHN)
II l	249 (4.03) 301 (3.80) 351 (4.065)	1642	1527	2.2-2.8 (m, CH_2-3 + 2 CH_2NMe), 2.32 (s, CH_3N), 3.01 (t, J = 6, CH_2-2), 3.56 (t, J = 5.4, 2 CH_2N), 7.25-7.75 (m, 4 H ar), 7.84 (s, =CHN)
IIm	247.5 (4.06) 358 (4.20)	1644	1527	2.30 (t, J = 6, CH_2-3), 2.78 (t, J = 6, CH_2-2), 3.49 (s, CH_3N), 7.1-7.8 (m, C_6H_5 + 4 H ar), 8.11 (s, =CHN)
IIn	250.5 (4.12) 372 (4.26)	1645	1533	2.03 (t, J = 6, CH_2-3), 2.48 (t, J = 6, CH_2-2), 7.1-7.8 (m, 2 C_6H_5 + 4 H ar), 8.20 (s, =CHN)

Table III

N,N-Disubstituted 4-Amino-3,3-dichloro-3,4,5,6-tetrahydro-2*H*-[1]benzothiepino[5,4-*b*]pyran-2-ones IIIa-e,h,i,m,n



Formula Number	NR_2	Yield %	Mp °C	Molecular Formula	Analyses % Calcd./Found C	H	N
IIIa	$N(CH_3)_2$	83	113 [a]	$C_{15}H_{15}Cl_2NO_2S$	52.33 52.30	4.39 4.32	4.07 4.06
IIIb	$N(C_2H_5)_2$	85	115 [a]	$C_{17}H_{19}Cl_2NO_2S$	54.84 54.82	5.14 5.10	3.76 3.81
IIIc	$N[CH(CH_3)_2]_2$	99	177 dec [b]	$C_{19}H_{23}Cl_2NO_2S$	57.00 56.73	5.79 5.78	3.50 3.38
IIId	$N(CH_3)CH_2C_6H_5$	95	136 [a]	$C_{21}H_{19}Cl_2NO_2S$	60.00 59.99	4.56 4.60	3.33 3.22
IIIe	$N(CH_3)CH_2CH_2C_6H_5$	85	102 [c]	$C_{22}H_{21}Cl_2NO_2S$	60.83 60.63	4.87 4.84	3.22 3.18
IIIh	1-Piperidinyl	72	109 [a]	$C_{18}H_{19}Cl_2NO_2S$	56.25 56.55	4.98 4.95	3.64 3.79
IIIi	4-Morpholinyl	76	149 [a]	$C_{17}H_{17}Cl_2NO_3S$	52.86 52.82	4.44 4.50	3.63 3.71
IIIm	$N(CH_3)C_6H_5$	92	114 [a]	$C_{20}H_{17}Cl_2NO_2S$	59.12 59.03	4.22 4.22	3.45 3.43
IIIn	$N(C_6H_5)_2$	97	238 dec [b]	$C_{25}H_{19}Cl_2NO_2S$	64.11 64.14	4.09 4.05	2.99 3.04

[a] From anhydrous diethyl ether. [b] From ethyl acetate. [c] From petroleum ether bp 40-70°-diethyl ether 1:1.

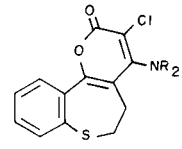
Table IV

IR and NMR Spectral Data of Compounds IIIa-e,h,i,m,n

Compound	IR, cm^{-1} C=O	IR, cm^{-1} C=C	NMR, δ
IIIa	1780	1682	2.38 (near t, J = 7.2, CH_2-5), 2.64 [s, $(CH_3)_2N$], 3.53 (t, J = 6.6, CH_2-6), 3.85 (near s, CH-4), 7.2-7.8 (m, 4 H ar)
IIIb	1778	1678	1.10 (t, J = 7.2, 2 CH_3), 2.36 (mc, CH_2-5), 2.93 (q, J = 7.2, 2 CH_2N), 3.56 (t, J = 6.6, CH_2-6), 4.00 (s, CH-4), 7.25-7.80 (m, 4 H ar)
IIIc	1775	1670	1.09 [d, J = 5.4, $(CH_3)_2C$], 1.19 [d, J = 5.4, $(CH_3)_2C$], 2.50 (near t, J ~ 6, CH_2-5), 3.18 (mc, 2 CHN), 3.57 (near t, J ~ 6, CH_2-6), 3.94 (s, CH-4), 7.15-7.85 (m, 4 H ar)
IIId	1780	1680	2.15-2.65 (m, CH_2-5), 2.46 (s, CH_3N), 3.52 (t, J = 6, CH_2-6), 4.02 (s, CH-4), 4.12 (s, CH_2Ph), 7.33 (mc, C_6H_5 + 4 H ar)
IIIe	1782	1680	1.89 (mc, CH_2-5), 2.52 (s, CH_3N), 2.76 (mc, CH_2-6), 3.20 (mc, CH_2N + CH_2Ph), 3.82 (s, CH-4), 7.1-7.8 (m, C_6H_5 + 4 H ar)
IIIh	1782	1680	1.50 (mc, 3 CH_2 pip), 2.37 (t, J = 6.3, CH_2-5), 2.6-3.4 (m, 2 CH_2N), 3.57 (t, J = 6.3, CH_2-6), 3.83 (s, CH-4), 7.53 (mc, 4 H ar)
IIIi	1782	1678	2.40 (t, J = 6.3, CH_2-5), 2.6-3.4 (m, 2 CH_2N), 3.45-3.75 (m, CH_2-6 + 2 CH_2O), 3.81 (s, CH-4), 7.45 (mc, 4 H ar)
IIIm	1783	1680	2.34 (t, J = 6.6, CH_2-5), 2.85 (s, CH_3N), 3.43 (t, J = 6.6, CH_2-6), 5.07 (s, CH-4), 6.7-7.9 (m, C_6H_5 + 4 H ar)
IIIn	1785	1685	2.51 (mc, CH_2-5), 3.61 (mc, CH_2-6), 5.39 (s, CH-4), 6.4-8.0 (m, 2 C_6H_5 + 4 H ar)

Table V

N,N-Disubstituted 4-Amino-3-chloro-5,6-dihydro-2*H*-[1]benzothiepino[5,4-*b*]pyran-2-ones IVa-n



Formula Number	NR_2	Yield %	Mp °C	Molecular Formula	Analyses % Calcd./Found C	H	N
IVa	$N(CH_3)_2$	94	158 [a]	$C_{15}H_{14}ClNO_2S$	58.53	4.58	4.55
					58.61	4.63	4.50
IVb	$N(C_2H_5)_2$	90	101 [b]	$C_{17}H_{18}ClNO_2S$	60.80	5.40	4.17
					60.97	5.38	4.23
IVc	$N[CH(CH_3)_2]_2$	90	152 [b]	$C_{19}H_{22}ClNO_2S$	62.71	6.09	3.85
					62.68	6.09	3.78
IVd	$N(CH_3)CH_2C_6H_5$	85	154 [a]	$C_{21}H_{18}ClNO_2S$	65.70	4.73	3.65
					65.55	4.66	3.62
IVe	$N(CH_3)CH_2CH_2C_6H_5$	95	116 [a]	$C_{22}H_{20}ClNO_2S$	66.40	5.07	3.52
					66.43	4.97	3.56
IVf	$N(CH_3)CH_2CH_2N(CH_3)_2$	35 [c]	99, 119 [b]	$C_{18}H_{21}ClN_2O_2S$	59.25	5.80	7.68
					59.40	5.69	7.84
IVg	1-Pyrrolidinyl	70 [d]	210 [a]	$C_{17}H_{16}ClNO_2S$	61.16	4.83	4.20
					60.91	4.84	4.29
IVh	1-Piperidinyl	93	176 [a]	$C_{18}H_{18}ClNO_2S$	62.15	5.22	4.03
					62.22	5.24	4.04
IVi	4-Morpholinyl	97	207 [a]	$C_{17}H_{16}ClNO_3S$	58.37	4.61	4.00
					58.15	4.54	3.98
IV l	1-(4-Methylpiperazinyl)	24 [e]	208 [a]	$C_{18}H_{19}ClN_2O_2S$	59.58	5.28	7.72
					59.40	5.22	7.82
IVm	$N(CH_3)C_6H_5$	86	190 [a]	$C_{20}H_{16}ClNO_2S$	64.95	4.36	3.79
					64.95	4.36	3.92
IVn	$N(C_6H_5)_2$	93	233 [a]	$C_{25}H_{18}ClNO_2S$	69.52	4.20	3.24
					69.22	4.18	3.24

[a] From ethyl acetate. [b] From anhydrous diethyl ether. [c] The precipitate obtained from the reaciton of IIf with dichloroketene plus the semi-solid residue obtained by evaporation of toluene were treated with water. The aqueous solution was made alkaline with sodium hydrogen carbonate and extracted thoroughly with diethyl ether. The ether extracts were dried (magnesium sulfate) and evaporated to give crude IVf. [d] Prepared by dehydrochlorination with DBN of the crude, unstable cycloadduct obtained from IIg and dichloroketene. [e] Prepared by dehydrochlorination with DBN of the crude cycloadduct hydrochloride obtained from II l and dichloroketene. Crude IV l was obtained from the hydrochloric acid solution by treatment with 1 *N* sodium hydroxide, followed by extraction with chloroform.

Table VI

UV, IR and NMR Spectral Data of Compounds IVa-n

Compound	UV, λ max nm (log ε)	IR, cm^{-1} C=O	IR, cm^{-1} C=C	NMR, δ
IVa	232 sh (3.97) 255.5 (4.07) 263 sh (4.05) 320 (4.04)	1695	1613 1522	2.58 (t, J = 6.6, CH_2-5), 3.10 [s, $(CH_3)_2N$], 3.56 (mc, CH_2-6), 7.3-7.9 (m, 4 H ar)
IVb	235 sh (4.08) 253.5 (4.08) 266 sh (3.99) 326.5 (4.17)	1698	1612 1507	1.16 (t, J = 7.2, 2 CH_3), 2.61 (t, J = 6.6, CH_2-5), 3.38 (q, J = 7.2, 2 CH_2N), 3.54 (t, J = 6.6, CH_2-6), 7.3-7.9 (m, 4 H ar)
IVc	236 (4.05) 255 sh (3.84)	1703	1612 1498	1.27 (d, J = 6, 4 CH_3), 2.70 (t, J = 6.6, CH_2-5), 3.3-4.1 (m, CH_2-6 + 2 CHN), 7.3-7.9 (m, 4 H ar)
IVd	235 sh (3.98) 255 (4.02) 265 sh (3.98) 323 (4.035)	1700	1613 1512	2.61 (t, J = 6.6, CH_2-5), 2.90 (s, CH_3N), 3.50 (t, J = 6.6, CH_2-6), 4.47 (s, CH_2N), 7.2-7.9 (m, C_6H_5 + 4 H ar)
IVe	232 sh (4.02) 255 (4.06) 265 sh (4.01) 324 (4.08)	1695	1610 1508	2.31 (t, J = 6, CH_2-5), 2.90 (t, J = 6, CH_2-6), 3.04 (s, CH_3N), 3.1-3.9 (m, CH_2N + CH_2Ph), 7.1-7.9 (m, C_6H_5 + 4 H ar)
IVf	234 (4.02) 255 (4.06) 266 sh (3.99) 325 (4.07)	1700	1613 1512	2.22 [s, $(CH_3)_2N$], 2.3-2.9 (m, CH_2-5 + CH_2N), 3.07 (s, CH_3N), 3.25-3.75 (m, CH_2-6 + CH_2N), 7.3-7.9 (m, 4 H ar)
IVg	231 sh (3.97) 257 sh (4.07) 265.5 (4.11) 318 (4.00)	1692	1613 1502	1.99 (mc, 2 CH_2 pyr), 2.60 (t, J = 6.6, CH_2-5), 3.2-3.9 (m, CH_2-6 + 2 CH_2N), 7.3-7.9 (m, 4 H ar)
IVh	233 (3.95) 254.5 (4.01) 264 sh (3.99) 323 (4.06)	1697	1613 1508	1.70 (mc, 3 CH_3 pip), 2.61 (t, J = 6, CH_2-5), 3.38 (mc, CH_2-6 + 2 CH_2N), 7.2-8.0 (m, 4 H ar)
IVi	235 sh (3.99) 253 (4.05) 264 sh (3.97) 323 (4.08)	1705	1612 1508	2.63 (t, J = 6.6, CH_2-5), 3.1-3.7 (m, CH_2-6 + 2 CH_2N), 3.84 (t, J = 4.2, 2 CH_2O), 7.2-7.9 (m, 4 H ar)
IV l	236 sh (4.00) 254 (4.07) 264 sh (4.00) 321 (4.06)	1704	1614 1508	2.37 (s, CH_3N), 2.62 (mc, CH_2-5 + 2 CH_2N), 3.52 (mc, CH_2-6 + 2 CH_2N), 7.3-7.9 (m, 4 H ar)
IVm	241 (4.25) 273 sh (3.825) 340 (4.07)	1717	1618 1513	2.34 (t, J = 6.6, CH_2-5), 2.87 (t, J = 6.6, CH_2-6), 3.38 (s, CH_3N), 6.7-7.9 (m, C_6H_5 + 4 H ar)
IVn	239 (4.18) 276.5 (4.22) 343 (4.08)	1705	1613 1508	2.40 (t, J = 4.2, CH_2-5 + CH_2-6), 6.9-8.0 (m, 2 C_6H_5 + 4 H ar)

3,4-Dihydro-4-hydroxymethylene-[1]benzothiepin-5(2*H*)-one (I).

This compound was prepared from 3,4-dihydro-[1]benzothiepin-5(2*H*)-one [8] (35.65 g, 0.2 mole), ethyl formate (22.22 g, 0.3 mole) and sodium methoxide (16.21 g, 0.3 mole) in toluene solution, following a previously described procedure [9], yield, 34.65 g (84%), mp 57° from petroleum ether bp 40-70°-diethyl ether 2:1 (lit [5] mp 55-56°); uv: λ max nm (log ε) 240 (4.15), 269 sh (3.68), 327 (3.75); ir (chloroform): ν max 1632, 1590, 1572, 1553 cm^{-1}; nmr (deuteriochloroform): δ 2.37 (t, J = 6.5, CH_2-3), 3.19 (t, J = 6.5, CH_2-2), 7.53 (mc, 4 H ar), 8.10 and 8.17 (2 br s, =CH-O), 14.93 and 15.01 (2 br s, OH; disappear with deuterium oxide).

Anal. Calcd. for $C_{11}H_{10}O_2S$: C, 64.05; H, 4.89. Found: C, 64.30; H, 4.83.

General Procedure for *N,N*-Disubstituted 4-Amino-3,3-dichloro-3,4,5,6-tetrahydro-2*H*-[1]benzothiepino[5,4-*b*]pyran-2-ones III (Table III).

Dichloroacetyl chloride (2.21 g, 15 mmoles) dissolved in anhydrous toluene (50 ml) was slowly added under nitrogen to a well stirred, ice-cooled solution of enaminone II (10 mmoles) and triethylamine (1.52 g, 15 mmoles) in the same solvent (150 ml). The mixture was stirred at room temperature for 30 minutes, filtered and the solution was evaporated under reduced pressure. The residue was treated with a little anhydrous diethyl ether to give a solid which was purified by recrystallization from a suitable solvent.

General Procedure for *N,N*-Disubstituted 4-Amino-3-chloro-5,6-dihydro-2*H*-[1]benzothiepino[5,4-*b*]pyran-2-ones IV (Table V).

1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) (2.48 g, 20 mmoles) dissolved in anhydrous toluene (20 ml) was added under nitrogen to a stirred solution of adduct III (10 mmoles) in the same solvent (80 ml). The mixture was stirred at 100° for 15 minutes, cooled and poured into a mixture of ice (80 g) and 1 *N* hydrochloric acid (40 ml). The toluene phase was separated and the acid solution was extracted three times with toluene (50 ml each time). The collected toluene solutions were washed with water, dried (magnesium sulfate) and evaporated under reduced pressure to yield a residue which was purified by treatment with a little anhydrous diethyl ether, followed by recrystallization of the solid so obtained from a suitable solvent.

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