# Cyanation of α-Ketoalkynes Catalyzed by Nickel in Water

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α-Ketoalkynes react with KCN, catalyzed by anionic Ni(0) cyano complexes in water, affording unsaturated hydroxylactams. The active anionic species, thought to be $[Ni(CN)_4]^{4-}$, can be formed in situ from Ni(II) cyano compounds under various reduction conditions. A possible mechanism, excluding Ni−hydride intermediates, is proposed.



## Introduction

The nickel-catalyzed hydrocyanation reaction of unsaturated substrates is a well-studied reaction and constitutes probably one of the best industrial application of homogeneous catalysis in the last decades.[1] In most cases it is through the addition of HCN, in the presence of Ni(0) complexes, that the reaction is performed,[2] although some examples catalyzed by cyanonickelate ions have been reported in which KCN is the cyanation entity in the presence of excess reducing agents such as $NaBH_4$.[3] In this last case, applied only to alkynyl substrates, the hydrocyanation is accompanied by a hydrogenation reaction leading to saturated nitriles.

Zerovalent nickel anions are also encountered in carbonylation reactions and have been used with a wide variety of substrates.[4−23] We report here the case of one of these substrates,[23] α-ketoalkynes, in which the carbonylation reaction was transformed into a nickel-mediated cyanation reaction in the presence of excess cyanide ions.

## Results and Discussion

The use of $Ni(CN)_2$ as a precursor for catalytic carbonylation reactions of various substrates under biphasic systems is well-documented. This anionic catalytic system replaces advantageously $Ni(CO)_4$-catalyzed carbonylations mainly because of its lower volatility and the ease with which it can be handled. The active species is thought to arise from the base attack of a cyano group, leading to loss of a carbamic acid moiety and reduction of nickel to zero valency,[9] the role of CO at this stage being thought to be simply to stabilize the Ni(0) anionic complex.

$$Ni^{II}(CN)_2 \xrightarrow[H_2O/HO^-]{CO} \underset{\mathbf{1}}{[Ni^0(CO)_3CN]^-} + HOOC-NH_2$$

Complex **1** has been used as a carbonylation catalyst with a wide variety of substrates, generally by a nucleophilic attack of the anion, followed by CO insertion.

In a recent study[23] in which α-ketoalkynes were cleanly carbonylated to unsaturated hydroxylactones, we observed, in trace amounts, the formation of the corresponding unsaturated hydroxylactam. This could conceivably arise from the introduction of a cyanide group instead of a CO insertion, corresponding formally to a hydrocyanation reaction, and might possibly be enhanced by replacing, in **1**, CO ligands by cyanide ions.

Such a ligand exchange could formally be schematized as follows:[24]

$$Ni(CO)_4 \rightleftarrows \underset{\mathbf{1}}{[Ni^0(CO)_3CN]^-} \rightleftarrows \underset{\mathbf{2}}{[Ni^0(CO)_2(CN)_2]^{2-}} \rightleftarrows \underset{\mathbf{3}}{[Ni^0(CO)(CN)_3]^{3-}} \rightleftarrows \underset{\mathbf{4}}{[Ni^0(CN)_4]^{4-}}$$

Treatment of non-4-yn-3-one under the "carbonylation" conditions[23] but in the presence of excess KCN

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(1) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley Interscience: New York, 1992.
(2) Tolman, C. A.; McKinney, R. J.; Siedel, W. C.; Druliner, J. D.; Stevens, W. R. *Adv. Catal.* **1985**, *33*, 1.
(3) Funabiki, T.; Sato, H.; Tanaka, N.; Yamazaki, Y.; Yoshida, S. *J. Mol. Catal.* **1990**, *62*, 157.
(4) Des Abbayes, H.; Alper, H. *J. Am. Chem. Soc.* **1977**, *99*, 98.
(5) Cole, K. C. T.; Slegeir, W.; Pettit, R. *J. Am. Chem. Soc.* **1978**, *100*, 3969.
(6) Januszkiewicz, K.; Alper, H. *J. Mol. Catal.* **1983**, *19*, 139.
(7) Del Rosario, R.; Stuhl, L. S. *J. Am. Chem. Soc.* **1984**, *106*, 1160.
(8) Hashem, K. E.; Petrignani, J. F.; Alper, H. *J. Mol. Catal.* **1984**, *26*, 285.
(9) Joó, F.; Alper, H. *Organometallics* **1985**, *4*, 1775.
(10) Joó, F.; Alper, H. *Can. J. Chem.* **1985**, *63*, 1157.
(11) Amer, I.; Bravdo, T.; Blum, J. *Tetrahedron Lett.* **1987**, *28*, 1321.
(12) Amer, I.; Alper, H. *J. Org. Chem.* **1988**, *53*, 5147.
(13) Amer, I.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 927.
(14) Alper, H.; Amer, I.; G. Vasapollo, G. *Tetrahedron Lett.* **1989**, *30*, 2615.
(15) Alper, H.; Vasapollo, G. *Tetrahedron Lett.* **1989**, *30*, 2617.
(16) Amer, I.; Alper, H. *J. Organomet. Chem.* **1990**, *383*, 573.
(17) Satyanarayana, N.; Alper, H.; Amer, I. *Organometallics* **1990**, *9*, 284.
(18) Lee, J. T.; Alper, H. *Tetrahedron Lett.* **1991**, *32*, 1769.
(19) Satyanarayana, N.; Alper, H. *Organometallics* **1991**, *10*, 804.
(20) Arzoumanian, H.; Cochini, F.; Nuel, D.; Petrignani, J. F.; Rosas, N. *Organometallics* **1992**, *11*, 493.
(21) Arzoumanian, H.; Cochini, F.; Nuel, D.; Rosas, N. *Organometallics* **1993**, *12*, 1871.
(22) Ben Taleb, A.; Jenner, G. *J. Organomet. Chem.* **1993**, *456*, 263.
(23) Arzoumanian, H.; Jean, M.; Nuel, D.; Cabrera, A.; Garcia Gutierrez, J. L.; Rosas, N. *Organometallics* **1995**, *14*, 5438.
(24) Burg, A. B.; Dayton, J. C. *J. Am. Chem. Soc.* **1949**, *71*, 3233.

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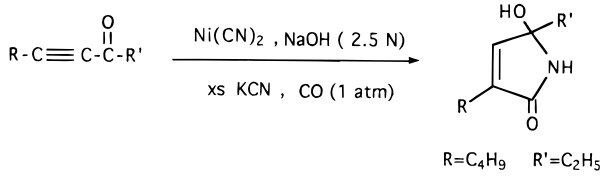
**Table 1. Reaction of α-Ketoalkynes with KCN in Water in the Presence of Ni(0) Anions**

| ketone | R | R′ | time (h) | temp (°C) | yield (%)[a] | lactam |
|---|---|---|---|---|---|---|
| **5** | *n*-$C_4H_9$ | $CH_3$ | 3 | 25 | 77 | **12** |
| **6** | *n*-$C_4H_9$ | $C_2H_5$ | 20 | 25 | 83 | **13** |
| **6** | *n*-$C_4H_9$ | $C_2H_5$ | 0.6 | 50 | 70 | **13** |
| **6** | *n*-$C_4H_9$ | $C_2H_5$ | 18 | 25 | 84 | **13**[b] |
| **6** | *n*-$C_4H_9$ | $C_2H_5$ | 2 | 25 | 65 | **13**[c] |
| **7** | *n*-$C_4H_9$ | *n*-$C_3H_7$ | 3 | 60 | 65 | **14** |
| **8** | *n*-$C_4H_9$ | *t*-$C_4H_9$ | 4 | 60 | 50[d] | **15** |
| **9** | $C_6H_5$ | $CH_3$ | 20 | 25 | 76 | **16** |
| **10** | $C_6H_5$ | $C_2H_5$ | 3 | 25 | 68 | **17** |
| **11** | $C_6H_5$ | *n*-$C_3H_7$ | 6 | 25 | 56 | **18** |

[a] Isolated yields with 100% conversion. Reaction catalyzed by $Ni(CN)_2$/CO/KCN. [b] Reaction catalyzed by $K_2Ni(CN)_4$/$NaBH_4$/KCN. [c] Reaction run with $K_2Ni(CN)_4$/Zn/KCN (see Experimental Section). [d] Isolated yield with 50% conversion.

gave as sole product the desired unsaturated hydroxylactam in good yield.



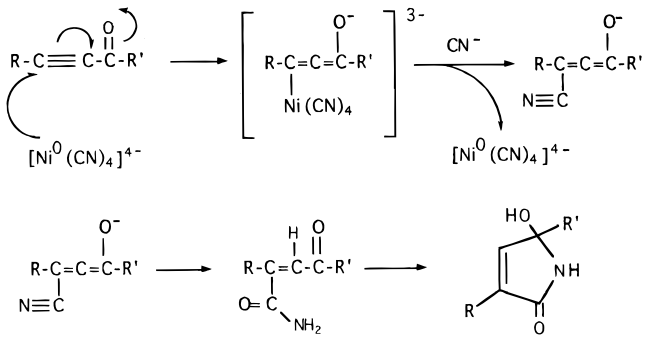

The nature of the active species, under these reaction conditions, is difficult to establish. Compound **2** has been characterized[25,26] and proposed as an intermediate,[27] whereas compound **3** has neither been isolated nor well characterized.[24] On the other hand compound **4**, first discovered in 1942,[28] has been shown to be active in hydrocyanation reactions;[3] it can be obtained directly in solution by reduction of $K_2[Ni(CN)_4]$ with $NaBH_4$ or metallic zinc in the presence of KCN.[3]

When non-4-yn-3-one was treated in water with $K_2[Ni(CN)_4]$, $NaBH_4$, and excess KCN, the unsaturated hydroxylactam was equally obtained as the only product, suggesting that the active species in all these reactions is indeed the anion $[Ni^0(CN)_4]^{4-}$ (**4**).[29] The results obtained with other α-ketoalkynes are given in Table 1, showing the general character of the reaction.

Hydrocyanation of unsaturated substrates catalyzed by Ni(0) species is a well documented reaction. The most known and studied system is the addition of HCN catalyzed by nickel(0) phosphite complexes in the presence or absence of Lewis acids.[2,30] It is well established that these reactions involve the intermediacy of a nickel hydride. Similarly, when anion **4** is reacted with alkynes in the presence of KCN and excess $NaBH_4$ or metallic zinc, a nickel hydride has been proposed as the intermediate and the reaction products are saturated nitriles arising from hydrocyanation and hydrogenation.[3]

The absence of any hydrogenated products, under our reaction conditions, seems to exclude the intermediacy of any hydridic species. Furthermore, the similarity of results observed with anion **4** obtained either via $NaBH_4$ or metallic zinc reduction of $K_2[Ni(CN)_4]$, or via anion **1** and excess KCN, in which no hydride can be generated, strongly suggests a pathway different from those reported earlier.[3,30]

A plausible mechanism could be analogous to the one retained for the unsaturated hydroxylactone formation, with the active species being here the anion **4**:[23]







Another pathway, proceeding by a prior coordination of the triple bond followed by a free cyanide nucleophilic attack, cannot be totally excluded, although it is less probable regarding the lack of reaction observed with $K_2[Ni(CN)_4]$ alone.[29]

In conclusion, $[Ni^0(CN)_4]^{4-}$ (**4**) obtained either via reduction of $[Ni(CN)_4]^{2-}$ or via replacement of CO ligands by cyanide ions on $[Ni(CO)_3CN]^-$ (**1**) appears to be a versatile hydrocyanation mediator. The scope of this novel reaction is presently being studied with other substrates.

## Experimental Section

**General Comments.** Solvents and reagents were reagent grade and used as received from commercial suppliers unless otherwise stated. α-Ketoalkynes were synthesized by a method described in the literature,[31] and checked for their purity with IR and $^1H$ and $^{13}C$ NMR techniques. NMR spectra were recorded on a Bruker AC 200, AC 100, or Varian Unity Plus 500 instrument. IR spectra were recorded on a Perkin-Elmer 1720X spectrophotometer. Elemental analyses were done by the microanalysis service of the University Aix-Marseille III.

**Synthesis of α-Ketoalkynes. General Procedure.**[31] To a 40 mL THF solution containing 100 mmol of alkyne (e.g. phenylacetylene), cooled to −60 °C, was added dropwise 100 mmol of an *n*-BuLi solution in *n*-hexane (40 mL, 2.5 N), with the temperature maintained below −50 °C and with vigorous stirring. A 90 mL THF solution containing 100 mmol of $ZnCl_2$ was then added, with the temperature kept below 10 °C. The resulting mixture was cooled to 0 °C, and 100 mmol of acyl chloride (e.g., propionyl chloride) was added while the temperature was kept below 10 °C during the addition. It was then alowed to reach room temperature and stirred for 45 min. The hydrolysis was done by adding to the reaction mixture cooled to −10 °C, 170 mL of an aqueous solution containing 0.4 mol of $NH_4Cl$. The organic phase was separated and the aqueous phase extracted with diethyl ether (4 × 50 mL). The combined extracts were washed with a saturated solution of $NH_4Cl$ (4 × 50 mL), dried over $MgSO_4$, and evaporated. The α-ketoalkyne (e.g., 1-phenylpent-1-yn-3-one) was purified by distillation under reduced pressure.

Compounds **5**,[32] **6**,[33] **8**,[34] **9**,[35] **10**,[36] and **11**[37] were prepared by this method. Their spectral (IR, $^1H$ NMR,$^{13}C$ NMR) and elemental analyses were in accord with those reported.

(25) Nast, R.; Schulz, H.; Moerler, H. D. *Chem. Ber.* **1970**, *103*, 777.
(26) Nast, R.; Roos, H. *Z. Anorg. Allg. Chem.* **1953**, *272*, 242.
(27) Del Rosario, R.; Stuhl, L. S. *Tetrahedron Lett.* **1982**, 3999.
(28) Eastes, J. W.; Burgess, W. M. *J. Am. Chem. Soc.* **1942**, *64*, 1189.
(29) Treatment of non-4-yn-3-one with $K_2[Ni(CN)_4]$, metallic zinc, and KCN, under stoichiometric conditions, yielded also the lactam. Furthermore, the use of $Ni(CN)_2$ or $K_2[Ni(CN)_4]$ alone under analogous experimental conditions resulted in the recovery of starting material.
(30) Bäckvall, J. E.; Andell, O. S. *Organometallics* **1986**, *5*, 2350.
(31) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: New York, 1988; Vol. 34, pp 24, 36, and 105.
(32) Hoye, T. R.; Suriano, J. A. *J. Org. Chem.* **1993**, *58*, 1659.
(33) Ma, D.; Yu, Y.; Lu, X. *J. Org. Chem.* **1989**, *54*, 1105.

**Reaction of α-Ketoalkynes with $Ni(CN)_2$/NaOH/CO/KCN. General Procedure.** A 5 N NaOH solution (25 mL) was saturated by *slowly* bubbling CO at room temperature for 30 min. To the solution was then added 2 mmol of $Ni(CN)_2 \cdot 4H_2O$ (366 mg), and stirring was continued under a CO atmosphere until a pale yellow solution was obtained. Addition of 15 mmol of KCN (975 mg) resulted in an immediate color change to orange. After stirring for 30 min, the orange solution was diluted with 25 mL of degassed water and the α-ketoalkyne (8 mmoles) was added. The evolution of the reaction was followed by TLC. The reaction time and temperature are given in Table 1 (note: the yields were generally higher when the CO atmosphere was kept throughout the reaction). At the end of the reaction, ethyl acetate (2 × 20 mL) was used to extract the product. Evaporation of the solvent after drying over $MgSO_4$ yielded nearly pure crystalline products.

**Reaction of Non-4-yn-3-one with $K_2[Ni(CN)_4]$/NaOH/$NaBH_4$/KCN.** Preparation of the reduced nickelate salt was done as described by Funabiki et al.[3] In a Schlenk tube, under a nitrogen atmosphere, were placed 240 mg (1 mmol) of $K_2[Ni(CN)_4]$, 490 mg (7.5 mmol) of KCN, and 189 mg (5 mmol) of $NaBH_4$. The solid mixture was stirred for 2 h before a 2.5 N NaOH solution (25 mL) was added yielding an orange solution that was stirred at room temperature for 1 h. After this period of time, acetone (300 mg) was added to eliminate the excess $NaBH_4$. The red solution obtained was stirred for 30 min before non-4-yn-3-one (4 mmol) was added. The orange solution obtained was stirred at room temperature for 18 h. Ethyl acetate (2 × 20 mL) was used to extract the product. Upon evaporation of the combined organic extracts, dried over $MgSO_4$, the lactam was isolated as a white solid in 84% yield.

**Reaction of Non-4-yn-3-one with $K_2[Ni(CN)_4]$/$H_2O$/Zn/KCN.** Preparation of the reduced nickelate salt was done as described by Funabiki et al.[3] In a Schlenk tube under a nitrogen atmosphere were placed $K_2[Ni(CN)_4]$ (2 mmol, 482 mg), KCN (4 mmol, 252 mg), and zinc powder (10 mmol, 378 mg). The solid mixture was vigorously stirred for 1 h. Water (10 mL) was then added to give a reddish suspension which was stirred for one additional hour before non-4-yn-3-one (2 mmol, 276 mg) was added. After the mixture was stirred for 2 h at room temperature, the product was extracted with ethyl acetate (2 × 20 mL) to give 65% lactam and 15% unreacted α-ketoalkyne.

**Dec-5-yn-4-one (7).**[38] Compound **7** was prepared as described in the general procedure for the synthesis of ynones from 1-hexyne (12.6 g, 0.153 mol) and butyryl chloride (16.3 g, 0.153 mol) and was obtained as a colorless liquid (bp 70 °C/2 mbar) with 77% yield. Anal. Calcd (found) for $C_{10}H_{16}O$: C, 78.90 (79.11); H, 10.59 (11.32). IR (selected, $cm^{-1}$): 2212 (C≡C), 1678 (CO). $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ (ppm): 0.94 (t, 3H, $CH_3CH_2CH_2CH_2$, $J = 7$ Hz), 0.95 (t, 3H, $CH_3CH_2CH_2$, $J = 7$ Hz), 1.39−1.76 (m, 6H, $CH_3CH_2CH_2$ and $CH_3CH_2CH_2CH_2$), 2.38 (t, 2H, $CH_3CH_2CH_2CH_2$, $J = 7$ Hz), 2.52 (t, 2H, $CH_3CH_2CH_2$, $J = 7$ Hz). $^{13}C$ {$^1H$} NMR (50 MHz, $CDCl_3$), $\delta$ (ppm): 13.3, 13.4 ($CH_3CH_2CH_2$ and $CH_3CH_2CH_2CH_2$), 17.4 ($CH_3CH_2CH_2CH_2$), 18.3 ($CH_3CH_2CH_2$), 21.7, 29.2 ($CH_3CH_2CH_2CH_2$), 47.2 ($CH_3CH_2CH_2$), 80.7, 93.8 (C≡C), 188.0 (C═O).

**3-Butyl-5-hydroxy-5-methyl-3-pyrrolin-2-one (12).** The product was obtained as described in the general procedure in 77% yield as a white solid (mp 105 °C). Mass spectrum: $m/z = 169$. IR (selected, $cm^{-1}$): 3368 (br, NH), 3201 (br, OH), 1691 (vs, CO). $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ ppm: 0.87 (t, 3H, $J = 7$ Hz, $CH_3(CH_2)_2CH_2$), 1.25−1.55 (m, 4H, $CH_3(CH_2)_2CH_2$), 1.53 (s, 3H, $CH_3COH$), 2.11 (dt, 2H, $J = 7$ Hz, 2 Hz, $CH_3(CH_2)_2CH_2$), 4.3 (s, 1H, OH), 6.46 (q, 1H, $J = 2$ Hz, C═CH), 7.27 (bs, 1H, NH). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) $\delta$ ppm: 13.7 ($CH_3(CH_2)_2CH_2$), 22.3, 24.3 ($CH_3(CH_2)_2CH_2$), 24.6 ($CH_3COH$), 29.4 ($CH_3(CH_2)_2CH_2$), 85.8 (COH), 138.0 (C═CH), 144.4 (C═CH), 172.8 (CO).

**3-Butyl-5-hydroxy-5-ethyl-3-pyrrolin-2-one (13).** The product was obtained as described in the general procedure in 83% yield as a white solid (mp 65 °C). Mass spectrum: $m/z = 183$. Anal. Calcd (found) for $C_{10}H_{17}NO_2$: C, 65.54 (65.75); H, 9.35 (9.13); N, 7.64 (7.72). IR (selected, $cm^{-1}$): 3388 (br, NH) 3200 (br, OH) 1689 (vs, CO). $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ ppm: 0.91, 0.92 (2 × t, 6H, $J = 7$ Hz, $CH_3(CH_2)_2CH_2$ and $CH_3CH_2COH$), 1.36 (sext, 2H, $J = 7$ Hz, $CH_3CH_2CH_2CH_2$), 1.51 (qn, 2H, $J = 7$ Hz, $CH_3CH_2CH_2$ $CH_2$), 1.83 (q, 2H, $J = 7$ Hz, $CH_3CH_2COH$), 2.20 (dt, 2H, $J = 7$ Hz, 2 Hz, $CH_3(CH_2)_2CH_2$), 4.30 (s, 1H, OH), 6.45 (q, 1H, $J = 2$ Hz, C═CH), 7.07 (bs, 1H, NH). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) $\delta$ ppm: 7.87, 13.37 ($CH_3(CH_2)_2CH_2$ and $CH_3CH_2COH$), 21.88, 24.09 ($CH_3(CH_2)_2CH_2$), 29.16, 30.72 ($CH_3(CH_2)_2CH_2$ and $CH_3CH_2COH$), 87.53 (COH), 138.83 (C═CH), 142.78 (C═CH), 172.31 (CO).

**3-Butyl-5-hydroxy-5-(1-propyl)-3-pyrrolin-2-one (14).** The product was obtained as described in the general procedure in 65% yield as a white solid (mp 68 °C). Anal. Calcd (found) for $C_{11}H_{19}NO_2$: C, 66.97 (67.02); H, 9.71 (9.60); N, 7.10 (7.08). IR (selected, $cm^{-1}$): 3370 (br, NH), 3205 (br, OH) 1692 (vs, CO). $^1H$ NMR (200 MHz, $(CD_3)_2CO$) $\delta$ ppm: 0.83 (t, 6H, $J = 7$ Hz, $CH_3(CH_2)_2CH_2$ and $CH_3CH_2$ $CH_2COH$), 1.22−1.46 (m, 6H, $CH_3(CH_2)_2CH_2$ and $CH_3CH_2CH_2COH$), 1.68 (t, 2H, $J = 7$ Hz, $CH_3CH_2CH_2COH$), 2.05 (dt, 2H, $J = 7$ Hz, 2 Hz, $CH_3(CH_2)_2CH_2$), 4.8 (s, 1H, OH), 6.47 (q, 1H, $J = 2$ Hz, C═CH), 7.53 (bs, 1H, NH). $^{13}C\{^1H\}$ NMR (50 MHz, $(CD_3)_2CO$) $\delta$ ppm: 14.1, 14.5 ($CH_3(CH_2)_2CH_2$ and $CH_3CH_2CH_2COH$), 18.0, 22.9, 25.1 ($CH_3(CH_2)_2CH_2$ and $CH_3CH_2CH_2COH$), 30.5, 41.4 ($CH_3(CH_2)_2CH_2$ and $CH_3CH_2CH_2COH$), 88.1 (COH), 138.9 (C═CH), 144.3 (C═CH), 172.7 (CO).

**3-butyl-5-hydroxy-5-(1,1-dimethylethyl)-3-pyrrolin-2-one (15).** The product was obtained as described in the general procedure in 50% yield as a white solid (mp 140 °C) (50% of the starting ketone was recovered). Anal. Calcd (found) for $C_{12}H_{21}NO_2$: C, 68.21 (67.27); H, 10.01 (10.15); N, 6.63 (5.94). IR (selected, $cm^{-1}$): 3361 (br, NH), 3256 (br, OH), 1687 (vs, CO). $^1H$ NMR (200 MHz, $(CD_3)_2CO$) $\delta$ ppm: 0.96 (t, 3H, $J = 7$ Hz, $CH_3(CH_2)_2CH_2$), 1.05 (s, 9H, $C(CH_3)_3$), 1.25−1.55 (m, 4H, $CH_3(CH_2)_2CH_2$), 2.12 (dt, 2H, $J = 7$ Hz, 2 Hz, $CH_3(CH_2)_2CH_2$), 4.8 (s, 1H, OH), 6.62 (q, 1H, $J = 2$ Hz, C═CH), 7.32 (bs, 1H, NH). $^{13}C\{^1H\}$ NMR (50 MHz, $(CD_3)_2CO$) $\delta$ ppm: 13.9 ($CH_3(CH_2)_2CH_2$), 22.5, 24.7 ($CH_3(CH_2)_2CH_2$), 25.2 ($C(CH_3)_3$), 29.7 ($CH_3(CH_2)_2CH_2$), 37.1 ($C(CH_3)_3$), 92.2 (COH), 139.2 (C═CH), 142.5 (C═CH), 173.5 (CO).

**3-Phenyl-5-hydroxy-5-methyl-3-pyrrolin-2-one (16).** The product was obtained as described in the general procedure in 76% yield as a white solid (mp 152 °C). Anal. Calcd (found) for $C_{11}H_{11}NO_2$: C, 69.82 (69.43); H, 5.86 (5.67); N, 7.40 (7.38). IR (selected, $cm^{-1}$): 3375 (br, NH), 3209 (br, OH), 1696 (vs, CO). $^1H$ NMR (200 MHz, $(CD_3)_2CO$) $\delta$ ppm: 1.59 (s, 3H, $CH_3$), 4.89 (s, 1H, OH), 7.19 (d, 1H, $J = 2$ Hz, C═CH), 7.30−7.38 (m, 3H, $C_6H_5$), 7.69 (bs, 1H, NH), 7.90−7.95 (m, 2H, $C_6H_5$). $^{13}C\{^1H\}$ NMR (50 MHz, $(CD_3)_2CO$) $\delta$ ppm: 25.6 ($CH_3$), 84.8 (COH), 128.1, 129.0, 129.3 ($C_6H_5$), 137.8 (C ipso), 139.2 (C═CH), 145.9 (C═CH), 173.5 (CO).

**3-Phenyl-5-hydroxy-5-ethyl-3-pyrrolin-2-one (17).** The product was obtained as described in the general procedure in 68% yield as a white solid (mp 130 °C). Anal. Calcd (found) for $C_{12}$ $H_{13}NO_2$: C, 70.91 (70.93); H, 6.45 (6.37); N, 6.89 (6.87). IR (selected, $cm^{-1}$): 3371 (br, NH), 3227 (br, OH), 1707 (vs, CO). $^1H$ NMR (200 MHz, $(CD_3)_2CO$) $\delta$ ppm: 0.93 (t, 3H, $J = 7$ Hz, $CH_3CH_2$), 1.87 (q, 2H, $J = 7$ Hz, $CH_3CH_2$), 4.85 (s, 1H, OH), 7.20 (d, 1H, $J = 2$ Hz, C═CH), 7.30−7.38 (m, 3H, $C_6H_5$), 7.62 (bs, 1H, NH), 7.90−7.95 (m, 2H, $C_6H_5$). $^{13}C\{^1H\}$ NMR (50 MHz, $(CD_3)_2CO$) $\delta$ ppm: 8.6 ($CH_3CH_2$), 32.0 ($CH_3CH_2$), 87.5

(34) Chopra, A. K.; Moss, G. P.; Weedon, B. C. L. *J. Chem. Soc., Perkin Trans. 1*, **1988**, 1371.
(35) (a) Bartoli, G.; Simarelli, C.; Palmieri, G.; Bosco, M.; Dalpozzo, R. *Tetrahedron Lett.* **1991**, 7091. (b) Also available commercially.
(36) Katrisky, A. R.; Lang, H. *J. Org. Chem.* **1995**, *60*, 7612.
(37) Yamaguchi, M.; Shibato, K.; Fujiwara, S.; Irao, I. *Synthesis* **1986**, *5*, 421.
(38) Castan, P.; Labarre, J. F. *C. R. Acad. Sci. Fr.* **1963**, *256*, 1715.

(*C*OH), 128.2, 129.1, 129.2 ($C_6H_5$), 138.2 (C ipso), 140.3 (*C*═CH), 144.6 (C═*C*H), 174.5 (*C*O).

**3-Phenyl-5-hydroxy-5-(1-propyl)-3-pyrrolin-2-one (18).** The product was obtained as described in the general procedure in 56% yield as a white solid (mp 127 °C). Anal. Calcd (found) for $C_{13}H_{15}NO_2$: C, 71.87 (71.89); H, 6.96 (6.99); N, 6.44 (6.23). IR (selected, $cm^{-1}$): 3357 (br, NH), 3235 (br, OH), 1708 (vs, CO). $^1$H NMR (200 MHz, $(CD_3)_2CO$) $\delta$ ppm: 0.95 (t, 3H, $J$ = 7 Hz, C$H_3$CH$_2$), 1.51 (sext, 2H, $J$ = 7 Hz, CH$_3$C$H_2$CH$_2$), 1.90 (t, 2H, $J$ = 7 Hz, CH$_3$CH$_2$C$H_2$), 5.01 (s, 1H, O*H*), 7.24 (d, 1H, $J$ = 2 Hz, C═C*H*), 7.36−7.43 (m, 3H, $C_6H_5$), 7.76 (bs, 1H, NH), 7.95−8.00 (m, 2H, $C_6H_5$). $^{13}$C{$^1$H} NMR (50 MHz, $(CD_3)_2$-CO) $\delta$ ppm: 14.5 (*C*H$_3$CH$_2$), 17.9 (CH$_3$*C*H$_2$), 41.3 (CH$_3$ CH$_2$*C*H$_2$), 87.0 (*C*OH), 128.1, 128.9, 129.2 ($C_6H_5$), 133.6 (C ipso), 135.1 (*C*═CH), 145.0 (C═*C*H), 171.2 (*C*O).

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