NEW TYPE OF TRANSFORMATION OF A 1,2,4-TRIAZINE RING TO PYRAZINE DERIVATIVES

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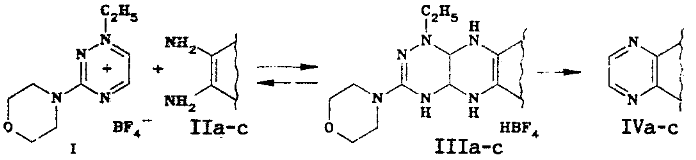
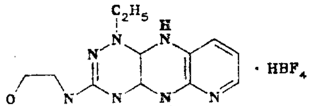
It is known that 1,2,4-triazines are prone to various types of ring transformation which occur both under the action of nucleophilic reagents [1-3], and on reaction with electron-rich dienophiles (the Diels—Alder reaction with reversed electron requirements) [1, 4].



IIa = o-phenylenediamine; IIb = 5,6-diaminopyrimidin-4-one; IIc = 2,3-diaminopyridine; IVa = quinoxaline; IVb = pteridin-4-one; IVc = pyrido[2,3-b]pyrazine.

We have discovered a new type of transformation of a triazine ring in which the 1-ethyl-1,2,4-triazine cation (I) participates. It has been established that the cation (I) reacts at 20°C with ortho-phenylenediamine (IIa) (in methylene chloride) and 5,6-diaminopyrimidin-4-one (IIb) (in 9:1 ethanol—DMF) with the formation of quinoxaline IVa (yield 43%) and pteridin-4-one IVb (yield 23%). This transformation is based on the susceptibility of the cation (I) to bi-addition of nucleophiles [5] and proceeds via the cyclic adducts IIIa,b which are then aromatized on account of separation of 3-morpholinoamidrazone.

In the reaction with 2,3-diaminopyridine IIc it was possible to isolate the primary products of the cyclization in the form of a mixture of two regio-isomers A and B in overall yield of 54%. On treating these adducts with potassium permanganate in acetone, instead of the expected aromatized tricyclic compound, pyridol[2,3-b]pyrazine (IVc) was obtained in 76% yield, which suggests that stabilization of the adducts III as a result of the separation of the morpholinoamidrazone is a more energetically favorable process.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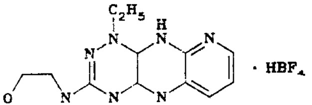
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The reaction products IVa-c were identified by comparison of their melting points and spectroscopic characteristics (NMR, mass-spectra) with those of samples whose structure is definitely known [6]. NMR spectrum of compound A (in acetone-D_6): 1.27 (3H, t, CH_3); 3.12 (2H, q, NCH_2); 3.3-4.0 (8H, m, morpholino); 4.96 and 5.44 (two d with ^3J = 4.4 Hz, 4a-H, 10a-H); 6.60 (1H, d d, $^3J_{8,7}$ = 5.1; $^3J_{8,9}$ = 7.6 Hz, 8-H); 6.97 (1H, d d, $^3J_{9,8}$ = 7.6, $^4J_{9,7}$ = 1.6 Hz, 9-H); 7.57 ppm (1H, d d, $^3J_{7,8}$ = 5.1, $^4J_{7,9}$ = 1.6 Hz, 7-H). The regio-isomer B was a minor formed in the ratio B:A = 1:3. The NMR spectrum of compound B: 4.74 and 5.55 ppm (two d, ^3J = 4.1 Hz, 4a-H and 10a-H); it was difficult to determine the chemical shift of the remaining proton signals on account of overlap by the absorptions of the corresponding groups of compound A.

The transformations detailed above appear to be a new type of 1,2,4-triazine transformation in which the triazine ring acts as a donor of a C—C fragment.

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