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A reinvestigation of the reactions of 3-substituted chromones with hydroxylamine. Unexpected synthesis of 3-amino-4*H*-chromeno[3,4-*d*]-isoxazol-4-one and 3-(diaminomethylene)chroman-2,4-dione

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ABSTRACT

Reactions of 3-substituted chromones (3-formylchromone, 3-formylchromone-3-oxime, and 3-cyanochromone) with hydroxylamine in alkaline medium were reinvestigated, and a proof of structures and a probable reaction pathway are presented. Syntheses of 2-aminochromone-3-carboxamide, 3-amino-4*H*-chromeno[3,4-*d*]isoxazol-4-one, and 3-(diaminomethylene)chroman-2,4-dione were developed.

Derivatives of 4*H*-1-benzopyran-4-one, also known as 4*H*-chromen-4-ones or chromones, are important natural products possessing a wide range of valuable physiological activities.[1] In addition, they represent useful synthetic building blocks in organic and medicinal chemistry.[2] The introduction of an electron-withdrawing group at the 3-position of the chromone system changes crucially the reactivity of the pyrone ring with respect to nucleophiles, and provides a broad synthetic potential of 3-substituted chromones. The diversity of properties of these compounds is due to the fact that, being highly reactive geminally activated push–pull alkenes with a good leaving group at the β-carbon atom, whose role is played by the phenolate anion (a fragment of the enol ether), they acquire the ability to undergo additional transformations related to γ-pyrone ring opening and heterocyclizations at the C-4 atom and/or at the substituent at the 3-position.[3]

The chemistry of 3-substituted chromones, mainly 3-formyl- and 3-cyanochromones, has been developed since the mid-1970s after the simple and convenient Vilsmeier–Haack method was proposed for the synthesis of 3-formylchromones from 2-hydroxyacetophenones, DMF, and $POCl_3$.[4] Treatment of 3-formylchromones **1** with hydroxylamine via 3-formylchromone-3-oximes **2** leads to 3-cyanochromones **3**.[5,6] In addition, **3** can be synthesized directly from 2-hydroxyacetophenones and hydroxylamine under the Vilsmeier–Haack conditions.[7] Among the diverse transformations of **3**, one of its more interesting reactions is its ability to interact with water at the C-2 atom followed by pyrone ring opening and cyclization at the CN group, leading to the formation of 2-amino-3-formylchromone **4**,[6,8] which in turn can be converted into 2-amino-3-formylchromone-3-oxime **5** and 2-amino-3-cyanochromone **6**.[6] Thus, the nitrile **3** is 'chemically equivalent' to the aminoaldehyde **4** under certain reaction conditions[9] (Scheme 1).

Continuing our studies on the synthetic potential of the chromone system,[10] we were interested in the course of oximation reactions of 3-substituted chromones **1–3**. This, at first glance simple reaction, has already been the subject of investigations. Ghosh et al. in 1979[11] studied the reaction of hydroxylamine hydrochloride with **3** in the presence of sodium acetate, and obtained a compound with mp 263 °C. Its composition corresponded to a 1:1 adduct, $C_{10}H_8N_2O_3$, which was assigned the structure **7** on the basis of ^{1}H NMR, IR, and mass spectra. The authors believed that the reaction occurred via 1,2-addition of hydroxylamine to the cyano group of **3**, and the stability of **7** was explained by two intramolecular hydrogen bonds. In this case, the structure of 2-amino-3-formylchromone-3-oxime **5** was not considered a possibility, because this oxime had been prepared earlier from **4** and its spectral characteristics differed from those of **7**.[6a] A compound of the same composition and spectral properties has been synthesized by Basiński and Jerzmanowska[12] in reactions of chromones **1–3**

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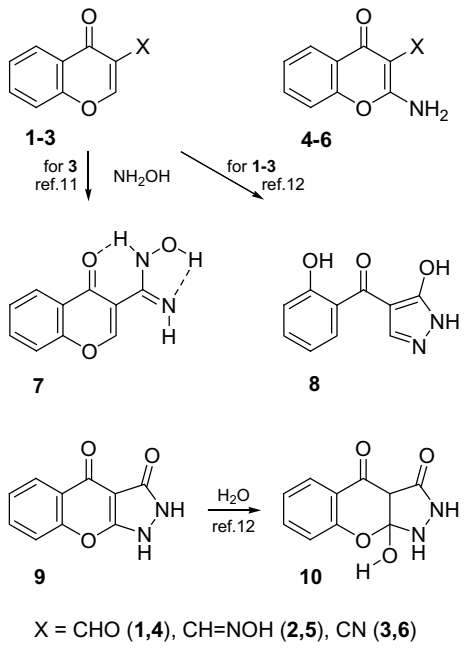
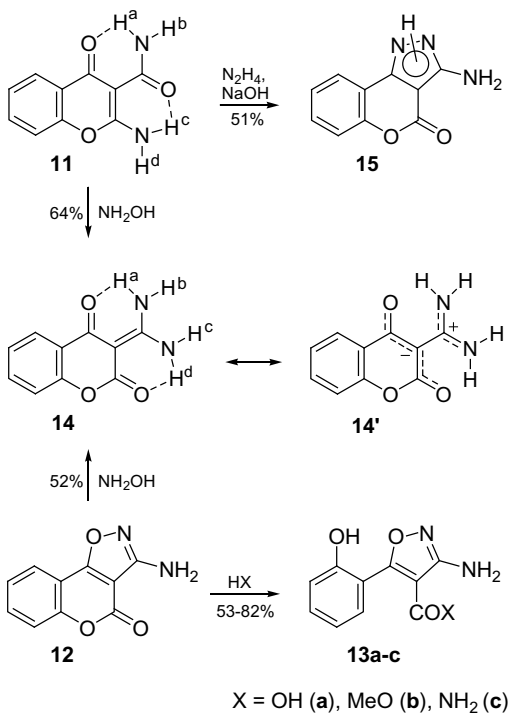


Scheme 1.



Scheme 2.

with hydroxylamine under different conditions affording contrasting yields. Based on a very doubtful mechanism, they proposed pyrazolone **8** as their product. In the same work,[12] the authors performed an important transformation, which, however, was not fully appreciated by them. When chromone **2** was treated with hydroxylamine hydrochloride (2 equiv) in the presence of NaOH (4 equiv) in aqueous ethanol, a compound of molecular formula $C_{10}H_6N_2O_3$ was obtained, which easily added water to form a product of molecular formula $C_{10}H_8N_2O_4$. Structures **9** and **10**, respectively, were assigned to these products, and chromones **3**, **5**, and **6** were indicated as non-isolable intermediates of the reaction;[12b] their claim has since been reviewed favorably[9] (Scheme 1).

We studied repeatedly the reactions of chromones **1–3** with hydroxylamine under the conditions described in Refs. 11 and 12 and confirmed the identity of compounds **7** and **8**. On the basis of ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy and using 2D HSQC and HMBC experiments we found that the product was, in fact, 2-amino-3-carbamoylchromone **11** (Scheme 2). The structural assignment for this compound as the aminoamide was based on four CD_3CO_2D exchangeable NH protons in the ^{1}H NMR spectrum [δ_H = 7.44 (H^b), 9.11 (H^d), 9.66 (H^a), and 10.50 (H^c)]. A literature search proved that this compound had been obtained before the reports of Ghosh[11] and Basiński[12] via acidic hydrolysis of **6**, which in turn was synthesized from 2-acetoxybenzoyl chloride and malononitrile in the presence of NaOH.[13] Although in 1978, the identity of the products prepared by hydrolysis of **6** and oximation of **3** was described in a Japanese patent,[14] the structures **7** and **8** are still valid in the chemical literature.[9]

Moreover, we repeated the treatment of chromone **2** with hydroxylamine according to Basiński and Jerzmanowska,[12b] and a perfect reproducibility of the reaction, as well as agreement of the spectral and chemical properties of the product with their description has been established. The same compound was also obtained as a result of the oximation of chromone **4** (yields 40–45% from **2** and **4**). However, we found that the reaction of both **2** and **4** with hydroxylamine in strongly basic solution leads not to **9**, but instead to 3-amino-4*H*-chromeno[3,4-*d*]isoxazol-4-one **12**, which was converted into acid **13a** when heated to boiling with a 10% solution of sodium hydroxide (Scheme 2). We confirmed the validity of the new structures using ^{1}H, ^{13}C, ^{15}N NMR, and IR spectroscopies. In addition, all the signals in the ^{1}H and ^{13}C NMR spectra of compound **12** were assigned on the basis of 2D ^{1}H–^{13}C HSQC and HMBC experiments.[15] Thus, the claimed compounds **9** and **10** are implausible, and are instead coumarino[3,4-*d*]isoxazole **12** and its acid **13a**.

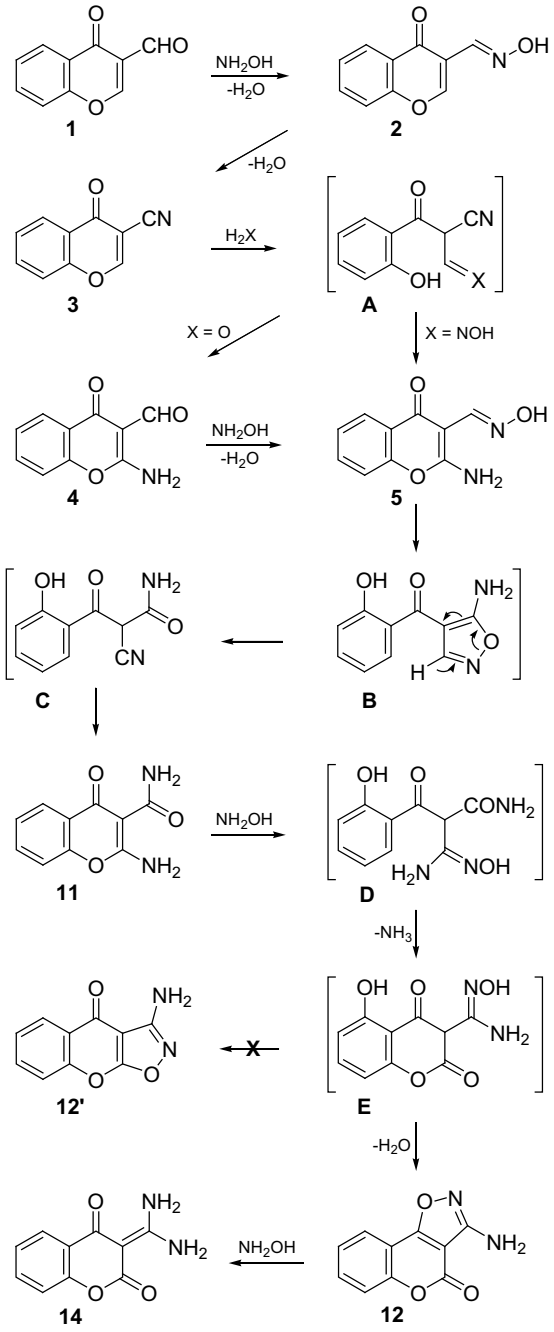
It was also found that the coumarin ring can easily be opened by the action not only of water,[12] but also of methanol and ammonia, which is a new route to prepare densely functionalized isoxazoles such as **13a–c** (Scheme 2). As mentioned above, compound **13a** had previously been incorrectly formulated as **10**,[12] which is contradicted by the spectral properties of this compound. For example, in the NMR spectrum of **13a** in DMSO-d_6, all the protons of the benzene ring are shifted to a higher field in comparison with those of **12** and, hence, opening of the α-pyrone ring took place under the action of water. The amino group and the phenolic hydroxyl appeared as two singlets at δ 5.90 (2H) and 10.03 (1H) ppm; the broad signal at δ 11.6–13.6 ppm is due to the resonance of the CO_2H proton. The IR spectra are also of diagnostic value in this isoxazole series (ν_{CO} = 1683–1712 cm^{-1}).

Following the same procedure,[12b] we also found that coumarino[3,4-*d*]isoxazole **12**, when treated with hydroxylamine under basic conditions, underwent transformation into a product of molecular formula $C_{10}H_8N_2O_3$, which was shown by a combination of ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy, including 2D ^{1}H–^{13}C, ^{1}H–^{15}N HSQC, and HMBC experiments, to be 3-(diaminomethylene)chroman-2,4-dione **14** (yield 52%). Thus, it turned out that the O–N bond in **12** is reduced under the action of hydroxylamine affording previously unknown compound **14**. Although the precise mechanism for this unusual reaction is unclear, the driving force for fission of the O–N bond is presumably the formation of a stable highly delocalized structure with two intramolecular hydrogen bonds. It is notable that the ^{13}C spectroscopic data for compound **14** show significant polarization of the C=C double bond [δ_C = 86.3 (C3) and 164.0 ppm (C3′)] and that the two nitrogen atoms are apparently equivalent (δ_N = 94.2 ppm). This may indicate a significant contribution from a fully charge-separated form

14′ in which there is a single bond but no free rotation of the $(NH_2)_2C^+$ grouping due to two strong intramolecular hydrogen bonds (Scheme 2). Besides the signals expected for the aromatic protons, the ^{1}H NMR spectrum of **14** showed two singlets (2H) at δ 9.82 (H^a, H^d) and 7.69 (H^b, H^c) ppm.[16] The simple and efficient syntheses of compounds **12–14** are of interest, because this class of organic compounds has remained inaccessible and unstudied until now.

Interestingly, when aminoamide **11** was treated with hydroxylamine under the same conditions, chroman-2,4-dione **14** was obtained in 64% yield. This unprecedented isomerization evidently involved firstly the formation of the coumarino[3,4-*d*]isoxazole **12**, followed by cleavage of the isoxazole ring. In accordance with this, the reaction of **11** with hydrazine hydrate in the presence of NaOH gave 3-aminochromeno[4,3-*c*]pyrazol-4-one **15** in 55% yield (Scheme 3). Previously, this compound was obtained by the reaction of 4-chloro-3-cyanocoumarin with hydrazine hydrate.[17] Of note is the fact that the ^{1}H NMR spectrum of **15** showed two sets of signals due to the possibility of annular prototropy of the pyrazole ring. Although annular tautomerism in NH azoles is a very fast process on the NMR time scale,[18] in our case, two singlets (NH_2) exhibiting broadening at lower frequency and two singlets (NH) at higher frequency were observed, indicating that coumarino[4,3-*c*]pyrazole **15** exists in DMSO-d_6 as a 77:23 mixture of 1*H*- and 2*H*-tautomers, respectively. The structural assignment was based on the signals due to the NH_2 groups at δ 6.60 ppm (1*H*-tautomer) and δ 5.62 ppm (2*H*-tautomer), the former of which is very similar in structure to that of **12**.

A possible route for the multi-step reaction of 3-formylchromone **1** with hydroxylamine in alkaline medium is outlined in Scheme 3. It includes several sequential nucleophilic 1,4- and 1,2-attacks of hydroxylamine and water molecules at the activated C-2 atom or at the 3-substituent of the chromone system. For the transformation **5**→**11** we favor a pathway involving the intermediacy of the 5-aminoisoxazole **B**, since its formation via intramolecular recyclization is especially facile under basic conditions. Subsequent deprotonation of **B** with concomitant isoxazole ring opening leads to the open chain intermediate **C**, which is cyclized involving the phenolic hydroxyl and cyano group to form aminoamide **11**. We suggest, therefore, that formation of **11** from **5** corresponds to the operation of a ring-to-ring interconversion.[2e,10b] In this context, it is important that when oxime **5** was treated with alkali without hydroxylamine, a 1:1 mixture of **11** and salicylic acid was isolated. An alternative mechanism, involving initial dehydration of **5** to form 2-amino-3-cyanochromone **6** followed by addition of water to form **11** was discarded owing to the failure of **6** to react with water to produce **11** under the conditions employed. In addition, attempts to detect **6** among the reaction products by ^{1}H NMR spectroscopy were unsuccessful, although it can be readily prepared from **4** and **5** in acidic solutions.[6]



Scheme 3.

We believe that hydroxylamine in alkaline medium first converts chromones **1–5** into the key intermediate **11**, which then undergoes further recyclization and reduction to give compound **14** via **12**. These products can result from the initial nucleophilic 1,2- or 1,4-additions of hydroxylamine to **11** due to the chemical equivalency of the 3-$CONH_2$ group and the C-2 atom (intermediate **D**). However, it seems more logical to us that the more nucleophilic nitrogen atom of the hydroxylamine would attack at the C-2 position of the chromone rather than at the 3-$CONH_2$ group. This behavior of **11** closely resembles (with the exception of a reduction stage) to that already reported for ethyl 2-alkyl- and 2-phenylchromone-3-carboxylates, which on treatment with hydroxylamine hydrochloride in refluxing acetic acid give 3-alkyl- and 3-phenyl-4*H*-chromeno[3,4-*d*]isoxazol-4-ones;[19] condensation of chromone- and 2-methylchromone-3-carboxylic acids with phenylhydrazine leads to 1-phenylchromeno[4,3-*c*]pyrazol-4(1*H*)-ones.[20]

It should be noted that the alternative cyclization of **E** involving the amidoxime hydroxyl and the lactone carbonyl to give 3-amino-4*H*-chromeno[3,2-*d*]isoxazol-4-one **12′** does not occur. The structure of the 3-amino-4*H*-chromeno[3,4-*d*]isoxazol-4-one **12** is not in doubt. That the compound is a coumarin and not a chromone is shown by the IR band at 1757 cm^{-1}, typical of the carbonyl group in coumarins[19] (the chromone carbonyl band is usually near 1660 cm^{-1}).

In support of the proposed pathway (Scheme 3), the reactions of chromones **1**, **3**, and **5** with hydroxylamine were studied under the conditions used for the synthesis of isoxazole **12** from **2** and **4** and chroman-2,4-dione **14** from **11** and **12**. In these cases, different

compositions of the mixtures of **11**, **12**, and **14** were obtained (**11:12:14** = 8:30:62 from **1** and 33:17:50 from **5**) in good combined yields (50–60%), whereas the same reaction with **3** yielded a mixture of compounds **12** and **14** in about equal amounts and **11** was not detected at all (the ratio of the products was determined by integration of the signals in the ^{1}H NMR spectra). Thus, the origin of these materials is explained and the overall reaction can be represented as a coherent process, the final product of which is chroman-2,4-dione **14**. Compounds **11** and **12** are isolable intermediates in this process, and the product structure depends on the nature of the starting materials and the reaction conditions. Since coumarins with 3,4-heterocyclic fused ring systems serve as useful synthetic intermediates and have attracted attention as key compounds for drug design,[21] it is expected that these reactions will have significant synthetic application.

In conclusion, 3-formylchromone represents a very reactive system and its reactions with hydroxylamine give a variety of products. Since the identity of some of these products was in doubt, we have reinvestigated the reactions and found that by varying the conditions, 2-aminochromone-3-carboxamide, 3-amino-4*H*-chromeno[3,4-*d*]isoxazol-4-one, and 3-(diaminomethylene)chroman-2,4-dione could be prepared in moderate to good yields. The resulting products are of considerable interest as useful precursors in the synthesis of other biologically and medicinally important organic materials. The generality of this simple and unrecognized method is being investigated further.

Acknowledgments

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15. *3-Amino-4H-chromeno[3,4-d]isoxazol-4-one* **12**. This compound was prepared from chromones **2** and **4** according to the procedure described previously for **9**.[12b] Yields 40–45%, mp 229–230 °C (lit.[12b] mp 228–229 °C); IR (KBr) 3457, 3364, 3300, 3195, 1757, 1646, 1616, 1597, 1566, 1528 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.45 (s, 2H, NH_2), 7.49 (ddd, 1H, H-8, J = 7.8, 7.4, 1.0 Hz), 7.58 (dd, 1H, H-6, J = 8.5, 1.0 Hz), 7.78 (ddd, 1H, H-7, J = 8.5, 7.4, 1.6 Hz), 7.99 (dd, 1H, H-9, J = 7.8, 1.6 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 97.23 (C3a), 110.58 (C9a), 117.31 (C6), 122.47 (C9), 125.08 (C8), 133.74 (C7), 153.63 (C5a), 156.40 (C3), 160.51 (C4), 168.74 (C9b); ^{15}N NMR (40 MHz, DMSO-d_6) δ 50.0 (NH_2), 342.3 (=N); MS (EI): *m/z* (%) 202 $[M]^+$ (100), 173 (11), 130 (10), 121 $[HOC_6H_4CO]^+$ (84), 120 $[OC_6H_4CO]^+$ (27), 104 $[C_6H_4CO]^+$ (18), 92 $[C_6H_4O]^+$ (33), 76 (27), 63 (23), 53 (10), 50 (16). Anal. Calcd for $C_{10}H_6N_2O_3$: C, 59.41; H, 2.99; N, 13.86. Found: C, 59.25; H, 2.90; N, 13.74.
16. *3-(Diaminomethylene)chroman-2,4-dione* **14**: Yield 64% (from 11), 52% (from 12), mp 259–261 °C; IR (KBr) 3429, 3290, 3157, 1684, 1633, 1610, 1568, 1487, 1473 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.28 (dd, 1H, H-8, J = 8.2, 1.2 Hz), 7.30 (ddd, 1H, H-6, J = 7.8, 7.3, 1.2 Hz), 7.63 (ddd, 1H, H-7, J = 8.2, 7.3, 1.7 Hz), 7.69 (br s, 2H, NH_2), 7.94 (dd, 1H, H-5, J = 7.8, 1.7 Hz), 9.82 (br s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ 86.26 (C3), 116.22 (C8), 120.71 (4a), 123.60 (C6), 125.44 (C5), 133.36 (C7), 152.46 (C8a), 163.93 (C2/C3′), 164.12 (C3′/2), 177.96 (C4); ^{15}N NMR (40 MHz, DMSO-d_6) δ 94.2 (NH_2); MS (EI): *m/z* (%) 204 $[M]^+$ (100), 187 (19), 159 (13), 121 $[HOC_6H_4CO]^+$ (40), 120 $[OC_6H_4CO]^+$ (39), 109 (17), 92 $[C_6H_4O]^+$ (24), 84 (20), 68 (20), 65 (13), 64 (13), 63 (12). Anal. Calcd for $C_{10}H_8N_2O_3 \cdot 0.25H_2O$: C, 57.56; H, 4.11; N, 13.42. Found: C, 57.39; H, 3.80; N, 13.04.
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