Functionalization of a Pyridine Framework via Intramolecular Reissert-Henze Reaction of *N*-Carbamoyloxypyridinium Salt and Unexpected Insertion of Ethereal Solvents

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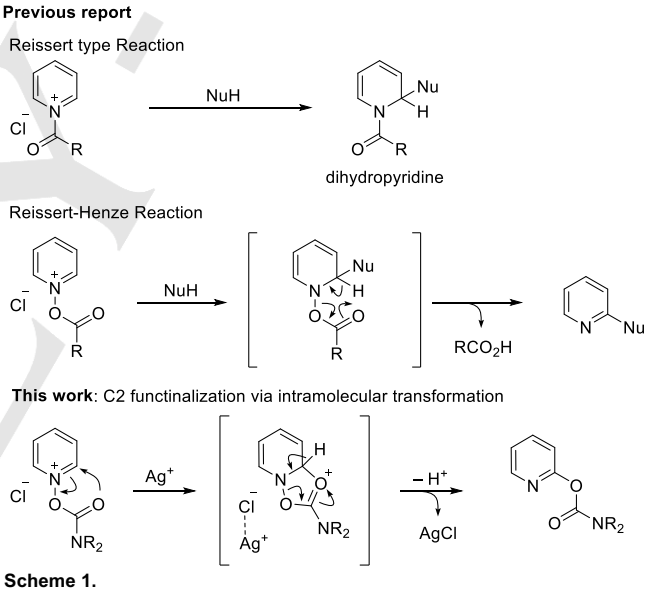
Dedication ((optional))

Abstract: A new strategy for synthesis of the 2-pyridyl carbamate is reported herein. This strategy exploits a novel intramolecular transformation of acyloxy group from *N*-carbamoyloxypyridinium salt (Reissert-Henze-type reaction) as the key step. Addition of silver salt effectively accelerates the intramolecular attack of the carbonyl oxygen at the 2-position of the pyridine ring. Additionally, a new rearrangement of the acyloxy group, combined with insertion of an ethereal solvent to afford pyridine derivatives having a coordinating tether, is reported.

Introduction

Functionalized pyridines are widely distributed in biologically active compounds,[1] ligands,[2] optical materials,[3] and so on. Nonetheless, direct functionalization of the pyridine ring is still challenging due to the relatively low electron density and high Lewis basicity of the ring nitrogen, which prevents functionalization by electrophilic processes. *N*-Acylation is one of the most important approaches for activation of the pyridine ring, where nucleophilic addition to functionalize the 2-position is facilitated. This is known as the Reissert-type reaction;[4],[5] however, the products are non-aromatic dihydropyridines (Scheme 1). This disadvantage is overcome by employing the Reissert-Henze-type reaction[6] using *N*-acyloxypyridinium halide, which affords 2-functionalized pyridines via rearomatization, accompanied by elimination of carboxylic acid. Although this reaction is applicable to a wide range of nucleophiles, to the best of our knowledge, no intramolecular rearrangement of the carbonyl oxygen has been reported. In this context, intramolecular attack of the carbonyl oxygen at the 2-position may occur when other nucleophiles are absent, which is a hitherto unknown process. To perform the desired transformation, the following strategies were implemented: (1) the use of carbamoyl chloride having an electron-donating amino group to increase the nucleophilicity at the carbonyl oxygen; (2) addition of a silver salt to keep the counter chloride anion away via the formation of a stable silver chloride having a small dissociation constant, thus increasing the electrophilicity of the pyridine ring.

Herein, we report a novel method for the synthesis of 2-functionalized pyridines via the reaction between pyridine *N*-oxide **1** and carbamoyl chloride **2** in the presence of silver salts. In this study, we demonstrate a new acyloxy group rearrangement, accompanied by insertion of an ethereal solvent.



Scheme 1.

Results and Discussion

Initially, the reaction of pyridine *N*-oxide **1A** with *N*,*N*-dimethylcarbamoyl chloride **2a** was investigated. *N*-Acyloxypyridinium salt **3Aa** was formed as a white precipitate when 2 equivalents of **2a** was added to a benzene solution of pyridine *N*-oxide. After stirring the mixture at room temperature, $AgNO_3$ (1.0 equiv.) was added, and the resultant mixture was heated at 150 °C in a sealed tube for 1 h. The desired product, 2-pyridinyl *N*,*N*-dimethylcarbamate **4Aa** was obtained by this process, albeit in just 4% yield (Table 1, entry 1). On the other hand, control experiments showed that no reaction took place in the absence of the silver salt (entries 2 and 3). Screening of various silver salts demonstrated that silver(I) oxide was the most effective and that its use increased the yield of **4Aa** to 51% (entries 1, 4–6). When methyl chloroformate or benzoyl chloride were used instead of carbamoyl chloride, *N*-oxide was

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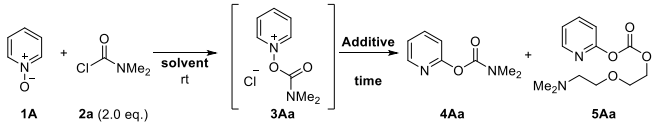
recovered without any detectable 2-functionalized pyridine. These results imply that the electron-donating amino group play an important role in the intramolecular transformation. Screening of several solvents for the reaction revealed that the formation of **4Aa** in 1,4-dioxane was superior to that in other solvents (entries 5–8). Lowering the reaction temperature to 60 °C produced slightly higher yields (entries 11 and 12), although longer reaction times were required. Therefore, the optimized reaction conditions for intramolecular transformation of the acyloxy group were 2 equivalents of carbamoyl chloride and an equimolar amount of Ag_2O in 1,4-dioxane at 60 °C. The present strategy furnishes pyridyl carbamate via a novel intramolecular Reissert-Henze-type reaction.

Table 1. Optimization of the intramolecular transformation of acyloxy group.



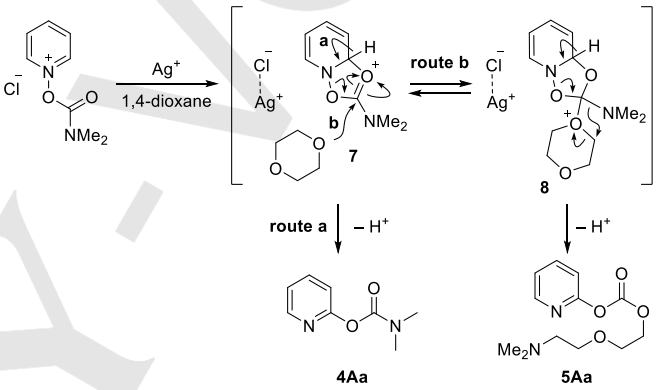
1A **2a** (2.0 eq.) **3Aa** **4Aa** **5Aa**

entry	additive	solvent	temperature (°C)	time (h)	yield (%)[a]	
					4Aa	**5Aa**
1	$AgNO_3$	benzene	150	1	4	–
2	None	benzene	150	1	0	–
3	$Cu(OAc)_2$	benzene	150	1	0	–
4	AgOAc	benzene	150	1	15	–
5	Ag_2CO_3	benzene	150	1	47	–
6	Ag_2O	benzene	150	1	51	–
7	Ag_2O	acetonitrile	150	1	33	–
8	Ag_2O	*c*-hexane	150	1	22	–
9	Ag_2O	CPME[b]	150	1	48	–
10	Ag_2O	1,4-dioxane	150	1	52	20
11	Ag_2O	benzene	60	24	50	–
12	Ag_2O	1,4-dioxane	60	24	61	33

[a] NMR yield. [b] Cyclopentyl methyl ether.

It is noteworthy that **5Aa** was formed via a competitive reaction when the reaction was conducted in 1,4-dioxane. Structural determination was performed as follows: in the ^{1}H NMR spectrum of **5Aa**, signals of four non-equivalent methylene protons were observed between 3.76 and 4.47 ppm, in addition to signals closely related to **4Aa**. In the ^{13}C NMR and IR spectra, a signal at 164.1 ppm and an absorption peak at 1697 cm^{-1} for the carbonyl group, respectively, were observed, which indicated that the product contains a carbonate ester group. Additionally, the MS data of **5Aa** (M^+ = 254) indicated that a $C_4H_8O_2$ (88) moiety is newly added to the framework of **4Aa** (166). These data clearly indicated the insertion of a dioxane molecule into the side chain, accompanied by ring opening.

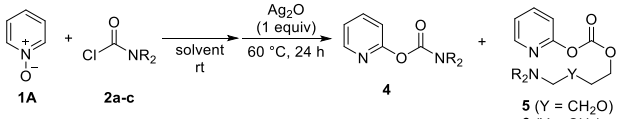
A plausible mechanism for this transformation is illustrated in Scheme 2. Addition of silver salt accelerates the intramolecular attack of the carbonyl oxygen at the 2-position of the pyridine ring to afford the highly electrophilic dioxazolopyridine **7**, which is an intermediate common to both **4Aa** and **5Aa**. While the deprotonation at the bridgehead position induces rearomatization to afford **4Aa** (route a), attack of a 1,4-dioxane molecule competitively occurs, leading to the formation of adduct intermediate **8** (route b). During rearomatization of the pyridine ring, rearrangement of the dimethylamino group results in dioxane ring opening to afford **5Aa**. To selectively obtain this intriguing product **5**, we reinvestigate the reaction conditions, such as solvent, temperature, time, amount of silver oxide, and concentration. Despite considerable efforts, the simultaneous production of **4Aa** could not be suppressed, and the product ratio of **4**/**5** was little changed. The difficulty to control the reaction paths could be attributed to that both products were formed via same intermediate **7**. We also studied the interconversion of both isolated product **4** and **5** under reaction conditions, however, the products were stable and not changed.



Scheme 2. A Plausible mechanism of the insertion of 1,4-dioxane.

This transformation was performed using another ethereal solvent, THF. Indeed, a similar reaction occurred to furnish **6Aa** (32%) in addition to **4Aa** (61%) (Table 2, entry 2). We then examined the effect of substituents on the nitrogen atom of the carbamoyl chloride in THF (Table 2). Even substrates with bulkier substituents on the nitrogen atom, i.e., *N*,*N*-dialkylcarbamoyl chlorides **2b** and **2c**, underwent similar reactions in THF, without loss of the total yield and selectivity (entries 3 and 4).

Table 2. Substituent effect of carbamoyl group.



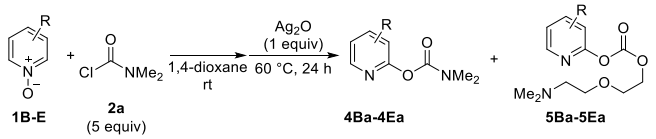
1A **2a-c** **4**

entry	**2**	R	solvent	yield (%)[a]		total
				4	**5**/**6**	
1	**2a**	Me	1,4-dioxane	**4Aa** (61)	**5Aa** (33)	94
2	**2a**	Me	THF	**4Aa** (61)	**6Aa** (32)	93
3	**2b**	Et	THF	**4Ab** (53)	**6Ab** (31)	84
4	**2c**	*i*-Pr	THF	**4Ac** (62)	**6Ac** (29)	91

[a] NMR yield.

Next, we attempted to extend the scope of this reaction to substituted pyridines, as shown in Table 3. The present reaction was considerably influenced by the electronic properties of the substituent, as reflected in the product yields and regioselectivity. Specifically, substrates **1B** and **1C** with the electron-donating methyl group provided the desired products in low yields, while pyridine *N*-oxides with electron-withdrawing groups, **1D** and **1E**, gave products **4** in higher yields. Notably, the reaction of 3-chloropyridine *N*-oxide **1E** with **2a** yielded the desired product **4Ea** in 77% total yield and with good regioselectivity (2-position/6-position = 90:10). This may be attributed to the inductive effect of the chloro group and the fact that the 2-position of the pyridine ring was more electrophilic.

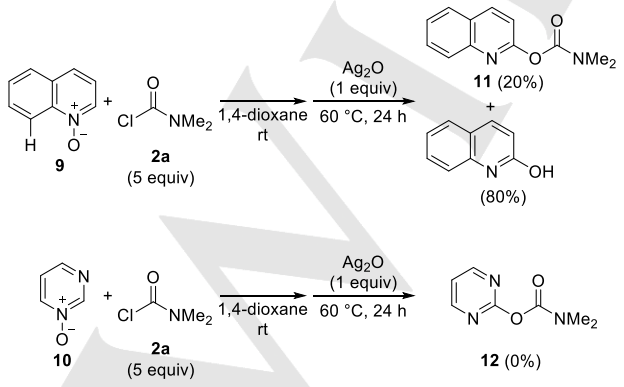
Table 3. Substituent effect of carbamoyl group.



entry	1	R	yield (%)[a,b]	
			4	5
1	1B	4-Me	10	trace
2	1C	3-Me	29 (38/62)	14 (50/50)
3	1D	4-CN	39	trace
4	1E	3-Cl	77 (90/10)	trace

[a] NMR yield. [b] Ratio of regioselectivity (2-position/6-position) were shown in the parentheses.

The 2-functionalization quinoline *N*-oxide (**9**) or pyrimidine *N*-oxide (**10**) with carbamoyl chloride **2a** was also tested under standard reaction conditions (Scheme 3). In the presence of silver salt, the reaction between substrate **9** and **2a** afforded the desired 2-quinolyl dimethylcarbamate **11** in 20% yield with 80% of 2-quinolonol as by-product. The low efficiency of the transformation of substrate **9** is probably due to the steric repulsion of *peri*-hydrogen. On the other hand, pyrimidine *N*-oxide (**10**) afforded a complex mixture under the same reaction conditions without detection of **12**.



Scheme 3. 2-Functionalization of other substrates.

In order to demonstrate the utility of the ethereal solvent-inserted products, we studied the binding ability of the products to metal ions. Figure 1 shows the ^{1}H NMR spectral changes for **5Aa** upon the addition of magnesium ions in CD_3CN. A shift of both the ethylene and pyridine proton signals was observed upon the addition of $Mg(ClO_4)_2$, which suggests that binding of **5Aa** to the magnesium ion occurred via both ring nitrogens and a tether at the 2-position. Details of the binding ability of the products and the structure of the corresponding metal complexes are now under investigation.

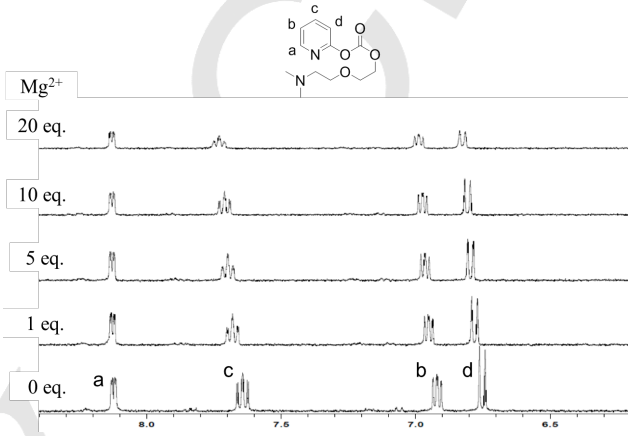


Figure 1. NMR spectral changes of **5Aa** upon addition of $Mg(ClO_4)_2$ in CD_3CN.

Conclusions

In conclusion, we have demonstrated novel functionalization of the pyridine framework to afford pyridyl carbamate **4** via the intramolecular Reissert-Henze-type reaction of *N*-carbamoyloxypyridinium salt. Addition of a silver salt effectively increased the electrophilicity of the pyridine ring due to keeping the counter chloride anion away as silver chloride. Moreover, unexpected insertion of ethereal solvents into the side chain of the pyridine ring, leading to pyridyl carbonate **5** and **6**, was detected. Products **4** and **5**/**6** were formed competitively via the common dioxazolopyridine intermediate **7**. Since these products have multi-coordination sites, they are expected to serve as novel ligands.

Experimental Section

General Information: Pyridine *N*-oxides **1A-E** and carbamoyl chlorides **2a-c** were purchased from commercial sources and directly used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX-400 spectrometer (400 MHz and 100 MHz, respectively) in $CDCl_3$ using TMS as an internal standard. ^{1}H NMR data is reported as follows: chemical shift (δ, ppm), (chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz). ^{13}C NMR data is reported in terms of chemical shift (δ, ppm). NMR signal assignments of dioxane inserted product **5Aa** were based on additional 2D-NMR spectroscopy (e.g., COSY, NOESY, HSQC, and HMBC). Horiba FT-200 IR Spectrometer was used to record infrared spectra and are reported in frequency of absorption. High-resolution

mass spectra were obtained on a JEOL JMS-700N mass spectrometer. Melting points were recorded with a Yanaco micro-melting-points apparatus and were uncorrected.

Typical Procedure for the Reaction of Pyridine *N*–Oxide 1 with Carbamoyl Chloride 2: To a solution of pyridine *N*-oxide **1a** (38 mg, 0.4 mmol) in solvent (3 mL), carbamoyl chloride **2** (0.8 mmol) was added and the resultant mixture was stirred at ambient temperature for several minutes. And then silver salt (0.4 mmol) was added. After heating of the solution at 60 °C for 24 h, the precipitate was filtered and washed with dichloromethane (10 mL × 2). The collected filtrate was concentrated under reduced pressure. The yield of the product were determined by ^{1}H NMR integration of the crude product using 1,1,2,2-tetrachloroethane as an internal standard. Further purification was achieved by flash column chromatography on silica gel (hexane/EtOAc = 50/50). The known carbamate products **4** were assigned with The assignment of In the case of several substituted pyridine *N*-oxides, attempts to isolate the pure product was failed due to the low yield and close R_f value.

2-Pyridyl *N,N*-Dimethylcarbamate (4Aa)[7]: brown oil, R_f = 0.15 (silica gel, hexane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.02 (s, 3H), 3.13 (s, 3H), 7.10 (ddd, *J* = 0.7, 0.9, 7.3 Hz, 1H), 7.17 (ddd, *J* = 0.9, 4.9, 7.3 Hz, 1H), 7.75 (ddd, *J* = 2.0, 7.3, 7.3 Hz, 1H), 8.36 (ddd, *J* = 0.7, 2.0, 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.7 (CH_3), 36.8 (CH_3), 116.4 (CH), 121.4 (CH), 139.4 (CH), 148.4 (CH), 154.1 (C), 158.8 (C); IR (NaCl) 1728, 1225, 1161 cm^{-1}.

2-Pyridyl *N,N*-Diethylcarbamate (4Ab)[7]: brown oil, R_f = 0.17 (silica gel, hexane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 3.40 (q, *J* = 7.1 Hz, 2H), 3.48 (q, *J* = 7.1 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 1H), 7.16 (dd, *J* = 4.9, 7.4 Hz, 1H), 7.75 (ddd, *J* = 2.0, 7.4, 8.8 Hz, 1H), 8.37 (dd, *J* = 2.0, 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4 (CH_3), 14.3 (CH_3), 42.2 (CH_2), 42.3 (CH_2), 116.5 (CH), 121.3 (CH), 139.3 (CH), 148.4 (CH), 153.5 (C), 158.9 (C); IR (ATR) 1713, 1209, 1148 cm^{-1}.

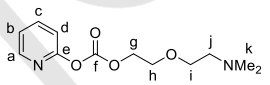
2-Pyridyl *N,N*-Diisopropylcarbamate (4Ac)[8]: reddish orange solid, R_f = 0.16 (silica gel, hexane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25–1.45 (m, 12H), 3.95–4.16 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.16 (dd, *J* = 4.8, 7.5 Hz, 1H), 7.74 (ddd, *J* = 2.0, 7.5, 8.2 Hz, 1H), 8.39 (dd, *J* = 2.0, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6 (CH_3), 21.6 (CH_3), 46.9 (CH), 116.7 (CH), 121.2 (CH), 139.2 (CH), 148.5 (CH), 152.9 (C), 158.8 (C); IR (ATR) 1697, 1200, 1148 cm^{-1}.

4-Methylpyridin-2-yl *N,N*-Dimethylcarbamate: brown oil, R_f = 0.17 (silica gel, hexane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 3.02 (s, 3H), 3.13 (s, 3H), 7.14 (d, *J* = 4.9 Hz, 1H), 8.30 (d, *J* = 4.9 Hz, 1H), 8.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8 (CH_3), 36.6 (CH_3), 37.0 (CH_3), 125.7 (CH), 139.8 (C), 144.2 (CH), 146.6 (CH), 147.4 (C), 154.1 (C); IR (NaCl) 1717, 1246, 1151 cm^{-1}. HRMS (EI) m/z calcd. for $C_9H_{12}N_2O_2$: 180.0899; found 180.0895.

4-Cyanopyridin-2-yl *N,N*-Dimethylcarbamate: yellowish brown solid, mp 127–129 °C, R_f = 0.13 (silica gel, hexane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (s, 3H), 3.14 (s, 3H), 7.40 (dd, *J* = 1.7, 5.0 Hz, 1H), 7.41 (dd, *J* = 0.9, 1.7 Hz, 1H), 8.53 (dd, *J* = 0.9, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.8 (CH_3), 37.0 (CH_3), 116.0 (C), 119.0 (CH), 122.9 (CH), 123.4 (C), 149.7 (CH), 153.2 (C), 159.3; IR (ATR) 2201 (CN), 1715, 1250, 1142 cm^{-1}. HRMS (EI) m/z calcd. for $C_9H_9N_3O_2$: 191.0695, found 191.0697.

3-Chloropyridin-2-yl *N,N*-Dimethylcarbamate: yellow solid, mp 109–110 °C, R_f = 0.34 (silica gel, hexane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.04 (s, 3H, H-1), 3.16 (s, 3H, H-2), 7.18 (dd, *J* = 4.8, 7.8 Hz, 1H, H-4), 7.80 (dd, *J* = 1.7, 7.8 Hz, 1H, H-3), 8.28 (dd, *J* = 1.7, 4.8 Hz, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.8 (CH_3), 36.9 (CH_3), 122.8 (CH), 124.2 (C), 139.6 (CH), 146.3 (CH), 153.1 (C), 154.9 (C); IR (ATR) 1705, 1234, 1153 cm^{-1}. HRMS (EI) m/z calcd. for $C_8H_9ClN_2O_2$: 200.0353, found 200.0354.

9-Aza-9-methyl-1,3,6-trioxa-2-oxo-1-(2-pyridyl)decane (5Aa):



5Aa

yellow oil, R_f = 0.24 (silica gel, hexane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89 (br s, 6H, H_k), 3.76 (t, *J* = 4.8 Hz, 2H, H_j), 3.85 (t, *J* = 4.8 Hz, 2H, H_i), 4.24 (t, *J* = 4.8 Hz, 2H, H_h), 4.47 (t, *J* = 4.8 Hz, 2H, H_g), 6.77 (ddd, *J* = 0.9, 1.7, 7.1 Hz, 1H, H_d), 6.85 (ddd, *J* = 1.7, 5.0, 7.1 Hz, 1H, H_b), 7.55 (ddd, *J* = 2.0, 7.1, 7.1 Hz, 1H, H_c), 8.12 (ddd, *J* = 0.9, 2.0, 5.0 Hz, 1H, H_a); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.1 (CH_3, C_k), 36.6 (CH_3, C_k), 64.7 (CH_2, C_j), 65.1 (CH_2, C_i), 69.8 (CH_2, C_h), 69.9 (CH_2, C_g), 111.5 (CH, C_d), 116.9 (CH, C_b), 138.7 (CH, C_c), 146.9 (CH, C_a), 156.6 (C, C_e), 163.8 (C, C_f); IR (ATR) 1697, 1273, 1186 cm^{-1}. HRMS (EI) m/z calcd. for $C_{12}H_{18}N_2O_4$: 254.1267, found 254.1272.

8-Aza-8-methyl-1,3-dioxa-2-oxo-1-(2-pyridyl)nonane (6Aa): yellow oil, R_f = 0.25 (silica gel, hexane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77–1.90 (m, 4H), 2.89 (br s, 6H), 4.14 (t, *J* = 6.3 Hz, 2H), 4.32 (t, *J* = 6.3 Hz, 2H), 6.71 (ddd, *J* = 0.8, 1.2, 7.1 Hz, 1H), 6.84 (ddd, *J* = 1.2, 5.1, 7.1 Hz, 1H), 7.55 (ddd, *J* = 2.0, 7.1, 7.1 Hz, 1H), 8.13 (ddd, *J* = 0.8, 2.0, 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9 (CH_2), 26.1 (CH_2), 36.0 (CH_3), 36.5 (CH_3), 65.2 (CH_2), 65.5 (CH_2), 111.2 (CH), 116.7 (CH), 138.6 (CH), 147.0 (CH), 156.9 (C), 164.1 (C); IR (ATR) 1697, 1285, 1182 cm^{-1}. HRMS (EI) m/z calcd. for $C_{12}H_{18}N_2O_3$: 238.1317, found 238.1314.

8-Aza-8-ethyl-1,3-dioxa-2-oxo-1-(2-pyridyl)decane (6Ab): brown oil, R_f = 0.30 (silica gel, hexane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, *J* = 7.1 Hz, 6H), 1.77–1.90 (m, 4H), 3.18–3.40 (m, 4H), 4.14 (t, *J* = 6.2 Hz, 2H), 4.32 (t, *J* = 6.2 Hz, 2H), 6.72 (d, *J* = 9.4 Hz, 1H), 6.84 (ddd, *J* = 0.8, 5.0, 7.5 Hz, 1H), 7.55 (ddd, *J* = 1.7, 7.5, 9.4 Hz, 1H), 8.13 (dd, *J* = 1.7, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8 (CH_3), 14.0 (CH_3), 26.0 (CH_2), 25.9 (CH_2), 41.4 (CH_2), 41.7 (CH_2), 64.9 (CH_2), 65.5 (CH_2), 111.2 (CH), 116.7 (CH), 138.6 (CH), 147.0 (CH), 156.2 (C), 164.1 (C); IR (ATR) 1694, 1269, 1169 cm^{-1}. HRMS (EI) m/z calcd. for $C_{14}H_{22}N_2O_3$: 266.1630, found 266.1621.

Quinolin-2-yl *N,N*-Dimethylcarbamate (11)[9]: brown oil, R_f = 0.18 (silica gel, hexane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (s, 3H), 3.18 (s, 3H), 7.24 (d, *J* = 8.7 Hz, 1H), 7.52 (ddd, *J* = 1.2, 7.0, 9.2 Hz, 1H), 7.70 (ddd, *J* = 1.0, 7.0, 9.1 Hz, 1H), 7.83 (dd, *J* = 1.2, 9.1 Hz, 1H), 8.00 (dd, *J* = 1.0, 9.2 Hz, 1H), 8.20 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.8 (CH_3), 36.9

(CH_3), 116.1 (CH), 126.3 (CH), 127.1 (C), 127.6 (CH), 128.7 (CH), 130.1 (CH), 139.8 (CH), 146.7 (C),154.2 (C), 157.2 (C); IR (NaCl) 1717, 1223, 1148 cm^{-1}

Keywords: Synthetic methods • Rearrangement • Nitrogen heterocycles • N,O ligands • Insertion

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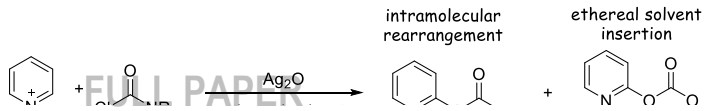

FULL PAPER

Key Topic*

*Haruyasu Asahara, Asuka Kataoka, Shotaro Hirao, and Nagatoshi Nishiwaki**

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Functionalization of a Pyridine Framework via Intramolecular Reissert-Henze Reaction of *N*-Carbamoyloxypyridinium Salt and Unexpected Insertion of Ethereal Solvents

Fiddler crab: A new strategy is provided which affords 2-pyridyl carbamate upon treatment of *N*-carbamoyloxypyridinium salt with silver oxide. Additionally, a new rearrangement of the acyloxy group, combined with insertion of an ethereal solvent to afford pyridine derivatives having a coordinating tether, is reported.