SYNTHESIS OF SOME 1-SUBSTITUTED 2,5-DIPHENYLIMIDAZOLES

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The synthesis of 1,2,5-triphenylimidazole derivatives was accomplished by reaction of ω-benzamidoacetophenone with primary aromatic amines in the presence of phosphorus trichloride.

Substituted imidazoles that contain aryl groups in the 2 and 5 positions are nitrogen analogs of 2,5-diaryloxazoles, which are known to be effective for photo- and radioluminescence [1]. However, in connection with the ability of nitrogen-unsubstituted imidazoles to undergo tautomerism [2], a study of the luminescence characteristics of 2,5-diphenylimidazole derivatives cannot give unambiguous results regarding the interrelationship between the molecular structures and the luminescence characteristics of these compounds. In this respect, 1,2,5-triaryl-substituted imidazoles are of interest. However, compounds of this series have not been described in the literature, which is apparently associated with the difficulty involved in their preparation. In fact, a method for the synthesis of substituted imidazoles from N-substituted amidines and ω-bromomethyl ketones, which makes it possible, in principle, to obtain compounds of the indicated series, is presented only in [3]. However, this method is inconvenient because of the low degree of accessibility and the high toxicity of the starting compounds.

In [4] it was demonstrated that 1,2-dibenzoylhydrazine gives high yields of 1,2,5-trisubstituted 1,3,4-triazoles on reaction with primary aromatic amines in the presence of phosphorus trichloride. According to our data, the previously described 1,2,5-triphenylpyrrole is formed under these conditions from 1,2-dibenzoylethane and aniline. It might have been assumed that ω-benzamidoacetophenone, which is the structural analog of the two indicated γ-dicarbonyl compounds, should form 1,2,5-triphenylimidazole on reaction with aniline under the described conditions. We obtained a substance with a high melting point, which is characteristic for 1,2,5-triphenyl-substituted five-membered heterocycles [4]. The percentage of nitrogen in it corresponded to 1,2,5-triphenylimidazole. The substance had a capacity for effective photo- and radioluminescence, which is characteristic for cyclic compounds.

On this basis, we deemed it possible to assign the 1,2,5-triphenylimidazole structure to the compound obtained and, in accordance with [4], to depict the reaction for its formation by the following scheme:

TABLE 1. 1,2,5-Triphenylimidazole Derivatives (I-V)

Comp.	R	mp, °C (from alcohol)	Empirical formula	N, %		Yield, %
				found	calc.	
I	H	250	$C_{21}H_{16}N_2$	9,3	9,4	55—60
II	4-OCH_3	217	$C_{22}H_{18}N_2O$	8,6	8,6	65
III	2-OCH_3	149—150	$C_{22}H_{18}N_2O$	8,5	8,6	30
IV	4-Cl	228—229	$C_{21}H_{15}ClN_2$	8,5	8,5	50
V	2-Cl	168—169	$C_{21}H_{15}ClN_2$	8,5	8,5	25

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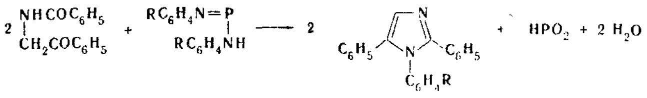
$$RC_6H_4NH_2 + PCl_3 \longrightarrow RC_6H_4N{=}P{-}NHC_6H_4R + 3\,RC_6H_4NH_2 \cdot HCl$$



I-V

Substituted anilines react with ω-benzamidoacetophenone to give 1,2,5-triphenylimidazole derivatives (I-V, Table 1) in yields of 50-60% for p-substituted compounds (II, IV) and 20-30% for o-substituted compounds (III, V). An attempt to introduce an aliphatic amine (n-propylamine) into the reaction gave only traces of a substituted imidazole.

Compounds I-V have blue-violet luminescence in benzene solution.

EXPERIMENTAL

1,2,5-Triphenylimidazole Derivatives (I-V, Table 1). A mixture of 0.6 mole of amine and 0.1 mole of phosphorus trichloride in 50 ml of chlorobenzene was heated to the boiling point, 0.1 mole of crystalline ω-benzamidoacetophenone was added, and the mixture was refluxed for 2.5-3 h. The mixture was filtered, and the filtrate was diluted with 75-100 ml of petroleum ether. The liberated oil was washed with another portion of petroleum ether, dried slightly, and dissolved in alcohol. The alcohol solution was neutralized to pH 8-9 with alcoholic KOH. The precipitated crystals of I-V were removed by filtration and purified by the usual methods.

LITERATURE CITED

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