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PHOTOCHEMICAL REACTION OF 7-AMINOCOUMARINS.

9.* [2 + 2]-CYCLOADDUCTS WITH trans, trans-1,4-DIPHENYL-1,3-BUTADIENE

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The photoreactions of 7-diethylaminocoumarin, 4-methyl-7-diethylaminocoumarin, 4-trifluoromethyl-7diethylaminocoumarin, and 4-N-morpholino-7-diethylaminocoumarin with trans, trans-1,4-diphenyl-1,3butadiene, which lead to the formation of [2 + 2]-cycloaddition products, were studied. It was established that photocycloaddition proceeds with the formation of adducts that have a 1-endo-styryl substituent and a 2exo-phenyl group. The effect of the substituent in the 4-position of the 7-aminocoumarin molecule on the effectiveness of cycloaddition is discussed.

It is known that products of [2 + 2]-cycloaddition at the 3-4 bond that have a phenyl group in the 1-endo-position are formed as a result of the photochemical reaction of 7-aminocoumarins with styrene and trans-stilbene. It has been shown that reactions of this type proceed through the singlet excited state of 7-aminocoumarins and are distinguished by high regioselectivity and stereoselectivity [2, 3].

Since the endo orientation of the 1-phenyl group suggests increased steric requirements in the transition state of cycloaddition, it seemed of interest to ascertain, first of all, how lengthening of the chain of conjugation between the phenyl groups in the olefin affects the stereochemistry of cycloaddition and, second, what effect the substituent in the 4 position of the 7-aminocoumarin molecule has on the effectiveness of the process.

To solve these problems we selected 1,4-trans,trans-diphenyl-1,3-butadiene as the olefin component and, as the substrates, a number of 7-diethylaminocoumarins that have groups with different electronic properties in the 4 position: 7-diethylaminocoumarin (I), 4-methyl-7-diethylaminocoumarin (II), 4-trifluoromethyl-7-diethylaminocoumarin (III), and 4-N-morpholino-7-diethylaminocoumarin (IV).

In all cases only [2 + 2]-cycloadducts V-VIII are formed as a result of the reactions. The actual amounts of V-VIII in the reaction mixtures approach 90-100%; however, as a consequence of a tendency for retrograde decomposition, some of the adduct decomposes during chromatography, and the preparative yields of the cycloadducts range from 60 to 70% (Table 1).

^{*}See [1] for Communication 8.

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Com				5		IR spectru	spectrum (in KBr), V.cm ⁻¹	·), v.cm ⁻	UV spectrum (in 2-propanol), λ_{max} Yield, %
punod		mpritcal tormua mp.				C=0	о —	c=c	nm (log E)
		C ₃₉ H ₂₈ NO ₂ C ₃₀ H ₃₁ NO ₂ · C ₆ H ₃ N ₃ O ₇ C ₃₀ H ₃₆ NO ₂ C ₃₃ H ₃₆ N ₂ O ₃	N ₃ O ₇	134 64 85	0,42 0,43 0,31 0,31	1758 1758 1758 1755	1615, 15 1635, 15 1628, 15 1628, 15 1625, 15	1558, 1520 1570, 1530 1558, 1525 1560, 1525	214 (4,79), 260 (4.63), 283 (4,17), 293 (4,13), 312 (397) 67 0,070 215 (4,39), 245 (4,16), 283 (4,21), 308 (3,86), 355 (2,59) 65 0,097 215 (4,55), 259 (4,56), 290 (4,18), 295 (4,14), 305 (4,03) 61 0,014 256 (4,54), 285 (4,23), 296 (4,13) 295 (4,14), 305 (4,03) 70 0,124
*The	duantum y	/ields of t	he photor	chemical	l reaction:	s (م) invol	ving the fo	mation o	*The quantum yields of the photochemical reactions (φ) involving the formation of IX and XI under similar conditions are 0.001 and 0.045, respectively.
TABL	TABLE 2. PMR Spectra of V-VIII	Spectra o	IIIV-V j						
						ט	Chemical sh	shift, δ, ppm	ppm (SSCC, J, Hz)*
pound	1H. dd (/=10,0; /=9,5)	2-H. dd 2 <i>a</i> -H. d (<i>J</i> =10,0; (<i>J</i> =10,0) <i>J</i> =10,0)	2a-H, d (<i>J</i> =10,0)	5-H, d (<i>J</i> =2,7)	7-H, dd (<i>J</i> =9.0; <i>J</i> =2,7)	b.H-8 (<i>J</i> =9,0)	NCH ₂ , q (<i>J</i> =7,0)	PCH ₂ CH ₂ CH,	Other protons
>	3,89*2	3,56	3,64*8	6,40	6,48	6,92	3,40	1,22	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$
N	3,10	3,55	3,21	6,33	6,42	6,93	3,33	1,12	m, 2C ₆ H ₃) 1.42 (3H, s, CH ₃); 6.00 (1H, dd, <i>J</i> =16,0, <i>J</i> =9.5, H—C=CHC ₆ H ₅); 6,44
ΠΛ	3,64	3,52	3,94	6,40	6,05	7,15	2,74*4	0,73	$(101, q, J = 10, 0, 0 - C(C_{615}) = C(T); I, 0 I, 0 (1011, m, 2C_{615})$ $5,92$ (1H, dd, $J = 16,0, J = 9,0, H - C = CH - C_{615}$); $6,25$ (1H, d, $J = 16,0,$ $U = C(C, U) = C(U) = 7,00, 0, 0 - C = CH - C_{615}$); $C = 25$
ШЛ	3,57	3,32	3,43	6,42	6,53	7,18	3,39	12,2	$\begin{array}{c} 1 & 1 \\ 2,52 & (14), 7 \\ 1 & -(16), 7 \\ -(16), 7 \\ -(16), 7 \\ -(16), 7 \\ -(16), 7 \\ -(16), 7 \\ -(16), 7 \\ -(16), 7 \\ -(16), 7 \\ -(16), 7 \\ -(16), 7 \\ -(16), 7 \\ -(10), 7$
- 4	- 2		-	(- 4	-		-	

*The PMR spectra of VII were recorded in C₆D₆, while the spectra of the remaining compounds were recorded in CDCl₃.

****J** = 10.0 Hz, J = 9.0 Hz, J = 9.0 Hz.

*******Doublet of doublets (J = 10.0 Hz, J = 8.0 Hz). ********Doublet of quartets (J = 7.0 Hz, J = 4.0 Hz).

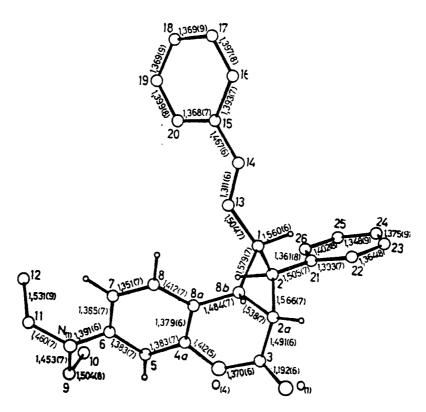


Fig. 1. Overall form of the V molecule and bond lengths in it.

TABLE 3. Bond Angles in V

Angle	w*	Angle	ധ്	Angle	ED.
$\begin{array}{c} C_{(3)}O_{(4)}C_{(4a)}\\ C_{(6)}N_{(1)}C_{(11)}\\ C_{(9)}N_{(1)}C_{(11)}\\ C_{(9)}N_{(1)}C_{(11)}\\ C_{(2)}C_{(1)}C_{(3b)}\\ C_{(2)}C_{(1)}C_{(3)}\\ C_{(2)}C_{(1)}C_{(3)}\\ C_{(1)}C_{(2)}C_{(21)}\\ C_{(1)}C_{(2)}C_{(22)}\\ C_{(2)}C_{(22)}C_{(22)}\\ C_{(2)}C_{(22)}C_{(3)}\\ C_{(2)}C_{(22)}C_{(3)}\\ C_{(3)}C_{(22)}C_{(3b)}\\ C_{(3)}C_{(22)}C_{(3b)}\\ O_{(1)}C_{(3)}O_{(4)}\\ O_{(1)}C_{(3)}C_{(22)}\\ O_{(4)}C_{(23)}C_{(22)}\\ O_{(4)}C_{(23)}C_{(22)}\\ O_{(4)}C_{(33)}C_{(22)}\\ O_{(4)}C_{(33)}C_{(23)}\\ O_{(4)}C_{(33)}\\ O_{(33)}C_{(23)}\\ O_{(33)}C_{(23)}\\ O_{(4)}C_{(33)}\\ O_{(33)}C_{(23)}\\ O_{(33)}C_{(23)}\\ O_{(33)}C_{(23)}\\ O_{(4)}C_{(33)}\\ O_{(33)}\\ O_{(33)}\\$	$\begin{array}{c} 121.6(3)\\ 121.5(4)\\ 121.8(4)\\ 116.1(4)\\ 88,0(3)\\ 119,1(4)\\ 121.8(4)\\ 86,2(3)\\ 119,8(4)\\ 121,0(4)\\ 116,7(4)\\ 89,2(3)\\ 120,2(4)\\ 116,7(4)\\ 126,2(4)\\ 116,5(4)\\ 112,7(4)\\ \end{array}$	$\begin{array}{c} O_{(4)}C_{(4a)}C_{(8a)}\\ C_{(5)}C_{(4a)}C_{(8a)}\\ C_{(4a)}C_{(5)}C_{(5)}\\ N_{(1)}C_{(6)}C_{(5)}\\ N_{(1)}C_{(6)}C_{(7)}\\ C_{(5)}C_{(6)}C_{(7)}\\ C_{(5)}C_{(6)}C_{(7)}\\ C_{(6)}C_{(7)}C_{(8)}\\ C_{(7)}C_{(8)}C_{(8a)}\\ C_{(4a)}C_{(8a)}C_{(8a)}\\ C_{(4a)}C_{(8a)}C_{(8a)}\\ C_{(4a)}C_{(8a)}C_{(2a)}\\ C_{(1)}C_{(8b)}C_{(2a)}\\ C_{(1)}C_{(8b)}C_{(2a)}\\ C_{(1)}C_{(8b)}C_{(8a)}\\ C_{(2a)}C_{(6b)}C_{(8a)}\\ N_{(1)}C_{(2)}C_{(10)}\\ N_{(1)}C_{(11)}C_{(12)}\\ C_{(1)}C_{(13)}C_{(14)}\\ \end{array}$	122,4(4)124,8(4)119,5(4)120,1(4)122,1(4)117,8(5)120,8(5)124,1(5)112,9(4)123,0(4)124,1(4)86,5(3)115,7(4)109,9(4)115,2(5)113,6(5)121,5(4)	$\begin{array}{c} C_{(13)}C_{(14)}C_{(15)}\\ C_{(14)}C_{(15)}C_{(16)}\\ C_{(14)}C_{(15)}C_{(20)}\\ C_{(16)}C_{(15)}C_{(20)}\\ C_{(15)}C_{(16)}C_{(17)}\\ C_{(16)}C_{(17)}C_{(18)}\\ C_{(17)}C_{(18)}C_{(19)}\\ C_{(15)}C_{(20)}C_{(19)}\\ C_{(15)}C_{(20)}C_{(19)}\\ C_{(21)}C_{(22)}C_{(22)}\\ C_{(22)}C_{(21)}C_{(25)}\\ C_{(22)}C_{(21)}C_{(25)}\\ C_{(22)}C_{(22)}C_{(25)}\\ C_{(22)}C_{(25)}C_{(25)}\\ C_{(21)}C_{(25)}C_{(25)}\\ C_{(21)}C_{(25)}C_{(25)}\\ C_{(21)}C_{(25)}C_{(25)}\\ C_{(21)}C_{(25)}C_{(25)}\\ C_{(21)}C_{(25)}C_{(25)}\\ C_{(21)}C_{(25)}C_{(25)}\\ \end{array}$	$\begin{array}{c} 127,8(4)\\ 118,5(4)\\ 124,0(4)\\ 117,5(4)\\ 120,2(5)\\ 121,0(5)\\ 119,5(6)\\ 122,5(5)\\ 122,5(5)\\ 122,3(4)\\ 119,6(4)\\ 118,0(5)\\ 121,3(5)\\ 121,3(5)\\ 120,2(6)\\ 120,2(6)\\ 120,6(5)\\ \end{array}$
Et ₂ N I-I	R 0 0 +	Ph Ph	EtzN		=Сң РЪ

I, V, R=H; II, VI R=CH₃; III, VII R=CF₃; IV, VIII R=N(CH₂CH₂)₂O

The aromatic 5-H, 6-H, and 8-H protons of the coumarin fragment, the signals of which have the characteristic multiplicity and spin-spin coupling constants (SSCC) [4], are readily identified in the PMR spectra of V-VIII (Table 2) recorded in deuterochloroform. The common structural peculiarities of adducts V-VIII also confirm the similarity in the

chemical shifts (CS) of the olefin protons of the styryl substituents. The small range in the changes in the CS of the 1'-H and 2'-H protons constitutes evidence for the remoteness of the styryl group from the variable substituent in the 8b position. The high ${}^{3}J_{1'2'}$ SSCC of 16 Hz indicates retention of the trans orientation of the 1'-H and 2'-H protons. In the spectrum of adduct VII one can observe a ${}^{5}J_{F,1'H}$ SSCC of ~2 Hz, which may serve as a confirmation of the endo orientation of the styryl residue.

In analogy with the data in [2, 3, 5] for all of cycloadducts V-VIII we assume cis fusion of the four-membered and lactone rings. The most difficult and fundamentally important task for the establishment of the stereochemistry of V-VII is the assignment of the signals of the cyclobutane protons, the multiplicity of which provides a basis for asserting that the styryl group is located in the 1 position. This conclusion is in agreement with data on the regiospecificity of the cycloaddition of styrene [2] and other terminal olefins [6] to 7-aminocoumarins.

In the assignment of the signals of the 1-H and 2-H protons we used the vicinal ${}^{3}J_{1,1'}$ SSCC as the reference. If it is assumed that the styryl group occupies the 1-endo position, a 2-exo orientation for the phenyl group is most likely in the case of a concerted reaction. This is confirmed by several pieces of evidence. First, the CS of the 2a-H and 1-H protons, which approach closely in space the 8b substituent, experience the most pronounced changes ($\Delta = -0.7$ ppm) in the V-VIII series, while the signals of the remote 2-endo-H protons change more slightly ($\Delta = 0.2$ ppm). In addition, in the spectra of V and VII the signals of the 2-H protons have a broadened structure ($\Delta h_{1/2} = -2$ Hz) as a consequence of the manifestation of long-range ${}^{4}J_{8b,2}$ and ${}^{5}J_{F,2-H}$ SSCC, which attests to their anti orientation. Similar coupling of the 1-H and 2a-H protons was not observed. Evidence in favor of this assumption is also provided by the close CS of the 2a-H protons in adducts V, VI, and VIII and the 2a-H protons in adducts of the same coumarins with trans-stilbene, where the phenyl group occupies a 2-exo position [3]. Rigorous confirmation of the correctness of the assignment of the signals of the 1-H, 2-H, and 2a-H protons for adduct VI was obtained as a result of the use of double resonance: irradiation of the signal at 3.10 ppm (1-H) led to simplification of the structure of the signals at 3.55 ppm (2-H) and 6.00 ppm (the α proton of the styryl substituent) to doublets.

Thus, for adducts V-VIII we propose a 1-endo orientation for the styryl substituent and a 2-exo orientation for the phenyl group. For definitive confirmation of the orientation of the substituents in the four-membered ring we carried out an x-ray diffraction study of cycloadduct V.

As in previously studied products of [2 + 2]-cycloaddition of styrene to coumarin II (IX) [2] and of stilbene to coumarin I (x) [3], in the V molecule the substituent attached to the C₍₁₎ atom is in an endo orientation, while the substituent attached to the C₍₂₎ atom is in an exo orientation (see Fig. 1 and Table 3). The geometry of the diethylaminocoumarin fragment of the V molecule coincides, within the error limits, with that found in the IX and X molecules, while the differences in the bond angles at the C₍₁₎ atom and in the puckered character of the four-membered ring are due to replacement of the phenyl substituent. The styryl group in adduct V is planar, evidently as a consequence of conjugation between the π systems of the C₍₁₃₎–C₍₁₄₎ double bond and the C₍₁₅₎–C₍₂₀₎ double bond of the phenyl ring. One should note the different orientations of the exo C₆H₅ groups attached to the C₍₂₎ atom of V and X: in the V molecule the C₍₂₁₎–C₍₂₆₎ plane actually coincides with the bisector plane of angle C₍₁₎C₍₂₎C₍₂₄₎ and torsion angle C₍₈₎C₍₂₎C₍₂₁₎C₍₂₂₎ is equal to 3.8(7)°, while the corresponding torsion angle in the X molecule is –72.0°.

Thus, in the series of investigated reactions with phenyl-substituted olefins (styrene, trans-stilbene, and trans, trans-1,4diphenyl-1,3-butadiene), we observed regiospecific and stereospecific formation of adducts that have the substituent attached to the $C_{(1)}$ atom in an endo orientation. It has been previously assumed [2, 6] that the regiospecificity of cycloaddition is due to the development of biradicals or biradical-like transition states, whereas the formation of 1-endo isomers is associated with secondary reactions of the substituents of the addends.

The mechanism of the investigated reactions is similar to that found for the [2 + 2]-cycloaddition of styrene and stilbene [2, 3].

It seemed of interest to evaluate the dependence of the rate of cycloaddition on the nature of the substituent in the 4 position of the 7-aminocoumarin molecule. With this end in mind, we measured the quantum yields of the reactions involving the formation of adducts V-VIII (Table 1). We found that the effectiveness of cycloaddition increases with an increase in the electron-donor properties of the substituent in the 4 position of the starting coumarin. We also established that, all other things being equal, the rate of formation of the adducts increases on passing from styrene to stilbene and to diphenylbutadiene, which is confirmed, for example, by the φ values measured for adduct IX and the adduct of the addition of coumarin II to stilbene (XI) [3] (Table 1). Considering the principles that we found, one might assume that the rate of cycloaddition of phenyl-substituted olefins depends, all other things being equal, on two factors: first, on the effectiveness of

TABLE 4. Coordinates of the Nonhydrogen Atoms (× 10⁴) in V

Atom	x	y	z	Atom	x	ÿ	z
$\begin{array}{c} O_{(1)} \\ O_{(4)} \\ N_{(1)} \\ C_{(2)} \\ C_{(2a)} \\ C_{(3)} \\ C_{(4a)} \\ C_{(6)} \\ C_{(6)} \\ C_{(8)} \\ C_{(8a)} \end{array}$	11039(3) 9919(3) 7764(4) 8483(4) 8562(4) 9915(4) 10369(4) 9246(4) 8828(4) 8190(4) 8019(5) 8437(5) 9061(4)	2216 (2) 3204 (2) 5471 (2) 2140 (3) 1871 (3) 2520 (3) 3648 (3) 4304 (2) 4809 (3) 4639 (3) 3990 (3) 3442 (3)	10812(3) 10220(2) 9278(4) 7379(4) 8591(4) 8892(4) 10036(4) 9335(4) 9698(4) 8925(4) 7808(4) 7489(4) 8235(4)	C(8b) C(9) C(10) C(11) C(12) C(13) C(14) C(15) C(15) C(15) C(15) C(17) C(18) C(19)	9524 (4) 7763 (5) 6779 (5) 7123 (5) 5722 (6) 7229 (4) 6808 (4) 5591 (4) 5591 (4) 5303 (5) 3267 (5) 3546 (5)	2732 (3) 5592 (3) 5171 (3) 6029 (3) 5876 (4) 2360 (3) 2079 (3) 2213 (2) 1825 (3) 1924 (4) 2400 (4) 2798 (4)	7885(4) 10438(5) 10840(5) 8490(5) 8029(6) 6651(4) 5653(4) 4870(4) 3867(4) 3112(4) 3339(5) 4309(5)

TABLE 5. Coordinates of the H Atoms (× 10³) in V

Atom	x	y	z	Atom	x	y	Z
$\begin{array}{c} H_{(1)} \\ H_{(2)} \\ H_{(2a)} \\ H_{(5)} \\ H_{(7)} \\ H_{(8)} \\ H_{(8b)} \\ H_{(9,1)} \\ H_{(9,2)} \\ H_{(10,2)} \\ H_{(10,2)} \\ H_{(10,3)} \\ H_{(11,1)} \\ H_{(11,2)} \\ H_{(12,1)} \\ H_{(12,2)} \\ H_{(12,3)} \\ H_{(13)} \end{array}$	892(3) 798(3) 1048(3) 895(4) 757(4) 825(4) 1012(4) 850(3) 773(4) 588(4) 674(3) 674(3) 698(4) 712(3) 746(4) 567(3) 506(4) 528(4) 675(3)	$\begin{array}{c} 177 (2) \\ 220 (2) \\ 187 (2) \\ 441 (2) \\ 495 (2) \\ 387 (2) \\ 281 (2) \\ 554 (2) \\ 613 (2) \\ 538 (2) \\ 538 (2) \\ 530 (2) \\ 468 (2) \\ 659 (2) \\ 602 (2) \\ 538 (2) \\ 588 (2) \\ 588 (2) \\ 623 (2) \\ 266 (2) \end{array}$	696 (3) 896 (3) 884 (3) 1047 (3) 731 (3) 675 (3) 745 (3) 1058 (3) 1058 (3) 1073 (3) 898 (3) 784 (3) 763 (3) 868 (3) 746 (3) 702 (3)	$\begin{array}{c} H_{(14)} \\ H_{(16)} \\ H_{(17)} \\ H_{(18)} \\ H_{(19)} \\ H_{(20)} \\ H_{(22)} \\ H_{(22)} \\ H_{(23)} \\ H_{(24)} \\ H_{(25)} \\ H_{(25)} \\ C_{(20)} \\ C_{(21)} \\ C_{(22)} \\ C_{($	743 (4) 590(3) 396(3) 241(4) 300(3) 476(3) 974(4) 930(3) 781(4) 684(3) 4703(5) 8349(4) 9081(5) 8862(6) 7880(6) 7146(6) 7374(5)	$\begin{array}{c} 170 (2) \\ 140 (2) \\ 166 (2) \\ 246 (2) \\ 320 (2) \\ 294 (2) \\ 61 (2) \\ -70 (2) \\ -100 (2) \\ 3 (2) \\ 118 (2) \\ 2688 (3) \\ 1068 (3) \\ 504 (3) \\ -222 (3) \\ -408 (3) \\ 126 (4) \\ 872 (3) \end{array}$	532(3) 375(3) 241(3) 277(3) 446(3) 573(3) 826(3) 855(3) 930(3) 947(3) 947(3) 5071(4) 8808(4) 8527(5) 8720(5) 9173(5) 9440(5) 9245(5)

the donor-acceptor type of interaction of the addends in the step involving the formation of the $C_{(1)}-C_{(8b)}$ bond, where the donor is the 7-aminocoumarin fragment, and the acceptor is the olefin fragment; second, on the steric hindrance that arises when the $C_{(1)}$ and $C_{(8b)}$ centers draw near to one another. These conclusions are in agreement with the possibility of the existence of an unsymmetrical transition state in a concerted reaction with the "late" formation of a $C_{(1)}-C_{(8b)}$ bond or an alternative biradical mechanism [8].

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a Perkin–Elmer 577 spectrometer. The UV spectra of solutions in 2-propanol were obtained with a Hitachi EPS-3T spectrophotometer. The PMR spectra of solutions in $CDCl_3$ were obtained with a Bruker WM spectrometer (250 Hz) with hexamethyldisiloxane (HMDS) as the internal standard.

The adducts were synthesized in 100-ml Pyrex reactors with a medium-pressure PRK-2 mercury lamp as the source of irradiation. The reaction mixtures were stirred with a stream of nitrogen and by means of a magnetic stirrer. The compositions of the reaction mixtures and the purity of the synthesized substances were monitored by means of TLC on Silufol UV-254 plates; the eluent was hexane-acetone, and the chromatograms were developed with UV light and iodine. The products were isolated by means of column chromatography with columns (15×5 and 25×2.5 cm) packed with Silpearl UV silica gel using hexane-acetone as the eluent.

The differential quantum yields of the photochemical reactions were calculated in accordance with [9] and were determined for solutions of the 7-aminocoumarins (0.08 mole/liter) and solutions of 1,4-diphenylbutadiene (0.30 mole/liter) (as well as

styrene and stilbene for IX and XI) in 1,4-dioxane. The rate of accumulation of the products was determined by means of liquid chromatography with a Du Pont apparatus and was simultaneously monitored with a Shimadzu CS-930 densitometer. In determining the φ values we used light with a wavelength of 370 nm, obtained by means of a Shimadzu NGF-16 monochromator. The intensity of the source was determined by means of a ferrioxalate actinometer [10] and amount to I₀ = 5.62 \cdot 10^{-10} erg/sec.

General Method for Obtaining V-VIII. A mixture of 5 mmoles of the starting coumarin (I-IV) and 50 mmoles of 1,4-diphenylbutadiene in 100 ml of 1,4-dioxane was irradiated for 8-10 h, after which the reaction mixture was evaporated in vacuo, and the residue was chromatographed on silica gel [elution with hexane-acetone (3:1)]. The isolated products V-VIII were recrystallized from hexane-acetone.

X-Ray Diffraction Study of Adduct V (Tables 4 and 5). The crystals for the x-ray diffraction study were grown by slow evaporation of a solution of V in hexane. The crystals of adduct V ($C_{29}H_{29}NO_2$) had the form of transparent tetragonal antiprisms, were monoclinic, and had the following parameters at 20°C: a = 10.993(1) Å, b = 18.054(1) Å, c = 12.387(1) Å, $\beta = 104.19(1)^\circ$, Z = 4, and space group P2₁c. The cell parameters and intensities of 1565 independent reflections with $I \ge 2\sigma$ (I) were measured with a Hilger–Watts four-circle diffractometer (λ MoKa, graphite monochromator, $\theta/2\theta$ scanning, $\theta \le 30^\circ$). The structure was decoded by the direct method and was refined by the total-matrix method of least squares within the anisotropic approximation for the nonhydrogen atoms. All of the H atoms were revealed from the differential series and were then refined with fixed $B_{iso} = 5$ Å². In the final stage the refinement was carried out with respect to 1478 reflections with $\sin \theta/\lambda \le 0.55$ and I > 4.5 σ (I). The final divergence factors were R = 0.060 and R_w = 0.060. All of the calculations were performed with an Eclipse S/200 computer by means of INEXTL programs [11].

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