HETERYLIMIDAZOLES

II.* SYNTHESIS OF 4,5-DIARYL-2-HETERYLIMIDAZOLES AND HETERO ANALOGS OF HEXAARYLBIIMIDAZOLYLS

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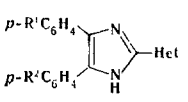
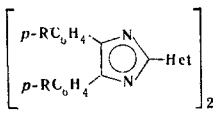
The condensation of heterocyclic aldehydes with aromatic α-diketones in the presence of ammonium acetate in acetic acid has given 4,5-diaryl-2-quinolinylimidazoles and 4,5-diaryl-2-(acridin-9-yl)imidazoles. The oxidation of the latter with $K_3Fe(CN)_6$ in an alkaline medium has given the corresponding biimidazolyls, which possess photochromic and thermochromic properties.

2,2',4,4',5,5'-Hexaarylbiimidazolyls, obtained by the oxidation of 2,4,5-triarylimidazoles, possess photochromic and thermochromic properties thanks to reversible dissociation on irradiation or heating into deeply colored free radicals. At the present time, the properties of biimidazolyls with carbocyclic substituents of the aromatic series containing various functional groupings have been widely studied [2]. Imidazolyl radicals containing carbazolyl, indol-3-yl [4], α-furyl, and α-thienyl [2] radicals as substituents are also known.

It appeared of interest to investigate the influence exerted by residues of six-membered nitrogen-containing heterocycles on the properties of the imidazolyl radicals and their dimers. We have previously [1] described the synthesis of the 2-hetero analogs of the triarylimidazoles containing quinoline and acridine residues as substituents in position 2 of the imidazole residue. In the present work we give the synthesis and properties of the previously undescribed 2-heteryl-4,5-diphenylimidazoles (I-XV, Table 1) and 4,4',5,5'-tetraaryl-2,2'-diheterylbiimidazolyls (XVI-XXX, Table 2).



I-XV



XVI-XXX

The synthesis of the imidazoles was effected by the usual method [5] with the gradual addition of an acetic acid solution of a heterocyclic aldehyde and an aromatic α-diketone to a boiling solution of ammonium acetate in acetic acid. It must be mentioned that the 2-heteryl-4,5-diphenylimidazoles (VII-XV) containing Br and NO_2 as substituents in the para position of the phenyl ring were obtained in low yields. As a rule, the products formed mixtures from which the required compound was isolated by chromatography on alumina after its recrystallization from a suitable solvent. The imidazoles (I-IV and VII-IX) are colorless, (V, VI, X, and XI) yellow, and (XII-XV) orange substances with high melting points. They dissolve in acetic acid and also in ethanolic alkalis with a deepening of their coloration which is particularly pronounced in the case of the nitro derivatives.

The most widely used method of synthesizing hexaarylbiimidazolyls is the oxidation of triarylimidazoles in ethanolic alkali with an aqueous solution of $K_3Fe(CN)_6$ at a low temperature [6]. However, under these conditions the 4,5-diaryl-2-quinolinylimidazoles do not form biimidazolyls, which is possibly due to

*For Communication I, see [1].

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TABLE 1. 4,5-Diaryl-2-heterylimidazoles (I-XV)

Comp.	Het	R^1	R^2	mp, °C	Purification*	Empirical formula	Found,•			Calculated,•			Yield, %
							C	H(Br) †	N	C	H(Br) †	N	
I	Quinolin-3-yl	OCH_3	OCH_3	264—265	A	$C_{26}H_{21}N_3O_2$	76,4	5,1	10,3	76,6	5,2	10,3	60
II	Quinolin-4-yl	OCH_3	OCH_3	227—228	B	$C_{26}H_{21}N_3O_2$	76,5	5,4	10,7	76,6	5,2	10,3	10
III	Quinolin-6-yl	OCH_3	OCH_3	132—133	A	$C_{26}H_{21}N_3O_2$	76,9	5,0	10,3	76,6	5,2	10,3	76
IV	Quinolin-7-yl	OCH_3	OCH_3	191—192	A	$C_{26}H_{21}N_3O_2$	76,3	5,9	9,9	76,6	5,2	10,3	82
V	Quinolin-8-yl	OCH_3	OCH_3	183—184	C	$C_{26}H_{21}N_3O_2$	76,4	5,3	10,6	76,6	5,2	10,3	51
VI	Acridin-9-yl	OCH_3	OCH_3	310—311	A	$C_{30}H_{23}N_3O_2$	78,5	5,3	9,1	78,7	5,1	9,2	67
VII	Quinolin-4-yl	Br	Br	269—271	D	$C_{24}H_{15}Br_2N_3$	57,8	(31,2)	8,3	57,2	(31,6)	8,3	19
VIII	Quinolin-6-yl	Br	Br	283—284	D	$C_{24}H_{15}Br_2N_3$	57,0	(31,3)	8,7	57,2	(31,6)	8,3	29
IX	Quinolin-7-yl	Br	Br	290—292	D	$C_{24}H_{15}Br_2N_3$	57,2	(31,2)	8,2	57,2	(31,6)	8,3	23
X	Quinolin-8-yl	Br	Br	188—190	D	$C_{24}H_{15}Br_2N_3$	57,1	(31,3)	8,7	57,2	(31,6)	8,3	18
XI	Acridin-9-yl	Br	Br	219—221	E	$C_{28}H_{17}Br_2N_3$	60,1	(27,7)	7,2	60,0	(27,7)	7,6	11
XII	Quinolin-4-yl	H	NO_2	213—214	F	$C_{24}H_{16}N_4O_2$	73,6	4,0	14,3	73,5	4,1	14,3	35
XIII	Quinolin-6-yl	H	NO_2	218—219	F	$C_{24}H_{16}N_4O_2$	73,7	4,3	13,9	73,5	4,1	14,3	30
XIV	Quinolin-7-yl	H	NO_2	271—272	A	$C_{24}H_{16}N_4O_2$	73,6	4,0	14,3	73,5	4,1	14,3	50
XV	Quinolyn-8-yl	H	NO_2	194—195	F	$C_{24}H_{16}N_4O_2$	73,8	4,2	14,1	73,5	4,1	14,3	25

*A – crystallization from ethanol and then from toluene; B – crystallization from concentrated HCl in the form of the hydrochloride, then crystallization of the base from dichloroethane and then from toluene; C – chromatography on Al_2O_3 (lower zone), and then crystallization from ethanol; D – chromatography on Al_2O_3 (second zone from the bottom) and then crystallization from xylene; E – chromatography on Al_2O_3 (bottom zone) and then crystallization from xylene; F – chromatography on Al_2O_3 (second zone from the bottom) and then crystallization from ethanol.

† The bromine content is given in parentheses.

TABLE 2. 4,4',5,5'-Tetraaryl-2,2'-diheterylbiimidazolyls (XVI-XXX)

Comp.	Het	R	mp, °C	Empirical formula	N, %		λ_{max} of radical in toluene, nm	Yield, %
					found	calc.		
XVI	Quinolin-3-yl	H	118—120	$C_{48}H_{32}N_6$	11,8	12,1	500, 586, 632	25
XVII	Quinolin-4-yl	H	197—203	$C_{48}H_{32}N_6$	11,7	12,1	—, 665, 736	27
XVIII	Quinolin-5-yl	H	177—179	$C_{48}H_{32}N_6$	11,9	12,1	450, 630, 690	20
XIX	Quinolin-6-yl	H	179—181	$C_{48}H_{32}N_6$	11,9	12,1	500, 597, 646	28
XX	Quinolin-7-yl	H	179—182	$C_{48}H_{32}N_6$	12,0	12,1	500, 599, 649	23
XXI	Acridin-9-yl	H	185—188	$C_{56}H_{36}N_6$	9,9	10,6	—, 515, 550	35
XXII	Quinolin-3-yl	CH_3	175—178	$C_{52}H_{40}N_6$	11,6	11,2	—, 590, 634	22
XXIII	Quinolin-4-yl	CH_3	162—165	$C_{52}H_{40}N_6$	11,6	11,2	428, 656, 720	32
XXIV	Quinolin-6-yl	CH_3	167—170	$C_{52}H_{40}N_6$	10,8	11,2	490, 600, 647	29
XXV	Quinolin-7-yl	CH_3	168—170	$C_{52}H_{40}N_6$	11,1	11,2	500, 600, 645	20
XXVI	Acridin-9-yl	CH_3	310	$C_{60}H_{44}N_6$	9,6	9,9	Red	36
XXVII	Quinolin-6-yl	OCH_3	135—137	$C_{52}H_{40}N_6O_4$	10,4	10,3	—, 610, 650	35
XXVIII	Quinolin-7-yl	OCH_3	137—140	$C_{52}H_{40}N_6O_4$	10,3	10,3	—, 610, 652	31
XXIX	Acridin-9-yl	OCH_3	137—140	$C_{60}H_{44}N_6O_4$	9,0	9,3	Red	25
XXX	Quinolin-3-yl	OCH_3	152—156	$C_{52}H_{40}N_6O_4$	10,5	10,3	Green	25

the poor solubility of the initial imidazoles. The biimidazolyls (XVI-XXX) were obtained by oxidizing the corresponding imidazoles with $K_3Fe(CN)_6$ in an emulsion of pyridine and aqueous alkali. In the oxidation of the trisubstituted imidazoles containing quinolin-4-yl and acridin-9-yl residues, in addition to the biimidazolyls (XVII and XXI), a considerable amount of the starting material was recovered from the reaction mixture even with a large excess of $K_3Fe(CN)_6$ and a prolonged reaction (up to 6 h). This is obviously due to the strong electron-accepting action of these substituents, which oppose the oxidation process. 4,5-Diphenyl-2-(quinolin-2-yl)imidazole and 4,5-diphenyl-2-(quinolin-8-yl)imidazole and their 4,5-di(p-tolyl) analogs do not, under these conditions, form biimidazolyls capable of dissociating into radicals. The products isolated consist in each case of a mixture of the initial compound and compounds of undetermined structure. It is also interesting to note that 2-(anthracen-9-yl)4,5-diphenylimidazole, unlike its acridin-9-yl analog, forms an orange nonphotochromic sparingly soluble compound with mp 206-210°C which cannot be recrystallized without decomposition. This compound is apparently the product of the recombination of radicals through the anthracene nucleus.

The biimidazolyls (XVI-XXX) obtained (Table 2) are yellow high-melting substances. They have no sharp melting points because of thermal dissociation into radicals during the melting process. When solutions of the biimidazolyls obtained are heated or irradiated with sunlight, they dissociate into deeply colored radicals which give an ESR signal and generate the DPPH radical from diphenylpicrylhydrazine. The quinolinyl-substituted radicals have a green coloration, and the acridinyl-substituted ones are red. In the dark at room temperature the color gradually disappears, and it reappears once more on heating or irradiation. The radicals differ considerably in stability. Thus, the dark-green color of a solution of (XVII) heated to 100-110°C disappears almost completely when the solution is cooled to room temperature. At the same time, the color of a solution of (XXVII) is retained for several hours. This confirms existing information [2] according to which electron-accepting substituents decrease the stability of triarylimidazolyl radicals and electron-donating substituents increase it.

EXPERIMENTAL

4,5-Diaryl-2-heterylazoles (I-XV). Over 2 h, a hot solution of 0.01 mole of a diketone and 0.01 mole of an aldehyde in 60 ml of acetic acid was added to a boiling solution of 5 g (0.065 mole) of ammonium acetate in 20 ml of glacial acetic acid. The reaction mixture was boiled for another 3 h, cooled, and poured onto 250 g of ice with an excess of concentrated aqueous ammonia solution. The precipitate was filtered off, washed with water, dried, chromatographed in chloroform on alumina, and recrystallized from a suitable solvent (Table 1).

4,4',5,5'-Tetraaryl-2,2'-diheterylbiimidazolyls (XVI-XXX). A 4,5-diaryl-2-heterylimidazole (0.01 mole) was dissolved in 80 ml of freshly distilled pyridine. The solution was cooled to 0-2°C and to it was slowly added a cooled solution of 11 g (0.196 mole) of KOH in 40 ml of water. Then, with stirring, 14.4 g (0.044 mole) of a finely ground powder of $K_3Fe(CN)_6$ was added to the reaction mixture. Stirring was continued for another 4 h at 0-2°C and the reaction mixture was slowly poured into 500 ml of water. The precipitate that deposited was filtered off, washed with water, and dried in a vacuum desiccator over solid KOH. The dried residue was dissolved in chloroform and chromatographed on Al_2O_3. The solvent was eliminated at room temperature. In the case of compounds (XVII, XIX, XXI), the resulting vitreous mass was triturated with 7 ml of acetone and the precipitate was filtered off and dried in a vacuum desiccator. In the case of compounds (XVI, XVIII, XX, XXII-XXX), after the elimination of the solvent the product was reprecipitated from toluene with petroleum ether. All the operations were performed in a darkened room.

The visible spectra of the radicals were recorded on an SF-2M spectrophotometer in solution in purified toluene in a thermostated cell at 80°C at an initial concentration of the biimidazolyl of 10^{-3} M. The thickness of the cell was 1 cm.

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