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OXIDATION OF BENZIMIDAZOLES TO BENZIMIDAZOLONES

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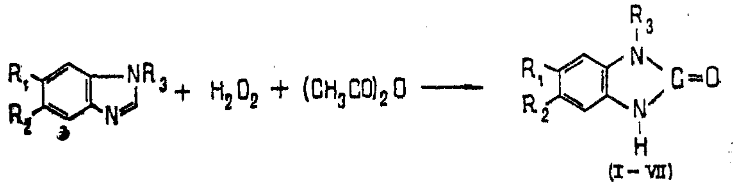
Two main methods of obtaining benzimidazolones are known: by the reaction of o-phenylenediames with urea or with phosgene [1, 2], but it is impossible to obtain certain benzimidazolones (for example, (III) and (VI), below) by these methods. This is due to the fact that not all substituted o-phenylenediamines are stable compounds and their use is accompanied by side reaction with the formation of azine dyes which leads to a marked decrease in the yield of the benzimidazolone derivative [3].

The aim of our work was to obtain substituted benzimidazolones by the oxidation of the corresponding benzimidazoles, since physiologically active compounds have been found among them [4, 5].

The oxidation reaction was carried out with hydrogen peroxide in acetic anhydride under conditions similar to those described by Sawlewicz [6] with our own simplifications in the isolation of the reaction products.



(I – VII)

Compound	R_1	R_2	R_3	Yield, %	mp, deg C (literature figures in parentheses)
I. Benzimidazolone	H	H	H	57	304–305 (305–306)
II. 5-Methylbenzimidazolone (III)	CH_3	H	H	41	291–292 (292)
III. 5-Methoxybenzimidazolone	CH_3O	H	H	23	218–219
IV. 5-Chlorobenzimidazolone	Cl	H	H	36	270–271 (269–270)
V. 5-Nitrobenzimidazolone	NO_2	H	H	22	305–306(306)
VI. 5,6-Dimethylbenzimidazolone	CH_3	CH_3	H	36	210–211
VII. 1-Methylbenzimidazolone	H	H	CH_3	35	191–192(191–192)

The optimum yields of reaction products were obtained by the action of one mole of the appropriate benzimidazole of 24 ml of 30% hydrogen peroxide in 80 ml of acetic anhydride. The reactions took place exothermically. After the reaction mixture had cooled, it was made weakly alkaline with 5 N NaOH and was then boiled for 1 h. After cooling, the reaction mixture was acidified with 4 N HCl and the resulting precipitate of benzimidazolone was filtered off, the unchanged benzimidazole being isolated from the acid filtrate by alkalinization. The benzimidazolones obtained were recrystallized from aqueous ethanol.

The benzimidazolones obtained were identified by mixed melting points with authentic samples obtained by a method described previously [1] and from their IR spectra. The IR spectra of compound (III) and (VI) each showed an absorption band at 1660-1680 cm^{-1} that is characteristic for C=O of a benzimidazolone ring.

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RADICAL ADDITION OF ALKYLPYRIDINES TO STYRENE

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The reaction of alkylpyridines with styrene in the presence of metallic sodium is known [1, 2]. The phenylpropylpyridines formed are of interest as fungicides, herbicides, and surface-active agents [3]. We have proposed a method for obtaining phenylpropylpyridines by the free-radical addition of alkylpyridines to styrene. The reaction of 2-, 3-, and 4-methylpyridines with styrene have been investigated under the conditions of thermal initiation at 250-350°C for 3 h. To limit the processes of telomerization and polymerization we used a ratio of methylpyridine to styrene of 75-100 : 1. With the 2-, 3-, and 4-methylpyridines the process took place with the formation of the corresponding 2-, 3-, and 4-phenylpropylpyridines (Ia-c) in accordance with the equation

$$\mathrm{PyCH_3 + CH_2{=}CH{-}Ar \rightarrow \underset{I\,a\text{-}c}{PyCH_2CH_2CH_2Ar},}$$

where Ar = C_6H_5, and Py = pyridin-2-, -3-, and -4-yl (Ia, b, and c, respectively) with yields of 31, 37, and 30% of theoretical, calculated on the styrene taken in the reaction, respectively.

In addition to the 1 : 1 adducts (Ia-c), the products of the oxidation and dehydrodimerization of the alkylpyridines were also detected and identified, their amount depending on the nature of the methylpyridine and the reaction conditions.

The experiments were performed in a three-liter steel autoclave under a pressure of the vapors of the reactants (20-70 atm). After the end of the reaction, the bulk of the methylpyridine was distilled off and the residue was analyzed by GLC using 4-benzylpyridine as internal standard. The individual adducts (Ia-c) were isolated with the aid of preparative GLC from the fractions obtained on vacuum distillation of the residue. Column 600 × 0.9 cm; stationary phase 20% of FFAP on Chromosorb W; column temperature 170-245°C (1°C/min), temperature of the detector 260°C and of the evaporator 250°C.

The physical constants of (Ia-c) coincided with those given in the literature [4]. The mass spectra of (Ia-c) contained peaks with m/z 197 (M^+) 106, 105, 92, and 91. The characteristics of the PMR spectra also confirmed the structures (Ia-c) given above.

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