VINYL DERIVATIVES OF 2,5-DIARYL-1,3,4-OXADIAZOLES

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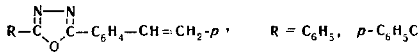
Vinyl derivatives of 2,5-diaryl-1,3,4-oxadiazoles have been synthesized and some of their physical properties have been studied.

Solid solutions of many 2,5-diaryl-1,3,4-oxadiazoles in polystyrene are effective plastic scintillators [1,2]. In the present communication we describe vinyl derivatives of 2,5-diaryl-1,3,4-oxadiazoles.



$R = C_6H_5,\ p\text{-}C_6H_5C_6H_4,\ \beta\text{-}C_{10}H_7$

By copolymerizing them with styrene or other monomers it is possible to obtain plastic scintillators the polymer chains of which contain the structural groupings responsible for the scintillation properties.

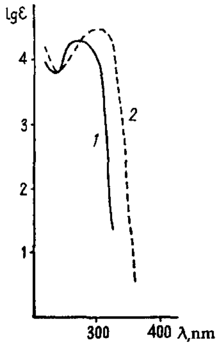
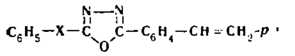


Fig. 1. UV spectra of: 1)2,5-diphenyl-1,3,4-oxadiazole; 2) 5-phenyl-2-(p-vinylphenyl)-1,3,4-oxadiazole.

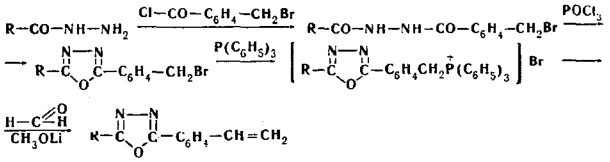
According to the literature [3,4] such scintillators are more effective than solid solutions of luminophores in polymers. It is not excluded that these copolymers will possess a high light fastness because of the capacity of the diaryloxazole links of the polymer chain for converting UV light into visible light which is less harmful to them.

In addition to the vinyl derivatives of the diaryloxazoles, vinyl monomers containing bridges interrupting the chain of conjugation between the heterocycle and the aryl radical have been obtained.



$X = CH_2,\ O\text{—}CH_2$

The synthesis of the monomers was effected by a method ensuring the production of compounds with a strictly fixed position of the vinyl group in the aromatic nuclei



In the acylation of the monohydrazides with acid chlorides, part of the hydrazide reacted with the hydrogen chloride liberated [5]. To decrease the loss of hydrazide, the reaction was frequently carried out in pyridine. The presence of a bromomethyl group in the molecule of p-bromomethylbenzoic acid, with which we worked, apparently leads to the formation of water-soluble pyridinium salts, which interfered with the formation and isolation of the dihydrazides.

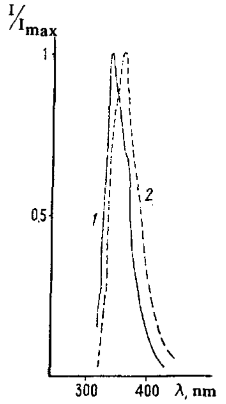


Fig. 2. Luminescence spectra of: 1) 2,5-diphenyl-1,3,4-oxadiazole; 2) 5-phenyl-2-(p-vinylphenyl)-1,3,4-oxadiazole.

As solvent we used chlorobenzene, at whose boiling point the monohydrazide hydrochloride decomposes,

Table 1

$R\text{—}CO\text{—}NH\text{—}NH\text{—}CO\text{—}C_6H_4\text{—}CH_2Br\text{-}p$

Compound	R	Mp, °C	Empirical formula	N, % found	N, % calculated	Yield, %
I	C_6H_5	198 —200	$C_{15}H_{13}BrN_2O_2$*	—	—	91
II	$p\text{-}C_6H_5C_6H_4$	215 —216	$C_{21}H_{17}BrN_2O_2$	6.73	6.84	28
III	$\beta\text{-}C_{10}H_7$	214.5—215.5	$C_{19}H_{15}BrN_2O_2$	7.53	7.31	80
IV	$C_6H_5CH_2$	168 —169	$C_{16}H_{15}BrN_2O_2$	8.31	8.07	42
V	$C_6H_5OCH_2$	180 —181	$C_{16}H_{15}BrN_2O_3$	7.78	7.71	56

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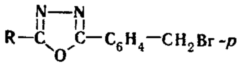
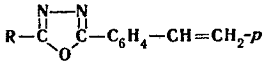
* Found, %: Br 23.91. Calculated, %: Br 24.02.

Table 2



Compound	R	Mp, °C	Empirical formula	Found, %		Calculated, %		Yield, %
				Br	N	Br	N	
VI	C_6H_5	156—157	$C_{15}H_{11}BrN_2O$	—	8.71	—	8.88	71
VII	p-$C_6H_5C_6H_4$	150—152	$C_{21}H_{15}BrN_2O$	20.49	—	20.46	—	24
VIII	β-$C_{10}H_7$	191—193	$C_{19}H_{13}BrN_2O$	—	7.41	—	7.67	25
IX	$C_6H_5CH_2$	204—205	$C_{16}H_{13}BrN_2O$	24.40	—	24.32	—	34
X	$C_6H_5OCH_2$	213—214.5	$C_{16}H_{13}BrN_2O_2$	—	8.13	—	8.11	25

Table 3



Compound	R	Mp, °C	UV spectra		Luminescence λ_{max}, nm	Empirical formula	N, %		Yield, %
			λ_{max}, nm	log ε			found	calculated	
XI	C_6H_5	82— 84	300	4.45	365	$C_{16}H_{12}N_2O$	11.20	11.29	40
XII	p-$C_6H_5C_6H_4$	148—150	312	4.73	370	$C_{22}H_{16}N_2O$	8.86	8.64	21
XIII	β-$C_{10}H_7$	116—117	310	4.54	370	$C_{20}H_{14}N_2O$	9.10	9.39	38.5
XIV	$C_6H_5CH_2$	231—232	280	4.42	365	$C_{17}H_{14}N_2O$	10.69	10.68	25
XV	$C_6H_5OCH_2$	168—169.5	270	3.38	—*	$C_{17}H_{14}N_2O_2$	9.70	10.07	35

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* Does not luminesce.

the hydrogen chloride being eliminated from the reaction zone. The starting materials were used in molecular amounts and the dihydrazides formed were used for further treatment without additional purification.

The last stages of the synthesis, the closure of the oxadiazole ring and the replacement of a bromomethyl group by a vinyl group by the Wittig method, took place without difficulties.

The monomers obtained were purified by crystallization from methanol, by chromatography of the benzene solutions on alumina (in columns protected from the light), and by recrystallization from methanol. The analyses and yields and some properties of the monomers and the intermediates for their synthesis are given in Tables 1–3.

The absorption and luminescence spectra of methanolic solutions of the monomers obtained did not differ in nature from one another nor from the spectra of their analogs containing no vinyl groups, but the vinyl groups caused a bathochromic displacement of the absorption maxima and, in the majority of cases, of the luminescence maxima (Figs. 1 and 2).

The replacement of the phenyl group in the vinyl derivative of diphenyloxazole by a biphenylyl or a β-naphthyl radical caused a similar bathochromic effect in the absorption and the luminescence spectra.

The introduction of a bridging grouping ($-OCH_2-$ and $-CH_2-$) interrupting the total chain of conjugation, led to a hypsochromic shift of the absorption spectra. The investigation of the scintillation efficiency of copolymers with styrene of the monomers that we have obtained will be the subject of a separate communication.

EXPERIMENTAL

1-Benzoyl-2-(p-bromomethylbenzoyl)hydrazine (I). A solution 2.72 g (0.02 mole) of benzhydrazide in 50 ml of chlorobenzene was treated with 4.66 g (0.02 mole) of p-bromomethylbenzoyl chloride and the mixture was boiled under reflux for about 3 hr, until the evolution of hydrogen chloride had ceased. First a gel-like mass was formed, and then a microdisperse precipitate separated out. After cooling, the precipitate was filtered off and washed with methanol. The yield of technical product with mp 196°–198° C was 6 g. After purification by crystallization from ethanol, it formed a colorless crystalline substance with mp 198°–200° C. Compounds II-V were obtained in the same way.

2-(p-Bromomethylphenyl)-5-phenyloxadiazole (VI). A mixture consisting of 3 g (0.009 mole) of I and 20 ml of phosphorous oxychloride was boiled for 1 hr, and the reaction mixture was poured onto ice. The solid substance was separated off, washed with water, dried, and crystallized from methanol. Yield 2 g (71%). Colorless crystalline substance, mp 156°–157° C.

Compounds VII-X were obtained in the same way.

5-Phenyl-2-p-vinylphenyloxadiazole (XI). A solution of 6.3 g (0.02 mole) of VI and 5.3 g (0.02 mole) of triphenylphosphine in 18 ml of dimethylformamide was boiled for 2 hr. The precipitate that deposited was filtered off and dissolved in 50 ml of methanol, and the solution was poured into a solution of 0.6 g (0.02 mole) of paraformaldehyde and 100 ml of 0.2 M lithium methoxide solution in methanol. The mixture was left for 3 hr with occasional stirring and was then diluted with water (100 ml); the precipitate that deposited was separated off, dried, and crystallized from ethanol, chromatographed on alumina in benzene, and again crystallized from ethanol. Yield 2 g (40%). Colorless crystalline substance; mp 82°–84° C. Compounds XII-XV were obtained similarly.

The absorption spectra were studied in a SF-4 spectrophotometer and the luminescence spectra in an apparatus consisting of a ZM-3 monochromator, a M-95 microammeter, and a FEU-18 [photoelectric multiplier]. The source of excitation was a DRSh-500 lamp, the exciting line at 313 nm of which was isolated by means of a DMR-4 monochromator.

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