Neighbouring Group Participation of the *N*-Acyl Function. I

A Selective Conversion of Nitriles into Carboxamides by Formic Acid

Klaus Friedrich*, Mohebullah Zamkanei, and **Ralph Zimmer**

Freiburg, Institut für Organische Chemie und Biochemie der Universität

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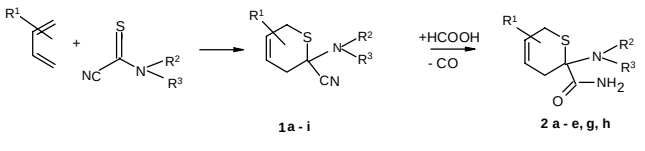
Abstract. Aliphatic α-(acylamino)nitriles react with formic acid at room temperature to give the corresponding α-(acylamino)carboxamides with concomitant formation of one mole of carbon monoxide. This new reaction, which was first observed with 2-acylamino-2-cyano-3,6-dihydro-2H-thiapyranes **1**, can also be used to convert other *N*-(α-cyanoalkyl) amides such as *N*-cyanomethylbenzamides **3**, **5** and the 3,4-dihydro Reissert compound **16** into the corresponding carboxamides. Another application is a synthesis of 2-formylaminoacetamides **11**. A mechanism for the reaction is proposed.

The thiocarbonyl group of *N*-acylated cyanothioformamides exhibits pronounced dienophilic reactivity. Thus, with a variety of 1,3-dienes, we obtained the corresponding Diels–Alder adducts **1** [1].

Investigating possible transformations of adducts **1**, we observed that dissolving them in concentrated formic acid at room temperature resulted in a specific conversion of the nitrile moiety into the corresponding carboxamides **2a**–**e**,**g**,**h** with concomitant formation of one mole of carbon monoxide. In most cases, the reaction was complete within 15–20 minutes and the amides could be isolated in 22–94% yield (Scheme1).



1/2	R1	R2	R3	Yield (%) 1 [1]	2
a		Ph	COMe	95	91
b		Ph	COPh	81	94
c	Me, Me	Ph	COPh	72	85
d		*p*-NO_2-Ph	COMe	88	79
e		*p*-NO_2-Ph	COPh	87	32
f		*p*-NO_2-Ph	H	77	–
g		Ph	COMe	53	22
h		Ph	COPh	76	59
i		Ph	H	50	–

Scheme 1 Reaction of 2-acylamino-2-cyano-3,6-dihydro-2*H*-thiapyranes with formic acid

In contrast to reported conversions of nitriles into carboxamides by formic acid which require either heating at 180–200 °C [2], or the presence hydrogen halides [3], our reaction occurs under rather mild conditions. In order to determine the structural features essential for this conversion and to study its scope, several other α-aminonitriles were treated with formic acid at room temperature.

Because the two α-aminonitriles **1f** and **1i** [1], both lacking the *N*-acyl functionality present in the other members of the group, were not altered by formic acid at room temperature, we came to the conclusion that the *N*-acyl group is essential for the reaction and that other special features such as the thioether moiety present in the Diels–Alder adducts **1** are no prerequisites for the reaction.

Accordingly, *N*-(cyanomethyl)benzanilide (**3**) [4] after 3 h gave the corresponding acetamide **4** in 93% yield together with 0.9 equivalents of carbon monoxide. The two cyano groups in *N*,*N*-bis(cyanomethyl)benzamide (**5**) [5] could also be converted into carboxamido groups, affording the triamide **6** in 74% yield. In this case, measured by the rate of carbon monoxide evolution, the conversion of the first nitrile needed about 16 h, whereas the whole reaction was complete after about 64 h (Scheme 2).

Whereas compounds **1**, **3** and **5** on treatment with formic acid yielded the corresponding amides, 2-(*N*-phenylbenzamido)isobutyronitrile (**7**) [6], the only other nitrile without α-hydrogen atoms studied, afforded 83% of acid **8** together with only 5% of amide **9**.

In a one-pot reaction α-(*N*-formyl)carboxamides **11a**–**c** could be synthesized from α-aminonitriles **10a**–**c** us-

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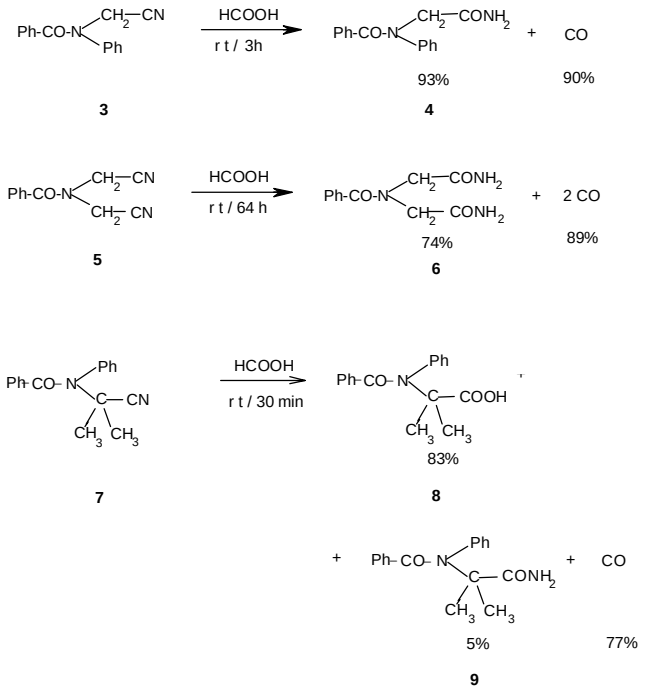
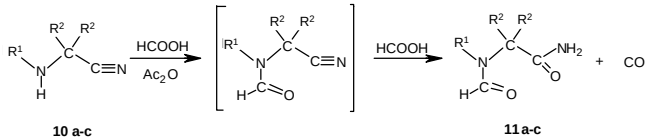


Scheme 2 Reaction of *N*-cyanomethylbenzamides

ing formic-acetic anhydride prepared *in situ* (Scheme 3).

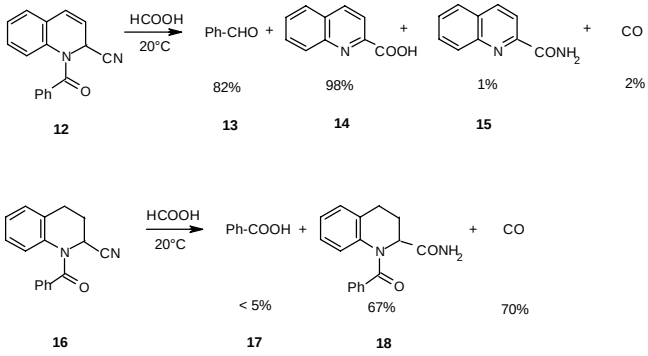


10/11	R¹	R²	react. cond.	yield (%)
a	H	H	r.t./5 h	50
b	H	Me	r.t./20 h	47
c	Ph	Me	r.t./3 h	72

Scheme 3 One-pot synthesis of 2-formylaminoacetamides

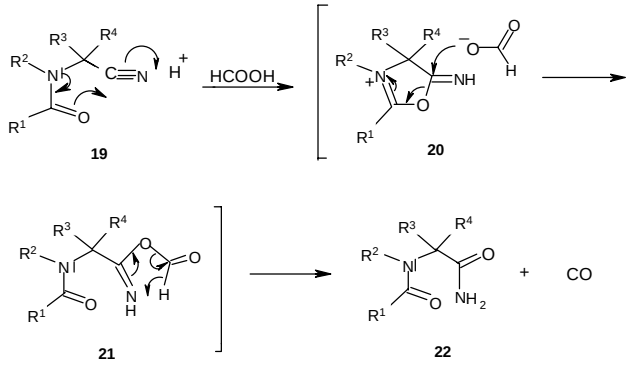
An alternative formulation of **11b** as 5,5-dimethyl-2-hydroxy-4-imidazolidone has been published [7, 8]. Because the IR spectra of **11a** and **11b** show a typical amide II absorption at 1 535 – 1 536 cm^{-1}, the open-chain structure for **11a – c** is preferred in accordance with related α-(formylamino)carboxamides [9].

Since *Reissert* compounds represent a special class of α-(acylamino)nitriles, it appeared worthwhile to test the reaction of **12** [10, 11] with formic acid. As *Reissert* analogs derived from 3,4-dihydro heterocyclic precursors fail to undergo the *Reissert* reaction [12], the 3,4-dihydro derivative **16** [13] was also included in the study. In formic acid, **12** underwent the classical acid-catalyzed *Reissert* reaction [10, 11], yielding 82% of benzaldehyde (**13**) and 98% of quinoline-2-carboxylic acid (**14**) together with 1% of the corresponding amide **15** and only 2% of carbon monoxide. The 3,4-dihydro compound **16** on the other hand afforded 67% of 1-benzoyl-1,2,3,4-tetrahydroquinoline-2-carboxamide (**18**), 70% of carbon monoxide and minor amounts of benzoic acid (**17**) (Scheme 4).



Scheme 4 Reaction of Reissert compounds with formic acid

For the reaction of α-acylaminonitriles with formic acid we propose a mechanism, in which the α-acylamino group acts by neighbouring group participation. In the first step, the nitrilium cation, formed by protonation of the α-acylaminonitrile **19**, cyclizes to give a dihydrooxazoliumimine cation **20** [15]. This activated iminolactone is then ring-opened by formate anion, furnishing an imidoylformate **21**. In the last step, **21** decomposes to give the carboxamide **22** and carbon monoxide, a step which may be formulated as an intramolecular hydride transfer (Scheme 5).



Scheme 5 Proposed mechanism for the formic acid reaction

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Experimental

IR: Perkin-Elmer 298. – NMR: Varian A 60D and WM 250. – MS: Finnigan MAT 44S; *m.p.* (uncorrected): Dr. Tottoli apparatus of Fa. Büchi.

Reaction of α-Acylaminonitriles with Formic Acid (General Procedure 1)

A 100 ml round bottomed flask containing 5 mmol of the appropriate α-acylaminonitrile (**1a**–**h**, **3**, **5**, **7**, **12**, **16**) was equipped with stirrer and pressure equalizing dropping funnel, whose top was connected *via* a bubbler to a gasometer. Then 50 ml of conc. formic acid were added all at once from the dropping funnel to the α-acylaminonitrile and the mixture stirred at room temperature until the evolution of carbon monoxide had ceased. The excess formic acid was evaporated at 50 °C/ 0.1 Torr and the remaining solid purified by recrystallization.

3,6-Dihydro-2-(N-phenylacetamido)-2H-thiapyran-2-carboxamide (**2a**)

According to the general procedure **1**, **1a** [1] after 45 min yielded 91% of **2a**; *m.p.* 169–171 °C (dichloromethane/ether). – ^{1}H NMR ($CDCl_3$, 60 MHz): δ/ppm = 1.73 (s, 3H), 2.37 (m, 2H), 3.20 (m, 2H), 5.50 (m, 1H), 6.10 (m, 1H), 7.48 (m, 5H).

$C_{14}H_{16}N_2O_2S$	Calcd.:	C 60.85	H 5.84	N 10.14	S 11.60
(276.3)	Found:	C 60.60	H 5.65	N 9.74	S 11.63.

3,6-Dihydro-2-(N-phenylbenzamido)-2H-thiapyran-2-carboxamide (**2b**)

According to the general procedure **1**, **1b** [1] after 15 min yielded 94% of **2b**; *m.p.* 217–219 °C (dichloromethane/*n*-hexane). – ^{1}H NMR (D_6-dmso, 60 MHz): δ/ppm = 2.21–3.43 (m, 4H), 5.58 (m, 2H), 7.16 (m, 10H).

$C_{19}H_{18}N_2O_2S$	Calcd.:	C 67.43	H 5.36	N 8.28	S 9.47
(338.4)	Found:	C 67.18	H 5.20	N 8.22	S 9.66.

3,6-Dihydro-4,5-dimethyl-2-(N-phenylbenzamido)-2H-thiapyran-2-carboxamide (**2c**)

According to the general procedure **1**, **1c** [1] after 20 min yielded 85% of **2c**; *m.p.* 188–192 °C (dichloromethane/ether). – ^{1}H NMR ($CDCl_3$, 60 MHz): δ/ppm = 1.47 (s, 3H), 1.73 (s, 3H), 2.30 (AB, J = 15 Hz, 2H), 3.06 (AB, J = 15 Hz, 2H), 7.0–7.67 (m, 10H).

$C_{21}H_{22}N_2O_2S$	Calcd.:	C 68.82	H 6.05	N 7.64	S 8.75
(366.5)	Found:	C 68.66	H 5.87	N 7.21	S 9.00.

3,6-Dihydro-4,5-dimethyl-2-(N-(4-nitrophenyl)acetamido)-2H-thiapyran-2-carboxamide (**2d**)

According to the general procedure **1**, **1d** [1] after 15 min yielded 79% of **2d**; *m.p.* 133–135 °C (dichloromethane/ether/*n*-hexane). – ^{1}H NMR ($CDCl_3$, 60 MHz): δ/ppm = 1.37 (s, 3H), 1.76 (s, 6H), 2.18 (AB, J = 15 Hz, 2H), 3.08 (AB, J = 15 Hz, 2H), 7.70 (m, 2H), 8.32 (m, 2H).

$C_{16}H_{19}N_3O_4S$	Calcd.:	C 55.00	H 5.48	N 12.03	S 9.18
(349.4)	Found:	C 54.96	H 5.68	N 11.81	S 9.21.

3-(N-(4-Nitrophenyl)benzamido)-2-thiabicyclo[2,2,1]hept-5-en-3-carboxamide (**2e**)

According to the general procedure **1**, **1e** [1] after 4 h yielded 32% of **2e**; *m.p.* 220–225 °C decomp. (dichloromethane/ether). – ^{1}H NMR ($CDCl_3$, 60 MHz): δ/ppm = 1.95 (m, 2H), 3.92 (m, 2H), 4.5 (m, 1H), 6.46 (m, 1H), 7.0–7.4 (m, 5H), 7.89 (A_2B_2, J = 9 Hz 4H).

$C_{20}H_{17}N_3O_4S$	Calcd.:	C 60.75	H 4.33	N 10.63	S 8.11
(395.4)	Found:	C 60.22	H 3.95	N 10.55	S 8.49.

3-(N-Phenylacetamido)-2-thiabicyclo[2,2,2]oct-6-en-3-carboxamide (**2g**)

According to the general procedure **1**, **1g** [1] after 20 min yielded 22% of **2g**; *m.p.* 163–165 °C (dichloromethane/ether). – ^{1}H NMR ($CDCl_3$, 60 MHz): δ/ppm = 1.07 (m, 4H), 1.63 (s, 3H), 3.17 (m, 1H), 3.5 (m, 1H), 4.91 (m, 1H), 5.90 (m, 1H, NH), 6.4 (m, 1H), 7.05–8.0 (m, 5H), 7.95–8.1 (m, 1H, NH).

$C_{16}H_{18}N_2O_2S$	Calcd.:	C 63.55	H 6.00	N 9.26	S 10.60
(302.4)	Found:	C 63.13	H 6.20	N 9.11	S 11.57.

3-(N-Phenylbenzamido)-2-thiabicyclo[2,2,2]oct-6-en-3-carboxamide (**2h**)

According to the general procedure **1**, **1h** [1] after 30 min yielded 59% of **2h**; *m.p.* 210–212 °C (dichloromethane/ether). – ^{1}H NMR ($CDCl_3$, 60MHz): δ/ppm = 1.0–2.28 (m, 4H), 3.47 (m, 2H), 4.75 (m, 1H), 5.82 (m, 1H, NH), 6.32 (m, 1H), 7.23 (m, 10H), 8.1 (m, 1H, NH).

$C_{21}H_{20}N_2O_2S$	Calcd.:	C 69.21	H 5.53	N 7.69	S 8.80
(364.5)	Found:	C 69.05	H 5.37	N 7.41	S 9.07.

2-(N-Phenylbenzamido)acetamide (**4**)

According to the general procedure **1**, *N*-cyanomethyl-*N*-phenylglycinonitrile (**3**) [4] after 3 h yielded 93% of amide **4**; *m.p.* 170–172.5 °C (*m.p.* [14] 175 °C) (dichloromethane/ether). – ^{1}H NMR ($CDCl_3$, 60 MHz): δ/ppm = 4.53 (s, 2H), 5.93 (m, 1H), 6.53 (m, 1H), 7.20 (m, 10H).

$C_{15}H_{14}N_2O_2$	Calcd.:	C 70.85	H 5.55	N 11.02	
(254.3)	Found:	C 70.99	H 5.79	N 11.07.	

N,N-Bis(carboxamido)methylbenzamide (**6**)

According to the general procedure **1**, *N*,*N*-Bis(cyanomethyl)benzamide (**5**) [5] after 64 h yielded 74% of triamide **6**; *m.p.* 225–226 °C (*m.p.* [5] 225–227 °C) (ethanol).

2-(N-Phenylbenzamido)isobutyric Acid (**8**) *and 2-(N-Phenylbenzamido)isobutyramide* (**9**)

According to the general procedure **1**, 0.36 g (1.36 mmol) of 2-(*N*-phenylbenzamido)isobutyronitrile (**7**) [6] in 10 ml of formic acid after 25 min. gave 0.77 equivalents of carbon monoxide. After removal of excess formic acid the crystalline residue (0.38 g) was stirred with 100 ml of aqueous 5% $NaHCO_3$ at 20 °C for 1 h and the insoluble 2-(*N*-phenylbenzamido)isobutyramide filtered off. Recrystallization from dilute ethanol afforded 0.02 g (5%) of **9** ($C_{17}H_{18}N_2O_2$ = 282.3); *m.p.* 182 °C (*m.p.* [15] 189 °C). – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.51 (s, 6H), 5.83 (s, 2H, NH_2), 7.05–7.30 (m, 10H). – MS (170 eV, CI–NH_3): *m/z* (%) = 283 (6) [MH^+], 266 (100)

[$MH^+ - NH_3$]. The filtrate was acidified with 2N HCl, the precipitate filtered off and air – dried. After recrystallization from dilute ethanol 0.32 g (83%) colourless crystals of **8** were obtained ($C_{17}H_{17}NO_3$ = 283.3); *m.p.* 187–190 °C (*m.p.* [15] 185 °C). – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.52 (s, 6H), 7.08–7.30 (m, 10H). – MS (170 eV, CI-isobutane): *m/z* (%) = 283 (3) [M^+], 239 (11) [$M^+ - CO_2$], 238 (20) [$M^+ - CHO_2$], 134 (23) [$M^+ - C_8H_5O_3$], 105 (100) [$M^+ - C_{10}H_{12}NO_2$], 77 (37) [$M^+ - C_{11}H_{12}NO_3$].

Reaction of α-Aminonitriles with Formic-Acetic Anhydride (General Procedure 2)

In 250 ml flask equipped with stirrer and dropping funnel, to 10–30 mmol of the starting α-aminonitriles **10a**–**c** was added a mixture of 90 ml of formic acid and 10 ml of acetic anhydride and the mixture stirred at room temperature. Because formic-acetic anhydride decomposes at room temperature at an appreciable rate giving off CO, the reaction was monitored by TLC (silica gel, cyclohexane/ethyl acetate 6/4) or by ^{1}H NMR. After the disappearance of the starting amine and the removal of the volatile components *in vacuo* the residue was purified by recrystallization.

2-Formylaminoacetamide (**11a**)

According to the general procedure 2, a mixture of 2.24 g (26 mmol) of aminoacetonitrile hydrochloride (98%) and 2.0 g (29 mmol) of sodium formate was stirred for 5 h with the reagent solution. Evaporation afforded a colourless oil which slowly crystallized to give 1.32 g (50%) of crude **11a**. Recrystallization from isopropanol yielded 0.83 g (31%) colourless crystals; *m.p.* 117–118 °C (*m.p.* [16] 117–118 °C). – IR (KBr): ν/cm^{-1} = 3312, 3170, 1704, 1648, 1536. – ^{1}H NMR (DMSO-d_6/d_5, 250 MHz): δ/ppm = 3.68 (s, 2H), 7.07 (s, 1H, NH_2), 7.4 (s, 1H, NH_2), 8.05 (s, 1H, CHO), 8.19 (s, 1H, NH). – MS (170 eV, CI-isobutane): *m/z* (%) = 103 [MH^+].

$C_3H_6N_2O_2$	Calcd.: C 35.30 H 5.92 N 27.44
(102.1)	Found: C 35.39 H 5.96 N 27.33.

2-Formylamino-2-methylpropanamide (**11b**)

According to the general procedure 2, 1.2 g of 2-amino-2-methylpropionitrile (**10b**) [17] after 20 h yielded 0.87 g (47%) crude **11b**, recrystallization from ethyl acetate gave 0.48 g (26%) colourless crystals; *m.p.* 160–163 °C (*m.p.* [7] 169 °C). – IR (KBr): ν/cm^{-1} = 3409, 3287, 3040, 1719, 1663, 1650, 1535. – ^{1}H NMR (DMSO-d_6/d_5, 250 MHz): δ/ppm = 1.38 (s, 6H), 6.93 (s, 1H, NH_2), 7.18 (s, 1H, NH_2), 7.90 (s, 1H, CHO), 8.05 (s, 1H, NH). – MS (170 eV, CI-isobutane): *m/z* (%) = 131 (100) [MH^+], 114 (24) [$MH^+ - NH_3$].

$C_5H_{10}N_2O_2$	Calcd.: C 46.15 H 7.74 N 21.52
(130.1)	Found: C 46.09 H 7.85 N 21.73.

2-(N-Formylanilino)-2-methylpropanamide (**11c**)

According to the general procedure 2, 1.50 g (9.36 mmol) of 2-anilino-2-methylpropionitrile (**10c**) [9] after 3 h gave 1.38 g (72%) of crude **11c**, which after recrystallization from ethyl acetate afforded 0.79 g (47%) of colourless crystals; *m.p.* 159–160 °C. – IR (KBr): ν/cm^{-1} = 3384, 3190, 1678, 1630, 1597. – ^{1}H NMR (DMSO-d_6/d_5, 250 MHz): δ/ppm = 1.28 (s, 6H), 6.97 (s, 1H, NH_2), 7.12 (s, 1H, NH_2), 7.25–7.70 (m, 5H), 8.02 (s, 1H, CHO). – MS (170 eV, CI-isobutane): *m/z* (%) = 207 (20) [MH^+], 190 (100) [$MH^+ - NH_3$].

$C_{11}H_{14}N_2O_2$	Calcd.: C 64.06 H 6.84 N 13.58
(206.2)	Found: C 63.80 H 6.87 N 13.24.

Reissert Reaction of 1-Benzoyl-2-cyano-1,2-dihydroquinoline (12) in Formic Acid

A solution of 1.10 g (4.23 mmol) of **12** [10] in 20 ml of formic acid was stirred at room temperature for 20 h. During this time a clear red solution was formed and 8 ml of CO were evolved. Allowing for 5–6 ml resulting from self-decomposition of the formic acid, about 2 ml (2%) had originated from the reaction with **12**. After dilution with 100 ml of water and neutralizing with saturated aqueous $NaHCO_3$, the *benzaldehyde* (**13**) was isolated by steam distillation and identified as 2,4-dinitrophenylhydrazone, 0.99 g (82%); *m.p.* 233 °C (*m.p.* [18] 234 °C). The solution remaining in the distillation flask was filtered and made slightly basic (pH = 9). Extraction with ether afforded 0.01 g (1%) of *quinoline-2-carboxamide* (**15**); *m.p.*129 °C (*m.p.* [10] 133 °C). – MS (70 eV, EI) *m/z* (%): 172 (36) [M^+], 129 (100) [$M^+ - CHNO$]. The aqueous layer was acidified with acetic acid to pH = 4 and the quinoline-2-carboxylic acid (**14**) precipitated by addition of a solution of 1.27 g (5.08 mmol) of $CuSO_4 \cdot 5H_2O$ in 75 ml of water. The yield of the air-dried bluish-green Cu^{++}-salt [5], identified by IR, was 0.85 g (98%).

Reaction of 1-Benzoyl-2-cyano-1,2,3,4-tetrahydroquinoline (16) with Formic Acid

The reaction of 0.07 g (0.27 mmol) of **16** [13] (general procedure 1) in 10 ml of formic acid was stopped, when 35 ml of CO had been evolved, because TLC (cyclohexane/ethyl acetate 1/1) showed the disappearance of **16** and the formation of traces of benzoic acid (**17**). After evaporation the residue was treated with 30 ml of 5% aqueous $NaHCO_3$ for 30 min, the solid collected, washed with a small amount of ice-water and air-dried. There remained 0.05 g (67%) of crude 1-benzoyl-1,2,3,4-tetrahydroquinoline-2-carboxamide (**18**). Recrystallization from ethanol afforded 0.03 g (41%) of **18**; *m.p.*187–189 °C (*m.p.* [12] 188–189 °C). – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.21–3.00 (m, 4H), 5.20 (dd, *J* = Hz, 1H), 6.72 (s, 1H, NH), 6.85 (dt, *Jd* = 2 Hz, *Jt* = 8 Hz, 1H), 7.03 (dt, *Jd* = 2 Hz, *Jt* = 8 Hz, 1H), 7.12–7.45 (m, 6H). – MS (70 eV, EI) *m/z* (%): 280 (2) [M^+], 236 (16) [$M^+ - CH_2NO$], 105 (100) [$M^+ - C_{10}H_{11}N_2O$], 77 (45) [$M^+ - C_{11}H_{11}N_2O_2$].

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Address for correspondence:
Prof. Dr. K. Friedrich
Institut für Organische Chemie und Biochemie
Universität Freiburg i. Br.
Albertstraße 21
D-79104 Freiburg i. Br.
Fax: Internat. code (0) 761/72976
e-Mail: friedrichku@t-online.de