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).

LITERATURE CITED

1. A. Dorlars, C. W. Schellhammer, and J. Schroeder, Angew. Chem., 87, 693 (1975).
2. K. H. Drexhage, J. Res. Nat. Bur. Stand., A80, 421 (1976).
3. B. H. Winters and H. J. Mandelberg, Appl. Phys. Lett., 25, 723 (1974).
4. R. J. Trebra and T. H. Koch, Appl. Phys. Lett., 42, 129 (1983).
5. G. Jones, W. R. Bergmark, and W. R. Jackson, Optic Commun., 50, 320 (1984).
6. G. Jones, S. F. Griffin, C. Choi, and W. R. Bergmark, J. Org. Chem., 49, 2705 (1984).
7. Yu. F. Pedash, V. F. Pedash, A. V. Luzanov, and M. I. Dzyubenko, "Electronic structures of the excited states of the coumarin molecule in a semiempirical model," Preprint [in Russian], Institute of Radiophysics and Electronics, Academy of Sciences of the Ukrainian SSR, Kharkov.
8. A. Martin and N. K. Ray, Indian J. Chem., B16, 517 (1978).
9. G. Jones and W. R. Bergmark, J. Photochem., 26, 179 (1984).
10. R. A. Pabon, D. J. Bellville, and N. L. Bauld, J. Am. Chem. Soc., 106, 2730 (1984).
11. A. G. Gonzales, J. T. Barroso, Z. D. Jorge, and L. F. Rodriguez, Fis. Nat., 75, 811 (1981).
12. S. K. Gorozhankin, M. A. Kirpichenok, N. A. Klyuev, and I. I. Grandberg, Izv. Timiryazev. Skh. Akad., No. 4, 151 (1986).
13. O. Buchardt, J. J. Christensen, and N. Harrit, Acta Chem. Scand., B30, 189 (1976).
14. G. R. Evanega and D. L. Fabing, J. Org. Chem., 35, 1970 (1970).
15. T. Naito, N. Nakayama, and C. Kaneko, Chem. Lett., No. 3, 423 (1981).
16. K. Somekawa, T. Shimou, and M. Atsuchi, Nippon Kagaku Kaishi, No. 7, 1013 (1978).
17. J. W. Hanifin and E. Cohen, Tetrahedron Lett., No. 13, 1419 (1966).
18. J. J. McCullough and C. W. Huang, Can. J. Chem., 47, 757 (1969).
19. R. J. Trebra and T. H. Koch, J. Photochem., 35, No. 1, 33 (1986).
20. L. M. Tolbert and M. B. Ali, J. Am. Chem. Soc., 104, 1742 (1982).
21. C. G. Hatchard and C. A. Parker, Proc. R. Soc., A235, 512 (1956).

PHOTOCHEMICAL REACTIONS OF 7-AMINOCOUMARINS. 2.[*] [2 + 2]-CYCLOADDUCTS WITH STYRENE

M. A. Kirpichenok, L. M. Mel'nikova,
D. S. Yufit, Yu. T. Struchkov, I. I. Grandberg,
and L. K. Denisov

UDC 547.587.51'538:141:535.217

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.

K. A. Timiryazev Moscow Agricultural Academy, Moscow 127550. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1176-1184, September, 1988. Original article submitted October 17, 1986; revision submitted July 3, 1987.

0009-3122/88/2409-0965$12.50

TABLE 1. Characteristics of VI-X

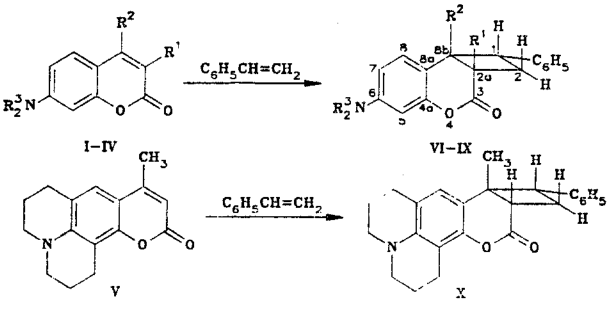
Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
VI	113,5	77,6	6,4	4,7	$C_{18}H_{17}NO_2$	77,4	6,1	5,0	47
VII	116,5	78,5	7,5	4,3	$C_{22}H_{25}NO_2$	78,8	7,5	4,2	62
VIII	93,0	75,4	6,4	4,4	$C_{21}H_{21}NO_3$	75,2	6,3	4,2	54
IX	58,0	73,9	7,5	3,5	$C_{26}H_{31}NO_4$	74,1	7,4	3,3	46
X	89,0	80,0	6,7	3,7	$C_{24}H_{25}NO_2$	80,2	7,0	3,9	32

TABLE 2. IR and UV Spectra of VI-X

Compound	IR spectrum, ν, cm^{-1}		UV spectrum, λ_{max}, nm (log ε)
	C=O	C=C	
VI	1742	1635, 1575	258 (3,76), 280 (3,55)
VII	1755	1633, 1565, 1530	214 (4,63), 240 (4,28), 272 (4,15), 280 (4,20), 300 (3,95)
VIII	1757	1635, 1572, 1530	215 (4,57), 242 (4,31), 275 (4,18), 283 (4,18), 304 (3,85)
IX	1761, 1710	1635, 1575, 1532	214 (4,59), 245 (4,27), 280 (4,21), 310 (3,90)
X	1759	1635, 1570	250 (3,81), 280 (3,70), 335 (3,74)

We have previously reported [1] the [2 + 2]-cycloaddition of vinyl butyl ether and acrylonitrile to 4-methyl-7-aminocoumarin (I) and 4-methyl-7-diethylaminocoumarin (II). It was found that exclusively regioisomers of the "head-to-tail" type are formed in these reactions. In the present paper we present data on the cycloaddition of styrene to coumarins I and II, as well as 7-(N-morpholino)coumarin (III), 3-carbethoxymethyl-4-methyl-7-diethylaminocoumarin (IV), and coumarin-102 (V). Styrene was selected because of its intermediate position from the point of view of the electronic donor-acceptor properties in a series of investigated olefins [1]. Consequently, in comparing the reactions of the selected olefins with the reactions of vinyl butyl ether and acrylonitrile one can more accurately evaluate the ratio of the "polar" and "steric" factors in [2 + 2]-cycloaddition.

The reactions were carried out in acetonitrile by irradiation of a 0.05 M solution of the corresponding 7-aminocoumarin with UV light through a Pyrex filter (λ > 300 nm) in excess styrene (15-20 equivalents) for 8-10 h. A single adduct (VI-X) was isolated as the principal product in all cases.



I, VI $R^1=R^3=H$, $R^2=CH_3$; II, VII $R^1=H$, $R^2=CH_3$, $R^3=C_2H_5$; III, VIII $R^1=R^2=H$, $R^3+R^3=-CH_2CH_2OCH_2CH_2-$; IV, IX $R^1=CH_2CO_2C_2H_5$, $R^2=CH_3$, $R^3=C_2H_5$

Despite their high percentages in the reaction mixtures (~90%), the preparation yields of the adducts did not exceed 60% (Table 1), since VI-X are rather unstable and undergo retrodecomposition during chromatographic isolation on silica gel and heating or under the influence of light.

To prove the structures of adducts VI-X we first used ordinary physicochemical methods (Tables 1-3). Thus a band of carbonyl absorption appears at 1745-1760 cm^{-1} in the IR spectra of VI-X; this is in agreement with other derivatives of this type [1, 2]. Absorption bands at 280-285 and 300-335 nm, which are characteristic for a saturated dihydrocoumarin

TABLE 3. PMR Spectra of VI-X

Compound	Chemical shift, δ, ppm, in $CDCl_3$ (J, Hz)							
	1-exo-H	2-exo-H	2-endo-H	2a-H	5-H	7-H	8-H (12-H)	other protons
VI	3,63 t (9,5)	2,46 ddd (9,5; 9,5; 1,25)	2,46 ddd (9,5; 9,5; 1,25)	3,20 t (9,5)	6,38 d (2,4)	6,05 dd (8,5; 2,4)	5,85 d (8,5)	1,52 (3H, s, 8b-CH_3); 3,75 (2H, s, NH_2); 6,89 (2H, ddd, $J_1=7,0$, $J_2=3,5$, $J_3=2,2$, $J_4=1,25$, o-C_6H_5); 7,20 (3H, m, p- and m-C_6H_5)
VII	3,57 t (9,5)	2,46 t (9,5)	2,46 t (9,5)	3,19 t (9,5)	6,27 d (2,6)	6,00 dd (9,0; 2,6)	5,85 d (9,0)	1,03 (6H, t, $J=7,0$, 2-CH_3); 1,48 (3H, s, 8b-CH_3); 3,22 (4H, q, $J=7,0$, 2-CH_2); 6,86 (2H, m, o-C_6H_5); 7,17 (3H, m, p- and m-C_6H_5)
VIII	4,04 ddd (10,0; 10,0; 7,9)	2,72 ddd (10,0; 9,0; 9,0)	2,68 ddd (9,0; 9,0; 9,0; 3,0)	3,58 ddd (9,0; 9,0; 7,9)	6,48 d (2,5)	6,26 dd (7,5)	6,03 d (7,5)	3,04 [4H, m, $N(CH_2)_2$]; 3,80 [4H, m, $O(CH_2)_2$]; 3,91 (1H, ddd, $J_1=J_2=7,9$; $J_3=3,0$, 8b-H); 6,84 (2H, m, o-C_6H_5); 7,15 (3H, m, p- and m-C_6H_5)
IX	3,61 dd (11,0; 8,0)	2,70 dd (11,0; 11,0)	2,20 dd (11,0; 8,0)	—	6,27 d (2,5)	5,99 dd (8,8; 2,5)	5,83 d (8,8)	1,09 (6H, t, $J=7,0$, 2-CH_3); 1,23 (3H, t, $J=7,0$, $OCH_2\mathbf{CH_3}$); 1,39 (3H, s, 8b-CH_3); 3,15 (1H, d, $J=17,0$, **H**—CHCO); 3,22 (4H, q, $J=7,0$, 2-CH_2); 3,44 (1H, d, $J=17,0$, H—CHCO); 4,08 (1H, dq, $J=14,0$, $J_q=7,0$, **H**—CHO); 4,11 (1H, dq, $J_d=14,0$, $J_q=7,0$, H—CHO); 6,82 (2H, m, o-C_6H_5); 7,15 (3H, m, o- and m-C_6H_5)
X	3,59 t (9,5)	2,35 t (9,5)	2,35 t (9,5)	3,09 t (9,5)	—	—	5,35 s	1,40 (3H, s, 12b-CH_3); 1,65 (2H, m, NCH_2CH_2); 1,85 (2H, m, $NCH_2C\mathbf{H_2}$); 2,62 (2H, t, $J=6,9$, $C\mathbf{H_2}$—Ar); 2,91 (2H, t, $J=6,9$, $C\mathbf{H_2}$—Ar); 2,9 . m 3,0 [4H, m, $N(CH_2)_2$]; 6,82 (2H, m, o-C_6H_5); 7,11 (3H, m, p- m-C_6H_5)

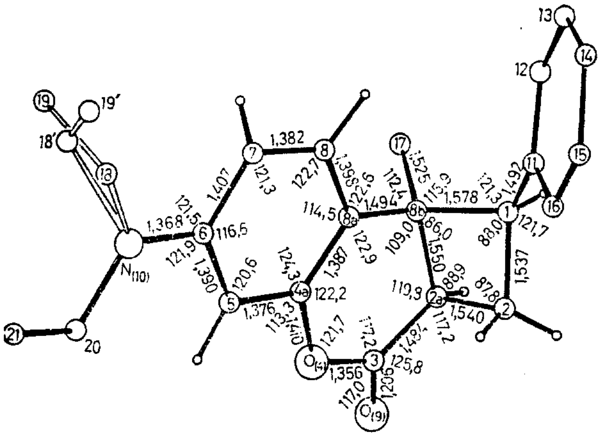


Fig. 1. Principal bond lengths and bond angles in the VII molecule.

fragment [3], are present in the UV spectra (Table 2). The mass-spectral fragmentation of VI-X resembles the fragmentation of 7-aminocoumarins [4] and is characterized by high-intensity peaks of starting coumarins I-V (relative intensities ~90-100%); this constitutes evidence for retro-[2 + 2]-decomposition. The intensities of the molecular-ion peaks are generally low and do not exceed 30%.

The principal information regarding the structures of derivatives VI-X follows from their PMR spectra (Table 3). In conformity with the literature data [1, 5, 6] cis fusion of the cyclobutane and lactone fragments was adopted for all of the adducts. Signals of aromatic 8-H, 7-H, and 5-H protons of the coumarin fragment at 5.8-5.9, 6.0-6.1, and 6.3 ppm, respectively, are readily distinguishable in the PMR spectra of VI-X. Attention is directed to the fact of the significant shift to strong field of the 8-H signals as compared with the starting coumarins (7.5 ppm) [7] or the adducts based on acrylonitrile and vinyl butyl ether (6.9-7.2 ppm) [1]. This regularity is evidently explained by the shielding effect of the phenyl substituents in VI-X.

The PMR spectra of adducts VI, VII, and X have a rather simple form as a consequence of the coincidence of the spin-spin coupling constants (SSCC) of the cyclobutane protons. Thus the spectrum of VI contains three groups of signals at 2.46, 3.20, and 3.63 ppm, which were assigned to the 2-H (exo and endo), 2*a*-H, and 1-H protons, respectively. The signals at 3.20 and 3.63 ppm have the form of triplets (J = 9.5 Hz) and are not linked by spin-spin coupling, as evidenced by the use of double resonance. On the other hand, suppression of the signal at 2.46 ppm leads to distortion or degeneration of the 1-H and 2*a*-H signals. The position and form of the signals of the cyclobutane protons of VI, VII, and X make it possible to assign them to isomers of the "head-to-tail" type. The absence in the spectra of long-range coupling of the 1-H and 2*a*-H protons, which, according to the data in [8], are equal to ~1.0 Hz in the case of an anti orientation, makes it possible to assume the presence of the phenyl substituent in the 1-endo position. This assumption is also confirmed by the absence of a shielding effect of the phenyl ring on the protons of the 8b-methyl group (see [1]), which is well known for phenyl-substituted cyclobutanes [9, 10]. A small degree of splitting to a doublet of the strong-field line of the triplet signal at 2.46 ppm (J = 1.25 Hz) can also be observed in the spectrum of VI. The indicated splitting correlates with the signals of the aromatic ortho protons of the phenyl group and was assigned to long-range W coupling of the 2-endo-H proton with one of the ortho protons.

Chemical shifts of cyclobutane protons are observed at 2.7-4.0 ppm in the PMR spectrum of adduct VIII. Signals of 1-H (4.02 ppm) and 8b-H (3.91 ppm) protons, which show up in the form of a doublet of triplets and are linked by spin-spin coupling with the 2-H (3.68 and 3.72 ppm) and 2*a*-H (3.58 ppm) protons, are located at weakest field. The constants of spin-spin coupling of the 8b-H proton with the 1-H and 2*a*-H β protons are identical and are equal to 7.9 Hz. This fact makes it possible to assume a cis orientation for the 8b-H and 1-H protons and, consequently, an endo orientation for the phenyl group. The ssignment of the 2-endo-H proton was made on the basis of the long-range $^4J_{2\text{-endo},8b}$ constant, which is 3.0 Hz. The analogy in the stereochemical structures of VIII and adducts VI, VII, and X is also confirmed by the close values of the remaining vicinal constants. A comparison of the PMR spectra of adducts VII and VIII indicates the appreciable shielding effect of

TABLE 4. Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors of the Nonhydrogen Atoms in the VII Molecule

Atom	x	y	z	B_{iso}^{eq}, (Å^2)
$C_{(1)}$	5827(2)	−1371(5)	4131(2)	3,4(1)
$C_{(2)}$	5782(3)	763(6)	3844(2)	4,1(1)
$C_{(3)}$	6538(3)	1132(5)	2650(2)	3,7(1)
$O_{(4)}$	7451(2)	1242(4)	2787(1)	4,33(7)
$C_{(4a)}$	7888(3)	−30(6)	3275(2)	3,7(1)
$C_{(5)}$	8811(3)	342(6)	3360(2)	4,7(1)
$C_{(6)}$	9354(3)	−858(7)	3790(2)	5,7(1)
$C_{(7)}$	8913(3)	−2458(7)	4115(2)	5,8(1)
$C_{(8)}$	7982(3)	−2768(6)	4027(2)	4,6(2)
$C_{(8a)}$	7428(2)	−1561(5)	3601(2)	3,1(1)
$C_{(2a)}$	5986(3)	−107(3)	3123(2)	3,7(1)
$C_{(8b)}$	6427(2)	−1939(5)	3487(2)	3,1(1)
$O_{(9)}$	6242(2)	2107(4)	2169(1)	4,64(8)
$N_{(10)}$	10266(3)	−487(7)	3902(2)	8,4(2)
$C_{(11)}$	6148(2)	−1800(5)	4857(2)	3,2(1)
$C_{(12)}$	6119(3)	−3752(6)	5105(4)	4,0(1)
$C_{(13)}$	6422(3)	−4201(6)	5771(2)	4,7(1)
$C_{(14)}$	6746(3)	−2740(6)	6216(2)	4,6(1)
$C_{(15)}$	6763(3)	−824(6)	5983(2)	4,6(1)
$C_{(16)}$	6471(3)	−341(6)	5311(2)	3,9(1)
$C_{(17)}$	6236(3)	−3973(6)	3164(2)	4,7(1)
$C_{(18)}$	10822(7)	−1395(15)	4486(5)	6,0(2)*
$C_{(18')}$	10958(9)	−2497(21)	4088(7)	9,8(3)*
$C_{(19)}$	11134(8)	−3387(17)	4047(6)	8,6(3)*
$C_{(19')}$	11112(11)	−2425(23)	4760(7)	11,3(4)*
$C_{(20)}$	10708(3)	1172(9)	3560(3)	8,0(2)
$C_{(21)}$	10952(4)	713(11)	2846(3)	10,5(3)

*The B_{iso} values are presented (these atoms were refined isotropically with G = 0.5).

the β-cis-methyl group, as a result of which the signals of the 1-exo-H and 2*a*-H protons in VIII are shifted ~0.4 ppm to weak field as compared with adduct VII.

In the PMR spectrum of IX the signals of the cyclobutane protons are observed at 3.61, 2.70, and 2.20 ppm. The signal at 3.61 ppm was assigned to the 1-exo-H proton on the basis of the characteristic chemical shift (compare VII-IX and X), and it is thus assumed that the phenyl group is in the 1-endo position. This conclusion is confirmed by the close values of the chemical shifts of the aromatic 8-H, 7-H, and 5-H aromatic protons in VII-IX, which attest to a monotypic configuration of the $C_{(1)}$ center in the adducts obtained. The signal at 2.70 ppm has the form of a triplet and was assigned to the 2-exo-H proton, since a deshielding effect of the carbonyl group [11] of the substituent in the 2*a* position can be expected for this proton. The presence of an ethoxycarbonylmethyl group in IX evidently leads to appreciable distortion of the cyclobutane fragment. This results in greater shielding of the 2-endo-H proton (2.20 ppm) by the β-phenyl group and an increase in the difference in the $^3J_{1\text{-exo},2\text{-endo}}$ (8.0 Hz) and $^3J_{1\text{-exo},2\text{-exo}}$ (11.0 Hz) constants as compared with the other adducts. The nonequivalence of the methylene protons in the CH_2CO and OCH_2 fragments of the carbethoxymethyl substituent (Table 3) may serve as an additional confirmation of the steric hindrance that develops.

On the whole, the PMR spectra of the synthesized cycloadducts VI-X have elements in common, and their interpretation is interdependent in many respects. Taking this into account, we conducted a special x-ray diffraction study of adduct VII and confirmed its structure as a compound with a cis-fused ring that is an isomer of the "head-to-tail" type with an endo orientation of the phenyl substituent.

The structure of the VII molecule in accordance with the results of x-ray diffraction analysis is shown in Fig. 1, and the coordinates of the atoms are presented in Tables 4 and 5. Most of the geometrical parameters have the expected values. In the VII molecule one observes the usual (for coumarin [12, 13] and 3,4-dihydrocoumarin [14] derivatives) difference in the $C_{(8)}C_{(8a)}C_{(4a)}$ [114.5(3)°] and $C_{(5)}C_{(4a)}C_{(8a)}$ [124.3(4)°] bond angles and $O_{(4)}$—$C_{(4a)}$ [1.410(4) Å] and $O_{(4)}$—$C_{(3)}$ [1.356(5) Å] bond lengths, as well as a certain

TABLE 5. Coordinates of the Hydrogen Atoms (×10^3) in the VII Molecule

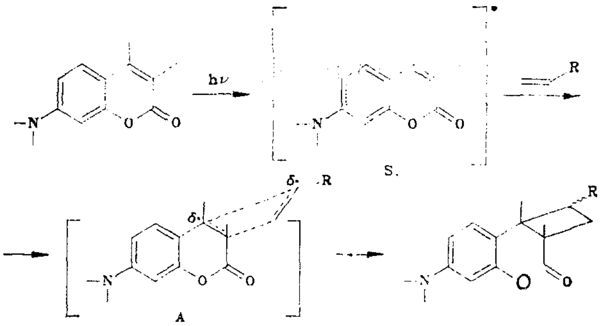
Atom	*x*	*y*	*z*
$H_{(1)}$	520(2)	−197(5)	406(2)
$H_{(2,1)}$	523(2)	144(5)	391(2)
$H_{(2,2)}$	630(2)	151(5)	398(2)
$H_{(2a)}$	541(2)	−41(5)	291(2)
$H_{(5)}$	765(2)	−382(5)	433(2)
$H_{(7)}$	926(2)	−327(5)	446(2)
$H_{(8)}$	908(2)	146(5)	310(2)
$H_{(12)}$	591(2)	−471(5)	480(2)
$H_{(13)}$	642(2)	−549(5)	593(2)
$H_{(14)}$	703(2)	−307(5)	676(2)
$H_{(15)}$	703(2)	−307(5)	676(2)
$H_{(16)}$	655(2)	109(5)	513(2)
$H_{(17,1)}$	661(2)	−407(5)	270(2)
$H_{(17,2)}$	652(2)	−492(5)	341(2)
$H_{(17,3)}$	558(2)	−413(5)	313(2)
$H_{(20,1)}$	1020(2)	257(5)	351(2)
$H_{(20,2)}$	1120(2)	144(5)	385(2)
$H_{(21,1)}$	1029(2)	23(5)	240(2)
$H_{(21,2)}$	1142(2)	−17(5)	286(2)
$H_{(21,3)}$	1119(2)	150(5)	262(2)

decrease in angle $O_{(4)}C_{(3)}O_{(9)}$ [117.0(3)°] as compared with the ideal value (120°). In the six-membered heteroring the $C_{(3)}$ and $C_{(2a)}$ atoms deviate from the plane [drawn with an accuracy of 0.011(4) Å] of the remaining four atoms by 0.060(4) Å and 0.404(4) Å, respectively, i.e., the conformation of this ring can be described as a distorted sofa (or a distorted boat). The modified (in accordance with [15]) Cramer–Pople parameters for this ring are as follows: $Q = 0.401$ Å, $\theta = 132.8°$, $\psi = 214.0°$, and $\sigma = 0.6°$. The four-membered ring is nonplanar, and its degree of bending with respect to the $C_{(1)}\ldots C_{(2a)}$ line is 32°. This value is characteristic for substituted cyclobutane derivatives (30 ± 6°) [16]. The $C_{(1)}-C_{(8b)}$ bond [1.578(5) Å] is substantially elongated as compared with the other three bonds of this ring; this is probably due to the strain of the condensed system with the six-membered heteroring and, particularly, the short nonbonding $C_{(11)}\ldots C_{(8a)}$ [3.092(5) Å] and $C_{(11)}\ldots C_{(8)}$ [3.215(5) Å] contacts.

The $C_{(19)}-C_{(18)}$ ethyl group is randomized with respect to two orientations in such a way that the $C_{(18)}$ and $C_{(18')}$ atoms deviate by −0.415(9) Å and 0.66(1) Å, respectively, on different sides of the plane of the benzene ring, while the $C_{(20)}$ atom of the other ethyl group virtually lies in this plane [its deviation is −0.078(6) Å]. The decrease in the endocyclic $C_{(5)}-C_{(6)}-C_{(7)}$ bond angle to 116.6(4)° is normal and is due to the electron-donor character of the diethylamino group.

Thus the structures of adducts VI-X indicate regiospecific cycloaddition. In combination with the stereospecificity of the reactions this may constitute evidence in favor of concerted character of the cycloaddition. The available rigorous ab initio calculations of the [2 + 2]-cycloaddition of unsymmetrical olefins (for example, see [17]) predict the energic preferableness of unsymmetrical transition states with different degrees of formed character of the chemical bonds. In [1] we demonstrated that the cycloaddition of coumarins I and II to terminal olefins, regardless of the donor-acceptor properties of the substituent in the olefin, leads to isomers of the "head-to-tail" type. With these data in mind, for the explanation of the regiospecificity of the reactions with monosubstituted olefins in a simplified way one can imagine the existence of a biradical intermediate or "biradical-like" transition state A with a more markedly formed $C_{(2a)}-C_{(2)}$ bond as compared with the $C_{(1)}-C_{(8b)}$ bond; this is depicted arbitrarily below by δ symbols (see scheme on following page).

This scheme suggests the participation of the excited state of the 7-aminocoumarin molecule in the reactions. To verify this assumption we studied the effect of the addition of triplet sensitizers (acetophenone), singlet quenchers ($CHBr_3$), and electron photocarriers



(triethylamine, 1,4-dicyanobenzene) on the quantum yields of the reaction to form adduct VII. The data obtained (Table 6) show a certain decrease in the effectiveness of cycloaddition under the influence of added acetophenone and 1,4-dicyanobenzene and pronounced quenching of the reactions by bromoform. These results, as well as previously obtained data [1], constitute evidence for the participation of the singlet excited state of 7-aminocoumarin in the cycloaddition. The satisfaction of the Stern–Volmer dependence [18] that we found in an investigation of the quenching of the fluorescence of coumarin II by styrene, which in the case of small degrees of conversion is linearly related to the quantum yields of reactions carried out at similar concentrations of the reagents, may serve as yet another confirmation of this.

A rather unexpected result was obtained in the reaction of coumarin II with styrene in the presence of excess triethylamine. Appreciable acceleration of cycloaddition was observed in this case; this is confirmed by the increase in the quantum yield of the reaction (Table 6). A probable explanation of this fact consists in the formation of a long-lived exciplex with the participation of triethylamine and the singlet excited state of the aminocoumarin. The development of such reactive exciplexes in [2 + 2]-cycloaddition reactions is well known [19, 20]. We established that the reaction of coumarin II with vinyl butyl ether and acrylonitrile is quenched weakly by triethylamine. In contrast to styrene, vinyl butyl ether, as a more electron-donor molecule, evidently itself can form exciplexes with the participation of the singlet excited state of the aminocoumarin [20]. The formation of such exciplexes should be partially suppressed in the presence of triethylamine. On the other hand, a strong electron acceptor – acrylonitrile – is capable of undergoing prior coordination with triethylamine and is thus removed from the reaction sphere. In both cases the addition of triethylamine should hinder cycloaddition, and this is actually observed.

Thus the concepts regarding the participation of the excited states of aminocoumarin I-V molecules in [2 + 2]-cycloaddition and the determining effect of the spin properties of the electron density localized on the $C_{(3)}$ atom on the course of the reaction make it possible to explain the regiospecificity of the processes. However, these concepts alone clearly are inadequate for the interpretation of the stereospecificity of the investigated reactions. The most consistent explanation for the observed principles can be given if one assumes secondary interactions in the step involving the formation of new σ bonds. In fact, we observed the formation of 1-endo isomers previously [1] in reactions involving cycloaddition of acrylonitrile to coumarins I and II. This signifies drawing together in the transition state of the phenyl ring of the 7-aminocoumarins and the acceptor nitrile group, which may facilitate their additional attraction. Similar coordination may also be assumed for styrene.

Thus stereocontrol in the investigated cycloaddition reactions may be realized under the influence of the aminobenzene fragment. In conclusion, we should add that the high sensitivity of reactions involving [2 + 2]-cycloaddition to donor-acceptor interactions in the transition state and their insensitivity to steric factors have frequently been mentioned in the literature [21].

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions in 2-propanol were recorded with a Hitachi EPS-3T spectrophotometer. The PMR spectra of solutions in $CDCl_3$ were obtained with a Bruker WM spectrometer (250 MHz) with hexamethyldisiloxane as the internal standard. The mass spectra were obtained

TABLE 6. Quantum Yields of the Reactions to Form Adducts VI-X in Acetonitrile*

Compound	Additive	Additive concn., M	Quantum yield (·10²)	Compound	Additive	Additive concn., M	Quantum yield (·10²)
VI	—	—	5,5	VII	p-$(CN)_2C_6H_4$	0,08	2,3
VII	—	—	4,1	VII	$(C_2H_5)_3N$	0,15	8,0
VII**	—	—	1,8	VIII	—	—	3,5
VII***	—	—	9,5	IX	—	—	2,4
VII	$C_6H_5COCH_3$	0,08	1,0	X	—	—	3,1
VII	$CHBr_3$	0,08	0,1				

*The concentration of coumarins I-V was 0.08 M in all cases, and the styrene concentration was 10.0 M.
**The styrene concentration was 5.0 M.
***The styrene concentration was 15.0 M.

with a Varian MAT-311A spectrometer with direct introduction of the samples into the ion source at an electron-ionization energy of 70 eV.

The syntheses of the adducts were carried out in 100-ml Pyrex reactors; the irradiation source was a PRK-2 medium-pressure mercury lamp. The products were isolated by means of column chromatography with columns (35 by 2.5 cm) packed with Silpearl UV-254 silica gel with hexane—acetone (3:1) as the eluent. The purity of the synthesized substances was monitored by TLC on Silufol UV plates by elution with hexane—acetone and benzene—acetone and development with UV light and iodine.

The quantum yields of the reactions were determined for 0.08 M solutions of the starting coumarine in acetonitrile by means of a Shimadzu CS-930 densitometer and were simultaneously monitored with a Du Pont liquid chromatograph from the rates of accumulation of the corresponding adducts. Ultraviolet light with a wavelength of 370 nm, which was obtained by means of a Shimadzu NGF-16 monochromator, was used for excitation of coumarin I-V molecules. The intensity of the source was determined in the standard way [22] and was $I_1 = 5.62 \cdot 10^{-10}$ ergs/sec. The quantum yields of the reactions of coumarin II with styrene in the presence of $N(C_2H_5)_3$ and $CHBr_3$ were determined by excitation with the same light, whereas in the case of $C_6H_5COCH_3$ and 1,4-$(CN)_2C_6H_4$ they were determined with irradiation by monochromatic light with a wavelength of 250 nm ($I_2 = 5.81 \cdot 10^{-10}$ ergs/sec) taking into account the absorption of the additive in this region.

The quenching of the luminescence of coumarin VII by styrene and the comparison with data on the quantum yields of the reactions to form adduct VII were investigated in acetonitrile at 20°C over the styrene concentration range 0-10.0 M at a coumarin concentration of $5.3 \cdot 10^{-6}$ M.

General Method for Obtaining Adducts VI-X. A mixture of 5 mmole of the coumarin (I-V) and 75-100 mmole of styrene was dissolved in 100 ml of freshly distilled deoxygenated acetonitrile, and the solution was irradiated for 8-10 h with vigorous stirring with a stream of nitrogen, as well as by means of a magnetic stirrer. The reaction mixture was evaporated in vacuo at no higher then 40-50°C, and the residue was subjected to rapid chromatography. The desired products were recrystallized from hexane—acetone.

1-endo-Phenyl-8b-methyl-6-amino-1,2-dihydrocyclobuta[c]benzopyran-3-one (VI). After irradiation for 9 h, 0.88 g (5 mmole) of coumarin I and 10.40 g (100 mmole) of styrene gave 0.65 g (47%) of VI with R_f 0.05 [hexane—acetone (3:1)]. Mass spectrum,* m/z (%): 279 (3), 231 (99).

1-endo-Phenyl-8b-methyl-6-diethylamino-1,2-dihydrocyclobuta[c]benzopyran-3-one (VII). After irradiation for 9 h, 1.16 g (5 mmole) of coumarin II and 8.3 g (80 mmole) of styrene gave 1.04 g (62%) of VII with R_f 0.38 [hexane—acetone (3:1)]. Mass spectrum, m/z (%): 335 (2), 279 (2), 266 (1), 242 (2), 231 (99).

---

*Here and subsequently, the fragment ions with masses no lower than that of the starting coumarin are presented.

A crystal for x-ray diffraction study was grown by slow evaporation of a solution of VII in hexane.

X-Ray Diffraction Study of VII. The crystals of adduct VII were monoclinic and had the following parameters at 20°C: $a = 14.601(1)$, $b = 6.7194(4)$, $c = 19.230(1)$ Å, $\beta = 91.267(6)°$, $V = 1886.1(2)$ Å^3, $d_{calc} = 1.18$ g/cm^3, $Z = 4$, space group $P2_1/c$. The cell parameters and intensities of 1991 reflections with $I \geq 2\sigma$ were measured with a Hilger–Watts automatic four-circle diffractometer (λ MoKα, graphite monochromator, $\theta/2\theta$ scanning, $\theta \leq 30°$). The structure was decoded by the direct method by means of the MULTAN program and was refined by the total-matrix method of least squares within the anisotropic approximation for all of the nonhydrogen atoms, except for the randomized carbon atoms of the ethyl group. Refinement of the populations of the $C_{(19)}$ and $C_{(18)}$ positions led to approximately equal values, and these atoms therefore were subsequently refined isotropically with half masses. All of the H atoms, except the H atoms in the disordered ethyl group, were revealed in a differential series; no attempt was made to localize them. The H atoms were refined with fixed $B_{iso} = 5$ Å^2. The final divergence factors $R = 0.068$ and $R_w = 0.061$. All of the calculations were made with an Eclipse S/200 computer by means of INEXTL programs [23].

1-endo-Phenyl-6-(N-morpholino)-1,2-dihydrocyclobuta[c]benzopyran-3-one (VIII). After irradiation for 9 h, 1.16 g (5 mmole) of coumarin III and 8.3 g (80 mmole) of styrene gave 0.90 g (54%) of VIII with R_f 0.35 [hexane–acetone (3:1)]. Mass spectrum, m/z (%): 335 (5), 231 (95).

1-endo-Phenyl-2a-carbethoxymethyl-8b-methyl-1,2-dihydrocyclobuta[c]benzopyran-3-one (IX). After irradiation for 9 h, 1.63 g (5 mmole) of coumarin IV and 10.40 g (100 mmole) of styrene gave 0.97 g (46%) of IX with R_f 0.29 [hexane–acetone (3:1)]. Mass spectrum, m/z (%): 421 (6), 325 (91).

1-endo-Phenyl-12b-methyl-1,2,6,7,10,11-hexahydro-3H,5H,9H-[1]-cyclobuta[c]benzopyrano[6,7,8-ij]quinolizin-3-one (X). After irradiation for 10 h, 1.28 g (5 mmole) of coumarin V and 10.40 g (100 mmole) of styrene gave 0.58 g (32%) of X with R_f 0.40 [hexane–acetone (3:1)]. Mass spectrum, m/z (%): 359 (1), 255 (95).

LITERATURE CITED

1. M. A. Kirpichenok, L. M. Mel'nikova, L. K. Denisov, and I. I. Grandberg, Khim. Geterotsikl. Soedin., No. 9, 1169 (1988).
2. T. Naito, N. Nakayama, and C. Kaneko, Chem. Lett., No. 3, 423 (1981).
3. A. G. Gonzalez, J. T. Barroso, Z. D. Jorge, and L. F. Rodriguez, Fis. Nat., 75, 811 (1981).
4. S. K. Gorozhankin, M. A. Kirpichenok, N. A. Klyuev, and I. I. Grandberg, Izv. Timiryazev. Skh. Akad., No. 4, 151 (1986).
5. D. J. Haywood, R. G. Hunt, C. J. Potter, and S. T. Reid, J. Chem. Soc., Perkin 1, No. 22, 2458 (1977).
6. J. W. Hanifin and E. Cohen, Tetrahedron Lett., No. 13, 1419 (1966).
7. M. A. Kirpichenok, I. I. Grandberg, L. K. Denisov, and L. M. Mel'nikova, Izv. Timiryazev. Skh. Akad. No. 3, 172 (1985).
8. G. R. Evanega and D. L. Fabing, J. Org. Chem., 35, 1757 (1970).
9. F. D. Lewis and R. J. De Voe, J. Org. Chem., 45, 948 (1980).
10. I. I. Grandberg, I. K. Yakushchenko, and L. B. Dmitriev, Zh. Org. Khim., 15, 89 (1979).
11. H. Günther, Introductory Course in NMR Spectroscopy [Russian translation], Mir, Moscow (1984), p. 480.
12. K. Ueno and N. Saito, Acta Cryst., B33, 283 (1977).
13. M. Kimura, W. H. Watson, P. Pacheco, and M. Silva, Cryst. Struct. Commun., 9, 257 (1980).
14. C. H. Schwalbe and P. G. Waterman, Acta Cryst., C39, 499 (1983).
15. N. S. Zefirov and V. A. Palyulin, Dokl. Akad. Nauk SSSR, 252, 111 (1980).
16. F. A. Cotton and B. A. Frenz, Tetrahedron, 30, 1587 (1974).
17. K. Raksanyi, M. Farkas, J. Fidy, and I. Tarjan, Acta Phys. Acad. Sci. Hung., 51, 51 (1981).
18. G. Barltrop and G. Coyle, Excited States in Organic Chemistry [Russian translation], Mir, Moscow (1978), p. 446.
19. H. Morrison and P. P. Wells, J. Am. Chem. Soc., 97, 154 (1975).
20. S. C. Shim and D. Y. Chi, Chem. Lett., No. 11, 1229 (1978).

21. F. D. Lewis, Acc. Chem. Res., 12, 152 (1979).
22. S. Parker, The Photoluminescence of Solutions [Russian translation], Mir, Moscow (1972), p. 510.
23. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, Kristallografiya, 28, 1029 (1983).

2-BENZOPYRYLIUM SALTS.

33.* 4-1'-DIMERIZATION OF 2-BENZOPYRYLIUM SALTS. FORMATION OF BENZ[*a*]ANTHRACENES

Yu. A. Zhdanov, S. V. Verin,
I. V. Korobka, and E. V. Kuznetsov

UDC 547.814.1'672.1

The conversion of 2-benzopyrylium salts to benz[*a*]anthracenes, which proceeds through prior dimerization of a new type, was observed. An intermediate dimer was isolated, its properties were studied, and assumptions regarding the mechanisms of its formation and conversion to benz[*a*]anthracenes, cenes were expressed.

We have recently described the formation of chrysenes from 1-(α)-methyl-2-benzopyrylium salts [2, 3]; it was shown [3] that in the presence of bases the reaction proceeds via prior α-1'-dimerization. Under these conditions the 2-benzopyrylium salt, acting as a CH acid, is deprotonated with the formation of the anhydro base, the unshielded (by substituents) nucleophilic exo-methylene group of which reacts with the cation of the unchanged salt. The anhydro base molecule can be regarded as a cyclic divinyl ether in which the reaction center is the exocyclic double bond; the endocyclic fragment of the vinyl ether does not participate in this reaction.

If, however, the 2-benzopyrylium salt is not deprotonated but adds a nucleophile, the vinyl ether fragment that develops in the resulting adduct is capable of participating in dimerization of a new type. However, only opening of the heteroring with the subsequent occurrence of intramolecular recyclization reactions has thus far been observed in adducts of the II type under the conditions used to realize the electrophilic-nucleophilic reaction of 2-benzopyrylium salts [4, 5].

We have observed that a product of new 4-1'-dimerization (IIIa) is formed in quantitative yield when 1-phenyl-3-methyl-2-benzopyrylium perchlorate Ia is maintained in the two-phase 10% aqueous alkali—ether system at 20°C (on top of following page).

The presence of two asymmetric centers in dimer IIIa molecule leads to its isolation from the reaction in the form of a mixture of two diastereomers in a ratio of ~1:1, from which one diastereomer (monitoring by means of the PMR spectra) was obtained after three recrystallizations from acetonitrile.

Absorption bands of two carbonyl groups at 1650 and 1725 cm^{-1} are present in the IR spectrum of this diastereomer. The weak-intensity band at 1675 cm^{-1} is related to the vibrations of the C═C bond of the vinyl ether of the isochromene ring. The retention of the isochromene ring is also confirmed by the weak splitting of the methyl group in the 3 position of the heteroring (J = 0.8 Hz), which is due to allylic coupling of the methyl group with the vinyl proton, the signal of which is also somewhat broadened.

---

*See [1] for Communication 32.

Scientific-Research Institute of Physical and Organic Chemistry, M. A. Suslov Rostov State University, Rostov-on-Don 344071. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1185-1189, September, 1988. Original article submitted April 6, 1987.

0009-3122/88/2409-0974$12.50