B) A solution of 4.1 g (0.02 mole) of phthaloyl chloride in 200 ml of absolute dioxane solution containing 0.6 g (0.01 mole) of anhydrous 1,2-diaminoethane and 6.1 g (0.06 mole) of triethylamine, after which the mixture was maintained for 3 min and then filtered. The filtrate was concentrated in vacuo (60-80 mm Hg) to a volume of 10 ml, and the precipitated crystals were removed by filtration and recrystallized from acetone. The yield was 1.7 g (53%). The constants were identical to those presented above.

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REACTIONS OF 4-METHYL-7-DIETHYLAMINOCOUMARIN WITH ELECTROPHILIC REAGENTS

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The reactions of 4-methyl-7-diethylaminocoumarin with various electrophilic reagents - acetic anhydride, complexes of unsaturated compounds (styrene, dihydropyran, phenylacetylene) with Lewis acids, and copper halides - were used to synthesize 3-, 6-, and 8-substituted coumarins. It was shown that the selectivity of reactions involving substitution in the 3 position increases with an increase in the "softness" of the Lewis acid.

The special interest in 7-aminocoumarins is due to their effective application as laser dyes [1]. Most of the publications dealing with 7-aminocoumarins are devoted to methods for their synthesis and physicochemical characteristics, whereas little study has been devoted to the chemistry of the indicated compounds [2]. We began a systematic investigation of the chemical properties of 7-aminocoumarins, and in the present paper we will discuss a number of electrophilic substitution reactions in the case of 4-methyl-7-diethylaminocoumarin(I) - a typical representative of this class.

Several electrophilic substitution reactions are known in the 7-aminocoumarin series [2], e.g., nitration [3], sulfonation [4], which, as a rule, proceed under severe conditions and nonselectively and give mixtures of products of 3-, 6-, and 8-substitution in high yields.

We attempted to realize a number of new reactions in the case of coumarin I under standard conditions. We tested acetic anhydride, acetyl chloride, benzyl chloride, and benzenediazonium chloride as electrophilic reagents. Dichloroethane, benzene, acetic anhydride,

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Com- pound*	т <sub>тр</sub> , •С	ν <sub>C=0</sub> cm <sup>-1</sup>	Found, %			Empirical	Calc., %			d, %	Degree of conver-
			с	н	N	formula	с	н	N	Yiel	sion,† %
IV	104—105	1735	70,5	7,1	5,3	C16H19NO3	70,3	7,0	5,1	7	50
v	127—128	1715	70,2	7,1	5,1	C <sub>16</sub> H <sub>19</sub> NO <sub>3</sub>	70,3	7,0	5,1	21	50
VIII	109—110	1710	48,0	4,4	12,7	$C_{19}H_{25}NO_3 \times 2C_eH_3N_2O_7$	48,4	4,0	12,7	24	45
IX	110—111	1710	57,1	5,8	9,4	$C_{24}H_{33}NO_4 \times C_6H_3NO_7$	57,5	5,5	8,9	17	45
XIII	133—134	1715	60,1	5,2	9,7	$C_{22}H_{24}NO_2 \times C_6H_3N_3O_7$	59,6	5,0	9,9	32	80
XIV	160—161	1695	55,4	4,6	11,3	$C_{22}H_{23}N_2O_4 \times C_6H_3N_2O_7$	55,2	4,5	11,5	9	80
XVI XVIII XIX XXI	194—195 110—111 108—109 113—114	1700 1700 1715 1700	77,4 78,9 63,3 47,1	6,3 7,1 6,0 4,4	5,4 4,3 5,5 4,0	C <sub>18</sub> H <sub>17</sub> NO <sub>2</sub> C <sub>22</sub> H <sub>23</sub> NO <sub>2</sub> C <sub>14</sub> H <sub>16</sub> CINO <sub>2</sub> C <sub>14</sub> H <sub>16</sub> INO <sub>2</sub>	77,4 79,3 63,3 47,1	6,1 7,0 6,1 4,5	5,0 4,2 5,3 3,9	25 23 87 75	75 90 100 100

TABLE 1. Characteristics of the Substituted 7-Aminocoumarins

\*For VIII, IX, XIII, and XIV the melting points and the results of microanalysis are presented for the picrates. +Given with respect to the starting coumarin.

dioxane, and methanol served as the solvents. Sulfuric acid, aluminum chloride, and titanium tetrachloride were used as catalysts, and we also varied the temperature conditions and the reagent ratios. In the overwhelming majority of cases the principal reaction products were II and III, which are formed as a result of N-dealkylation of the starting coumarin under the influence of Lewis acids. The only exception was acylation with acetic anhydride in the presence of sulfuric acid, which, under severe conditions, led to 6- and 8-acetyl derivatives IV and V in 7 and 21% yields, respectively, vis-à-vis an 80% degree of conversion of the starting coumarin.



Let us especially point out that in everything that follows we carried out the reactions of coumarin I with incomplete degrees of conversion; this substantially reduced the occurrence of secondary processes and facilitated the isolation of the desired products (see Table 1).

The presence of an acetyl substituent in the 6 and 8 positions in IV and V follows from their PMR spectra. As we have previously noted [5], the chemical shifts in the PMR spectra and the form of the signals of the aromatic protons of the 7-aminocoumarin fragment are quite characteristic values. In particular, for coumarins IV and V the signals of the 3-H protons appear in the form of broad singlets at 6.0-6.1 ppm, the 5-H protons are observed at the weakest field (~7.5 ppm), and the signals of the 6-H (for V) and 8-H (for IV) protons are observed at 6.94 and 6.75 ppm, respectively. Data from the PMR and IR spectra of IV and V are presented in Tables 1 and 2, and the UV spectra are described in the experimental section. One's attention is directed to the absence of luminescence for coumarins IV and V. This fact is evidently explained by the steric effect of the acetyl groups, which disrupt the conjugation of the diethylamino group with the aromatic ring.

Let us note that the primary formation of V is in agreement with the results of a quantum-chemical calculation of coumarin [6], as well as with data from the <sup>13</sup>C NMR spectra of 7-aminocoumarins [5, 7], which predict the greatest localization of the electron density on the  $C_{(8)}$  atom.

Com-	δ. ppm (J, Hz)								
pound	5-H	6-H	8-H	4-CH3 (S)	NCH₂CH₃	other protons			
II	7,32 d	6,50 dd	6,42 d	2,32	3,20q; 1,28t	4,28 (1H, s, NH);			
ш	(0,0) 7,45 d	(0,0; 2,0) 6,68 dd	6,55 d	2,37	( <i>1</i> ,0) —	$5,50$ (1H, s, $5H_2$ ); $5,60$ (2H, s, $NH_2$ ); 5,00 (1H s, 3H)			
IV	(8,6) 7,52 s	(0,0; 2,2)	6,75 s	2,27	3,12 q, 0,98 t	2,48 (3H, s, CH <sub>3</sub> CO);			
v	7,46 d	6,94d	—	2,35	3,14q; 1,05 t	(3,00,01,11,1,1,1,11) 2,57 (3H, s, CH <sub>3</sub> CO);			
VIII	(9,1) 7,35 d (8,8)	(9,1) 6,45 dd (8,8; 2,1)	6,16d (2,1)	2,52	(7,0) 3,29 q; 1,16 t (6,9)	1,2-1,8 (6H, m, <i>cyclo</i> -CH <sub>2</sub> ); 3,5-5,0 (3H, m, <i>cyclo</i> -OCH, OCH.)			
IX	7,25 d (8,8)	6,48 dd (8,8; 2,7)	6,29 d (2,7)	2,48	3,31 q; 1,09 t (6,9)	1,1-2,8 (11H,m, <i>cyclo</i> -CH, CH <sub>2</sub> ); 3,5-5,2 (6H,m, <i>cyclo</i> -OCH, OCH <sub>2</sub> )			
XIII	7,21 d (9,0)	6,47 d (9,0)	6,30 s	2,12	3,27 q; 1,08 t (6,8)	$I_{220} = 0.011_{2}$ $I_{1,63} = (3H, d, J = 7,0 Hz, CH_3);$ $I_{4,57} = (1H, q, J = 7,0 Hz, CH);$ $I_{220} = (5H, m, C, H_2)$			
XIV	7,20 d	6,46 dd	6,28 d	2,37	3,23q;1,05 t	$(3H, m, CHCH_2);$ (3H, m, CHCH_2); (7.20) (5H, m, C+H_2);			
XVI	(8,9) 7,25 d (8,9)	(8,9) 6,49 d (8,9)	6,30 s	2,25	( <sup>1,1)</sup> -	(1,2) (3H, dt, $J=7,1$ Hz, CH <sub>3</sub> ); 4,55 (1H, q, $J=7,1$ Hz, CH); 7,25 (5H, m, C <sub>2</sub> H <sub>5</sub> );			
XVII	7,36 s		6,51 s	2,31	-	5,20 (2H, s, NH <sub>2</sub> ) 1,55 (3H, d, $J = 7,0$ Hz, CH <sub>3</sub> ); 4,20 (1H, q, $J = 7,0$ Hz, CH); 5,94 (1H, s, 3-H); 5 00 (0H, s, NH <sub>2</sub> )			
XVIII	7,49 d (8,8)	6,67 dd (8,8; 2,6)	6,45 d (2,6)	2,26	3,44 g 1,17 t (6,8)	5,95 (211, $g$ ; 1412) 5,20 (1H, $d$ ; $J = 1,5$ Hz, =CH); 5,93 (1H, $d$ ; $J = 1,5$ Hz =CH); 7,2-74 (5H m C/H)			
XIX	7,19d	6,37 dd	6,26 d	2,44	3,26  g, 1,07  t				
XXI	7,45 d (9,2)	6,65 dd (9,2; 2,6)	6,50 d (2,6)	2,40	3,38q; 1,18t (7,0)	-			

TABLE 2. PMR Spectra of Substituted 7-Aminocoumarins

The reason for the inertness of coumarin I in the investigated reactions apparently consists in initial attack of strong electrophiles at the nitrogen atom in the diethylamino group, which deactivates the coumarin system with respect to subsequent substitution. In fact, the diazo coupling of benzenediazonium chloride with such a close analog of aminocoumarin I as 4-methylumbelliferone (VI), which we carried out under similar conditions, proceeds appreciably faster and leads to azo coupling product VII in 33% yield (65% degree of conversion).



One should bear in mind that coumarins generally have a tendency to undergo polarization as a result of manifestation of the aromatic character of benzopyrylium system Ia [5]. 7-Aminocoumarins are potentially capable of even greater charge separation due to participation of the amino group; this can be represented arbitrarily as an increase in the contribution of resonance structure Ib.



Thus, two basicity centers - the nitrogen atom in the amino group and the oxygen atom in the carbonyl fragment - exist in 7-aminocoumarin molecules. The fact of deactivation of 4-methyl-7-diethylaminocoumarin in the investigated reactions confirms that the diethylamino group is the most strongly basic and hardest center here. One might have assumed that the use of soft electrophilic reagents would facilitate substitution reactions as a consequence of prior coordination of the electrophile at the softer basic center - the exocyclic oxygen atom in the Ib structure. Assuming that this assumption is valid, one might also have expected that electrophilic substitution in this case would occur at the  $C_{(3)}$  atom.

To verify this hypothesis we investigated the reaction of coumarin I with softer electrophilic reagents - complexes of unsaturated compounds with soft Lewis acids - zinc, mercury, and copper(I) chlorides. Styrene, dihydropyran, and phenylacetylene were selected for the reactions. To ensure homogeneity of the medium and to exclude side reactions it was desirable to use polar low-nucleophilic solvents. Nitromethane and nitrobenzene proved to be most suitable for this purpose. Compound VIII was obtained in 24% yield (45% degree of conversion) when coumarin I was refluxed with excess dihydropyran in nitromethane in the presence of catalytic amounts of zinc chloride. Substituted coumarin IX (17% yield) was also isolated as a side product.



The formation of VIII can be represented as being the result of alkylation of the starting coumarin by the complex (X) of dihydropyran with zinc chloride, the electrophilic center of which is concentrated primarily in the  $\alpha$  position relative to the oxygen atom. This complex is evidently capable of capturing yet another molecule of dihydropyran with the formation of electrophilic particle XI, the attack of which on the starting coumarin leads to IX. Similar results were obtained when mercury chloride and cuprous chloride were used. On the other hand, carrying out of the reaction of 4-methyl-7-diethylaminocoumarin with dihydropyran in the presence of aluminum chloride leads to a decrease in the yields of the alkylation products and to an increase in the relative percentage of N-dealkylation products II and III. The formation of 3-substituted coumarins VIII and IX may serve as a confirmation of coordination of soft electrophilic complexes X and XI at the exocyclic oxygen atom of coumarin I in transition state XII. The possibility of this sort of coordination of metals, which leads to regioselective substitution reactions, is well known (for example, see [8]). The structures of VIII and IX were established primarily on the basis of mass-spectrometric data. Thus, an intense molecular-ion peak  $(M^+ 315)$  and fragments of unsubstituted coumarin\* (230) and a tetrahydropyranyl residue (85) are present in the mass spectrum of coumarin VIII. The fragmentation of the molecular ion of VIII is accompanied by the formation of  $[M - CH_3]^+$ ,  $[M - CO]^+$ , and  $[M - N(C_2H_5)_2]^+$  fragments, which are characteristic for 7-dialkylaminocoumarins [9], as well as processes involving the detachment and capture of hydrogen atoms in different (with respect to degree) stages of the fragmentation of the molecule. The latter principle is known for various ethers; Shriner and coworkers [10] explain this by H° transfers during ion-molecular collisions. In addition to an M<sup>+</sup> peak at 399, ions at 230 and 169, which confirm cleavage of the bond between the alkyl substituent in the 3 position and the heterocyclic ring, are recorded in the mass spectrum of coumarin IX. Ions at  $111 (C_{7H_{1}}O)$ and 110  $(C_7H_{10}O)$ , which evidently have vinyltetrahydro- and vinyldihydropyran structures, also constitute evidence for the presence of a bond between two tetrahydropyranyl residues. The bonding of the coumarinyl residue with the  $\alpha$  position of the pyranyl substituents in coumarins VIII and IX is confirmed by the presence in the mass spectra of these compounds of a peak at 258, which was assigned to the  $[RC=0]^+$  ion, where R is the radical of the starting coumarin.

The PMR spectra of VIII and IX have a rather complex form at 1.5-5 ppm; however, the presence of a substituent in the 3 position is confirmed by the characteristic signals of aromatic 5-H, 6-H, and 8-H protons at ~7.3, ~6.5, and ~6.2 ppm, respectively (see Table 2). A band of carbonyl absorption of a coumarin fragment at 1710 cm<sup>-1</sup> is present in the IR spectra of the indicated substances. Data from the UV and the luminescence spectra of coumarins VIII and IX are presented in Table 3.

\*Here and subsequently, the m/z values are given for the ion peaks.

Com-	Solvent		Luminescence			
pound		$(\log \varepsilon)$	<sup>λ</sup> ex <sup>•</sup> mm	λ <sub>max</sub> , nm	quantum yield•	
VIII	C₂H₅OH	250 (3,70), 320 (2,93), 380 (3,76)	370	460	0,57	
IX	$CH_3CN$ $C_2H_5OH$	$\begin{bmatrix} 246 & (3,70), & 320 & (3,21), & 380 & (3,76) \\ 248 & (4,11), & 316 & (3,44), & 379 & (4,14) \\ 246 & (3,95), & 316 & (3,33), & 374 & (4,06) \\ \end{bmatrix}$	370 370 270	446 460	0,53	
XIII	C <sub>2</sub> H <sub>5</sub> OH	252 (4,17), 308 (3,41), 318 (3,50), 377 (4,30)	380	460	0,63	
xvi	CH₃CN C₂H₅OH	245 (4,15), 310 (3,58), 319 (3,68) 272 (3,57), 360 (4,22) 270 (3,46) 350 (4,07)	380 360	450 439 495	0,58 0,66	
XVII	C <sub>2</sub> H <sub>5</sub> OH	228 (4,20), 300 (3,49), 357 (4,28)	352	438	0,48	
XVIII	CH₃CN C₂H₅OH	227 (4,24), 300 (3,62), 346 (4,26) 246 (4,41), 280 (3,65), 306 (3,51), 319 (3,55), 371 (4,47)	352 380	420 466	0,54 0,74	
	CH₃CN	244 (4,34), 280 (3,61), 309 (3,59), 319 (3,68) 376 (4,38)	380	458	0,32	
XIX	C₂H₅OH	252 (4,17), 282 (3,17), 310 (3,36), 252 (4,17), 282 (3,17), 310 (3,36), 282 (4,26)	380	476	0,81	
	CH₃CN	250 (4,18), 282 (3,25), 310 (3,46), 281 (4,50)	380	466	0,74	
xx	C₂H₅OH	253 (4,26), 282 (3,43), 308 (3,47), 200 (3,51)	390	479	0,51	
	CH₃CN	320 (3,51), 390 (4,47) 251 (4,27), 284 (3,43), 308 (3,52), 321 (3,62), 386 (4,53)	390	479	0,18	

TABLE 3. UV and Luminescence Characteristics of Coumarins VIII, IX, XIII, XV, and XVI-XX

\*3-Aminophthalimide was used as the standard for  $\lambda_{\rm ex}$  > 380 nm, and quinine bisulfate was used as the standard for  $\lambda_{\rm ex}$  < 380 nm.

The reaction of coumarin I with styrene, which leads to alkylation product XIII in moderate yield (32% vis-à-vis an 80% degree of conversion), proceeds similarly. In addition, substituted coumarin XIV was also isolated from the reaction mixture in appreciable amounts (up to 9%) in this case.



The structure of XIV indicates a side reaction involving the nitration of styrene. The signals of the protons of the aminocoumarin fragments, which confirm the presence of substituents in the 3 position, are readily distinguishable in the PMR spectra of XIII and XIV. The chemical shifts of the protons of the  $CHCH_2NO_2$  fragment of XIV have approximately identical values and form a difficult-to-resolve ABC system at 5.1 ppm. Measurement of the integral intensities confirms the presence of three protons in this region. The mass spectrum of coumarin XIV, in which, in addition to a molecular-ion peak (M<sup>+</sup> 380), fragments with masses of 149, 104, and 60, which are assigned to  $[C_6H_5CH=CHNO_2]^+$ ,  $[C_6H_5CH=CH_2]^+$ , and  $[CH_2NO_2]^+$  particles, respectively, may serve as an additional confirmation of the structure of coumarin XIV.

Vibrations of carbonyl groups of a lactone ring appear at 1715 and 1695 cm<sup>-1</sup> in the IR spectra of XIII and XIV. The presence of a primary nitro group in XIV is confirmed by the absorption at 1560 and 1360 cm<sup>-1</sup>. It should also be noted that the presence of a nitro group leads to quenching of the luminescence in coumarin XIV. This principle is observed for all of the known nitro derivatives of the 7-aminocoumarin series.

In order to investigate the general character of reactions involving alkylation by olefins we also studied the reaction of 4-methyl-7-aminocoumarin (XV) with styrene. 3-Substituted coumarin XVI was isolated as the principal product in 25% yield (75% degree of conversion) in this case.



However, the selectivity of the process is lower in this case, and, judging from the PMR spectroscopic and TLC data, 6-isomer XVII and products of alkylation of the amino group are present in the reaction mixture in small amounts (up to 10%).

In our study of the possibility of the introduction of various substituents into the 3 position of 7-aminocoumarins we also investigated the reaction of coumarin I with phenylacetylene. Coumarin XVIII was obtained in 23% yield vis-á-vis a 90% degree of conversion when a mixture of the reagents in solution in nitromethane was heated at 100°C for 15 h in the presence of catalytic amounts of mercury chloride.



In addition to signals of an aminocoumarin fragment at 7.3 ppm, a multiplet signal of phenyl protons of a substituent in the 3 position is observed in the PMR spectrum of coumarin XVIII. The presence of a terminal methylene group is confirmed by doublet signals at 5.9 and 5.2 ppm with geminal constant  $^{2}J = 1.5$  Hz. The other physicochemical characteristics of XVIII are presented in Tables 1-3 and in the experimental section.

A special topic in the study of substitution reaction in coumarin I was an investigation of methods for the synthesis of 3-halo derivatives from it. We observed that the reaction of coumarin I with copper(II) halides is an effective method for the introduction of Cl or Br atoms into the 3 position. Thus, 3-chloro-4-methyl-7-diethylaminocoumarin (XIX) was obtained in 87% yield (100% degree of conversion) when the starting coumarin was refluxed with 1.5 equivalents of CuCl<sub>2</sub> in nitromethane for 15 h. The corresponding 3-bromo derivative XX was obtained in 81% yield under similar conditions. The oxidative iodination of coumarin I with iodine in acetonitrile in the presence of hydrogen peroxide was used for the synthesis of 3-iodo-4-methyl-7-diethylaminocoumarin (XXI). The yield of XXI reached 75% in this case.



Quenching of the luminescence properties under the influence of a heavy atom can be graphically observed in the case of 3-halo derivatives XIX-XXI[11]. Thus, in solution in ethanol the luminescence quantum yield of XIX is 0.81 (with 3-aminophthalimide as the standard); this value is 0.51 for coumarin XX, whereas XXI has virtually no luminescence.

In conclusion, let us briefly correlate the physicochemical properties of the synthesized 3-substituted 7-aminocoumarins VIII, IX, XIII, XIV, XVI, and XIX-XXI.

The 5-, 6-, and 8-H protons of a coumarin fragment are readily distinguishable in the PMR spectra of the indicated compounds (Table 2). In conformity with the available data [5], the 5-H signal, which shows up in the form of a doublet  $(J_{56} \approx 8-9 \text{ Hz})$ , is observed at weakest field at 7.2-7.5 ppm. The signal of the 8-H proton is observed at 6.3-6.5 ppm, also usually in the form of a doublet as a result of spin-spin coupling with the 6-H proton  $(J_{86} \approx 2-3 \text{ Hz})$ . The chemical shift of the 6-H proton occupies the intermediate region 6.5-6.7 ppm; the 6-H signal, correspondingly, is split into a doublet of doublets.

The most characteristic absorption in the IR spectra of the synthesized coumarins is the absorption of a carbonyl group of a lactone ring at 1695-1735 cm<sup>-1</sup> (Table 1).

Data on the UV and luminescence spectra of VIII, IX, XIII, and XVI-XX, which have appreciable luminescence ( $\phi > 0.1$ ), is presented in Table 3. Data on the UV spectra of the remaining compounds are presented in the experimental section. The general tendency in the

electronic spectra of the 7-aminocoumarins consists in a shift to the short-wave region of the absorption bands or emission with an increase in the electron-donor properties of the substituent in the 3 position (for example, compare VIII and IX and XIX and XX).

Thus, the specific characteristic of coumarin consists in a tendency for charge separation within the molecule. Whereas the amino group is capable of stabilizing the positive charge effectively, the maximum electron density is localized primarily on the exocyclic oxygen atom and the  $C_{(3)}$  atom of the pyrone ring. Let us also point out that the tendency of 7-aminocoumarin molecules to undergo this sort of polarization should be manifested in strong p- $\pi$  conjugation in the nitrogen atom-carbonyl oxygen atom system. This fact is actually confirmed by the NMR spectroscopic data [7]. The charge separation in 7-aminocoumarins actually means that the molecules of these compounds may potentially act as electron donors. Of particular interest in this connection is a study of the reactions of coumarin I, as well as other 7-aminocoumarins, under electron-transfer conditions. This topic will be the subject of our next publication.

## EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV and luminescence spectra were obtained with a Hitachi EPS-3T spectrophotometer with a G-3 luminescence adapter. The relative luminescence quantum yields were determined with respect to quinine bisulfate or 3-aminophthalimide by the method in [12]. The PMR spectra of solutions in CDCl<sub>3</sub> were recorded with a Brucker 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 reaction products were isolated by chromatography with a column  $(30 \times 2.5 \text{ cm})$  packed with Silpearl UV-254 silica gel in hexane-acetone and benzene-ethyl acetate systems. The purity of the substances was monitored by TLC on Silufol UV-254 plates. The degree of conversion was determined from the amount of unchanged coumarin that was isolated after chromatographic separation of the mixture.

Compounds VIII, IX, XIII, and XIV, which are isolated in the form of oils, were converted, for additional identification, to the picrates by mixing ether solutions of the corresponding coumarin and a twofold to threefold excess of picric acid; the resulting crystals were removed by filtration, washed with ether, and dried.

<u>General Method for Obtaining Coumarins (II, III, VIII, IX, XIII, XIV, and XVI-XXI)</u>. A mixture of 6.5 mmole of 4-methyl-7-diethylaminocoumarin (I) and 1.0-10.0 mmole of the Lewis acid ( $ZnCl_2$ ,  $HgCl_2$ , etc.) was heated in dry nitromethane or acetonitrile with an equivalent or excess amount of the corresponding reagent at 80-100°C for 15-30 h, after which the reaction mixture was evaporated, 20 ml of water was added, and the aqueous mixture was made alkaline to pH 6-8 with sodium carbonate and extracted with ethyl acetate. The solvent was removed by distillation, and the residue was separated by chromatography.

<u>4-Methyl-7-ethylamino- and 4-Methyl-7-aminocoumarins (II and III)</u>. From 1.5 g (6.5 mmole) of coumarin I and 0.87 g (6.5 mmole) of aluminum chloride, after refluxing for 20 h in 20 ml of acetonitrile, we obtained, from the fraction with  $R_f$  0.31 [hexane-acetone (2:1)], 0.40 g (38% yield; 80% degree of conversion) of II with mp 147°C (from hexane-acetone). Found: M<sup>+</sup> 203.  $C_{12}H_{13}NO_2$ . Calculated: M<sup>+</sup> 203 [13]. From the fraction with  $R_f$  0.13 [hexane-acetone (2:1)] we obtained 0.25 g (28% yield; 80% degree of conversion) of III with mp 223°C (from methanol). Found: M<sup>+</sup> 175.  $C_{10}H_9NO_2$ . Calculated: M<sup>+</sup> 175 [13].

 $\frac{4-\text{Methyl-6-acetyl-7-diethylaminocoumarin (IV) and 4-\text{Methyl-8-acetyl-7-diethylaminocoumarin (V)}}{\text{marin (V)}. A mixture of 1.50 g (6.5 mmole) of coumarin I, 5 ml of acetic anhydride, and 0.12 ml (2.5 mmole) of sulfuric acid was refluxed for 25 h, after which the excess anhydride was removed in vacuo, and the residue was separated by chromatography. From the fraction with R<sub>f</sub> 0.23 [benzene-ethyl acetate (1:1)] we obtained 0.06 g of IV with mp 104-105°C (from methanol). UV spectrum (in 2-propanol), <math display="inline">\lambda_{max}$  (log  $\varepsilon$ ): 237 (4.38), 260 (4.10), 348 nm (4.20). From the fraction with R<sub>f</sub> 0.20 [benzene-ethyl acetate (1:1)] we obtained 0.19 g of V with mp 127-128°C (from methanol). UV spectrum (in 2-propanol),  $\lambda_{max}$  (log  $\varepsilon$ ): 242 (4.32), 250 (4.03), 255 (4.13), 350 nm (4.28).

<u>4-Methyl-7-hydroxy-8-phenylazocoumarin (VII)</u>. An 18-ml sample of an aqueous solution of benzenediazonium chloride (13.5 mmole) was added with stirring at  $-10^{\circ}$ C in the course of 15 min to a mixture of 1.58 g (9.0 mmole) of 4-methylumbelliferone and 14 ml of a 1 N aqueous

solution of sodium carbonate (14.0 mmole), after which the reaction mixture was stirred for another hour at 20°C. The precipitate was removed by filtration and purified by chromatography to give 0.54 g (33% yield; 65% degree of conversion) of VII with mp 222-223°C (from methanol) and  $R_f$  0.10 [hexane-acetone (10:1)]. IR spectrum (KBr): 1730 cm<sup>-1</sup> (C=O). UV spectrum (in 2-propanol),  $\lambda_{max}$  (log  $\varepsilon$ ): 237 (4.13), 244 (4.09), 330 (4.53), 342 nm (4.53). PMR spectrum (CDCl<sub>3</sub>): 7.05 (2H, m, o-CH in C<sub>6</sub>H<sub>5</sub>), 6.88 (1H, d, J = 9.0 Hz, 5-H), 6.67 (3H, m, m- and p-CH in C<sub>6</sub>H<sub>5</sub>), 6.06 (1H, d, J = 9.0 Hz, 6-H), 5.37 (1H, s, 3-H), 3.20 (1H, s, 0H), 2.12 (3H, s, CH<sub>3</sub>). Found, %: C 68.8; H 4.5; N 9.8.  $C_{16}H_{12}N_2O_3$ . Calculated, %: C 68.6; H 4.3; N 10.0.

<u>3-(2-Tetrahydropyranyl)-4-methyl-7-diethylaminocoumarin (VIII) and 3-[3-(2-Tetrahydropyranyl)-2-tetrahydropyranyl]-4-methyl-7-diethylaminocoumarin (IX)</u>. From 1.50 g (6.5 mmole) of coumarin I, 3.0 g (35.7 mmole) of dihydropyran, and 0.10 g (0.7 mmole) of zinc chloride, after refluxing for 30 h in 10 ml of nitromethane, we obtained, from the fraction with  $R_f$  0.19 [hexane-acetone (8:1)], 0.22 g of VIII in the form of an oil. Mass spectrum, m/z (relative intensity, %): 315 (98); 300 (98); 287 (18); 286 (26); 272 (26); 270 (25); 258 (61); 244 (48); 242 (27); 169 (52); 111 (22); 110 (23); 97 (47); 85 (100). The picrate had mp 109-110°C. From the fraction with  $R_f$  0.13 [hexane-acetone (8:1)] we obtained 0.20 g of IX in the form of an oil. Mass spectrum (relative intensity, %): 399 (4); 258 (5); 244 (30); 230 (6); 216 (18); 169 (12); 120 (10); 111 (23); 110 (19); 55 (100). The picrate had mp 110°C.

<u>4-Methyl-3-(1-phenylethyl)-7-diethylaminocoumarin (XIII) and 4-Methyl-3-(2-nitro-1-phenylethyl)-7-diethylaminocoumarin (XIV)</u>. From 1.50 g (6.5 mmole) of coumarin I, 3.0 g (28.9 mmole) of styrene, and 0.50 g (3.7 mmole) of zinc chloride, after refluxing for 32 h in 6 ml of nitromethane, from the fraction with  $R_f$  0.15 [hexane-acetone (9:1)] we obtained 0.56 g of XIII in the form of an oil. From the fraction with  $R_f$  0.20 [hexane-ethyl acetate (6:1)] we obtained 0.18 g of XIV in the form of an oil. IR spectrum (KBr): 1695 (C=0), 1560, 1360 cm<sup>-1</sup> (NO<sub>2</sub>). Mass spectrum (relative intensity, %): 380 (5); 219 (18); 160 (40); 149 (8); 117 (40); 104 (52); 91 (39); 78 (100); 60 (18). The picrate had mp 160-161°C.

 $\frac{3-(1-\text{Phenylethyl})-4-\text{methyl}-7-\text{aminocoumarin (XVI) and } 6-(1-\text{Phenylethyl})-4-\text{methyl}-7-}{\text{aminocoumarin (XVII)}}.$  From 1.05 g (6.0 mmole) of 4-methyl-7-aminocoumarin, 1.37 g (13.2 mmole) of styrene, and 0.16 g (0.6 mmole) of mercury chloride, after refluxing for 20 h in 15 ml of nitromethane, we obtained, from the fraction with R<sub>f</sub> 0.22 [benzene-ethyl acetate (8:1)], XVI with mp 194-195°C (from acetone). From the fraction with R<sub>f</sub> 0.18 [benzene-ethyl acetate (8:1)] we obtained 0.11 g (8% yield; 75% degree of conversion) of XVII with mp 242-243°C (from acetone). IR spectrum (KBr): 1695 cm<sup>-1</sup> (C=0). Found: M<sup>+</sup> 279. C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>.

<u>3-(1-Phenylvinyl)-4-methyl-7-diethylaminocoumarin (XVIII)</u>. From 1.50 g (6.5 mmole) of coumarin I, 1.33 g (13.0 mmole) of phenylacetylene, and 0.24 g (0.9 mmole) of mercury chloride, after refluxing for 15 h in 12 ml of nitromethane, we obtained 0.45 g of XVIII with mp 110-111°C (from hexane-acetone) and  $R_f$  0.40 [benzene-ethyl acetate (10:1)].

<u>3-Chloro-4-methyl-7-diethylaminocoumarin (XIX)</u>. From 1.50 g (6.5 mmole) of coumarin I and 1.31 g (9.7 mmole) of anhydrous copper(II) chloride, after refluxing for 15 h in 10 ml of nitromethane, we obtained 1.50 g of XIX with mp 108-109°C (from hexane-acetone) and  $R_f$  0.35 [benzene-ethyl acetate (5:1)].

<u>3-Bromo-4-methyl-7-diethylaminocoumarin (XX)</u>. From 1.50 g (6.5 mmole) of coumarin I and 3.36 g (9.7 mmole) of anhydrous copper(II) bromide, after refluxing for 10 h in 15 ml of nitromethane, we obtained 1.15 g (81% yield; 70% degree of conversion) of XX with mp 92-93°C (from hexane-acetone) [according to the data in [14], this compound had mp 93°C and  $R_f$  0.35 [benzene-ethyl acetate (5:1)]].

<u>3-Iodo-4-methyl-7-diethylaminocoumarin (XXI)</u>. A mixture of 1.50 g (6.5 mmole) of coumarin I, 1.65 g (6.5 mmole) of elementary iodine, and 1.0 ml (8.81 mmole) of a 30% aqueous solution of hydrogen peroxide was heated at 80°C for 15 h in 15 ml of acetonitrile, after which the solvent was evaporated, and the residue was purified by chromatography to give 1.73 g of XXI with mp 113-114°C (from hexane-acetone) and  $R_f$  0.38 [benzene-ethyl acetate (5:1)].

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INTRAMOLECULAR CYCLIZATION OF 5-(o-CARBOXYPHENYL)PYRROLE DERIVATIVES

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A new method is proposed for the synthesis of derivatives of indeno[1,2-b]pyrrole-4-ones by intramolecular cyclization of the corresponding 5-(o-carboxyphenyl)pyrroles by trifluoroacetic anhydride.

In a previous communication [1] we reported the synthesis of 3-carbethoxyindeno[1,2-b]pyrrole-4-ones (IIa-d) by intramolecular cyclization of the acid chlorides of 3-carbethoxy-5-(o-carboxyphenyl)pyrroles (Ia-d) under Friedel-Crafts conditions. However, we did not succeed in preparing derivatives of indeno[1,2-b]pyrrole-4-one containing acetyl and carboxyl groups at position 3 of the pyrrole ring, or derivatives of indeno[1,2-b]pyrrole with position 3 unoccupied, by this method. With the aim of preparing the latter, we used trifluoroacetic anhydride as a cyclizing medium and this made it possible to obtain previously unknown derivatives of indeno[1,2-b]pyrrole-4-one (IIf- $\ell$ ) and the previously described indenopyrrolones IIa-e from the corresponding 5-(o-carboxyphenyl)pyrroles (Ia- $\ell$ ) in one stage with yields greater than by the method which we put forward previously [1].



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