OXIDATION AND REACTIVITY OF THIOPTERIDINES

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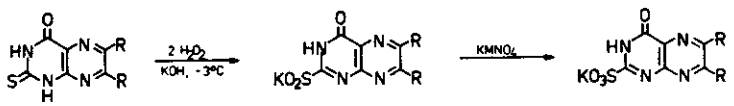
Recent investigations in the field of thiopteridines indicated that the thioxo group reveals an interesting functionality of versatile synthetic purpose. Since so far only S-alkylations have been performed in this series we focussed our attention on the various oxidation products and their chemical reactivity. We found that 2-thiolumazine and its derivatives are easily oxidized in basic medium at low temp. with two equivalents of H_2O_2 to the corresponding 4-oxo-3,4-dihydropteridine-2-sulfinates, whereas further oxidation led to the analogous sulfonates. Both types of compounds can be isolated and are well characterized by physical means.



The chemical reactivity of both series differs to some extent. Acidic hydrolysis leads in both cases to lumazines, which are also obtained under basic conditions, but here are the sulfinates more reactive than the sulfonates. Attempts to form the free sulfinic acid can result in SO_2 elimination showing a striking parallelism to the decarboxylation reaction. Nucleophilic displacement reactions with amines proceed again more readily with the sulfinates whereas the sulfonates afford usually some boiling. It was also recognized that in 2-thiolumazines the sulfur can directly be displaced by amines at room temp. if H_2O_2 is added for activation.

Analogous reactions have also been performed with 4-thiolumazines and will be discussed in detail. 7-Thiolumazines are even more unique since here the complete series of oxidation products, the disulfides, the sulfenates, the sulfinates, and the sulfonates could be synthesized. 1,3,6-Trimethyllumazine-7-sulfenic acid turned out to be a new unusually stable free sulfenic acid showing interesting properties and reactivities towards various nucleophiles.