HETERYLIMIDAZOLES

I. SYNTHESIS OF 2-HETERYL-4,5-DIARYLIMIDAZOLES

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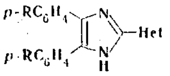
2-Quinolyl- or 2-(9-acridinyl)-4,5-diarylimidazoles were obtained by the condensation of benzil or p,p'-dimethylbenzil with heterocyclic aldehydes in acetic acid in the presence of ammonium acetate.

2,4,5-Triarylimidazoles are oxidized in alkaline media to give 2,2',4,4',5,5'-hexaaryldiimidazolyls, which have photochromic and thermochromic properties [1-3]. However, heterosubstituted diimidazolyls have not been described up until now. At the same time, it seems of considerable interest to investigate the effect of introduction of a heteroatom into the aromatic ring on the photochromic and thermochromic properties of diimidazoles. The present paper is devoted to the synthesis of the previously unknown 2-heteryl-4,5-diphenyl- [or di-(p-tolyl)-]imidazoles (I-XV) (Table 1), which contain quinoline and acridine residues, with the aim of studying their capacity to form photochromic and thermochromic diimidazolyls on oxidation.



I-XV

R=H, CH_3

The most convenient method for obtaining triarylimidazoles is condensation of α-diketones with aldehydes in a refluxing solution of ammonium acetate in acetic acid [4]. However, when benzil and 4-formylpyridine are used, one observes the formation of a large amount of 2,4,5-triphenylimidazole as a side prod-

TABLE 1. 2-Heteryl-4,5-diarylimidazoles (I-XV)

Compound	R	Het	Mp, °C*	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	N	C	H	N	
I	H	2-Quinolinyl	189—191	$C_{24}H_{17}N_3$	82,6	5,0	12,1	83,0	4,9	12,1	41
II	H	3-Quinolinyl	273—274	$C_{24}H_{17}N_3$	82,8	5,0	12,0	83,0	4,9	12,1	53
III	H	4-Quinolinyl	304—305	$C_{24}H_{17}N_3$	83,3	5,4	11,7	83,0	4,9	12,1	47
IV	H	5-Quinolinyl	298—299	$C_{24}H_{17}N_3$	83,0	4,7	11,7	83,0	4,9	12,1	55
V	H	6-Quinolinyl	235—237	$C_{24}H_{17}N_3$	83,2	5,4	11,6	83,0	4,9	12,1	94
VI	H	7-Quinolinyl	241—242	$C_{24}H_{17}N_3$	82,8	5,0	12,1	83,0	4,9	12,1	45
VII	H	8-Quinolinyl	155—156	$C_{24}H_{17}N_3$	83,4	5,3	12,1	83,0	4,9	12,1	45
VIII	H	9-Acridinyl	296—297	$C_{28}H_{19}N_3$	84,8	4,8	10,6	84,6	4,8	10,6	44
IX	CH_3	2-Quinolinyl	193—194	$C_{26}H_{21}N_3$	83,2	5,7	10,9	83,2	5,6	11,2	40
X	CH_3	3-Quinolinyl	275—277	$C_{26}H$[illegible]$_{1}N_3$	82,7	5,7	11,1	83,2	5,6	11,2	58
XI	CH_3	4-Quinolinyl	256—257	$C_{26}H_{21}N_3$	83,3	5,9	11,4	83,2	5,6	11,2	57
XII	CH_3	5-Quinolinyl	270—272	$C_{26}H_{21}N_3$	83,1	5,8	11,5	83,2	5,6	11,2	49
XIII	CH_3	6-Quinolinyl	248—250	$C_{26}H_{21}N_3$	83,0	5,6	11,0	83,2	5,6	11,2	64
XIV	CH_3	7-Quinolinyl	273—274	$C_{26}H_{21}N_3$	82,8	5,5	11,3	83,2	5,6	11,2	60
XV	CH_3	8-Quinolinyl	145—147	$C_{26}H_{21}N_3$	83,3	5,7	10,9	83,2	5,6	11,2	31

*Compounds I, VII, and XIII-XV were recrystallized from toluene, III and VIII were recrystallized from dioxane, IX was recrystallized from xylene, while the remaining compounds were recrystallized from alcohol.

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uct, which can be avoided by slow addition of the solution of aldehyde and diketone to the refluxing solution of ammonium acetate in acetic acid [5]. Since we also observed the formation of triphenylimidazole in the condensation of 9-formylacridine, 2-formylquinoline, and 8-formylquinoline with benzil when all of the reagents were mixed simultaneously, we adopted the order of mixing the reagents in conformity with [5], which made it possible to obtain imidazoles I-XV in satisfatory yields (Table 1).

Imidazoles I-XV are yellow or colorless high-melting substances that dissolve in acetic acid with deepening of their color. The IR spectra of II-VI and VIII-XIV contain absorption bands of the N—H bond of the imidazole ring at 3432-3450 cm^{-1} ($CHCl_3$). The decrease in the absorption frequency of the N—H bond in solutions of VII to 3300 cm^{-1} (CCl_4) and of XV to 3280 cm^{-1} ($CHCl_3$) attests to the presence of intramolecular hydrogen bonding. There are also characteristic absorption bands of the imidazole ring [6] at 1500-1511 cm^{-1}, the frequency of which does not depend substantially on the aggregate state of the substance.

As will be shown in subsequent communications, imidazoles II-VI, VIII, and X-XIV form photochromic and thermochromic diimidazolyls when they are oxidized in alkaline media.

EXPERIMENTAL

The 4-, 6-, 7-, and 8-formylquinolines were obtained by the method in [7], 2-formylquinoline was prepared as in [8], 9-formylacridine was obtained by the method in [9], and p,p'-dimethylbenzil was prepared in accordance with [10].

2-Heteryl-4,5-diarylimidazoles (I-XV, Table 1). A warm solution of a mixture of 0.01 mole of benzil (or p,p'-dimethylbenzil) and 0.01 mole of aldehyde in 30 ml of acetic acid was added dropwise in the course of 2 h to a refluxing solution of 5 g of ammonium acetate in 20 ml of glacial acetic acid. The reaction mass was refluxed for another 3 h, cooled, and poured into 250 g of ice containing excess concentrated NH_4OH. The precipitate was removed by filtration, washed with water, dried, and recrystallized from a suitable solvent (Table 1). Imidazoles I, VI, IX, and XV were chromatographed in chloroform on aluminum oxide prior to recrystallization.

The IR spectra of chloroform solutions (VII in CCl_4) were recorded at 2800-3500 cm^{-1} with a UR-10 spectrophotometer, while mineral oil pastes were used to obtain the spectra at 1400-1700 cm^{-1}.

LITERATURE CITED

1. T. Hayashi and K. Maeda, Bull. Chem. Soc. Japan, 33, 560 (1960).
2. H. Zimmermann, H. Baumgärtel, and F. Bakk, Angew. Chem., 73, 808 (1961).
3. T. Hayashi, K. Maeda, and M. Takeuchi, Bull. Chem. Soc. Japan, 37, 1717 (1964).
4. D. Davidson, M. Weiss, and M. Jelling, J. Org. Chem., 2, 319 (1937).
5. J. H. M. Hill, J. Org. Chem., 32, 3214 (1967).
6. D. M. White and J. Sonnenberg, J. Org. Chem., 29, 1926 (1964).
7. V. M. Rodionov and M. A. Berkengeim, Zh. Obshch. Khim., 14, 330 (1944).
8. A. H. Cook, I. M. Heilbron, and L. Steger, J. Chem. Soc., 413 (1943).
9. A. E. Porai-Koshits, Yu. I. Aushkap, and N. K. Amsler, Zh. Russk. Fiz.-Khim. Obshchestva, 43, 517 (1911).
10. West German Patent No. 913,891; Chem. Abstr., 52, 14,691 (1958).