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Temperature-Controlled Synthesis of Substituted Pyridine Derivatives via the [5C + 1N] Annulation of 1,1-Bisalkylthio-1,4-pentanedienes and Ammonium Acetate

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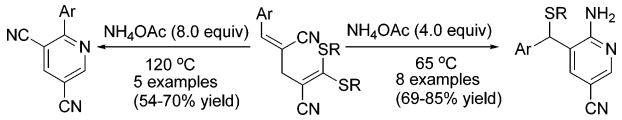

A novel temperature-controlled one-pot synthesis of substituted pyridine derivatives via [5C + 1N] annulation of 1,1-bisalkylthio-1,4-pentanedienes and ammonium acetate is developed, and possible mechanisms leading to the divergent formation of the two types of pyridines are discussed.

Pyridines and their benzo-/hetero-fused analogues represent an important class of organic molecules for their presence in numerous natural products along with useful bio-, physio- and pharmacological activities.[1] Although many creative and practical methods for pyridine preparation have been developed,[2,3] which employ [5 + 1],[2b,3a,4] [2 + 2 + 1 + 1],[5] [2 + 2 + 2],[6] [3 + 3],[7] [4 + 2][8] and [3 + 2 + 1][9] synthetic strategies with respect to pyridine ring disconnection, each synthesis must be carefully planned due to the incompatibility of certain functional groups. Therefore, there is a continuing need to generate new and improved methods for pyridine synthesis. The [5 + 1] annulation of 1,5-dicarbonyl compounds and their equivalents with ammonia represents one of the most simple and reliable routes due to its straightforward concept.[2b,4] However, the problem associated with this transformation is the availability of suitable starting materials. Thus, it is of great importance to explore more appropriate precursors for efficient synthesis of pyridine derivatives via a [5 + 1] annulation strategy.

In view of the above and our interest in the synthesis of carbo- and heterocyclic compounds,[10−14] the [5C + 1C],[12] [5C + 1N],[13] and [5C + 1S][14] annulation strategies have been developed based on the new 1,5-bielectrophilic alkenoyl ketene-(*S*,*S*)-acetal precursors. Recently, by combining the advantages of functionalized ketene-(*S*,*S*)-acetals[11−15] and Morita−Baylis−Hillman

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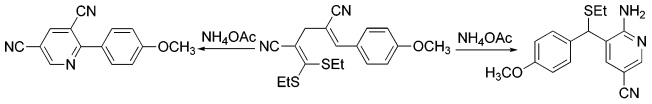
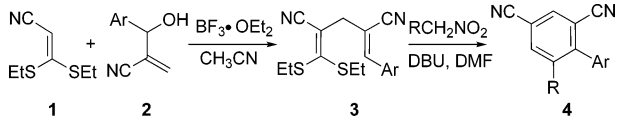
TABLE 1. Reaction of 3a with NH_4OAc under Different Conditions

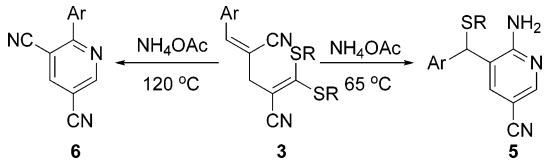


entry	NH_4OAc (equiv)	*T* (°C)	solvent	time (h)	yield (%) **5a**	yield (%) **6a**
1	1.0	65	DMF	12.0	10	0
2	4.0	65	DMF	6.0	83	0
3	8.0	65	DMF	6.0	82	0
4	4.0	65	DMSO	6.0	78	0
5	4.0	25	DMF	6.0	0	0
6	4.0	40	DMF	6 .0	16	0
7	4.0	90	DMF	6.0	64	10
8	4.0	120	DMF	6.0	28	32
9	8.0	120	DMF	1.0	trace	54

SCHEME 1



SCHEME 2



(MBH) adducts[16] in organic synthesis, we realized the efficient direct C−C coupling reaction between α-cyanoketene-(*S*,*S*)-acetals **1** and MBH adducts **2** (Scheme 1). As a result, the new 1,5-dielectrophiles, substituted 1,1-bisalkylthio-1,4-pentanedienes **3**, were prepared and successfully used for the synthesis of the unsymmetrical biaryls **4** via a [5C + 1C] annulation (Scheme 1).[12b] As part of our continuing studies on the development of the synthesis of substituted pyridine derivatives from the 5C precursor, 1,1-bisalkylthio-1,4-pentanediene **3** via [5C + 1N] annulation strategy, in this contribution, the remarkable temperature-controlled synthesis of two types of substituted pyridine derivatives **5** and **6** from the same precursors (**3** and ammonium acetate) is reported (Scheme 2).

According to our previous work,[12b] the [5C + 1N] annulation of 2-(bisethyl(ethylthio)methylene)-4-(4-methoxybenzylidene)-pentanedinitrile (**3a**) with ammonium acetate was focused on at first (Table 1). After many attempts, it was found that a pyridine derivative, 6-amino-5-(ethylthio(4-methoxyphenyl)-methyl)nicotinonitrile (**5a**), could be isolated in 83% yield when the reaction of **3a** and ammonium acetate was performed in DMF at 65 °C for 6 h (Table 1, entry 2). The reaction was then carried out under various conditions to optimize the yield. The experiments revealed that the addition of 4.0 equiv of ammonium acetate was enough for a high transformation from **3a** to **5a** (Table 1, entries 1−3). In addition, the reaction is greatly affected by the solvent. For example, no desired product **5a** was obtained in the solvents such as toluene, dichloromethane, ethanol, THF and acetonitrile, and **5a** was obtained in a little lower yield with DMSO as the solvent (Table 1, entry 4). It is worth emphasizing that the reaction is very sensitive to temperature. For example, when the reaction was carried out at room temperature, no desired product **5a** was observed (Table 1, entry 5). When the reaction temperature was maintained at 65 °C, **5a** was formed in high yields (Table 1, entries 2 and 5−8). Interestingly, when the temperature was higher than 90 °C, a new pyridine derivative 2-(4-methoxyphenyl)pyridine-3,5-dicarbonitrile (**6a**) was obtained along with the formation of pyridine **5a** (Table 1, entries 7 and 8), and **6a** could be obtained exclusively with good yield within 1 h when the reaction was performed at 120 °C and 8.0 equiv of ammonium acetate was added (Table 1, entry 9). In addition, **5a** was stable in the presence of 8.0 equiv of ammonium acetate at 120 °C. In fact, selective synthesis has been a formidable challenge in organic synthesis, especially controlled highly selective synthesis beginning from the same starting materials.[17] So far, to the best

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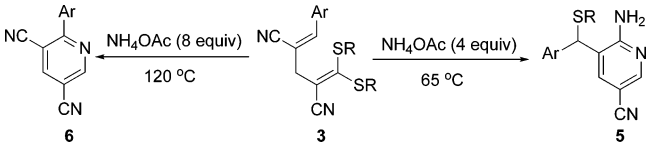
TABLE 2. [5C + 1N] Annulation of 3 with NH_4OAc to Pyridines 5[a] and 6[b]



entry	substrate **3**	Ar	R	time (h)	pyridine **5** or **6**	yield[c] (%)
1	**3b**	3,4-$O_2CH_2C_6H_3$	Et	6.0	**5b**	85
2	**3c**	2-$MeOC_6H_4$	Et	8.0	**5c**	75
3	**3d**	3-$MeOC_6H_4$	Et	10.0	**5d**	69
4	**3e**	4-$EtOC_6H_4$	Et	10.0	**5e**	74
5	**3f**	4-$MeOC_6H_4$	Me	10.0	**5f**	73
6	**3g**	4-$MeOC_6H_4$	*n*-Bu	10.0	**5g**	69
7	**3h**	4-$MeOC_6H_4$	Bn	10.0	**5h**	77
8	**3i**	Ph	Et	48.0	**5i**	36[d,e]
9	**3j**	4-ClC_6H_4	Et	48.0	**5j**	0[f]
10	**3b**	3,4-$O_2CH_2C_6H_3$	Et	3.0	**6b**	70
11	**3c**	2-$MeOC_6H_4$	Et	5.0	**6c**	54
12	**3d**	3-$MeOC_6H_4$	Et	4.0	**6d**	56
13	**3e**	4-$EtOC_6H_4$	Et	3.0	**6e**	56
14	**3f**	4-$MeOC_6H_4$	Me	3.0	**6e**	52
15	**3g**	4-$MeOC_6H_4$	*n*-Bu	3.0	**6e**	57
16	**3h**	4-$MeOC_6H_4$	Bn	3.0	**6e**	54
17	**3j**	4-ClC_6H_4	Et	48.0	**6j**	0[f]

[a] Reaction conditions unless otherwise noted: **3** (1.0 mmol), NH_4OAc (4.0 mmol), DMF (10 mL) at 65 °C. [b] Reaction conditions: **3** (1.0 mmol), NH_4OAc (8.0 mmol), DMF (10 mL) at 120 °C. [c] Isolated yields. [d] The reaction was performed at 120 °C with 8.0 equiv of NH_4OAc. [e] 63% of **3i** was recovered. [f] **3j** was recovered.

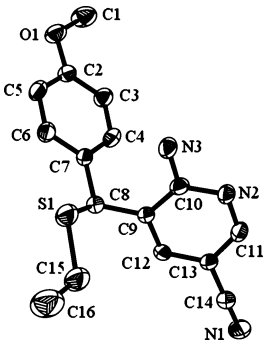
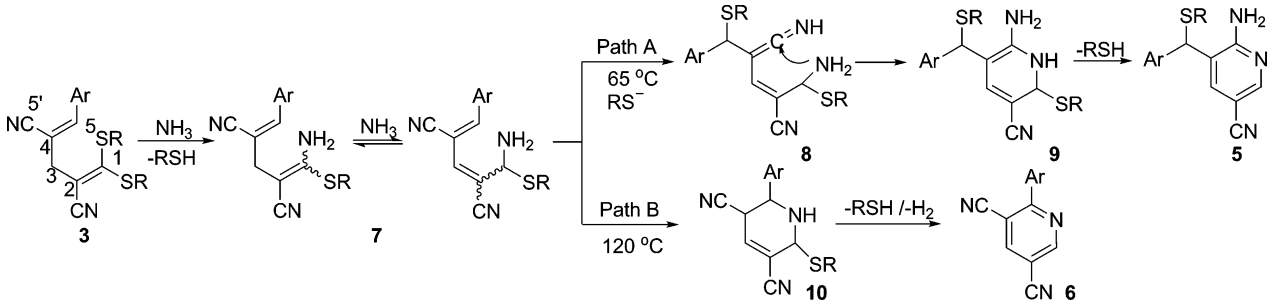


FIGURE 1. ORTEP drawing of **5a**.

SCHEME 3. Proposed Mechanisms for the Temperature-Controlled Pyridines Syntheses



of our knowledge, there are no reports for the divergent synthesis of two types of substituted pyridine derivatives from the same 5C fragment and ammonium acetate via a [5C + 1N] annulation.

Subsequently, the reactions of a series of available 1,1-bisalkylthio-1,4-pentanedienes **3**[12b] with ammonium acetate were carried out to understand the efficiency of the temperature-controlled synthesis of substituted pyridine derivatives. At 65 °C and under the reaction conditions as indicated in Table 1, entry 2, the reactions between **3b**−**3h** and ammonium acetate (4.0 equiv) proceeded smoothly to afford the corresponding trisubstituted pyridines **5b**−**5h** in good to high yields (Table 2, entries 1−7). The structure of **5a** was further confirmed by single-crystal X-ray diffraction analysis (Figure 1).

On the other hand, for the reactions performed at 120 °C as shown in Table 1, entry 9, the reactions of **3b**−**3e** with 8.0 equiv of ammonium acetate, gratifyingly, did result in the formation of the corresponding pyridines **6b**−**6e** in good yields (Table 2, entries 10−13). Furthermore, **6e** could also be obtained in good yields starting from **3f**−**3h**, regardless of the difference of the alkylthio groups of **3** (Table 2, entries 14−16). However, in the case of the reactions between **3i** and ammonium acetate, under the conditions described in Table 1, entry 2, no reaction occurred; under the conditions described in Table 1, entry 9, and reacted for 48 h, **5i** was obtained in 36% isolated yield with 63% of **3i** recovered (Table 2, entry 8), and no product **6i** was detected. In addition, for precursor **3j**, with an electron-withdrawing chloro group on the aryl ring, under both conditions described in Table 1, entry 2 and entry 9, no reactions occurred, and only **3j** was recovered (Table 2, enties 9 and 17). The significant difference between the reactivities of **3i**, **3j**, and **3a**−**3h** may indicate that the electron-donating nature of the aryl substitute of **3** plays an important role in the annulation reaction.

On the basis of all above experiments and our previous works,[12] the possible mechanisms for the formation of pyridine derivatives **5** and **6** are proposed as shown in Scheme 3. The intermediates **7** is first formed via aza-Michael-S_NV reaction of 1,1-bisalkylthio-1,4-pentanediene **3** with ammonia and the subsequent transformations can be temperature dependent. When the temperature is controlled at 65 °C, an intermolecular thia-Michael addition of thiolate anion through path A is preferred, which leads to intermediate **8**. By this way, pyridine **5** is finally provided through the consecutive intramolecular aza-annulation. Whereas, when the temperature is raised to 120 °C, the intramolecular aza-Michael addition of **7** through path B is more likely to occur, which leads to intermediate **10**. Finally, pyridine **6** can be formed via the subsequent elimination of an alkylthiol and oxidation process.

It should be noted that the highly selective formation of two types of pyridines can be attributed to the promising structural features of the five-carbon fragments **3**, which include: (1) the potential dual 1,5-bielectrophilic units as shown in Scheme 3; (2) the important multiple role of the dialkylthio group acting as leaving group in the S_NV process (for example, in the transformation from **3** to **7** in Scheme 3), elimination (for example, from **9** to **5** and **10** to **6** in Scheme 3) to meet the aromatic requirements, and the adjustment to the annulation by the intermolecular thia-Michael addition from **7** to **8** as shown in Scheme 3.

In summary, the novel temperature-controlled efficient synthesis of pyridine derivatives through one-pot [5C + 1N] annulation reactions of the 1,1-bisalkylthio-1,4-pentanedienes **3** and ammonium acetate has been developed. Two types of pyridine derivatives **5** and **6** were synthesized in good to high yields, which can be attributed to the notable features of 1,1-bisalkylthio-1,4-pentanedienes **3**. The expansion of this methodology and the further synthetic application of **3** are in progress.

Experimental Section

General Procedure for the Preparation of 5 (with 5a as an example). To a well-stirred solution of **3a** (344 mg, 1.0 mmol) and ammonium acetate (308 mg, 4.0 mmol) in 5 mL of *N*,*N*-dimethylformamide (DMF). The reaction mixture was well stirred at 65 °C for 6.0 h (monitored by TLC). Then the above mixture was poured into ice−water, extracted with dichloromethane (10 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by a flash silica gel column chromatography to give product **5a** (248 mg, 83%) as a yellow solid (eluent: diethyl ether/petroleum ether = 1/1).

Selected data for 5a: mp 130−132 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.25 (t, J = 7.5 Hz, 3H), 2.43 (q, J = 7.5 Hz, 2H), 3.83 (s, 3H), 4.97 (s, 1H), 5.42 (s, 2H), 6.91 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 7.53 (s, 1H), 8.30 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.4, 26.5, 49.0, 55.6, 99.2, 114.8, 118.3, 120.1, 129.2, 129.9, 139.7, 151.7, 158.9, 159.7; IR (KBr) 3113, 2361, 2216, 1641, 1250; MS (*m*/*z*): 300.1 $[(M + 1)]^+$; Anal. Calcd for $C_{16}H_{17}N_3OS$: C, 64.19; H, 5.72; N, 14.04; Found C, 64.26; H, 5.69; N, 13.99.

General Procedure for the Preparation of 6 (with 6a as an example): To a well-stirred solution of **3a** (344 mg, 1.0 mmol) and ammonium acetate (616 mg, 8.0 mmol) in 5 mL of *N*,*N*-dimethylformamide (DMF). The reaction mixture was well stirred at 120 °C for 1.0 h (monitored by TLC). Then the above mixture was poured into ice−water, extracted with dichloromethane (10 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by a flash silica gel column chromatography to give product **6a** (127 mg, 54%) as a yellow solid (eluent: diethyl ether/petroleum ether = 1/15).

Selected data for 6a: mp 162−164 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.91 (s, 3H), 7.08 (d, J = 8.5 Hz, 2H), 8.06 (d, J = 8.5 Hz, 2H), 8.29 (s, 1H), 9.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz)

δ 55.5, 106.5, 107.1, 114.2, 114.5, 115.0, 116.3, 127.8, 131.1, 145.0, 154.3, 162.6; IR (KBr) 3153, 2978, 2360, 2342, 1589, 1446, 1262; MS (*m/z*): 236.1$[(M + 1)]^+$; Anal. Calcd for $C_{14}H_9N_3O$: C, 71.48; H, 3.86; N, 17.86; Found C, 71.39; H, 3.90; N, 17.51.

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Supporting Information Available: Experimental details and full characterization data, copies of ^1H and ^{13}C NMR spectra for all new compounds, CIF for compound **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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