

Synthesis of 2-Acetyl-1-pyrroline, the Principal Rice Flavor Component

Norbert G. De Kimpe,* Christian V. Stevens, and Marian A. Keppens

Department of Organic Chemistry, Faculty of Agricultural and Applied Biological Sciences,
University of Gent, Coupure Links 653, B-9000 Gent, Belgium

A new straightforward synthesis of 2-acetyl-1-pyrroline, the principal rice flavor component with a cracker-like flavor, is reported. The reaction sequence involves the conversion of pyrrolidine into tripyrroline, subsequent hydrocyanation of the latter into 2-cyanopyrrolidine, oxidation into 2-cyano-1-pyrroline, and Grignard addition of methylmagnesium iodide, affording an overall yield of 16-19% from pyrrolidine. In similar way, 2-propionyl-1-pyrroline, a recently discovered flavor component of popcorn, was prepared in addition to several higher analogues, i.e., 2-acyl-1-pyrrolines. Also, the synthesis of 2-(acetyl- d_3)-1-pyrroline, a deuterated derivative of the rice flavor compound which is useful for the stable isotope dilution assay, is described.

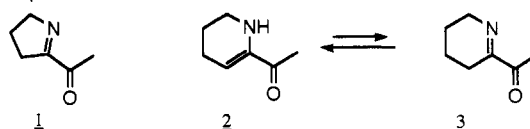
INTRODUCTION

A variety of heterocyclic compounds, originating from enzymatic reactions of several substrates and nonenzymatic browning reactions, are distributed in food flavors. The nonenzymatic browning reaction between reducing sugars and α -amino acids is known as the Maillard reaction, which becomes more important at higher temperatures. Some of the heterocyclic Maillard products display a characteristic strong cracker-like flavor. 2-Acetyl-1,2,3,4-tetrahydropyridine (2), which occurs in tautomeric equilibrium with its imino form 3, is a very potent cracker-like flavor and is considered to be the principal bread flavor component (Hunter et al., 1969; Schieberle and Grosch, 1983, 1984). The lower analogue, 2-acetyl-1-pyrroline (1), has a similar cracker-like flavor and is considered to be the most important flavor component of cooked rice (Buttery et al., 1982, 1983a, 1986, 1988; Lin et al., 1990; Teranishi and Buttery, 1985). 2-Acetyl-1-pyrroline (1) has been identified and isolated from different varieties of cooked rice (Buttery et al., 1982, 1983a, 1986, 1988; Lin et al., 1990) and the crust of wheat and rye breads (Schieberle and Grosch, 1985, 1987; Schieberle, 1988). It is remarkable that 2-acetyl-1-pyrroline (1) has been found in Pandan leaves (*Pandanus amaryllifolius* Roxb) (Buttery et al., 1983b). It has long been the practice in India and other parts of Asia to use leaves of *Pandanus* species in the cooking of common rices to impart a resemblance of the aroma of the more costly scented rice. 2-Acetyl-1-pyrroline (1) is also present in the flavor of cooked beef, where it contributes to the "roasted" aroma (Gasser and Grosch, 1988). Compound 1 was recently tentatively identified in the urine of tigers, which use it for territorial and sexual connotations (Brahmachary and Sarkar, 1990).

The aroma character of a dilute solution of 2-acetyl-1-pyrroline (1) is very similar to that of cooked rice (Buttery et al., 1982). The odor threshold value of this compound is extremely low, i.e., 0.1 ppb (in H_2O) (Buttery et al., 1988). Therefore, this compound has been used in flavoring foods, particularly in imparting a scented rice flavor to foods (Buttery et al., 1984, 1985).

At present, only one synthetic route to 2-acetyl-1-pyrroline (1) has been published (Buttery et al., 1983a, 1984, 1985). This synthesis entails hydrogenation of 2-acetylpyrrole with rhodium on alumina, followed by oxidation of the resulting amino alcohol by means of an excess of silver carbonate, absorbed on Celite, in benzene (Schieberle and Grosch, 1985). The drawbacks of this

Scheme I



procedure are the use of very expensive reagents (rhodium and silver salts), the low overall yield of 10%, the use of toxic chemicals, e.g., benzene, in the last step of the sequence, and the virtual inaccessibility of the compound on a larger scale (the flavor compound was isolated by preparative gas chromatography to separate it from several side products).

We disclose here now a straightforward and attractive synthetic route to 2-acetyl-1-pyrroline (1) (De Kimpe et al., 1991). The procedure utilizes cheap, basic chemicals and is amenable to large-scale production of the flavor material.

EXPERIMENTAL PROCEDURES

Synthesis of 2-(Methoxycarbonyl)-1-pyrroline (6) (Poisel and Schmidt, 1975; Häusler and Schmidt, 1979). A solution of 5.16 g (40 mmol) of methyl proline (5) (Guttman, 1961) in 70 mL of dry ether was treated with 4.43 g (40.8 mmol) of *tert*-butyl hypochlorite at 0 °C. After 45 min of stirring at 0 °C, 4.12 g (40.8 mmol) of triethylamine was added, and stirring was continued at room temperature for 18 h. The heterogeneous reaction mixture was filtered, the filter cake washed with dry ether, and the filtrate evaporated in vacuo. The residue was treated again with dry ether and filtered and the filtrate evaporated to afford 4.88 g (96%) of pure 2-(methoxycarbonyl)-1-pyrroline (6): bp 41-44 °C (12 mmHg) [lit. bp 43 °C (13 mmHg) (Häusler and Schmidt, 1979)].

Reaction of 2-(Methoxycarbonyl)-1-pyrroline (6) with Methylmagnesium Iodide. The reaction of α -iminoester 6 with methylmagnesium iodide in ether was performed with various molar equivalents (1.1-1.3) of the Grignard reagent at temperatures from 0 °C to room temperature during 3 to 20 h. In all cases, variable mixtures of starting material 6, 2-acetyl-1-pyrroline (1), and 2-(1-hydroxy-1-methylethyl)-1-pyrroline (7) were obtained after aqueous workup (see Results and Discussion). The best result was obtained with 1.2 equiv of methylmagnesium iodide in ether at 0 °C during 20 h. The reaction mixture contained then 83% 2-acetyl-1-pyrroline (1) and 8% each of starting material 6 and the alcohol 7. The three compounds were separated by preparative gas chromatography. 2-Acetyl-1-pyrroline (1) was identical in all aspects (IR, MS, 1H NMR) to the data reported in the literature (Buttery et al., 1982, 1983a). In addition, the ^{13}C NMR spectrum supported the structure: δ

22.32 (t, CH₂), 33.27 (t, CH₂C=N), 62.66 (t, CH₂N), 26.00 (q, Me), 174.35 (s, C=N), 197.72 (s, C=O).

2-(1-Hydroxy-1-methylethyl)-1-pyrroline (7): ¹H NMR (CDCl₃) δ 1.36 (6H, s, Me₂), 1.7–2.3 (2H, m, CH₂), 2.4–2.8 (2H, m, CH₂C=N), 3.7–4.0 (2H, m, CH₂N), 4.2 (1H, s, br, OH); ¹³C NMR δ 23.87 (t, CH₂), 28.04 (q, Me₂), 32.93 (t, CH₂C=N), 59.96 (t, CH₂N), 71.05 (s, COH), 183.59 (s, C=N); IR (NaCl) 3100–3600 (OH), 1642 cm⁻¹ (C=N); mass spectrum *m/z* (%) 127 (M⁺, 0.2), 126 (1), 112 (21), 84 (7), 70 (25), 69 (14), 68 (10), 59 (25), 43 (100), 42 (24), 41 (38).

Reaction of 2-(Methoxycarbonyl)-1-pyrroline 6 with Methylolithium in Ether. A solution of 0.508 g (4 mmol) of α-iminoester 6 in 20 mL of dry ether was treated dropwise with 4 mL of 1.06 M methylolithium in ether at –30 °C (nitrogen atmosphere). The reaction mixture was stirred for 20 h during which time the temperature rose to room temperature. The mixture was poured into water, and extraction was performed three times with pentane. The combined extracts were dried (MgSO₄) and evaporated to give 80 mg of a clear oil, consisting of 2-acetyl-1-pyrroline (1) and 2-(1-hydroxy-1-methylethyl)-1-pyrroline (7) in a 4:1 ratio, respectively (GC, ¹H NMR). The aqueous layer was then extracted three times with dichloromethane, and the combined extracts were dried (MgSO₄) and evaporated to afford 300 mg of an oil, consisting of a 1:1 ratio of 1 and 7 (GC, ¹H NMR). The total yields of 2-acetyl-1-pyrroline (1) and the alcohol 7 were 47% and 32%, respectively.

Synthesis of 2-Cyanopyrrolidine (10). Pyrrolidine (8) was oxidized to 1-pyrroline trimer 9 by aqueous sodium peroxodisulfate as described in the literature (Ogawa et al., 1982). The crude trimer 9, obtained from 7.1 g (0.1 mol) of pyrrolidine, was directly treated with aqueous hydrogen cyanide, prepared from 0.2 mol of potassium cyanide and 0.2 mol of 4 N HCl (hood!) under cooling with an ice bath. If necessary, some additional 12 N HCl was added dropwise to acidify the solution. The mixture was stirred at ambient temperature for 1 h. Sodium hydroxide pellets were added under cooling till alkaline. The aqueous phase was extracted three times with dichloromethane, and the organic phases were dried (MgSO₄) and evaporated in vacuo to leave an oil, which was distilled in vacuo to afford 6.2 g (65%) of 2-cyanopyrrolidine (10): bp 70–75 °C (14 mmHg) [lit. bp 168–172 °C (Bonnett et al., 1959)]; ¹H NMR (CDCl₃) δ 1.7–2.3 (4H, m, CH₂CH₂), 3.13 (2H, t, *J* = 6 Hz, NCH₂), 4.10 (1H, t, *J* = 5.5 Hz, CHN); ¹³C NMR (CDCl₃) δ 24.22 (t, CH₂), 30.89 (t, CH₂), 45.95 (t, NCH₂), 47.49 (d, NCH), 121.76 (s, C=N); IR (NaCl) 3340 (NH), 2220 cm⁻¹ (C=N).

Synthesis of 2-Cyano-1-pyrroline (12). A solution of 3.84 g (0.04 mol) of 2-cyanopyrrolidine (10) in 50 mL of dry ether was treated with 4.34 g (0.04 mol) of *tert*-butyl hypochlorite at 0 °C. After 1 h of stirring at this temperature, 4.04 g (0.04 mol) of triethylamine was added, and stirring was continued for an overnight period. The precipitate was filtered and washed with dry ether, and the filtrate was evaporated without heating in vacuo. The remaining *tert*-butyl alcohol was evacuated under high vacuum (0.05 mmHg) for 30 min. The remaining imido-cyanide (12) was obtained in 90–95% yield and was used immediately in the next step. This compound can be distilled [bp 80 °C (15 mmHg)], but it offers no advantage: ¹H NMR (CDCl₃) δ 2.0 (2H, quintet, *J* = 6 Hz, CH₂), 2.5–2.9 (2H, m, CH₂C=N), 3.9–4.3 (2H, m, CH₂N); ¹³C NMR (CDCl₃) δ 21.65 (t, CH₂), 38.95 (t, CH₂), 63.12 (t, CH₂N), 114.42 (s, C=N); 151.40 (s, C=N); IR (NaCl) 2220 (C=N), 1670 cm⁻¹ (C=N); mass spectrum *m/z* (%) 94 (M⁺, 94), 93 (63), 79 (9), 66 (100), 54 (25), 52 (9), 42 (41), 41 (31).

Synthesis of 2-Acetyl-1-pyrroline (1). Freshly prepared 2-cyano-1-pyrroline (12) (3.76 g, 0.04 mol), obtained as described above, was dissolved in 20 mL of dry ether, and this solution was cooled in an ice bath. This cold solution was added dropwise to a vigorously stirred solution of freshly prepared methylmagnesium iodide in ether at –20 °C (the Grignard reagent was prepared from 0.12 mol of magnesium turnings and 0.12 mol of iodomethane in 120 mL of dry ether under reflux for 1 h). After complete addition of the imido-cyanide (12), stirring was continued for 1 h. The supernatant was cautiously poured into a stirred ice-cold aqueous ammonium chloride solution in an Erlenmeyer. The viscous residue remaining in the reaction flask was triturated with the ice-cold mixture from the Erlenmeyer. The clear organic

and aqueous layers were vigorously stirred for 20 min at ambient temperature. The organic layer was isolated, and the aqueous phase was extracted twice with ether. The combined ether extracts were dried (MgSO₄) for 30 min. The drying agent was filtered and replaced for a fresh portion of MgSO₄. After drying overnight at 5 °C, the drying agent was filtered and the solvent removed in vacuo without heating to afford 2.2 g (40%) of light yellow oil, which consisted of pure (purity ≥96%; GC, ¹H NMR) 2-acetyl-1-pyrroline (1) (see data above). This compound darkened rapidly on standing at room temperature in neat form. The compound is preferably kept in dilute solution (pentane, dichloromethane; 1% w/v) at –20 °C. After an initial decantation from a small amount of dark viscous liquid (after 1 week at –20 °C), the clear solution is stable for several months at –20 °C (up to now, under the latter conditions, a good stability over a period of 2 years was observed).

Synthesis of 2-(Propionyl)-1-pyrroline (14). This popcorn flavor component was prepared from imido-cyanide 12 and ethylmagnesium bromide (1.5 molar equiv) in ether at room temperature for 30 min, using the procedure described above for the synthesis of 2-acetyl-1-pyrroline (1): yield 67%; bp 74–76 °C (16 mmHg); ¹H NMR (CDCl₃) δ 1.12 (3H, t, *J* = 7 Hz, Me), 1.93 (2H, quintet, *J* = 7 Hz, CH₂), 2.5–3.2 (4H, m, CH₂C=N, CH₂C=O), 3.9–4.3 (2H, m, CH₂N); ¹³C NMR (CDCl₃) δ 7.66 (q, Me), 22.12 (t, CH₂), 31.59 (t, CH₂Me), 33.53 (t, CH₂C=N), 62.59 (t, CH₂N), 174.07 (s, C=N), 200.82 (s, C=O); IR (NaCl) 1700 (C=O), 1622 cm⁻¹ (C=N); mass spectrum *m/z* (%) 125 (M⁺, 6), 124 (3), 97 (62), 96 (22), 70 (12), 69 (59), 68 (22), 57 (97), 42 (19), 41 (100). This mass spectrum matches satisfactorily the data reported for compound 14 prepared according to an alternative method (Schieberle, 1991).

Synthesis of 2-(2-Methylpropionyl)-1-pyrroline (15). This compound was prepared from imido-cyanide 12 and isopropylmagnesium bromide (1.5 molar equiv) in ether at room temperature for 30 min, using the procedure described for the synthesis of 2-acetyl-1-pyrroline (1): yield 14%; bp 74–76 °C (14 mmHg); ¹H NMR (CDCl₃) δ 1.11 (6H, d, *J* = 7 Hz, Me₂), 1.92 (2H, quintet, *J* = 7 Hz, CH₂), 2.5–2.9 (2H, m, CH₂C=N), 3.61 (1H, septet, *J* = 7 Hz, CHC=O), 3.9–4.3 (2H, m, CH₂N); ¹³C NMR (CDCl₃) δ 18.42 (q, Me), 22.08 (t, CH₂), 33.88 (t, CH₂C=N), 35.71 (d, CHMe₂), 62.70 (t, CH₂N), 173.57 (s, C=N), 203.59 (s, C=O); IR (NaCl) 1700 cm⁻¹ (C=O), 1620 cm⁻¹ (C=N); mass spectrum *m/z* (%) 139 (M⁺, 4), 111 (10), 110 (6).

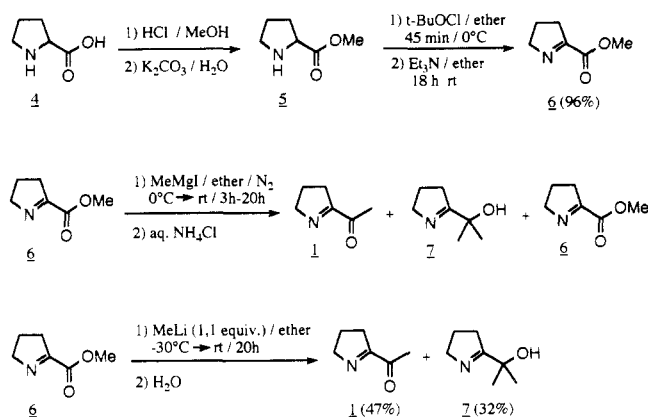
Synthesis of 2-(Valeroyl)-1-pyrroline (16). This compound was prepared from imido-cyanide 12 and butylmagnesium bromide (1.5 molar equiv) in ether at room temperature for 30 min, using the procedure described for the synthesis of 2-acetyl-1-pyrroline (1): yield 22%; bp 98–101 °C (17 mmHg); ¹H NMR (CDCl₃) δ 0.90 (3H, t, *J* = 7 Hz, Me), 1.1–1.7 (4H, m, CH₂CH₂), 1.90 (2H, quintet, *J* = 7 Hz, CH₂), 2.5–3.0 (4H, m, CH₂C=N, CH₂C=O), 3.8–4.3 (2H, m, CH₂N); ¹³C NMR (CDCl₃) δ 13.80 (q, Me), 22.13 (t, CH₂), 22.39 (t, CH₂), 25.94 (t, CH₂), 33.51 (t, CH₂C=N), 38.03 (t, CH₂C=O), 62.59 (t, CH₂N), 174.37 (s, C=N), 200.13 (s, C=O); IR (NaCl) 1698 (C=O), 1620 cm⁻¹ (C=N); mass spectrum *m/z* (%) 153 (M⁺, 11), 138 (8), 125 (8), 124 (16), 110 (5), 98 (57), 97 (29), 85 (13), 83 (12), 70 (20), 69 (100), 68 (13), 57 (46), 55 (8), 41 (88), 39 (36).

Synthesis of 2-(Acetyl-d₃)-1-pyrroline (17). This compound was synthesized from imido-cyanide 12 (0.03 mol) and methylmagnesium-d₃ iodide (1.5 molar equiv; prepared from 99+ atom % D methyl-d₃ iodide and magnesium turnings in ether; 30-min reflux) in ether for 1 h at room temperature, using the procedure described for the synthesis of 2-acetyl-1-pyrroline (1): yield 55%; ¹H NMR (CDCl₃) δ 1.93 (2H, quintet, *J* = 7.5 Hz, CH₂), 2.5–3.0 (2H, m, CH₂C=N), 3.8–4.3 (2H, m, CH₂N); ¹³C NMR (CDCl₃) δ 22.42 (t, CH₂), 33.28 (t, CH₂C=N), 62.67 (t, CH₂N), 174.53 (s, C=N), 197.55 (s, C=O), CD₃ invisible; IR (NaCl) 1695 (C=O), 1620 cm⁻¹ (C=N); mass spectrum *m/z* (%) 114 (M⁺, 12), 113 (4), 112 (4), 111 (3), 94 (6), 86 (11), 85 (4), 84 (3), 70 (11), 69 (14), 68 (9), 67 (2), 66 (4), 46 (100), 45 (35), 44 (23), 43 (12), 42 (56), 41 (30), 40 (35), 39 (11).

RESULTS AND DISCUSSION

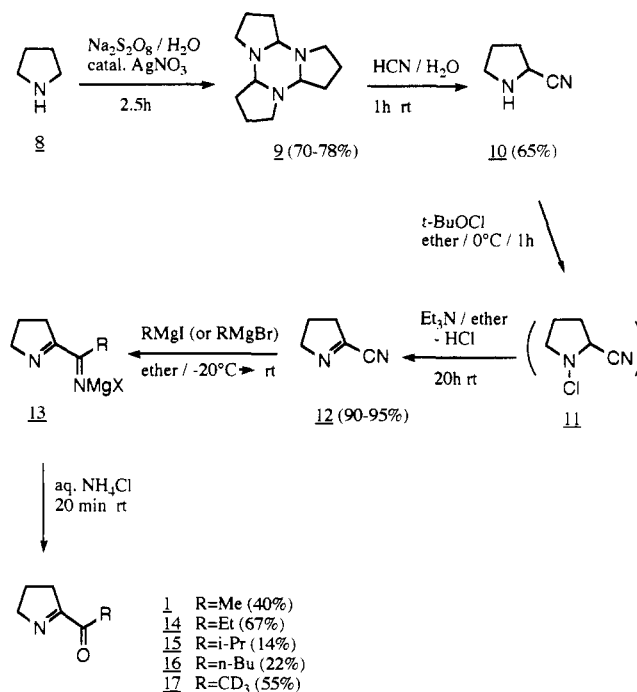
Due to the fact that 2-acetyl-1-pyrroline (1) has a major potential for use in bakery products and rice preparations,

Scheme II



synthetic attempts were directed toward the obtention of a final product which was free of side products, which might hamper use in the flavor industry. The first efforts focused on the conversion of the methoxycarbonyl moiety of 2-(methoxycarbonyl)-1-pyrroline (6) into an acetyl moiety. 2-(Methoxycarbonyl)-1-pyrroline (6) was prepared from proline (4) via esterification with hydrogen chloride in methanol and subsequent N-chlorination of methyl prolinates (5) with *tert*-butyl hypochlorite and following dehydrochlorination with triethylamine (Poisel and Schmidt, 1975; Häusler and Schmidt, 1979). The reaction of 2-(methoxycarbonyl)-1-pyrroline (6) with methylmagnesium iodide (1.1–1.3 equiv) in ether at 0 °C to room temperature led to mixtures of the desired 2-acetyl-1-pyrroline (1), the alcohol 7, and starting material 6 in variable ratios depending on the number of molar equivalents of the Grignard reagent and the temperature. 2-Acetyl-1-pyrroline was formed in 45–83% yield, while the yield of alcohol 7 ranged from 6 to 29%. The starting material was always present in 8–39% yield. Also, methyllithium in ether converted α -iminoester 6 into a mixture of 2-acetyl-1-pyrroline (1) (47%) and the alcohol 7 (32%). Both the Grignard reagent and the alkyl lithium reagent gave rise to a further addition of the desired ketone 1. Despite the fact that neither method allowed the preparation of 2-acetyl-1-pyrroline (1) without interference of side products, these methods give a simple access to the flavor compound from proline in a way much faster and easier than reported procedures (Buttery et al., 1982, 1983a) using expensive rhodium and silver reagents. Instead of utilizing more selective 2-(alkoxycarbonyl)-1-pyrrolines or analogues, or instead of using more selective organometallic methyl-transfer reagents, attention was paid to an attractive alternative solution to the problem, namely the addition of a Grignard reagent to the nitrile moiety of 2-cyano-1-pyrroline (12). This imidoyle cyanide 12 was prepared via a sequence of reactions (Scheme III), involving oxidation of pyrrolidine (8) with aqueous sodium peroxodisulfate in the presence of catalytic amounts of silver nitrate (Ogawa et al., 1982), the resulting tripyrroline 9, i.e., 1,6,11-triazatetracyclo[10.3.0.0^{2,6}.0^{7,11}]pentadecane, being hydrocyanated into 2-cyanopyrrolidine (10). This α -aminonitrile 10 was oxidized via N-chlorination with *tert*-butyl hypochlorite and subsequent dehydrochlorination using triethylamine. The resulting imidoyle cyanide 12 was obtained in 90–95% yield from 2-cyanopyrrolidine (10). Reaction of imidoyle cyanide 12 with methylmagnesium iodide in ether at -20 °C afforded the magnesium salt of 2-acetimidoyle-1-pyrroline (13), which was hydrolyzed with aqueous ammonium chloride to give 2-acetyl-1-pyrroline (1) in 60% yield, free of side products. In similar way, addition of ethylmagnesium bromide to

Scheme III



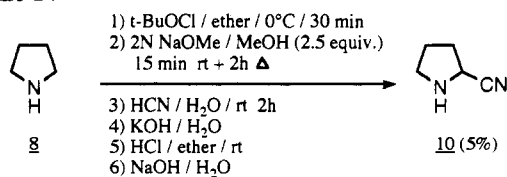
imidoyle cyanide 12 produced 2-propionyl-1-pyrroline (14) in 67% yield. Recently, this compound 14 was identified as an important flavor component of popcorn (Schieberle, 1991) and was synthesized by condensation of 2-pyrrolylmagnesium iodide with propionyl chloride, followed by hydrogenation and partial oxidation of the resulting β -amino alcohol. According to this literature paper, compound 14 was obtained in an unspecified yield and was purified by preparative gas chromatography (Schieberle, 1991).

2-Propionyl-1-pyrroline (14) has an odor threshold value comparable to that of 2-acetyl-1-pyrroline (1) (Schieberle, 1991). Higher analogues, such as 2-(2-methylpropionyl)-1-pyrroline (15) and 2-valeroyl-1-pyrroline (16), were prepared by addition of isopropylmagnesium bromide or butylmagnesium iodide, respectively, to imidoyle cyanide 12. Recently, it was found that the higher homologues 2-butanoyl- and 2-hexanoyl-1-pyrroline, which do not occur in foodstuffs, have a 10⁵ higher odor threshold value than 2-(2-propionyl)- and 2-acetyl-1-pyrroline (Schieberle, 1991).

The method described above also allowed the synthesis of deuterated 2-acetyl-1-pyrroline, useful for the stable isotope dilution assay (Schieberle and Grosch, 1987). The reaction of 2-cyano-1-pyrroline (12) with methylmagnesium-*d*₃ iodide in ether afforded, after hydrolytic workup with aqueous ammonium chloride, 2-(acetyl-*d*₃)-1-pyrroline (17) in 55% yield. There is no obvious reason why this yield was higher than for the synthesis of 2-acetyl-1-pyrroline. Up to now, only ring-deuterated 1-acetyl-2-pyrroline was available in the literature (Schieberle and Grosch, 1987). The present method, affording specifically deuterated 2-acetyl-1-pyrroline (deuterated exclusively at the methyl group), offers now a well-defined tool for the quantitative analysis of the rice flavor component 1 using the stable isotope dilution assay (Schieberle and Grosch, 1987). However, it should be verified if this labeling is stable during workup procedures, because deuteration α to a carbonyl group facilitates a protium/deuterium exchange in aqueous medium.

Instead of preparing 1-pyrroline trimer 9 and performing the subsequent cyanation, we tried to obtain 2-cyanopyrrolidine (10) from pyrrolidine (8) without the isolation of

Scheme IV



intermediates. To this end, pyrrolidine was reacted with *tert*-butyl hypochlorite in ether, and the resulting *N*-chloropyrrolidine was treated with sodium methoxide in methanol under reflux. The reaction mixture, containing presumably 1-pyrroline and the trimer **9**, was treated with aqueous hydrogen cyanide. After neutralization with aqueous potassium hydroxide, 2-cyanopyrrolidine (**10**) was obtained in very poor yield (overall yield 5%), after purification via its hydrochloride form (Scheme IV). Therefore, it seems that the cyanation of pyrrolidine via 1-pyrroline without isolation of the corresponding trimer is not a suitable synthetic way. More expensive alternatives include the cyanation of 4-aminobutanal diethylacetal in acid medium (Bonnett et al., 1959) or the cyanation of pyrrolidine using phenylseleninic anhydride and trimethylsilyl cyanide (Barton et al., 1985).

ACKNOWLEDGMENT

The Belgian National Fund for Scientific Research is thanked for financial support of this project.

LITERATURE CITED

- Barton, D.; Billon, A.; Boivin, J. *Tetrahedron Lett.* **1985**, *26*, 1229–1232.
 Bonnett, R.; Clark, V. M.; Giddey, A.; Todd, A. *J. Chem. Soc.* **1959**, 2087–2093.
 Brahmachary, R. L.; Sarkar, M. P. *Nature* **1990**, *344*, 26.
 Buttery, R. G.; Ling, L. C.; Juliano, B. O. *Chem. Ind.* **1982**, 958–959.

- Buttery, R. G.; Ling, L. C.; Juliano, B. O.; Turnbaugh, J. G. *J. Agric. Food Chem.* **1983a**, *31*, 823–826.
 Buttery, R. G.; Juliano, B. O.; Ling, L. C. *Chem. Ind.* **1983b**, 478.
 Buttery, R. G.; Ling, L. C.; Juliano, B. O. U.S. Pat. 500,049, Feb 3, 1984.
 Buttery, R. G.; Ling, L. C.; Juliano, B. O. U.S. Pat. 4,522,838, June 11, 1985.
 Buttery, R. G.; Ling, L. C.; Mon, T. R. *J. Agric. Food Chem.* **1986**, *34*, 112–114.
 Buttery, R. G.; Turnbaugh, J. G.; Ling, L. C. *J. Agric. Food Chem.* **1988**, *36*, 1006–1009.
 De Kimpe, N.; Stevens, C.; Schamp, N. Eur. Pat. Appl. EP 436,481 (Cl. C07D207/20), July 10, 1991; Appl. 90/870,004, Jan 4, 1990; *Chem. Abstr.* **1991**, *115*, 158981.
 Gasser, U.; Grosch, W. *Z. Lebensm. Unters. Forsch.* **1988**, *186*, 489–494.
 Guttman, S. *Helv. Chim. Acta* **1961**, *44*, 721–744.
 Häusler, J.; Schmidt, U. *Liebigs Ann. Chem.* **1979**, 1881–1889.
 Hunter, I. R.; Walden, M. K.; Scherer, J. R.; Lundin, R. E. *Cereal Chem.* **1969**, *46*, 189–195.
 Lin, C. F.; Hsieh, T. C. Y.; Hoff, B. J. *J. Food Sci.* **1990**, *55*, 1466–1469.
 Poisel, H.; Schmidt, U. *Chem. Ber.* **1975**, *108*, 2547–2553.
 Ogawa, K.; Nomura, Y.; Takeuchi, Y.; Tomoda, S. *J. Chem. Soc., Perkin Trans. 1* **1982**, 3031–3035.
 Schieberle, P. *Getreide, Mehl Brot* **1988**, *220*, 334–335.
 Schieberle, P. *J. Agric. Food Chem.* **1991**, *39*, 1141–1144.
 Schieberle, P.; Grosch, W. *Z. Lebensm. Unters. Forsch.* **1983**, *177*, 173–180.
 Schieberle, P.; Grosch, W. *Z. Lebensm. Unters. Forsch.* **1984**, *178*, 479–483.
 Schieberle, P.; Grosch, W. *Z. Lebensm. Unters. Forsch.* **1985**, *180*, 474–478.
 Schieberle, P.; Grosch, W. *J. Agric. Food Chem.* **1987**, *35*, 252–257.
 Teranishi, R.; Buttery, R. G. In *Chemical Changes in Food during Processing*; Richardson, T., Finley, J. W., Eds.; AVI Publishing: Westport, CT, 1985; Chapter 15, p 327.

Received for review February 9, 1993. Accepted June 2, 1993.