

PREPARATION OF ETHYL 1-ARYL-2-(2-PYRIDYL)ETHENYL CARBAMATES  
AND THEIR BIOLOGICAL ACTIVITIES

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*Abstract* — Anions of *N*-silylenamines, generated from 2-(trimethylsilylmethyl)pyridine and *p*-substituted benzonitriles in the presence of LDA, reacted with ethyl chloroformate to give a mixture of ethyl (*E*)- and (*Z*)-1-aryl-2-(2-pyridyl)ethenyl carbamates. Their insecticidal or fungicidal properties were evaluated.

In the course of our investigations on the reactions of  $\alpha$ -silylcarbanions with carbonyl compounds or their analogs, we have reported three results. Lithiated 2-(trimethylsilylmethyl)pyridine (**1**) reacts with imines to give (*E*)-2-alkenylpyridines stereospecifically;<sup>1</sup> it reacts with benzonitrile (**2a**) to give (*E*)-1-phenyl-2-(2-pyridyl)-1-(trimethylsilylamino)ethene, (*E*)-**3a**, under kinetically controlled conditions; but (*Z*)-**3a** was predominantly obtained under thermodynamically controlled conditions.<sup>2</sup> These *N*-silylenamines are ambident nucleophiles possessing N and C atoms as reaction centers, and are expected to become a useful material for synthetic organic chemists. We have found that these *N*-silylenamines reacts with ethyl chloroformate to afford ethyl carbamate derivatives, which are expected to show strong biological activities.<sup>3</sup> Here we report this reaction of *N*-silylenamines with ethyl chloroformate and biological properties of the products as an insecticide or a fungicide.

The *N*-silylenamines, 1-aryl-2-(2-pyridyl)-1-(trimethylsilylamino)ethenes (**3a**) ~ (**3d**), were generated from **1** and *p*-substituted benzonitriles, (**2a**) ~ (**2d**), according to the procedure reported previously.<sup>2</sup> The resulting reaction mixtures without further purification were allowed to react with ethyl chloroformate (**4**) to afford the final products: ethyl 1-aryl-2-(2-pyridyl)ethenyl carbamates (**5a**) ~ (**5d**) in moderate yields (Eq. 1). Generally, a 8 : 2 mixture of (*E*)- and (*Z*)-**5** was obtain-

ed. The results are summarized in Table 1. In this one-pot reaction, a considerable amount of  $\underline{3}$  was formed together with  $\underline{5}$ . This low reactivity of  $\underline{3}$  was in agreement with the fact that  $\underline{3a}$ , purified by distillation,<sup>2</sup> also gave a small amount of  $\underline{5a}$  (16%) together with a large amount of phenacylpyridine (42%), which was formed from the unreacted  $\underline{3a}$  by hydrolysis<sup>2,4</sup> during a column chromatography on silica gel.

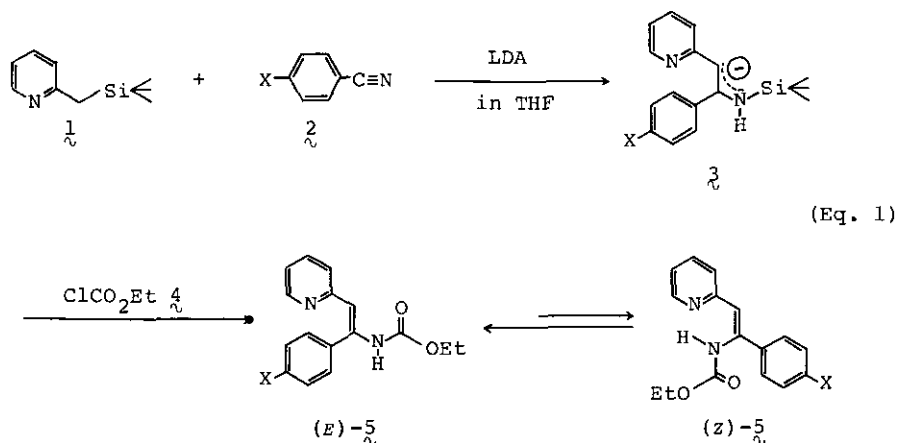


Table 1. Yields and physical properties of  $\underline{5}$

X	Yield <sup>a</sup> (%)	Mp (°C)	(from)	E : Z <sup>b</sup>
a H	38	138.5 - 139.3	(benzene)	80 : 20
b Cl	13	149.3 - 150.5	(ligloin)	75 : 25
c CH <sub>3</sub>	21	133.4 - 134.4	(ligloin)	81 : 19
d OCH <sub>3</sub>	33	155.3 - 156.3	(ligloin)	80 : 20

a) Determined by hplc (SiO<sub>2</sub>). b) Determined by <sup>1</sup>H-nmr.

The structure of  $\underline{5}$  was spectrometrically determined.<sup>5,6,7,8</sup> For example, the ms of  $\underline{5a}$  shows a molecular ion (M<sup>+</sup>) peak at m/z 268 (molecular weight 268), and the <sup>1</sup>H-nmr spectrum of  $\underline{5a}$  consists of two kinds of ethyl groups ( $\delta$  0.7, 0.6H and 3.7, 0.4H for the z-isomer;  $\delta$  1.1, 2.4H and 4.1, 1.6H for the E-isomer)<sup>9</sup> and singlet-like phenyl protons of the E-isomer, complicated with two ABCX systems for the 2-pyridyl protons, alkenyl protons, N-H protons, and multiplet phenyl protons of the z-isomer. By adding deuterium oxide, the N-H protons disappeared. Furthermore,

neither a methylene group nor a methine group was observed in either  $^1\text{H}$ -nmr or  $^{13}\text{C}$ -nmr. The ir spectrum of  $\underline{5a}$ , measured in KBr disk, suggested the presence of the enamine system ( $\nu_{\text{NH}}$  3350  $\text{cm}^{-1}$  and  $\nu_{\text{C=C}}$  1620  $\text{cm}^{-1}$ ) together with the ester group ( $\nu_{\text{C=O}}$  1645  $\text{cm}^{-1}$ ). No absorption due to a C=N bond was observed. These facts suggest that ethoxycarbonylation did not occur on the C atom, but rather on the N-atom of the enamine system. That is, this reaction is a kind of an aminolysis of  $\underline{4}$  by the *N*-silylenamine  $\underline{3}$ . This differs from a result reported for a reaction of  $\underline{3a}$  with phenacyl bromide.<sup>10</sup>

Biological activities<sup>11</sup> of  $\underline{5b}$  and  $\underline{5d}$  as a herbicide, an insecticide, or a fungicide were evaluated. The *p*-chloro derivative,  $\underline{5b}$ , showed a strong insecticidal activity against adult small brown planthoppers, *Laodelphax steriatellus* Fallen on rice plant seedlings, which were dipped in the sample solution (1000 ppm) and dried in air (mortality after 48 h, 70%); while that of the *p*-methoxyl derivative ( $\underline{5d}$ ) was lower (50%). Neither  $\underline{5b}$  nor  $\underline{5d}$  showed any insecticidal activity at all against other insects employed (house flies, *Musca domestica* (L.); azuki bean weevil, *Callosobruchus chinensis* Linne; larvae of common cutworms, *Spodoptera litura* Fabricius; two-spotted spider mites, *Tetranychus urticae* Koch; southern root-knot nematodes, *Meolilogyne incognita* Kofoid et White). In addition,  $\underline{5b}$  showed a fungicidal activity, *in vivo*, against stem rot of beans by *Sclerotinia sclerotiorum* (disease-control rate was 50% using a 500 ppm solution of  $\underline{5b}$ ). The other,  $\underline{5d}$ , however, showed no activity as a fungicide, and no herbicidal activity was found in  $\underline{5b}$  or  $\underline{5d}$ .

In a typical run, 20 mmol of  $\underline{1}$  was lithiated with 20 mmol of LDA in THF at  $-75\text{ }^\circ\text{C}$  and the resultant solution was treated with 20 mmol of  $\underline{2}$  at  $-75\text{ }^\circ\text{C}$ . The resultant mixture was stirred for 1 h at  $-75\text{ }^\circ\text{C}$  and for 2 h at room temperature,<sup>2</sup> followed by treatment with 20 mmol of  $\underline{4}$  at  $-75\text{ }^\circ\text{C}$  (exothermic). After stirring for 1 h at  $-75\text{ }^\circ\text{C}$  and for 2 h at room temperature, the reaction mixture was quenched with 50 ml of water at  $0\text{ }^\circ\text{C}$ , and then completely extracted with ether. The extract was dried over  $\text{Na}_2\text{SO}_4$ , and evaporated *in vacuo*. The residue was recrystallized from an appropriate solvent to give a pure product.

## REFERENCES AND NOTES

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2. T. Konakahara and K. Sato, *Bull. Chem. Soc. Jpn.*, 1983, 56, 1241.
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4. T. Konakahara and Y. Takagi, *Heterocycles*, 1980, 14, 393.
5. All new compounds gave satisfactory results for C, H, N analyses.  $\bar{5}a$ : ir(KBr) 3350( $\nu_{\text{NH}}$ ), 1645( $\nu_{\text{C=O}}$ ), 1620  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ );  $^1\text{H-nmr}$ (60 MHz,  $\text{CDCl}_3$ )  $\delta$  0.7(0.6H, t,  $-\text{CH}_3$  of the *Z*-isomer), 1.1(2.4H, t,  $-\text{CH}_3$  of the *E*-isomer), 3.7(0.4H, q,  $-\text{CH}_2-$  of the *Z*-isomer), 4.1(1.6H, q,  $-\text{CH}_2-$  of the *E*-isomer), 6.3 ~ 8.4(11H, singlet-like Ph-H of the *E*-isomer, multiplet Ph-H of the *Z*-isomer, and two ABCX systems for 2-Py-H complicated with =CH and NH); ms(70 eV)  $m/z$ (rel intensity) 268( $\text{M}^+$ , 44), 267(76), 222(18), 221(100), 119(61).
6.  $\bar{5}b$ : ir(KBr) 3310( $\nu_{\text{NH}}$ ), 1660( $\nu_{\text{C=O}}$ ), 1630  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ );  $^1\text{H-nmr}$ (60 MHz,  $\text{CDCl}_3$ )  $\delta$  0.6[0.8H, t,  $-\text{CH}_3$ (*Z*)], 1.1[2.2H, t,  $-\text{CH}_3$ (*E*)], 3.5[0.5H, q,  $-\text{CH}_2-$ (*Z*)], 4.0 [2.5H, q,  $-\text{CH}_2-$ (*E*)], 6.4 ~ 8.3(10H, m, Py-H, ph-H, =CH, and NH); ms(70 eV)  $m/z$ (rel intensity) 302( $\text{M}^+$ , 47), 301(72), 255(100), 119(54).
7.  $\bar{5}c$ : ir(KBr) 3370( $\nu_{\text{NH}}$ ), 1650( $\nu_{\text{C=O}}$ ), 1610  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ );  $^1\text{H-nmr}$ (60 MHz,  $\text{CDCl}_3$ )  $\delta$  0.7[0.6H, t,  $-\text{CH}_3$ (*Z*)], 1.1[2.4H, t,  $-\text{CH}_3$ (*E*)], 2.1[2.4H, s, Ph- $\text{CH}_3$ (*E*)], 2.3[0.6H, s, Ph- $\text{CH}_3$ (*Z*)], 3.7[0.4H, q,  $-\text{CH}_2-$ (*Z*)], 4.0[1.6H, q,  $-\text{CH}_2-$ (*E*)], 6.0 ~ 8.4(10H, m, Py-H, Ph-H, =CH, and NH); ms(70 eV)  $m/z$ (rel intensity) 282( $\text{M}^+$ , 48), 281(65), 235(100), 119(59).
8.  $\bar{5}d$ : ir(KBr) 3350( $\nu_{\text{NH}}$ ), 1645( $\nu_{\text{C=O}}$ ), 1620  $\text{cm}^{-1}$  ( $\nu_{\text{C=C}}$ );  $^1\text{H-nmr}$ (60 MHz,  $\text{CDCl}_3$ )  $\delta$  0.8[0.6H, t,  $-\text{CH}_3$ (*Z*)], 1.2[2.4H, t,  $-\text{CH}_3$ (*E*)], 3.4 ~ 5.4(5H, m,  $-\text{CH}_2-$  and  $-\text{OCH}_3$ ), 6.0 ~ 8.6(10H, m, Py-H, Ph-H, =CH, and NH); ms(70 eV)  $m/z$ (rel intensity) 298( $\text{M}^+$ , 66), 297(71), 251(100), 119(47).
9. The configuration of  $\bar{5}$  was determined by a comparison of the spectral data of (*E*)- and (*Z*)- $\bar{3}a$  reported in ref. 2. in addition, the ir spectra of  $\bar{5}a$  in cyclohexane suggested the presence of two isomers( $\nu_{\text{NH}}$  3500, 3300  $\text{cm}^{-1}$ ), which were analyzed by hplc using a column of silver nitrate on silica gel support (*E* : *Z* = 8 : 2).
10. O. Tsuge, K. matsuda and S. Kanemasa, *Heterocycles*, 1983, 20, 593.
11. Evaluation of biological activities of these compounds was performed at SDS Biotech K.K. Tokyo Research Laboratory.

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