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## PHOTOCHEMICAL REACTIONS OF 7-AMINOCOUMARINS.

3.\* REACTION OF 4-METHYL-7-DIETHYLAMINOCOUMARIN WITH OLEFINS AND ACETYLENES CONTAINING ELECTRON-WITHDRAWING SUBSTITUENTS

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The photochemical reactions of 4-methyl-7-diethylaminocoumarin with the dimethyl ester of acetylenedicarboxylic acid, diethyl ester of maleic acid, and N-phenyl-maleimide in the presence of oxygen and acetophenone give products of the heterocyclization at  $C_{(6)}$  and  $C_{(8)}$  of coumarin fragment with participation of the diethylamino group. The stereochemical structure of the compounds synthesized was demonstrated using PMR spectroscopy. A mechanism was proposed for this reaction involving the formation of an  $\alpha$ -amino radical and its addition to the acetylene or olefin, accompanied by attack on the aromatic ring with subsequent aromatization.

7-Aminocoumarins upon photoirradiation with olefins having not more than one electronwithdrawing substituent form [2 + 2]-cycloaddition adducts at the  $C(_3)-C(_4)$  bond [1, 2]. In order to expand the scope of these reactions, we attempted to carry out the reaction of the dimethyl ester of acetylenedicarboxylic acid as well as olefins with two electron-withdrawing substituents, namely diethyl maleate and N-phenylmaleimide, with 4-methyl-7-diethylaminocoumarin (I). [2 + 2]-Cycloadducts are not formed under conditions described in our previous work [1, 2] in the absence of a sensitizer in an inert atmosphere. On the other hand, the irradiation of mixtures of reagents in acetonitrile upon saturation with air in the presence of a triplet sensitizer (acetophenone) gives heterocyclization products II-VI (see scheme on following page).

The yields of II-VI are 15-40% with the incomplete conversion of the starting coumarin (the conversion is 60-75%) (Table 1). The reaction should not be carried out with a greater conversion from a preparative viewpoint due to the formation of side-products. Saturation of the solution with pure oxygen or the addition of peroxides are also inefficient for the same reason.

\*See [1] for Communication 2.

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Com- pound	Chemical formula	.mp, °C	¢ <sup>280 *</sup>	Conver- sion, %	Yield,
II III IV	C <sub>20</sub> H <sub>21</sub> NO <sub>6</sub> C <sub>20</sub> H <sub>21</sub> NO <sub>6</sub> C <sub>24</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub>	127 159 240 (dec.)	0,0072 0,0095 0,0290; 0,0185**;	65 65 60	16 18 39
V VI	C <sub>22</sub> H <sub>27</sub> NO <sub>6</sub> C <sub>22</sub> H <sub>27</sub> NO <sub>6</sub>	93 86,5	0,0000*** 0,0124 0,0155	75 75	26 20

TABLE 1. Characteristics of II-VI and the Quantum Yields for Their Formation in Acetonitrile

\*The quantum yields are measured for 0.08 M coumarin I, 0.80 M, and 0.15 M acetophenone at 20°C. \*\*The acetophenone concentration was 0.08 M. \*\*\*In a nitrogen atmosphere.



IV  $R^{1}+R^{3}=-CONC_{6}H_{5}CO-$ ,  $R^{2}=R^{4}=H$ ; V  $R^{1}=R^{3}=CO_{2}C_{2}H_{5}$ ,  $R^{2}=R^{4}=H$ ; VI  $R^{1}=R^{3}=H$ ,  $R^{2}=R^{4}=CO_{2}C_{2}H_{5}$ 

The photolyses were carried out with the complete light of a medium-pressure mercury lamp in quartz reactors upon the irradiation of 0.05 M solutions of coumarin I in acetonitrile with a tenfold excess of the unsaturated compound over 10-20 h. Close-to-equivalent amounts (1.5 equivalents) of acetophenone were used. The presence of a sufficient concentration of the sensitizer is significant. For example, this indicates the dependence of the quantum yields for the formation of IV on the acetophenone concentration (Table 1). These reactions do not proceed at all in the absence of sensitizer. The quantum yields of other reactions of other reactions are given in Table 1.

4-Methyl-7-ethylaminocoumarin (VII) and 4-methyl-7-aminocoumarin (VIII) [3] were also observed in these reactions as side products in up to 15% yield. The formation of these compounds is accelerated in the presence of acetophenone. In the absence of olefin, VII and VIII become the major photolysis products. Thin-layer chromatographic and NMR spectral data also indicate the presence of small amounts of other compounds, which are apparently isomers or products of oxidation [4] and secondary transformations. Desired products II-VI were isolated by chromatography and identified by ordinary methods (Tables 1-3).

The IR spectra of II-VI have bands for the carbonyl groups of the coumarin fragment and substituents at 1700-1740 cm<sup>-1</sup>. The absorption of the carbon bonds of the aromatic rings is usually observed as two bands at 1590-1630 cm<sup>-1</sup> (Table 2). The UV spectra also confirm the retention of the 7-aminocoumarin structure. Characteristic absorption maxima are observed at 240-250, 270-290, 320-325, and 360-370 nm (Table 2). Products II and III have weak luminescence, while IV-VI have strong luminescence (Table 3).

The detailed structure of II-VI follows primarily from their PMR spectra taken at 250 MHz (Table 3). Thus, the fusion of the dihydropyridine ring with  $C_{(6)}$  and  $C_{(7)}$  of the coumarin fragment is seen by the presence of singlets at 7.15 and 6.49 ppm, assigned to aromatic protons 5-H and 10-H, respectively [5]. The retention of a free position at  $C_{(3)}$  is indicated by the signal for 3-H at 5.91 ppm, which appears as a poorly resolved quartet as a re-

1	*		0		7	ç.
e	$\varphi_{\mathrm{f1}}$	0,11	0,11	0,5;	0,7	0,7
escenc	hmax,	546	546	475	451	450
Lumin	A <sub>exc</sub> ,	430	430	365	370	370
		324	366	366	308	308
6		(4,19),	(4,47),	(3,73),	(3,70),	(3,48);
u, xi		273 4,14)	292	322	283	283 283 (4,36)
ο <b>υ,</b> λ <sub>mέ</sub>		(4,31), , 430 (	(4,34),	(3,90),	(4,21),	(4,04), (369),
orpti	(ມ ຜ	245 (4,16)	261 (4,11)	282	248	246 (3,71)
Abso	lor)	(4,35), (, 363	(4,34), 1, 420	(4,18),	(4,24),	4,08), 320
		217 (4,19)	253 (4,23)	236 (	243 () 243 ()	$\left  \begin{array}{c} 240\\ 240\\ (3,60) \end{array} \right $
cm-1	c≖c	1600	1605, 1595	1630,	1603,	1630,
v	C=0	1737, 1735,	1740, 1738,	1725,	1710,	1730,
pu -	рол. Сош	11	III	IV	>	

TABLE 2. Spectral Characteristics of Coumarins II-VI

\*3-Aminophthalimide was used as the standard.

TABLE 3. PMR Spectra of II-VI

oupling constant, J, Hz)	other protons	19 (3H, d, 7,0, 8-CH <sub>3</sub> ); 1,35 (3H, t, 7,0, CH <sub>2</sub> CH <sub>3</sub> ); 3,35and3,47 (1H, d.q, 7,0; 4.0: NCH <sub>3</sub> ): 3.76 and 3.87 (3H, s, OCH <sub>3</sub> )	(12 (3H, t, 7,0, CH <sub>2</sub> CH <sub>3</sub> ); 1,24 (3H, d, 7,0, 8-CH <sub>3</sub> ); 3,39 and 3,50 (1H, d.q, 7,0;	.0: 14.0, NCH2); 3:00 and 3:32 (201, 5; OCH3) ,12 (3H, d, 6.9, 8:CH3); 1,19 (3H, t, 7,0, CH2CH3); 3,31 and 3,64 (1H, d-q, 6,9; 4,0, NCH2); 7,307,50 (5H, m, CsH5)	(16 (3H, d, 8-CH <sub>3</sub> ); 1,20 and 1,22 (3H, t, 7,0, OCH <sub>2</sub> CH <sub>3</sub> ); 3,28 and 3,51 (1H, d.q.	03 (3) (4) (4) (3) (1) (1) (3) (4) (7) (2) (2) (2) (4) (1) (1) (2) (6) (4) (0) (0) (2) (3) (3) (3) (3) (3) (3) (3) (3) (3) (3	
ó, ppm (c	4-CH3**	2,33	2,21	2,34	2,31	2,30	-
	H-01	6,49 s		4,65 (d, 8,2)	4,72 s	4,22 (d,3,9)	
	H-6	1	[	4.02 (d.d.	3,49 s	3,25 (d.d, 3,9; 10,8)	
	H-8	4,66 (q.7.0)	4,40	(q, ', ') 3,45 (d.q.5,5;	4,23	( <b>d</b> . <b>q</b> ,7,0; ( <b>d</b> . <b>q</b> ,7,0; (0,8)	
	6-H, đ	1	6,42	(0,6)	6,57	() () () () () () () () () () () () () (	
	5-H	7,15 s	7,20	(d, 9,0) 7,30 (d, 9,0)	7,36	7,35 7,35 (d,9,1)	-
	3-H*	5,91	5,77	6,05	5,92	5,93	
.b.	unod -ພວງ	Π	III	N	>	17	•

\*Quartet, J = 1.25 Hz. \*\*Doublet, J = 1.25 Hz. sult of long-range coupling with the  $4\text{-CH}_3$  protons. The diastereotopic protons of the NCH<sub>2</sub> fragment are seen as mutually symmetrical sextets (doublet of quartets) at 3.35 and 3.47 ppm. The signal for 8-H in the cyclic N-CH fragment appears as a quartet at 4.66 ppm. On the other hand, doublets are seen in the downfield area at 7.20 and 6.42 ppm for isomeric product III, which are assigned to 5-H and 6-H, respectively [5]. The signal for 3-H is found at 5.77 ppm. The structures of the signals for II and III are otherwise identical (Table 3).

The signals for aromatic protons 6-H and 3-H of the coumarin fragment in the PMR spectrum of IV are found at 6.69 and 6.05 ppm. By analogy to II and III, the 3-H signal is subject to weak splitting due to the 4-CH<sub>3</sub> group protons. The 5-H signal is found at 7.3-7.5 ppm and is overlapped by the phenyl proton multiplet. The protons of the methylene group of the N-ethyl fragment, as in II and III, are diastereotopic and their signals appear as symmetrically distorted sextets (combination of a doublet of quartets) at 3.31 and 3.64 ppm (<sup>2</sup>J = 14.0 and <sup>3</sup>J = 6.9 Hz). The chemical shifts of the protons of the tetrahydropyridine ring at positions 8, 9, and 10 appear at 4.02, 3.45, and 4.65 ppm, respectively. The doublet for 10-H (J<sub>9,10</sub> = 8.2 Hz) is found furthest downfield. The 9-H signal is a doublet of doublets (J<sub>9,10</sub> = 8.2 and J<sub>8,9</sub> = 5.5 Hz). The 8-H signal is a doublet of quartets degenerate into a quintet with broad central lines (J<sub>8,CH3</sub> = 6.9 Hz). The low values of the vicinal coupling constants of the protons at positions 8-10 indicate their cis arrangement [6] and, thus, the cis orientation of the three substituents in the tetrahydropyridine (THP) ring. Taking account of the conformational mobility of the nitrogen atom in such compounds [7], the N-ethyl group may be assigned a pseudoequatorial position, while the 8-CH<sub>3</sub> group may be assigned an equatorial position.

The identification of V and VI as products of the heterocyclization at the coumarin  $C_{(8)}$  atom may be made on the basis of the characteristic signals for the aromatic protons 5-H, 6-H, and 3-H at 7.4, 6.6, and 5.9 ppm (Table 3). The detailed arrangement of the substituents in the THP ring follows from the vicinal coupling constants at positions 8-10. Thus, the signals for 10-H and 9-H for V appear as singlets at 4.72 and 3.49 ppm, which indicates the lack of coupling of 9-H with 8-H and 10-H. In principle, this condition may be met by two isomers. The first isomer has cis arrangement of the 9-ethoxycarbonyl and 8-methyl groups and trans arrangement of the two ester groups. This requires that we assume the existence of two conformers. In one such conformer, the  $CO_2C_2H_5$  groups occupy axial positions, the methyl group occupies an equatorial position, and the  $H-C_{(s)}-C_{(s)}-H$  and  $H-C_{(9)}-C_{(10)}-H$  dihedral angles approach 90°. Thus, the vicinal coupling constants may be zero. On the other hand, the ester groups in the other conformer occupy equatorial positions and the methyl group occupies an axial position. The 9-H and 10-H protons for this conformer are found in trans-axial positions and the  ${}^{3}J_{9,10}$  constant should be large. Since the activation free energies corresponding to the transition from the equatorial to the axial conformer are comparable for the methyl and carbonyl groups according to different evaluations [8, 9] (AGe, a 0.8-1.1 kcal/mole). A given conformer should be comparable in stability with the former (or more stable). Further support for this proposition may be found in the high stability of the e,e-conformers of 1,2-dicarbalkoxycyclohexenes [10]. Thus, the isomer examined is not in good accord with the observed PMR spectrum.

The isomer with a cis,cis arrangement of the methyl and ethoxycarbonyl groups is more probable. Despite the formal analogy with IV, the ester groups in this isomer have rather sufficient conformational mobility and the  $H^{-}C_{(9)}^{-}C_{(10)}^{-}H$  and  $H^{-}C_{(8)}^{-}C_{(9)}^{-}H$  dihedral angles may approach 90°. The most stable conformer (Va) with equatorial arrangement of the methyl and 10-ethoxycarbonyl groups and axial orientation of  $9-CO_2C_2H_5$  also corresponds to this condition. The fragment of the THP ring in the conformational transformation of isomer V is given below. Thus, we also assume the existence of an isomer with a cis arrangement of the substituents at  $C_{(8)}^{-}C_{(10)}^{-}$  for V.



The arrangement of the substituents in isomer VI was established by analyzing the signals for 8-H, 9-H, and 10-H, which appear at 4.19, 3.25, and 4.22 ppm, respectively. The 10-H signal is a doublet overlapped by the signals of the OCH<sub>2</sub> fragments (4.24 ppm). The 8-H proton is discernible on the background of the OCH<sub>2</sub> signals as a doublet of quartets. The value for  ${}^{3}J_{8,9}$  (10.8 Hz) indicate a trans relationship for 8-H and 9-H. In this case, a cis arrangement should be adopted for the ester groups and the most stable conformer (VIa) should have the methyl and 9-CO<sub>2</sub>Et groups in equatorial positions and the 10-CO<sub>2</sub>Et group in an axial position:



Thus, the isomer with a trans, cis arrangement of the  $8-CH_3$ ,  $9-CO_2Et$ , and  $10-CO_2Et$  groups is most probable for VI.

In order to explain the formation of II-VI, we may assume the scheme given below for the case of the reaction with olefins. Acetophenone absorbs a light quantum and converts to the triplet excited state  $(T_1)$ , in which it may act as a one-electron oxidizing agent and react with coumarin I to form radical-cation Ia (see below). This step is supported by the high tendency of coumarin I to undergo one-electron oxidation [11] (comparable to the tendency of triethylamine). We also note that electron transfer upon the irradiation of tertiary amines with triplet sensitizers such as acetophenone is a well-known phenomenon [12]. Then, radical-cation Ia is capable of abstracting an  $\alpha$ -proton and convert to "nucleophilic" radical Ib. In principle, radical-cation Ia may also arise in the reaction of the excited triplet state of the dye molecule with an oxygen molecule in the ground state [13].

An alternate explanation involves the direct formation of radical Ib upon the reaction of coumarin I as a hydrogen donor with an acetophenone molecule in the  $T_1$  state or with singlet oxygen [14], whose generation is sensitized by the starting coumarin [15].

In the next step, radical Ib attacks the olefin or acetylene molecule to form "electrophilic" radical Ic, which attacks one of the ortho positions of the benzene ring. The last step entails the oxidation of radical Id by oxygen with restoration of the aromatic 7-aminocoumarin structure. In any case, the participation of acetophenone is required in at least one of these steps. Carrying out the reactions in a monochromator cell showed that the formation of products IV-VI proceeds efficiently upon irradiation at the acetophenone absorption band ( $\lambda_{max}$  280 nm) and virtually does not proceed upon irradiation at the long-wavelength band of coumarin I ( $\lambda_{max}$  367 nm). Thus, the quantum yields for the formation of IV-VI (Table 1) were calculated relative to acetophenone (see Experimental).



The question of the regioselectivity of these reactions is rather interesting. While the reaction of coumarin I with the dimethyl ester of acetylenedicarboxylic acid is nonselective, the  $C_{(8)}$ -isomers are predominantly formed in the reactions with olefins (see above). The formation of the  $C_{(8)}$ -isomers is in accord with the <sup>13</sup>C NMR spectral data, which predicts maximal electron density specifically at  $C_{(8)}$  of 7-aminocoumarins [5]. Thus, the formation of IV-VI confirms the electrophilic nature of radicals Ic (see the above scheme). The lack of selectivity in the case of the acetylenic derivative may be explained by the additional steric hindrance arising between the planar methoxycarbonyl group and unshared pairs of the oxygen atom of the pyrone ring in the addition step. The factor of the enhanced reactivity of the vinyl radical (analog of Ic) in comparison with alkyl radicals [16] should act in the same direction.

## EXPERIMENTAL

The IR spectra of II-VI were taken in KBr pellets on a UR-20 spectrometer. The UV and luminescence spectra in ethanol were taken on a Hitachi EPS-3T spectrometer with a G-3 luminescence attachment. The PMR spectra were taken on an XL-100 spectrometer at 100 MHz and Bruker-WM spectrometer at 250 MHz in  $CDCl_3$  with HMDS as the internal standard.

The photolyses were carried out in 100-ml quartz reactors. A PRK-2 medium-pressure mercury lamp was the source of UV radiation. The products were isolated by column chromatography on  $35 \times 2.5$  cm columns packed with Silpearl UV silica gel with hexane-acetone or hexane-ethyl acetate as the eluent. The purity of the products was monitored by thin-layer chromatography on Silufol UV-254 plates with the same eluents.

The quantum yields for the formation of II-VI in the presence of acetophenone were determined for 0.08 mole/liter acetonitrile solutions of coumarin I using a Shimadzu CS-930 densitometer. UV light at 280 nm obtained using a Shimadzu NGF-16 monochromator was employed in determining the quantum yields ( $\varphi^{280}$ ). The intensity of the source (I<sub>0</sub> = 6.02 \cdot 10<sup>-10</sup> E/sec) was found by a standard procedure [17]. The quantum yields were calculated using the relationship to acetophenone and subtracting the absorption of coumarin I at 280 nm (Table 2). The elemental analysis data for C, H, and N were in accord with the calculated values.

<u>Compounds II-VI.</u> A mixture of 5 mmoles coumarin I, 10-50 mmoles corresponding acetylene or olefin, and 7.5 mmoles acetophenone in 100 ml acetonitrile was irradiated at 15-20° for 10-20 h with vigorous stirring by air. The reaction mixture was evaporated in vacuum and the residue was subjected to chromatography. The desired products were recrystallized from hexane-acetone.

 $\frac{2-0 \times o-4,8-\text{dimethyl-6},7-\text{dimethoxycarbonyl-9-ethyl-8},9-\text{dihydro-2H-pyrano[3,2-g]quinoline}{(II)} and 2-0 \times o-4,8-\text{dimethyl-9},10-\text{dimethoxycarbonyl-7-ethyl-7},8-\text{dihydro-2H-pyrano[3,2-h]quinoline}{(III)}. A mixture of 1.16 g (5 mmoles) coumarin I and 7.1 g (50 mmoles) dimethyl ester of acetylenedicarboxylic acid after irradiation for 10 h gave 0.20 g II from the fraction with R<sub>f</sub> 0.09 (3:1 hexane-acetone) and 0.22 g III from the fraction with R<sub>f</sub> 0.08 (3:1 hexane-acetone).$ 

<u>N-Phenylimide of 2-oxo-4,8-dimethyl-7-ethyl-7,8,9,10-tetrahydro-2H-pyrano[3,2-h]quin-oline-9,c-10-dicarboxylic acid (IV)</u> was obtained from a mixture of 1.16 g (5 mmoles) coumarin I and 1.73 g (10 mmoles) N-phenylmaleimide after irradiation for 10 h from the fraction with  $R_f$  0.10 (3:1 hexane-acetone). The product yield was 0.47 g.

 $\frac{2-0xo-4, r-8-dimethyl-9, c-10-diethoxycarbonyl-7-ethyl-7, 8, 9, 10-tetrahydro-2H-pyrano[3, 2-h]quinoline (V) and 2-0xo-4, r-8-dimethyl-9, t-10-diethoxycarbonyl-7-ethyl-7, 8, 9, 10-tetrahydro-2H-pyrano[3, 2-h]quinoline (VI) was obtained from a mixture of 1.16 g (5 mmoles) coumarin I and 8.60 g (50 mmoles) diethyl maleate after irradiation for 20 h from the fraction with Rf 0.30 (3:1 hexane-ethyl acetate). The yield of V was 0.39 g. The fraction with Rf 0.28 (3:1 hexane-ethyl acetate) gave 0.29 g VI.$ 

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REACTION OF TETRANITRODIBENZO-18-CROWN-6 WITH SODIUM ALKOXIDES

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UDC 547.898'546.04

It is shown that the reaction of tetranitrodibenzo-18-crown-6 with sodium alkoxides in aprotic solvents at room temperature occurs with initial cleavage of the macroheterocycle and formation of an intermediate - substituted o-dinitrobenzene - whereas the reaction in protonated solvents occurs with substitution of the nitro groups. From among other derivatives of dibenzo-18crown-6 containing azole rings linked to the benzene ring, only the furoxancontaining crown ether is cleaved under similar conditions.

We have previously shown that the reaction of tetranitrodibenzo-18-crown-6 (I) with sodium methoxide or ethoxide in the ratio 1:6 at room temperature occurs with formation of trialkoxynitrobenzene (II) [1]. Since the initial compound I has several reaction centers capable of undergoing nucleophilic substitution, the question has remained open as to which occurs first - substitution of the nitro groups or cleavage of the macroheterocycle.

From the mixture of products formed by reaction of crown ether I with sodium methoxide in the ratio 1:2, in addition to trimethoxynitrobenzene (II) it was possible to isolate odinitrobenzene III in 18% yield together with trace amounts of isomers IV. Compound III is readily converted under the reaction conditions to trialkoxynitrobenzene II whereas crown ether IV does not decompose under these conditions. The results obtained show conclusively that cleavage of the macrocycle occurs at the first stage of this reaction (see scheme on following page).

Chromatographic monitoring of the reaction mixture showed that even after 5 min decomposition products II and III are present in it. When the reaction mixture was treated with acid to pH 7, it was also possible to detect diethylene glycol among the reaction products. When the rate of agitation is 120 rpm, the reaction is complete after 20-25 min.

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