ring potential for each compound corresponded to the foot of the first oxidation wave on the disk. A saturated calomel electrode served as the comparison electrode. The number of electrons was calculated by comparison with the one-electron wave of N,N-tetramethyl-p-phenylenediamine.

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HETERYLIMIDAZOLES.

VI.* 2-(N,N'-DIMETHYLBENZIMIDAZOLON-5-YL)-4,5-DIARYLIMIDAZOLES

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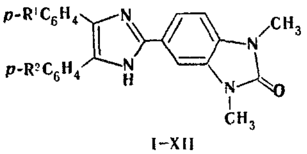
Condensation of 5-formyl-N,N'-dimethylbenzimidazolone with aromatic α-diketones gave 2-(N,N'-dimethylbenzimidazolon-5-yl)-4,5-diarylimidazoles, which are easily oxidized in alkaline media to imidazolyl free radicals. Some of the investigated heterylimidazoles also form radicals when chloroform solutions of them are irradiated. It is shown that the synthesized compounds are inhibitors of the thermal oxidative destruction of polyethylene oxide.

We have previously [1] investigated 4(5)-(N,N'-dimethylbenzimidazolon-5-yl)-2,5(4)-diarylimidazoles. The present paper is devoted to the synthesis and study of the properties of 2-DMBI-4,5-diarylimidazoles (I-XII).†



I-XII

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*See [1] for communication V.

†The abbreviation "DMBI" stands for N,N'-dimethylbenzimidazolon-5-yl.

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Heterylimidazoles I-XII (Table 1) were obtained by condensation of 5-formyl-N,N'-dimethylbenzimidazolone with the appropriate diketones in refluxing acetic acid in the presence of ammonium acetate.

As in the spectrum of 2,4,5-triphenylimidazole, two absorption bands with well-expressed maxima at 230 and 320 nm are observed in the UV spectra of most of the synthesized imidazoles I-XII (Table 1). Neither a ureylene grouping nor the introduction of para substituents in the phenyl rings in the 4 and 5 positions of imidazole substantially changes the character of the spectrum. Only the introduction of a nitro group gives rise to the appearance of another absorption band at 390 nm.

Like their 4-DMBI isomers [1], the 2-DMBI-substituted imidazoles are readily oxidized by sodium hypobromite in alkaline media to free radicals. Solutions of the radicals in toluene are green. They also generate a diphenylpicrylhydrazyl (DPPH) radical from α,α-diphenyl-β-picrylhydrazine and give an ESR signal.

Substituents have a greater effect on the spectra of the radicals (Fig. 1 and Table 1) than on the spectra of the corresponding imidazoles. Replacement of the phenyl residue in the 2,4,5-triphenylimidazolyl radical (XIIIa) by a DMBI residue in both the 2 position (Ia) and in the 4(5) position of the imidazole ring (2,4-diphenyl-5-DMBI-imidazolyl radical, XIVa) leads to a 160-170 nm bathochromic shift of the long-wave absorption band, while the methoxy group in the 2-(p-anisyl)-4,5-diphenylimidazolyl radical shifts this band only 50 nm [2]. The introduction of a second ureylene grouping (2,4-bis-DMBI-5-phenylimidazolyl radical, XVa) is accompanied by a further increase in the λ_{max} value of this band, although it is of lower magnitude.

In the series of free radicals corresponding to imidazoles I-XI the spectra in the visible region differ only slightly from one another, and only the radical containing a nitro group (XIIa) has an additional absorption band with λ_{max} at 480 nm.

It was observed that solutions of I, III, and XV in chloroform take on a green coloration (which gradually changes to red) when they are irradiated with sunlight or UV light in a test tube made of ordinary glass. The green solutions give an ESR signal. The diimidazolyl radical obtained from imidazole XV displays similar properties. In the latter case the green color develops more rapidly and is of higher intensity.

The spectrum of an irradiated solution of XV at 600-800 nm (Fig. 2) is similar to the spectrum of the corresponding radical (Fig. 1), but the optical density at 400-600 nm is considerably higher than in the case of the radical. When diphenylamine is added to the solution, the green color vanishes, and the solution becomes red (λ_{max} 517 nm). However, the addition of hydroquinone decolorizes this solution almost completely.

Thus it may be assumed that irradiation of I, III, and XV in chloroform gives imidazolyl radicals, which are converted upon further irradiation to a compound that probably has a quinoid structure. However, the latter assumption requires more rigorous proof.

It is known that triarylimidazoles and their heteroanalogs are inhibitors of the thermal oxidative destruction of polymers [3-5]. To evaluate the inhibiting ability of the compounds obtained we studied the thermal oxidative destruction of polyethylene oxide in the presence of I-XII. The effectiveness of the compounds as antioxidants was characterized from the duration of the induction period (τ_{ind}). For nonstabilized polyethylene oxide τ_{ind} is 60 min, as compared with 70 min in the presence of 2,4,5-triphenylimidazole.

It is apparent from the τ_{ind} values presented in Table 1 that most of the DMBI-substituted imidazoles display appreciable antioxidant activity. As expected, replacement of a phenyl residue in 2,4,5-triphenylimidazole by a DMBI residue, which has electron-donor properties, leads to an increase in the effectiveness of the compounds as antioxidants.

EXPERIMENTAL

The spectra of $1 \cdot 10^{-5}$ M solutions of I-XII in alcohol and of the radicals in toluene with starting imidazole concentrations of $5 \cdot 10^{-3}$ M were recorded with a Perkin-Elmer 420 spectrophotometer. The cuvette thickness was 1 cm. The photochemical transformations of I, III, and XV in chloroform ($2 \cdot 10^{-2}$ M, l = 2 cm) were investigated with an SF-2M spectrophotometer. Solutions in quartz cuvettes were irrradiated with a PRK-4 lamp.

TABLE 1. Heterylimidazoles I-XII

Compound	R^1	R^2	mp, °C	Found, %			Empirical formula	Calc., %			UV spectra, λ_{max}, nm (log ε)	Yield, %	Spectra of the radicals, λ_{max}, nm	τ_{ind}, min
				C	H(Cl, Br)[a]	N		C	H(Cl, Br)[a]	N				
I	H	H	253—254	75,5	5,3	14,9	$C_{24}H_{20}N_4O$	75,7	5,3	14,7	224 (4,84); 322 (4,69)	80	542, 716	240
II	CH_3	H	255—256	76,3	5,2	14,6	$C_{25}H_{22}N_4O$	76,1	5,6	14,2	221 (4,63); 320 (4,48)	62	540, 710	140
III	CH_3	CH_3	272—273	76,2	5,6	13,7	$C_{26}H_{24}N_4O$	76,4	5,9	13,7	218 (4,77); 323 (4,62)	68	540, 704	140
IV	OCH_3	H	238—239	73,3	5,2	13,5	$C_{25}H_{22}N_4O_2$	73,1	5,4	13,6	216 (4,64); 321 (4,49)	71	540, 714	170
V	OCH_3	OCH_3	210—211	70,7	5,6	12,9	$C_{26}H_{24}N_4O_3$	70,9	5,5	12,7	218 (4,76); 322 (4,57)	78	542, 708	—
VI	OC_2H_5	H	234—235	77,6	5,6	13,1	$C_{26}H_{24}N_4O_2$	73,5	5,7	13,2	219 (4,62); 321 (4,48)	72	539, 713	170
VII	Cl	H	268—269	69,2	(8,8)	13,5	$C_{24}H_{19}ClN_4O$	69,5	(8,5)	13,5	219 (4,64); 320 (4,54)	60	548, 726	—
VIII	Br	H	274—275	63,0	(17,5)	12,5	$C_{24}H_{19}BrN_4O$	62,7	(17,4)	12,2	216 (4,66); 320 (4,54)	58	546, 727	90
IX	Br	Br	295—296	53,2	(29,6)	10,5	$C_{24}H_{19}Br_2N_4O$	53,6	(29,7)	10,4	213 (4,64); 320 (4,52)	49	556, 748	90
Xb	—	—	287—288	78,2	5,3	13,2	$C_{28}H_{22}N_4O$	78,1	5,2	13,0	222 (4,56); 320 (4,51)	61	540, 736	70
XIc	—	—	281—282	78,0	5,1	13,2	$C_{28}H_{22}N_4O$	78,1	5,2	13,0	227 (4,99); 322 (4,77)	74	632, 738	80
XII	NO_2	H	326—327	67,5	4,7	16,3	$C_{24}H_{19}N_5O$	67,8	4,5	16,5	220 (4,64); 318 (4,38) 394 (4,10)	52	480, 552 (sh)	100

a) The percentage of halogen is given in parentheses. b) 2-DMBI-4-(α-naphthyl)-5-phenylimidazole. c) 2-DMBI-4-(β-naphthyl)-5-phenylimidazole.

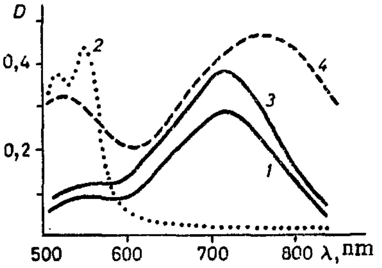

Fig. 1

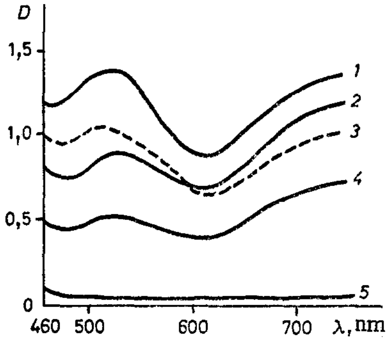

Fig. 2

Fig. 1. Spectra of the radicals from imidazoles I, XIII, and XV in toluene: 1) Ia; 2) XIIIa; 3) XIVa; 4) XVa.

Fig. 2. Spectral changes in XV during UV irradiation (chloroform solution): 1) 20 min; 2) 15 min; 3) 60 min; 4) 3 min; 5) 0 min.

2-(N,N'-Dimethylbenzimidazolon-5-yl)-4,5-diarylimidazoles I-XII were obtained similarly from 4(5)-DMBI-substituted imidazoles [1]. Imidazole II was crystallized from dimethylformamide, VII was crystallized from dioxane—dichloroethane (1:3), VII and IX were crystallized from xylene, and the remaining compounds were crystallized from ethanol. The synthesis of XIV and XV is described in [1].

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