chemistry proceedings

MDPI

Proceeding Paper

Heterocyclization of 2-Imino-2H-Chromeno-3-Carbonitriles with Some N,N-Binucleophiles †

Anna A. Meshcheryakova [1,*], Ekaterina A. Konstantinova [2], Karina A. Melkonyan [1], Daria V. Vidlatskaya [1] and Vitaliy V. Sorokin [1]

[1] Institute of Chemistry, N.G. Chernyshevsky Saratov National Research State University, 83 Ulitsa Astrakhanskaya, 410012 Saratov, Russia; vidlatska6@gmail.com (D.V.V.); sorokinviv@gmail.com (V.V.S.)
[2] Institute of Biochemistry and Physiology of Plants and Microorganisms—Subdivision of the Federal State Budgetary Research Institution Saratov Federal Scientific Centre of the Russian Academy of Sciences (IBPPM RAS), 13 Prospekt Entuziastov, 410049 Saratov, Russia; kate-uliana@mail.ru
* Correspondence: meshcheryakova321@gmail.com or karina_yo_14@mail.ru
† Presented at the 28th International Electronic Conference on Synthetic Organic Chemistry (ECSOC 2024), 15–30 November 2024; Available online: https://sciforum.net/event/ecsoc-28.

Abstract: One-pot three-component and stepwise reactions of malononitrile and salicylic aldehydes (salicylic, 5-bromsalicylic) with N,N-nucleophiles such as hydrazine hydrate, nitrobenzhydrazides and o-phenylenediamine under various conditions were investigated. This work reports the synthesis of novel chromeno[4,3-c]pyrazoles and chromeno[4,3-e][1,4]diazepines. The influence of reaction parameters, such as solvent type and temperature was studied. The structures of the synthesized compounds were established using spectroscopic data (IR, NMR).

Keywords: 2-imino-2H-chromene-3-carbonitriles; chromeno[4,3-c]pyrazoles; chromeno[4,3-e][1,4]diazepines; chromenes; three-component synthesis; green chemistry

Citation: Meshcheryakova, A.A.; Konstantinova, E.A.; Melkonyan, K.A.; Vidlatskaya, D.V.; Sorokin, V.V. Heterocyclization of 2-Imino-2H-Chromeno-3-Carbonitriles with Some N,N-Binucleophiles. *Chem. Proc.* **2024**, *6*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s): Name

Published: 15 November 2024

Copyright: © 2024 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

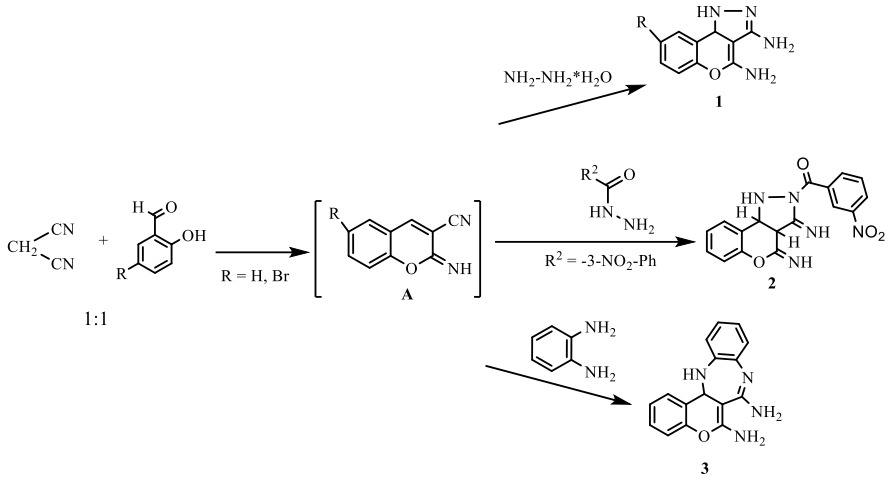
1. Introduction

Heterocyclic-fused chromene derivatives with a chromenopyrazole or chromenodiazepine skeleton have a wide spectrum of biological activity, including antitumor [1,2], antimicrobial, antibacterial [2–6], antifungal [3], antioxidant [4,6], etc. Also, hybrid condensed chromene derivatives have great interest in the fundamental research of organic chemistry.

Previously, we described the preparation of new 2-imino-2H-chromeno-3-carbonitrile and 2-(2-amino-3-cyano-4H-chromen-4-yl)malononitrile derivatives via one-pot and stepwise reactions of salicylic aldehydes (salicylic, 5-bromsalicylic) and different equivalents of malononitrile [7]. This work is the continuation of the studies on the preparation of new derivatives of 2-(2-amino-3-cyano-4H-chromen-4-yl)malononitrile using reactions with various N,N-binucleophiles. The possibility of synthesizing chromeno[4,3-c]pyrazoles and chromeno[4,3-e][1,4]diazepine under various conditions was studied in this paper.

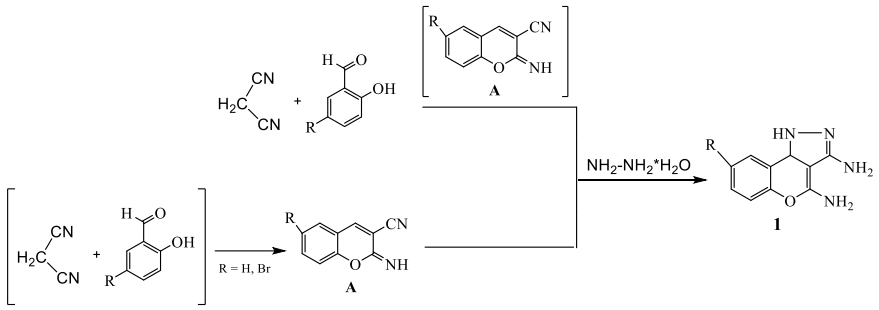
2. Results and Discussion

The use of hydrazine hydrate, benzhydrazides of aromatic or heteroaromatic acids, or orthophenylenediamine as N,N-nucleophiles in three-component and stepwise reactions with malononitrile and salicylic aldehyde leads to the formation of new compounds of the chromeno[4,3-c]pyrazoles **1**, **2** and chromeno[4,3-e][1,4]diazepine **3** series (Scheme 1).



Scheme 1. The synthesis of chromeno[4,3-c]pyrazoles **1a**,**b**, **2** and chromeno[4,3-e][1,4]diazepine **3.**

The novel 8-R-1,9b-dihydrochromeno[4,3-c]pyrazole-3,4-diamines (**1a**,**b R = H**, **Br**) were synthesized by one-pot three-component reaction of malononitrile and salicylic aldehydes with unsubstituted hydrazine hydrate under magnetic stirring in isopropyl alcohol at 40 °C. Chromeno[4,3-c]pyrazoles **1** were similarly prepared by two-step reaction method: preliminary preparation of 6R-2-imino-2H-chromeno-3-carbonitrile **A**, and subsequent introduction of substrate A into the reaction with hydrazine hydrate (Scheme 2).



Scheme 2. The synthesis of chromeno[4,3-c]pyrazoles **1a**,**b** via one-pot three-component and stepwise reactions.

The formation of chromeno[4,3-c]pyrazoles **1** proceeds according to the following scheme. Malononitrile and salicylic aldehyde undergo Knoevenagel condensation and intramolecular O-cyclization reactions in the presence of the basic catalyst triethylamine to form the intermediate 2-imino-2H-chromeno-3-carbonitrile A. Subsequently, new products 1,9b-dihydrochromeno[4,3-c]pyrazole-3,4-diamine 1 are formed by nucleophilic attack of hydrazine on 6R-2-imino-2H-chromeno-3-carbonitrile A and subsequent intramolecular cyclization.

The structure of 8-R-1,9b-dihydrochromeno[4,3-c]pyrazole-3,4-diamines (**1a**,**b R = H**, **Br**) was confirmed by IR and NMR spectroscopy data.

The ^{1}H NMR spectra of the **1a** (**R = H**) and **1b** (**R = Br**) (Figure 1) showed characteristic signals of singlets at 5.96 and 7.04 ppm (**1a**), 6.67 and 7.33 ppm (**1b**) for the amino groups and at 11.32 ppm (**1a**), 11.51 ppm (**1b**) for the imino group, and at 6.34 ppm (**1a**), 6.77 ppm (**1b**) for the methine proton H^{9b}. The two-dimensional ^{1}H/^{13}C HSQC spectrum of **1a** displayed correlations between the methine proton H^{9b} and the sp3-hybridized carbon atom C^{9b}, respectively: 6.34/47.98 (**1a**), 6.77/50.86 (**1b**).

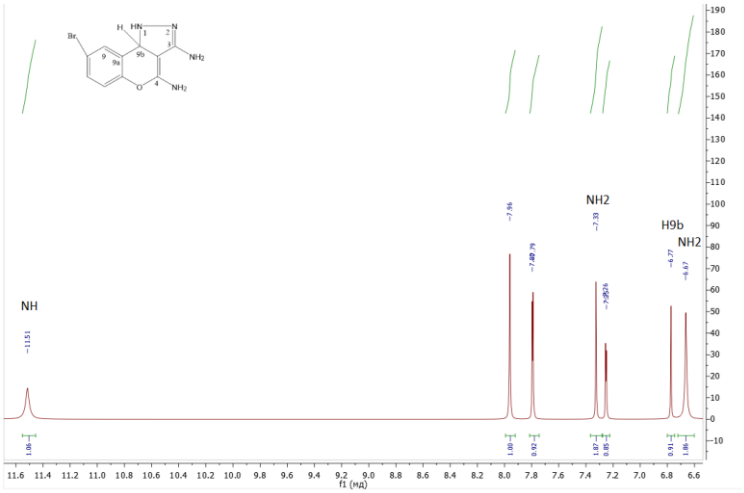
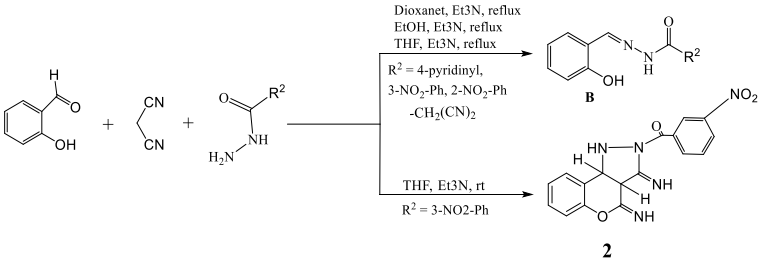


Figure 1. ^{1}H NMR spectrum of 8-bromo-1,9b-dihydrochromeno[4,3-c]pyrazole-3,4-diamine **1b.**

Three-component reaction of equimolar amounts of malononitrile, salicylic aldehyde and hydrazides (isoniazid, 2-, 3-nitrobenzhydrazide) under boiling in ethanol, dioxane or THF in the presence of catalytic amounts of triethylamine predominantly leads to the formation of Schiff bases—N′-(2-hydroxybenzylidene)-hydrazides **B** [8]. A three-component reaction of malononitrile, salicylic aldehyde, and 3-nitrobenzhydrazide at room temperature using THF as a solvent led to the formation of new (3,4-diimino-1,3a,4,9b-tetrahydrochromeno[4,3-c]pyrazol-2(3H)-yl)(3-nitrophenyl)methanone **2** (Scheme 3).



Scheme 3. The reactions of the formation of Schiff bases **B** and (tetrahydrochromeno[4,3-c]pyrazolyl)(3-nitrophenyl)methanone **2**.

The ^{1}H NMR spectrum of (tetrahydrochromeno[4,3-c]pyrazolyl)(3-nitrophenyl)methanone **2** showed characteristic signals of doublet at 4.80 ppm and doublet of doublets at 5.84 ppm for the vicinal protons H^1 and H^2, respectively, and also singlets at 7.80, 7.85, 10.99 ppm for the imino groups (Figure 2).

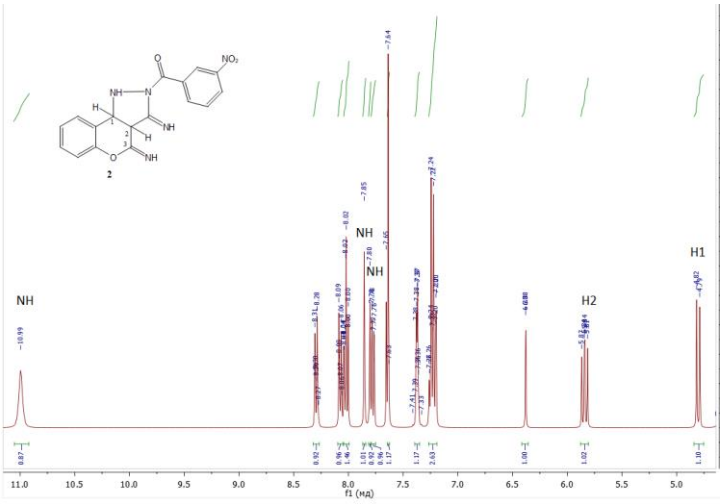


Figure 2. ^{1}H NMR spectrum of (3,4-diimino-1,3a,4,9b-tetrahydrochromeno[4,3-c]pyrazol-2(3H)-yl)(3-nitrophenyl)methanone **2**.

The two-dimensional ^{1}H/^{13}C HSQC spectrum of the compound **2** displayed correlations between the vicinal protons H^1 and H^2 and the sp3-hybridized carbon atoms C^1 and C^2, respectively: 4.8/51.85 (H^1/C^1), 5.84/53.71 (H^2/C^2). The main correlations in the ^{1}H/^{13}C HMBC spectrum are 4.81/53.70 (H^1/C^2); 4.8/144.79 (H^1/C^{10}); 4.8/163.35 (H^1/C^{16}); 4.8/187.42 (H^1/C^3); 5.84/51.85 (H^2/C^1); 5.84/187.42 (H^2/C^3) (Figure 3).

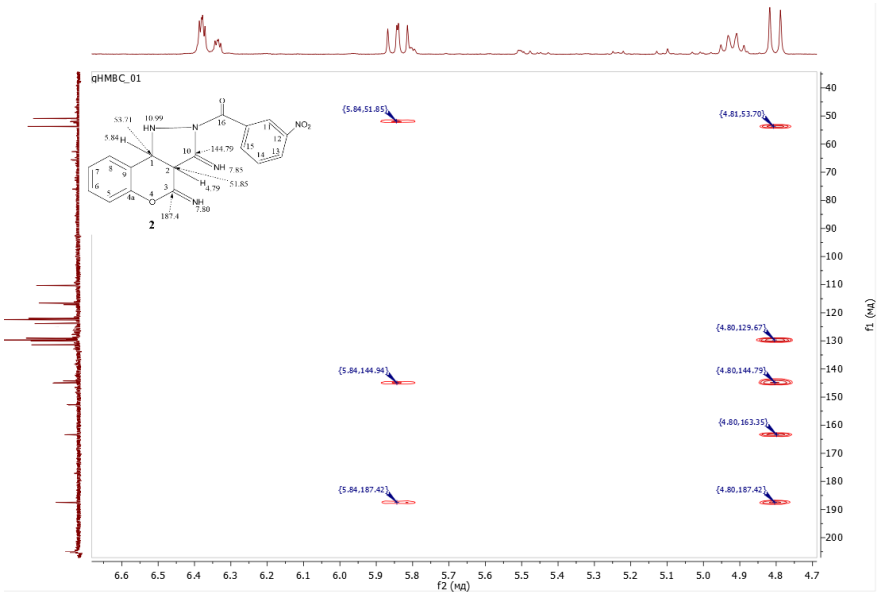
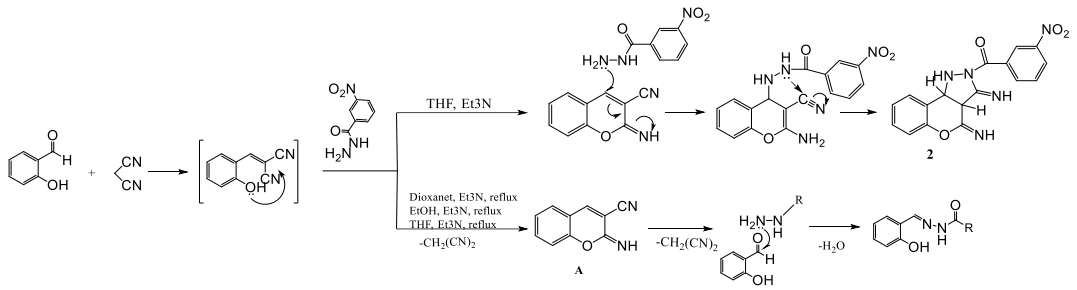


Figure 3. NMR HMBC ^{1}H/^{13}C spectrum and main correlations in the NMR HMBC ^{1}H/^{13}C and HSQC ^{1}H/^{13}C spectrum of (3,4-diimino-1,3a,4,9b-tetrahydrochromeno[4,3-c]pyrazol-2(3H)-yl)(3-nitrophenyl)methanone **2**.

Stepwise reaction of 2-imino-2H-chromeno-3-carbonitrile between 3-nitrobenzhydrazide at room temperature in the THF similarly led to the formation of the target chromeno[4,3-c]pyrazole **2**.

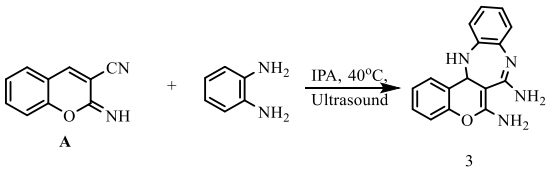
The proposed reaction mechanism is similar to that described above and includes an initial Knoevenagel condensation to form an intermediate 6R-2-imino-2H-chromeno-3-carbonitrile A, subsequent nucleophilic attack of 3-nitrobenzhydrazide and heterocyclization to form the product **2**.

Heating of 2-imino-2H-chromeno-3-carbonitrile with benzhydrazides can lead to the formation of Schiff base due to a nucleophilic attack by the hydrazide with opening of the benzopyran ring and elimination of malononitrile (Scheme 4). The effect of temperature on 2-imino-2H-chromeno-3-carbonitrile may also contribute to the ring-opening process. Reactions leading to the opening of the benzopyran ring of 2-imino-2H-chromeno-3-carbonitrile or similar chromene derivatives during intense heating (or boiling) are described in the literature [9,10].



Scheme 4. Proposed mechanism of reactions of salicylic aldehyde, malononitrile and 3-nitrobenzhydrazide under different conditions.

The reaction of 2-imino-2H-chromene-3-carbonitrile and orthophenylenediamine in isopropyl alcohol under ultrasonic activation conditions proceeds with the formation of new 13,13a-dihydrobenzo[b]chromeno[4,3-e][1,4]diazepine-6,7-diamine **3** (Scheme 5).



Scheme 5. The synthesis of chromeno[4,3-e][1,4]diazepine **3.**

The structure 13,13a-dihydrobenzo[b]chromeno[4,3-e][1,4]diazepine-6,7-diamine **3** was confirmed by IR and NMR spectroscopy data.

The ^{1}H NMR spectra of the **3** showed characteristic signals of singlets at 7.14 and 7.20 ppm for the amino groups and at 6.30 ppm for the imino group, and also at 6.49 ppm for the methine proton H^{1} (Figure 4). The two-dimensional ^{1}H/^{13}C HSQC spectrum of **3** displayed correlations between the methine proton H^{1} and the sp3-hybridized carbon atoms C^{1}, respectively: 6.49/50.68 (H^{1}/C^{1}).

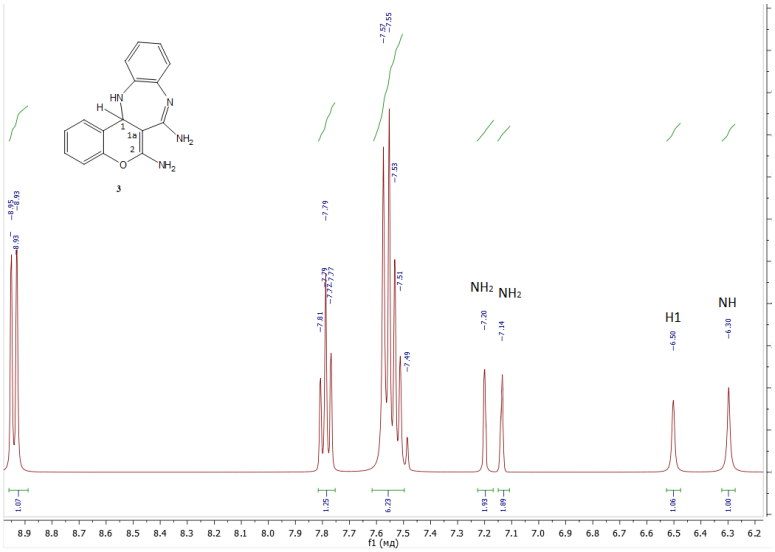


Figure 4. ^{1}H NMR spectrum of 13,13a-dihydrobenzo[b]chromeno[4,3-e][1,4]diazepine-6,7-diamine **3.**

3. Experimental

3.1. General Information, Instrumentation, and Chemicals

The IR spectra were recorded on an FSM 1201Fourier spectrometer in KBr pellets. The 1H, 13C, 1H/13C HSQC, 1H/1H COSY, and 1H/13C HMBC spectra were recorded on a Varian 400 MHz spectrometer at 400 MHz (1H), the 13C spectra were recorded at 100 MHz. NMR spectra were recorded in CDCl3, (CD3)2CO, and DMSO-d6, internal standard TMS. Elemental analysis was performed on a Vario MICRO Cube automatic CHNS analyzer. The melting points were determined in an open capillary. The reaction pro-gress was monitored by TLC on Fluka Silicagel/TLC-cards, eluent hexane–ethyl ace-tate–chloroform (2:2:1), and visualized by exposure to UV light and iodine vapor. Ul-trasonic synthesis was performed in a Sapphire TTC ultrasonic bath (2.8 L, heated).

3.2. Synthesis and Characterization of the Compounds

- **1,9b-dihydrochromeno[4,3-c]pyrazole-3,4-diamine 1a**

(A) 0.004 mol (0.26 g) of malononitrile, 0.004 mol of salicylic aldehyde and 0.008 mol of hydrazine hydrate were stirred in isopropyl alcohol for 1 h at 40 °C. The formed precipitate is filtered off, washed with isopropyl alcohol and dried in a vacuum. (B) 0.004 mol (0.82 g) of 2-imino-2H-chromene-3-carbonitrile, 0.008 mol of hydrazine hydrate were stirred in isopropyl alcohol for 1 h at 40 °C. The formed precipitate is filtered off, washed with isopropyl alcohol and dried in a vacuum.

M.p. = 306–308 °C. Yellow crystals. Calculated, %: C, 59.40; H, 4.98; N, 27.71; O, 7.91. $C_{10}H_{10}N_4O$. Found, %: C 59.19; H 4.95; N 27.55. IR, ν, cm^{-1}: 3442, 3350, 3238, 3188 (NH); 3050(Ar-H); 2925 (Csp3-H); 1550 (C=C); 1157 (C-O-C). ^{1}H NMR (DMSO-d6), δ, ppm: 5.96 (-NH_2, s, 2H); 6.34 (H^{9b}, s, 1H), 7.04 (-NH_2, s, 2H), 7.09–7.64 (C_6H_4, m, 4H); 11.32 (NH, s, 1H). ^{13}C NMR (DMSO-d6), Cδ, ppm: 47.98 (C^{9b}); 71.92 (C^{3a}); 116.68 (C^{6} Ar); 132.87 (C^{7} Ar); 124.55 (C^{8} Ar); 129.13 (C^{9} Ar); 147.10 (C^{5a}); 158.77 (C-NH_2); 165.30 (C-NH^2). ^{1}H/^{13}C HSQC (DMSO-d6), δ, ppm: 6.34/47.98 (H^{9b}/C^{9b}). Yield: 54.5% (A), 45% (B).

- **8-bromo-1,9b-dihydrochromeno[4,3-c]pyrazole-3,4-diamine 1b**

(A) 0.004 mol (0.26 g) of malononitrile, 0.004 mol (0.8) of 5-bromsalicylic aldehyde and 0.008 mol of hydrazine hydrate were stirred in isopropyl alcohol for 3 h at 40 °C. The formed precipitate is filtered off, washed with isopropyl alcohol and dried in a vacuum. (B) 0.004 mol (1 g) of 6-bromo-2-imino-2H-chromene-3-carbonitrile, 0.008 mol of

hydrazine hydrate were stirred in an ultrasonic bath in isopropyl alcohol at 40 °C for 3 h. The formed precipitate is filtered off, washed with isopropyl alcohol and dried in desiccators.

M.p. = 287–288 °C. Dark yellow crystals. Calculated, %: C, 42.73; H, 3.23; Br, 28.42; N, 19.93; O, 5.69. $C_{10}H_9BrN_4O$. Found, %: C, 42.85; H, 3.22; N, 20.08. ^{1}H NMR (Acetone-d6), δ, ppm: 6.67 (-NH_2, s, 2H), 6.77 (H^{9b}, s, 1H), 7.25 (ArH^6, d, 1H. J = 6.9 Hz), 7.33 (-NH_2, s, 2H), 7.79 (ArH^7, d, 1H. J = 7.0 Hz,), 7.96 (ArH^9, s, 1H,), 11.51 (NH, s, 1H). ^{13}C NMR (Acetone-d6), Cδ, ppm: 50.86 (C^{9b}); 64.13 (C^{3a}); 116.21 (C^8); 119.59 (C^6 Ar); 134.66 (C^7 Ar); 142.15 (C^9 Ar); 151.46 (C^{5a}); 158.89 (C-NH_2); 160.55 (C-NH^2). ^{1}H/^{13}C HSQC (Acetone-d6), δ, ppm: 6.77/50.86 (H^{9b}/C^{9b}); 7.24/119.59 (H^6/C^6); 7.79/134.66 (H^7/C^7); 7.96/142.15 (H^9/C^9).

Yield: 69% (A), 75% (B).

- **(3,4-diimino-1,3a,4,9b-tetrahydrochromeno[4,3-c]pyrazol-2(3H)-yl)(3-nitrophenyl)methanone 2.**

(A) Equimolar amounts of malononitrile 0.002 mol (0.13 g,), salicylic aldehyde (0.002 mol) and 3-nitrobenzhydrazide 0.002 mol (0.36 g,) were stirred in THF at room temperature under magnetic stirring for 4 h. The formed precipitate is filtered off, washed with isopropyl alcohol and dried in desiccators. (B) 0.002 mol (0.41 g) of 2-imino-2H-chromene-3-carbonitrile, 0.003 mol (0.54 g) of 3-nitrobenzhydrazide were stirred in THF at room temperature under magnetic stirring for 4 h. The formed precipitate is filtered off, washed with isopropyl alcohol and dried in desiccators. The product is recrystallized from isopropyl alcohol.

M.p. = 275–278 °C. Light brown crystals. Calculated, %: C, 58.12; H, 3.73; N, 19.93; O, 18.22. $C_{17}H_{13}N_5O_4$. Found, %: C 58.19; H 3.75; N 20.02. IR, ν, cm^{-1}: 3421, 3255 (NH); 3065 (Ar-H); 2961, 2870 (Csp3-H); 1133 (C-O-C). ^{1}H NMR (Acetone-d6), δ, ppm: 4.79–4.82 (H^1, d, 1H. J = 8.7 Hz); 5,84 (H^2, dd, 1H. J = 9 Hz); 6.38 (ArH^5, d, 1H. J = 3.7 Hz); 7.19–7.28 (ArH^6, m, 1H); 7.33–7.41 (ArH^7, m, 1H); 7.64 (ArH^{11}, s, 1H); 7.76–7.78 (ArH^8, d, 1H. J = 8.5 Hz); 7.80 (=NH, s, 1H); 7.85 (=NH, s, 1H); 8.02 (ArH^{14}, t, 1H. J = 7.6 Hz); 8.07 (ArH^{15}, d, 1H. J = 8.4 Hz); 8.29 (ArH^{13}, d, 1H. J = 8.4 Hz); 10.99 (NH, s, 1H). ^{13}C NMR (DMSO-d6), Cδ, ppm: 53,71 (C^2); 51,85 (C^1); 110,3 (C^5); 116.61 (C^7); 122.02 (C^{14}); 122,43 (C^{11}); 123.88 (C^{13}); 129.18 (C^{15}); 129.64 (C^6); 131.42 (C^8); 144.79 (C^{10}); 163.35 (C^{16}); 187.42 (C^3). ^{1}H/^{13}C HSQC (Acetone-d6), δ, ppm: 4.8/51,85 (H^1/C^1); 5,84/53,71 (H^2/C^2); 6,38/110,3 (H^5/C^5); 7.23/129.64 (H^6/C^6); 7.37/116.61 (H^7/C^7); 7,64/122,43 (H^{11}/C^{11}); 7.78/131.42 (H^8/C^8); 8.01/122.02 (H^{14}/C^{14}); 8.07/129.18 (H^{15}/C^{15}); 8.29/123.88 (H^{13}/C^{13}). ^{1}H/^{13}C HMBC (Acetone-d6), δ, ppm: 4.81/53.70 (H^1/C^2); 4.8/144.79 (H^1/C^{10}); 4.8/163.35 (H^1/C^{16}); 4.8/187.42 (H^1/C^3); 5.84/51.85 (H^2/C^1); 5.84/187.42 (H^2/C^3). Yield: 60% (A), 63% (B).

- **13,13a-dihydrobenzo[b]chromeno[4,3-e][1,4]diazepine-6,7-diamine 3.**

(A) Equimolar amounts of 2-imino-2H-chromene-3-carbonitrile 0.002 mol (0.41 g,) and orthophenylenediamine 0.002 mol (0.22 g) were stirred in an ultrasonic bath in isopropyl alcohol at 50 °C for 4 h. The formed precipitate is filtered off, washed with hexane, and dried in desiccators. The product is recrystallized from isopropyl alcohol.

M.p. = 289–291 °C. The beige crystals. Calculated, %: C, 69.05; H, 5.07; N, 20.13; O, 5.75. $C_{16}H_{14}N_4O$. Found, %: C 69.30; H 5.10; N 20.27. ^{1}H NMR (DMSO-d6), δ, ppm: 6.30 (NH, s, 1H), 6.50 (H^1, s, 1H), 7.14 (-NH_2, s, 2H), 7.20 (-NH_2, s, 2H), 7.49–7.57 (ArH, m, 6H,), 7.78 (ArH, t, 1H. J = 7.9 Hz,), 8.94 (ArH, d, 1H. J = 8.5 Hz,). ^{13}C NMR (DMSO-d6), Cδ, ppm: 50.68 (C^1); 108.94 (C^{1a}); 118.90 (C Ar); 125.38 (C Ar); 125.92 (C Ar); 134.90 (C Ar); 142.58 (C^{3a}); 152.26 (C-NH_2); 152.64 (C-NH_2). ^{1}H/^{13}C HSQC (DMSO-d6), δ, ppm: 6.49/50.68 (H^1/C^1). ^{1}H/^{13}C HMBC (Acetone-d6), δ, ppm: 6.29/142.58 (NH/ C^{3a}). Yield: 74% (A).

4. Conclusions

Thus, the novel chromeno[4,3-c]pyrazoles **1,2** and chromeno[4,3-e][1,4]diazepine **3** were synthesized. Compounds **1b**, **3** were synthesized using the «green chemistry»

approach under ultrasonic activation. The influence of reaction parameters, such as temperature, solvent type and activation type was studied.

Three-component reactions of malononitrile, salicylic aldehyde and hydrazides under heating led mainly to the formation of the Schiffe base, but three-component and stepwise reactions of malononitrile, salicylic aldehyde and 3-nitrobenzhydrazides in THF led to the new chromeno[4,3-c]pyrazole **2**. Thus, the reaction conditions significantly affect the direction and depth of the reaction of malononitrile, salicylic aldehyde and hydrazides.

Author Contributions: All authors contributed equally to this work. All authors have read and agreed to the published version of the manuscript.

Funding: Please add: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Yin, Y.; Hu, J.Q.; Wu, X.; Sha, S.; Wang, S.F.; Qiao, F.; Song, Z.C.; Zhu, H.L. Design, synthesis and biological evaluation of novel chromeno [4,3-c] pyrazol-4 (2H)-one derivates containing sulfonamido as potential PI3Kα inhibitors. *Bioorg. Med. Chem.* **2019**, *27*, 2261–2267. https://doi.org/10.1016/j.bmc.2019.04.021.
2. Alshaye, N.A.; Ibrahim, M.A. Synthesis, characterization and biological evaluation of the novel chromenopyridothiazolopyrimidines and chromenopyridopyrimidothiazolo-pyrimidines. *Synth. Commun*. **2023**, *53*, 332–344. https://doi.org/10.1080/00397911.2023.2172684.
3. Renuka, N.; Kumar, K.A. Synthesis and biological evaluation of fused pyrans bearing coumarin moiety as potent antimicrobial agents. *Philipp J. Sci*. **2015**, *144*, 91–96.
4. Hamdi, N.; Fischmeister, C.; Carmen Puerta, M.; Valerga, P. A rapid access to new coumarinyl chalcone and substituted chromeno [4, 3-c] pyrazol-4 (1 H)-ones and their antibacterial and DPPH radical scavenging activities. *Med. Chem. Res*. **2011**, *20*, 522–530. https://doi.org/10.1007/s00044-010-9326-1.
5. Allehyani, E.S. Synthetic strategies, characterization and antimicrobial evaluation of novel angular heteroannulated furo [3,2-g] chromenes. *Synth. Commun*. **2023**, *53*, 1568–1578. https://doi.org/10.1080/00397911.2023.2238311.
6. Fauziah, F.; Bakhtra, D.D.A. LC-HRMS Profile of Chemical Compounds in Penicillium citrinum XT6 Extract. *IJPSM* **2023**, *8*, 80–102. https://doi.org/10.47760/ijpsm.2023.v08i06.007.
7. Meshcheryakova, A.A.; Konstantinova, E.A.; Melkonyan, K.A.; Khrustaleva, A.A.; Sorokin, V.V. The Synthesis of Various 2-Imino-2H-chromene-3-carbonitrile Derivatives. *Chem. Proc*. **2023**, *14*, 42. https://doi.org/10.3390/ecsoc-27-16125.
8. dos Santos PV, P.; Ribeiro, C.M.; Pavan, F.R.; Corbi, P.P.; Bergamini, F.R.; Carvalho, M.A.; D'Oliveria, K.A.; Cuin, A. Promising Ag (I) complexes with N-acylhydrazones from aromatic aldehydes and isoniazid against multidrug resistance in tuberculosis. *J. Mol. Struct*. **2021**, *1234*, 130193. https://doi.org/10.1016/j.molstruc.2021.130193.
9. Elumalai, D.; Gnanasekaran, R.; Leelakrishnan, S.; Nachimuthu, G.; Kannan, T.; Paramasivam, T.P.; Jayabal, K. InCl3-Assisted Eco-Friendly Approach for N-Fused 1, 4-Dihydropyridine Scaffolds via Ring Opening Michael Addition of Cyclic Nitroketene and Iminocoumarin: Synthesis and DFT Studies. *ChemistrySelect* **2018**, *3*, 2070–2079. https://doi.org/10.1002/slct.201702718.
10. Alizadeh, A.; Ghanbaripour, R.; Zhu, L.G. Recyclization of 2-Iminochromenes via Ketene Aminal Intermediates: One-Pot, Three-Component Reaction for Synthesis of 1, 4-Dihydropyridines-fused-1, 3-diazaheterocycles. *Synth. Commun*. **2013**, *43*, 2575–2582. https://doi.org/10.1080/00397911.2012.714040.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.