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REACTIONS OF 4-METHYL-7-DIETHYLAMINOCOUMARIN THAT PROCEED WITH ELECTRON TRANSFER

M. A. Kirpichënok, S. K. Gorozhankin, and I. I. Grandberg

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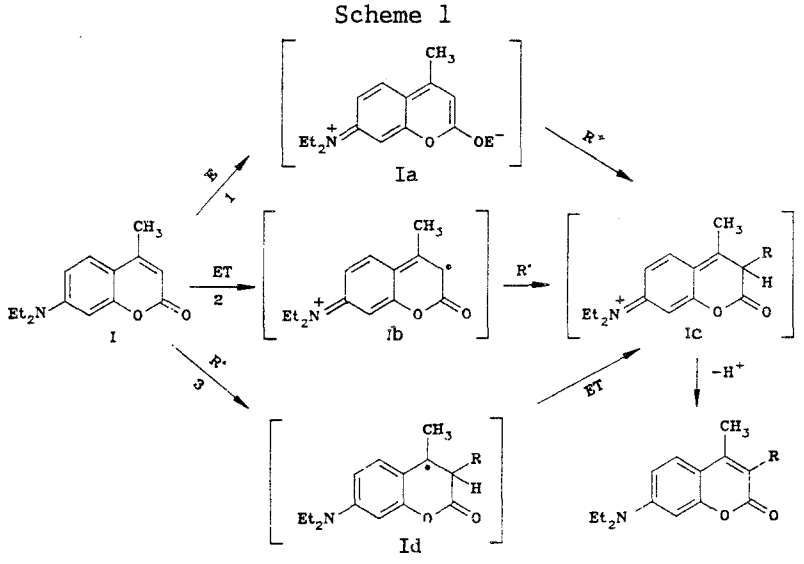
The reactions of 4-methyl-7-diethylaminocoumarin with various oxidizing agents, viz., nitrous acid, nitromethane in the presence of Lewis acids, tetranitromethane, lead tetraacetate, phenyliodosodiacetate, and p-benzoquinone, as well as with typical one-electron oxidizing agents [$(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$, $NOBF_4$, $NOSbCl_6$, $[Fe(biPy)_3](ClO_4)_3$], were studied. It was shown that most of the reactions can be interpreted as proceeding with the intermediate formation of the cation radical of the starting coumarin and lead to new substituted 7-aminocoumarins when suitable substrates (unsaturated compounds, radicals, etc.) are present.

We have previously reported [1] electrophilic substitution reactions in 4-methyl-7-diethylaminocoumarin (I). It was shown that relatively mild Lewis acids ($ZnCl_2$, $HgCl_2$) are capable of coordinating with the exocyclic oxygen atom with the formation of polarized complexes Ia, which are subject to regioselective electrophilic attack at the $C(_3)$ atom (Scheme 1, pathway 1).

Considering the high tendency of 7-aminocoumarins to undergo one-electron oxidation* [2], it seemed of interest to evaluate the behavior of coumarin I under oxidative conditions; one might have assumed the formation of cation radical Ib, in which the cationic and radical centers are markedly dispersed (Scheme 1).

Scheme 1



E=$ZnCl_2$, $HgCl_2$ etc.

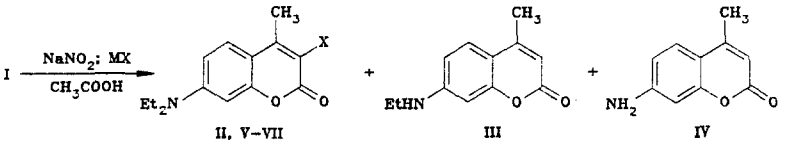
*According to electrochemical data [2], coumarin I is comparable to triethylamine in this respect.

K. A. Timiryazev Moscow Agricultural Academy, Moscow 127550. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 888-897, July, 1989. Original article submitted December 16, 1987.

In fact, quantum-chemical calculation [3] for the coumarin cation radical predicts localization of the unpaired electron primarily between the $C_{(3)}$ atom and the carbonyl oxygen atom. This regularity seems promising in the search for new nontraditional substitution reactions in the coumarin fragment. In this connection the aim of the present research consisted in the study of methods for the generation of cation radical Ib and the investigation of its reactivity.

To obtain cation radical Ib we investigated the reaction of coumarin I with a number of oxidizing agents that are potentially capable of one-electron transfer, viz., $NaNO_2$ in CH_3COOH and CF_3COOH, CH_3NO_2 in the presence of Lewis acids, $Pb(CH_3COO)_4$, $C_6H_5I(OCOCH_3)_2$, $C(NO_2)_4$, and p-benzoquinone, as well as with typical one-electron oxidizing agents [$(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$, $NOBF_4$, $NOSbCl_6$, and $[Fe(biPy)_3](ClO_4)_3$]. Acetic acid, CF_3COOH, CH_3NO_2, and CH_3CN were tested as solvents.

It was found that the use of the $CH_3COOH + NaNO_2$ system as the oxidizing agent in the absence of other reagents leads to nitration of coumarin I in the 3 position. The yield of 3-nitro-4-methyl-7-diethylaminocoumarin (II) [4] in the case of brief stirring in the cold of equivalent amounts of the starting coumarin and sodium nitrite is 30-35%. The known [1] 4-methyl-7-ethylaminocoumarin (III) and 4-methyl-7-aminocoumarin (IV) are side products in this and most of the other investigated reactions.



M=Na, K; II X=NO_2; V X=I; VI X=Br; VII X=SCN

Let us note that the occurrence of side reactions via a purely radical or ionic mechanism has not found confirmation in the literature [5, 6]. According to the available concepts [5], this reaction can be regarded as evolving via an ion-radical mechanism in which a nitrosonium cation or nitrogen oxide is the one-electron oxidizing agent, and the formation of nitro derivative II is interpreted as being the result of reaction between cation radical Ib or the starting coumarin and an NO_2 particle (Scheme 1, pathways 2 and 3, respectively).

To verify this hypothesis we subjected salts of inorganic acids that undergo oxidation relatively readily – KI, KBr, and KSCN – to reaction with coumarin I in $CH_3COOH + NaNO_2$. As a result we isolated 3-iodo- (V), 3-bromo- (VI) [1], and 3-thio-cyanato-4-methyl-7-diethylaminocoumarin (VII) in 45%, 55%, and 67% yields, respectively. Salts of the $NaOCOCH_3$, KCN, KCl, and KF type, which undergo oxidation with greater difficulty, did not undergo a similar reaction.

Thus the probable mechanism of the process includes radical attack in the 3 position of cation radical Ib or coumarin I. In the latter case radical Id undergoes oxidation (Scheme 1). The hypothesis regarding attack on cation radical Ib directly by X^- anions (X = halogen, SCN, etc.), as is assumed, for example in [6], has not yet been adequately confirmed in our case. It should, however, be borne in mind that the presence of electrophilic particles of the X^+ or $XOCOCH_3$ type [7] and manifestation of the catalytic properties of nitrogen oxide [8] are possible in the reactions under consideration, and, consequently the problem of distinguishing between ionic and ion-radical mechanisms, strictly speaking, remains unsolved, as in most similar cases [5, 9]. The high selectivity of substitution reactions may serve as additional evidence in favor of the ion-radical mechanism. Despite the rather severe reaction conditions, products of substitution in the 6 and 8 positions were not detected. Similar principles were observed when the $CF_3COOH + NaNO_2$ oxidative system was used. Moreover, the iodination of coumarin I with elementary iodine in CH_3COOH (or CF_3COOH) at the same reagent ratios and under similar temperature conditions but in the absence of sodium nitrite leads only to the insignificant formation of coumarin V. It is interesting to note that in the reaction to obtain coumarin V one also observes the partial formation of coumarin II, the relative amount of which increases with time. An independent experiment shows that conversion of coumarin V to coumarin II may occur under the reaction conditions. A similar process was observed for the conversion of coumarin V to coumarins VI and VII. These reactions recall the well-known ipso substitution in aromatic compounds in ion-radical reactions [10].

TABLE 1. IR and UV Spectra and Luminescence Characteristics of Coumarins VII, VIII, and X–XIV

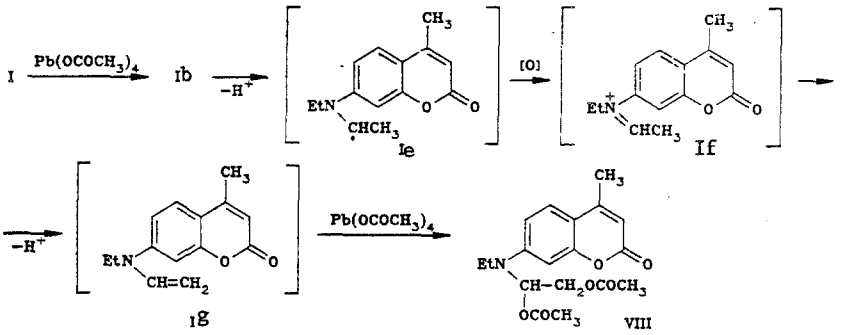
Compound	Empirical formula	T_{mp}, °C	IR spectrum, $\nu_{C=O}$, cm^{-1}	UV spectrum		Luminescence			Yield, %
				solvent	λ_{max}, nm (log ε)	λ_{exc}, nm	λ_{max}, nm	quantum yield*	
VII	$C_{15}H_{16}N_2O_2$	128,5	1710	C_2H_5OH	255 (4,15), 284 (3,52), 409 (4,55)	410	474	0,09	67
VIII	$C_{18}H_{21}NO_6$	132	1779, 1752, 1710	C_2H_5OH	241 (4,25), 276 (3,41), 312 (3,71), 364 (4,40)	360	440	1,0	42
X	$C_{20}H_{21}NO_4$	303	1680	i-C_3H_7OH	245 (4,12), 306 (3,90), 318 (3,89), 375 (4,53)	—	—	—	56
XI**	$C_{20}H_{27}NO_2 \cdot C_6H_3N_3O_7$	140 ... 141	1700	C_2H_5OH	250 (4,14), 280 (3,31), 318 (3,58), 375 (4,35)	370	460	0,60	35
XII**	$C_{26}H_{37}NO_2 \cdot C_6H_3N_3O_7$	133 ... 134	1700	C_2H_5OH	250 (4,07), 308 (3,47), 318 (3,55), 375 (4,27)	370	460	0,72	17
XIII	$C_{30}H_{27}NO_4$	84	1695	i-C_3H_7OH	254 (4,46), 387 (4,32)	—	—	—	27
XIV	$C_{30}H_{27}NO_4$	115	1695	i-C_3H_7OH	254 (4,53), 400 (4,32)	—	—	—	22

*3-Aminophthalimide was used as the standard.
**Melting point of the picrate.

TABLE 2. PMR Spectra of Coumarins VII, VIII, and X-XIV

Compound	Chemical shifts, δ, ppm (J, Hz)						
	5-H	6-H	8-H	4-CH_3	NCH_2	NCH_2CH_3	other protons
VII	7,29 d (9,0)	6,45 d.d (2,8; 9,0)	6,22 d (2,8)	2,55 s	3,30 q (7,0)	1,11 t (7,0)	—
VIII	7,45 d (9,0)	6,81 d.d (2,6; 9,0)	6,68 d (2,6)	2,35 d	3,50 q (7,0)	1,21 t (7,0)	2,08 (6H, s $2CH_3CO$), 3,66 (2H, d, J=5,5, CH_2O), 6,02 (1H, q, J=1,2, 3-H), 6,93 (1H, t, J=5,5, NCHO)
X	7,50 d (8,9)	6,60 d.d (2,5; 8,9)	6,44 d (2,5)	2,09 s	3,35 q (7,0)	1,13 t (7,0)	6,53 (1H, d, $J_{4,6}$=2,0, 6-H), 6,68 (1H, d, $J_{3,4}$=7,5, 3-H), 6,72 (1H, d, d, $J_{4,6}$=2,0, $J_{3,4}$=7,5, 4-H), 8,51 (1H, s, OH), 8,72 (1H, s, OH)
XI	7,37 d (9,2)	6,47 d.d (2,4; 9,2)	6,40 d (2,4)	2,29 s	3,29 q (7,0)	1,08 t (7,0)	1,5...2,2 (6H, m, *cyclo*-CH_2), 3,92 (1H, m, *cyclo*-CH), 5,60 (2H, m, *cyclo*-CH=CH)
XII	7,21 d (9,1)	6,34 d.d (2,3; 9,1)	6,28 d (2,3)	2,26 s	3,42 q (7,0)	1,11 t (7,0)	1,20...2,11 (14H, m, *cyclo*-CH_2), 3,55 (1H, m, *cyclo*-CH), 3,91 (1H, m, *cyclo*-CH), 5,25 (1H, m, *cyclo*-CH)
XIII	7,59 d (9,0)	6,83 d.d (2,6; 9,0)	6,62 d (2,6)	2,29 s	3,40 q (7,0)	1,20 t (7,0)	7,34 (1H, s, =CHCO), 7,35...7,60 (6H, m, $2C_6H_5$), 7,91 (2H, m, *o*-C_6H_5), 8,09 (2H, m, *o*-C_6H_5)
XIV	7,50 d (8,9)	6,73 d.d (2,5; 8,9)	6,58 d (2,5)	2,57 s	3,41 q (7,0)	1,19 t (7,0)	7,29 (1H, s, =CHCO), 7,30...7,60 (6H, m, $2C_6H_5$), 7,82 (2H, m, *o*-C_6H_5), 8,05 (2H, m, *o*-C_6H_5)

The structures of II and V–VII follow from spectral data and a comparison with the available (for coumarins II, V, and VI) literature data [1, 4]. Thus signals of aromatic 5-H (7.3-7.5 ppm), 6-H (6.4-6.7 ppm), and 8-H (6.2-6.5 ppm) protons are observed in the PMR spectra of coumarins II and V–VII, and signals of a 3-H proton are absent; this confirms the presence of a substituent in the 3 position. A band of carbonyl absorption in the IR spectra is observed at 1710 cm^{-1}, as in the case of most other 7-aminocoumarins [11]. The presence of a nitro group in coumarin II is proved by the absorption at 1570 and 1340 cm^{-1} [4], while the presence of a thiocyanato group in coumarin VII is proved by the absorption at 2157 cm^{-1}. Data from the electronic spectra of coumarin VII are presented in Table 1.

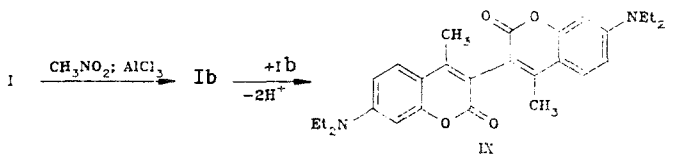


In the course of our search for reactions that indicate the participation of cation radical Ib more definitively we investigated the oxidation of coumarin I with lead tetraacetate. Coumarin VIII was isolated in 42% yield when the reagents were heated in acetonitrile. In addition to signals of aromatic 3-H, 5-H, 6-H, and 8-H protons, doublet (3.66 ppm) and triplet (6.93 ppm) signals belonging, respectively, to two and one protons that participate in spin-spin coupling (J = 5.5 Hz) are present in the PMR spectrum of VIII. These signals are related to a $CH–CH_2$ fragment bonded to an N-ethylamino group. A singlet signal of methyl protons of two acetyl groups is observed at 2.08 ppm (Table 2).

One can also conceive of the formation of VIII from cation radical Ib if one assumes the detachment of a proton in the α position relative to the nitrogen atom that is usually observed for lead(IV) salts [12]. The subsequent oxidation of the resulting α-amino radical Ie to iminium salt If and the elimination of a β proton lead to olefin Ig, which is converted

to a 1,2-glycol diether under the reaction conditions. This reaction has sufficient literature analogies and confirms the existence of reactive cation radical Ib as an intermediate of the chemical transformations.

The reaction of coumarin I with nitromethane in the presence of $AlCl_3$ or $ZnCl_2$ or with phenyl iodosodiacetate in acetonitrile or nitromethane may serve as another more convincing example. In these cases bis(coumarin) IX is formed in the reaction mixture in 30-50% yields [4].



The highest yields of IX (up to 70%) are achieved in the oxidation of coumarin I with purely one-electron oxidizing agents such as $(p\text{-}BrC_6H_4)N^{\dot{+}}SbCl_6^-$ or $[Fe(biPy)_3](ClO_4)_3$ in acetonitrile solutions. On the other hand, the use of nitrosonium salts $NOBF_4$ and $NOSbCl_6$ as the oxidizing agents under normal conditions led to the nitration of coumarin I to coumarin II. It is apparent that the production of bis(coumarin) IX formally can be regarded as being the result of dimerization of cation radicals Ib, i.e., as an analog of the classical Fries–Lohman reaction [13].

Considering the fact that the oxidative properties of the CH_3NO_2 + Lewis acid system are sufficient for the generation of cation radical Ib, it seemed of interest to verify if the cation radical under investigation would be converted to 3-nitrocoumarin II in nitromethane solution in the presence of some source of $NO_2^{\cdot}$ radicals in analogy with the reaction with nitrous acid. We selected tetranitromethane as a source of this type and as an effective one-electron oxidizing agent. The reaction of coumarin I with tetranitromethane in nitromethane solution in the presence of catalytic amounts of $ZnCl_2$ led to nitro derivative II in high yield (64%). Thus, in a preparative respect, the reaction with tetranitromethane should be preferred over all of the remaining investigated nitration reactions, including nitration with the usual nitrating mixture, which leads to a mixture of 3-, 6-, and 8-nitro derivatives [14]. The probable nitration mechanism (Scheme 2) includes electron transfer (1), dissociation of the tetranitromethyl anion radical (2), and recombination of cation radical Ib and the $NO_2^{\cdot}$ radical (3).

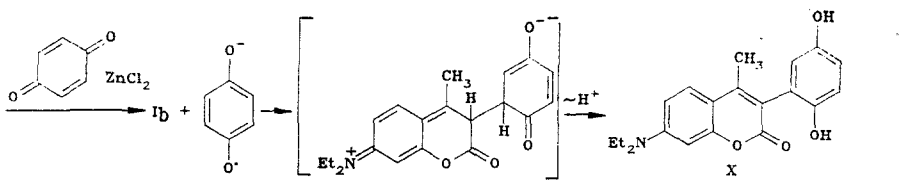
Scheme 2

$$C(NO_2)_4 + I \xrightarrow{ET} Ib + C(NO_2)_4^{\dot{-}} \quad (1)$$

$$C(NO_2)_4^{\dot{-}} \longrightarrow NO_2^{\cdot} + C(NO_2)_3^{-} \quad (2)$$

$$Ib + NO_2^{\cdot} \longrightarrow II \quad (3)$$

To elucidate the possibility of oxidation of coumarin I by p-benzoquinone we studied the reaction of the reagents in acetonitrile. An acetonitrile solution of equivalent amounts of the starting coumarin and p-benzoquinone has an intense brown coloration that is evidently due to the formation of a charge-transfer complex. A 1:1 adduct that was only slightly soluble in most organic solvents, to which we assign formula X as being the most probable formula, was isolated in 56% yield when the solution was heated in the presence of catalytic amounts of $ZnCl_2$.

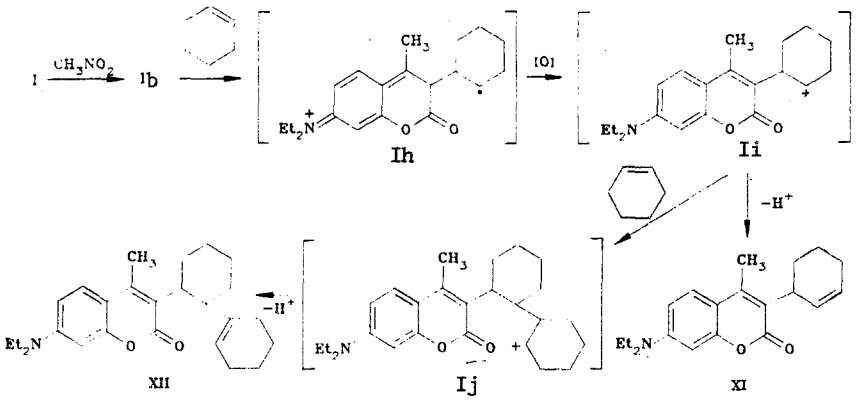


The correspondence of the synthesized compound to formula X is confirmed by data from the mass spectrum, in which an intense molecular-ion peak M^+ (m/z 339, relative intensity 100%) is present. In addition to $[M - CH_3]^+$ (m/z 324, 99%) $[M - CH_3 - C_2H_4]^+$ (m/z 296, 68%) and other fragmentation processes that are similar to those for other 7-aminocoumarins [15],

$[M - 1]^+$ (55%) and $[M - 2]^+$ (6%) ions, which are characteristic for diatomic phenols, are observed; the processes involving the loss and capture of hydrogen atoms are also observed for more than the profound fragmentation steps. Protons of 4-methyl-7-diethylaminocoumarin fragment and aromatic protons of the phenyl ring of the substituent are present in the PMR spectrum of X. The signals of the 3'–H (6.68 ppm) and 6'–H (6.53 ppm) protons in the hydroquinone fragment have the form of doublets as a result of spin-spin coupling with the 4'–H proton (6.72 ppm). Consequently, the signal of the 4'–H proton is a doublet of doublets with constants $J_{4',3'}$ = 7.5 Hz and $J_{4',6'}$ = 2.0 Hz. Singlet signals of protons of phenolic groups are observed at 8.51 and 8.72 ppm. In the IR spectrum of X the band of carbonyl absorption has a somewhat depressed value (1680 cm^{-1}); this may be due to the formation of an intermolecular hydrogen bond with one of the hydroxy groups of the substituent.

We assume that the described reaction also includes an electron-transfer step with the initial formation of cation radical Ib and a semiquinone anion radical, which, in the simplest variant, recombine with subsequent proton migration to give X.

The reaction of coumarin I with cyclohexene in nitromethane in the presence of zinc or mercury chloride is yet another example that confirms the possibility of the formation of a new $C(_3)$–C bond via an ion-radical pathway. In this case, in contrast to the previously investigated [1] reactions of coumarin I with dihydropyran and styrene, the usual 3-alkylation products were not detected. Instead of this, we isolated XI and XII, which retain unsaturation in the cyclohexane fragment. The yields of coumarins XI and XII are 35% and 17%, respectively.



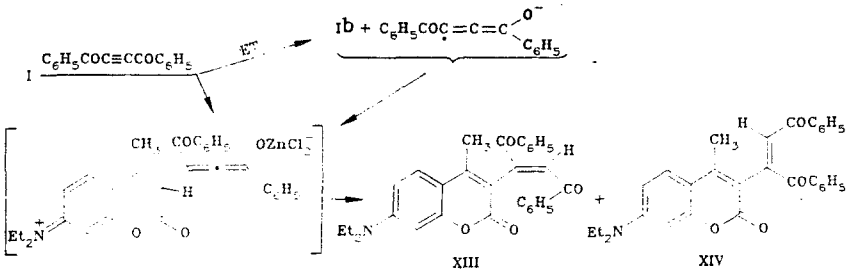
Signals of protons of a 3-substituted 4-methyl-7-diethylaminocoumarin fragment are present in the PMR spectra of XI and XII. The presence of cyclic olefin protons in XI is confirmed by the multiplet signal at 5.60 ppm, which corresponds in integral intensity to two protons. A multiplet signal of one allylic proton bonded to the α-carbon atom of the 2-cyclohexenyl substituent is observed at 3.92 ppm. The signals of the remaining cyclohexane protons show up in the form of two broad multiplets at 1.7 and 2.0 ppm. On the other hand, only one cyclic olefin proton is present in the PMR spectrum of coumarin XII at 5.25 ppm, while multiplet signals of two methylidyne protons of a CH–CH fragment included between the 3,4 bond and the double bond of the other cyclohexene substituent are located at 3.55-3.90 ppm. Signals of cyclohexane protons are located at 1.20-2.10 ppm.

Peaks of molecular ions with m/z 311 (29%) and m/z 393 (38%), which, respectively, attest to retention of unsaturated in the cycloalkyl substituents, are quite appreciable in the mass spectra of coumarins XI and XII. In addition to the fragmentation pathways that are usual for 7-diethylaminocoumarins [15], diverse processes involving the degradation of the cycloalkyl substituents are observed in the mass spectra of XI and XII; peaks with m/z 257 (25-33%), which are probably related to the 3-vinyl-4-methyl-7-diethylaminocoumarin ion, are observed for both coumarins. It is interesting that an ion with m/z 311 (25%), which corresponds to the molecular ion for coumarin XI, is also present in the mass spectrum of XII. This fact confirms the genetic relationship between the structures of the compounds under consideration.

A band of carbonyl absorption at 1700 cm^{-1} is present in the IR spectra of XI and XII; this confirms retention of the coumarin part of the molecules.

The formation of coumarins XI and XII becomes explainable within the framework of an ion-radical mechanism with the participation of cation radical Ib. The most probable scheme of the process includes the addition of cation radical Ib to cyclohexene with the formation of radical Ih, which is then oxidized to cation Ii. The latter, as a result of the elimination of a proton, may either undergo conversion to product XI or capture yet another molecule of cyclohexene, which ultimately leads to XII. The reason for the special behavior of cyclohexene in our opinion, consists in its decreased (as compared with styrene or dihydropyran) tendency to undergo coordination with Lewis acids. As a result, the formation of the primary reaction center occurs preferably in the 7-aminocoumarin molecule rather than in the olefin molecule.

In the presence of zinc chloride in nitromethane coumarin I also reacts with dibenzoylacetylene to give a mixture of isomeric coumarins XIII and XIV, which were isolated in 27% and 22% yields, respectively. The mechanism of this reaction is difficult to interpret unequivocally, since both ionic and ion-radical pathways in this case should lead to the same products.



The structures of XIII and XIV as 3-substituted coumarins are confirmed by data from the mass spectra, in which the usual pathways of fragmentation of the 7-aminocoumarin fragment (for example, the formation of $[M - CH_3]^+$ ions) are observed. However, elimination of one benzoyl group is the dominant process, so that intense peaks of $[M - COC_6H_5]^+$ (m/z 360, 54-56%) and $COC_6H_5^+$ (m/z 105, 100%) ions are observed in the mass spectra of XIII and XIV. In the PMR spectrum of XIV the chemical shift of the olefinic β-H proton (7.34 ppm) is found at weaker field than in the case of the analogous proton in the XIII (7.29 ppm). On the other hand, the signal of the protons of the 4-methyl group in isomer XIII (2.57 ppm) is shifted ∿0.3 ppm to weak field as compared with the signal of the $4\text{-}CH_3$ protons in isomer XIV. We assume XIV is the s-cis isomer. This conclusion is in agreement with the stronger $CH_3...(\alpha\text{-}COC_6H_5)$ steric interactions that one must expect in E isomer XIII as compared with Z isomer XIV. The UV spectrum of XIV, in which the long-wave absorption band experiences a bathochromic shift (λ_{max} 400 nm) as compared with the analogous band in the spectrum of isomer XIII (λ_{max} 387 nm), may serve as an additional confirmation; this indicates more effective conjugation between the coumarinyl and trans-β-benzoyl fragments.

In conclusion, in the case of coumarin I it may be concluded that the creation of special or even unique conditions, including the following, is evidently required for the unambiguous manifestation of the reactions of cation radicals: the presence of a sufficiently strong one-electron oxidizing agent, the absence of strong "purely electrophilic" properties in the given oxidizing agent and the other reagents under the reaction conditions, decreased reductive properties in the other reagents as compared with the reagent under investigation, and the presence of a suitable substrate that is inclined to undergo reactions with the cation radical under investigation.

The search for such conditions is, in our opinion, one of the most urgent tasks in the evolving synthetic chemistry of ion radicals.

EXPERIMENTAL

The IR spectra were recorded with a Jasco spectrometer. The UV and luminescence spectra were obtained with a Hitachi EPS-3T spectrophotometer. The relative fluorescence quantum yields were determined with respect to quinine sulfate by the method in [16]. The PMR spectra of solutions in $CDCl_3$ were recorded with a Bruker WM-250 spectrometer with hexamethyldisiloxane (HMDS) as the internal standard. The mass spectra were obtained with a Varian MAT-311A mass spectrometer (ionizing voltage 70 eV).

The isolation of the reaction products was carried out by chromatography with a column (30 by 2.5 cm) packed with Silpearl UV-254 silica gel in hexane–acetone and benzene–acetone systems. The synthesized products were recrystallized from hexane–acetone. The purity of the substances was monitored by means of TLC on Silufol UV-254 plates. The characteristics of the newly synthesized substances are presented in Tables 1 and 2. The results of elementary analysis of these substances were in agreement with the calculated values.

3-Nitro-4-methyl-7-diethylaminocoumarin (II). A. A mixture of 1.50 g (6.49 mmole) of coumarin I, 2.27 g (6.5 mmole) of tetranitromethane, and 0.30 g of anhydrous zinc chloride was heated at 40-60°C in 40 ml of nitromethane for 3 h, after which it was evaporated in vacuo. The residue was treated with 40 ml of 10% aqueous sodium bicarbonate solution, and the mixture was extracted with ethyl acetate (three 20-ml portions). The combined organic layers were evaporated, and the residue was separated by chromatography in a hexane–acetone system (4:1) with collection of the fraction with R_f 0.17 to give 1.14 g (64%) of coumarin II with mp 158.5°C (mp 158.5°C [4]) and M^+ 276 (by mass spectrometry).

B. A 0.55-g (31%) sample of II, with mp 157-158°C, was obtained from 1.50 g (6.5 mmole) of coumarin I and 0.90 g (13.0 mmole) of sodium nitrite after stirring in 30 ml of acetic acid at 40-50°C for 8 h.

3-Iodo-4-methyl-7-diethylaminocoumarin (V). A 1.04-g (45%) sample of coumarin V, with mp 113.5°C (mp 113-114°C [1]), R_f 0.21 [hexane–acetone (4:1)], and M^+ 357 (by mass spectrometry), was obtained from 1.50 g (6.5 mmole) of coumarin I, 1.00 g (4.5 mmole) of sodium nitrite, and 1.33 g (8.0 mmole) of potassium iodide after stirring in 40 ml of acetic acid at 15°C for 8 h.

3-Bromo-4-methyl-7-diethylaminocoumarin (VI). A 1.11-g (55%) sample of coumarin VI, with mp 93°C (mp 92-93°C [1]) and R_f 0.19 [hexane–acetone (4:1)], was obtained from 1.50 g (6.5 mmole) of coumarin I, 1.00 g (14.5 mmole) of sodium nitrite, and 0.95 g (8.0 mmole) of potassium bromide after stirring in 40 ml of acetic acid at 20°C for 8 h.

3-Thiocyanato-4-methyl-7-diethylaminocoumarin (VII). A 1.25-g sample of coumarin VII, with R_f 0.36 [hexane–acetone (4:1)], was obtained from 1.50 g (6.5 mmole) of coumarin I, 1.00 g (14.5 mmole) of sodium nitrite, and 0.78 g (8.0 mmole) of potassium thiocyanate after stirring in 40 ml of acetic acid at 60-80°C for 8 h.

4-Methyl-7-ethyl(1',2'-diacetoxyethylamino)coumarin (VIII). A 0.73-g sample of VIII, with R_f 0.21 [hexane–acetone (4:1)], was obtained from 1.15 g (5 mmole) of coumarin I and 4.43 g (10 mmole) of lead tetraacetate after heating in 50 ml of acetonitrile at 80°C for 6 h.

Bis-3,3'-(4-methyl-7-diethylaminocoumarin) (IX). A. A 0.71-g (47%) sample of IX, with mp 222°C (mp 222°C [4]) and R_f 0.40 [hexane–acetone (2:1)], was obtained from 1.50 g (6.5 mmole) of coumarin I and 1.70 g (13.0 mmole) of aluminum chloride after refluxing in 35 ml of nitromethane for 28 h.

B. A 0.48-g (32%) sample of IX, with mp 222°C, was obtained from 1.50 g (6.5 mmole) of coumarin I and 2.09 g (6.5 mmole) of phenyl iodosodiacetate after refluxing in 40 ml of acetonitrile for 6 h.

C. A 0.69-g (69%) sample of IX, with mp 222°C, was obtained from 0.10 g (0.43 mmole) of coumarin I and 0.71 g (0.86 mmole) of $[Fe(biPy)_3](ClO_4)_3$ after stirring in 30 ml of acetonitrile at 20°C for 2 h.

3-(2,5-Dihydroxyphenyl)-4-methyl-7-diethylaminocoumarin (X). A 1.31-g sample of X, with R_f 0.13 [hexane–acetone (4:1)], was obtained from 1.60 g (6.9 mmole) of coumarin I, 2.10 g (19.4 mmole) of p-benzoquinone, and 0.70 g (5.2 mmole) of zinc chloride after refluxing in 40 ml of acetonitrile for 25 h.

3-(2-Cyclohexenyl)-4-methyl-7-diethylaminocoumarin (XI) and 3-[2-(1-cyclohexenyl)cyclohexanyl]-4-methyl-7-diethylaminocoumarin (XII). Workup of the fraction with R_f 0.64 [hexane–acetone (5:1)] obtained from 2.00 g (8.7 mmole) of coumarin I, 20.0 g (243.9 mmole) of cyclohexene, and 1.00 g (7.4 mmole) of zinc chloride after refluxing in 30 ml of nitromethane for 30 h gave 0.95 g of XI in the form of an oil with M^+ 311 (by mass spectrometry). Compound XI was converted to the picrate by mixing with a saturated ether solution of picric acid.

Workup of the fraction with R_f 0.74 [hexane–acetone (5:1)] gave 0.58 g of XII in the form of an oil with M^+ 393 (by mass spectrometry). Compound XII was converted to the picrate.

3-(E-1,2-Dibenzoylvinyl)-4-methyl-7-diethylaminocoumarin (XIII) and 3-(Z-1,2-Dibenzoylvinyl)-4-methyl-7-diethylaminocoumarin (XIV). Workup of the fraction with R_f 0.28 [hexane–acetone (4:1)] obtained from 1.50 g (6.5 mmole) of coumarin I, 1.75 g (7.4 mmole) of dibenzoylacetone, and 0.30 g (2.2 mmole) of zinc chloride after refluxing in 45 ml of toluene for 10 h gave 0.81 g of XIII with M^+ 465 (by mass spectrometry).

Workup of the fraction with R_f 0.23 [hexane–acetone (4:1)] gave 0.66 g of XIV with M^+ 465 (by mass spectrometry).

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