Novel Syntheses of the Major Flavor Components of Bread and Cooked Rice

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A new synthetic pathway toward the Maillard flavor compounds 6-acyl-1,2,3,4-tetrahydropyridines and 2-acetyl-1-pyrroline is presented. The reaction sequence involves deprotonation of a vicinal diimine and subsequent alkylation with an N,N-diprotected ω-bromoalkylamine, followed by deprotection and intramolecular transimination of the functionalized intermediate. Acidic workup affords the above-mentioned heterocycles, which are principal flavor constituents of bread and cooked rice, respectively. In addition, the synthesis of the more stable diethyl acetal of 2-acetyl-1-pyrroline is described.

Keywords: *Rice flavor; bread flavor; 2-acetyl-1-pyrroline; 6-acetyl-1,2,3,4-tetrahydropyridine; Maillard*

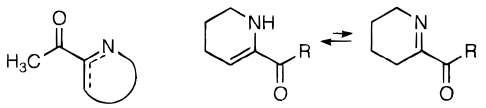
INTRODUCTION

A wide range of heterocyclic compounds play an important role in food science as food flavors, formed by either enzymatic or nonenzymatic processes. The nonenzymatic browning reaction, better known as the Maillard reaction, takes place between reducing sugars and the free amino groups of amino acids or proteins. Several Maillard products, more specifically azaheterocycles with the structural unit **1** (Scheme 1), in which the nitrogen atom and the adjacent carbon atom are part of a ring structure, exhibit biscuit- or cracker-like odors (Folkes and Gramshaw, 1981).

6-Acetyl-1,2,3,4-tetrahydropyridine (**2**) is the principal bread flavor component, which occurs in tautomeric equilibrium with its imino form **3** (Scheme 1). This compound displays a characteristic strong cracker-like flavor in freshly baked bread (Hunter et al., 1969) and in the crust of rye bread (Schieberle and Grosch, 1983, 1984). The higher analogue, 6-propionyl-1,2,3,4-tetrahydropyridine (**4**), and its imino tautomer **5** have also been identified as Maillard products with a cracker-like flavor (Schreier, 1981; Ledl and Schleicher, 1990).

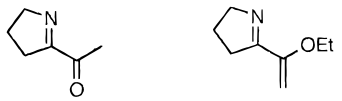
2-Acetyl-1-pyrroline (**6**) (Scheme 2) also belongs to the group of cracker-like compounds and is considered to be the major flavor component of cooked rice (Buttery et al., 1982, 1983a, 1986, 1988; Lin et al., 1990). With an odor threshold value of 0.1 ppb in water (Buttery et al., 1988), it appears to be one of the most potent members of this group of Maillard flavor components. 2-Acetyl-1-pyrroline (**6**) was also found to be a character-impact compound in wheat bread crust and a minor flavor in rye bread crust (Schieberle and Grosch, 1985, 1987; Schieberle, 1988). In contrast with the six-membered ring analogue **3**, which always occurs in tautomeric equilibrium with its enamino tautomer **2**, the enamino form of 2-acetyl-1-pyrroline (**6**) has never been observed in significant amounts next to **6**. Since its first identification in cooked rice, 2-acetyl-1-pyrroline (**6**) has also been isolated from entirely different sources, e.g. Pandan leaves (*Pandanus amaryllifolius* Roxb) (Buttery et al., 1983b), cooked beef (Gasser and Grosch, 1988), and even the urine of tigers, which is used for territorial and sexual connotations (Brahmachary and Sarkar, 1990). Since the aroma character of a dilute solution of 2-acetyl-1-pyrroline (**6**) shows great resemblance to that of cooked rice (Buttery et al., 1982), this compound has been used as a flavorant to impart a scented rice flavor to foods (Buttery et al., 1985).

Scheme 1



1 **2** R = Me, **4** R = Et **3** R = Me, **5** R = Et

Scheme 2



6 **7**

Because of the considerable instability of 2-acetyl-1-pyrroline (**6**), recent synthetic efforts focused on more stable, carbonyl-protected analogues, such as the 1-ethoxyethenyl derivative **7** (Duby and Huynh, 1993). After hydrolytic conversion of compound **7** into **6** and immediate encapsulation on carbohydrate matrices, the flavoring agent **6** remained stable during a period of 110 days at −20 °C (Duby and Huynh, 1993). Likewise, upon addition of the encapsulated compound **7** to foods, it would hydrolyze gradually, thus providing a slow release of 2-acetyl-1-pyrroline (**6**).

At present, only a limited number of synthetic routes toward the flavor components **2**, **4**, and **6** have been reported (Hunter et al., 1969; Büchi and Wüest, 1971; Buttery et al., 1983a; De Kimpe and Stevens, 1993, 1995; De Kimpe et al., 1993a; Duby and Huynh, 1993; Rewicki et al., 1993), all of which are restricted to one or two of these flavor compounds. In this paper, a straightforward, attractive, and versatile synthetic route to all three aroma compounds **2**, **4**, and **6**, as well as a convenient synthesis of a stable, carbonyl-protected analogue of 2-acetyl-1-pyrroline, is disclosed.

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EXPERIMENTAL PROCEDURES

Synthesis of 6-Acetyl-1,2,3,4-tetrahydropyridine (2). A solution of 5.04 g (30 mmol) of α-diimine **9a** (Armesto et al., 1987; De Kimpe et al., 1991) in dry THF (10 mL) was added dropwise at 0 °C under nitrogen to an in situ prepared stirred solution of 30.6 mmol of lithium diisopropylamide (LDA) in dry THF (from diisopropylamine and *n*-butyllithium). After 6 h of stirring at 0 °C, a solution of 9.24 g (33 mmol) of stabase derivative **10a** (Djuric et al., 1981) in dry THF (10 mL) was added. The stirred reaction mixture was allowed to reach room temperature during 15 h, after which time it was poured into 100 mL of an aqueous NaOH solution (0.5 N), extracted with ether (3 × 50 mL), and dried (K_2CO_3). After filtration of the drying agent and evaporation in vacuo, the residue was dissolved in 100 mL of MeOH, and after addition of 12.42 g (90 mmol) of K_2CO_3, the resulting suspension was stirred under gentle reflux for a period of 3 h. The reaction mixture was then poured into 150 mL of water, extracted with CH_2Cl_2 (3 × 100 mL), and dried (K_2CO_3). After filtration and evaporation of the solvent, the residue was dissolved in 100 mL of ether, after which a solution of 7.56 g (60 mmol) of $(COOH)_2 \cdot 2H_2O$ in 100 mL of water was added. This two-layer system was shaken thoroughly, and the aqueous phase was isolated. After further extraction of the latter phase with ether (2 × 100 mL), it was basified with solid NaOH and extracted with CH_2Cl_2 (3 × 100 mL), after which the combined CH_2Cl_2 layers were dried (K_2CO_3). After filtration and evaporation of the solvent, the residue (2.45 g, 65% yield) consisted of a 1:4 mixture of 6-acetyl-1,2,3,4-tetrahydropyridine (**2**) and its imino tautomer **3**, respectively (purity ≥95%; GC−MS, ^{1}H NMR, ^{13}C NMR). The ratio of **2** to **3** gradually changed upon standing until the tautomeric equilibrium was reached, at which point this ratio amounted to approximately 3:1, respectively. The reaction mixture may be distilled (bp 23−29 °C/0.01 mmHg), but the yield dropped dramatically (0.83 g, 22%); distillation did not result in any significant further purification (purity 96%; GC). All spectral data (^{1}H and ^{13}C NMR, IR, MS) of compounds **2** and **3** were consistent with an earlier literature report (De Kimpe and Stevens, 1993).

Synthesis of 6-Propionyl-1,2,3,4-tetrahydropyridine (4). The procedure used to prepare **4** starting from diimine **9b** is essentially the same as described above for the synthesis of 6-acetyl-1,2,3,4-tetrahydropyridine (**2**). For the preparation of **4**, 1.05 equiv of LDA and 1.2 equiv of **10a** were used. Starting from 5.46 g (30 mmol) of **9b**, 2.81 g (67%) of nearly pure **4**+**5** was obtained (purity ≥98%; ^{1}H and ^{13}C NMR, GC−MS). The reaction mixture was distilled (bp 71−76 °C/7 mmHg) but resulted again in a poor yield (1.50 g, 36%). IR (NaCl) 1645−1695 cm^{-1} (C═O and C═N). Other spectral data of **4** and **5** were deduced from a sample containing a tautomeric mixture of **4** and **5**. The mass spectral data of tautomers **4** and **5** were consistent with an earlier literature report (Ledl and Schleicher, 1990).

Spectral data of **4**: ^{1}H NMR ($CDCl_3$) δ 1.11 (3H, t, J = 7.59 Hz, Me), 1.8−1.9 (2H, m, CH_2CH$_2$N), 2.2−2.3 (2H, m, CH$_2$C═C), 2.67 (2H, q, J = 7.59 Hz, CH$_2$C═O), 3.16 (2H, ∼t, CH$_2$N), 5.64 (1H, t, J = 4.46 Hz, CH═), NH invisible; ^{13}C NMR ($CDCl_3$) δ 8.99 (Me), 21.89 and 22.66 (each CH$_2$), 28.95 (*C*H$_2$C═O), 40.99 (CH$_2$N), 108.01 (CH═), 141.40 (═CN), 197.41 (C═O); mass spectrum, *m*/*z* (%) 139 (M$^+$, 81), 124 (57), 97 (42), 96 (100), 82 (43), 79 (16), 69 (85), 68 (43), 55 (41), 54 (24), 44 (43), 43 (87), 42 (54), 41 (60).

Spectral data of **5**: ^{1}H NMR ($CDCl_3$) δ 1.07 (3H, t, J = 7.26 Hz, Me), 1.6−1.8 [4H, m, (CH_2)$_2$CH$_2$C═N], 2.3−2.4 (2H, m, CH$_2$C═N), 2.84 (2H, q, J = 7.26 Hz, CH$_2$C═O), 3.7−3.8 (2H, m, NCH$_2$); ^{13}C NMR ($CDCl_3$) δ 7.85 (Me), 18.81 and 21.70 (each CH$_2$), 23.97 (*C*H$_2$C═N), 29.54 (*C*H$_2$C═O), 50.13 (CH$_2$N), 166.84 (C═N), 202.67 (C═O); mass spectrum, *m*/*z* (%) 139 (M$^+$, 81), 138 (21), 124 (34), 111 (30), 110 (24), 96 (16), 84 (23), 83 (92), 82 (85), 80 (15), 68 (11), 67 (12), 57 (80), 56 (19), 55 (84), 54 (100), 53 (19), 52 (11), 44 (16), 42 (17), 41 (34).

Synthesis of 2-Acetyl-1-pyrroline (6). 2-Acetyl-1-pyrroline (**6**) was prepared from α-diimine **9a** (30 mmol) and stabase derivative **10b** in essentially the same way as described above for the synthesis of **2**. According to ^{1}H and ^{13}C NMR data and GC analysis, the residue obtained after acidic and basic workup with two equiv of $(COOH)_2 \cdot 2H_2O$ was a mixture of 2-acetyl-1-pyrroline (**6**) (81%), its isomer **12** (8%), and some unidentified, slightly higher boiling compounds (11%). The yield of **6** in the reaction mixture was 43%. Distillation of this residue did not result in any further purification (bp 22−24 °C/0.25 mmHg). 2-Acetyl-1-pyrroline (**6**) was isolated from this mixture via preparative gas chromatography. All spectral data (^{1}H and ^{13}C NMR, IR, MS) were identical to data reported in the literature (De Kimpe et al., 1993a). As mentioned above, no traces of the enamino form of 1-pyrroline **6** could be detected (^{1}H and ^{13}C NMR).

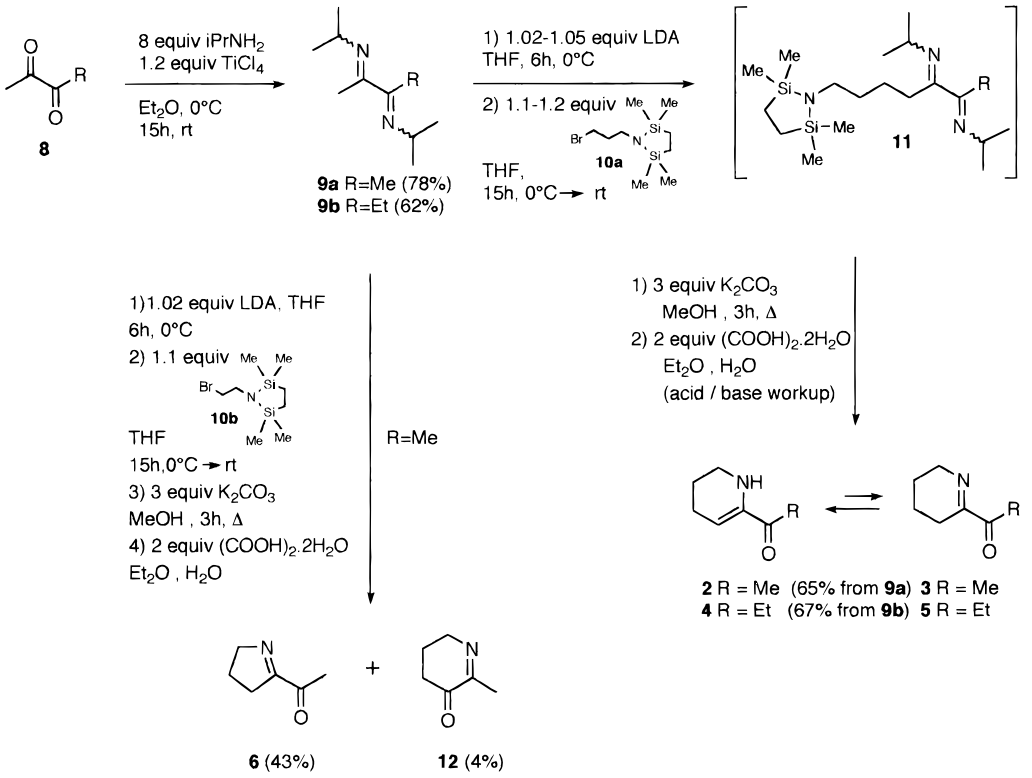
Synthesis of 2-(1,1-Diethoxyethyl)-1-pyrroline (18). The procedure used to prepare **18** from α,α-diethoxyimine **17** (De Kimpe and Stevens, 1995) and stabase derivative **10b** is essentially the same as described above for the synthesis of piperideine **2** from diimine **9a**. For the preparation of **18**, 1.2 equiv of LDA was used, and only 1 equiv of $(COOH)_2 \cdot 2H_2O$ was used for the acidic and basic workup. Starting from 35 mmol of imine **17**, 4.12 g (64%) of pure 1-pyrroline **18** was obtained after flash chromatography (pentane:Et$_2$O 3:7, R_f = 0.27; purity ≥99%; GC−MS, ^{1}H and ^{13}C NMR). Spectral data of **18**: ^{1}H NMR ($CDCl_3$) δ 1.22 (6H, t, J = 6.92 Hz, 2 × OCH$_2$C*H*$_3$), 1.50 [3H, s, *Me*C(OEt)$_2$], 1.89 (2H, ∼pent., J = ∼7.92 Hz, C*H*$_2$CH$_2$N), 2.60 (2H, txt, J_1 = 8.58 Hz, J_2 = 1.98 Hz, CH$_2$C═N), 3.45 (2H, dxq, J_1 = 9.23 Hz, J_2 = 6.92 Hz, OCH$_2$), 3.55 (2H, dxq, J_1 = 9.23 Hz, J_2 = 6.92 Hz, OCH$_2$), 3.94 (2H, txt, J_1 = 7.26 Hz, J_2 = 1.98 Hz, CH$_2$N); ^{13}C NMR ($CDCl_3$) δ 15.40 (2 × OCH$_2$*C*H$_3$), 22.44 [*Me*C(OEt)$_2$], 22.53 (CH$_2$), 34.88 (*C*H$_2$C═N), 57.11 (2 × OCH$_2$), 61.35 (NCH$_2$), 100.07 (Cq), 178.45 (C═N); IR (NaCl) 1648 cm^{-1} (C═N); mass spectrum, *m*/*z* (%) 185 (M$^+$, <1), 141 (13), 140 (38), 117 (47), 112 (84), 96 (10), 95 (11), 94 (9), 89 (40), 70 (33), 68 (14), 61 (100), 45 (13), 44 (13), 43 (94), 42 (19), 41 (52). Anal. Calcd for $C_{10}H_{19}O_2N$: N, 7.56. Found: N, 7.70.

Hydrolysis of 1-Pyrroline 18. A mixture of 1.85 g (10 mmol) of **18** and 50 mL (100 mmol) of 2N HCl aqueous solution was stirred at room temperature for 2 days, after which time it was cooled to −5 °C. Under vigorous stirring at this temperature, a 1 N aqueous solution of NaOH was added dropwise very slowly (caution!) until the solution was alkaline. This aqueous solution was extracted with CH_2Cl_2 (3 × 30 mL) and dried ($MgSO_4$). After filtration and evaporation of the solvent, the residue (1.02 g, 92% yield) was analyzed immediately (GC, ^{1}H and ^{13}C NMR) and consisted of 2-acetyl-1-pyrroline (**6**) and its structural isomer **12** in a ratio of 47:53, respectively. Both compounds **6** and **12** were isolated via preparative gas chromatography. All spectral data (^{1}H and ^{13}C NMR, IR, MS) of 2-acetyl-1-pyrroline (**6**) were consistent with literature data (De Kimpe et al., 1993). Spectral data of **12**: ^{1}H NMR ($CDCl_3$) δ 2.08−2.12 (2H, m, CH_2CH$_2$N), 2.12 (3H, s, Me), 2.52 (2H, ∼t, J = 6.93 Hz, CH$_2$C═O), 3.81−3.86 (2H, m, NCH$_2$); ^{13}C NMR ($CDCl_3$) δ 18.60 (Me), 22.70 (CH$_2$), 35.33 (CH$_2$), 48.65 (NCH$_2$), 163.00 (C═N), 189.90 (C═O); IR (NaCl) 1695 (C═O), 1630 cm^{-1} (C═N); mass spectrum, *m*/*z* (%) 111 (M$^+$, 35), 83 (27), 55 (81), 54 (8), 44 (54), 43 (22), 42 (100), 41 (43).

RESULTS AND DISCUSSION

For the syntheses of the bread flavor compounds **2** and **4**, the principal rice flavor component **6** and its protected form **18**, a recently developed strategy for the synthesis of cyclic imines was used (De Kimpe et al., 1993). This procedure involved α-deprotonation with LDA and α-alkylation of a suitable imine with a stabase-protected ω-bromoalkylamine **10**, which led to an amino-protected functionalized imine (such as **11**) as the key intermediate (Scheme 3). Deprotection of the primary amine function resulted in spontaneous cyclization via transimination and formation of the desired azaheterocycle. To synthesize the flavor components **2**, **4**, and **6** in this way, the diimines **9** were prepared from the corresponding α-diones **8** (Armesto et al., 1987; De

Scheme 3

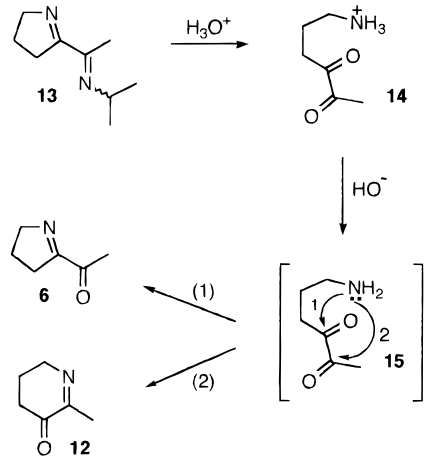


Kimpe et al., 1991). Elaboration of α-diimine **9a** in the above-described strategy with stabase derivative **10a** as alkylating agent and acid/base workup of the resulting heterocycle provided a convenient synthesis of the principal bread flavor compound **2** (purity ≥95%). The freshly prepared crude reaction mixture consisted of enamine **2** and its imino tautomer **3** in a 1:4 ratio, respectively. Upon distillation, this ratio altered to 2:3, after which it changed further to approximately 3:1, at which point tautomeric equilibrium was obtained.

The higher homologue, 6-propionyl-1,2,3,4-tetrahydropyridine (**4**), which is also a Maillard flavor compound isolated from the bread crust, was synthesized in an essentially similar manner as described for **2**, starting from α-diimine **9b**. The purity of this flavor compound **4** in the reaction mixture (after acid/base workup) was excellent (>98%) because of the more selective deprotonation (exclusively at the least substituted side) of **9b**, as compared to that of the lower analogue **2**. The ratio of enamino form **4** to imino form **5** changed similarly on standing. Starting from a 1:4 ratio in the crude reaction mixture, the ratio of **4** to **5** mounted to 2:5 upon distillation, after which it slowly changed further to approximately 7:3 (tautomeric equilibrium).

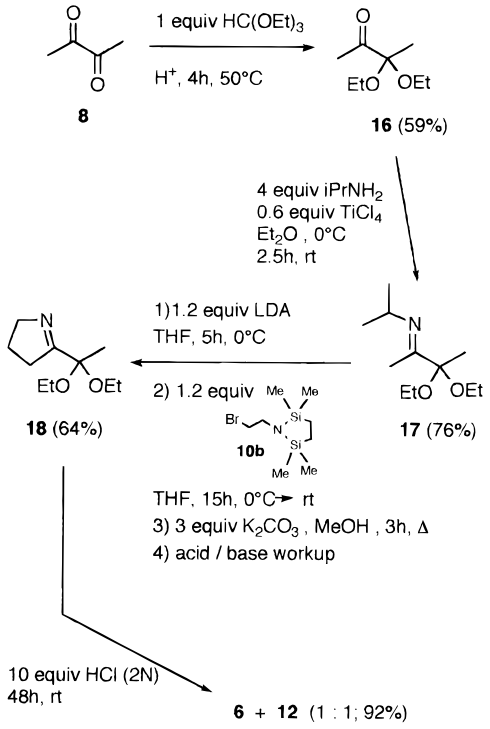
In view of the excellent results achieved in the synthesis of 6-acyl-1,2,3,4-tetrahydropyridines **2** and **4**, the research was headed toward the synthesis of 2-acetyl-1-pyrroline (**6**), the principal rice flavor component. To prepare this compound, α-diimine **9a** and stabase derivative **10b** were applied in the same synthetic pathway as described above (Scheme 3). This procedure resulted in a reaction mixture containing the desired flavor compound **6** in moderate yield (43%), next to the structural isomer **12** (4%) and several minor unidentified impurities. The latter impurities are probably due to the above mentioned—and in this case more pronounced—lack of selectivity during deprotonation and alkylation of the symmetrical α-diimine **9a**. This

Scheme 4



weaker selectivity led to the formation of α,α′-dialkylated derivatives in minor amounts, and an equal amount of nonalkylated α-diimine **9a**, both resulting in a significantly lower yield of 2-acetyl-1-pyrroline (**6**). According to GC−MS analysis, the relative amount of compounds originating from double alkylation in the reaction mixture was approximately 10−15%. The formation of 6-methyl-5-oxo-2,3,4,5-tetrahydropyridine (**12**) can be explained as follows (Scheme 4): When 2-imidoyl-1-pyrroline (**13**), which is formed after the deprotection step, is subjected to the usual acid/base workup, ring opening occurs, leading to the intermediate α-dione **14**. Upon basification, the primary amine attacked both carbonyl functions of the α-dione moiety, resulting in the two structural isomers **6** and **12**. An important factor that affects the ratio of **6** to **12** seemed to be the excess of acid used. The use of only 1 equiv of oxalic acid (instead of 2) led to a mixture containing only 39% of the desired 2-acetyl-1-pyrroline (**6**) and 50% of compound **12**, next to 11% of the earlier mentioned

Scheme 5

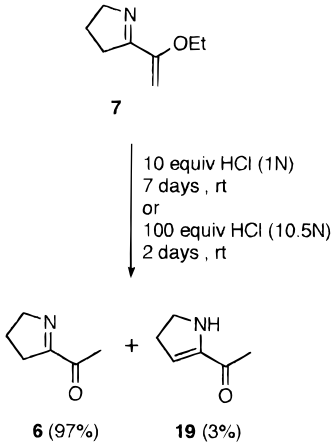


impurities. A thorough investigation concerning this reaction step is currently under way.

Because of the instability of 2-acetyl-1-pyrroline (**6**) and the potential of carbonyl-protected forms of **6** as "slow-release" flavorants, synthetic efforts were finally directed toward the synthesis of the protected analogue **18**. Such synthetic endeavours could also provide a simple solution to the difficulties encountered during the direct synthesis of 2-acetyl-1-pyrroline (**6**) (vide supra). Compound **18** was prepared according to the same sequence of reactions as described for the synthesis of **6**, but in this case starting from α,α-diethoxyketimine **17**. The latter imine was prepared from α-dione **8** via α-keto acetal **16** (De Kimpe and Stevens, 1995) (Scheme 5). According to a sequence of reactions involving α-deprotonation of **17**, α-alkylation with stabase electrophile **10b**, N,N-deprotection, and transimination, the protected rice flavor component **18** was obtained, free of side products, in good yield after flash chromatography. An additional advantage of this particular compound **18** in its potential use as flavoring agent in foods is the fact that two natural products are formed upon gradual hydrolysis, i.e., ethanol and the principal rice flavor component **6**.

In a recent literature report, the synthesis of the protected analogue **7** was described (Duby and Huynh, 1993); **7** is structurally very similar to our synthesized analogue **18**. According to this paper, 1-pyrroline derivative **7** could be hydrolyzed into the flavor compound **6** (purity 97%), along with a minor amount of 2-acetyl-2-pyrroline (**19**) (3%), using a large excess of hydrochloric acid under various conditions (Scheme 6). Applying this procedure of hydrolysis to our analogue **18** resulted in an approximately 1:1 mixture of the desired 2-acetyl-1-pyrroline (**6**) and its structural isomer **12**. Although this result is consistent with our earlier observations concerning the hydrolysis of 2-imidoyl-1-pyrroline **13** (Scheme 4), it seems quite strange that no similar reaction has been observed during the hydrolysis of pyrroline **7** (Duby and Huynh, 1993). Also, the (albeit minor) presence of the enamino tautomer **19** in the

Scheme 6



mixture after hydrolysis of **7** does not fit our findings, nor any other earlier literature reports. It might be that the structural identification of **19** was wrong (Duby and Huynh, 1993) and that it in fact concerned the isomeric compound **12**, characterized in the present research.

In conclusion, a convenient and straightforward synthetic pathway toward three major rice and bread flavor components is presented. Furthermore, an attractive synthesis of a carbonyl-protected analogue of 2-acetyl-1-pyrroline is described, which could be a potential flavoring agent in rice preparations and bakery products.

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