6. V. G. Brovchenko and E. V. Kuznetsov, Khim. Geterotsikl. Soedin., No. 1, 125 (1986).
7. P. A. Klare, General Organic Chemistry [Russian translation], Vol. 8, Izd. Khim., Moscow (1985), p. 280.
8. C. Van der Plas, Khim. Geterotsikl. Soedin., No. 7, 867 (1978).
9. J. K. Stamos, Tetrahedron Lett., 23, 459 (1982).
10. G. P. Safaryan, I. V. Shcherbakova, G. N. Dorofeenko, and E. V. Kuznetsov, Khim. Geterotsikl. Soedin., No. 12, 1608 (1981).
11. S. Agurell, J. Granelli, K. Leander, B. Luning, and J. Rosenblom, Acta, Chem. Scand., Ser. B, 28, 239 (1974).
12. J. M. Holland and D. W. Jones, J. Chem. Soc., C, No. 3, 608 (1971).
13. M. Maleni and A. C. Hopkinson, Tetrahedron Lett., 24, 4911 (1983).
14. K. Takeuchi, T. Kitagawa, and K. Okamoto, Chem. Commun., No. 1, 7 (1983).

PHOTOCHEMICAL REACTIONS OF 7-AMINOCOUMARINS.

4.* REACTION OF 4-METHYL-7-DIETHYLAMINOCOUMARIN WITH COMPOUNDS TENDING TO PHOTOLYTIC DISSOCIATION

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The photochemical reactions of 4-methyl-7-diethylaminocoumarin with a series of alkyl halides including isopropyl iodide, allyl iodide, bromoacetone α-bromoethyl acetate, phenacyl bromide, p-bromophenacyl bromide, and chloroacetonitrile, and aryl iodides including iodobenzene, 2-nitroiodobenzene, 3,4-dimethoxyiodobenzene, and 3-iodo-4-methyl-7-diethylaminocoumarin proceed by a radical addition mechanism to give 3-substituted aminocoumarins. A series of 3-substituted 7-aminocoumarins was also obtained as a result of the photochemical reactions of 4-methyl-7-diethylaminocoumarin, with other reagents, having photolabile chemical bonds such as dioxanyl peroxide, phenyl iodosodiacetate, and nitromethane. The luminescence characteristics of the compounds synthesized were studied.

We have previously reported about the [2 + 2] photocycloaddition reactions of 7-aminocoumarins [2, 3] and unusual photoreactions of 4-methyl-7-diethylaminocoumarin (I) with unsaturated compounds, which affect the diethylamino group [1]. In the present article, we describe the photochemical reactions of coumarin I with alkyl and aryl halides and some other compounds, which tend to undergo photolytic dissociation.

7-Dialkylaminocoumarins lose alkyl groups at the nitrogen atom upon irradiation in nitroaromatic solvents [4]. The dealkylation also proceeds upon the photooxidation of dialkylaminocoumarins by atmospheric oxygen, which attacks the α-position relative to the nitrogen atom or the alkyl group at $C_{(4)}$ [5, 6]. Since these processes occur with the formation of radical intermediates [5], we might expect that coumarin I would also react with other compounds, which are potential radical sources in photochemical reactions. A priori, two primary directions for the radical reactions may be proposed for coumarin I: loss of a hydrogen atom from 4-methyl group or from the methylene group in the α-position to the nitrogen atom. Addition or substitution reactions at the $C_{(3)}-C_{(4)}$ bond also appeared to be probable.

We initially studied the reaction of the starting coumarin with alkyl halides, which tend to act as acceptors in electron transfer processes [7] and also give direct dissociation of C—Hal bonds by the action of short-wavelength UV light. A preliminary comparison of the reactivity of alkyl halides in the series RCl→RBr→RI showed that the use of alkyl iodides is best from the preparative viewpoint relative to coumarin upon irradiation by the full light of a PRK-2 mercury lamp, while, in the case of functionally substituted compounds, alkyl bromides,

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*For Communication 3, see [1].

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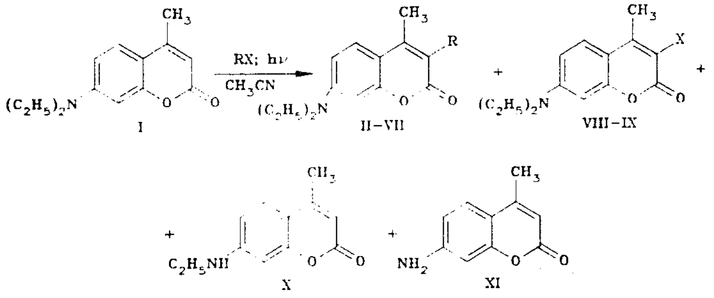
which are more active than alkyl chlorides and less susceptible to side reactions such as reduction and the loss of hydrogen halide, are preferable to the corresponding alkyl iodides. As a result, isopropyl iodide, allyl iodide, bromoacetone, ethyl α-bromoacetate, ω-bromoacetophenone, and p-bromophenacyl bromide were studied in the reaction with the coumarin studied. The photolysis was carried out in a quartz reactor for 0.02-0.05 M solutions of the reagents in acetonitrile in a nitrogen atmosphere with irradiation for 8-40 h. In all cases, the major products of the photoreactions were 3-substituted coumarins II-VII. The yields of these products were 10-30%; the conversion was 40-60%. 3-Iodo- (VIII) or, correspondingly, 3-bromo-4-methyl-7-diethylaminocoumarin (IX) are found as side products in the reaction mixtures. Jones et al. [5] reported X and XI, which are the major photolysis products in the absence of alkyl halide.



II $R=i\text{-}C_3H_7$; III $R=CH_2{=}CHCH_2$; IV $R=CH_2COCH_3$; V $R=CH_2CO_2C_2H_5$; VI $R=$ $=CH_2COC_6H_5$; VII $R=CH_2COC_6H_4Br\text{-}p$; VIII $X=I$; IX $X=Br$

We observed a marked increase in the yields of X and XI (up to 40-80% total yield) in the presence of acetophenone and benzophenone, which indicates the capacity of 7-dialkylaminocoumarins to act as hydrogen donors in the photoreduction of ketones and is in accord with the work of Jones et al. [5] by an N-deethylation scheme. It was then found that the selectivity of the photosubstitution increases markedly in the presence of 1-10 eq triethylamine, which suppresses undesirable reactions giving VIII-XI. In this case, the yields of the 3-alkyl-7-aminocoumarins II-VII may be increased to 15-50% for the same conversions (Table 1).

The structures of II-VII were established using the usual physicochemical methods, elemental analysis, and, in some cases, by conversion to picrates (Table 1). Signals of aromatic protons 5-H, 6-H, and 8-H, which are characteristic for 3-substituted 7-aminocoumarins [8],

TABLE 1. Characteristics of Substituted 7-Aminocoumarins

Compound	Chemical formula	mp	R_f†	ν(C=O), cm^{-1}	Yield, %	Conversion, %
II	$C_{17}H_{23}NO_2 \times C_6H_3N_3O_7$	127...129	0,56	1713	15	50
III	$C_{17}H_{21}NO_2 \times C_6H_3N_3O_7$	129	0,54	1700, 1710	18	40
IV	$C_{17}H_{21}NO_3 \times C_6H_3N_3O_7$	114	0,20	1700, 1705	31	40
V	$C_{18}H_{23}NO_4$	107...107,5	0,24	1701, 1720	35	50
VI	$C_{22}H_{23}NO_3$	77	0,22	1702, 1710	36	45
VII	$C_{22}H_{22}BrNO_3$	108...108,5	0,25	1700, 1710	50	60
XII	$C_{21}H_{21}NO_3$	88...89	0,19	1702	10	65
XIV	$C_{20}H_{21}NO_2$	133...133,5	0,29	1693	27	58
XV	$C_{20}H_{20}N_2O_4$	156...156,5	0,17	1709	25	60
XVI	$C_{22}H_{25}NO_4$	126...127	0,20	1713	21	65
XVII	$C_{28}H_{32}N_2O_4$	222	0,15	1673	20	50
XVIII	$C_{18}H_{23}NO_4$	76	0,20	1720	11	55
XIX	$C_{16}H_{18}N_2O_2$	94...95	0,17	1702	33	50
XX	$C_{14}H_{16}N_2O_4$	158...158,5	0,21	1710	30	50
XXI	$C_{28}H_{27}NO_3$	141...141,5	0,31	1673, 1715	20	40

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*The chemical formulas were confirmed by determination of the content of C, H, and N. The formulas and melting points of the picrates were obtained for II-IV.

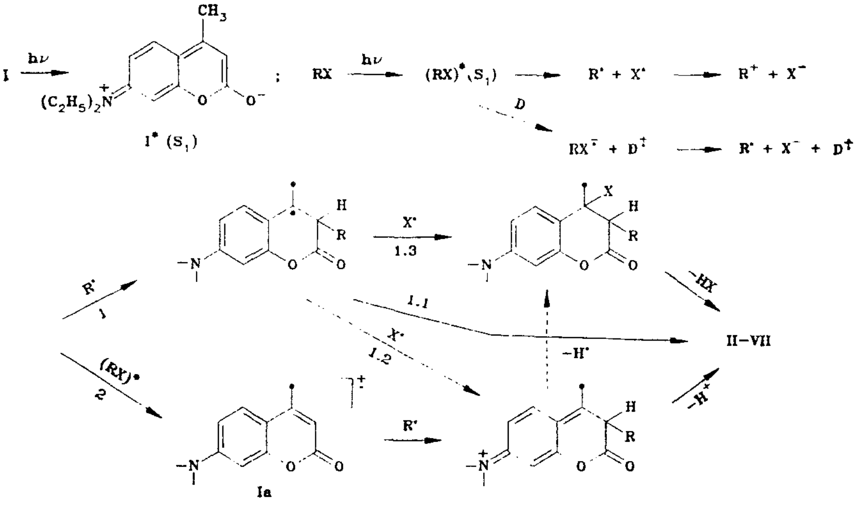
†The R_f values were given for Silufol UV-254 plates with 3:1 hexane—acetone as the eluent.

TABLE 2. PMR Spectra of Coumarins II-VII, XII, and XIV-XXI

Compound	δ, ppm., multiplicity (J, Hz)					
	5-H	6-H	8-H	4-CH$_3$	NCH$_2$CH$_3$	other substituent protons
II	7,32 d (9,0)	6,48 d.d	6,29 d (2,7)	2,25 s	3,30 q (6,9); 1,09 t	1,27 and 3,27 (6H, d and 1H, m 6,85, 3-CH(CH$_3$)$_2$)
III	7,05 d (9,0)	6,67 d.d	6,15 d (2,3)	2,16 s	3,22 q (7,0); 1,15 t	3,20 (2H, m, 3-CH$_2$); 4,78 (1H, s, =C—H trans); 4,93 (1H, d, 7,0, =CH-cis; 5,63 (1H, m, =CH—CH$_2$)
IV	7,25 d (9,7)	6,49 d.d	6,35 d (2,5)	2,18 s	3,30 q (7,0); 1,10 t	2,18 (3H, s, COCH$_3$); 3,65 (2H, s, 3-CH$_2$)
V	7,40 d (9,0)	6,59 d.d	6,48 d (2,8)	2,31 s	3,39 q (7,0); 1,19 t	1,26 and 4.14 (3H, t, 7,0 and 2H, q, 7,0, OCH$_2$CH$_3$); 3,65 (2H, s, 3-CH$_2$)
VI	7,35 d (10,0)	6,51 d.d	6,46 d (2,9)	2,25 s	3,35 q (7,0); 1,10 t	4,27 (2H, s, 3-CH$_2$); 7,42 and 8,01 (3H, m, and H, m, COC$_6$H$_5$)
VII	7,38 d (9,2)	6,58 d.d	6,47 d (2,4)	2,25 s	3,37 q (7,0); 1,17 t	4,26 (2H, s, 3-CH$_2$); 7,57 and 7,90 (each 2H, d 8,6, COC$_6$H$_4$)
XII	7,27 d (9,1)	6,48 d.d	6,39 d (2,8)	2,19 s	3,32 q (7,0); 1,12	7,1 . . . 7,3 and 7,72 (3H, m, and 2H, m, COC$_6$H$_5$)
XIV	7,56 d (9,6)	6,75 d.d	6,52 d (2,6)	2,22 s	3,52 q (7,1); 1,23 t	7,36 (5H, m, 3-C$_6$H$_5$)
XV	7,25 d (9,0)	6,48 d.d	6,35 d (2,9)	1,96 s	3,31 q (7,0); 1,10 t	6,40 and 6,82 (3H, m, and 1H, d 9,1, C$_6$H$_4$)
XVI	7,51 d (9,1)	6,70 d.d	6,49 d (2,8)	2,10 s	3,48 q (7,0); 1,19 t	3,73 and 3,83 (each 3H, s, 2-OCH$_3$); 6,56 (1H, d.d, 8,2, 2,5, 6′-H); 6,61 (1H, d, 2,5, 2′-H); 7,05 (1H, d, 8,2, 5′-H)
XVII	7,43 d (9,1)	6,60 d.d	6,51 d (2,8)	2,22 s	3,41 q (7,0); 1,19 t	—
XVIII	7,28 d (9,3)	6,39 d.d	6,32 d (2,9)	2,44 s	3,26 q (6,9); 1,09 t	3,69 and 5,06 [6H, m, 3-*cyclo*-(CH$_2$) and 1H, m, *cyclo*-(CH)]
XIX	7,26 d (9,3)	6,45 d.d	6,29 d (2,9)	2,35 s	3,29 q (6,9); 1,11 t	3,59 (2H, s, CH$_2$CN)
XX	7,20 d (9,2)	6,44 d.d	6,26 d (2,7)	2,22 s	3,35 q (7,0); 1,15 t	—
XXI	7,19 or 6,94 s	—	6,47 s	2,11 d (1,5)	2,97 q (7,0); 0,93 t	5,99 (1H, q, 1,5, 3-H); 6,94 or 7,19 (1H, s, 6-CH); 7,20 and 7,90 [6H, m, and 4H, m (C$_6$H$_5$)$_2$]

are found at δ 6.2-7.4 ppm in the PMR spectra of these coumarins (Table 2). Other reference signals for the compounds synthesized may be found in the 4-methyl group singlet at 2.1-2.5 ppm and the quartet splitting of the signals at 3.5 and 1.1 ppm, which characterizes the diethylamino group. The lactone ring carbonyl band at 1700-1715 cm^{-1} is characteristic for the IR spectra of coumarins II-VII. Data on the UV and luminescence parameters of the compounds synthesized are given in Table 3.

Considering the capacity of alkyl halides and the radicals formed from these compounds to undergo electron transfer [9, 10], we would expect the generation of different active species in the reaction mixtures upon photolysis such as $R^{\cdot}$, $Hal^{\cdot}$, R^{+}, Hal^{-}, and $RHal^{\bar{\cdot}}$ (see below). Furthermore, we should bear in mind that the structure of 7-aminocoumarin in the excited singlet state (S_1) is best described by bipolar form (I^{*}) with intermolecular charge transfer (ICT state [11]). If we limit ourselves only by these initial conditions, we may propose the following probable scheme formally for substitution at $C_{(3)}$:



Let us consider the reactions in this scheme in greater detail. We could initially assume that the reactions are related to the direct photolysis of the alkyl halide and involve radical attack at $C_{(3)}$ in coumarin I in the S_0 state (pathway 1). On the other hand, electron transfer processes as, for example, in pathway 2, involving singlet excited states of the alkyl halide or coumarin also appeared likely [12]. Finally, the presence of compounds containing heavy atoms such as RI and RBr and the products of their photolysis (halogen atoms and anions) as well as triplet sensitizers, in a number of cases, such as bromoketones does not exclude the generation and participation fo the triplet excited state (T_1) of the dye in these reactions.

In order to clarify this question, we determined the spectral range, which gives the photosubstitution. The photoreactions with alkyl halides virtually do not proceed upon the excitation of coumarin I by monochromatic light in the long-wavelength absorption band (λ_{max} 367 nm). Thus, the existence of a singlet excited state (S_1) of the starting coumarin is not sufficient or even necessary for the photosubstitution. An analogous conclusion is also valid for other excited states (T_1, TICT state [11]) of the coumarin studied. An efficient reaction of coumarin I with alkyl halides was observed only upon UV irradiation at 230-255 nm. Thus, we may assume that the step involving photoexcitation of the alkyl halide is significant for these reactions.

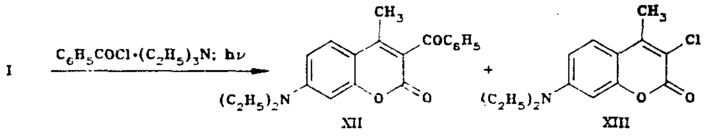
According to Kropp [10], the formation of reactive ions is possible upon the photolysis of alkyl bromides and iodides. In order to study the possible ionic nature of these reactions, we studied quenching of the proposed radical reactions by carbon tetrachloride and oxygen. Indeed, the yields of the 3-substitution products (II-VII) are reduced by a factor of 2-5 upon the addition of an excess (5-10 eq) CCl_4 or saturation with oxygen. The effect of these and other additives on the quantum yields of the reactions leading to coumarin V determined upon monochromatic irradiation at 230 nm taking account of the absorption of the additive is given as an example in Table 4 (see Experimental). A significant increase in the fraction of the 3-halo derivative VIII or IX is also observed by the effect of oxygen. We also note

TABLE 3. UV and Luminescence Characteristics of Coumarins II-VII, XII, and XIV-XXI

Compound	Solvent	UV spectrum, λ_{max}, nm (log ε)	Luminescence		
			λ_{exc}, nm	λ_{max}, nm	φ
II	C_2H_5OH	246 (4,12), 254 (4,11), 308 (3,58), 318 (3,67), 371 (4,34)	375	460	0,49
	CH_3CN	243 (4,24), 252 (4,19), 308 (3,77), 319 (3,90), 365 (4,47)	375	442	0,39
III	C_2H_5OH	247 (4,14), 254 (4,12), 306 (3,50), 318 (3,62), 375 (4,29)	380	460	0,54
	CH_3CN	244 (4,10), 251 (4,07), 306 (3,48), 320 (3,65), 368 (4,34)	380	427	0,62
IV	C_2H_5OH	256 (4,31), 306 (3,73), 319 (3,80), 377 (4,50)	370	465	0,69
	CH_3CN	246 (3,98), 252 (3,93), 318 (3,50), 373 (4,23)	370	450	0,42
V	C_2H_5OH	248 (4,21), 306 (3,51), 316 (4,60), 378 (4,42)	370	464	0,80
	CH_3CN	245 (4,14), 253 (4,09), 318 (3,61), 372 (4,36)	370	448	0,71
VI	C_2H_5OH	246 (4,47), 280 (3,54), 308 (3,57), 318 (3,69), 377 (4,48)	400	478	0,01
	CH_3CN	244 (4,42), 280 (3,43), 308 (3,57), 320 (3,71), 372 (4,42)	400	470	0,01
VII	C_2H_5OH	257 (4,90), 318 (3,61), 379 (4,42)	370	460	<0,1
	CH_3CN	255 (4,45), 318 (3,66)	370	454	0,06
XII	*i*-C_3H_7OH	250 (4,31), 353 (4,04), 396 (4,28)	—	—	—
XIV	C_2H_5OH	218 (4,15), 257 (4,19), 306 (3,53), 318 (3,61), 383 (4,49)	380	475	0,86
	CH_3CN	244 (4,18), 256 (4,22), 306 (3,61), 318 (3,74), 377 (4,57)	380	488	0,61
XV	*i*-C_3H_7OH	251 (4,37), 306 (3,73), 318 (3,75), 382 (4,48)	—	—	—
XVI	C_2H_5OH	250 (4,28), 276 (3,84), 306 (3,69), 318 (3,77), 379 (4,55)	375	460	0,66
	CH_3CN	242 (4,19), 250 (4,17), 278 (3,77), 322 (3,79), 375 (4,50)	375	442	0,39
XVII	C_2H_5OH	252 (4,14), 282 (3,38), 310 (3,45), 320 (3,50), 402 (4,48)	400	479	0,11
	CH_3CN	248 (4,17), 282 (3,38), 310 (3,55), 322 (3,62), 395 (3,57)	400	479	0,17
XVIII	C_2H_5OH	252 (4,30), 283 (3,33), 308 (3,44), 318 (3,53), 385 (4,47)	380	464	0,61
	CH_3CN	250 (4,15), 283 (3,27), 308 (3,49), 318 (3,66), 378 (4,44)	380	454	0,60
XIX	C_2H_5OH	250 (4,22), 282 (3,45), 306 (3,54), 385 (4,46)	380	470	0,36
	CH_3CN	244 (4,15), 252 (4,13), 282 (3,35), 306 (3,52), 318 (3,61), 380 (4,42)	380	470	0,36
XX	*i*-C_3H_7OH	250 (4,22), 286 (3,50), 320 (3,53), 413 (4,43)	—	—	—
XXI	C_2H_5OH	246 (4,37), 270 (4,04), 338 (4,06)	—	—	

that the usual electrophilic substitution reactions for 7-aminocoumarins are not selective and give a mixture of 3-, 6-, and 8-isomers [13]. On the other hand, in the reactions studied, formation of the 6- and 8-alkylation products was not observed. Furthermore, further alkylation did not proceed at all in the photolysis of 3-substituted coumarins II-VII themselves with alkyl halides. Thus, ionic reactions, including those involving the ground state of coumarin I, are not predominant in these reactions.

For indirect confirmation of this conclusion, we carried out the reaction of coumarin I with a strong electrophilic reagent, which is also relatively stable to the effect of light, namely the complex of benzoyl chloride with triethylamine. If the photolytic reactions proceeded by an ionic mechanism, we would expect an increase in the yield of the substitution product. Indeed, 3-benzoyl derivative XII was isolated upon the irradiation of coumarin I in acetonitrile in the presence of an equivalent amount of $C_6H_5COCl \cdot N(C_2H_5)_3$ over 35 h. However, the yield of XII was rather low (10% for 65% conversion). Furthermore, 3-chlorocoumarin XIII was found in the reaction mixture in comparable amounts.



The formation of coumarin XII was not observed at all upon using benzoyl fluoride in an analogous reaction. These findings are in best accord with a radical or radical-ion course for the observed photoreactions. Additional support for this hypothesis is found in the chromato-mass spectral detection of products of purely radical origin such as acetophenone (M^+ 120) and 1,2-dibenzoylethane (M^+ 238) in the reaction mixture in the case of the reaction of coumarin I with ω-bromoacetophenone.

In this study of the mechanism of these reactions, we investigated the effect of various triplet sensitizers such as naphthalene, acetophenone, benzophenone, and p-benzoquinone on the photosubstitution reaction. All these sensitizers decrease the rate of accumulation of 3-alkylation products (Table 4) and accelerate the formation of X and XI. The photoalkylation was also suppressed in the presence of additives containing heavy atoms ($CHBr_3$ and CBr_4), which are capable of $S_1 \rightarrow T_1$ intercombinational conversion. These findings exclude the participation of a triplet excited state of coumarin I in the photosubstitution reaction.

Since acetophenone, benzophenone, and p-benzoquinone may also act as hydrogen acceptors and one-electron oxidizing agents [14], the results of these experiments apparently provide additional information and, in particular, indicate that the formation of radical-cations Ia does not hold great importance for these reactions. This conclusion is supported by the lack of the product of the dimerization of coumarinyl radical-cations in the reaction mixtures. Additives of typical one-electron oxidizing agents in photochemical reactions such as 1,4-dicyanobenzene and tetracyanoquinodimethane also do not lead to an acceleration of the photoalkylation.

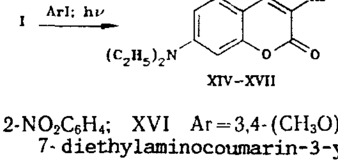
Significant evidence for the realization of pathway, in our view, is found in the effect of triethylamine on the photosubstitution. The lack of formation of 3-halocoumarins VIII and IX and an increase in the relative yield of the 3-alkylation product are observed upon the addition of 1-10 eq triethylamine to the reaction mixtures. The accelerating effect of triethylamine is also indicated by the increase in the quantum yield of the formation of V and VI (Table 4). Triethylamine may accelerate the formation of alkyl radicals as a result of electron transfer [15]:

$$RX \xrightarrow{h\nu} (RX)^{*} \xrightarrow{N(C_2H_5)_3} RX^{\bar{\cdot}} + N(C_2H_5)_3^{\dot{+}} \longrightarrow R^{\cdot} + X^{-} + N(C_2H_5)_3^{\dot{+}}$$

The observed behavior is apparently not in good accord with pathway 2, in which the formation of radical-cation Ia plays the predominant role and triethylamine should act as a quencher.

Thus, the key step of these photoreactions is apparently the attack of the coumarin molecule at $C_{(3)}$ by the alkyl radical. In this case, we consider the realization of pathway 1 most likely although, in principle, the question of the participation of excited states of coumarin I in the photosubstitution reactions remains unresolved. The following step may feature hydrogen atom abstraction (pathway 1.1), one-electron oxidation (pathway 1.2), or addition of a halogen atom (pathway 1.3). As implied by the scheme, these pathways are qualitatively indistinguishable for halo derivatives. Thus, the final step may involve elimination of a proton or a hydrogen halide molecule.

In a continuation of the photochemical reactions of coumarin I, we investigated its reaction with aryl halides. In this case, comparison of the reactivity in the series ArCl→ArBr→ArI showed that the use of aryl iodides is most effective for the substitution reactions. The irradiation of acetonitrile solutions of the starting coumarin and aromatic iodides such as iodobenzene, 2-nitroiodobenzene, and 3,4-dimethoxyiodobenzene in the presence of triethylamine gave 3-aryl-substituted coumarins XIV-XVI. Under analogous conditions, the reaction of coumarin I with 3-iodocoumarin VIII gave bis-coumarin XVII. The characteristics of XIV-XVII are given in Table 1-3.



XIV–XVII

XIV $Ar=C_6H_5$; XV $Ar=2\text{-}NO_2C_6H_4$; XVI $Ar=3,4\text{-}(CH_3O)_2C_6H_3$; XVII Ar=4-methyl 7-diethylaminocoumarin-3-yl

TABLE 4. Quantum Yields for the Formation of Coumarins V, VI, and XIV in Acetonitrile

Compound	Additive	Additive concentration, mole/liter	Quantum yield*
V	—	—	0,058
V	CCl_4	0,50	0,021
V	O_2†	—	0,027
V	$C_6H_5COCH_3$	0,15	0,031
V	$(C_2H_5)_3N$	1,00	0,110
VI	—	—	0,091
VI	$(C_2H_5)_3N$	0,50	0,154
XIV	—	—	0,067

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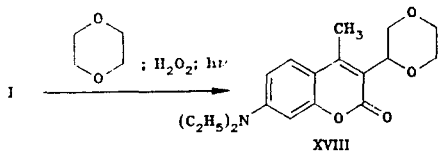
*The quantum yields were determined for 0.1 M solutions of coumarin I and 1.0 M solutions of the halo derivatives in acetonitrile at 20°C taking account of the absorption of the corresponding additive (see also Experimental).

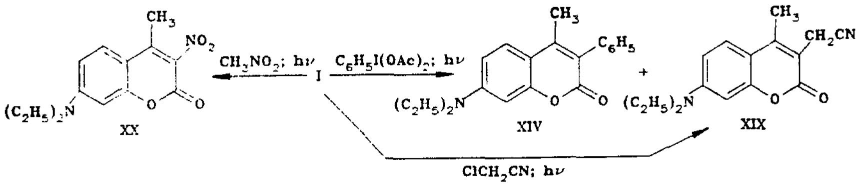
†Oxygen-saturated solution in CH_3CN at 20°C.

The yields of XIV-XVII obtained under identical photoalkylation conditions were 20-30% for conversions of 50-65%. In the case of XIV, we established that the photoalkylation proceeds most efficiently upon irradiation by short-wavelength UV light (λ 230-250 nm). This finding supports a radical course also for this case. Further evidence for the analogy between the photochemical alkylation and arylation reactions may be found in the value of the quantum yield, which we found for XIV (Table 4), and the data from a chromato-mass spectrometric study of the composition of the reaction mixture obtained upon the photolysis of coumarin I with iodobenzene. In this case, a number of compounds arising from radicals such as diiodobenzene (M^+ 330), iododiphenyl (M^+ 280), and, in particular, 3,4-dihydro-3-phenyl-4-methyl-7-diethylaminocoumarin (M^+ 309) formed from the corresponding 3-phenylcoumarinyl radical were detected along with the usual products.

In light of the tendency of coumarin I to undergo radical substitution reactions, we also studied the reaction of this compound with several other reagents capable of photolytic dissociation. Thus, the photolysis of 1,4-dioxane solutions of coumarin I in the presence of hydrogen peroxide or dioxanyl peroxide gave coumarin XVIII in 11% yield upon 55% conversion:



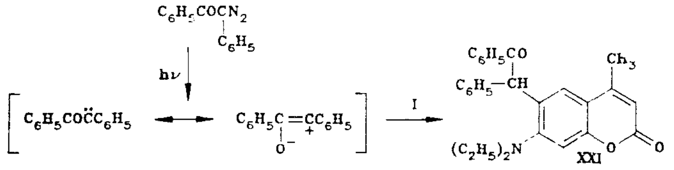
The irradiation of coumarin I in the presence of phenyl iodosodiacetate in acetonitrile gave 3-phenylcoumarin XIV in 15% yield (50% conversion). Coumarin XIX was also detected in yields not exceeding 5%. The formation of XIX may be explained assuming the presence of $^{\bullet}CH_2CN$ radicals, which arise as a result of hydrogen atom abstraction from acetonitrile. The "nucleophilic" $^{\bullet}OAc$ radicals formed in the photolysis of phenyl iodosodiacetate may act as the $H^{\bullet}$ atom acceptors. For preparative purposes, XIX was also obtained by convergent synthesis in the photolysis with chloroacetonitrile. In this case, the yield of coumarin XIX is 33% (50% conversion).



The irradiation of nitromethane solutions of coumarin I in a quartz reactor for 5-10 h leads to the formation of 3-nitrocoumarin XX. The yield of XX at 30-50% conversion is 30%.

In our view, this photochemical nitration is more convenient for preparative purposes than, for example, the well-known nitration of coumarin I by nitric acid [13], since it proceeds selectively and gives 3-nitro-4-methyl-7-diethylaminocoumarin uncontaminated with other isomers.

A somewhat unusual result was obtained in a study of the photochemical reaction of coumarin I with phenylbenzoyldiazomethane. In this case, we also expected reactions at the $C_{(3)}$—$C_{(4)}$ bond. However, coumarin XXI was obtained in 10% yield (60% conversion) upon the irradiation of an equimolar mixture of the reagents in benzene for 12 h.



The formation of the product of substitution at $C_{(6)}$ apparently proceeds through an intermediate electrophilic carbene, which attacks coumarin I at the least hindered site susceptible to electrophilic attack. The structure of XXI follows, for example, from its PMR spectrum, in which the signal for 3-H is found at 5.99 ppm as a poorly resolved quartet as a result of long-range coupling with the CH_3 group (^4J = 1.5 Hz). Protons 5-H and 8-H appear at 7.19 and 6.47 ppm, respectively, as singlets. The IR spectrum of coumarin XXI has a band at 1673 cm^{-1} assigned to the C=O fragment of the substituent at $C_{(6)}$ in addition to the carbonyl absorption for the lactone ring at 1715 cm^{-1}.

On the whole, the photochemical reaction of coumarin I with compounds having bonds, which tend to undergo photolytic dissociation, apparently may serve for the controlled synthesis of substituted 7-aminocoumarins.

Most of the 3-substituted 7-aminocoumarins synthesized have strong fluorescence at 440-490 nm (Table 3). An exception is found for compounds containing a nitro group (XV and XX) as well as heavy atoms (VIII) and a benzoyl group (VI, VII, and XII). The lack of luminescence for coumarin XXI may be attributed to a breakdown in the conjugation of the amino group with the coumarin fragment as a result of steric hindrance or intramolecular energy transfer to the carbonyl group of the substituent at $C_{(6)}$, which is accompanied by $S_1 \rightarrow T_1$ intercombinational conversion [16].

EXPERIMENTAL

The IR spectra were taken for KBr pellets on a UR-20 spectrophotometer. The UV and luminescence spectra were taken on a Hitachi EPS-3T spectrophotometer equipped with a G-3 luminescence attachment. The relative luminescence quantum yields (φ) were determined relative to quinine bisulfate or 3-aminophthalimide according to Parker [17]. The PMR spectra were taken on a Bruker WM spectrometer at 250 MHz with HMDS as the internal standard and $CDCl_3$ as the solvent. The mass spectra were taken on a Varian MAT-311A mass spectrometer at 70 eV. The chromato-mass spectrometric studies were carried out on an 80 × 0.2-cm glass column packed with 3.0% Merck OV-101 on Merck 100-200 mesh Chromosorb WHR. The helium gas carrier flow rate was 20 ml/min, while the column temperature was 90-290°C and the heating rate was 5°C/min.

The reaction products were separated by chromatography on a 30 × 2.5-cm column packed with Silpearl UV-254 silica gel. Hexane—acetone and benzene—ethyl acetate were used as the eluting systems. The purity of the products was monitored by thin-layer chromatography on Silufol UV 254 plates. The conversion was determined relative to the amount of unreacted coumarin isolated after chromatographic separation of the mixture. The characteristics of products II-XXI are given in Tables 1-4.

The apparent differential quantum yields of the photochemical reactions were calculated according to a standard procedure [12] and determined for 0.1 M solution of coumarin I and 1.0 M solutions of halo derivatives in acetonitrile using a Shimadzu CS-930 densitometer. In order to determine the quantum yield, we used UV light with wavelength 230 nm (for V) and 250 nm (for VI and XIV) obtained using a Shimadzu NGF-16 monochromator. The source intensity was measured by a standard procedure [17] and found to be $4.52 \cdot 10^{-10}$ einsteins/sec at 230 nm and $5.81 \cdot 10^{-10}$ einsteins/sec at 250 nm.

Preparation of Coumarins II-VII, XII, XIV-XVII, and XIX. A mixture of 5 mmoles (1.15 g) coumarin I, 5-10 mmoles (0.5-1.0 g) triethylamine, and 5-10 mmoles of the corresponding reagent in acetonitrile was irradiated using a medium-pressure PRK-2 mercury lamp in a 100-150-ml quartz reactor with stirring by a nitrogen stream for 8-40 h. The reaction mixture was evaporated and the residue was separated chromatographically. The products isolated were recrystallized from hexane—acetone. Products II-IV were isolated as oils, which were converted to picrates by mixing ethereal solutions of the corresponding coumarin and a 2-3-fold excess of picric acid. The crystalline residue was filtered off, washed with ether, and dried.

4-Methyl-7-ethylamino- and 4-Methyl-7-amino-2H-benzopyran-2-one (X and XI). Irradiation of 1.15 g (5 mmoles) coumarin I in acetonitrile in the presence of 1.20 g (10 mmoles) acetophenone for 17 h and isolation of the fraction with R_f 0.18 (3:1 hexane—acetone) gave 0.49 g (60% yield, 80% conversion) X, mp 147°C (from hexane—acetone). M^+ 203 (mp 147°C [18]).

The fraction with R_f 0.10 (3:1 hexane—acetone) gave 0.09 g (13% yield, 80% conversion) XI, mp 223°C (from methanol). M^+ 175 (mp 223°C [18]).

3-Phenyl-4-methyl-7-diethylamino-2H-benzopyran-2-one (XIV) and 3-Cyanomethyl-4-methyl-7-diethylamino-2H-benzopyran-2-one (XIX). Irradiation of 1.15 g coumarin I and 1.61 g (5 mmoles) phenyl iodosodiacetate in 100 ml acetonitrile for 10 h gave 0.09 g (15% yield, 50% conversion) XIV and 0.03 g (5% yield, 50% conversion) XIX.

3-(1,4-Dioxanyl)-4-methyl-7-diethylamino-2H-benzopyran-2-one (XVIII). Irradiation of 1.15 g (5 mmoles) coumarin I and 11 ml (10 mmoles) 30% hydrogen peroxide in 1,4-dioxane for 24 h gave 0.10 g XVIII.

3-Nitro-4-methyl-7-diethylamino-2H-benzopyran-2-one (XX). Irradiation of 1.15 g (5 mmoles) coumarin I in nitromethane for 20 h gave 0.21 g XX.

6-(Benzoylphenylmethyl)-4-methyl-7-diethylamino-2H-benzopyran-2-one (XXI). Irradiation of 1.15 g (5 mmoles) coumarin I and 2.23 g (10 mmoles) benzoylphenyldiazomethane in acetonitrile for 40 h gave 0.17 g XXI.

LITERATURE CITED

1. M. A. Kirpichenok, L. M. Mel'nikova, L. K. Denisov, I. I. Grandberg, and N. P. Akimova, Khim. Geterotsikl. Soedin., No. 1, 30 (1989).
2. M. A. Kirpichenok, L. M. Mel'nikova, L. K. Denisov, and I. I. Grandberg, Khim. Geterotsikl. Soedin., No. 9, 1169 (1988).
3. M. A. Kirpichenok, L. M. Mel'nikova, D. S. Yufit, Yu. T. Struchkov, I. I. Grandberg, and L. K. Denisov, Khim. Geterotsikl. Soedin., No. 9, 1176 (1988).
4. D. Dopp and J. Heufer, J. Photochem., 32, 243 (1986).
5. G. Jones, W. R. Bergmark, and W. R. Jackson, Opt. Commun., 50, 320 (1984).
6. R. J. Trebra and T. H. Koch, Appl. Phys. Lett., 42, 129 (1983).
7. P. J. Kropp, G. S. Poindexter, N. J. Pienta, and D. C. Hamilton, J. Am. Chem. Soc., 98, 8135 (1976).
8. M. A. Kirpichenok, I. I. Grandberg, L. K. Denisov, and L. M. Mel'nikov, Izv. TSKhA, No. 3, 172 (1985).
9. R. S. Davidson, J. W. Goodin, and G. Kemp, Adv. Phys. Org. Chem., 20, 191 (1984).
10. P. J. Kropp, Acc. Chem. Res., 17, 131 (1984).
11. G. Jones, W. R. Jackson, C. Choi, and W. R. Bergmark, J. Org. Chem., 49, 2705 (1984).
12. G. O. Becker, Introduction to Organic Photochemistry [Russian translation], Izd. Khimiya, Leningrad (1976).
13. I. I. Grandberg, L. K. Denisov, and O. A. Popova, Khim. Geterotsikl. Soedin., No. 2, 147 (1987).
14. M. Julliard and M. Chanon, Chem. Rev., 83, 425 (1983).
15. N. J. Bunce, P. Pilon, L. O. Ruzo, and D. J. Sturch, J. Org. Chem., 41, 3023 (1976).
16. J. A. Barltrop and J. Coyle, Excited States in Organic Chemistry [Russian translation], Izd. Mir, Moscow (1978).
17. S. Parker, Solution Photoluminescence [Russian translation], Izd. Mir, Moscow (1972).
18. M. A. Kirpichenok, S. L. Levchenko, and I. I. Grandberg, Khim. Geterotsikl. Soedin., No. 10, 1324 (1987).