Acylation of 5-Amino-3*H*-1,3,4-Thiadiazolin-2-one

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Acylation of 5-amino-3*H*-1,3,4-thiadiazolin-2-one (**2**) was undertaken selectively at either the 3-NH position or at 5-amino group depending on reaction conditions. The 3-NH is highly acidic and acylation takes place with acid anhydrides at this position in high yields in the presence of pyridine or triethylamine. The diacylation of both the 3-position and the 5-amino group was only possible *via* the 5-amino-3-acyl-1,3,4-thiadiazolin-2-one intermediates **4**. Under neutral conditions, acylation only occurs at the 5-amino group with acyl chlorides forming 5-acylamino-3*H*-1,3,4-thiadiazolin-2-ones **5**. 5-Acetylamino-3*H*-1,3,4-thiadiazolin-2-one can also be synthesized by the thermal transformation of 5-amino-3-acetyl-1,3,4-thiadiazolin-2-one in acetic acid.

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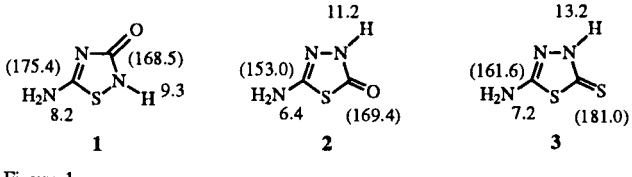
Introduction

Within the framework of our systematic efforts to obtain new analogs of pyrimidine bases and their derivatives as potential insecticidal, herbicidal, fungicidal and pharmaceutical agents, we have reported the synthesis and tautomeric study of 5-amino-2*H*-1,2,4-thiadiazolin-3-one (**1**) [1-5], 5-amino-3*H*-1,3,4-thiadiazolin-2-one (**2**) [1,6], 5-amino-3*H*-1,3,4-thiadiazoline-2-thione (**3**) [7] and their derivatives [1-7]. Compound **1** is an analog of cytosine on the basis of the well-known correspondence between a -CH=CH- group in benzenoid hydrocarbons and the divalent sulfur in their heterocyclic analogs. Compound **2** is an isomer of compound **1**. The ^1H and ^{13}C nmr chemical shifts of compounds **1**, **2** and **3** are shown in Figure 1 with the ^{13}C nmr chemical shifts in parentheses.



1 **2** **3**

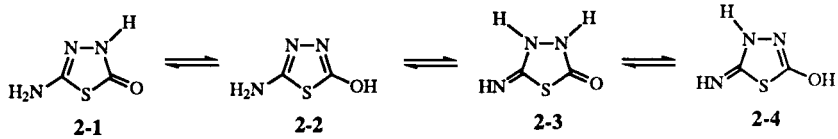
Figure 1.

The structure of **2** can be represented as the following tautomers shown in Figure 2. It was established by ^{13}C nmr [8] and ^{15}N nmr [9] spectroscopy that **2** exists in the lactam form, **2-1** as does **1** [5]. Most studies of **2** [1,6,8-13] deal with synthesis, while very little is known about its reactivity [9]. Thus, we have chosen to examine the relationship between the structure and reactivity of **2** based on acylation reactions.

Results and Discussion.

When attempting to acetylate the amino group of compound **2** by a conventional method 3-acetyl-5-amino-1,3,4-thiadiazolin-2-one (**4a**) was obtained in high yield, as shown in Table 1, instead of the expected 5-acetylamino-3*H*-1,3,4-thiadiazolin-2-one (**5a**). Under the same conditions a mixture of **4** and 5-acylamino-3*H*-1,3,4-thiadiazolin-2-ones **5** were obtained with an acyl chloride as the acylating agent. However, with an aroyl chloride, aroylation gave a mixture of **4** and 3-aroyl-5-aroylamino-1,3,4-thiadiazolin-2-ones **6**. It was necessary to use acid anhydrides under basic conditions, such as the use of pyridine or triethylamine, to synthesize the 3-acyl-5-amino-1,3,4-thiadiazolin-2-ones **4**. The 3-NH group is more acidic than the 5-amino group. The 3-NH group of **2** is deprotonated by either pyridine or triethylamine and the acylation reaction is regioselective at the 3-position under these basic conditions. The formation of **4** is quite similar to the alkylation of 3-NH group in sodium hydroxide or sodium hydride [1].

In contrast, under neutral conditions, acylation is regioselective at the 5-NH_2 group forming 5-acylamino-3*H*-1,3,4-thiadiazolin-2-ones **5** with acyl chlorides. The melting point and other physical properties of 5-acetylamino-3*H*-1,3,4-thiadiazolin-2-one (**5a**) were in agreement with those of an authentic sample prepared by acetylation and deethylation of 2-amino-5-ethoxy-1,3,4-thiadiazole [6] as shown in Scheme 1. The ^1H nmr, ^{13}C nmr, and ir spectra were in support of structure **5a**. In the ir spectrum, the amide and lactam carbonyl groups are diagnostic as strong bands at 1770 and 1650 cm^{-1}, respec-



2-1 **2-2** **2-3** **2-4**

Figure 2.

Table 1

Acylated Products of 5-Amino-3*H*-1,3,4-thiadiazolin-2-one

Compound No.	Reaction Temperature (°C)	Reaction Time (hours)	Mp (°C)	Yield (%)	Moelcular Formula (Mol wt)	Analysis (%) Calcd. (Found) C	H	N	S
4a	rt	2	224	74	$C_4H_5N_3O_2S$	30.19	3.17	26.40	20.14
					(159.16)	30.20	3.27	25.65	20.25
4b	rt	2	137-140	81	$C_6H_9N_3O_2S$	38.49	4.85	22.44	17.12
					(187.22)	38.42	4.82	22.43	17.32
4c	rt	2.5	130-131	99	$C_6H_9N_3O_2S$	38.49	4.85	22.44	17.12
					(187.22)	38.19	4.96	21.96	16.57 [e]
4d	rt	5	146-149	88	$C_7H_{11}N_3O_2S$	41.77	5.51	20.89	15.93
					(201.25)	41.99	5.90	21.16	15.90
4e	-2-2	1	157-158	40 [a]	$C_9H_7N_3O_2S$	48.86	3.19	18.99	14.49
					(221.23)	48.48	3.28	19.06	14.26
5a [6]	rt	6	318-319	69	$C_4H_5N_3O_2S$ (159.16)				
5e [6]	rt	6	269-270	31	$C_9H_7N_3O_2S$ (221.23)				
6a	100	2	199-200	95 [b]	$C_6H_7N_3O_3S$	35.82	3.51	20.88	15.93
					(201.20)	36.31	3.44	20.74	15.84
6c	98-100	16	116	43 [c]	$C_{10}H_{15}N_3O_3S$	46.68	5.88	16.33	12.46
	98-100	4		73 [d]	(257.31)	46.79	6.14	16.83	12.72
6e	rt	2	176-178	89	$C_{16}H_{11}N_3O_3S$	59.07	3.41	12.92	9.85
					(325.34)	58.84	3.82	12.92	9.78
6f	rt	2	221	92	$C_{18}H_{15}N_3O_3S$	61.18	4.28	11.89	9.07
					(353.40)	61.82 [e]	4.19	11.99	8.71
6g	rt	2	256-257	93	$C_{16}H_9N_3O_3SCl_2$	48.75	2.30	10.66	8.13
					(394.23)	49.62	2.22	10.64	8.07

[a] Not optimized yield. [b] Acetylation of **4a** with acetic anhydride in acetic acid. [c] Diisobutyrylation of **2** with isobutyric anhydride. [d] Isobutyrylation of **4c** with isobutanoyl chloride. [e] After repeated analyses, more satisfactory values could not be obtained.

Table 2

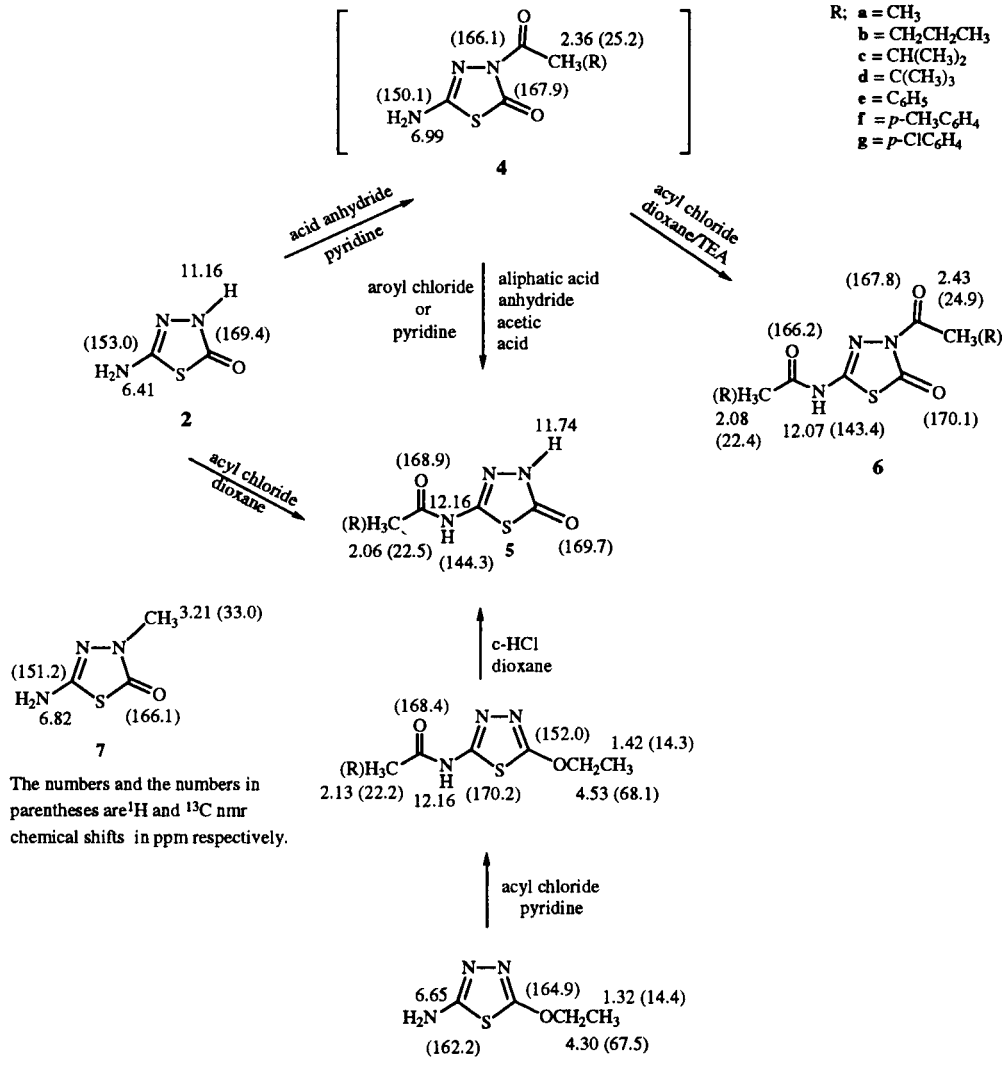
Spectral data of acylated products of 5-amino-3H-1,3,4-thiadiazolin-2-one

Compound No.	R	IR Spectrum (cm^{-1}, potassium bromide) ^1H NMR (ppm, dimethyl-d_6 sulfoxide) ^{13}C NMR (ppm, dimethyl-d_6 sulfoxide)
4a	CH_3	3400, 3250 (NH), 3200 (CH), 1700, 1630 (C=O), 1580 (C=N) 6.99 (2H, b, NH_2), 2.36 (3H, s, Me) 167.9 (C=O), 166.1 (amide), 150.1 (C=N), 25.2 (Me)
4b	CH_2CH_2Me	3400, 3250 (NH), 3200, 3170 2970 (CH), 2940, 2880, 1700, 1630 (C=O), 1580 (C=N) 7.09 (2H, b, NH_2), 2.73 (2H, t, CH_2), 1.53 (2H, q, CH_2), 0.99 (3H, t, Me) 169.0 (C=O), 167.7 (amide), 150.0 (C=N) 38.5 (CH_2), 17.1 (CH_2), 13.5 (Me)
4c	$CH(CH_3)_2$	3550, 3200 (NH), 3000, 2950, 2900 (CH), 1760, 1710 (C=O), 1630 (C=N) 7.46 (2H, b, NH_2), 3.28 (1H, septet, CH), 1.22 (6H, d, CH_3) 173.2 (C=O), 167.6 (amide), 150.1 (C=N), 34.1 (CH), 18.5 (Me)
4d	$C(CH_3)_3$	3460 (NH), 3400, 3300 (NH), 3000, 2850 (CH), 1720, 1660 (C=O), 1600 (C=N) 7.04 (2H, b, 2NH), 1.30 (9H, s, 3Me) 174.4 (C=O), 167.8 (amide), 148.6 (C=N), 42.1 (CMe_3), 26.4 (Me)
4e	C_6H_5	3400, 3250, 3220 (NH), 2980, 1720, 1690 (C=O), 1610 (C=N) 7.83-7.53 (5H, m, C_6H_5), 7.24 (2H, b, NH_2) 168.2 (C=O), 165.2 (amide), 150.2 (C=N), 1338, 132.3, 129.3, 128.0 (ph)
5a [6]	CH_3	3200, 3180 (NH), 3070, 2850 (CH), 1770, 1650 (C=O), 1590 (C=N) 12.16 (1H, b, NH), 11.74 (1H, b, NH), 2.06 (3H, s, Me) 169.7 (C=O), 168.9 (amide), 144.3 (C=N), 22.5 (Me)
5e [6]	C_6H	3180 (NH), 3050 (CH), 1660, 1640 (C=O), 1580 (C=N) 12.34 (1H, b, NH), 12.15 (1H, b, NH), 8.02-7.48 (5H, m, ph) 169.8 (C=O), 165.4 (amide), 144.6 (C=N) 132.7, 131.6, 128.5, 128.1
6a	CH_3	3210, 3150 (NH), 3050 (CH), 1730, 1700, 1660 (C=O), 1590 (C=N) 12.07 (1H, b, NH), 2.43 (3H, s, Me), 2.08 (3H, s, Me) 170.1 (C=O), 167.8 (amide), 166.2 (amide), 143.4 (C=N), 24.9 (Me), 22.4 (Me)

Table 2 (continued)
Spectral data of acylated products of 5-amino-3H-1,3,4-thiadiazolin-2-one

Compound No.	R	IR Spectrum (cm^{-1}, potassium bromide) ^1H NMR (ppm, dimethyl-d_6 sulfoxide) ^{13}C NMR (ppm, dimethyl-d_6 sulfoxide)
6c	$CH(CH_3)_2$	3270 (NH), 2980 (CH), 1752, 1700, 1660 (C=O), 1600 (C=N) 12.27 (1H, b, NH), 3.43 (1H, septet, CH), 2.62 (1H, septet, CH), 1.15 (6H, d, Me_2), 1.06 (6H, d, Me_2) 176.8 (C=O), 173.2 (amide), 167.6 (amide), 143.6 (C=N), 33.9 (CH), 33.8 (CH), 18.7 (Me), 18.4 (Me)
6e	C_6H_5	3270 (NH), 3050 (CH), 1730, 1670 (C=O), 1590 (C=N) 12.92 (1H, b, NH), 8.23-7.48 (10H, m, 2ph) 168.0 (C=O), 166.4 (amide), 165.4 (amide), 144.6 (C=N) 133.3, 133.0, 132.7, 131.0, 129.9, 128.6, 128.4, 128.3
6f	*p*-$CH_3C_6H_4$	3295 (NH), 3050, 2920 (CH), 1730, 1660 (C=O), 1590 (C=N) 12.62 (1H, b, NH), 7.96-7.33 (8H, dd, 2ph), 2.40 (3H, s, Me), 2.32 (3H, s, Me) 167.9 (C=O), 166.1 (amide), 165.2 (amide), 144.4 (C=N), 143.7, 143.6, 130.1, 129.7, 129.2, 128.8, 128.4, 128.2, 21.2, 21.1
6g	*p*-ClC_6H_4	3290 (NH), 3070 (CH),1730, 1680, 1660 (C=O) 1590 (C=N) 12.79 (1H, b, NH), 8.04-7.55 (8H, dd, 2ph) 167.9 (C=O), 165.4 (amide), 164.3 (amide), 144.4 (C=N), 138.2, 137.7, 131.6, 131.6, 130.3, 129.8, 128.7, 128.3

Scheme 1
Acylation of 5-amino-3*H*-1,3,4-thiadiazolin-2-one



tively, while the C=N band appeared as a weak absorption at 1590 cm^{-1}. The ^1H nmr spectra indicated the presence of the lactam NH at 12.16 ppm, the amide NH at 11.74 ppm and the acetyl group at 2.06 ppm for **5a**. The ^{13}C nmr provided additional evidence for the structure of **5a**. The lactam, amide and C=N carbon signals appeared at 169.7, 168.9 and 144.3 ppm, respectively. The melting points of analytical data of **5** are recorded in Table 1. Table 2 contains spectroscopic data for compounds **5**. Compound **2** was diacylated forming 3-acyl-5-acylaminothiadiazolin-2-one (**6**) *via* the 3-acyl-5-amino-1,3,4-thiadiazolin-2-one intermediate. The 3-acyl-5-amino-1,3,4-thiadiazolin-2-ones (**4**) and 3-acyl-5-acylaminothiadiazolin-2-ones **6** were synthesized as shown in Scheme 1.

The structure of **4a** was verified as 5-amino-3-acetyl-1,3,4-thiadiazolin-2-one by ^1H and ^{13}C nmr, ir and elemental analyses. The disappearance of the 3-NH (11.16 ppm) signal in the ^1H nmr spectrum of **2** and appearance of the acetyl group signal (2.36 ppm) served as supporting evidence for the acetylation of **2** to give **4a**. Along with ^1H nmr, amide and lactam carbonyl signals clearly appear in the ir spectra at 1700 and 1630 cm^{-1} as diagnostic structural reporters. The C=N stretching band appears at 1580 cm^{-1}. A mass spectrometric study of the McLafferty rearrangement fragmentation also supported the structure of **4** [14]. Compound **4a** was thermally transformed to the more stable 5-acetylamino-3*H*-1,3,4-thiadiazolin-2-one (**5a**) in refluxing acetic acid (see Experimental). The elemental analyses and melting points of compounds **4** are given in Table 1. Table 2 contains the spectroscopic data of compounds **4**.

An efficient route for the diacylation of **2** is a two step process; acylation with an acid anhydride in base yielding compounds **4** followed by acylation of compounds **4** with an acyl halide in triethylamine-dioxane. The solubility of **4a** in pyridine and triethylamine-dioxane is low. The acetylation of **4a** was carried out with acetic anhydride in acetic acid. Using an acyl halide, diacylation is more problematic since compounds **4** and compounds **5** are both formed as intermediates under the necessary basic conditions. Diacylation could then be accomplished using an acid anhydride but harsh reaction conditions are required and the yields are low.

However, diaroylation of **2** differs from diacylation. Aroylation with an aroyl chloride affords a mixture of compounds **4** and compounds **6**, not compounds **5**. Consequently, diaroylation could be smoothly carried out in high yield with an aroyl chloride in pyridine or triethylamine-dioxane in manner similar to that for compound **1** [5]. The carbonyl groups of aroyl chlorides are less electrophilic than those of acyl chlorides. This difference in reactivity was illustrated by the yields of **5e** and **5a**; the former being half of the latter under the same reaction conditions. It appears that the reaction pattern of an aroyl chloride towards compound **2** is the same as an aliphatic acid anhydride although its reactivity is more than that of an aliphatic acid anhydride.

The structures of the new compounds **6** were established on the basis of their elemental analyses, ^1H and ^{13}C nmr and ir spectra. All of the spectral and experimental data support the structures of 3-acyl-5-acylamino-1,3,4-thiadiazolin-2-ones. In the case of 3-acetyl-5-acetylamino-1,3,4-thiadiazolin-2-one (**6a**), the chemical shifts were identified as shown in Scheme 1. The ^1H and ^{13}C nmr chemical shifts of 3-acetyl-5-acetylamino-1,3,4-thiadiazolin-2-one match those of 5-acetylamino-3*H*-1,3,4-thiadiazolin-2-one and 5-amino-3-acetyl-1,3,4-thiadiazolin-2-one at structurally similar positions. Furthermore, the elemental analyses of the new compounds **6** were in a good agreement with their proposed structures (Table 1). Table 2 contains the spectroscopic data for compounds **6**.

In conclusion, acylation of **2** is regioselective at either 3-NH or 5-NH_2 and diacylation is undertaken through intermediate **4**. These acylations present clear experimental evidence that compound **2** exists as lactam **2-1** among four possible tautomers under these reaction conditions.

EXPERIMENTAL

All melting points were determined on an electrically heated Thomas-Hoover capillary melting point apparatus but uncorrected. The ir spectra were measured on a Jasco Report-100 spectrophotometer. The ^1H and ^{13}C nmr spectra were recorded on either a 80 MHz Bruker AC-80 or a 300 MHz Bruker AM-300 using tetramethylsilane as the internal standard. Elemental analyses were carried out on a Elementar Analysensysteme GmbH Vario EL, at the Basic Science Research Institute, Seoul, Korea. The progress of the reaction and the purity of all compounds were checked by thin layer chromatography on precoated glass plates with silica gel 60 F-254 as the absorbent (purchased from Whatman Catalog No. 4861110. The eluent for tlc was used a mixture of *n*-hexane, ethyl acetate and acetic acid (4:8:1, v/v). Most of the commercially available starting materials and solvents were purchased from Aldrich Chemical Company, Milwaukee, WI.

5-Amino-3*H*-1,3,4-thiadiazoline-2-one was prepared by the published procedure [6].

Synthesis of 3-Acetyl-5-amino-1,3,4-thiadiazolin-2-one (**4a**) from 5-Amino-3*H*-1,3,4-thiadiazolin-2-one (**2**).

5-Amino-3*H*-1,3,4-thiadiazolin-2-one (0.5 g, 4.3 mmoles) was dissolved in anhydrous dioxane (10 ml) and triethylamine (0.72 ml, 5.13 mmoles) was added. Acetic anhydride (0.4 ml, 4.3 mmoles) was added dropwise for 15 minutes while stirring and allowed to react for 2 hours. The end of the reaction was monitored by tlc. The R_F values of the starting compound **2** and product **4a** are 0.55 and 0.63 respectively on the silica gel using a mixture of *n*-hexane, ethyl acetate and acetic acid (4:8:1, v/v)

as the eluent. The white precipitate was filtered and washed with water and *n*-hexane to give 3-acetyl-5-amino-1,3,4-thiadiazolin-2-one (0.5 g, 74%). To obtain the analytical sample it was recrystallized from ethanol. The yields, melting points, elemental analysis and spectral data of the products are shown in Tables 1 and 2.

All other 3-acyl-5-amino-1,3,4-thiadiazolin-2-ones **4** were obtained by the same procedure.

Synthesis of 5-Acetylamino-3*H*-1,3,4-thiadiazolin-2-one (**5a**) [6] from 5-Amino-3*H*-1,3,4-thiadiazolin-2-one (**2**).

5-Amino-3*H*-1,3,4-thiadiazolin-2-one (**2**) (0.5 g, 4.3 mmoles) was dissolved in dioxane (20 ml). Acetyl chloride (0.3 ml, 4.3 mmoles) in dioxane (20 ml) was added dropwise to the stirred mixture for 20 minutes. The mixture was allowed to react for 6 hours at room temperature. The resulting precipitate was filtered and washed with water to give 5-acetylamino-3*H*-1,3,4-thiadiazolin-2-one (0.4 g, 60%). The precipitate was recrystallized from ethanol to afford the analytical sample. The melting point and spectral data of the product were identical with the authentic sample which was synthesized by deethylation and acetylation of 2-amino-5-ethoxy-1,3,4-thiadizole [6]. The data are shown in Tables 1 and 2.

Transformation of 3-Acetyl-5-amino-1,3,4-thiadiazolin-2-one (**4a**) to 5-Acetylamino-3*H*-1,3,4-thiadiazolin-2-one (**5a**).

The 5-amino-3-acetyl-1,3,4-thiadiaolin-2-one (**4a**) (0.5 g, 3.1 mmoles) was dissolved in acetic acid (10 ml). The mixture was refluxed for 3 hours. The reaction mixture was cooled to room temperature. The resulting precipitate was filtered and washed with water to give 5-acetylamino-3*H*-1,3,4-thiadiazolin-2-one (**6a**) (0.34 g, 67%). To obtain the analytical sample it was recrystallized from ethanol. The melting point and spectral data of the product were identical with those of the **5a** which was synthesized from the acetylation of **2** with acetyl chloride in dioxane.

Synthesis of 5-Acetylamino-3-acetyl-1,3,4-thiadiazolin-2-one from 5-Amino-3-acetyl-1,3,4-thiadiazolin-2-one (**4a**).

5-Amino-3-acetyl-1,3,4-thiadiazolin-2-one (**4a**) (1.43 g, 9 mmoles) was suspended in acetic acid (40 ml) and acetic anhydride (2.6 ml, 27 mmoles) was added to reaction mixture. It was stirred for 2 hour at 100°. After reaction, the reaction mixture was cooled and the solvent was removed under reduced pressure. The residue was washed with water to afford 5-acetylamino-3-acetyl-1,3,4-thiadiazolin-2-one (1.71 g, 95%). It was recrystallization from ethanol, mp 199-200°; ^{1}H nmr (dimethyl sulfoxide-d_6, δ, ppm): 12.07 (1H, b, NH), 2.43 (3H, s, Me), 2.08 (3H, s, Me); ^{13}C nmr (dimethyl sulfoxide-d_6, δ, ppm): 170.1 (C=N), 167.8 (amide CO), 166.2 (amide CO), 143.4 (C=O), 24.9 (Me), 22.4 (Me); ir (potassium bromide, ν, cm^{-1}) : 3210, 3150 (NH), 3050 (CH), 1730 (C=O), 1700 (C=O), 1660 (C=O), 1590 (C=N).

Anal. Calcd. for $C_6H_7N_3O_3S$: C, 35.82; H, 3.51; N, 20.88; S, 15.93. Found: C, 36.31; H, 3.44; N, 20.74; S, 15.90.

Synthesis of 3-Isobutanoyl-5-isobutanoylamino-1,3,4-thiadiazolin-2-one (**6c**) from 5-Amino-3*H*-1,3,4-thiadiazolin-2-one (**2**). Method 1.

5-Amino-3*H*-1,3,4-thiadiazolin-2-one (**2**) (0.5 g, 4.3 mmoles) was dissolved in anhydrous dioxane (20 ml) and triethylamine (1.7 ml, 112.8 mmoles). Isobutanoic anhydride (2.1 ml, 12.8 mmoles) was added to the reaction mixture. It was refluxed for 16 hours. After the reaction, the solvent was evaporated under reduced pressure. The residue was recrystallized from ethanol to give **6c** (0.46 g, 43%). The yield, melting point and spectral data of the product are shown in Tables 1and 2.

Synthesis of 5-Isobutanoylamino-3-isobutanoyl-1,3,4,-thiadiazolin-2-one (**6c**) from 5-Amino-3-isobutanoyl-1,3,4,-thiadiazolin-2-one (**4c**).

5-Amino-3-isobutanoyl-1,3,4,-thiadiazolin-2-one (0.5 g, 2.67 mmoles) was dissolved in dioxane (20 ml) and triethylamine (0.56 ml, 4 mmoles). Isobutanoyl chloride (0.42 ml, 4 mmoles) was added to the reaction mixture and refluxed for 4 hours. The reaction mixture was cooled and the solvent was removed under reduced pressure. The residue was recrystallized from ethanol and **6c** (0.5 g, 73%) was collected. The melting point and spectral data of the product are identical with the product synthesized by Method 1.

Synthesis of 3-Benzoyl-5-benzoylamino-1,3,4-thiadiazolin-2-one (**6e**) from 5-Amino-3*H*-1,3,4-thiadiazolin-2-one (**2**).

5-Amino-3*H*-1,3,4-thiadiazolin-2-one (**2**) (0.5 g, 4.3 mmoles) was dissolved in pyridine (10 ml). Benzoyl chloride (1.16 ml, 10 mmoles) was added dropwise to the stirred mixture in the course of 3 minutes and the mixture was stirred for one and half hours at room temperature. After the mixture was cooled down in ice bath, the resulting precipitate was filtered off and washed with water to give the 3-benzoyl-5-benzoylamino-1,3,4-thiadiazolin-2-one (1.23 g, 89%). To obtain an analytical sample, the precipitate was recrystallized from ethanol. The yield, melting point and spectral data of the product are shown in Tables 1 and 2. All other 3-aroyl-5-aroylamino-1,3,4-thiadiazolin-2-ones were obtained by the same procedure.

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REFERENCES AND NOTES

[1] C. Parkanyi, M. L. Yuan, N. S. Cho, J. H. J. Jaw and T. E. Woodhouse, *J. Heterocyclic Chem.*, **26**, 1331 (1989).

[2] N. S. Cho, H. I. Shon and C. Parkanyi, *J. Heterocyclic Chem.*, **28**, 1645 (1991).

[3] N. S. Cho, H. I. Shon and C. Parkanyi, *J. Heterocyclic Chem.*, **28**, 1725 (1991).

[4] N. S. Cho, Y. C. Park, D. Y. Ra and S. K. Kang, *J. Korean Chem. Soc.*, **39**, 564 (1995).

[5] N. S. Cho, C. S. Ra, D. Y. Ra, J. S. Song and S. K. Kang, *J. Heterocyclic Chem.*, **33**, 1201 (1996).

[6] N. S. Cho, J. J. Cho, D. Y. Ra, J. H. Moon, J. S. Song and S. K. Kang, *Bull. Korean Chem. Soc.*, **17**, 1170 (1996).

[7] N. S. Cho, K. N. Kim and C. Parkanyi, *J. Heterocyclic Chem.*, **30**, 397 (1993).

[8] H. Kristinsson and T. Winkerler, *Helv. Chim. Acta*, **65**, 2606 (1982).

[9] H. Fritz, H. Kristinsson and T. Winkerler, *Helv. Chim. Acta*, **66**, 1755 (1983).

[10] E. Akerblom and K. Skagius, *Acta Chem. Scand.*, **16**, 1103 (1962).

[11] F. Kurzer, *J. Chem. Soc. (C)*, 2927, (1971).
[12] R. Esmail and F. Kurzer, *Tetrahedron*, **33**, 2007 (1977).
[13] H. Kristinsson, British UK Patent Appl. GB. 1,049,791 (1982), *Chem. Abstr.*, **98**, 53911 (1983).
[14] U. C. Lee, W. Lee, Y. J. Kim, S. J. Park, D. Y. Ra and N. S. Cho, *Phosphorus, Sulfur, Silicon*, **63**, 000 (1997).