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One-pot synthesis of a chromeno[4,3,2-*de*]-1,6-naphthyridine derivative from 4-chlorocoumarin-3-carbaldehyde

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Dedicated to Acad. Dimiter Ivanov on the occasion of his 120th birth anniversary

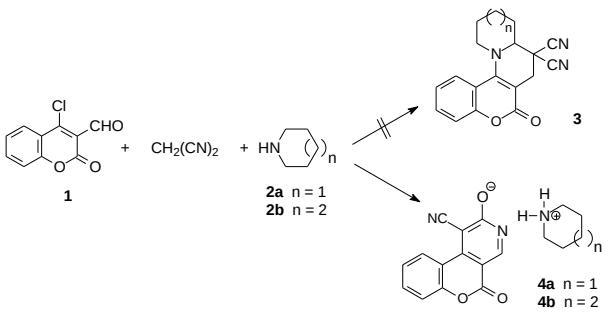
In the reaction of 4-chlorocoumarin-3-carbaldehyde with malononitrile in the presence of piperidine a crystalline piperidinium salt of a novel tetracyclic chromeno[4,3,2-*de*]-1,6-naphthyridine-2-carboxylic acid was isolated instead of the expected product of the "*tert*-amino effect". The structure of this piperidinium salt and its corresponding acidic form was characterized through spectral methods (IR, NMR, MS) and elemental analysis. In addition, the structure was established by means of X-ray crystallographic analysis. A theoretical multistep mechanism for this one-pot synthesis is discussed.

Key words: 4-chlorocoumarin-3-carbaldehyde, chromeno[4,3,2-*de*]-1,6-naphthyridine, X-ray crystallographic analysis, malononitrile

INTRODUCTION

In a previous paper we described some new examples of the so-called "*tert*-amino effect" reaction [1] starting from 4-chlorocoumarin-3-carbaldehyde and ethyl cyanoacetate as a CH-acid in the presence of piperidine. This reaction occurred *via* intermediate Knoevenagel condensation with the formyl group and led to the formation of 1,2 fused 5*H*-chromeno[4,3-*b*]pyridin-5-ones of type **3** (Scheme 1). We found that under the same reaction conditions but employing malononitrile in place of ethyl cyanoacetate [2] the corresponding aminium salts of 2-hydroxy-5-oxo-5*H*-chromeno [3,4-*c*]pyridine-1-carbonitrile (**4a**,**b**) could be obtained. In continuation of our interest in the development of new and simple methods for the synthesis of polyfunctionally substituted heterocycles with anticipated biological activity [3] we now wish to report the use of 4-chlorocoumarin-3-carbaldehyde (**1**) for the one-pot synthesis of a new chromeno[4,3,2-*de*]-1,6-naphthyridine (**5a**,**b** -Scheme 2).

Many known methods for the preparation of 5*H*-chromeno[4,3-*b*]pyridine or 5*H*-chromeno[3,4-*c*] pyridine derivatives involve coumarin derivatives as starting compounds or intermediates, e. g. [4-6]. Further detailed information on the synthesis and application of various 3,4-fused chromenopyridines is summarized in two review articles [3,7] and a recent paper [8]. We have also developed some synthetic procedures leading to the formation of substituted 5*H*-chromeno[4,3-*b*]pyridines *via* Knoevenagel condensation [9], *via* Wittig reaction followed by Vilsmeier conditions [10], or even *via* the Erlenmeyer-Ploechl reaction [11], all of them starting from coumarin-3-carbaldehydes. The preparation of some novel 5*H*-chromeno[3,4-*c*]pyridines was also reported by us [12,13].



Scheme 1. Reaction of 4-chlorocoumarin-3-carbaldehyde (**1**) with malononitrile, *cf.* [1,2].

The synthesis of some [1]benzopyrano[4,3-*b*] pyrrol-4(1*H*)-ones from 4-chlorocoumarin-3-carb-

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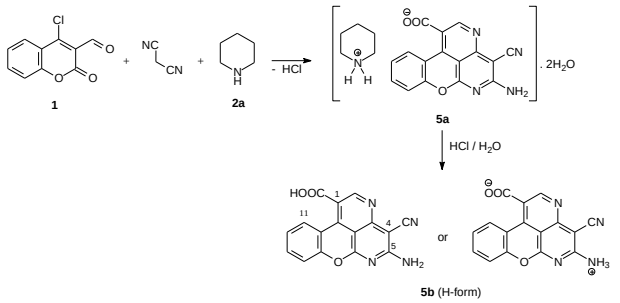
aldehyde (**1**) has also been described [14]. An efficient preparation of novel chromeno-2,6,9-trioxabicyclo-[3.3.1]nonadiene scaffolds was performed by mild base mediated reaction of 4-chloro-3-formylcoumarin (**1**) and *o*-hydroxy-acetophenones [15]. The synthesis of some novel chromeno [4,3-*b*]pyridine-2,5-diones with antimicrobial activity was reported recently, starting from 4-chloro-3-formylcoumarin (**1**) and acetoacetamides in polyethylene glycol as a recoverable solvent [16].



Scheme 2. Synthesis of 5-amino-4-cyanochromeno-[4,3,2-*de*]-1,6-naphthyridine-1-carboxylic acid (**5**) – as piperidinium salt (**5a**) and the acidic form (**5b**).

EXPERIMENTAL

General Remarks

The FTIR spectra were recorded on a Nicolet iS10 FT-IR Spectrometer from Thermo Scientific (USA) using ATR technique. The NMR experiments on Bruker Avance II+ 600 MHz NMR spectrometer in DMSO-d_6 allow the assignment of the structures. The precise assignment of the ^{1}H and ^{13}C NMR spectra (resolved signals) was accomplished by measurement of 2D homonuclear correlation (COSY), DEPT-135 and 2D inverse detected heteronuclear (C–H) correlations (HMQC and HMBC). LC-MS: Shimadzu LC-MS 2020 (ESI detector) equipped with a C18 reversed-phase analytical column at 37°C using a mobile phase H_2O-MeCN [90:10 (v/v)] + 0.1% HCOOH. Elemental analyses were performed by the Microanalytical Laboratory, Institute of Chemistry, University of Vienna, Austria. TLC: silica gel 60 GF_{254} Merck pre-coated aluminum sheets, eluted by hexane-chloroform-acetone 5:3:2 (vol. parts); the spots were visualized under UV irradiation (λ = 254 nm) and/or by treatment with I_2 (vapor).

*Piperidinium 5-amino-4-cyano-chromeno[4,3,2-de]-1,6-naphthyridine-1-carboxylate dihydrate (**5a**)*

Drawn on Scheme 2. To a solution of 1.04 g (5.0 mmol) of 4-chlorocoumarin-3-carbaldehyde (**1**) (prepared according to lit. [10,17]) and 0.66 g (10 mmol) of malononitrile in 20 ml of anhydr. ethanol, 1.08 ml (0.93 g; 10.9 mmol) of piperidine (**2a**) was added dropwise for 5 min under vigorous stirring at 20-25°C. The reaction mixture turned into a red solution and after stirring for additional 15 min orange-yellow crystals of compound **4a** separated. This product was reported elsewhere [2]. The separated crystals were filtered, recrystallized from ethanol (2 × 10 ml) and air-dried to yield 0.45 g (28%) of **4a** with m.p. 255-256°C.

After a 12 h stay at room temperature a yellow solid crystallized from the ethanolic filtrate. It was filtered, washed with cold ethanol (2 × 10 ml) and air-dried to yield 0.89 g (41%) of crystalline, TLC homogeneous product **5a**. A small sample for X-ray analysis was additionally recrystallized from ethanol to give yellow crystals of **5a** with m.p. 206.5-207.3°C, insoluble in chloroform. FTIR (ATR): ν(cm^{-1}) = 3460 (OH/$NH_{assoc.}$), 3056 (Ar-H), 3200-2400 ($NH_{assoc.}$), 2210, 2168, 2144 (CN), 1733 (w) (C=O), 1591, 1557, 1514, 1491, 1444, 1258, etc. ^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.62-1.56 (m, 2H, 4'-H), 1.61-1.65 (m, 4H, 3'-H and 5'-H), 3.00-3.02 (m, 4H, 2'-H and 6'-H), 7.42 (dd, J^3 = 8.3 Hz, J^4 = 1.2 Hz, 1H, 8-H), 7.45 (ddd, J^4 = 1.2 Hz, J^3 =7.2 Hz, J^3 =8.3 Hz, 1H, 10-H), 7.70 (ddd, J^4 = 1.3 Hz, J^3 =7.2 Hz, J^3 = 8.3 Hz, 1H, 9-H), 8.22 (bs, 2H, NH), 8.84 (s, 1H, 2-H), 8.98 (dd, J^3 = 8.3 Hz, J^4 = 1.3 Hz, 1H, 11-H). ^{13}C NMR (150 MHz, DMSO-d_6): δ (ppm) = 21.6 (C-4'), 22.3 (C-3' and C-5'), 43.8 (C-2' and C-6'), 83.1 (C-4), 106.0 (C-11c), 115.4 (C-11a), 117.5 (CN), 118.0 (C-8), 119.1 (C-1), 120.5 (C-11b), 124.5 (C-10), 125.3 (C-11), 133.6 (C-9), 144.0 (C-7a), 152.7 (C-6a), 154.1 (C-2), 158.6 (C-3a), 166.3 (C=O). Calcd. for $C_{21}H_{19}N_5O_3$ (389.41) (water loss on drying): C 64.77, H 4.92, N 17.98; found C 64.70, H 4.49, N 17.80.

*5-Amino-4-cyanochromeno[4,3,2-de]-1,6-naphthyridine-1-carboxylic acid (**5b**)*

Drawn on Scheme 2. After acidification of the aqueous solution of **2b** (0.15 g in 50 ml of water) with HCl (to pH ≈ 2) compound **5b** was isolated as yellow powder with m.p. 313°C (dec.), insoluble in chloroform. FTIR (ATR): ν(cm^{-1}) = 3489 and 3415 (NH_2), 3086 (Ar-H), 2210, 2190 (CN), 1714 (s, C=O), 1589 (s), 1570 (m), 1444, 1423 (w), 1261 (s), 1207 (m), etc. H-Form: ^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) = 7.42 (dd, J^3 = 8.3 Hz, J^4 = 1.2 Hz, 1H, 8-H), 7.45 (ddd, J^3 = 7.2 Hz, J^3 = 8.3 Hz, J^4 = 1.2 Hz, 1H, 10-H), 7.70 (ddd, J^3 =7.2 Hz, J^3 = 8.3 Hz, J^4 = 1.3 Hz, 1H, 9-H), 8.84 (s, 1H, 2-

H), 8.97 (dd, J^3 = 8.3 Hz, J^4 = 1.3 Hz, 1H, 11-H). 8.97 (dd, Hz, 1H, 8-H), 8.84 (s, 1H, 2-H), 7.70 (m_c, 1H, 9-H), 7.41-7.46 (m, 2H, 10-H and 11-H). ^{13}C NMR (150.9 MHz, DMSO-d_6): δ (ppm) = 83.2 (C-4), 106.0 (C-11c), 115.4 (C-11a), 117.5 (CN), 118.0 ($CH_{arom.}$,C-8), 119.1 (C-1), 120.5 (C-11b), 124.5 ($CH_{arom.}$, C-10), 125.4 ($CH_{arom.}$, C-11), 133.6 ($CH_{arom.}$, C-9), 144.1 (C-7a), 152.7 (C-6a), 154.0 ($CH_{arom.}$,C-2), 158.6 (C-3a), 166.1 (C=O). $C_{16}H_8N_4O_3$ (304.26). LC-MS (ESI, pos. mode): *m/z* = 425 $[M–CO_2 + 4MeCN + H]^+$, 343 $[M–CO_2 + 2MeCN + H]^+$, 327 $[M + Na]^+$.

*Crystal structure determination of compound **5a** (Table 1)*

Data collection: Bruker APEX II Software Suite, 2008; cell refinement: Bruker APEX II Software Suite, 2008; data reduction: Bruker APEX II Software Suite, 2008; program used to solve structure: SHELXS-97 [18]; program used to refine structure: SHELXL-97 [19]; molecular graphics: SHELXTL-Plus, XP [20].

X-ray single-crystal diffraction data were collected on a Bruker Kappa APEX II Duo diffractometer (Bruker AXS GmbH, Karlsruhe, Germany), using graphite monochromatized MoK_α radiation (λ = 0.71073 Å). A single crystal, coated with perfluorinated oil, was mounted on a teflon loop. Unit cell parameters, obtained by indexing the peaks in the first 36 frames, were refined by employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects. The crystal was measured at low temperature [100 (2) K]. The structure was solved by direct method using SHELXS-97 [18]. Refinement was evaluated on F^2 against all reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors (gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on all data will be even larger. All nonhydrogen atoms were located and refined anisotropically by full-matrix least squares using SHELXL-97 [19]. The carbon bonded hydrogen atoms were placed in idealized positions. The nitrogen bonded hydrogen atoms were found in the final difference Fourier map and were allowed to refine freely with isotropic displacement para-meters. For the preparation of the structural images the program SHELXTL-Plus [20] was used. The deposition number CCDC 992210 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

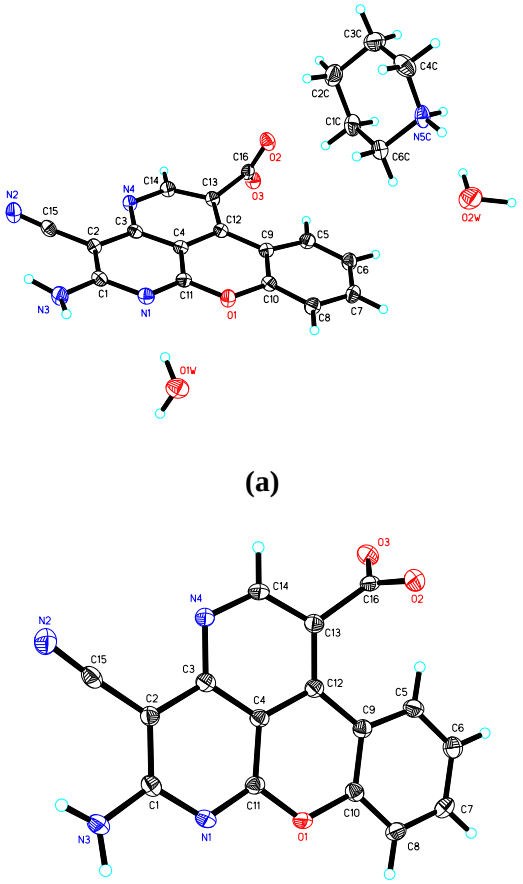
Table 1. Crystal data, data collection and structure refinement details for **5a**.

Chemical formula	**$C_{16}H_7N_4O_3 \cdot C_5H_{12}N \cdot 2(H_2O)$**
M_r	425.44
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	110
a, *b*, *c* (Å)	8.3890 (5), 10.9439 (7), 11.6018 (8)
α, β, γ (°)	98.979 (4), 96.261 (3), 109.626 (3)
V (Å^3)	975.93 (11)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.11
Crystal size (mm)	0.16 × 0.13 × 0.10
Data collection	
Diffractometer	Bruker Kappa APEX II Duo difractometer
Absorption correction	Multi-scan Blessing, 1995
T_{min}, T_{max}	0.717, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	28545, 3992, 3091
R_{int}	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.628
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.043, 0.109, 1.05
No. of reflections	3992
No. of parameters	310
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, -0.23

RESULTS AND DISCUSSION

The IR spectra of **5a** displays a split band for cyano group in the range 2144-2210 cm^{-1} and a carbonyl band at 1733 cm^{-1}. The acidic form **5b** shows absorption at 3489 and 3415 cm^{-1} for primary amino group whereas the cyano group absorbs at 2210 and 2190 cm^{-1}. In the ^{1}H NMR spectrum of **5a** a typical singlet for 2-H is observed at δ = 8.84 ppm (same shift in the H-form **5b**) as are the corresponding multiplets for five methylene groups due to the piperidinium ion. Both ^{13}C NMR spectra of **5a,b** contain the same ^{13}C signals due to the anionic part of **5a,b**, i.e. the only difference

between them is the cationic moiety. The assigned ^{13}C NMR signals are close to those of compounds **5c,d** described by O'Callaghan [21]. The single crystal X-ray crystallography (Table 1) confirmed the structure of the product **5a** (Fig. 1; crystallographic numbering) [Cambridge Crystallographic Data Centre (CCDC): deposit No. 992210].

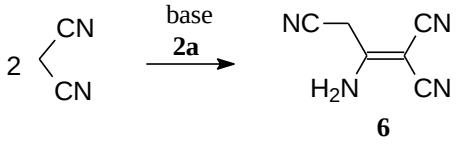


(a)

(b)

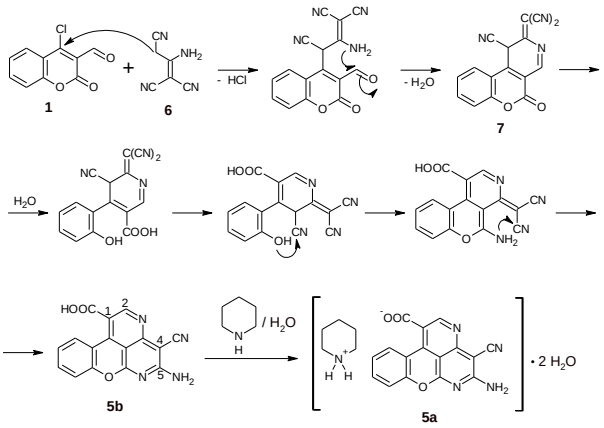
Fig. 1. ORTEP representation of the molecular structure of **5a** in the solid state with displacement ellipsoids at the 50% probability level: (a) whole structure; (b) anion only.

We suggest the following mechanistic sequence for the formation of **5a**: As an initial step, the base-catalyzed dimerization of malononitrile [22,23] into 2-amino-1-propene-1,1,3-tricarbonitrile (**6**) could be assumed (Scheme 3). This dimer has attracted a great deal of interest due to its wide applications in the field of heterocyclic synthesis [24]. The reagent was used for the synthesis of pyridines, pyrimidines, pyridazines, thiophenes, thiazoles and their analogs with diverse pharmaceutical activities including against neurological disorders, as receptor antagonists, as antidiabetics, tubulin inhibitors, kinase inhibitors and anticancer agents [25,26].



Scheme 3. Dimerization of malononitrile.

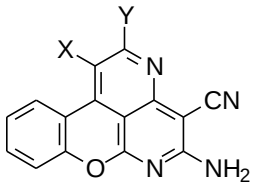
The next step of the suggested mechanism (Scheme 4) is the nucleophilic addition of the trinitrile **6** to the chloroaldehyde **1** accompanied by elimination of HCl. Further, heterocyclisation to the benzopyrano[4,3-*b*]pyridine derivative **7** is followed by lactone ring opening, re-cyclizing to 2-aminochromene and finally closing of the new pyridine ring to give the stable carboxyllic acid **5b** which readily transforms into the crystallizing piperidinium salt **5a**.



Scheme 4. Suggested mechanism for the formation of compounds **5a**,**b**.

Stable adducts, relevant to **7**, were prepared from salicylaldehyde and malononitrile and were reported earlier [21,27]. They were used for the synthesis of the already known [l]benzo-pyrano[4,3,2-*de*][1,6]naphthyridine derivatives **5c**,**d** (Fig. 2). The synthetic pathway for these compounds, as described by O'Callaghan [21], differs substantially from that of **5a**,**b** reported here. The essential difference here is that we used 4-chlorocoumarin-3-carbaldehyde (**1**) as starting material in the presence of piperidine. As a result, a 1-carboxylated compound **5a** without any substituent at position 2 and getting stabilized as a piperidinium salt was formed.

Shaker [28] reported the synthesis of some benzo[5,6]chromeno[4,3,2-*de*][1,6]naphthyridines, related to **5a-d**, starting from a 1*H*-benzo-[*f*] chromene trinitrile derivative with CH-acids in order to obtain a series of polyfunctionally substituted heterocyclic compounds with expected biological activity.



5 c X = CN, Y = NH_2
5 d X = $COOCH_3$, Y = CH_3

Fig. 2. Known chromeno[4,3,2-*de*][1,6]naphthyridine derivatives **5c**,**d**.

CONCLUSION

We developed a rare example of heterocyclic synthesis where a multiply substituted tetracyclic system **5a**,**b** arises directly in one reaction vessel as a main product. The proposed domino type mechanism (Scheme 4) is based on several one-step processes that are already known from the literature. The possibility the final product to stabilize as a piperidinium salt is obviously an important driving force for this complex multi-step synthetic route to proceed.

Full spectral characterization (IR, NMR and MS) is presented. In addition, suitable crystals of compound **5a** were successfully prepared in order crystallographic X-ray analysis to be carried out (see Table 1 for major X-ray data). Thus, the molecular structure of the product **5a** is unambiguously proven. The acidic form (compound **5b**) of the isolated piperidinium salt has also been characterized.

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ЕДНОСТЪПКОВ СИНТЕЗ НА ХРОМЕНО[4,3,2-*d*,*e*]-1,6-НАФТИРИДИНОВО ПРОИЗВОДНО ОТ 4-ХЛОРОКУМАРИН-3-КАРБАЛДЕХИД

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Постъпила на 24 април 2014 г.; Коригирана на 16 юли 2014 г.

(Резюме)

Изолирана е пиперидиниевата сол на едно ново тетрациклично производно на хромено[4,3,2-*d*,*e*]-1,6-нафтиридина вместо очаквания продукт на "*трет*-амино ефект" при взаимодействие на 4-хлорокумарин-3-карбалдехид с малононитрил в присъствие на пиперидин. Молекулният строеж на пиперидиниевата сол и на съответната Н-форма е охарактеризиран чрез спектрални методи (ИЧ, ЯМР, МС) и елементен анализ. Структурата е допълнително потвърдена и с помощта на рентгеноструктурен кристалографски анализ.