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CONVERSION OF COUMARINS ACCOMPANIED BY OPENING AND RECYCLIZATION OF THE LACTONE RING. 1. STUDY OF THE REACTION OF 3-ETHOXYCARBONYL(3-ACYL)COUMARINS WITH CYANOACETYLHYDRAZINE AND ITS DERIVATIVES

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A stepwise sequence for the interaction of 3-ethoxycarbonyl(acyl)coumarins with cyanoacetylhydrazine, its N-acetyl and N-isopropylidene derivatives, leading to the formation of 3-cyanocoumarins, is proposed and demonstrated. It was established that the 3-cyanocoumarins formed are also able to participate in further conversions by a type of Michael reaction.

Keywords: cyanoacetylhydrazine derivatives, 3-ethoxycarbonyl(acyl)coumarins, mass spectrometry, Michael reaction, recyclization of coumarin lactone rings.

It is known that coumarins substituted in position 3 with electron-withdrawing groups enter into the Michael reaction with compounds containing an active methylene group. Products of addition at position 4 of the initial coumarin are formed in this way [1]. In a series of cases this reaction does not stop at the addition stage but leads to the product of opening of the coumarin lactone ring [2]. We have also discovered that the reaction between 3-ethoxycarbonyl(acetyl)coumarins [3], their 5,6-benzo analogs, and 7-methoxy-substituted derivatives [4], and cyanoacetylhydrazine, its N-acetyl and N-isopropylidene derivatives in the presence of a secondary amine (piperidine), i. e. under Michael reaction conditions, does not stop at the two stages indicated above, but unexpectedly leads to the formation of the corresponding 3-cyanocoumarins. In developing these studies we established that 6-(8)-methoxy-, 3-ethoxycarbonyl-6-methylcoumarins, and 3-acetyl-8-methoxycoumarin are subject to an analogous conversion (see Scheme 1).

It is obvious that the observed conversion is the result of a series of sequentially occurring steps leading finally to the formation of the corresponding 3-cyanocoumarins. We propose the following scheme for this process. The initially formed product of addition at position 4 of the initial coumarin **A** is subject to opening of the lactone ring with the formation of anion **B**, which may be transformed into the final 3-cyanocoumarin in two directions, differing in the sequence of removal of a molecule of hydrazine and the appropriate β-dicarbonyl compounds. Route 1 is the recyclization of anion **B** with the intermediate formation of the 3-cyano-3,4-dihydrocoumarin **C**, fission from which of a molecule of malonic or acetoacetic (benzoylacetic) ester leads to

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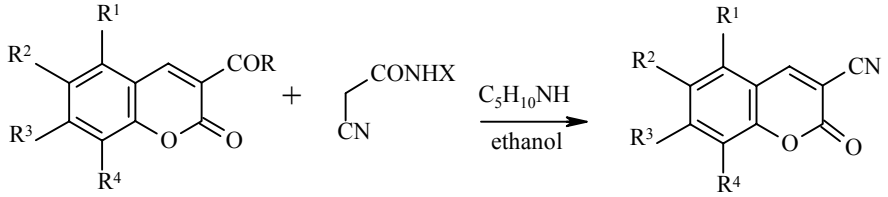
Scheme 1

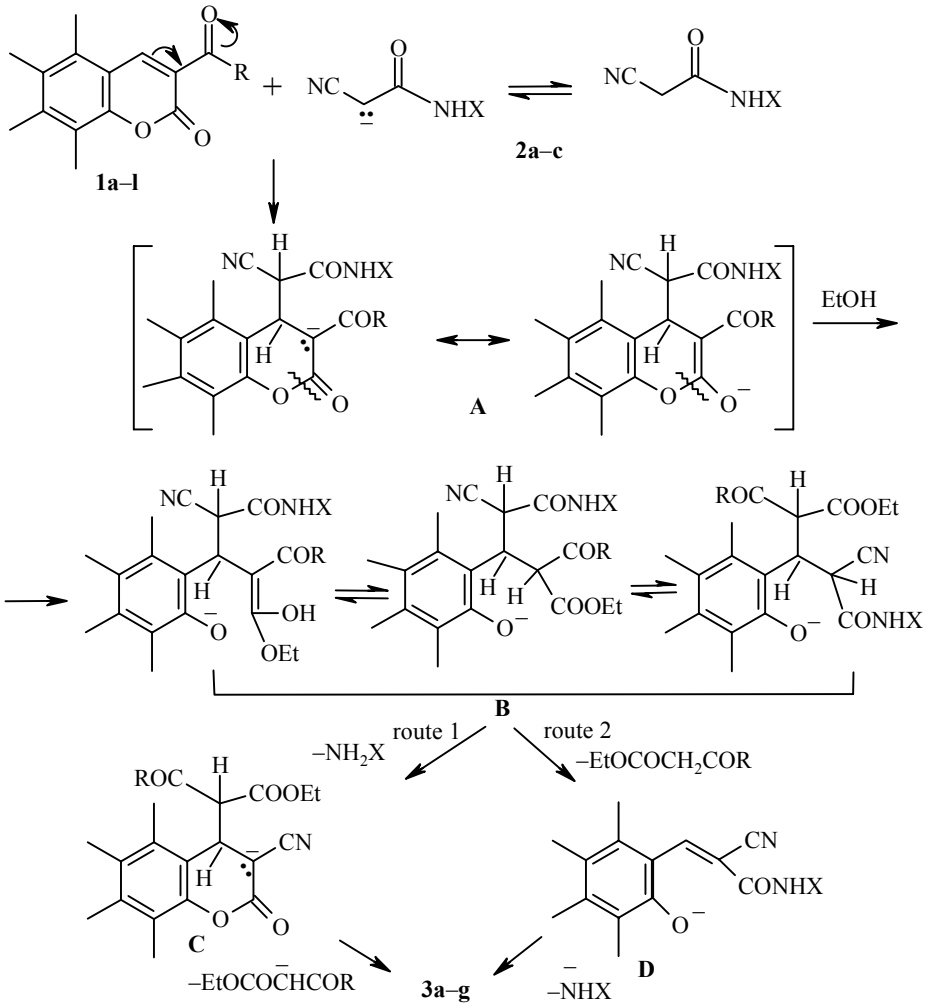


1a–l **2a–c** **3a–g**

1a,**d**,**f**,**h-j**,**l** R = OEt, **b**,**e**,**g**,**k** R = Me, **c** R = Ph; **a-c**,**f-l** R^1 = H, **d**,**e** $R^1 + R^2 = o\text{-}C_6H_4$;
a-c,**f**,**g**,**j**,**k** R^2 = H, **h** R^2 = OMe, **i** R^2 = Me, **l** R^2 = Br; **a-e**,**h-l** R^3 = H, **f**,**g** R^3 = OMe;
a-i,**l** R^4 = H, **j**,**k** R^4 = OMe; **3 a**,**c-g** R^1 = H, **b** $R^1+R^2 = o\text{-}C_6H_4$; **a**,**c**,**d** R^2 = H, **e** R^2 = Me, **f** R^2 = OMe, **g** R^2 = Br;
a,**b**,**d-g** R^3 = H, **c** R^3 = Me; **a-c**,**e-g** R^4 = H, **d** R^4 = OMe; **2 a** X = NH_2, **b** X = NHCOMe, **c** X = $N{=}CMe_2$

the final 3-cyanocoumarins. Route 2 is the conversion of anion **B** into the benzylidene derivative **D**, also recyclizing subsequently into 3-cyanocoumarins (see Scheme 2). It should be kept in mind that all the intermediate compounds shown in the Scheme in the form of anions exist in the reaction mixture in equilibrium with the corresponding neutral molecules.

Scheme 2



With the aim of investigating the conversion of 3-ethoxycarbonyl(3-acyl)coumarins into 3-cyanocoumarins by mass spectrometry, reaction mixtures formed by the interaction of **1a-c,f,l** with **2a**, **1a,c** with **2c**, and also **1a-c,f,h-j** with **2c** were studied. The corresponding 3-cyanocoumarins **3** were separated first in the precipitate. Then preparative resolution of the mixture was carried out by TLC and the mass spectra of the isolated fractions were studied.

According to the data obtained, the initial coumarins **1**, cyanoacetylhydrazines **2**, and the final reaction products, the 3-cyanocoumarins **3**, were present in the mixtures investigated. In addition a significant number of compounds were observed, probably existing as intermediates and byproducts in the formation of 3-cyanocoumarins and as products of further conversions of the 3-cyanocoumarins*. Compounds identified by us are given in Tables 1 and 2, however it must be stressed that the reaction mixtures proved to be so complex that the identification of the separated components has been unsuccessful up to the present.*[2]

As expected the interaction of 3-substituted coumarins with cyanoacetylhydrazines begins with a Michael reaction with addition of the latter at position 4 of the lactone ring (structure **A**) with its subsequent opening (structure **B**). The presence of the neutral forms of anions **A** and **B** was successfully recorded in the reaction mixtures formed in the interaction of the coumarins **1** with N-acetylcyanoacetylhydrazine **2b** and N-isopropylidenecyanoacetylhydrazine **2c**. This is indicated by the presence in the electron capture mass spectra of peaks for the corresponding molecular ions (see Table 1). In addition, in the chemical ionization mass spectrum of the reaction mixture formed on interacting **1a** + **2c**, peaks were observed for the protonated molecular ions MH^+ at 358 (**A**), 404 (**B**).

The preferred direction for the fragmentation of the molecular ions of compounds **B** is caused by the elimination from them of –OEt, EtOH, and –COOEt. The fragments $[M\text{-EtOH}]^+$ naturally have the same mass number as the molecular ions of the unopened structure **A**. It was concluded that compounds having structure **A** were present in the mixture together with compounds **B** on the basis of the significant redistribution of the intensities of the peaks for M_A^+ and M_B^+ during the evaporation of specimens.

Compounds **A** were not recorded in reaction mixtures obtained using cyanoacetylhydrazine **2a** in several cases (**1a** + **2a**, **1b** + **2a**, **1c** + **2a**, **1f** + **2a**). When using **2a** compound **B** was not recorded practically anywhere in the reaction, which is evidently linked with the high recyclization rate of the latter into cyanocoumarins **3**. In addition, in the case of the interaction of **2a** with 3-ethoxycarbonylcoumarins **1a,f,h,j**, an additional route is possible for the further conversion of structure **A** linked with cyclization into tricyclic structures through the elimination of ethanol*[3].

An additional route emerges in the case of the reactions of **2a** with 3-acylcoumarins **1b,c** for the cyclization of structure **A** through interaction with the carbonyl of the acyl group*[4] (Scheme 3).

In this case the appropriate peaks for the molecular ions at 269 (**1b** + **2a**) and 331 (**1c** + **2a**) were observed in the spectra, but compound **A** was not recorded. It is interesting to note that, judging by the mass spectrometric decomposition, the molecular ions of **E** were found partially in the open form **E'**. This is indicated by the ease of the breaking away of 40 m. u. ($NCCH_2$ group) from the molecular ions at the same time as elimination of a CONH group seemingly corresponding to the tricyclic form **E** of the molecular ions.

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* Further analysis showed that products isolated during the reaction interact with one another, with the initial reactants, and with the final 3-cyanocoumarins.

*[2] Since the reaction masses were multicomponent mixtures analysis of the evaporation curves of separate characteristic ions was widely used when considering the mass spectra. This significantly facilitated assignment of peaks to the spectrum of one or another component of the mixture being considered.

*[3] This route will be considered in more detail below.

*[4] The problem of which center (carbonylacyl group or the position 4 of the coumarin ring) initiates the interaction of the cyanoacetylhydrazine with 3-acylcoumarins remains.

TABLE 1. Mass Spectra of the Main Coumarin-containing Products

No.	Initial mixture	Molecular masses of reaction products													
		A	**B**	**C**	**3**	**E**	**F**	**G**	**I**	**J**	**A-2H**	**C-2H**	M	**N**	**K** and **I-2H**
1	**1a+2a**				171		204	250						269	268
2	**1b+2a**				171	269							267		
3	**1c+2a**				171	331							329		
4	**1a+2b**	359			171		246	292			357			311	310
5	**1b+2b**	329			171						327				310
6	**1b+2c**	327			171						325				308
7	**1a+2c**	357	403	331	171		244		310	284	355	329			308
8	**1f+2a**				201		234	280						299	298
9	**1k+2c**	387	433	361	201		274		340	314	385				338
10	**1h+2c**	387	433		—*					314					
11	**1i+2c**	371	417		185		258			298					322
12	**1j+2c**	387	433	361	201					314					
13*[2]	**1l+2a**	395/397			249/251		282/284	328/330			393/397	407/409			346/348
14	**1c+2c**	389	435	363							387				308

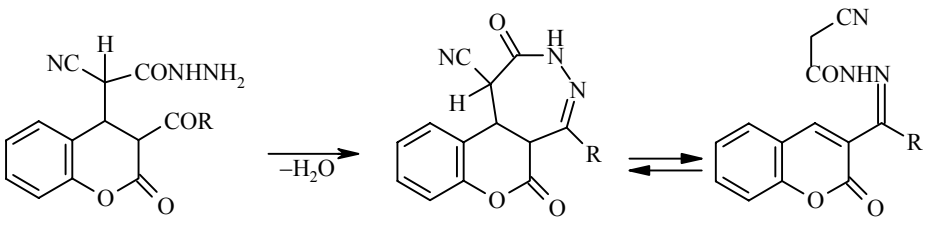
* The presence of 3-cyanocoumarin was not recorded mass spectrometrically in the reaction mixture after separating it in the precipitate.

*[2] The masses of ions containing $^{79}Br/^{81}Br$ are indicated.

TABLE 2. Mass Spectra of the Main Hydrazine Derivatives in the Reaction

Reaction products	Molecular masses of products													
	1a+2a	**1b+2a**	**1c+2a**	**1a+2b**	**1b+2b**	**1b+2c**	**1a+2c**	**1f+2a**	**1f+2c**	**1h+2c**	**1i+2c**	**1j+2c**	**1l+2a**	**1c+2c**
NH_2X				74	74	72	72		72	72	72	72		72
$XNHCOCH_2COOEt$	146			188			186	146	186	186	186	186	146	
Pyrazolidine-3,5-dione	100							100					100	
3-Methyl(phenyl)pyrazol-5-one		98	160											
$Me_2NNHCOCH_2COPh$														218

Scheme 3



A **E** **E'**

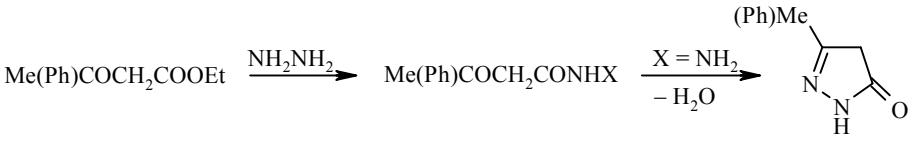
R = Me, Ph

The fact that recyclization of structures **B** into cyanocoumarins **3** occurs with the separation of hydrazines and β-keto esters (malonic, acetoacetic, or benzoylacetic) is confirmed by the presence in the mass spectra of the reaction mixtures with **2b** and **2c** of intense peaks for the corresponding molecular ions $NH_2NHCOMe^+$ (74) and $NH_2N{=}CMe_2^+$ (72) (see Table 2). In the spectra of the mixtures obtained in reactions with cyanoacetylhydrazine **2a** the molecular peak of hydrazine $NH_2NH_2^+$ (32) is outside the range of recording mass spectra (50-800 m. u.), however there is no doubt that hydrazine is formed since products of its interaction with β-keto esters formed in the course of the reaction are observed. In the interaction of cyanoacetylhydrazines **2a-c** with 3-ethoxycarbonylcoumarins **1a,f** intense peaks were observed in the mass spectra belonging to the spectrum of malonic ester monohydrazide. The values of the mass numbers of the molecular ions (146 for the interaction with **2a**, 188 with **2b**, and 186 with **2c**) and the daughter ions $[M\text{-}OEt]^+$, $[M\text{-}EtOH]^+$, and $[M\text{-}NHNH_2]^+$ completely confirm the structure of the hydrazides. Judging by the intensity of the peaks the monohydrazides of malonic ester are one of the main components of the reaction mixtures after the separation of the 3-cyanocoumarins*.

On using hydrazine **2a** in the reaction, formed malonic ester monohydrazide unsubstituted at the terminal nitrogen atom is partially cyclized into pyrazolidine-3,5-dione, which is indicated by the significant redistribution of intensities of the molecular ions of the monohydrazide (M^+ 146) and pyrazolidine-3,5-dione (100) during the temperature fractionation of the sample.

On interacting **2a** with 3-acetyl- and 3-benzoylcoumarins **1b,c** an analogous reaction takes place between the unsubstituted hydrazine separated on recyclization and acetoacetic (benzoylacetic) ester, however the hydrazides formed in this way readily cyclize with the formation of the corresponding pyrazolones (see Scheme 4).

Scheme 4



In the mass spectra of the mixtures mentioned above intense peaks were observed for the appropriate molecular ions at 98 (**1b** + **2a**) and 160 (**1c** + **2a**) and also peaks for the daughter ions $[M\text{-}HCO]^+$ and $[M\text{-}CH_2CO]^+$ characteristic of the decomposition of pyrazolones [5]. The structure of the isopropylidene-substituted hydrazide of benzoylacetic acid ester (see Table 2) is observed in the mixture formed on interaction of 3-benzoylcoumarin **1c** with hydrazine **2c**.*[2]

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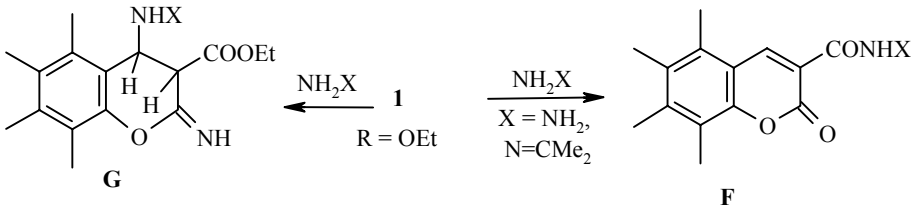
* Malonic acid dihydrazide is most probably formed in minor amounts since peaks for the corresponding ions are of low intensity in all cases.

*[2] Hydrazides were not recorded in the reaction mixtures obtained on interacting 3-acetylcoumarin **1b** with N-substituted hydrazines **2b,c**.

Hydrazines split off in the process of recyclization also react with the initial 3-ethoxycarbonylcoumarins **1a,f-l**, and the interaction proceeds both at the carbethoxy group with the formation of the corresponding hydrazides of coumarin-3-carboxylic acid **F,** and by way of addition of hydrazines at the 4 position of the lactone ring (structure **G**) (see Scheme 5).

Scheme 5

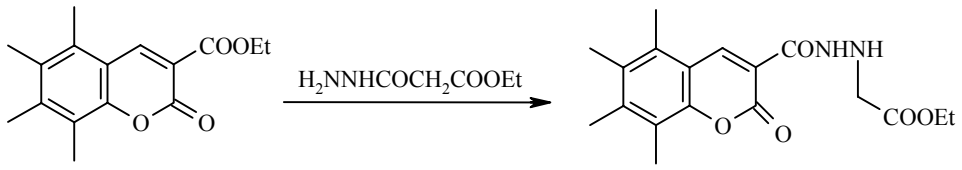


The formation of hydrazides is evidently the conversion preferred since the corresponding products are observed in almost all reaction mixtures, it is confirmed by the presence of molecular ion peaks in the electron impact spectra*, and by the characteristic decomposition direction with the formation of the $[M\text{-}NHX]^+$ ion.

Products of addition of hydrazine at position 4 of the lactone ring were observed in mixtures of **1a** + **2a**, **1a** + **2b**, **1f** + **2a**, and **1l** + **2a**. The corresponding peaks for the molecular ions of **G** have mass numbers 250, 292, 280, and 328/330*[2]. Although the molecular mass of ions **F** coincide with that of the $[M_G\text{-}EtOH]^+$ ion formed on mass spectrometric decomposition of the molecular ion of **G**, the conclusion as to the formation of compounds **F** follows from the temperature redistribution of the intensities of the peaks for the M_F and M_G ions. In addition, structure **F** was observed in the spectra of the reaction mixtures obtained using **2c**, where, by virtue of the presence of the isopropylidene-substituent at the terminal nitrogen atom of the hydrazine, elimination of EtOH from the molecular ion of **G** is impossible.

It is interesting to note that the N-unsubstituted malonic acid hydrazide formed in the reactions of **1a** + **2a**, **1f** + **2a**, and **1l** + **2a** also reacts with the initial 3-ethoxycarbonylcoumarin at the ethoxycarbonyl group with the formation of the corresponding hydrazides (see Scheme 6).

Scheme 6



Peaks were observed in the mass spectra for the molecular ions at 318 (**1a** + **2a**), 348 (**1f** + **2a**), and 396/398 (**1l** + **2a**).

As already mentioned above the recyclization into 3-cyanocoumarin may be effected with a different sequence of splitting away molecules of hydrazine and β-keto esters. Consideration of the mass spectra of all the mixtures studied shows that the intermediate structure **C** (route 1) is present in the reaction mixtures obtained on

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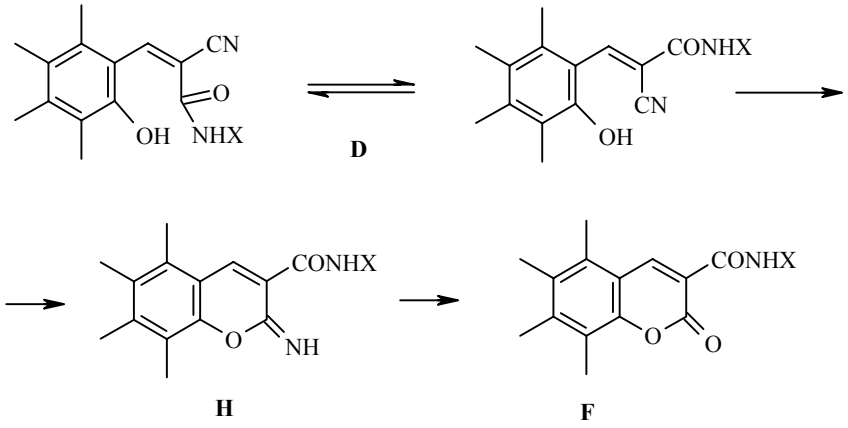
* In the chemical ionization spectrum of the reaction mixture obtained on interacting **1a** + **2c** a peak was recorded for the corresponding structure **F** as the quasimolecular ion MH^+ 245.

*[2] Here and subsequently the masses of the ions containing $^{79}Br/^{81}Br$ are indicated.

interacting **1a** + **2c** (M_C 331), **1f** + **2c** (M_C 361), and **1j** + **2c** (M_C 361). Finally it is impossible to exclude that structure **C** is not the direct product of the recyclization of **B**, as shown in Scheme 2, but is formed on further interaction of the isolated 3-cyanocoumarin **3** with the malonic ester split off at a previous stage. However this hypothesis seems less probable, since neither the free malonic ester nor the product of its addition to the initial 3-ethoxycarbonylcoumarin were recorded in these mixtures. Probably the malonic ester is mainly linked with the separated hydrazine.

Concerning the second possible reaction route through the formation of the intermediate benzylidene derivative **D**, structure **D** was not recorded in any mixture. Either this route does not occur or this structure has a short life span. It is possible that compound **D**, due to intramolecular cyclization involving the nitrile group and the phenolic hydroxyl, is readily converted into the 2-imino derivative of coumarin-3-carboxylic acid hydrazide **H**, and subsequent hydrolysis of **H** under the reaction conditions leads to the formation of the corresponding hydrazide of coumarin-3-carboxylic acid **F**, as shown in Scheme 7 [6, 7]. At the same time, the fact that hydrazides **F** are observed only in mixtures where the initial coumarin had an ethoxycarbonyl group in position 3 permits the assumption that the formation of **F** is linked preferably with the interaction of the hydrazine with the ethoxycarbonyl group, as was considered above. An unequivocal answer to the problem of the occurrence of the second pathway may only be obtained by studying the reaction dynamics with recording of the intermediate structures **D** and **H**.

Scheme 7



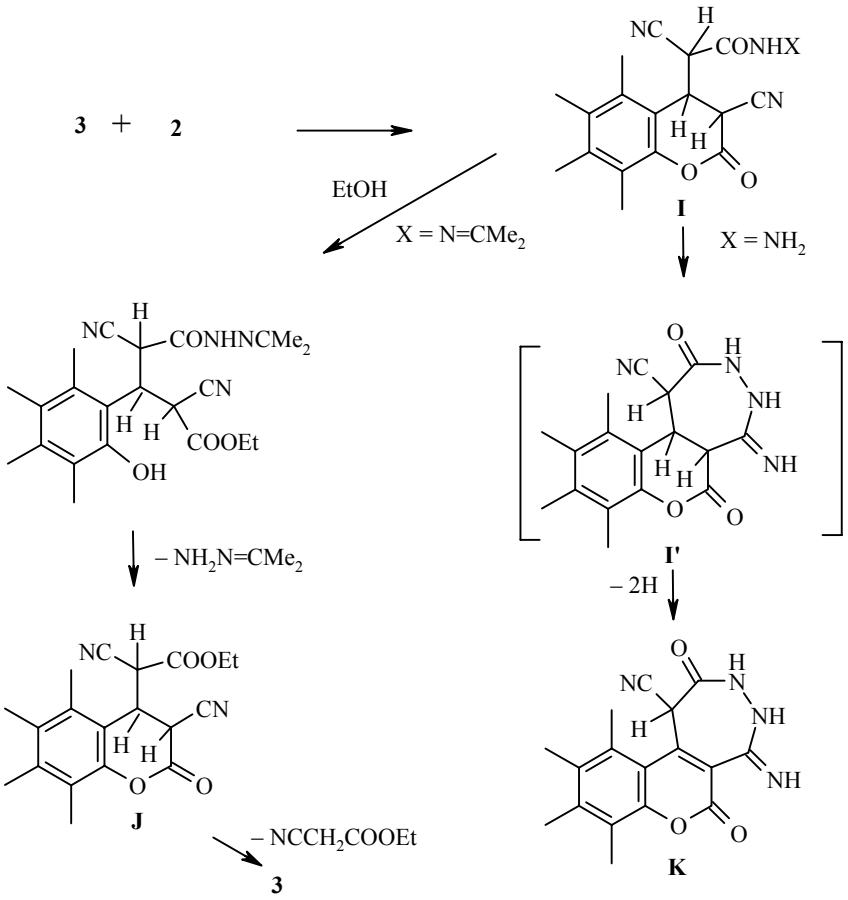
The resulting 3-cyanocoumarins **3** are also obviously capable of undergoing a Michael reaction with the initial cyanoacetylhydrazines **2**. In the case of reaction mixtures obtained on interacting **1a** + **2c** and **1f** + **2c** the molecular ions corresponding to structure **I** were successfully recorded at 310 and 340. The Michael adducts formed are probably capable of recyclization proceeding by a mechanism analogous to that considered above in Scheme 1. Recyclization leads to the formation of hydrazine, cyanoacetic ester, 3-cyanocoumarin and adduct **J** (see Scheme 8).

Cyanoacetic ester was not recorded in the mass spectra of the reaction mixtures investigated, however in the case of the interaction of N-isopropylidenecyanoacetylhydrazine **2c** with coumarins **1a,f,h-j** peaks for molecular ions were observed in the spectra corresponding to structure **J** at 284 (**1a** + **2c**), 298 (**1i** + **2c**), and 314 (**1f,h,j** + **2c**).

As was shown in [1] using **3a** as example, adduct **J** is readily formed on interacting 3-cyanocoumarins with cyanoacetic ester in the presence of catalytic amounts of piperidine. The absence of compounds **J** from reaction mixtures obtained involving hydrazine **2a** is possibly linked with additional stabilization of adduct **I** as a result of cyclization into the tricyclic structure **I'** [8] with subsequent dehydrogenation into structure **K**

(Scheme 8). A similar dehydrogenation was noted when obtaining benzopyranopyrimidine and pyridocoumarin derivatives, when during the synthesis compounds were also isolated having a molecular mass 2 m. u. lower than expected [9].

Scheme 8



The ability to dehydrogenate is evidently a property of products with an unsaturated 3-4 bond formed in the given mixtures. Dehydrogenation proceeds especially readily in tricyclic systems. This relates to structures **E** (in the interaction of **2a** with acylcoumarins), **I'**, and also the tricyclic structures **L**, which are formed from adduct **A** (in the interaction of **2a** with ethoxycarbonyl-substituted coumarins) by way of cyclization with elimination of EtOH (Scheme 6).

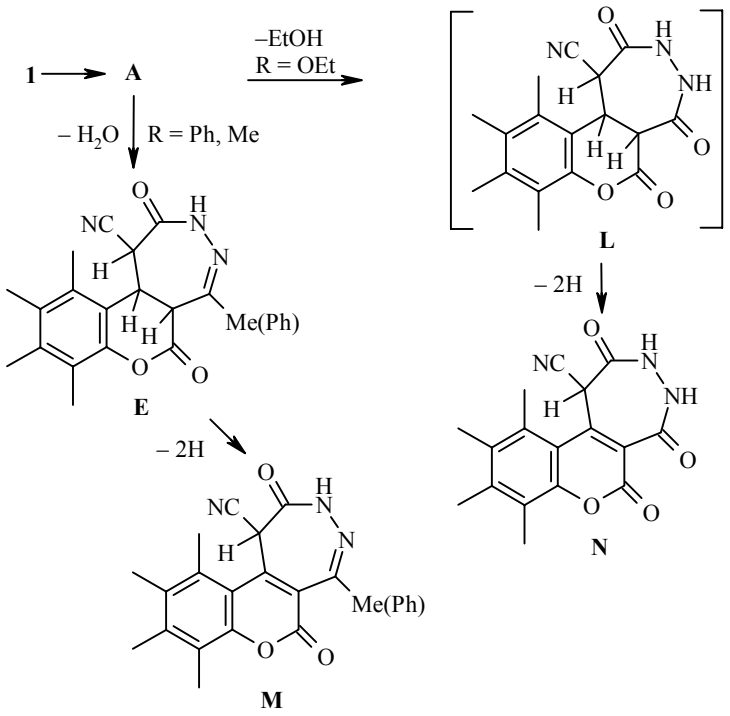
Essentially, when both compounds **E** and the dehydrogenation products **M** are successfully observed in the case of acyl coumarins, then structures **I'** and **L** are not recorded when **2a** interacts with ethoxycarbonylcoumarins **1a,h-j**. Only the dehydrogenated products **K** and **N*** are observed (see Scheme 9).

To a lesser extent dehydrogenation is natural for Michael adducts by virtue of their structures being incapable of cyclization. Dehydrogenation probably has a thermal character. In the process of evaporating samples in all mixtures with **2c**, where compounds **A**, **C**, and **I** are recorded, the intensity of their molecular ion

* It is impossible to exclude the fact that the formation of tricyclic structures may occur as a result of the interaction of not only the terminal NH_2 group but also the amide N atom of the hydrazine fragment, which will lead to the formation of isomeric **K** and **N** tricyclic structures containing a six-membered ring with an exocyclic NH_2 group.

peaks M^+ is reduced, peaks for $[M-2H]^+$ ions appear, and their intensity grows in proportion to the degree of heating of the sample.

Scheme 9



It should be noted that, as already mentioned above, all the products of the interaction of cyanoacetyl hydrazines with 3-substituted coumarins with the structures represented have not been exhausted. The large number of reactive centers and the possibility of interaction with hydrazines and β-keto esters formed during the reaction does not exclude the probability of forming dimeric and more complex structures.

To confirm the data of mass spectrometry given above with the aid of ^{1}H NMR spectroscopy, the course of the reaction of 3-ethoxycarbonylcoumarin **1a** with cyanoacetylhydrazine **2a** was studied directly in the ampule by recording the NMR spectra of the reaction mixture formed at definite time intervals. The reaction was carried out in CD_3OD and CH_3OD at an equimolar ratio of the initial reactants in the presence of a catalytic amount of piperidine. In the first step of the reaction it was established that directly after mixing **1a** and **2a,** even without adding piperidine, the formation of trace amounts of 3-cyanocoumarin **3a** was observed, as was shown by the appearance in the NMR spectrum of a low intensity signal for $C_{(4)}$–H at 8.66 ppm. In addition signals were observed corresponding to the protons of the COOEt fragment of malonic ester and its monohydrazide (triplet at 1.28 (CH_3) and quartet at 4.18 ppm (CH_2)). After adding piperidine the process accelerates sharply and leads to an increase of up to 36-40% in the content of 3-cyanocoumarin **3a** (10 min after adding piperidine). Simultaneously the intensity of the multiplet for aromatic protons at 6.7-7.3 ppm in the spectrum increased and new signals appeared for the COOEt group. At the present time a paper on the study of this reaction by NMR spectroscopy is being prepared.

EXPERIMENTAL

The mass spectra were recorded on a Finnigan SSQ-710 chromato-mass spectrometer with direct insertion of samples into the ion source. Energy of ionizing electrons was 70 eV, ion source temperature 150°C. Chemical ionization spectra were obtained using isobutane as reactant gas. The IR spectra were taken in nujol on a Perkin–Elmer 457 instrument. The NMR spectra were recorded on a Varian Unity 400 (400 MHz) spectrometer, internal standard was TMS.

Reaction masses 1-14 (see Table 1), the compositions of which were studied by mass spectrometry, were obtained by the interaction of hydrazines **2a-c** with the appropriate coumarins under the conditions indicated previously in [4], after separating the precipitated 3-cyanocoumarins **3** and evaporating the obtained filtrate from the ethanol used as reaction medium.

3-Cyano-8-methoxycoumarin (3d, $C_{11}H_7NO_3$). A. Piperidine (3 drops) was added to a suspension of coumarin **1j** (0.5 g, 2 mmol) and hydrazine **2c** (0.28 g, 2 mmol) in ethanol (20 ml). The reaction mixture was stirred for 1 h at 20°C. The precipitated solid was filtered off, washed with chilled ethanol (5 ml), and air-dried. Cyanocoumarin **3d** (0.3 g: 74%) was obtained; mp 221-223°C (ethanol). IR spectrum, ν, cm^{-1}: 2225 (CN), 1720 (C=O).

B. Cyanocoumarin **3d** (0.32 g, 65%) was obtained from coumarin **1k** (0.5 g, 2.3 mmol) and hydrazine **2c** (0.32 g, 2.3 mmol) under the conditions of method A and was identical both in mp and in spectral characteristics to the product synthesized by method A. According to [10] mp 222-223°C.

3-Cyano-6-methoxycoumarin (3f) was obtained under the conditions of synthesis of **3d** by method A on interacting coumarin **1h** (0.3 g, 1.2 mmol) with **2c** (0.17 g, 1.2 mmol). The yield of **3f** was 0.23 g (94%) of a bright yellow crystalline substance; mp 218-220°C (ethanol). IR spectrum, ν, cm^{-1}: 2225 (CN), 1725 (CO). Found, %: C 65.92; H 3.61; N 6.73. M^+ 201. $C_{11}H_7NO_3$. Calculated, %: C 65.67; H 3.48; N 6.96. M 201.

3-Cyano-6-methylcoumarin (3e, $C_{11}H_7NO_2$) was obtained under the conditions of synthesis of **3d** by method A on interacting coumarin **1i** (0.4 g, 1.7 mmol) with **2c** (0.24 g, 1.7 mmol). The yield of **3e** was 0.1 g (40%) of white thread-like crystals; mp 203-205°C (ethanol). IR spectrum, ν, cm^{-1}: 2225 (CN), 1720 (CO). According to [11] mp 205-206°C.

In order to study the dynamics of the interaction of 3-ethoxycarbonylcoumarin **1a** with cyanoacetylhydrazines **2a,c** the ^1H NMR spectra were taken of both the initial components and of mixtures of these compounds (in CD_3OD and DMSO-d_6). The mixtures were taken both in the absence of catalyst and in its presence (drop of piperidine).

Plottings were made at the following time intervals: directly after mixing the reactants, after 10, 20, 30, 40 min, 1, 2, 4 h, 1, 2, 3 days, and finally 7 d after the beginning of the reaction.

For the purpose of identifying the products formed the NMR spectra of samples mixed with 3-cyanocoumarin **3a** were taken.

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