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CONVERSION OF PYRIMIDO[5,4-e]-as-TRIAZINE 4-OXIDES INTO PYRROLO[3,2-d]PYRIMIDINES BY THE 1,3-DIPOLAR CYCLOADDITION REACTION

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The 1,3-dipolar cycloaddition reaction of fervenulin 4-oxides (6,8-dimethylpyrimido[5,4-e]-as-triazine-5,7(6H,8H)-dione 4-oxides: 1a-c) with acetylenic esters leading to pyrrolo[3,2-d]pyrimidines (9-deazapurines) has been investigated.

Reaction of (1a-c) with Dimethyl acetylenedicarboxylate (DMAD)

Heating of (1a-c) with DMAD in toluene at 95° for 30 min afforded the corresponding pyrrolo[3,2-d]pyrimidines (2a-c) in 55-64% yields. When (1a) was treated with DMAD in toluene under reflux, the unexpected pyrrolo[3,2-d]pyrimidine (3) was formed in 65% yield.

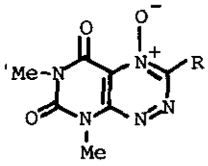
Reaction of (1a-c) with Methyl propiolate (MP)

Treatment of (1a) with MP in toluene at 95° for 30 min provided pyrrolo[3,2-d]pyrimidine (4) in 53% yield, and none of the expected (2a) could be isolated. The reaction of (1b-c) with MP in toluene under the same conditions yielded the respective (2b-c) in 72-75% yields.

Reaction of (1a-c) with Ethyl phenylpropiolate (EPP)

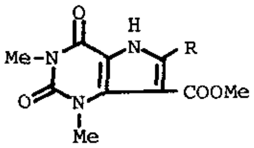
Heating of (1a) with EPP in toluene at 95° for 30 min furnished pyrrolo[3,2-d]pyrimidine (5) in 79% yield, while the treatment of (1b-c) with EPP in toluene afforded the corresponding pyrrolo[3,2-d]pyrimidine (6b-c) in 53-54% yields.

The mechanism for the formation of pyrrolo[3,2-d]pyrimidines is presented.

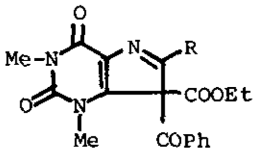


1a-c

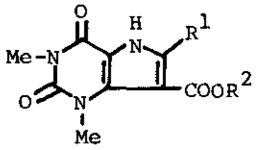
a, R=H
b, R=Me
c, R=Et



2a-c



6b-c



3; R^1=COCOOMe
R^2=Me

4; R^1=CHO
R^2=Me

5; R^1=COPh
R^2=Et