THE BECKMANN REARRANGEMENT OF OXIMES OF β-SUBSTITUTED β-(3-INDOLYL) KETONES

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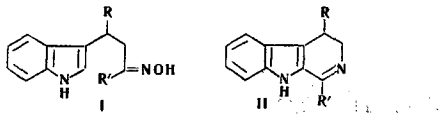
Earlier [1, 2], one of us had found that oximes of α-substituted β-(3-indolyl) ketones cyclize on undergoing the Beckmann rearrangement with the formation of 3-substituted 3, 4-dihydro-β-carbolines.

In an attempt to extend the method to oximes of β-substituted ketones (I), it was found that both the methods given previously [1, 2] and the classical procedures for performing the Beckmann rearrangement could not always be applied to this case. Only compounds in which R' was a phenyl radical reacted smoothly under the action of p-toluenesulfonyl chloride in pyridine and gave the normal rearrangement products, β-(3-indolyl)-β-R-propionanilides. For example, the oxime of 1, 3-diphenyl-3-(3-indolyl)propanone (I, R = R' = C_6H_5) [3], on treatment with p-toluenesulfonyl chloride in pyridine solution at 20° C for 8 hr, was converted almost quantitatively into β-(3-indolyl)-β-phenylpropionanilide, mp 193°—195° C. Found, %: C 81.1; H 6.1; N 8.0. Calculated for $C_{23}H_{20}N_2O$, %: C 81.2; H 5.9; N 8.2. IR spectrum (paraffin oil), ν, cm^{-1}: 3400 (N—H of an indole), 3270, 1643, 1530 (amide).



In numerous experiments, oximes with methyl substituents in the oximino function (I, R' = CH_3) either remained unchanged or underwent far-reaching decomposition. The reaction could be carried out only by using PCl_5 in such polar solvents as nitrobenzene and nitromethane. Under these conditions cyclization to 1, 4-disubstituted 3, 4-dihydro-β-carbolines (II) took place. Thus, the oxime of 4-(3-indolyl)-2-pentanone (I, R = C_3H_7, R' = CH_3) [3] after brief heating with PCl_5 in nitrobenzene at 70° C, was converted into the unstable 1-methyl-4-propyl-3, 4-dihydro-β-carbolene (II, R = CH_3, R' = C_3H_7), which was isolated in the form of the hydrochloride, mp 203°—204° C. Found, %: C 68.7; H 7.0; N 10.6. Calculated for $C_{15}H_{18}N_2 \cdot HCl$, %: C 68.6; H 7.3; N 10.7. UV spectrum (ethanol), λ_{max}, nm (log ε): 214 (4.36), 246 (4.14), 353 (4.47).

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SYNTHESIS OF 8-BENZYLGUANINE

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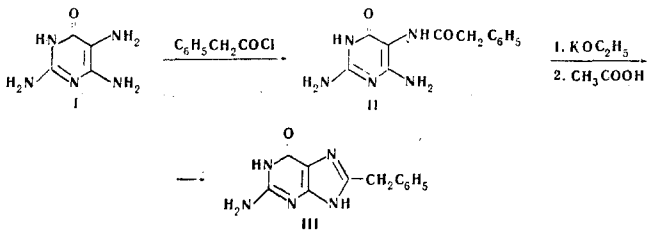
In order to study the physiological activity of purine derivatives we have synthesized 8-benzylguanine (III), the guanine analog of 2-benzylbenzimidazole, for the first time and have studied its antitumoral activity.

The synthesis was carried out by the following route.



2, 4-Diamino-5-phenylacetylamino-6-hydroxypyrimidine (II) was obtained by a published method for acylating the 5-amino group of pyrimidines [1] with a yield of 65% in the form of a colorless substance with mp 299°—300° C (decomp.). Found, %: C 55.00; H 5.11; N 26.87. Calculated for $C_{12}H_{13}N_5O_2$, %: C 55.59; H 5.02; N 27.02.

The cyclization of II into III was performed by a slight modification of the method of Haggerty et al. [2]. Compound III was obtained with a yield of 20% in the form of a light yellow substance with mp 303°—305° C (decomp., from aqueous ethanol). Found, %: C 58.92; H 5.04; N 29.02. Calculated for $C_{12}H_{11}N_5O$, %: C 59.45; H 4.56; N 29.20.

The two substances were characterized by ascending chromatography on FN 12 paper and by their UV spectra.

The antitumoral activity of compound III was studied on Walker's carcinosarcoma and Pleace's lymphosarcoma. The substance exhibited