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NEW METHOD OF SYNTHESIS OF 1,1′-DIALKYL-2,2′-DIBENZIMIDAZOLILES

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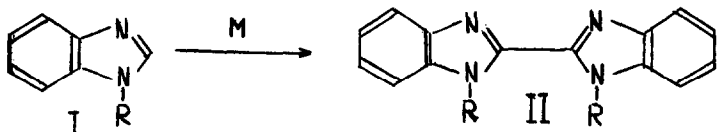
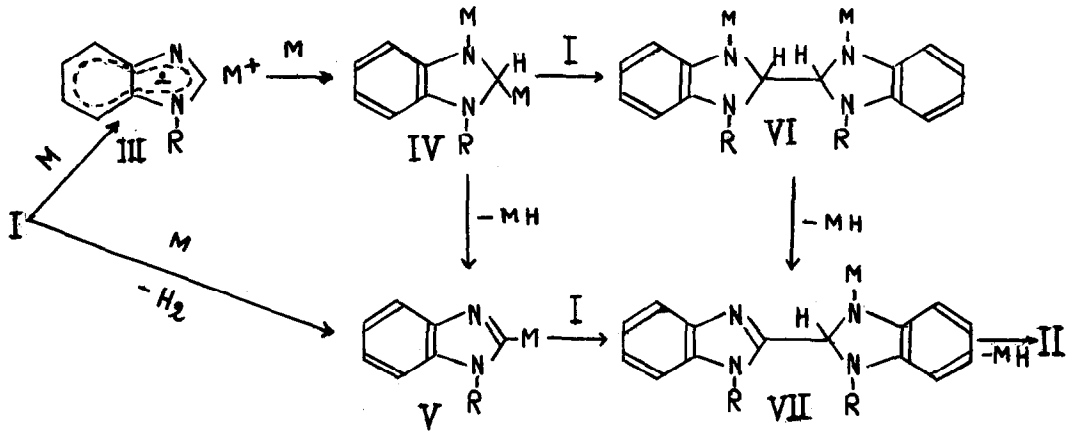
It is common knowledge that the reaction between o-phenylendiamines and oxalic acid gives the corresponding 2,3-dioxyquinoxalines and not the benzimidazole derivatives. As indicated in the work[1], 2,2′-dibenzimidazoliles with free NH-groups may be synthesized from o-phenylendiamines and oxamides. 2,2′-Dibenzimidazoliles are also formed when Ag-salts of benzimidazoles interact with iodine[2].

Among the alkylating dibenzimidazoliles we distinguish 1,1′-dimethyl-2,2′-dibenzimidazolile which was prepared from 1-methylbenzimidazole and butyllithium[3].

The method described in the present paper of obtaining 1,1′-dialkyl-2,2′-dibenzimidazoliles lies in the fact that metallic sodium and potassium act on 1-alkylbenzimidazole.

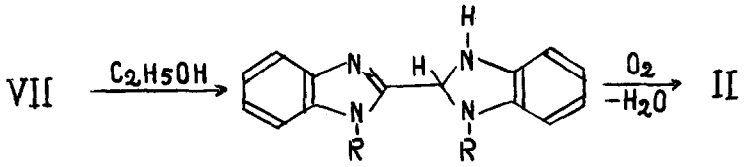


The appearing of an intermediate π -or- σ -complex in the process of reaction from anion radical /II/ and unreacted base, as has been observed in the case of pyridine[4], is unlikely due to the absence of a visible signal in the e.s.r. spectrum of the reaction mixture. As the reaction is accompained by the liberation of hydrogen and is remained sensitive to the inductive influence of N-substitute when potassium is being substituted by sodium (see table I), it may be concluded that of the three possible ways of formation II from I



the way I - V - VII - II is mainly realized.

It should be noted that in the conditions of this reaction VII does not completely convert into II as the yield of II somewhat increases if the reaction mixture after its treatment with ethanol is subject to the action of oxygen.



It is remarkable that when using a liquid alloy K - Na (4:1) instead of potassium or sodium the compound II is formed in small amount although we do observe the liberation of hydrogen.

The following general procedure was employed for the synthesis of 1,1′-dialkyl-2,2′-dibenzimidazolilles. Powdered potassium or sodium (0.033 g-atom) in 30 ml of benzene was activated with 2-3 drops of isoamyl alcohol and N-substituted benzimidazole (0.033 mole) was added with stirring in an atmosphere of nitrogen. The reaction was carried out at 25-30° for 2 hours. When the reaction was over the metal which had not reacted was removed by treatment with ethanol and for 1-1$\frac{1}{2}$ hours a moderate current

of air was passed through the mixture. Extraction of the base with 10% HCl and treatment of the combined aqueous layers with aqueous ammonia gave usually a mixture of oil and crystals. After standing for 8-10 hours crystals were filtered, washed with ethanol and dried. 1,1′-Dialkyl-2,2′-dibenzimidazolilles were recrystallized from ethanol.

The results of synthesis are given in the table I.

TABLE I

Initial compounds	Metal	Obtained compounds	Yield %	Melting point, °C	I R spectrum
1-methyl-benzimid-asole	K	1,1′-dimethyl-2,2′-dibenzimid-azolile	50.4	210,5-211°	1612 1584 1480 1008 964 744
	Na		42		
	K-Na (4:1)		14		
1-ethyl-benzimid-azole	K	1.1′-diethyl-2,2′-dibenzimid-azolile	44.5	188-189°	1586 1512 1480 1002 970 749
	Na		5		
	K-Na (4:1)		3.4		
1-propyl - benzimid-azole	K	1,1′-dipropyl-2,2′-dibenzimid-azolile	30.1	153-154°	1588 1480 1004 946 734
	Na		0.		
	K-Na (4:1)		0		

The results of elementary analysis of the obtained compounds correspond to the calculated data.

In the IR spectrum of all the 1,1′-dialkyl-2,2′-dibenzimidazolilles we find aromatic C = C and C = N - bonds, a benzene ring of benzimidazole[5] and o-substituted benzene ring.

That the dipol moments of 1,1′-dimethyl-and 1,1′-diethyl-2,2′-dibenzimidazoliles are equal to 1,41 and 1.94 D (benzene,25°) is confirmed by the fact that in a solution these compounds exist in angular conformations close to trans-forms.

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