REACTION OF 4,5-DIHALOPYRIMIDINES WITH 2-TOSYLMETHYLAZAHETARENES — ONE-STEP METHOD FOR OBTAINING CONDENSED POLYNUCLEAR SYSTEMS

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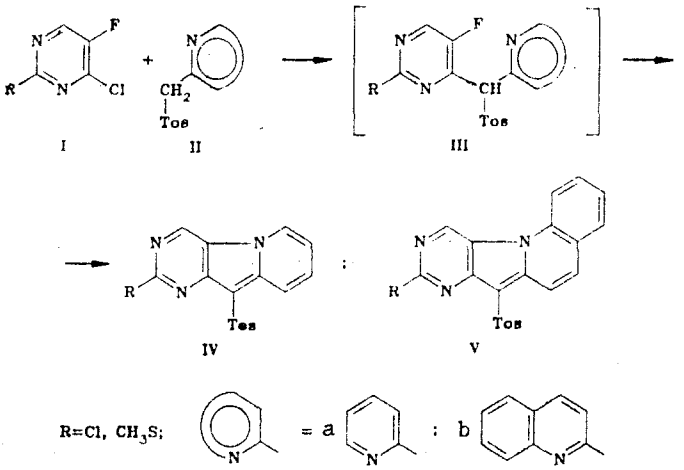
It is known that in the 4,5-dihalopyrimidine series the halogen atom in the 4 position is extremely labile in nucleophilic substitution reactions [1, 2], while the other halogen atom is essentially inert [3]. We have found that 4-chloro-5-fluoropyrimidines I react with carbanions generated from 2-tosylmethylazahetarenes IIa, b in the presence of potassium carbonate in refluxing DMF. However, the reaction does not stop at the step involving replacement of the chlorine atom (structure III) but concludes by cyclization to give polynuclear systems IV and V.



Unequivocal evidence in favor of the structures presented above is provided by the presence of the Overhauser effect in the PMR spectra: a 15% increase in the intensity of the 6-H signal on irradiation of 4-H is observed in the case of the formation of structure IV, while an 11% increase in the intensity of the 1-H signal on irradiation of 11-H is observed for structure V. This makes it possible to affirm the spatial closeness of the protons of the pyrimidine and pyridine (IV) or quinoline (V) rings, which is possible only in the structures presented above.

Compound IVa (R = Cl). This compound had mp 293°C (from chlorobenzene) and R_f 0.54 [here and subsequently, Silufol UV-254, toluene—isopropyl alcohol (7:3)]. PMR spectrum (CF_3CO_2D): 2.39 (3H, s, CH_3), 7.35-8.42 (7H, m, H_{Ar}), 9.34 (1H, d, 6-H), 9.67 ppm (1H, s, 4-H). The yield was 98%.

Compound IVa (R = CH_3S). This compound had mp 300°C (from DMF) and R_f 0.62. PMR spectrum (CF_3CO_2D): 2.47 (3H, s, CH_3), 2.95 (3H, s, CH_3S), 7.45-8.74 (7H, m, H_{Ar}), 9.10 (1H, d, 6-H), 9.43 ppm (1H, s, 4-H). The yield was 97%.

Compound Vb (R = CH_3S). This compound had mp 300°C (from DMF) and R_f 0.58. PMR spectrum (d_6-DMSO): 2.34 (3H, s, CH_3), 2.67 (3H, s, CH_3S), 7.40-8.53 (9H, m, H_{Ar}), 8.79 (1H, d, 1-H), 9.93 ppm (1H, s, 11-H). The yield was 92%.

IR spectra of IVa, b and Vb (KBr): intense absorption bands at 1335-1360 and 1160-1170 cm^{-1} ($R—SO_2—R^1$).

LITERATURE CITED

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