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SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF 4,4'-DI(2-OXAZOLYL)-STILBENES AND 4,4'-DI(2-OXAZOLYL)TOLANS

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A new method is proposed for the synthesis of 4,4'-di(2-oxazolyl)stilbenes and 4,4'-di(2-oxazolyl)tolans by condensation of oxazolyl-substituted benzyl bromides or benzal dibromides under the influence of strong bases (KOH, potassium tert-butoxide) in dipolar aprotic solvents [dimethylformamide (DMF) and dimethyl sulfoxide (DMSO)]. The synthesized compounds luminesce intensely over the spectral range 386-492 nm.

Compounds of the stilbene and tolan series that contain oxazole fragments have intense luminescence in the blue region of the spectrum [1, 2]. 4,4'-Di(2-oxazolyl)stilbenes are used as optical bleaches [1]. In addition, 4,4'-di(2-oxazolyl)stilbene is known as an active substance for lasers [3]. Less study has been devoted to the difficult-to-obtain 4,4'-di(2-oxazolyl)tolans; however, there are data that indicate that they can also be used as optical bleaches [4].

At present there are no convenient methods for the preparation of dioxazolyl-substituted stilbenes and tolans, and this significantly hinders the study of their spectral-luminescence properties. The usual methods for the synthesis of 4,4'-di(2-oxazolyl)stilbenes are based on the cyclodehydration of substituted amides of stilbene-4,4'-dicarboxylic acid [1, 5]. The specific method for their preparation consists in the oxidative dimerization of 2-(p-tolyl)oxazoles [1, 6]. The synthetic methods based on the Wittig—Horner reac-

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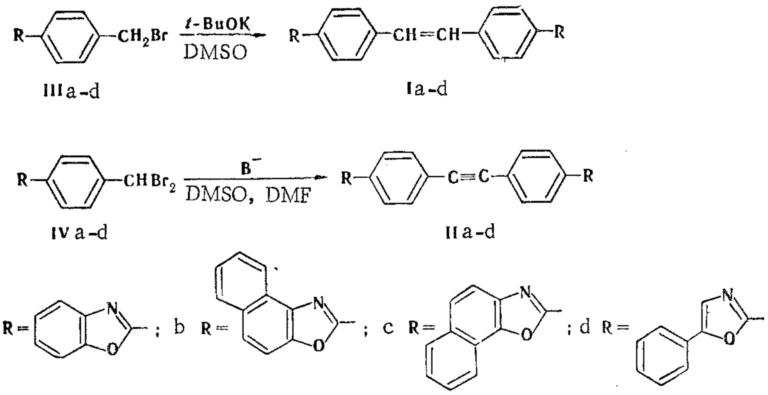
TABLE 1. Benzyl Bromides (IIIa-d) and Benzal Dibromides (IVa, d)

Compound	mp, °C	Found, %	Empirical formula	Calc., %	Yield, %
		Br (N)		Br (N)	
III a	173 [13]	—	$C_{14}H_{10}BrNO$	—	91
III b	210	(3,9)	$C_{18}H_{12}BrNO$	(4,1)	96
III c	218	(4,0)	$C_{18}H_{12}BrNO$	(4,1)	93
III d	130 [14]	—	$C_{16}H_{12}BrNO$	—	98
IV a	120	43,5	$C_{14}H_9Br_2NO$	43,5	92
IV d	204	40,8	$C_{16}H_{11}Br_2NO$	40,7	89

tion [7] or on the dehydrogenation of the corresponding dibenzils [8] use difficult-to-obtain starting compounds. The only known method for the preparation of 4,4'-di(2-oxazolyl)-tolans is condensation of derivatives of tolan-4,4'-dicarboxylic acid with o-aminophenols [2, 4]. Most of the indicated reactions are carried out at high temperatures, while the yields are low in the remaining cases.

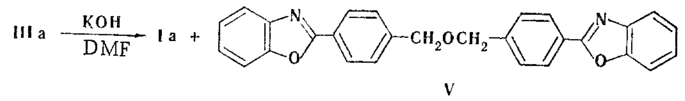
For the synthesis of 4,4'-di(2-oxazolyl)stilbenes (Ia-d) and 4,4'-di(2-oxazolyl)tolans (IIa-d) we used the condensation of oxazolyl-substituted benzyl bromides (IIIa-d) or benzal dibromides (IVa-d) under the influence of strong bases in dipolar aprotic solvents.



The method for the preparation of stilbenes from benzyl halides is quite well known [9, 10], but we used it for the first time for the preparation of dioxazolylstilbenes. The method for the synthesis of dioxazolyltolans from the corresponding benzal dibromides is new and was recently proposed in [11]. We showed that this method can also be used to synthesize other symmetrical tolans [12]. The peculiarities of the reaction will be set forth in a separate communication.

Starting benzyl bromides IIIa-d and benzal dibromides IVa-d were obtained by bromination of the corresponding 2-(p-tolyl)oxazoles with N-bromosuccinimide (NBS) (Table 1). The bromination of isomeric 2-(p-tolyl)naphthoxazoles stops at the step involving the benzyl bromides, and IVb, c were therefore obtained by condensation of α,α-dibromo-p-toluic acid with aminonaphthol hydrochlorides in polyphosphoric acid esters (resinification is observed in the acid itself).

4,4'-Di(2-benzoxazolyl)stilbene (Ia) (7%) and 4,4'-di(2-benzoxazolyl)dibenzyl ether (V) (51%) — the product of nucleophilic substitution of the bromine atom — were obtained in the reaction of 4-(2-benzoyl)benzyl bromide (IIIa) with powdered KOH in DMF and 20°C for 1 h.



A considerable amount of V is also formed in DMSO in the presence of KOH. The reaction of IIIa with a stronger base, viz., potassium tert-butoxide in DMSO, leads to individual Ia in 92% yield. Under the same conditions IIIb-d are converted to the corresponding Ib-d in ∿90% yields (Table 2).

The joint formation of Ia and V constitutes evidence for competition between deprotonation, which is the first step in the conversion of benzyl halides to stilbenes [9], and

TABLE 2. 4,4'-Di(2-oxazolyl)stilbenes (Ia-d) and 4,4'-Di(2-oxazolyl)tolans (IIa-d)

Compound	mp, °C	λ_{max} abs, nm (log ε)[a]	λ_{max} lum, nm (η, %)[a]	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
Ia	362 [6]	354 (4,75), 370 (4,77), 388[b] (4,49)	408, 433[a], 457; (68)				$C_{28}H_{18}N_2O_2$				92
Ib	322 [15]	372[b] (4,71), 388 (4,75), 406[b] (4,56)	436, 461[c], 492[b]; (66)				$C_{36}H_{22}N_2O_2$				99
Ic	325	372 (4,72), 387 (4,76), 406[b] (4,53)	429, 455[c], 483; (70)	83,8	4,5	5,2	$C_{36}H_{22}N_2O_2$	84,0	4,3	5,4	97
Id	247 [5]	366[b] (4,73), 380 (4,76)	425, 449[c], 477[b] (87)				$C_{32}H_{22}N_2O_2$				86
IIa	351 [4]	348 (4,84), 372 (4,72)	386[c] 408, 430[b], (89)				$C_{28}H_{16}N_2O_2$				95
IIb	336	371 (4,83), 392 (4,68)	415, 439[c], 463; (74)	84,2	4,1	5,6	$C_{36}H_{20}N_2O_2$	84,4	3,9	5,5	94
IIc	328	368 (4,79), 390 (4,66)	409, 432[c], 457; (64)	84,3	4,0	5,5	$C_{36}H_{20}N_2O_2$	84,4	3,9	5,5	87
IId	230	362 (4,80), 385 (4,68)	403[c] 424, 448[b], (77)	82,6	4,6	6,0	$C_{32}H_{20}N_2O_2$	82,7	4,3	6,0	46

[a] In chloroform. [b] Shoulder. [c] Chief maximum.

nucleophilic substitution. When the basicity of the medium is increased, deprotonation predominates over nucleophilic substitution, and this leads to an increase in the yield of the stilbene.

In contrast to benzyl bromide IIIa, 4-(2-benzoxazolyl)benzal dibromide (IVa) reacts with KOH in DMF to give a condensation product, viz., 4,4'-di(2-benzoxazolyl)tolan (IIa) (64%) rather than a nucleophilic substitution product. Thus the introduction of another bromine atom in the bromomethyl group of IIIa evidently increases the acidity of the hydrogen atom so much that deprotonation (the first step in the condensation [16]) proceeds readily in a less basic medium than in the case of IIIa. Under the same conditions tolan IId is formed from benzal dibromide IVd in 46% yield. The reaction of IVa-c with potassium tert-butoxide in DMSO leads to IIa-c in ~90% yields.

Absorption bands at 970 cm^{-1}, which are characteristic for the deformation vibrations of the C–H bonds of trans-disubstituted alkenes [17], are present in the IR spectra of stilbenes Ia-d. The structure of IIa was confirmed by alternative synthesis.

The electronic absorption and luminescence spectra of the synthesized compounds were measured (Table 2). Dioxazolylstilbenes Ia-d absorb in a longer-wave region that the corresponding tolans IIa-d, in agreement with the data in [2]. In each series of compounds substituted 5-phenyloxazole and naphthoxazole fragments with a longer effective conjugation chain also have the longest-wave absorption. A fine structure appears in the spectra of stilbenes Ia-d; the fine structure is less resolved in the spectra of tolans IIa-d.

Solutions of all of the investigated compounds luminesce intensely in the blue region of the spectrum. The Stokesian shifts for stilbenes Ia-d are 63-73 nm, as compared with 38-64 nm for tolans IIa-d. The synthesized dioxazolylstilbenes and dioxazolyltolans have high absolute luminescence quantum yields (η); this is characteristic for compounds in which the oxazole groups are conjugated with stilbene or tolan fragments [18].

A study of the generation properties of the synthesized compounds showed that they are efficient transformers of laser emission that generate in the 410-435 nm spectral range with high transformation coefficients [19, 20].

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The electronic absorption spectra of solutions of the compounds in chloroform were recorded with a Hitachi-356 spectrophotometer. The luminescence spectra were recorded with an apparatus assembled on the basis of an MDR-3 monochromator. The luminescnece was excited by the light of a DKSSh-200 lamp isolated with a UFS-2 filter. The absolute luminescence quantum yields (η) were determined by a relative method with an ethanol solution of 3-aminophthalimide (η 60%) as the standard [21]. The PMR spectrum of a solution of V in trifluoroacetic acid was recorded with a Tesla BS-467 spectrometer (60 MHz) with tetramethylsilane as the internal standard. The mass spectrum of V was obtained with a Varian Match-6 spectrometer.

The starting 2-(p-tolyl)oxazoles were obtained by known methods [22].

Benzyl Bromides (IIIa-d) and Benzal Dibromides (IVa, d) (Table 1). The necessary amount of N-bromosuccinimide (NBS) (0.011 mole for the benzyl bromides and 0.022 mole for the benzal dibromides) and a catalytic amount of azobisisobutyronitrile were added with stirring to a suspension of 0.01 mole of 2-(p-tolyl)oxazole in 50 ml of refluxing CCl_4, and the mixture was refluxed for 3 h. The CCl_4 was removed by distillation, and the residue was washed thoroughly with boiling water, dried, and recrystallized from a suitable solvent (heptane, ethyl acetate, ethanol, and acetone).

Benzal Dibromides (IVb, c). A mixture of 1.96 g (10 mmole) of aminonaphthol hydrochloride and 10 g of polyphosphoric acid esters was heated to 100°C, 4.41 g (15 mmole) of α,α-dibromo-p-toluic acid [23] was added, and the mixture was stirred at 120-140°C for 45 min. It was then cooled and treated with ice, and the precipitate was removed by filtration, washed successively with water, $NaHCO_3$ solution, and water, and dried. The substances obtained [2.5 g (60%)] were used without further purification.

Reaction of 4-(2-Benzoxazolyl)benzyl Bromide (IIIa) with KOH in DMF. A 2.25-g sample of powdered KOH was added with stirring to a solution of 2.88 g of IIIa in 100 ml of DMF, and the mixture was stirred at 20°C for 1 h. It was then acidified with 10% HCl while cooling with ice, and the precipitate was removed by filtration, washed to neutrality with water, and dried. The product (1.4 g) was chromatographed on Al_2O_3 with chloroform. Workup of the first fraction gave 1.1 g (51%) of dibenzyl ether V with mp 235-237°C (from xylene). PMR spectrum, δ: 7.4-8.7 (s, 16H, aromatic) and 4.86 ppm (s, 4H, CH_2). Found: C 77.7; H 4.6; N 6.1%. M (by mass spectrometry) 432. $C_{28}H_{20}N_2O_3$. Calculated: C 77.8; H 4.7; N 6.5%; M 432. The last fraction contained stilbene Ia {0.14 g (7%) with mp 358-360°C [6]}.

Stilbenes (Ia-d) and Tolans (IIa-c) (Table 2). A 0.04- or 0.08-mole (4.5 or 9 g) sample of potassium tert-butoxide was added with stirring to a solution of 0.01 mole of benzyl bromide or benzal dibromide in 100 ml of DMSO, and the mixture was stirred at 20°C for 1 h. It was then acidified with 10% HCl while cooling with ice, and the precipitate was removed by filtration, washed to neutrality with water, and dried. To obtain analytical samples the substances were recrystallized from DMF or trichlorobenzene.

4,4'-Bis(5-phenyl-2-oxazolyl)tolan (IId). This compound was obtained in 46% yield by the method used to obtain tolans IIa-c in DMF in the presence of powdered KOH.

4,4'-Di(2-benzoxazolyl)tolan (IIa). This compound was also obtained from tolan-4,4'-dicarboxylic acid dichloride and o-aminophenol by the method in [4].

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ORGANODIMAGNESIUM DERIVATIVES OF THIOPHENE.

3.* SYNTHESIS OF AN ORGANODIMAGNESIUM DERIVATIVE OF HEXABROMO-2,2'-DITHIENYL AND ITS REACTION WITH OXALIC ACID ESTERS

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It was established that the reaction of hexabromo-2,2'-dithienyl with magnesium in the presence of ethyl bromide gives an organodimagnesium derivative, which reacts with oxalic acid esters to give 3,3',4,4'-tetrabromo-5,5'-dithienyl-diglyoxalic acid esters. Reduction of the latter with ethylmagnesium bromide leads to 3,3',4,4'-tetrabromo-5,5'-dithienyl-2,2'-diglycolic acid esters.

In contrast to monomagnesium derivatives, organodimagnesium compounds are substances to which little study has been devoted both in a theoretical respect and with respect to their practical application; this is reflected in the amount of published data pertaining to these classes of compounds [2]. The formation of an organodimagnesium derivative of thiophene was established for the first time by Thomas [3] and was subsequently confirmed by others [4, 5]. After this, these compounds did not attract the attention of researchers for a long time, although the possibility of the simultaneous introduction of two functional groups in the thiophene ring by means of organodimagnesium compounds is of doubtless interest, as confirmed by research on dilithium compounds [6].

It was subsequently shown that 2,5-diiodothiophene [7] and 3,4-dibromo- and 3-bromo-2,5-diiodothiophenes in the presence of ethyl bromide smoothly form organodimagnesium compounds [8]. An organodimagnesium derivative was also obtained under the same conditions in the 2,2'-dithienyl series from 5,5'-dibromo-2,2'-dithienyl [1].

In a continuation of these studied we investigated the possibility of the preparation of an organodimagnesium derivative from hexabromo-2,2'-dithienyl (I) and its reaction with oxalic acid esters (II).

As in the case of 5,5'-dibromo-2,2'-dithienyl, attempts to obtain an organodimagnesium derivative (III) of hexabromo-2,2'-dithienyl by direct reaction between the components or "accompanied" by 1,2-dibromoethane (at a molar ratio of I to dibromoethane of 1:8) in ether

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*See [1] for Communication 2.

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