SYNTHESIS OF CONDENSED TETRAHYDROPTERIDINES BY THE CYCLIZATION OF THE 8-ETHYLPTERIDINIUM CATION WITH DINUCLEOPHILES*

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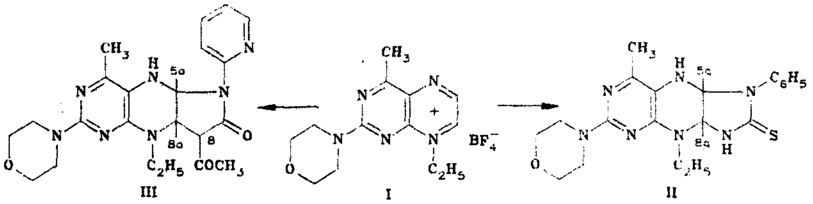
It was previously established in a series of published works that 1,4-diazinium cations can produce polycyclic compounds in reactions with dinucleophiles; the very diverse five- and six-membered nitrogen-, oxygen-, and sulfur-containing heterocycles are annelated to the pyrazine fragment in these polycyclic compounds (see the reviews [2, 3]). The only example of such a cyclization, which was described in pteridine series, is the formation of 5,5a,8a,9-tetrahydrofuro[2,3-g]pteridines in the reaction of unsubstituted pteridine with β-dicarbonyl compounds showing the properties of 1,3-C,O-dinucleophiles [4]. Information on the reaction of pteridines with other types of dinucleophile is absent from the literature. Attempts to cyclize N,C- and N,N-dinucleophiles with pteridines proved to be unsuccessful [5].

In the present work, the possible participation of pteridines, activated by charge, in cyclizations with dinucleophiles is reported. As a result of the reactions of 2-morpholino-4-methyl-8-ethylpteridinium borofluoride (I) with phenylthiourea and N-(α-pyridyl)acetoacetamide in ethanol at 20-30°C in the presence of triethylamine, the derivatives of 5,5a,6,7,8a,9-hexahydro-8H-imidazo[4,5-g] (II) and 5,5a,7,8,8a,9-hexahydro-6H-pyrrolo[2,3-g]pteridine (III) were correspondingly obtained in high yields. The structure of the compounds II and III was established by the comparison of their PMR spectra with the spectra of compounds of a similar structure in the quinoxaline series for which the detailed analysis was given in the work [6].



The conversions found are the first case of the participation of pteridinium cations in cyclizations with dinucleophiles, and they permit the accomplishment of the single-stage synthesis of derivatives of the new heterocyclic systems: pyrrolo- and imidazo-pteridines.

Compound (II). The mp was 200-202°C; the yield was 64%. The PMR spectrum (in $CDCl_3$) was as follows: 1.26 (3H, triplet, CH_3), 1.74 (3H, singlet, CH_3), 2.9-4.3 (2H, multiplet, $N\text{-}CH_2$), 3.72 (8H, multiplet, protons of the morpholine ring), 5.38 (1H, doublet, 8a-H, $^3J_{5a,8a} = 7.7$ Hz), 5.82 (1H, double doublet, 5a-H, $^3J_{5,5a} = 3.5$ Hz), 7.0-7.7 (5H, multiplet, phenyl), and 8.05 ppm (1H, broad singlet, NH).

Compound (III). The mp was 149-150°C; the yield was 79%. The PMR spectrum (in $CDCl_3$) was as follows: 1.19 (3H, triplet, CH_3), 2.13 (3H, singlet, CH_3), 2.54 (3H, singlet, $COCH_3$) 3.0-4.3 (2H, multiplet, $N\text{-}CH_2$), 3.71 (8H, multiplet, protons of the morpholine ring), 4.01 (1H, doublet, 8-H, $^3J_{8,8a} = 8.2$ Hz), 4.75 (1H, multiplet, 8a-H), 5.25 (1H, broad singlet,

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NH), 5.58 (1H, double doublet, 5a-H, ${}^3J_{5,5a} = 2.9$, ${}^3J_{5a,8a} = 5.7$ Hz) and 6.9-8.6 ppm (4H, multiplet, protons of the pyridine ring).

Satisfactory data of the elemental analysis were obtained for the compounds II and III.

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SYNTHESIS OF 2,3-DIPHENYL-5,6-DIHYDRO-1,3-OXAZINIUM HEXACHLOROANTIMONATE FROM 2-PHENYL-1,3-DIOXANE

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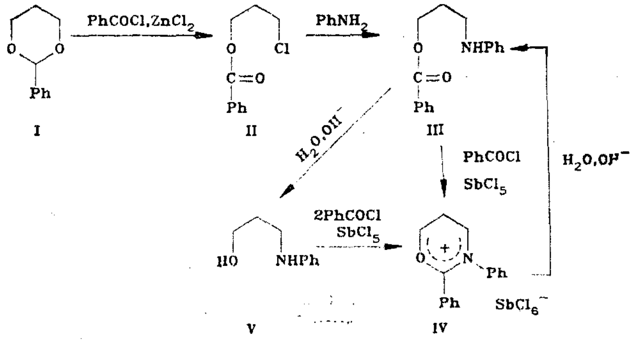
We have found a method for the synthesis of 1,3-oxazinium salts, taking as an example the previously unknown 2,3-diphenyl-5,6-dihydro-1,3-oxazinium hexachloroantimonate (IV). The main features of the proposed scheme are the acylation of 2-phenyl-1,3-dioxane (I) by benzoyl chloride, the exchange reaction of chlorine for the amino group in the resulting γ-chloroester IIa, and the subsequent acylation of compound III by benzoyl chloride in the presence of $SbCl_5$.

The secondary aminoalcohol V is formed on the alkaline hydrolysis of 1-phenylamino-3-benzoyloxypropane (III). Compound V also gives the salt IV by the action of benzoyl chloride and $SbCl_5$ in the ratio of 2:1.



The structure and composition of the salt IV were confirmed by the data of IR spectroscopy and elemental analysis, as well as by a chemical method. Hydrolysis of the salt IV leads to the opening of the ring with the formation of the γ-aminoester (III). The methods of [1] and [2] were employed to obtain 2-phenyl-1,3-dioxane I and 1-benzoyloxy-3-chloropropane (II) respectively.

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