NEW DIPOLAR CYCLOADDITIONS
WITH SULFUR-CONTAINING ZWITTERIONS

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In the course of our recent investigations feasible reaction pathways to sulfur-containing
zwiterionic pyridine derivatives (e.g. 1) have been elaborated [1]. These new zwitterions as
1,3-dipoles readily reacted with dipolarophiles in cycloaddition reactions and provided new
derivatives of five membered heterocycles fused to the pyridine ring [2].

We have found in some cases that even if the expected cycloaddition occurs (e.g. reaction of
zwiterion 1 and dimethyl acetylenedicarboxylate – “DMAD” – yields the bicyclic fused
pyrazole 2), a spontaneous subsequent transformation takes place, and as a result of a ring
transformation the pyrrole fused ring system 3 is formed. The $2 \rightarrow 3$ transformation was
interpreted as a [1,5]-sigmatropic rearrangement.

Extension of the scope of zwitterionic model compounds and dipolarophiles resulted in
observation of novel regioselective cycloadditions. Experimental details and possible reaction
mechanisms will be discussed.

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