

IMIDAZOLONES

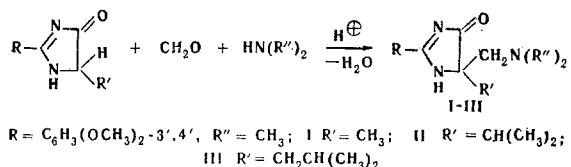
IV.* AMINOMETHYLATION AND PHOSPHORYLATION OF 2,5(4)-SUBSTITUTED 4(5)-IMIDAZOLONE

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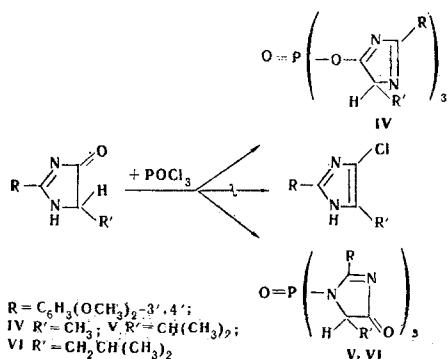
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2,5(4)-Substituted 4(5)-imidazolones undergo the Mannich reaction with formaldehyde and give phosphorylation products with phosphorus oxychloride. The structures of the isolated compounds were confirmed by IR and UV spectra.

In a continuation of our research in [1], we attempted to investigate the reaction of 2,5(4)-substituted 4(5)-imidazolones with formaldehyde and phosphorus oxychloride. The experiments demonstrated that 2,5(4)-substituted 4(5)-imidazolones, in contrast to the 2-substituted derivatives [2], do not react with formaldehyde under the conditions of the Knoevenagel condensation but react smoothly with formaldehyde when an equimolecular amount of dimethylamine is added to give the corresponding products of the Mannich reaction.



The structures of I-III were confirmed by their IR and UV spectra. The electronic absorption spectra of the starting imidazolones with a maximum at 280 nm, apparently caused by $\pi - \pi^*$ transitions (K band), do not change their character after carrying out the Mannich reaction; this attests to the immutability of the imidazolone ring in I-III. In addition, the presence of absorption frequencies characteristic for NH and C=O groups (Table 1) and the appearance of new absorption maxima at 1100 cm^{-1} due to the valence vibrations of an unconjugated C=N bond [3], are in agreement with the proposed structure of these compounds.



* See [1] for communication III.

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TABLE 1. Spectral Characteristics of I-VI*

Comp.	IR spectra, cm^{-1}						UV spectra in ethanol, λ_{max} , nm (log ϵ)
	CH_2-N	$\text{P}=\text{O}$	NH	$\text{C}=\text{N}$	$\text{C}=\text{O}$	NH	
I	1090 s	—	1585 m	1625 m	1715 s	3100 m, b	280 (4,10)
II	1095 m,b	—	1585 m	1615 m	1695 s	3175 m,b	276 (4,01)
III	1105 m,b	—	1585 m	1610 m	1690 s	3150 m,b	278 (4,03)
IV	—	—	—	1625 m	—	—	—
V	—	1275 s	—	1615 m	1680 s	—	—
VI	—	1280 s	—	1610 m	1690 s	—	—

*The letters s, m, and b are abbreviations for strong, medium, and broad, respectively.

TABLE 2. Compounds Synthesized

Comp.	Mp, °C	Empirical formula	Found, %				Calc., %				Yield, %
			C	H	N	P	C	H	N	P	
I	138—139	$\text{C}_{15}\text{H}_{21}\text{N}_3\text{O}_3$	61,5	7,1	14,2	—	61,9	7,2	14,4	—	44
II	151—153	$\text{C}_{17}\text{H}_{25}\text{N}_3\text{O}_3$	64,4	8,0	13,4	—	64,1	7,9	13,2	—	37
III	141—143	$\text{C}_{18}\text{H}_{27}\text{N}_3\text{O}_3$	64,6	7,9	12,4	—	64,8	8,1	12,6	—	41
IV*	224—226	$\text{C}_{36}\text{H}_{49}\text{N}_6\text{O}_{10}\text{P}$	—	—	11,1	4,3	—	—	11,3	4,2	62
V	292—294	$\text{C}_{42}\text{H}_{61}\text{N}_6\text{O}_{10}\text{P}$	—	—	9,8	3,9	—	—	10,1	3,7	54
VI†	298—300	$\text{C}_{45}\text{H}_{57}\text{N}_6\text{O}_{10}\text{P}$	—	—	9,5	3,7	—	—	9,6	3,6	73

* Found: mol. wt. 737. Calculated: mol. wt. 747.

† Found: mol. wt. 853. Calculated: mol. wt. 873.

The corresponding phosphorylation products (IV—VI) were obtained instead of the expected chloro derivatives on treatment of the 2,5(4)-substituted 4(5)-imidazolones with phosphorus oxychloride.

The IR spectra of V—VI (Table 1) contain absorption bands with maxima at 1690, 1275, and 715 cm^{-1} due to the valence vibrations of the $\text{C}=\text{O}$ and $\text{P}=\text{O}$ groups [3] and the $\text{P}-\text{N}$ bond [3].

The IR spectrum of IV does not contain an absorption band characteristic for the NH group but, in contrast to V—VI, here the absorption band of the $\text{C}=\text{O}$ group vanishes, and a new intense band with a maximum at 1780 cm^{-1} appears and can be assigned to the valence vibrations of an ester grouping of the

$\text{—O—P} \begin{smallmatrix} \text{O} \\ \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$ type [4]. A listing of the compounds obtained is given in Table 2.

EXPERIMENTAL

2-(3',4'-Dimethoxyphenyl)-5(4)-methyl-5(4)-dimethylaminomethyl-4(5)-imidazolone (I). A mixture of 1.37 g (0.006 mole) of 2-(3',4'-dimethoxyphenyl)-5(4)-methyl-4(5)-imidazolone, 1 ml of 20% aqueous dimethylamine, 0.45 ml of 36% aqueous formaldehyde, and 7 ml of acetic acid was heated to 60°. The clear solution was allowed to stand at room temperature for 24 h and made alkaline with dilute sodium hydroxide. The resulting precipitate was filtered, washed with water, and dried in a vacuum desiccator over potassium hydroxide. Crystallization from benzene—absolute ethanol (3:1) gave 0.62 g of I. Compounds II and III were similarly obtained.

Tris[2-(3',4'-dimethoxyphenyl)-5-isobutyl-4-oxo-1-imidazolyl]phosphine Oxide. A 0.3-ml sample of freshly distilled dimethylaniline was added to 1.37 g (0.006 mole) of 2-(3',4'-dimethoxyphenyl)-5(4)-isobutyl-4(5)-imidazolone in 5 ml of dry benzene, and 1.5 ml of phosphorus oxychloride was added with stirring to the cooled mass. The reaction mass was then refluxed for 3 h. The precipitate was filtered and washed first with water and then with ethanol. The precipitate was insoluble in the usual organic and inorganic solvents. The melting point of VI remained constant after it was washed with hot benzene and acetone. A total of 1.06 g of VI was obtained. Products IV and V were similarly obtained. Compound IV was purified by crystallization from dimethylformamide (50:1).

The molecular weights were determined by the Rast method. The IR spectra of mineral oil suspensions were recorded with an IKS-12 spectrometer. The UV spectra of ethanol solutions were recorded with an SF-16 spectrophotometer.

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