SYNTHESIS OF HETEROCYCLIC CARBAMATES WITH POTENTIAL ACTIVITY IN PLANT PROTECTION

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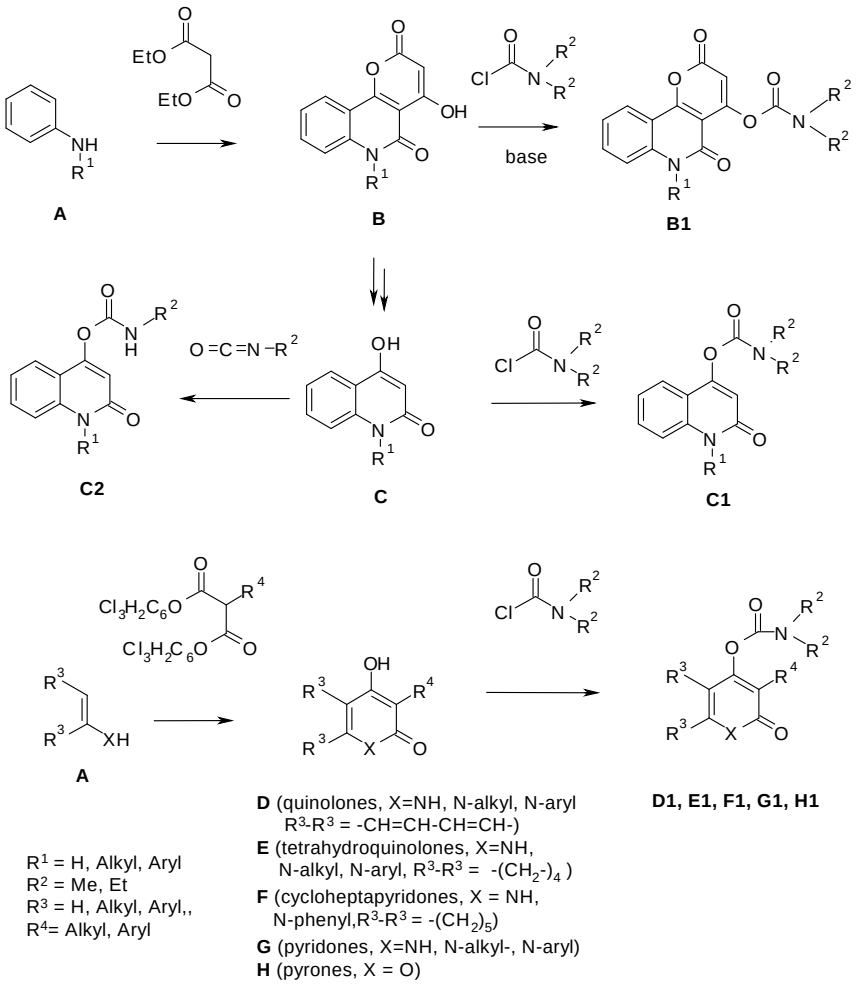
Abstract

Aryl- and heteroaryl carbamates are known as plant protection agents. Because many pests develop resistances, new carbamate structures are of interest in plant protection research.

Our synthetic approach started with the preparation of heterocyclic enoles such as hydroxypyrones **B** and **H**, hydroxyquinolones **C,** hydroxytetrahydroquinolines **E**, hydroxy-cycloheptapyridones **F** and hydroxypyridones **G**. They were obtained from 1,3-dinucleophiles such as anilines or azomethines **A** by cyclocondensation with malonates. Monocyclic hydroxypyridones were also accessible from dehydracetic acid, followed by oxygen exchange with amines.

These heterocyclic enols **B - H** react with dialkylcarbamoylchlorides in the presence of a base to carbamates **B1 - H1**. With alkyl- or arylisocyanates carbamates **C2** are formed.



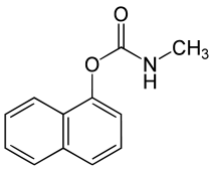
R^1 = H, Alkyl, Aryl
R^2 = Me, Et
R^3 = H, Alkyl, Aryl,,
R^4= Alkyl, Aryl

D (quinolones, X=NH, N-alkyl, N-aryl R^3-R^3 = -CH=CH-CH=CH-)
E (tetrahydroquinolones, X=NH, N-alkyl, N-aryl, R^3-R^3 = $-(CH_2-)_4$)
F (cycloheptapyridones, X = NH, N-phenyl,R^3-R^3 = $-(CH_2)_5$)
G (pyridones, X=NH, N-alkyl-, N-aryl)
H (pyrones, X = O)

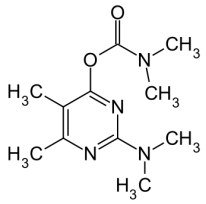
The evaluation of the biological activity shows, that representatives from structures **C1** and **G1** exhibit strong plant protection properties.

Introduction

Aryl- and heteroaryl carbamates such as *Carbaryl* or *Pirimicarb* are well known since several decades as plant protection agents [1,2]. Both carbamates are insecticides and act as inhibitors of the enzyme acetylcholinesterase.



Carbaryl



Pirimicarb

The latter one is registered in the European Union since 2006 as a selective carbamate insecticide used to control aphids on vegetable, cereal and orchard crops by inhibiting acetylcholinesterase activity, but does not affect useful predators [3,4]. Because many pests are known to develop resistances against carbamates, new types of carbamate structures are of interest in plant protection research [5].

The aim of our work was to synthesize heterocyclic carbamates starting from N,N-dialkylcarbamoylchlorides or alkylisocyanates and heterocyclic enols in order to search for new and active derivatives in plant protection. The synthesis of reactive enols started from 1,3-dinucleophiles such as anilines, azomethines or phenols, which were cyclized with malonates to pyridone or pyrone derivatives.

Results and Discussion

1. Carbamates from 4-hydroxyquinolones

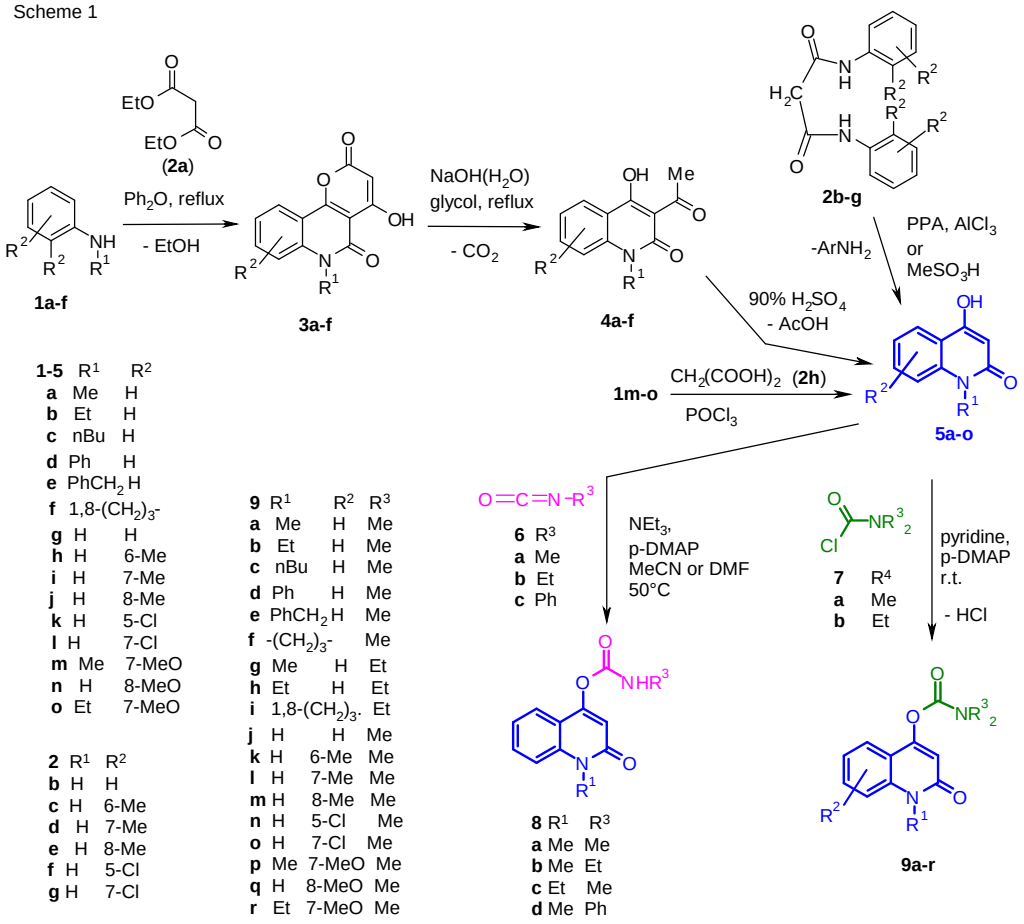
1.1 *Carbamates from 3-unsubstituted 4-hydroxyquinolones 5:*

1-Alkyl- and 1-aryl-4-hydroxyquinolones **5a-f** are formed in a 3-step reaction [6] via the "*pyrono route*" [6e] from N-alkyl- and N-arylanilines **1a-f** and 2 equivalents of malonate **2a**. In the first step, pyronoquinolones **3a-f** are obtained in refluxing diphenyl ether, while 4 molecules of ethanol are distilled off from the reaction mixture. Basic ring-opening of the pyrono ring and thermal decarboxylation in acidic media gives 3-acetylquinolones **4a-f** which are deacetylated with 90% sulfuric acid in an *ipso*-substitution to yield quinolones **5a-f**. 1-Unsubstituted 4-hydroxyquinolones **5g-l** are synthesized from malonodianilides **2g-l**. The cyclization takes place in a Friedel-Crafts type reaction using acidic catalysts such as PPA, aluminiumchloride or methane sulfonic acid [6e, 7]. Methoxy-substituted quinolones **5m-o** are synthesized from anilines **1m-o** and malonic acid **2h** with phosphorylchloride as condensing agent [8] (Scheme 1).

The 4-hydroxy group of quinolones **5** possesses phenolic properties and is easily esterificated either by addition reaction with isocyanates or by attack with acyl chlorides. Alkyl- or arylisocyanates **6** give with **5** N-monosubstituted carbamates **8a-d** using a basic catalyst. Best results were obtained with tri-

ethylamine as the base and p-dimethylaminopyridine (p-DMAP) as acylating agent. The reaction of hydroxyquinolones **5** with N,N-dialkylcarbamoyl chlorides **7** leads to N,N-dialkylcarbamoyloxy-quinolones **9a-r**. In this reaction, best results were obtained with a mixture of pyridine and p-DMAP acting as solvent, basic catalyst and acid trapping agent (Scheme 1).

Scheme 1



Spectral data confirm the structures of carbamates **8** and **9**. Infrared spectra of **8** and **9** show ester carbonyl signals between 1725 - 1740 cm^{-1}, and amide carbonyl signals between 1630 - 1650 cm^{-1}. ^{1}H-NMR spectral data of the methylamino groups in **8** show one dublet between 2.7 - 2.9 ppm. The diethylamino groups are visible as triplets between 1.0 - 1.3 ppm (methyl group), and one multiplet between 2.9 - 3.3 ppm (methylene group). The dimethylamino groups in **9** show two singlets between 2.75 - 2.85 ppm. The diethylamino groups show one multiplet between 0.9 - 1.4 ppm (2 methyl signals), and a further multiplet between 3.0 - 3.5 ppm (2 methylene groups).

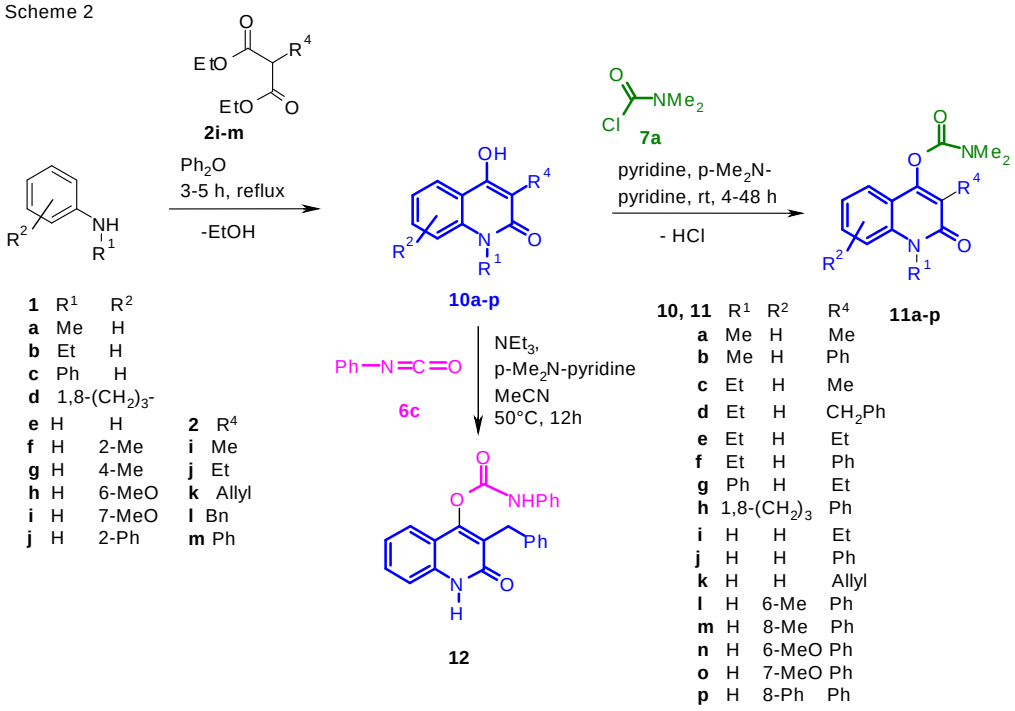
1.2 *Carbamates from 3-alkyl- and 3-arylsubstituted 4-hydroxyquinolones 10:*

2-Alkyl- or 2-arylmalonates **2i-m** react with anilines **1** in a thermal induced cyclization reaction without catalyst to 3-alkyl- and 3-aryl-4-hydroxyquinolones **10** [9]. The reaction proceeds as a one-pot reaction via 2 steps, in the first step forming at about 200 °C a malonoesteranilide, which is then cleaved in a second step at temperatures above 250 °C to give a ketene-anilide intermediate [6d]. The

ketene attacks easily the *ortho*-position of the aniline part to cyclize to the desired quinolone **10** (Scheme 2).

The reaction of 4-hydroxyquinolones **10** with N,N-dialkylcarbamoyl chlorides **7** leads to N,N-dialkylcarbamoyloxy-quinolones **11a-p**. Best results were obtained with a mixture of pyridine and p-DMAP as solvent and basic catalyst. Alkyl- or arylisocyanates **6** react with the reactive enol group at position 4 of quinolones **10** to give N-monosubstituted carbamates **12** using again triethylamine and p-dimethylaminopyridine (p-DMAP) as basic catalysts (Scheme 2).

Scheme 2



1 R^1 R^2
a Me H
b Et H
c Ph H
d 1,8-$(CH_2)_3$-
e H H
f H 2-Me
g H 4-Me
h H 6-MeO
i H 7-MeO
j H 2-Ph

2 R^4
i Me
j Et
k Allyl
l Bn
m Ph

10, 11 R^1 R^2 R^4
a Me H Me
b Me H Ph
c Et H Me
d Et H CH_2Ph
e Et H Et
f Et H Ph
g Ph H Et
h 1,8-$(CH_2)_3$ Ph
i H H Et
j H H Ph
k H H Allyl
l H 6-Me Ph
m H 8-Me Ph
n H 6-MeO Ph
o H 7-MeO Ph
p H 8-Ph Ph

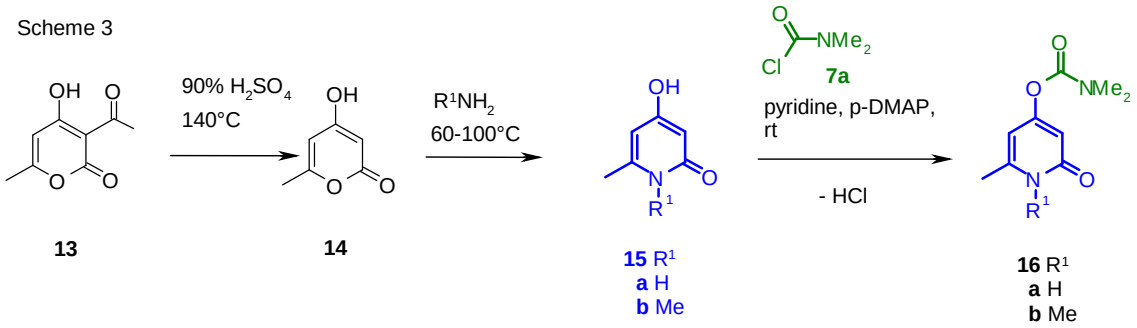
Infrared spectral data of **11** and **12** show ester carbonyl signals between 1725 - 1735 cm^{-1}, and amide carbonyl signals between 1630 - 1670 cm^{-1}. ^{1}H-NMR spectral data of the dimethylamino groups in **11** show one dublet at 2.7 - 2.85 ppm. The phenyl group in **12** is confirmed by the ratio of aromatic protons (14 H) compared with the benzylic CH_2 group (2 H). The NH group of the carbamate is visible at 10.0 ppm, while the ring-NH appears at 11.6 ppm.

2. Carbamates from pyridones and fused pyridones

2.1. Carbamates from 4-hydroxypyridones

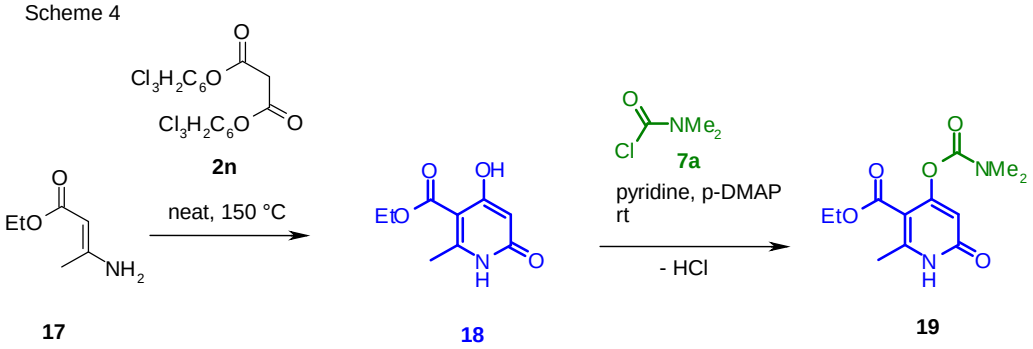
4-Hydroxy-6-methylpyridones **15** are easily obtained from commercially available dehydroacetic acid (**13**), which is deacetylated in the first step to 4-hydroxy-6-methyl-2-pyrone (**14**) and then converted to pyridones **15** by reaction with ammonia or aliphatic amines [11]. The reaction of 4-hydroxy-6-methylpyridones **15** with N,N-dimethylcarbamoyl chloride **7a** in pyridine as solvent and p-DMAP as basic catalyst leads to N,N-dimethylcarbamoyloxy-pyridones **16a,b** (Scheme 3).

Scheme 3



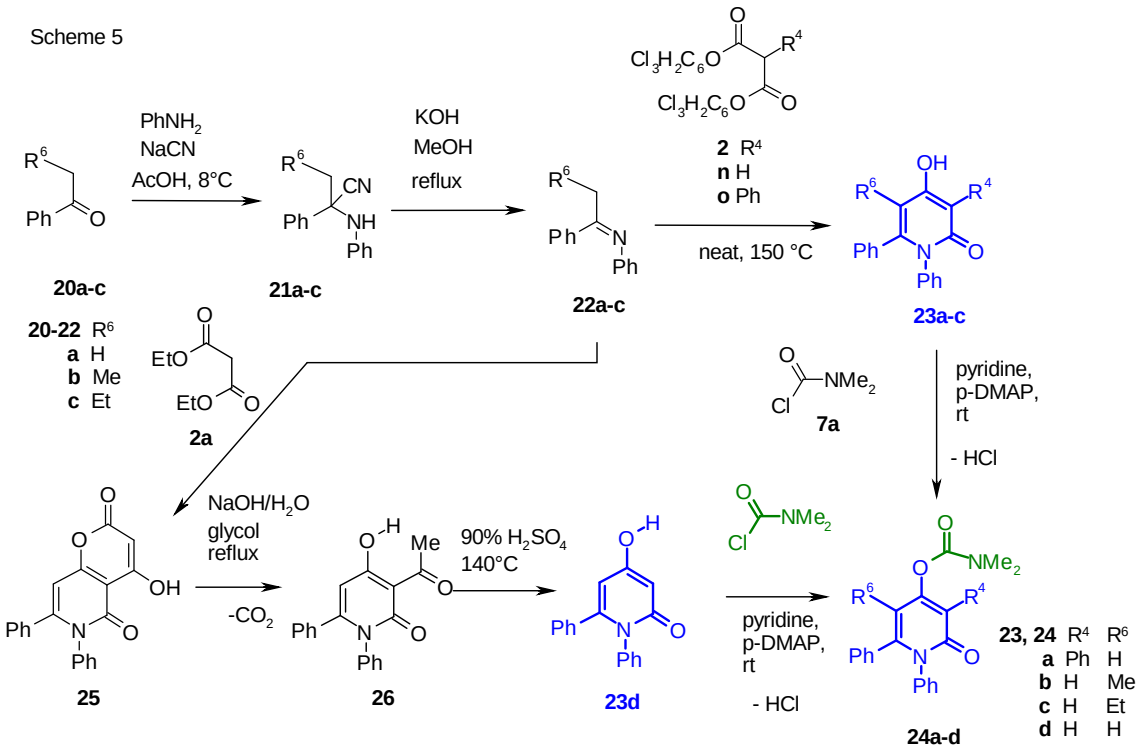
5-Carbethoxy-4-hydroxy-6-methylpyridones **18** are obtained from β-aminocrotonate (**17**) and bis-(2,4,6-trichlorophenyl)malonate (**2n**) as a reactive malonyl derivative [6d, 12, 17]. The reaction of 5-carbethoxy-4-hydroxy-6-methylpyridones **18** with N,N-dimethylcarbamoyl chloride **7a** in pyridine as solvent and p-DMAP as basic catalyst leads to N,N-dimethylcarbamoyloxy-pyridones **19** (Scheme 4).

Scheme 4



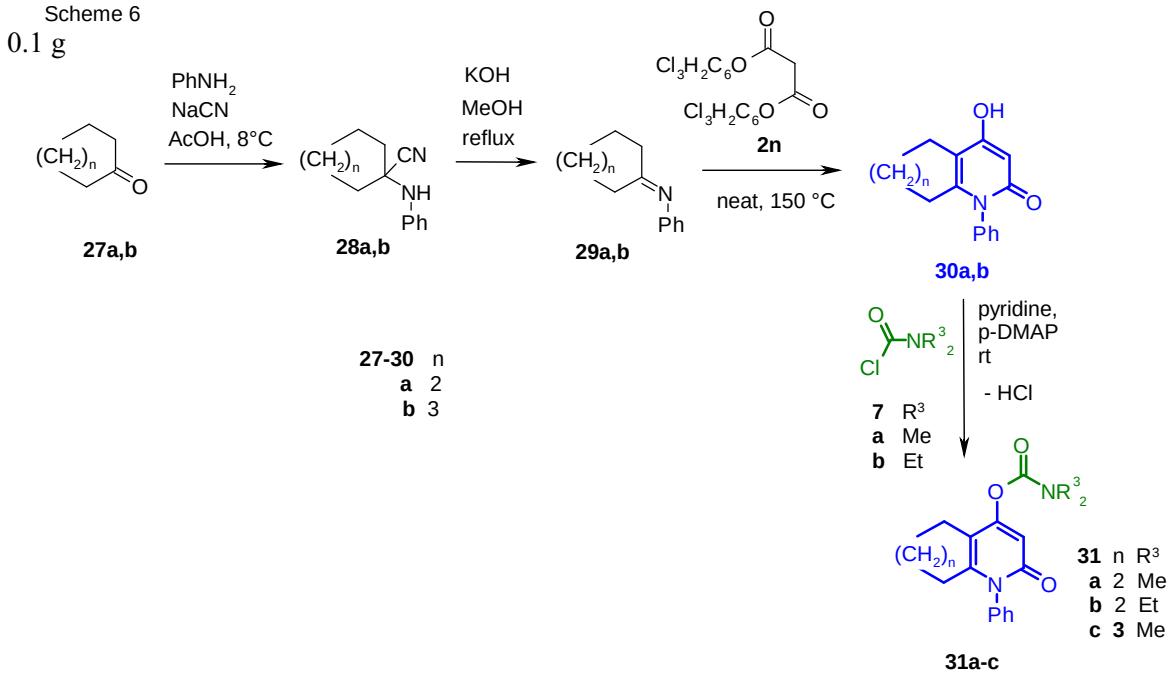
Another approach to 4-hydroxypyridones allows a versatile substitution pattern in position 1, 3, 5 and 6. The starting 1,3-dinucleophiles are azomethines **22**, which are best obtained from the appropriate ketones **20** in a mild two step reaction via aminonitriles **21** followed by subsequent elimination of hydrogen cyanide [12b, 13]. The direct formation of the Schiff bases **22** by reaction with anilines or aliphatic amines gives lower yields and large amounts of impurities caused by the high temperatures and the necessary acidic catalysts [7b]. Aniles **22** react in good yields with bis-(2,4,6-trichlorophenyl)malonates **2n,o** to 4-hydroxypyridones **23** [7b, 14] (Scheme 5)**.**

For 3-unsubstituted pyridone-derivatives, alternatively the "*pyrono route*" - already described for the sequence from **1** → **3** → **4** → **5** - was applied here, which gives in excellent yields 4-hydroxypyridone **23d** [14b]. The reaction of 4-hydroxypyridones **23** with N,N-dimethylcarbamoyl chloride **7a** in pyridine as solvent and p-DMAP as basic catalyst leads to N,N-dimethylcarbamoyloxy-pyridones **24** (Scheme 5).



2.2. Carbamates from 4-hydroxy-tetrahydroquinolones and 4-hydroxy-cyclopenta[b]pyridones

Cyclohexanone **27a** (n=2) and cycloheptanone **27b** (n=2) were transformed in the same manner as shown for the sequence **20** → **21** → **22** [11d] via nitriles **28** to aniles **29** and then cyclized with bis-(2,4,6-trichlorophenyl)malonate **2n** to 4-hydroxy-tetrahydroquinoline **30a** (n=2) and 4-hydroxy-cyclopenta[b]pyridone **30b** [15]. The reaction of 4-hydroxy-tetrahydroquinoline **30a** with N,N-dialkyl-carbamoyl chlorides **7a,b** in pyridine as solvent and p-DMAP as basic catalyst leads to 4-N,N-dialkyl-carbamoyloxy-5,6,7,8-tetrahydroquinolones **31a,b** (Scheme 5). 4-Hydroxy-cyclopenta[b]pyridone **30b** gives with N,N-dimethylcarbamoyl chlorides **7a** under the same conditions 4-N,N-dimethylcarba-moyloxy-2,5,6,7,8,9-hexahydro-1-phenyl-1H-cyclohepta[b]pyridone **31c** (Scheme 6).

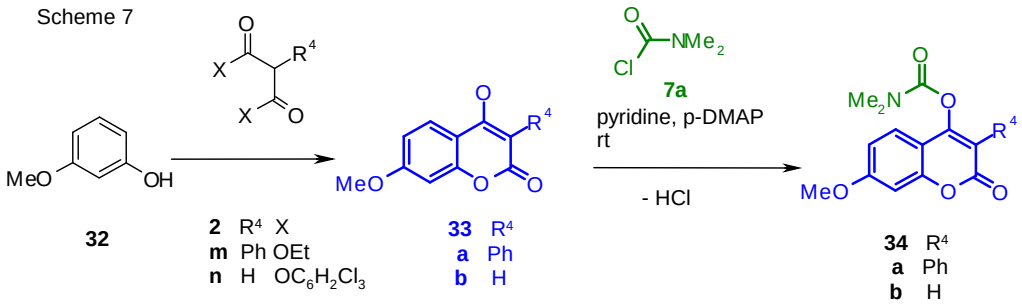


Spectral data confirm the structures of carbamates **16**, **19**, **24** and **31**. IR spectra show ester-carbonyl signals between 1720-1740 cm^{-1} and amide-carbonyl signals between 1640 and 1670 cm^{-1}. The methyl signals of the dimethylcarbamoyloxy groups in ^{1}H-NMR spectra appear as 2 singlets between 2.75 and 3.05 ppm, the ethyl signal of the diethylcarbamoyloxy group in **31b** as methyl signale at 1.1 ppm as triplet and the CH_2 signal at 3.2 as quartet.

3. Carbamates from pyrones and fused pyrones

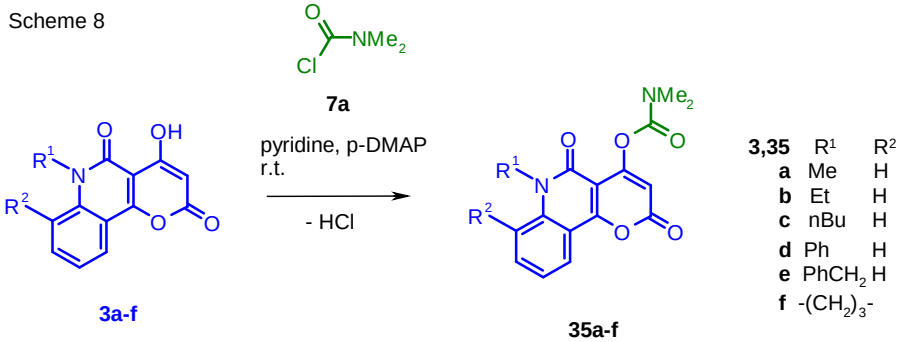
Carbamates from commercially available pyranones and coumarins are already known and show some insecticidal properties [16]. To extend this class of compounds, we synthesized 7-methoxycoumarins **33** from m-anisol **32** and 2-phenylmalonate **2m** [6d, 9] or from the active malonate **2n** [6d, 7d, 12] using the procedures described above for hydroxy-compounds **10** and **23**. The reaction of 4-hydroxycoumarines **33** with N,N-dimethylcarbamoyl chloride **7a** in pyridine as solvent and p-DMAP as basic catalyst leads to N,N-dimethylcarbamoyloxy-coumarins **34** (Scheme 7).

Scheme 7



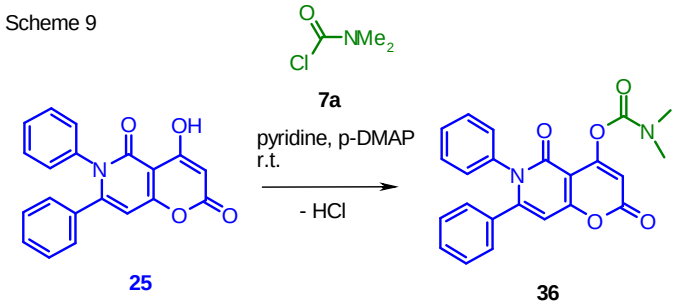
Fused pyranones **3** and **25** were obtained during the synthesis of quinolones (Scheme 2) and pyridones (Scheme 5) via the "*pyrono route*" as described above. The reaction of 4-hydroxy-pyrano[3,2-c]quinolones **3** with N,N-dimethylcarbamoyl chloride **7a** in pyridine as solvent and p-DMAP as basic catalyst leads to N,N-dimethylcarbamoyloxy-pyrano[3,2-c]quinolones **35** (Scheme 8)

Scheme 8



In a similar manner, the reaction of 4-hydroxy-pyrano[3,2-c]pyridones **25** with N,N-dimethyl-carbamoyl chloride **7a** in pyridine as solvent and p-DMAP as basic catalyst leads to N,N-dimethyl-carbamoyloxy-pyrano[3,2-c]pyridones **36** (Scheme 9)

Scheme 9



The structures of carbamates **34, 35** and **36** are confirmed by spectral data. IR spectra show ester-carbonyl signals between 1725-1740 cm^{-1} and amide-carbonyl signals between 1650 and 1670 cm^{-1}. The methyl signals of the dimethylcarbamoyloxy groups in ^{1}H-NMR spectra appear as 2 singlets between 2.75 and 3.2 ppm.

Conclusion

It could be shown, that heterocyclic enols could be easily esterificated with either dialkylcarbamoylchloride or alkyl- and arylisocyanates in a smooth reaction and good yields to give carbamates. As catalyst and solvent pyridine or triethylamine werde used, in combination with p-dimethylaminopyridine to accelerate the acylation reaction. The biological properties - especially for plant protection purposes - were investigated by academic and industrial cooperation. It could be detected that 2 representatives (**9a** and **16b**) possess insecticidal properties to control aphids comparable with Pirimicarb.

Methods and Experimental

General

IR spectra were taken either on a Bruker Alpha-P with Attenuated Total Reflectance (ATR) measurement, using a reflexion method, or with a Mattson Galaxy Series FTIR 7020 instrument in KBr discs.
NMR spectra were measured on a Bruker AMX 360 instrument (360 MHz ^{1}H) or a Bruker Avance III instrument (300 MHz ^{1}H). Chemical shifts are given in ppm (δ) from the internal TMS standard.
Elemental analyses were performed at the Microanalytical Laboratory of the University of Vienna, Austria.

Melting points were determined with a Stuart SMP3 melting point apparatus.
Thin layer chromatography was carried out on 0.2 mm silica gel F 254 plates (Merck, Darmstadt, Germany) using UV light (254 and 366 nm) for detection.

Preparation of representative compounds

General method for the synthesis of hetaryl alkyl- and arylcarbamates* (8, 12) *from isocyanates:

To a solution of 4-hydroxyquinolone **5** or **10** (10 mmol) and isocyanate **6** (25 mmol) in dry acetonitrile (20 mL), p-N,N-dimethylaminopyridine (0.1 g) and triethylamine (1 mL) were added and the mixture stirred at 50 °C for 12 h. Then the reaction mixture was poured onto ice/water (50 mL), and after 30 min filtered by suction.

The remaining solid was extracted in portions with hot petroleum benzin (ligroin, bp 120-140 °C) and the residue recrystallized from the solvent given below.

1-Ethyl-2-oxo-1,2-dihydroquinolin-4-yl methylcarbamate (**8c**): yield 70%, colorless prisms, mp 148 °C (ethanol). IR (ATR): 3188 w, 2979 w, 2934 w, 2897w, 1722 w, 1632 s, 1532 s cm^{-1}. ^{1}H-NMR (DMSO-d_6, 360 MHz): δ = 1.15 (t, J = 7 Hz, 3 H, ethyl-CH_3), 2.80 (d, J = 7 Hz, 3 H, NH-Me), 4.20 (q, J = 7 Hz, 2 H, ethyl-CH_2), 7.10-8.10 (m, 4 H, ArH), 10.0 (m, NH). Anal. calcd for $C_{13}H_{14}N_2O_3$ (246.27): C, 63.40; H, 5.73; N, 11.38. Found: C, 63.68; H, 5.61; N, 11.22.

General method for the synthesis of hetaryl dialkylcarbamates (**9, 11, 16, 19, 24, 31, 34, 35**, **36**) ***from dialkylcarbamoylchlorides:***

A mixture of the appropriate 4-hydroxy compound (**3, 5, 10, 25, 18, 23, 30, 33**) (10 mmol), N,N-dialkylcarbamoylchloride **7** (15 mmol) and 0.1 g p-N,N-dimethylaminopyridine in dry pyridine was stirred at room temperature for 12 h unless otherwise stated. The reaction mixture was then taken to dryness i.vac., the residue poured onto ice/water (100 mL), the solid filtered by suction and purified by extraction with hot ligroin (bp 120-140 °C). Then the solid was dried i. vac. and recrystallized from the solvent given below.

1-Methyl-2-oxo-1,2-dihydroquinolin-4-yl dimethylcarbamate (**9a**): 4 h; yield 64%, yellowish prisms, mp 118 °C (ethanol/water). IR (KBr): 3160-2940 w, 1745 s, 1660 s, 1650 sh, 1595 m, 1505 w cm^{-1}. ^{1}H-NMR (DMSO-d_6. 360 MHz): δ = 2.90 (s, 2 H, N-Me), 3.10 (s, 3 H, N-Me), 3.60 (s, 3 H, 1-Me), 6.45 (s, 3-H), 7.10-7.80 (m, 4 H, ArH). Anal. calcd for $C_{13}H_{14}N_2O_3$ (246.27): C, 63.40; H, 5.73; N, 11.38. Found: C, 63.68; H, 5.45; N, 11.20.

5-Oxo-6-phenyl-2,3-dihydro-1H,5H-pyrido[3,2,1-ij]quinolin-7-yl dimethylcarbamate (**11h**): 4 h; yield 54%, yellowish platelets, mp 206-208 °C (ethanol/water). IR (KBr): 3060-2930 w, 1730 s, 1650 s, 1630 m, 1595 w cm^{-1}. ^{1}H-NMR (DMSO-d_6, 360 MHz): δ = 1.70-2.20 (m, 4 H, 2 CH_2), 2.65 (s, 2 H, CH_2), 2.75 and 3.00 (2 s, 6 H, 2 N-Me), 3.80-4.10 (m, 2 H, N-CH_2), 7.00-7.70 (m, 7 H, ArH), 8.00 (dd, J = 1.5 and 7 Hz, 8-H). Anal. calcd for $C_{21}H_{20}N_2O_3$ (348.41): C, 72.40; H, 5.79; N, 8.04. Found: C, 72.78; H, 5.54; N, 7.87.

1,6-Dimethyl-2-oxo-1,2-dihydropyridin-4-yl dimethylcarbamate (**16b**): yield 70%. colorless prisms, mp 117-118 °C (ligroin). IR (ATR): 3073 w, 2921 w, 1732 sh, 1711 s, 1651 s, 1585 m cm^{-1}. ^{1}H-NMR (DMSO-d_6, 300 MHz): δ = 2.34 (s, Me), 2.89 and 2.97 (2 s, 2 carbamide-N-Me), 3.38 (s, NMe), 6.01-6.02 (and 6.06-6.07 (2 s, 2 H, 3- and 5-H). Anal. calcd for $C_{10}H_{14}N_2O_3$ (210.23): C, 57.13; H, 6.71; N, 13.32. Found: 57.44; H, 6.42; N, 13.06. IR (ATR): 3051 w, 2929 w, 1718 s, 1650 s, 1615 m, 1577 m cm^1.

1,3,6-Trimethyl-2-oxo-1,2-dihydropyridin-4-yl dimethylcarbamate (**24b**): yield 72%, yellowish prisms, mp 209 °C (ethanol). IR (ATR): 3051 w, 2929 w, 1718 s, 1650 s, 1615 m, 1577 m cm^{-1} ^{1}H-NMR (DMSO-d_6, 300 MHz): δ = 2.78 (s, 3 H, Me), 2.81 (s, 3 H, Me), 6.39 (s, 1 H, 5-H), 7.19-7.27 (m, 10 H, ArH), 7.38-7.40 (m, 3 H, ArH), 7.41-7.42 (m, 2 H, ArH). Anal. calcd for $C_{26}H_{22}N_2O_3$ (410.48): C, 76.08; H, 5.40; N, 6.82. Found: 76.37; H, 5.65; N, 6.49.

2-Oxo-1-phenyl-2,5,6,7,8,9-hexahydro-1H-cyclohepta[b]pyridin-4-yl dimethylcarbamate (**31c**):

Step 1: ***1-Phenylamino-cycloheptancarbonitril*** (**28b**): Cycloheptanone (**27**) (33.7 g, 0.3 mol) in glacial acetic acid (120 mL) was combined with aniline (33.5 g, 0.36 mol) and cooled to 7-8 °C. Then sodium cyanide (26.7 g, 0.54 mol) was added and the temperature kept between 7-10 °C. The reaction mixture was stirred for 12 h and then poured onto ice/water (250 mL). The product was filtered by suction, washed first with water and then

with hexane, and dried. The yield was 55.4 g (86%), mp 81-82 °C. IR (KBr): 3390 s, 2890 - 3110 m, 2230 m, 1600 s, 1510 s cm^{-1}.

Step 2: ***N-Cycloheptylidenphenyl-amin*** (**29b**): 1-Phenylamino-cycloheptancarbonitril (**28b**) (55.0 g, 0.26 mol) in methanol (300 mL) was heated to reflux and then potassium hydroxide (58 g, 1.0 mol) added slowly through the condenser and heated then 1 h under reflux. The mixture was cooled to room temperature, then water (800 mL) was added and the formed oily product extracted in several portions with hexane. The combined hexane-extracts were dried with sodium sulphate, the solvent removed i.vac. and the residue crystallized in a crystallization dish. The yield was 14.56 g (48%) yellow crystals. IR (KBr): 3350 s, 2840 - 3100 m, 1630 m, 1590 cm^{-1}.

Step 3: ***4-Hydroxy-1-phenyl-1,5,6,7,8,9-hexayhydro-cyclohepta[b]pyridin-2-on*** (**30b**): N-Cycloheptyliden-phenyl-amin (**29b**) (14.56 g, 0.078 mol) was mixed with bis-(2,4,6-trichlorophenyl)malonate **2n** (36.9 g, 0.80 mol) [17] and heated in a melt for 30 min to 150 °C. After cooling, the residue was extracted several times with hot hexan and diethylether and dried. The yield was 10.8 g (54%) yellow needles, mp 294 °C; lit. mp. 290-295°C [15]. IR (KBr): IR: 3100-2700 b, m, 1660 m, 1615s, 1590 m; identical with an authentic sample from ref. [15b].

Step 4: ***2-Oxo-1-phenyl-2,5,6,7,8,9-hexahydro-1H-cyclohepta[b]pyridin-4-yl dimethylcarbamate*** (**31c**): Obtained from **30b**; yield 89%, yellowish prisms, mp 163-165 °C (ethanol/water). IR (ATR): 3068 w, 2921 m, 2852 w, 1738 s, 1724 sh, 1661 s, 1600 w, 1587 m, 1529 s cm^{-1}. ^{1}H-NMR (DMSO-d_6, 300 MHz): δ = 1.39-1.42 (m, 2 H, CH_2), 1.43-1.52 (m, 2 H, CH_2), 1.67-1.70 (m, 2 H, CH_2), 2.37-2.41 (m, 2 H, CH_2), 2.50-2.52 (m, 2 H, CH_2), 2.92 (s, N-Me), 3.04 (s, N-Me), 6.06 (s, 3-H), 7.20-7.23 (d, J = 7 Hz, 2 H, ArH), 7.40-7.56 (m, 3 H, ArH). Anal. calcd for $C_{19}H_{22}N_2O_3$ (326.40): C, 69.92; H, 6.79; N, 8.58. Found: C, 69.65; H, 6.36; N, 8.89.

7-Methoxy-2-oxo-2H-chromen-4-yl dimethylcarbamate (**34**): yield 62%, yellowish prisms, mp 113-114 °C (toluene). IR (ATR): 3131w, 3069 w, 3007 w, 2944 w, 2852 w, 1740 m, 1715 s, 1619 s, 1564 w cm^{-1}. ^{1}H-NMR (DMSO-d_6, 300 MHz): δ = 2.97 (s, 3 H, N-Me), 3.12 (s, 3 H, N-Me), 3.87 (s, 3 H, MeO), 6.28 (s, 3-H), 6.97-6.98 (dd, J = 1.5 and 7 Hz, 1 H, 6-H), 7.07-7.08 (d, J = 7 Hz, 1 H, 8-H), 7.66-7.69 (d, J = 7 Hz, 1 H, 5-H). Anal. calcd for $C_{13}H_{13}NO_5$ (263.25): C, 59.31; H, 4.98; N, 5.32. Found: C, 59.56; H, 4.71; N, 5.39.

8,11-Dioxo-5,6,8,11-tetrahydro-4H-pyrano[3,2-c]pyrido[3,2,1-ij]quinolin-9-yl dimethylcarbamate (**35f**): 4 h; yield 50%, yellow prisms, mp 212-214 °C (DMF). IR (KBr): 3080-2880 w, 1745 s, 1665 s, 1615 m, 1560 m cm^{-1}. ^{1}H-NMR (CF_3COOH, 360 MHz): δ = 1.80-2.30 (m, 4 H, 2 CH_2), 2.40-2.60 (m, 2 H, CH_2) 2.70-3.20 (m, 6 H, 2 N-Me), 4.00-4.40(m, 2 H, N-CH_2), 5.90 (s, 1 H, 10-H), 7.10-7.70 (m, 2 H, ArH), 8.05 (dd, J = 1.5 and 7 Hz, 1-H). Anal. calcd for $C_{18}H_{16}N_2O_5$ (340.34): C, 63.53; H, 4.74; N, 8.23. Found: C, 63.82; H, 4.66; N, 8.01.

2,5-Dioxo-6,7-diphenyl-5,6-dihydro-2H-pyrano[3,2-c]pyridin-4-yl dimethylcarbamate (**36**): yield 56%, yellowish prisms, mp 168 °C (ethanol). IR (KBr): 1755 sh, 1740 s, 1670 s, 1615 w, 1565 w, 1540 s cm^{-1}. ^{1}H-NMR (DMSO-d_6, 300 MHz): δ = 2.90 and 3.00 (2 s, 6 H, 2 N-Me), 6.25 and 6.60 (2 s, 2 H, H-3 and H-8), 7.10-7.50 (m, 10 H, 2 Ph). Anal. calcd for $C_{23}H_{18}N_2O_5$ (402.41) C, 68.65; H, 4.51; N, 6.96. Found: C, 68.90; H, 4.61; N 6.87.

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