Chemistry of Heterocyclic Compounds, Vol. 39, No. 6, 2003

NEW PATHWAY TO THE SYNTHESIS OF SUBSTITUTED 4H-3,1-BENZOXAZINES

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The intramolecular rearrangement of N-acyl-2-cyclopropylanilines by the action of protic acids gives substituted 4H-3,1-benzoxazines. The reaction proceeds in high yield through the formation of benzoxazine precursors, namely, the corresponding 3,1-benzoxazinium ions, which are stable in acid solution. N-Acylamino-2-alkenylbenzenes, in which the double bond of the alkyl chain is conjugated with the benzene ring, are capable of undergoing a similar rearrangement.

Keywords: N-acylamino-2-alkenylbenzenes, N-acyl-2-cyclopropylanilines, 4H-3,1-benzoxazines, 4H-3,1-benzoxazinium ions, rearrangement.

The chemical and biological properties of 4H-3,1-benzoxazines have hardly been studied, largely due to the lack of general and efficient methods for their synthesis. Individual 4H-3,1-benzoxazines have been synthesized by intramolecular cyclization of the corresponding *o*-acylaminobenzyl alcohols or *o*-aminobenzyl chlorides [1]. However, limitations related to difficulty in obtaining these chlorides have prevented the use of these reactions for the synthesis of 4H-3,1-benzoxazines. Examination of the possible schemes for these chlorides from *o*-acylaminobenzyl alcohols would lead us to expect formation of the desired heterocyclic products if the starting aromatic substrate has a fragment, in which a benzylic carbenium site can be generated, while an NH–C(R)=O group exists adjacent to this fragment, in which the oxygen atom is capable of manifesting nucleophilic properties.

We have found that N-acyl-2-cyclopropylanilines **3-17** (Table 1) indeed are capable of converting to the corresponding 4H-3,1-benzoxazines **18-32** in high yield under the conditions of the acid-catalyzed reactions of phenylcyclopropanes [2-4] (Table 2). This reaction is initiated by the proton-catalyzed opening of the cyclopropane ring and generation of benzylic carbenium ion **A**. Subsequent intramolecular stabilization of ions **A** by the nucleophilic oxygen atom of the amide fragment leads to heterocyclic ions **B**, which are precursors of neutral rearrangement products **18-32**.

Special experiments showed that benzoxazinium ions **B** formed immediately upon mixing the rearrangements are so stable in concentrated sulfuric acid at 20°C that they do not undergo isomerization for at least 3-4 months. This stability of heterocyclic ions **B** permits us to carry out the reaction at 20°C. The yields of 4H-3,1-benzoxazines in this case are almost as high but the reaction is completed in much less time (Table 3).

In test variants of this rearrangement under milder conditions, we attempted to use trifluoroacetic acid as the initiator for opening the cyclopropane ring since the small ring in phenylcyclopropane is opened by the action of this acid [5].

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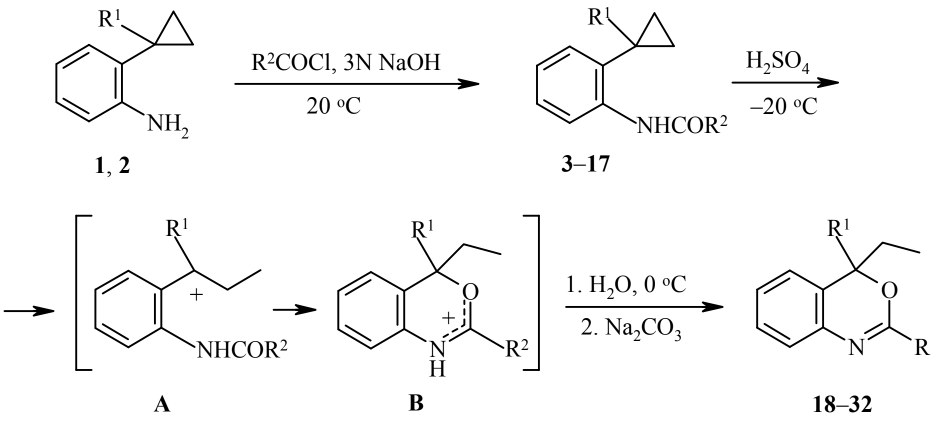
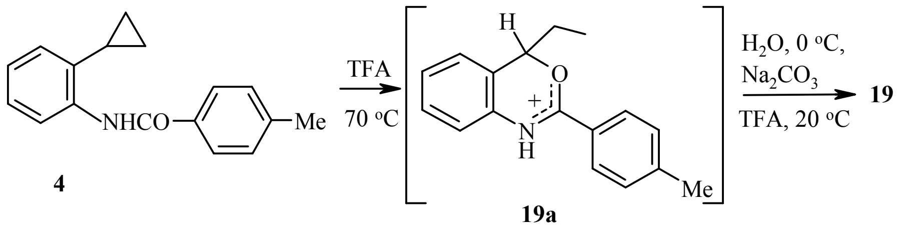
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 922-929, June, 2003. Original article submitted November 17, 2000.



1, 3-11, 18-26 R^1 = H; **2**, **12-17**, **27-32**, R^1 = Me; **3**, **13**, **18**, **28** R^2 = Ph; **4**, **10, 19, 25**
R^2 = *p*-MeC_6H_4; **5**, **14**, **20, 29** R^2 = *o*-ClC_6H_4; **6**, **15**, **21, 30** R^2 = *p*-ClC_6H_4; **7**, **16, 22, 31**
R^2 = *o*-BrC_6H_4; **8**, **17, 23, 32** R^2 = *p*-BrC_6H_4; **9, 24** R^2 = *m*-$MeOC_6H_4$;
11, **26** R^2 = *p*- $O_2NC_6H_4$; **12, 27,** R^2 = Me

In the case of anilide **4**, we found that trifluoroacetic acid cannot initiate the rearrangement at 20°C. However, anilide **4** is converted quantitatively to 4-ethyl-2-(*p*-tolyl)-4H-3,1-benzoxazinium ion (**19a**) upon warming the solution of this amide in trifluoroacetic acid.

We should note that the use of trifluoroacetic acid as the initiator for the rearrangement and the solvent yielded further evidence for the formation of the corresponding ionic precursors of 3,1-benzoxazines **18-32** directly in solutions of this acid.



This evidence is found in the ^{1}H NMR spectra of the reaction mixture obtained upon treating acylaniline **4** upon warming and recooling to room temperature, and of authentic 4-ethyl-2-(*p*-tolyl)-4H-3,1-benzoxazine (**19**) in the same acid (the high viscosity of the solutions of **4** and **19** in concentrated sulfuric acid prevented high-quality ^{1}H NMR spectra). The two spectra proved identical and the multiplicity of the proton signals as well as the integral intensities and chemical shifts correspond to ion **19a** (Table 2).

Thus, trifluoroacetic acid may be used in the synthesis of 4H-3,1-benzoxazines from the corresponding N-acyl-2-cyclopropylanilines. In general, this procedure is preferable to using concentrated sulfuric acid since trifluoroacetic acid has virtually no oxidizing properties.

Then, in order to demonstrate the general nature of the synthesis of substituted 4H-3,1-benzoxazines from anilides containing a substituent in the *ortho* position to the amide fragment, from which a benzylic carbenium site can be generated by the action of acid, we synthesized an anilide with a propenyl group in the *ortho* position (**34**) and studied its conversion upon the action of trifluoroacetic acid. Thus, N-acyl-2-alkenylanilines **34** upon the action of trifluoroacetic acid, similar to the corresponding cyclopropane derivatives, are capable of rearrangement to give 4H-3,1-benzoxazines. This reaction is accomplished under milder conditions than for the rearrangement of the cyclopropylanilides.

TABLE 1. Characteristics of N-Acyl-*o*-cyclopropylanilides **3-17** and *o*-Propenylanilide **34**

Com-pound	Empirical formula	Found, % / Calculated, %			mp, °C	^{1}H NMR spectrum, δ, ppm. (*J*, Hz)*			Yield, %
		C	H	N		Aliphatic protons	Aromatic protons	NH*	
1	2	3	4	5	6	7	8	9	10
3	$C_{16}H_{15}NO$	81.38 80.98	6.61 6.37	5.86 5.90	145-146	0.71 (2H, m); 0.92 (2H, m); 2.08 (1H, m)	7.04 (1H, m); 7.21 (2H, m); 7.46 (1H, m); 7.55 (3H, m); 8.01 (2H, m)	9.83 (1H, br. s)	78
4	$C_{17}H_{17}NO$	81.09 81.24	6.81 6.82	5.46 5.57	123-124	0.52 (2H, m); 0.93 (2H, m); 1.84 (1H, m); 2.41 (3H, s)	7.16 (1H, m); 7.29 (1H, m); 7.33 (2H, d, *J* = 8.2); 7.39 (1H, m); 7.78 (2H, d, *J* = 8.2); 7.88 (1H, s)	8.01 (1H, br. s)	79
5	$C_{16}H_{14}ClNO$	70.21 70.72	5.01 5.19	4.95 5.15	114-115	0.72 (2H, m); 0.97 (2H, m); 1.81 (1H, m)	7.09 (1H, m); 7.21 (1H, m); 7.29 (1H, m); 7.41 (3H, m); 7.82 (1H, m); 8.33 (1H, d, *J* = 8.0)	8.51 (1H, br. s)	72
6	$C_{16}H_{14}ClNO$	70.41 70.72	5.16 5.19	5.01 5.15	122-123	0.63 (2H, m); 0.93 (2H, m); 2.07 (1H, m)	7.01 (1H, m); 7.19 (2H, m); 7.43 (1H, m); 7.49 (2H, d, *J* = 8.8); 8.02 (2H, d, *J* = 8.8)	9.81 (1H, s)	81
7	$C_{16}H_{14}BrNO$	60.69 60.77	4.38 4.46	4.29 4.42	146-147	0.66 (2H, m); 0.96 (2H, m); 2.12 (1H, m)	6.99 (1H, m); 7.18 (2H, m); 7.39 (1H, m); 7.48 (1H, m); 7.56 (2H, m); 7.69 (1H, m)	9.79 (1H, s)	74
8	$C_{16}H_{14}BrNO$	60.61 60.77	4.52 4.46	4.31 4.42	147-148	0.72 (2H, m); 1.02 (2H, m); 1.87 (1H, m)	7.09 (1H, m); 7.25 (2H, m); 7.68 (2H, d, *J* = 8.6); 7.79 (2H, d, *J* = 8.6); 8.41 (1H, d, *J* = 8.8)	8.55 (1H, s)	78
9	$C_{17}H_{17}NO_2$	76.62 76.38	6.39 6.41	5.09 5.24	77-78	0.63 (2H, m); 0.96 (2H, m); 2.09 (1H, m); 3.88 (3H, s)	6.99-7.22 (4H, m); 7.39 (1H, t); 7.49 (1H, m); 7.57 (2H, m)	9.71 (1H, s)	82
10	$C_{17}H_{17}NO_2$	76.46 76.38	6.27 6.41	5.17 5.24	106-107	0.64 (2H, m); 0.93 (2H, m); 2.08 (1H, m); 3.87 (3H, s)	7.01 (3H, 2d); 7.15 (2H, m); 7.51 (1H, d, *J* = 8.4); 7.98 (2H, d, *J* = 8.2)	9.51 (1H, s)	84

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10
11	$C_{16}H_{14}N_2O_3$	68.22 68.07	4.77 4.99	9.21 9.92	153-154	0.68 (2H, m); 0.95 (2H, m); 2.09 (1H, m)	7.01 (1H, m); 7.19 (2H, m); 7.41 (1H, m); 8.25 (2H, d, *J* = 9.0); 8.37 (2H, d, *J* = 9.0)	10.11 (1H, s)	64
12	$C_{12}H_{15}NO$	75.92 76.16	7.77 7.99	7.23 7.40	112-113	0.81 (4H, s); 1.27 (3H, s); 2.19 (3H, s)	7.05 (1H, t); 7.16 (1H, t); 7.27 (1H, d, *J* = 8.0); 7.57 (1H, d, *J* = 8.0)	8.57 (1H, s)	73
13	$C_{17}H_{17}NO$	81.01 81.24	6.69 6.82	5.41 5.57	108-110	0.72 (2H, s); 0.88 (2H, s); 1.35 (3H, s)	7.12-7.77 (9H, m)	9.45 (1H, s)	76
14	$C_{17}H_{16}ClNO$	71.54 71.45	5.83 5.64	—	38-40	0.72 (2H, s); 0.85 (2H, s); 1.32 (3H, s)	7.16 (1H, t); 7.25 (1H, t); 7.37 (1H, d, *J* = 7.8); 7.51 (3H, m); 7.70 (2H, m)	9.27 (1H, s)	81
15	$C_{17}H_{16}ClNO$	71.12 71.45	5.74 5.64	4.71 4.90	96-97	0.91 (4H, m); 1.36 (3H, s)	7.09 (1H, m); 7.32 (2H, m); 7.51 (2H, d, *J* = 8.2); 7.87 (2H, d, *J* = 8.2); 8.43 (1H, d, *J* = 8.0)	8.71 (1H, s)	76
16	$C_{17}H_{16}BrNO$	62.01 61.83	4.83 4.88	4.42 4.24	59-60	0.72 (2H, m); 0.83 (2H, m); 1.32 (3H, s)	7.27 (2H, m); 7.37-7.65 (5H, m); 7.78 (1H, d, *J* = 8.2)	9.43 (1H, br. s)	78
17	$C_{17}H_{16}BrNO$	62.25 61.83	4.82 4.88	4.47 4.24	104-106	0.71 (2H, s); 0.86 (2H, s); 1.29 (3H, s)	7.23 (1H, m); 7.39 (1H, m); 7.57 (1H, m); 7.77 (2H, d, *J* = 9.0); 7.93 (2H, d, *J* = 9.0)	9.45 (1H, br. s)	77
34	$C_{17}H_{17}NO$	81.03 81.24	6.68 6.82	5.31 5.57	137-138	1.29 (3H, d, *J* = 6.4); 2.41 (3H, s); 6.16 (1H, m, $=C\underline{H}-CH_3$); 6.51 (1H, m, $C\underline{H}=CH-CH_3$)	7.16 (1H, m); 7.29 (1H, m); 7.31 (2H, d, *J* = 8.2); 7.36 (1H, m); 7.57 (1H, m); 7.93 (2H, d, *J* = 8.2)	9.71 (1H, s)	72

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* Spectra for compounds **3**, **6**, **7**, **9-14**, **16**, **17**, **34** taken in DMCO-d_6, for compounds **4**, **5**, **8**, **15** – in $CDCl_3$.

TABLE 2. Characteristics of 2-R-4H-3,1-Benzoxazines **18-32***

Compound	Empirical formula	Found, % / Calculated, %			^{1}H NMR spectrum, ppm (*J*, Hz)*^{2}	Yield, %
		C	H	N		
1	2	3	4	5	6	7
18	$C_{16}H_{15}NO$	$\frac{81.13}{80.98}$	$\frac{6.52}{6.37}$	$\frac{6.28}{5.90}$	1.01 (3H, t, $C\underline{H}_3$–CH_2–); 1.93 (2H, m, CH_3–$C\underline{H}_2$–); 5.28 (1H, t, H-4 benzoxazine); 6.81-7.57 (7H, m); 7.92-8.16 (2H, m, ArH)	91
19	$C_{17}H_{17}NO$	$\frac{79.85}{81.24}$	$\frac{6.61}{6.82}$	$\frac{5.41}{5.57}$	1.05 (3H, t, $C\underline{H}_3$–CH_2–); 1.92 (2H, m, CH_3–$C\underline{H}_2$–); 2.41 (3H, s, CH_3–Ar); 5.45 (1H, t, H-4 benzoxazine); 7.17 (3H, m); 7.28 (3H, m); 7.94 (2H, d, *J* = 8.0, ArH)	85
19a	$C_{17}H_{17}NO + H^+$	—	—	—	1.25 (3H, t, $C\underline{H}_3$–CH_2–); 2.31 (2H, m, CH_3–$C\underline{H}_2$–); 2.56 (3H, s, CH_3); 6.12 (t, 4-H benzoxazine); 7.36 (1H, m); 7.50 (1H, m); 7.56 (4H, m); 8.11 (2H, d, J_o = 8.2, ArH)	—
20	$C_{16}H_{14}ClNO$	$\frac{70.41}{70.72}$	$\frac{5.10}{5.19}$	$\frac{4.90}{5.15}$	1.08 (3H, t, $C\underline{H}_3$–CH_2–); 2.04 (2H, m, CH_3–$C\underline{H}_2$–); 5.46 (1H, t, H-4 benzoxazine); 7.04 (1H, d, *J* = 8.0); 7.23 (1H, m); 7.28-7.39 (4H, m); 7.45 (1H, dd, *J* = 8.0 and 1.6); 7.74 (1H, dd, *J* = 8.0, *J* = 2.0, ArH)	88
21	$C_{16}H_{14}ClNO$	$\frac{70.58}{70.72}$	$\frac{4.91}{5.19}$	$\frac{5.01}{5.15}$	1.07 (3H, t, $C\underline{H}_3$–CH_2–); 1.91 (2H, m, CH_3–$C\underline{H}_2$–); 5.34 (1H, m, H-4 benzoxazine); 6.99 (1H, d, *J* = 8.0); 7.25 (3H, m); 7.41 (2H, d, *J* = 8.2); 8.11 (2H, d, *J* = 8.2, ArH)	81
22	$C_{16}H_{14}BrNO$	$\frac{60.21}{60.77}$	$\frac{4.23}{4.46}$	$\frac{4.18}{4.42}$	1.06 (3H, t, $C\underline{H}_3$–CH_2–); 2.06 (2H, m, CH_3–$C\underline{H}_2$–); 5.48 (1H, t, H-4 benzoxazine); 7.05 (1H, d, *J* = 7.8); 7.24 (1H, dt, J_o = 7.8, J_m = 2.2); 7.28-7.35 (3H, m); 7.38 (1H, dt, J_o = 7.8, J_m = 1.4); 7.69 (1H, dd, J_o = 7.8, J_m = 1.4); 7.69 (1H, dd, J_o = 7.8, J_m = 2.2, ArH)	86
23	$C_{16}H_{14}BrNO$	$\frac{60.39}{60.77}$	$\frac{4.31}{4.46}$	$\frac{4.21}{4.42}$	1.05 (3H, t, $C\underline{H}_3$–CH_2–); 1.91 (2H, m, CH_3–$C\underline{H}_2$–); 3.85 (3H, s, OCH_3); 5.47 (1H, t, H-4 benzoxazine); 7.07-7.43 (6H, m); 7.61 (1H, s); 7.69 (1H, d, *J* = 8.4, ArH)	87
24	$C_{17}H_{17}NO_2$	$\frac{76.01}{76.38}$	$\frac{6.11}{6.41}$	$\frac{4.99}{5.24}$	1.05 (3H, t, $C\underline{H}_3$–CH_2–); 1.90 (2H, m, CH_3–$C\underline{H}_2$–); 3.87 (3H, s, OCH_3); 5.44 (1H, t, H-4 benzoxazine); 7.01 (2H, d, *J* = 8.8); 7.15 (3H, m); 7.29 (1H, t); 8.05 (2H, d, *J* = 8.8, ArH)	90
25	$C_{17}H_{17}NO_2$	$\frac{76.12}{76.38}$	$\frac{6.09}{6.41}$	$\frac{5.01}{5.24}$	1.05 (3H, t, $C\underline{H}_3$–CH_2–); 1.95 (2H, m, CH_3–$C\underline{H}_2$–); 5.58 (1H, t, H-4 benzoxazine); 7.15-7.38 (4H, m); 8.38 (4H, s, ArH)	88

TABLE 2 (continued)

1	2	3	4	5	6	7
26	$C_{16}H_{14}N_2O_3$	$\underline{67.74}$ 68.07	$\underline{4.77}$ 4.99	$\underline{9.61}$ 9.92	1.05 (3H, t, $C\underline{H}_3$–CH_2–); 1.95 (2H, m, CH_3–$C\underline{H}_2$–); 5.58 (1H, t, H-4 benzoxazine); 7.15-7.38 (4H, m); 8.38 (4H, s, ArH)	71
27	$C_{12}H_{15}NO$	$\underline{75.88}$ 76.16	$\underline{7.76}$ 7.99	$\underline{7.14}$ 7.40	0.84 (t, $C\underline{H}_3$–CH_2–); 1.61 (3H, s, CH_3); 1.81-1.94 (2H, m, CH_3–$C\underline{H}_2$–); 2.11 (3H, s, CH_3); 6.98-7.26 (4H, m, ArH)	74
28	$C_{17}H_{17}NO$	$\underline{80.95}$ 81.24	$\underline{6.66}$ 6.82	$\underline{5.31}$ 5.57	0.97 (t, $C\underline{H}_3$–CH_2–); 1.74 (3H, s, CH_3); 2.07 (2H, m, CH_3–$C\underline{H}_2$–); 7.12 (1H, m); 7.29 (2H, m); 7.42 (3H, m); 8.12 (2H, m, ArH)	97
29	$C_{17}H_{16}NOCl$	$\underline{71.01}$ 71.45	$\underline{5.22}$ 5.64	$\underline{4.82}$ 4.90	0.99 (t, $C\underline{H}_3$–CH_2–); 1.75 (3H, s, CH_3); 2.14 (2H, m, CH_3–$C\underline{H}_2$–); 7.09 (1H, d, *J* = 8.0); 7.21-7.48 (6H, m); 7.84 (1H, d, *J* = 8.0, ArH)	84
30	$C_{17}H_{16}NOCl$	$\underline{70.95}$ 71.45	$\underline{5.31}$ 5.64	$\underline{4.68}$ 4.90	0.94 (t, $C\underline{H}_3$–CH_2–); 1.71 (3H, s, CH_3); 2.01 (2H, m, CH_3–$C\underline{H}_2$–); 7.08 (1H, d, *J* = 8.0); 7.19 (1H, m); 7.24 (2H, m); 7.41 (2H, d, *J* = 8.2, ArH)	84
31	$C_{17}H_{16}NOBr$	$\underline{61.66}$ 61.83	$\underline{4.71}$ 4.88	$\underline{4.01}$ 4.24	0.99 (t, $C\underline{H}_3$–CH_2–); 1.76 (3H, s, CH_3); 2.08 (2H, m, CH_3–$C\underline{H}_2$–); 7.07 (1H, m); 7.19-7.41 (5H, m); 7.67 (2H, m, ArH)	92
32	$C_{17}H_{16}NOBr$	$\underline{61.53}$ 61.83	$\underline{4.76}$ 4.88	$\underline{3.96}$ 4.24	0.88 (t, $C\underline{H}_3$–CH_2–); 1.67 (3H, s, CH_3); 1.98 (2H, m, CH_3–$C\underline{H}_2$–); 7.14-7.32 (4H, m); 7.68 (2H, d, *J* = 8.2); 8.01 (2H, d, *J* = 8.2, ArH)	89

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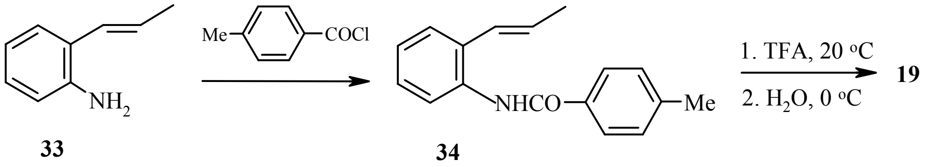
* Mp, °C: **21** 47-48; **23** 44-45; **25** 46-47; **26** 77-78, other compounds are viscous oils.

*[2] Spectra for compounds **18-20**, **22-32** obtained in $CDCl_3$, for compound **21** – in DMSO-d_6, for compound **19a** – in CF_3COOH, internal standard TMS.

TABLE 3. Effect of the Isomerization Temperature (IT) on the Rearrangement of N-(4-Methylbenzoyl)-2-cyclopropylaniline **4** by the Action of Concentrated Sulfuric Acid

IT, °C	Reaction time, h	Product yields, %
-35	3.5	88
-20	2.0	93
0	1.0	93
+20	0.5	94



Since substituted alkenylanilines **33** are readily easily formed from the corresponding cyclopropylanilines, 4H-3,1-benzoxazines, which cannot be synthesized from cyclopropylanilides by the action of concentrated sulfuric acid, likely can be prepared through the scheme shown above.

EXPERIMENTAL

The ^1H NMR spectra were taken on a Varian VXR-400 spectrometer at 400 MHz in $CDCl_3$ with TMS as the internal standard and a Bruker AM-300 spectrometer at 300 MHz in DMSO-d_6. The purity of the products was carried out by thin-layer chromatography on grade II alumina plates using 1:1:3 ether–chloroform–hexane as the eluent. The indices of the products synthesized for the first time are given in Tables 1 and 2.

2-Cyclopropylanilines 1 and 2 were obtained by the reduction of the corresponding 2-nitrophenylcyclopropanes as described in our previous work [6, 7]. N-(4-Nitrobenzylidene)-2-cyclopropylaniline was obtained by the condensation of 2-cyclopropylaniline **1** with *p*-nitrobenzaldehyde according to our previous procedure.

2-Propenylaniline (33). A sample of N-(4-nitrobenzylidene)-2-cyclopropylaniline (2.66 g, 10 mmol) was added in small portions to concentrated sulfuric acid (30 ml), maintaining the temperature at -20°C, and stirred at this temperature for 1 h. The reaction mixture was poured onto ground ice (100 g) and extracted with ether to remove *p*-nitrobenzaldehyde. The aqueous layer was made slightly basic by adding aqueous NaOH and extracted with ether. The ethereal extract was dried over $MgSO_4$. Evaporation of the solvent and distillation of the residue in vacuum gave 0.85 g (64%) **33**; bp 85-87°C (2 mm Hg) (bp 63-65°C (0.6 mm Hg) [8]).

N-Acyl-2-cyclopropylanilines (3-17) and N-(4-Methylbenzoyl)-2-propenylaniline (34) (General Method). A sample of acid chloride derivative of the corresponding acid (1.5 mmol) in dioxane (3 ml) and 3 N NaOH (5.6 g) was added with stirring at the same time gradually to a solution of **1** (or **2**) or **33** (1.5 mmol) in dioxane (40 ml). The reaction mixture was stirred for 1 h at 20°C and poured into water (150 ml). The crystalline precipitate formed was filtered off, washed with water, and recrystallized from ethanol.

Isomerization of N-Acyl-2-cyclopropylanilines 3-17 by the Action of Concentrated Sulfuric Acid. A sample of the corresponding N-acylaminophenylcyclopropane (1.5 mmol) was added in portions with stirring to concentrated sulfuric acid (2.5 ml) cooled to -10°C. The temperature was brought to 20°C. The reaction mixture was stirred for 30 min, poured into ice water (50 ml), and neutralized by adding Na_2CO_3. The organic products were extracted using two 15-ml chloroform portions and the extract was dried over $MgSO_4$. After evaporation of the solvent, the residue was subjected to chromatography on grade-II alumina using 1:3 ether–hexane as the eluent. The yields of 4H-3,1-benzoxazines **18-32** and their physicochemical indices are given in Table 2.

Isomerization of N-(4-Methylbenzoyl)-2-propenylaniline (34) by the Action of Trifluoroacetic Acid. A sample of **34** (0.38 g, 1.5 mmol) was added in portions to trifluoroacetic acid (3 ml). After 15 min, the temperature of the reaction mixture had risen to 30°C. The mixture was cooled to 20°C and poured into ice water (50 ml). Then, the mixture was treated and the desired product was isolated as described above. The yield of 4-ethyl-2-(*p*-tolyl)-4H-3,1-benzoxazine (**19**) 0.33 g (88%).

Benzoxazines 21, 25, and **30** were obtained from **6, 10,** and **15** in 85, 91, and 93% yield, respectively, according to an analogous procedure.

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