

# SYNTHESIS OF 5-AZIDOPYRIMIDINES. PHOTOCHEMICAL CONVERSION OF 5-AZIDO-4-PHENYLPYRIMIDINE TO 5H-PYRIMIDO[5,4-b]INDOLE

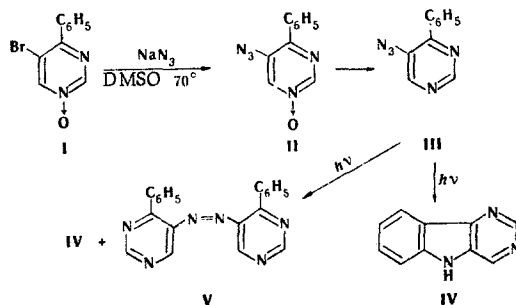
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5-Azidopyrimidines have not been described in the literature; this is associated, in particular, with the reduced reactivity of the halogen atom in 5-halopyrimidines [1]. The introduction of an N-oxide group in the pyrimidine molecule enabled us to synthesize 5-azido-4-phenylpyrimidine 1-oxide (II) [in 50% yield, mp 155-157°C (dec., from benzene)], which is the first representative of azidopyrimidines with an N-oxide group, from 5-bromo-4-phenylpyrimidine 1-oxide (I). Treatment of II with  $\text{PCl}_3$  converted it to 5-azido-4-phenylpyrimidine (III) [in 80% yield, mp 79-80°C (from petroleum ether)]. Azide II is quite stable with respect to diffuse light during storage, and its mass spectrum contains an  $\text{M}^+$  peak (m/e 213) with an intensity of 100% (70 eV, direct introduction, 100°C). The stability of azide III with respect to light is considerably lower, and the  $\text{M}^+$  peak (m/e 197) in its mass spectrum has an intensity of 7% (70 eV, direct introduction, 30°C).

The possibility of the synthesis of 5-azidopyrimidines through 5-hydrazinopyrimidines is limited by the accessibility of the latter. We were able to obtain 5-azido-2-methylsulfonylpyrimidine (VI) [in 55% yield, mp 142-145°C (dec., from alcohol)] by nitrosation of the corresponding 5-hydrazinopyrimidine, and the possibility of nucleophilic substitution of the  $\text{CH}_3\text{SO}_2$  group in VI makes it possible to obtain 2-substituted 5-azidopyrimidines; in particular, 2-methoxy derivative VII (mp 42-43°C) was obtained with  $\text{CH}_3\text{ONa}$ .

A mixture of five substances, the principal components of which are 5H-pyrimido[5,5-b]indole (IV) [in 15% yield, mp 239-241°C (from benzene)] and azopyrimidine V [in 37% yield, mp 186-189°C (with sublimation). UV spectrum (in alcohol),  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 268 (4.35) and 341 (4.01) nm] is formed when azide III is irradiated (in  $\text{CH}_2\text{Cl}_2$  with a DRSh-500 quartz lamp). Photolysis in  $\text{CF}_3\text{COOH}$  solution (in Pyrex with an SVD-120A lamp) made it possible to obtain IV in 90% yield. The principal fragmentation lines in the mass spectrum of indole IV, viz.,  $\text{M}^+$ ,  $(\text{M}-27)^+$ , and  $(\text{M}-54)^+$ , are similar to the data obtained for 9H-pyrimido[4,5-b]indole [2]. UV spectrum of IV (in alcohol),  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 212 (4.41), 239 (4.33), 257 (4.31), 298 (4.16), and 349 (3.41).



The IR spectra of II, III, VI, and VII contain absorption bands of an azide group at 2100-2200  $\text{cm}^{-1}$ , and the spectrum of azide II also contains a band at 1245  $\text{cm}^{-1}$  ( $\text{N} \rightarrow \text{O}$ ).

The structures of the compounds obtained are confirmed by the data from the PMR spectra ( $\delta$ , ppm): II [ $d_6$ -DMSO- $\text{CDCl}_3$  (2:1)] 8.80 (d,  $J = 2$  Hz, 2-H), 8.72 (d, 6-H), and 7.32-8.03 (m, 5H, Ph); III ( $\text{CDCl}_3$ ) 9.05 (s, 2-H), 8.66 (s, 6-H), and 7.37-8.12 (m, 5H, Ph); IV ( $d_6$ -DMSO) 11.71 (s, NH), 9.00 (s, 2-H and 4-H), 8.22 (d,  $J = 8$  Hz, 6-H), and 7.17-7.67 (m, 7-H, 8-H and 9-H); V ( $\text{CDCl}_3$ ) 9.34 (s, 2H, 2-H), 8.82 (s, 2H, 6-H), and 7.45-8.02 (m, 10H, Ph); VI ( $\text{CDCl}_3$ ) 8.70 (s, 4-H and 6-H) and 3.31 (s,  $\text{CH}_3$ ); VII ( $\text{CDCl}_3$ ) 8.35 (s, 4-H and 6-H) and 4.00 (s,  $\text{CH}_3$ ). The results of elementary analysis were in agreement with the calculated values.

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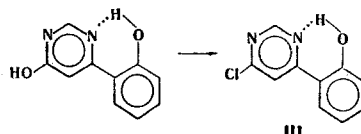
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## CONVENIENT METHOD FOR THE SYNTHESIS OF CHLOROPYRIMIDINES CONTAINING AN o-HYDROXYPHENYL GROUP

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The synthesis of 4-chloro-2-(o-hydroxyphenyl)quinazoline (I) by  $\text{COCl}_2$ -dimethylformamide (DMF) system has been described [1]. For selective chlorination we used the  $\text{SOCl}_2$ -DMF system (10:1, at 85-90°C for 1 h and 40 min), which makes it possible to avoid the difficulties involved in working with phosgene. This method was checked in the case of the synthesis of chloroquinazoline I from II and in the synthesis of 4-chloro-6-(o-hydroxyphenyl)pyrimidine (III) [in quantitative yield, mp 152-153°C (from isooctane)]. PMR spectrum: 12.01 (1H, s, OH), 9.05 (1H, s, 2-H), 8.35 (1H, s, 5-H), and 6.78-8.25 ppm (4H, m, Ph), 4-chloro-2-(o-hydroxyphenyl)pyrimidine [mp 100-102°C. PMR spectrum: 12.65 (1H, s, OH), 8.87 (1H, d,  $J_{65} = 5.5$  Hz, 6-H), 7.66 (1H, d, 5-H), and 6.80-8.46 ppm (4H, m, Ph)], 2-chloro-4-(1-hydroxyphenyl)pyrimidine [mp 147-148°C. PMR spectrum: 11.83 (1H, s, OH), 8.81 (1H, d,  $J_{65} = 5.5$  Hz, 6-H), 8.25 (1H, d, 5-H), and 6.85-8.18 ppm (4H, m, Ph)], and 2-chloro-4-phenyl-6-(o-hydroxyphenyl)pyrimidine [mp 160-161°C. PMR spectrum: 11.33 (1H, s, OH), 8.64 (1H, s, 5-H), and 6.73-8.44 ppm (9H, m, Ph)] from the corresponding hydroxypyrimidines. When



a starting spot was observed for the crude chloropyrimidines (on Silufol UV-254, elution with  $\text{CH}_2\text{Cl}_2$  or benzene), they were sublimed in vacuo or solutions in  $\text{CH}_2\text{Cl}_2$  or benzene were passed through a thin layer of silica gel. The results of elementary analysis were in agreement with the calculated values. The PMR spectra were obtained from solutions in DMSO.

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