SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF 7-DIETHYLAMINO-4-(2-ARYLETHENYL)COUMARINS

I. I. Tkach, N. A. Andronova, L. P. Savvina,
and E. A. Luk'yanets

UDC 547.814.1.04:535.37

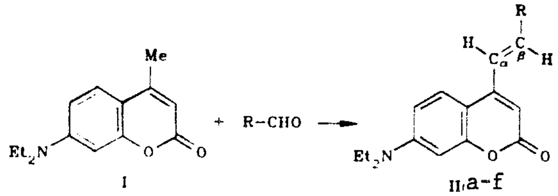
A number of 7-diethylamino-4-(2-arylethenyl)coumarins were obtained by condensation of 7-diethylamino-4-methylcoumarin with aromatic aldehydes, while only a product of addition to the carbon—nitrogen double bond is formed with benzalaniline. The spectral-luminescence properties of the compounds obtained were investigated.

Coumarin derivatives with electron-donor substituents in the 7-position are of interest as organic luminophores [1] and effective laser dyes of the blue-green region of the spectrum [2].

It is known that the introduction of substituents into the pyran part of the molecule has a substantial effect on the spectral-luminescence properties of coumarin derivatives. The presence of an activated methyl group in the 4 position for most luminophores of the coumarin series makes realization of condensation reactions with its participation tempting, particularly for obtaining previously unknown 7-diethylamino-4-(2-arylethenyl)coumarins by a condensation of the Knoevenagel type in the reaction of 7-diethylamino-4-methylcoumarin (I) with aromatic aldehydes.

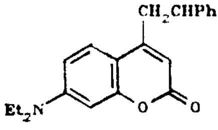
4-Styrylcoumarins (with a free 7 position) have been previously obtained either by condensation of 4-coumarinylacetic acid with aromatic aldehydes [3-6], which gives the products in low yields, or from 2-hydroxychalcones as a result of their reaction with phenylacetic acid derivatives (only 3-aryl-substituted 4-styrylcoumarins) [4] of with $Ph_3P{=}CHCOOEt$ via the Wittig reaction [7]. The known attempts to obtain 4-styrylcoumarins by condensation of 4-methylcoumarins with various aldehydes were unsuccessful [4], presumably because of the low reactivity of the CH_3 group in the 4 position of coumarin [8].

We have accomplished the condensation of coumarin I with aromatic aldehydes in strongly basic media. Derivatives IIa-f were obtained in 9-50% yields when tert-BuOK was used as the condensing agent in DMSO at room temperature. Electron-acceptor substituents in the aldehyde molecule promote the reaction, while electron-donor substituents (p-hydroxy, p-methoxy, and p-amino groups), on the other hand, hinder it markedly. 7-Diethylamino-4-[2(4-aminophenyl)ethenyl]coumarin (IIg) was obtained by reduction of IIe.



II a $R{=}C_6H_5$; b R= 1-naphthyl; c R=4-pyridyl d $R{=}4\text{-}C_6H_4CHO$; e $R{=}4\text{-}C_6H_4NO_2$;
f $R{=}2\text{-}OH\text{-}4\text{-}Et_2NC_6H_3$

A product (III) of addition to the carbon—nitrogen double bond of benzalaniline is formed instead of the expected IIa in the reaction of I with benzalaniline.



III

The structures of the compounds obtained were confirmed by the results of elementary analysis and the PMR and mass spectra (Tables 1 and 2).

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 319-322, March, 1991. Original article submitted September 27, 1989; revision submitted May 21, 1990.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	mp, °C	Mass spectrum, M^+	Spectral luminescence characteristics				Yield, %
				solvent	λ_{max}^{abs}, nm (log ε)	λ_{max}^{lum}, nm	quantum yield, η	
I	$C_{14}H_{17}NO_2$	73...74	—	a	243 (4,16), 315 (3,54), 375 (4,38)	450	0,50±0,02	—
				b	318 sh(3,65), 360 (4,34)	425	0,62±0,02	
II a	$C_{21}H_{21}NO_2$	138...139	319	a	278 (3,95), 320 (4,20), 415 (4,11)	570	0,15±0,02	30
				b	283 (4,14), 344 (4,00), 387 (4,20)	490	0,16±0,02	
II b	$C_{25}H_{23}NO_2$	173...174	369	a	258 (4,04), 325...335 sh (3,95), 370 (4,18)	470, 565	0,16±0,02	16
				b	330 (4,20), 360 (4,20)	430, 535	0,12±0,02	
II c	$C_{20}H_{20}N_2O_2$	147...148	320	a	297 (4,30), 330...340sh (4,00), 420 (4,04)	585	0,10±0,02	12
				b	287 (4,14), 348 (4,20), 405 (4,14)	495	0,26±0,03	
II d	$C_{22}H_{21}NO_3$	165...166	347	a	266 (4,04), 327 (4,40), 415 sh (3,90)	585	0,05±0,02	48
				b	280 sh (4,13), 329 (4,27), 390 (4,03)	635	0,12±0,03	
II e	$C_{21}H_{20}N_2O_4$	231...232	364	a	265 (4,04), 335 (4,54), 432 sh (4,00)	Very weak luminescence		51
				b	282 sh(4,10), 345 (4,37), 425 (3,80)	550	0,12±0,03	
II f	$C_{25}H_{30}N_2O_3$	227...228	406	a	278 (4,32), 423 (4,48)	575	0,18±0,03	9
				b	280 sh (4,19), 398 (4,42)	535	0,12±0,02	
II g	$C_{21}H_{22}N_2O_2$	147...148	334	a	282 (4,26), 395 (4,40)	560	0,11±0,02	74
				b	280 (4,19), 378 (4,38)	520	0,09±0,02	
III	$C_{27}H_{28}N_2O_2$	150...151	412	a	247 (4,37), 382 (4,30)	465	0,08±0,02	48
				b	305 sh(3,82), 370 (4,34)	425	0,34±0,03	

Note. a) Ethanol; b) toluene.

TABLE 2. PMR Spectra of II in $CDCl_3$

Compound	Chemical shifts, ppm						SSCC (J, Hz)		
	3-H, s	5-H, d	6-H, dd	8-H, d	α-H, d	β-H, d	J_{56}	J_{68}	$J_{\alpha,\beta}$
IIa	6,25	7,56	6,59	6,53	7,46	7,37	8,9	2,5	14,9
IIb	6,36	7,59	6,59	6,55	8,04	7,34	9,1	2,6	15,7
IIc	6,23	7,50	6,59	6,53	7,47	7,16	8,9	2,6	16,0
IId	6,24	7,54	6,59	6,53	7,42	7,28	9,0	2,6	16,1
IIe	6,23	7,52	6,59	6,52	7,43	7,28	9,0	2,5	16,1
IIf	6,41	7,66	6,60	6,54	7,83	7,12	9,0	2,5	15,9
IIg	6,20	7,57	6,57	6,51	7,21	7,08	9,0	2,6	16,0
IIa*	6,27	7,25	6,25	6,43	7,01	6,86	8,9	2,5	16,1

*The spectrum of IIa was recorded in C_6D_6.

In the PMR spectra of II in $CDCl_3$ the signals of the protons of the coumarin system are found in the region that is customary for such compounds [9], while the signals of the α-H and β-H protons attached to the double bond are found at 7.0-8.1 ppm in the form of two doublets with SSCC $J_{\alpha,\beta}$ ~16 Hz, which is evidence in favor of a trans-configuration for these compounds.

According to the spectral-luminescence characteristics, the long-wave absorption maximum of all coumarins II except IIb undergoes a significant bathochromic shift as compared with starting coumarin I; the intensity of the long wave band does not change when the substituent in the 4 position has electron-donor character and decreases when an electron-acceptor substituent is present in this position. The slight effect of substitution on the position of the long wave absorption band of IIb is possibly due to the large volume of substituent R (R = naphthyl) attached to the ethylene double bond.

An additional band at 330-350 nm in toluene and 320-335 nm in ethanol with an intensity that, in a number of cases, exceeds that of the long-wave band appears in the absorption spectra of IIa-e.

Compounds II have fluorescence; however, its quantum yield is low ($\eta < 0.2$) with a Stokesian shift of up to 165 nm. The large Stokesian shift is evidently due to the fact that the molecule in the excited state becomes more planar, and the effective conjugation chain increases [10].

EXPERIMENTAL

The PMR spectra of saturated solutions of II in $CDCl_3$ were recorded with a Bruker AM-400 spectrometer under pulse-buildup conditions at 40°C with an internal standard [tetramethylsilane (TMS)]. The electronic absorption spectra were recorded with an SF-26 spectrophotometer. The fluorescence spectra were measured with an apparatus of the SDL-1 type with a DKSSh-1000 lamp as the source of excitation. The spectra were corrected for the sensitivity of the apparatus. The fluorescence quantum yield (η) was measured relative to a standard, viz., 3-aminophthalimide ($\eta = 6.0$ [11]). The mass spectra were recorded with an MKh-1320 mass spectrometer at an ionizing voltage of 50 eV.

The results of elementary analysis of IIa-g and III for C, H, and N were in agreement with the calculated values.

General Method for Obtaining 7-Diethylamino-4-(2-arylethenyl)coumarins (IIa-f). A mixture of 10 mmoles of coumarin I and 10 mmole of tert-BuOK in 15 ml of DMSO was stirred for 10 min, after which 15 mmole of the aromatic aldehyde was added, and the mixture was stirred (~20°C, 5 h). The reaction mass was then poured into 100 ml of water, and the aqueous mixture was neutralized with acetic acid. The precipitated coumarins IIa, b, e were recrystallized from aqueous DMF, while coumarins IIc, d, f were recrystallized from aqueous ethanol; IIa, b, c, f were purified beforehand by column chromatography (silica gel, benzene—ethyl acetate).

7-Diethylamino-4-[2-(4-aminophenyl)ethenyl]coumarin (IIg). A 0.78-g (14 mmole) sample of activated iron powder was added to a suspension of 0.73 g (2 mmole) of IIe in 20 ml of 90% ethanol, and the reaction mass was refluxed for 1.5 h. The sludge was removed by filtration and washed with 30 ml of hot ethanol, the combined filtrate was poured into 200 ml of water, and the product was extracted with ethyl acetate (three 70-ml portions). The extract was dried over $CaCl_2$, the solvent was evaporated in vacuo, and the residue was recrystallized from aqueous ethanol to give 0.50 g (74%) of IIg.

7-Diethylamino-4-(2-anilino-2-phenylethyl)coumarin (III). A solution of 2.31 g (10 mmoles) of coumarin I, 2.72 g (15 mmole) of benzalaniline, and 2.24 g (20 mmole) of tert-BuOK in 20 ml of DMFA was stirred for 2 h at 40-45° in a stream of argon, after which the reaction mixture was poured into 200 ml of water, and the aqueous mixture was neutralized with 5% hydrochloric acid. The product was extracted with ethyl acetate (three 70-ml portions), and the extract was dried over $CaCl_2$ and evaporated in vacuo. The residue was purified by column chromatography [silica gel, benzene—ethyl acetate (5:1)] and recrystallized from benzene—heptane to give 1.98 g (48%) of III.

LITERATURE CITED

1. B. M. Krasovitskii and B. M. Bolotin, *Organic Luminophores* [in Russian], Khimiya, Moscow (1984), p. 145.
2. L. K. Denisov and B. M. Uzhinov, *Khim. Geterotsikl. Soedin.*, No. 6, 723 (1980).
3. B. B. Dey and K. K. Row, *J. Indian Chem. Soc.*, 1, 107 (1924).
4. H. S. Mahal and K. Venkataraman, *J. Chem. Soc.*, 616 (1933).
5. A. Mustafa and M. Kamel, *J. Am. Chem. Soc.*, 77, 1828 (1955).
6. A. Mustafa and M. Kamel, *J. Am. Chem. Soc.*, 78, 4692 (1956).
7. U. K. Joshi, R. M. Kelkar, and M. V. Paradkar, *Indian J. Chem.*, 22B, 1151 (1983).
8. G. P. Ellis, in: *Comprehensive Heterocyclic Chemistry*, Vol. 3, A. R. Katritzky and C. W. Rees (eds.), Pergamon Press, Oxford—New York (1984), p. 690.
9. M. A. Kirpichёnok, I. I. Grandberg, L. K. Denisov, and L. M. Mel'nikova, *Izv. Timiryazev. Sel'skokhoz. Akad.*, No. 3, 172 (1985).
10. E. M. Vernigor, M. V. Koz'menko, S. A. Lebedev, E. A. Luk'yanets, L. P. Savvina, and V. K. Shalaev, *Khim. Geterotsikl. Soedin.*, No. 6, 820 (1987).
11. J. N. Demas and G. A. Grosby, *J. Phys. Chem.*, 75, 997 (1971).

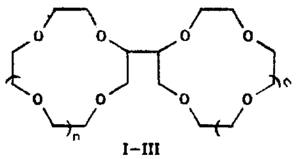
MASS SPECTROMETRY OF MACROHETEROCYCLES.
1. MASS SPECTRA OF ISOMERIC BICYCLIC CROWN ETHERS

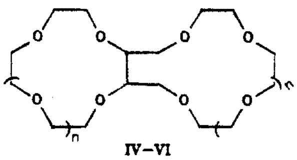
A. I. Gren', A. V. Mazepa, A. V. Lobach,
N. G. Luk'yanenko, and O. S. Timofeev

UDC 547.543.51:547.898

The fundamental, fragmentation paths under electron impact of bridged crown ethers and the condensed, bicyclic crown ethers isomeric to them have been established by means of a combination of techniques (DADI, metastable defocusing, high resolution). The mass spectral criteria of the compounds in the series considered have been determined, as well as the characteristic ion peaks, the intensity of which permit the isomeric compounds to be distinguished.

The fragmentation of the basic kinds of crown ethers by electron impact has been studied in [1-7]. It has been shown that, for crown ethers with the general formula 3n-crown-n and for macrocyclic, polyoxaethylenethioureas, the nonvalance C—H···O [1] and N—H···O [5] interactions in the molecules of these compounds determine the path of dissociative ionization under the conditions of the mass-spectroscopic experiment. In a continuation of our investigations [8], the present work deals with a study of the fragmentation paths of bicyclic, crown ethers of type I-VI.


I-III


IV-VI

I, IV n=1; II, V n=2; III, IV n=3

A. V. Bogatskii Physical Chemical Institute, Academy of Sciences of the Ukrainian SSR, Odessa. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 323-326, March, 1991. Original article submitted July 24, 1989; revision submitted October 2, 1989.