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UNEXPECTED FORMATION OF 2-PHENYLOXAZOLO[3,2-*a*]BENZIMIDAZOLE FROM 2-CHLORO-1-PHENACYLBENZIMIDAZOLE AND AN EXAMPLE OF ITS TRANSFORMATION INTO 3-PHENYL-1,4-DIHYDRO-1,2,4-TRIAZINO-[4,3-*a*]BENZIMIDAZOLE BY THE ACTION OF HYDRAZINE HYDRATE

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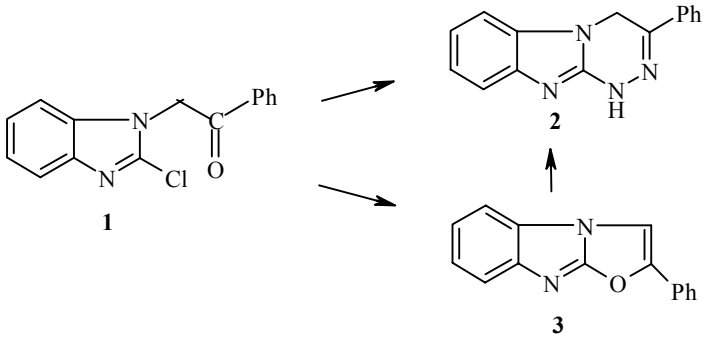
Keywords: 2-chloro-1-phenacylbenzimidazole, 2-phenyloxazolo[3,2-*a*]benzimidazole, hydrazine hydrate, ring expansion, 1,4-dihydro-3-phenyl-1,2,4-triazino[4,3-*a*]benzimidazole.

We have found that heating 2-chloro-1-phenacylbenzimidazole (**1**) in DMF at reflux with aminoguanidine for 2 h leads to 3-phenyl-1,4-dihydro-1,2,4-triazino[4,3-*a*]benzimidazole (**2**), which is identical to the product of the reaction of ketone **1** with hydrazine hydrate [1].

The reaction of the compound **1** with acetophenone aminoguanylhydrazone $H_2NCH(=NH)NHN=C(Me)Ph$ under the same conditions proceeds differently and gives previously unreported 2-phenyloxazolo[3,2-*a*]benzimidazole (**3**). Product **3** was also obtained in 76% yield by heating ketone **1** with sodium benzoate in DMF at reflux for 2 h. This method is analogous to the synthesis of oxazolotheophylline from 8-bromo-7-phenacyltheophylline [2].

At heating of the compound **3** with hydrazine hydrate in DMF at reflux for 4 h the expansion of the oxazole ring to a 1,2,4-triazine ring has been observed for the first time, triazinobenzimidazole **2** being formed in the reaction.



1 **2** **3**

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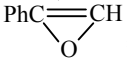
3-Phenyl-1,4-dihydro-1,2,4-triazino[4,3-*a*]benzimidazole (2) was obtained in 86% yield; mp 305-307°C (aq. DMF) (306-308°C [1]). Mass spectrum, *m/z* (I_{rel}, %): 249 (24) $[M + 1]^+$, 248 (100) M^+, 145 (43) $[M - PhCN]^+$, 144 (29), 119 (10), 118 (36) $[M - PhCN - HCN]^+$, 91 (10) $[M - PhCN - 2HCN]^+$, 77 (11) Ph^+.

2-Phenyloxazolo[3,2-*a*]benzimidazole (3) was obtained in 49% yield; mp 235-237°C (aq. DMF). IR spectrum (KBr): ν_{C-O-O} 1080, benzimidazole fragment 1490, 1150, 995, 850 cm^{-1} (see [3]). Mass spectrum, *m/z* (I_{rel}, %): 236 (6) $[M + 1]^+$, 234 (100) M^+, 233 (14), 206 (34) $[M - CO]^+$, 205 (50) $[M - COH]^+$, 118 (32)  ; $C_7H_4N_2$ 116 (14), 89 (19), 77 (25) Ph^+ (see data on the fragmentation of oxazole derivatives [4]). Found, %: C 77.20; H 4.22; N 12.12. $C_{15}H_{10}N_2O$. Calculated, %: C 76.91; H 4.30; N 11.96.

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