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PHOTOCHEMICAL REACTIONS OF 7-AMINOCOUMARINS

1. [2 + 2]-CYCLOADDUCTS WITH VINYL BUTYL ETHER AND ACRYLONITRILE

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Adducts of [2 + 2]-cycloaddition to the 3–4 bond were isolated in the photochemical cycloaddition of vinyl butyl ether and acrylonitrile to 4-methyl-7-diethylaminocoumarin. The stereochemical structures of the compounds obtained as isomers of the "head-to-tail" type with an endo or exo orientation of the substituents were established by means of PMR spectroscopy. As a result of an evaluation of the effect of sensitizers and one-electron oxidizing and reducing agents it was found that the investigated reactions proceed through the singlet excited states of 7-aminocoumarins. It is assumed that the regiospecificity of the [2 + 2]-cycloaddition is determined by the $C_{(3)}$ reaction center of the coumarin fragment.

The interest in 7-aminocoumarins is due primarily to their intensive luminescence [1, 2]. However, despite the large number of studies involving the photophysical investigation of aminocoumarin dyes, insignificant study has been devoted to their photochemical reactions. The aim of the present research consisted is an investigation of the photochemical reaction of 4-methyl-7-diethylaminocoumarin (I) and 4-methyl-7-aminocoumarin (II) with olefins.

It is known that 7-aminocoumarins, in contrast to other coumarins, are not inclined to form [2 + 2]-photodimers in solution [3]. Successive N-dealkylation occurs in the irradiation of 7-dialkylaminocoumarins [4], whereas photooxidation of the alkyl substituents attached to the nitrogen atom occurs under the influence of oxygen [5]. The unique character of the structures of 7-aminocoumarins consists in their capacity for pronounced charge separation upon photoexcitation [6]. The available quantum-chemical calculations of the structures of various coumarins [7, p. 18; 8] confirm high localization of the charge on the 3–4 bond, as well as of the spin density on the $C_{(3)}$ atom in the singlet and triplet excited states. This fact makes it possible to assume that the photoexcitation of coumarins I and II in the presence of olefins should lead to regioselective reactions with the participation of the 3–4 bond. The experiments carried out confirmed this assumption.

We studied the possibility of the synthesis of cycloadducts of 7-aminocoumarins I and II with olefins that contain substituents with different electronic properties – vinyl butyl ether and acrylonitrile. Cyclobutane derivatives III and IV were obtained as a result of the reaction of coumarin I with vinyl butyl ether. Only V and VI were obtained as the principal products in the reactions of coumarins I and II with acrylonitrile.*

*According to the results of TLC and mass spectroscopy, other isomeric adducts are present in small amounts (<5%) in the reaction mixtures in this case.

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TABLE 1. Characteristics of III-VI

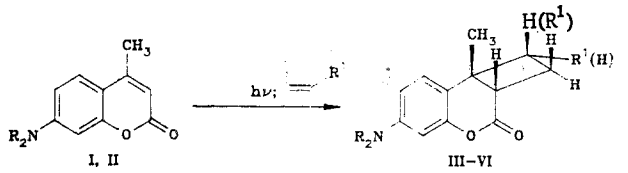
Compound	mp, °C	IR spectrum, ν, cm^{-1}	λ_{max}, nm (log ε), in 2-propanol	Found, %			Empirical formula	Calc., %			Yield %
				C	H	N		C	H	N	
III	Oil	1740, 1603, 1550	216 (4,33), 246 (4,03), 279 (4,02), 312 (3,54)	72,3	9,0	4,7	$C_{20}H_{29}NO_3$	72,5	8,8	4,2	28
IV	Oil	1745, 1610, 1545	215 (4,39), 244 (4,08), 280 (4,07), 312 (3,74)	72,6	8,8	4,2	$C_{20}H_{29}NO_3$	72,5	8,8	4,2	22
V*	189,5	2238, 1750, 1535	215 (4,41), 258 (4,22), 286 (3,91), 296 (3,83), 320 (3,56)	54,1	4,6	13,7	$C_{17}H_{20}N_2O_2\times$ $\times C_6H_3N_3O_7$	53,8	4,5	13,6	49
VI	186,0	2235, 1745	224 (4,18), 261 (3,77), 292 (3,50)	68,3	5,3	12,2	$C_{13}H_{12}N_2O_2$	68,4	5,3	12,3	58

*The melting point and the results of microanalysis are presented for the picrate.

TABLE 2. Quantum Yields of the Reactions to Form III-VI

Compound	Additive	Concn., M		Quantum yield*	Compound	Additive	Concn., M		Quantum yield*
		olefin	additive				olefin	additive	
III	—	10,0	—	0,025	V	—	5,0	—	0,035
	$C_6H_5COCH_3$	10,0	0,04	0,013		—	10,0	—	0,076
	$CHBr_3$	10,0	0,08	0,002		—	15,0	—	0,114
IV	—	10,0	—	0,023		$C_6H_5COCH_3$	10,0	0,04	0,020
	$C_6H_5COCH_3$	10,0	0,04	0,011		$CHBr_3$	10,0	0,08	0,001
	$CHBr_3$	10,0	0,08	0,002		1,4-$(CN)_2C_6H_4$	10,0	0,08	0,025
					VI	—	10,0	—	0,084

*Measured for 0.08 M solutions of coumarins I and II in acetonitrile at 20°C. Ultraviolet light with a wavelength of 370 nm was used. Source intensity $I_0 = 5.62\cdot10^{-10}$ ergs/sec.



I, III—V R=C_2H_5; II, VI R=H; III R^1=exo-OC_4H_9; IV R^1=endo-OC_4H_9; V, VI R^1=endo-CN

The syntheses were carried out in solutions in acetonitrile in a nitrogen atmosphere by irradiation for 8-10 h of 0.05 mole/liter solutions of the aminocoumarin in excess olefin with the unfiltered light of a medium-pressure mercury lamp in a Pyrex reaction (λ > 300 nm). The yields of III-VI reached 20-60% (Table 1); the efficiency of cycloaddition decreased on passing from acrylonitrile to vinyl butyl ether. The quantum yields of the reactions to form adducts III-VI confirm this regularity (Table 2). The rate of the reactions also increased with an increase in the olefin concentration (see, for example, the data for adduct V in Table 2), the optimum values of which were selected over the range 0.5-1.0 M. In all cases photodimers of coumarins I and II were not detected in the reaction mixtures. In the case of coumarin I 7-ethylaminocoumarin VIII and 7-aminocoumarin II were detected as side products (overall yield <5%).

Since 7-aminocoumarins have a high tendency to undergo one-electron oxidation [9], in addition to ionic and biradical intermediates, the possibility of the formation of ion radicals should have been taken into account in the description of the [2 + 2]-cycloaddition (see, for example, [10]). Thus the regioselectivity and stereoselectivity of the investigated reactions have not been previously apparent. For this reason we directed special attention to proving the structures of III-VI. This task proved to be rather difficult, since many of the adducts decomposed on silica gel during chromatographic isolation. The compositions of III-VI were confirmed by the results of microanalysis (Table 1); the picrate was identified for V. The IR spectra of adducts III-VI confirm the presence of a saturated lactone ring with carbonyl absorption at 1740-1750 cm^{-1}, which resembles the absorption of 3,4-dihydrocoumarins [11]. The UV spectra of III-VI contain absorption at 280-300 and 312-320 nm, which is in the shorter-wavelength region as compared with the spectra of the starting coumarins. As expected, III-VI, in contrast to coumarins I and II, do not have luminescence.

Peaks of molecular ions, the intensities of which are low and, as a rule, do not exceed 10%, are observed in the mass spectra of III-VI. Adduct V, for which the intensity of the molecular-ion peak reaches 35%, constitutes an exception. The peaks corresponding to the starting coumarins are particularly intense (relative intensities 75-100%); this confirms the tendency of the cyclobutane derivatives to undergo retrodecomposition. Consequently, the principles of the fragmentation of the adducts obtained resemble in many respects the mass-spectral fragmentation of 7-aminocoumarins [12]. A comparison of the intensities of the high-molecular-weight peaks in the mass spectra of isomers III and IV may be most useful. Low-intensity peaks corresponding to the following processes are observed for both compounds: $[M - CH_3]^+$, $[M - C_4H_9]^+$, $[M - OC_4H_9]^+$, and $[M - C_4H_9 - CH_2O]^+$ (see the Experimental section). The reduction of the intensities of these processes to a single scale reveals an increased tendency (by a factor of ~1.5) for stepwise fragmentation of precisely exo isomer III; this is evidently explained by the steric effect of the β-cis-methyl group.

The PMR spectra give the greatest amount of information regarding III-VI; however, the interpretation of these spectra presents certain difficulties. According to the data in [13, 14], the ^2J and ^3J spin—spin coupling constants (SSCC) of substituted cyclobutanes are not characteristic for these compounds and by themselves cannot serve as a criterion in the assignment of the structures. The structures of adducts III-VI were established on the basis of an analysis of the PMR spectra recorded at 250 MHz (Table 3), the use of the double-resonance method, and by comparison of our data and the literature data on the PMR spectra of [2 + 2]-cycloadducts based on coumarin [15], 2-pyridone [13], and 4,6,6-trimethyl-5,6-dihydro-2-pyridone [16]. In conformity with the data in [13, 15], cis fusion of the rings was adopted for all adducts III-VI. Let us examine the spectra of III-VI in greater detail.

As we have already noted, two isomeric adducts III and IV are formed in the reaction of coumarin I with vinyl butyl ether. The weak-field parts of the PMR spectra of these

TABLE 3. Chemical Shifts, Multiplicities of the Signals, and

Compound	1-H	2-exo-H	2-endo-H	2a-H	5-H, d	7-H, dd
III	3,76 t (7,0)	2,41 ddd (10,8; 10,0; 7,0)	2,49 m	2,84 dd (10,0; 5,8)	6,15 (2,7)	6,32 (8,8; 2,7)
IV	3,76 dd (8,0; 9,0)	2,51 dd (9,0; 8,0)	2,00 q (9,0)	2,60 t (9,0)	6,27 (2,6)	6,47 (9,0; 2,6)
V	3,20 dd (10,0; 8,5)	2,59 dt (11,0; 8,5)	2,31 dt (11,0; 10,0)	3,25 dd (10,0; 8,5)	6,10 (2,7)	6,35 (9,0; 2,7)
VI	3,22 dd (10,0; 8,5)	2,72 dt (11,5; 8,5)	2,46 dt (11,5; 10,0)	3,20 dd (10,0; 8,5)	6,37 (2,8)	6,59 (9,1; 2,8)

compounds are similar. For example, the signals of the aromatic 8-H, 7-H, and 5-H protons at 7.0, 6.5, and 6.3 ppm, respectively are readily distinguishable in the spectrum of adduct III. The weakest-field 8-H signal has the form of a doublet (J_{7_8} = 8.8 Hz). The 5-H signal is located at strongest field and is also split into a doublet (J_{5_7} = 2.7 Hz). Correspondingly, the 7-H signal has the form of a doublet of doublets. Triplet (SSCC 7.0 Hz) and doublet-doublet (SSCC 8.0 and 9.0 Hz) signals, which we assigned to the methylidyne 1-H proton in the α position relative to the butoxy group, are observed in the spectra of both isomers at 3.76 ppm. Thus both isomers have a structure of the "head-to-tail" type. This assertion is in agreement with the principles of the addition of ketene diethylketal to coumarin [17] and vinyl methyl ether to 2-pyridone [13]. In the case of the formation of isomers of the "head-to-head" type the signal of the 2a-H proton should have the form of a doublet (which is not observed), while the 2-H signal should have a more complex form and include SSCC with the remaining three protons. However, the indicated constants differ, as evidenced by the forms of the other signals. Thus for III the signal at 2.84 ppm, which is a doublet of doublets (SSCC 10.0 and 5.8 Hz), is readily distinguishable. Signals of yet another two protons in the form of a multiplet and a distorted doublet of triplets (SSCC 10.8 and 7.0 Hz) are located at stronger field at 2.49 and 2.41 ppm. In analogy with the data in [13, 16], the signal at 2.84 ppm was assigned to the 2a-H proton, the signals at 2.49 and 2.41 ppm were assigned to 2-endo-H and 2-exo-H protons, respectively, and III itself was identified as the 1-exo isomer. The correctness of the assignment is confirmed by the large values of the geminal $^2J_{2\text{-endo},2\text{-exo}}$ constant (10.8 Hz), as well as the $^3J_{2a,2\text{-exo}}$ constant (10.0 Hz), as compared with the $^3J_{2a,2\text{-endo}}$ constant (5.8 Hz); this is also observed for closely related compounds [13, 16]. The signals of the protons of the OCH_2 and NCH_2 fragments in adduct III are found at 3.2-3.4 ppm (Table 3).

The PMR spectrum of the isomeric endo adduct IV contains signals of two protons at 2.51 and 2.60 ppm in the form of superimposed doublet of doublets and a triplet with SSCC 8.0 and 9.0 Hz. The indicated signals were assigned to the 2-exo-H and 2a-H protons. The 2-exo-H signal correlates with the signal of the 1-H proton, while the 2a-H proton is linked by spin-spin coupling with the 2-endo-H proton, the signal of which, in contrast to isomer III, is shifted substantially to strong field and shows up at 2.00 ppm in the form of a broad quartet with $J_{2a,2\text{-endo}} = J_{2,2} = J_{1,2\text{-endo}} = 9.0$ Hz. The observed strong-field shift of the signal of the 2-endo-H proton can be explained by the shielding effect of the β-cis-butoxy group; this corresponds to the data in [13]. A small shift (Δ ~ 0.05-0.15 ppm) of the signals of the γ-methylene and methyl protons of the butoxy group to strong field as compared with exo isomer III is also observed in the PMR spectrum of endo isomer IV; this is probably explained by entry of these fragments into the cone of anisotropy of the aromatic ring. On the other hand, the protons of the 8b-CH_3 group is more strongly shielded in isomer III under the influence of the butoxy group, for which the signal is shifted to strong field (Δ = 0.11 ppm, Table 3).

The PMR spectra of adducts V and VI are also similar and, with respect to the signals of the aromatic protons, coincide with the spectra of the butoxy derivatives (Table 3). The chemical shifts of the protons of the cyclobutane fragment in adducts V and VI are located at 2.5, 2.7, and 3.2 ppm in the form of three groups of signals. A comparison of the spectra of these compounds with the spectra of the adducts of acrylonitrile and 2-pyridone leads to the conclusion that both cyclobutane derivatives are isomers of the "head-to-tail" type with an endo orientation of the nitrile group. Let us examine, for example

Spin-Spin Coupling Constants (J, Hz) in the PMR Spectra of III-VI

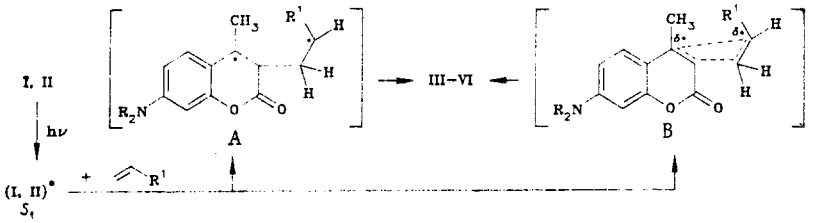
8-H, d	8b-CH_3, s	Other protons
6,89 (8,8)	1,37	0,93 (3H, t, J=7,0, $O(CH_2)_3\mathbf{CH_3}$), 1,14 (6H, t, J=7,0, 2 $NCH_2\mathbf{CH_3}$); 1,40 (2H, m, $\mathbf{CH_2}CH_3$), 1,49 (2H, m, $OCH_2\mathbf{CH_2}$) 3,30 (4H, q, J=7,0, 2 NCH_2); 3,31 (2H, q, J=7,0, OCH_2)
7,04 (9,0)	1,48	0,88 (3H, t, J=7,0, $O(CH_2)_3\mathbf{CH_3}$); 1,14 (6H, t, J=7,0, 2 $NCH_2\mathbf{CH_3}$); 1,25 (2H, m, $\mathbf{CH_2}CH_3$); 1,46 (2H, m, $OCH_2\mathbf{CH_2}$); 3,31 (4H, q, J=7,0, 2 NCH_2); 3,45 (2H, q, J=7,0, OCH_2)
7,02 (9,0)	1,45	1,07 (6H, t, J=7,0, 2 $NCH_2\mathbf{CH_3}$); 3,22 (4H, q, J=7,0, 2 NCH_2)
7,23 (9,1)	1,55	3,80 (2H, s, NH_2)

the PMR spectrum of VI. The signals of the 2a-H and 1-H protons are located at 3.2 ppm and have the form of superimposed doublets of doublets with constants $J_{2a,2\text{-exo}} = J_{1,2\text{-exo}} =$ 8.5 Hz and $J_{2a,2\text{-endo}} = J_{1,2\text{-endo}} = 10.0$ Hz. Let us note that in the case of the "head-to-head" isomer the 2a-H signal, to a first approximation, would be a doublet [13]. The shielded (by the nitrile group [18]) signal of the 2-endo-H proton, which forms a doublet of triplets with constants $J_{2a,2\text{-endo}} = J_{1,2\text{-endo}} = 10.0$ Hz and $J_{2,2} = 11.5$ Hz, is located at stronger field at 2.46 ppm. This assignment of the signals can be made on the basis of not only the chemical shifts but also the large value of the geminal $^2J_{2,2}$ constant, as well as the $J_{2a,2\text{-endo}}$ and $J_{1,2\text{-exo}}$ constants, as compared with the $J_{2a,2\text{-exo}}$ and $J_{1,2\text{-exo}}$ constants [13, 15]. The endo orientation of the nitrile group in VI is confirmed by the absence of any appreciable splitting of the 2a-H and 1-H signals, which could occur in the exo isomer as a result of long-range couplings [14], as well as by the relatively weak-field signal of the 8b-methyl protons at 1.55 ppm (compare III and VI), which arenot shielded by the nitrile group [18]. The same principles are observed in the spectrum of adduct V on the whole; however, the chemical shifts of the 2 -H and 1-H protons (3.25 and 3.20 ppm respectively) are close to the methylene protons of the diethylamino group (3.22 ppm), and the interpretation of these signals is therefore difficult.

Thus [2 + 2]-cycloadducts of the "head-to-tail" type are formed as a result of photoreactions of 7-aminocoumarins I and II with unsymmetrical olefins. Since the starting 7-aminocoumarins have high fluorescence quantum yields in acetonitrile, the participation of the triplet excited state of coumarin I or II in [2 + 2]-cycloaddition reactions seems unlikely. The experiments on the sensitization and quenching of photoreactions in the case of coumarin I confirm this assumption. Thus even small amounts (0.5 of an equivalent) of added acetophenone lead to quenching of the reactions under consideration (Table 2). Two new adducts, which, according to the PMR data, are isomers of the "head-to-head" type, develop in the case of vinyl butyl ether in the presence of excess (up to 40 equivalents amounts of acetophenone in the reaction mixture. Appreciable quenching of cycloaddition reactions is also observed in the presence of compounds that contain heavy atoms (bromoform, carbon tetrabromide, etc.). For example, when 1 equivalent of bromoform is added, the quantum yields of the reactions to form adducts III and IV decrease by more than an order of magnitude (Table 2).

Since 7-aminocoumarin molecules readily undergo one-electron oxidation [6, 19], the occurrence of ion-radical processes also was not excluded. To elucidate this possibility we studied the effect of the addition of 1,4-dicyanobenzene – a typical one-electron oxidizing agent. The data in Table 2 provide evidence for appreciable quenching of cycloaddition reactions under the influence of even equivalent amounts of 1,4-dicyanobenzene.

The observed principles make it possible to conclude that the singlet excited states of the I and II molecules participate in the reactions under consideration. The identical orientation of the terminal olefins that contain substituents with different electronic properties makes it possible to exclude a purely ionic description of the investigated reactions from consideration. It follows from the stereochemical structures of III-VI that the spin characteristics of the excited 7-aminocoumarin molecules play a decisive role in the primary orientation of the addends. The cycloaddition process can be formally conceived of as proceeding through biradical intermediate A or unsymmetrical "biradical-like" transition state B:



In each case the $C_{(3)}$ atom of the 7-aminocoumarin is the reaction center that controls the regiospecificity of [2 + 2]-cycloaddition. A probable explanation of the high stereoselectivity of the cycloaddition of acrylonitrile consists in secondary interactions that may arise between the electron-donor aminobenzene fragment and the electron-acceptor nitrile group in intermediate A or transition state B. The possibility of this sort of coordination for [2 + 2]-photoreactions has already been noted in the literature [20]. Analogous interactions are not favorable for vinyl butyl ether, and the cycloaddition process is not stereoselective.

EXPERIMENTAL

The IR spectra of thin layers (for III and IV) and KBr pellets (for V and VI) were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in 2-propanol were obtained with a Hitachi EPS-3T spectrophotometer. The PMR spectra of solutions in CDC_{13} were obtained with a Bruker WM spectrometer (250 MHz) with hexamethyldisiloxane as the internal standard. The mass spectra were recorded with a Varian MAT-311 A mass spectrometer with direct introduction of the samples into the ion source at an electron-ionization energy of 70 eV.

Photolysis was accomplished in 100-ml Pyrex reactors. The source of irradiation was a PRK-2 medium-pressure mercury lamp. The reaction mixtures were stirred with a stream of nitrogen. The compositions of the reaction mixtures and the purity of the synthesized substances were monitored by means of TLC on Silufol UV-254 plates by elution with hexane–acetone and development with UV light and iodine. The products were isolated by means of column chromatography with columns (35 by 2.5 cm) packed with Silpearl UV silica gel by elution with hexane–acetone.

The quantum yields of the reactions were determined for 0.08 M solutions of the starting coumarins in acetonitrile by means of a Shimadzu NGF-16 monochromator. Light with a wavelength of 370 nm was used for excitation. The intensity of the source was determined by means of a ferrioxalate actinometer [21] and was $I_0 = 5.62 \cdot 10^{-10}$ ergs/sec. The decrease in light absorption by the coumarin at 370 nm in the presence of the additives was taken into account on the basis of the absorption spectra in acetonitrile.

1-exo-Butoxy-8b-methyl-6-diethylamino-1,2,2a,8b-tetrahydro-3H-cyclobuta[c]chromen-3-one (III) and 1-endo-Butoxy-8b-methyl-6-diethylamino-1,2,2a,8b-tetrahydro-3H-cyclobuta[c]-chromen-3-one (IV). A mixture of 1.16 g (5 mmole) of coumarin I and 10.0 g (100 mmole) of vinyl butyl ether in 100 ml of acetonitrile was irradiated for 8 h, after which it was evaporated in vacuo, and the residue was chromatographed. Workup of the fraction with R_f 0.56 [hexane–acetone (3:1)] gave 0.47 g (28%) of III in the form of an oil. Mass spectrum, m/z (%): 331 (6.9), 316 (5.3), 274 (12.9), 258 (16.3), 244 (10.9), 231 (81.5). Workup of the fraction with R_f 0.50 [hexane–acetone (3:1)] gave 0.37 g (22%) of IV in the form of an oil. Mass spectrum, m/z (%): 331 (2.0), 316 (1.2), 274 (2.8), 258 (2.0), 244 (3.1), 231 (77.1).

1-endo-Cyano-8b-methyl-6-diethylamino-1,2,2a,8b-tetrahydro-3H-cyclobuta[c]chromen-3-one (V). A mixture of 1.16 g (5 mmole) of coumarin I and 2.65 g (50 mmole) of acrylonitrile in 100 ml of acetonitrile was irradiated for 10 h, after which it was evaporated in vacuo, and the residue was chromatographed with collection of the fraction with R_f 0.14 [hexane–acetone (3:1)], which yielded 0.70 g (49%) of V in the form of an oil. Mass spectrum, m/z (%): 284 (5.5), 269 (22.1), 231 (100.0).

For analytical purposes V was converted to the picrate, with mp 189.5°C, which precipitated when ether solutions of V and picric acid were mixed.

1-endo-Cyano-8b-methyl-6-amino-1,2,2a,8b-tetrahydro-3H-cyclobuta[c]-chromen-3-one (VI). This compound was obtained from 0.88 g (5 mmole) of coumarin II and 2.65 g (50 mmole) of

acrylonitrile by a procedure similar to that used to prepare V. Workup gave 0.66 g (58%) of a product with R_f 0.15 [hexane–acetone (2:1)]. Mass spectrum, m/z (%): 228 (4.2), 175 (100.0).

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PHOTOCHEMICAL REACTIONS OF 7-AMINOCOUMARINS.

2.* [2 + 2]-CYCLOADDUCTS WITH STYRENE

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The photocycloaddition of styrene to 4-methyl-7-aminocoumarin, 4-methyl-7-diethylaminocoumarin, 7-(N-morpholino)coumarin, 3-ethoxycarbonylmethyl-4-methyl-7-diethylaminocoumarin, and coumarin-102 (2,3,6,7-tetrahydro-9-methyl-1H,5H,11H-[1]-benzopyrano[6,7,8-ij]quinolizin-11-one) was investigated. Adducts of regio- and stereospecific [2 + 2]-cycloaddition to the 3–4 bond were isolated. It was established by means of x-ray diffraction analysis that the phenyl group in the cycloadducts occupies the 1-endo position. The participation of the singlet excited states of the 7-aminocoumarin molecules in [2 + 2]-cycloaddition was demonstrated.

*See [1] for Communication 1.

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