HETERYLIMIDAZOLES

V.* SYNTHESIS AND PROPERTIES OF HETEROANALOGS OF TRIARYLIMIDAZOLES

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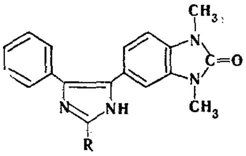
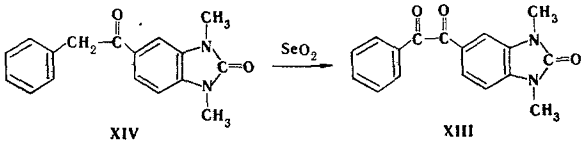
2-Aryl-4(5)-phenyl-5(4)-(N,N'-dimethyl-5-benzimidazolonyl)imidazoles were obtained by condensation of 1-(N,N'-dimethyl-5-benzimidazolonyl)-2-phenylglyoxal with aromatic aldehydes in acetic acid in the presence of ammonium acetate. It was shown that these compounds are either retarders or inhibitors of the radical polymerization of styrene.

This paper is devoted to the synthesis and investigation of the properties of 2,4,5-tri-substituted imidazoles containing an N,N'-dimethyl-5-benzimidazolonyl group in the 4(5) position of the imidazole ring and substituted phenyl, naphthyl, and N,N'-dimethyl-5-benzimidazolonyl groups in the 2 position (Table 1).



I-XII

Imidazoles I-XII were synthesized by condensation of 1-(N,N'-dimethyl-5-benzimidazolonyl-2-phenylglyoxal (XIII) with the appropriate aldehydes in refluxing acetic acid in the presence of ammonium acetate. In contrast to the well-known method [2], we synthesized XIII by condensation of phenylacetic acid with N,N'-dimethylbenzimidazolone in polyphosphoric acid with subsequent oxidation of the resulting ketone XIV with selenium dioxide:



XIV XIII

An attempt to obtain XIV under the conditions of the Friedel–Crafts reaction with phenylacetyl chloride was unsuccessful.

As in the spectrum of triarylimidazoles, two well-expressed absorption maxima at 230 and 320 nm are observed in the UV spectra of I-XII (Table 1). Replacement of the phenyl group in the 4(5) position of the imidazole by a N,N'-dimethylbenzimidazolone residue or introduction of substituents into the phenyl ring in the 2 position of the imidazole do not substantially change the character of the spectra. Napthyl-substituted imidazoles X and XI have more complex spectra.

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*See [1] for communication IV.

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TABLE 1. Heterylimidazoles (I-XII)

Compound	R	T. mp, °C	Crystallization solvent	Epirical formula	Found, %			Calculated, %			λ_{max}, nm (lg ε)	Yield, %
					C	H	N	C	H	N		
I	Phenyl	276—278	Dioxane*	$C_{24}H_{20}N_4O$	75,8	5,3	14,3	75,8	5,4	14,2	230 (4,23); 310 (4,18)	62
II	p-Methoxyphenyl	284—285	Dioxane*	$C_{25}H_{22}N_4O_2$	73,3	5,7	13,5	73,2	5,4	13,6	228 (4,36); 311 (4,42)	73
III	p-Dimethylaminophenyl	284—285	Ethanol, butanol*	$C_{26}H_{25}N_5O$	74,0	5,8	17,0	73,8	5,7	16,6	226 (4,56); 317 (4,53)	26
IV	p-Diethylaminophenyl	148—149	Xylene*	$C_{28}H_{29}N_5O$	74,5	6,5	15,0	74,9	6,2	15,5	226 (4,28); 330 (4,39)	74
V	3,4-Dimethoxyphenyl	211—213	Dioxane toluene	$C_{26}H_{24}N_4O_3$	70,4	5,8	12,2	70,8	5,5	12,7	227 (4,18); 314 (4,41)	73
VI	p-Chlorophenyl	313—314	Dioxane	$C_{24}H_{19}ClH_4O$	69,1	4,7	13,9	69,4	4,6	13,6	231 (4,47); 316 (4,49)	65
VII	p-Bromophenyl	330—331	Dioxane butanol	$C_{24}H_{19}BrH_4O$	62,5	4,1	12,3	62,8	4,2	12,2	227 (4,51); 320 (4,52)	43
VIII	m-Nitrophenyl	310—312	DMFA + alcohol	$C_{24}H_{19}N_5O_3$	67,7	4,5	16,5	67,7	4,5	16,5	231 (4,46); 314 (4,39)	75
IX	p-Nitrophenyl	336—337	DMFA	$C_{24}H_{19}N_5O_3$	67,7	4,5	16,5	67,4	4,2	16,3	228 (4,36); 302 (4,08); 400 (4,3)	73
X	α-Naphthyl	313—314	Toluene, xylene	$C_{28}H_{22}N_4O$	78,4	4,9	13,5	78,1	5,2	13,1	232 (4,59); 285 (4,08); 323 (4,33); 350 (infl)	62
XI	β-Hydroxy-α-naphthyl	152—153	Ethanol, butanol	$C_{28}H_{22}N_4O_2$	75,0	5,1	12,1	75,3	5,0	12,5	229 (4,57); 311 (4,14); 350 (infl)	42
XII	N,N'-Dimethyl-5-benzimidazolonyl	300—302	DMFA, bromobenzene	$C_{27}H_{24}N_6O_2$	69,5	5,4	18,1	69,8	5,2	18,1	231 (4,56); 322 (4,6)	59

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* The compounds were purified prior to crystallization: I, II, and IV were purified by chromatography on aluminum oxide (elution with chloroform), and III was purified by reprecipitation from a solution in concentrated hydrochloric acid by the addition of alkali solution.

TABLE 2. Inhibiting Capacities of the Investigated Compounds*

Compour	$V_p \cdot 10^5$, mole/liter sec†	F	$\frac{K_z}{K_p}$	τ_{inh}, sec
Triphenylimidazole	8,41	0,01	22,2	0
I	5,97	0,71	31,5	0
VII	4,71	1,21	39,9	0
XII	5,97	0,71	31,5	0
II	—	—	—	1190
Neozone D	—	—	—	1190
Diphenylamine	—	—	—	1970

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* Symbols: V_p is the rate of inhibited polymerization, τ_{inh} is the inhibition time, F is the inhibition factor, and K_z/K_p is the ratio of the inhibition constant to the chain-propagation rate constant.

† The rate of polymerization of styrene in the absence of an inhibitor is 8.55 moles/liter·sec.

Imidazoles I-X and XII are readily oxidized in toluene to the corresponding free radicals by shaking with an aqueous solution of sodium hypobromite at room temperature, as a consequence of which the solutions take on an intense green coloration. When a solution of diphenylpicrylhydrazine (DPPH) is added to them, the green coloration changes to violet owing to the development of the DPPH radical (λ_{max} 530 nm). Solutions of imidazolyl radicals give an ESR signal (singlet, g 2.003). A solution obtained by oxidation of XI has a red coloration, gives only a weak ESR signal, and does not generate a radical from diphenylpicrylhydrazine. The product of oxidation of XI is evidently the corresponding quinone [3].

Some of the synthesized heteroanalogs of triarylimidazoles were tested as inhibitors of the radical-initiated polymerization of styrene. The kinetic parameters of the inhibited radical polymerization that characterize their inhibiting capacity were found for the investigated substances (Table 2). 2,4,5-Triphenylimidazole (lophine) and the widely known stabilizers Neozone D and diphenylamine were used for comparison. It is apparent from the results obtained that the synthesized heterylimidazoles manifest a large inhibiting effect as compared with lophine, but are somewhat inferior to Neozone D and diphenylamine. Compounds I, VII, and XII are retarders of the radical polymerization of styrene, whereas, in contrast to them, II displays a more pronounced inhibiting effect with a clearly expressed induction period.

EXPERIMENTAL

The UV spectra of alcohol solutions of imidazoles I-XII were recorded with a Perkin–Elmer 402 spectrophotometer. The cuvette thickness was 1 cm, and the concentration was $3.32 \cdot 10^{-5}$ M. The kinetics of the inhibited radical polymerization of styrene were studied by a thermometric method with a differential isothermal calorimeter [4]. The styrene was vacuum distilled three times in a stream of argon with subsequent degassing by repeated freezing out (n_D^{20} 1.5468, d_4^{20} 0.9060, and bp 144 [5]). Azobisisobutyronitrile, which was recrystallized three times from methanol (mp 103°), was used as the initiator of the radical polymerization. The inhibited radical polymerization was investigated under steady-state conditions at 60° and small degrees of conversion (up to 0.5%). The kinetic parameters of the radical polymerization were found by known methods [6, 7].

N,N'-Dimethyl-5-phenylacetylbenzimidazolone (XIV). Orthophosphoric acid (10 ml) was added in portions with stirring in the course of 10 min to 15 g of phosphorus pentoxide, during which no measures were taken to prevent the pronounced spontaneous generation of heat. The mixture was heated at 200-250° until the phosphorus pentoxide had dissolved completely, after which it was cooled to 100°, and 7.52 g (0.046 mole) of N,N'-dimethylbenzimidazolone and 10.9 g (0.08 mole) of phenylacetic acid were added. The mixture was stirred at 150-155° for 3 h, after which it was cooled to 80-90°, diluted to 300 ml with water, made alkaline to pH 8 with saturated sodium carbonate solution, and refluxed for 15-20 min with maintenance of a weakly alkaline reaction medium. The hot suspension was filtered, and the slightly brown precipitate was washed with water and dried. It was then crystallized successively from alcohol and toluene to give a product with mp 185-186°. Found: C 72.6; H 5.8; N 10.0%. $C_{17}H_{14}N_2O$. Calculated: C 72.8; H 5.8; N 10.0%.

Diketone XIII. A 19.7-g (0.18 mole) sample of selenium dioxide was added in portions with stirring in the course of 10 min to a refluxing solution of 28 g (0.1 mole) of ketone XIV in 210 ml of dry xylene. The mixture was refluxed for another 3 h and filtered hot. The yellow precipitate that formed on cooling was removed by filtration and washed with a small amount of alcohol to give a product with mp 196-197° (mp 194° [2]) in 80% yield.

2-Aryl-4(5)-(N,N'-dimethyl-5-benzimidazolonyl)-5(4)phenylimidazoles (I-XII). A warm solution of a mixture of 0.01 mole of aldehyde and 2.94 g (0.01 mole) of diketone XIII in 45 ml of acetic acid was added in the course of 2 h to a refluxing solution of 0.082 mole of ammonium acetate in 45 ml of glacial acetic acid. The mixture was refluxed for another 3 h, cooled, and poured with stirring into a mixture of excess concentrated ammonium hydroxide and ice. The resulting precipitate was removed by filtration, washed with water, and dried. The methods used to purify I-XII are presented in Table 1.

LITERATURE CITED

1. Yu. A. Rozin, V. F. Gryazev, V. E. Blokhin, Z. V. Pushkareva, and G. É. Martina, Khim. Geterotsikl. Soedin., 1536 (1974).
2. A. V. El'tsov, Zh. Obshch. Khim., 33, 1327 (1963).
3. E. I. du Pont de Nemours et Co., French Patent No. 1395112 (1965); Chem. Abstr., 63, 1793 (1965).
4. L. G. Surovtsev and M. A. Bulatov, Vysokomol. Soedin., 14-A, 2108 (1972).
5. Concise Chemist's Handbook [in Russian], Khimiya, Moscow (1954), p. 150.
6. L. G. Surovtsev, M. A. Bulatov, K. A. Charushnikov, and S. S. Spasskii, Zh. Fiz. Khim., 46, 2684 (1972).
7. Kh. S. Bagdasaryan, Theory of Radical Polymerization [in Russian], Izd. Akad. Nauk SSSR, Moscow (1959).