REACTION OF PYRIDINIUM OR ISOQUINOLINIUM KETENE DITHIOACETALS WITH AROMATIC N-IMINES OR S-IMINES

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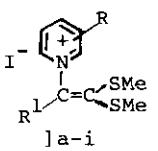
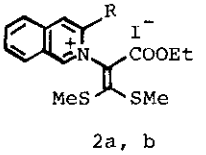
We now wish to report reaction of pyridinium or isoquinolinium ketene dithioacetals(1a-i, 2a, b) with aromatic N-imines(3a-m, 4,5) or S-imines(6, 7, 8). Reaction of 1-[1-substituted 2,2-bis(methylthio)ethenyl]pyridinium iodides(1a-f) with 1-aminopyridinium mesitylenesulfonates(3a-g) in the presence of triethylamine in ethanol gave the corresponding 3-substituted 2-methylthiopyrazolo[1,5-a]pyridines (11a-f) and 3-substituted 2-methylthioimidazo[1,2-a]pyridines(9a-e). Benzoyl compounds, 1-[1-benzoyl-2,2-bis(methylthio)ethenyl]pyridinium iodides(9h, i) were reacted with 3a to give only 3-benzoyl-2-methylthioimidazo[1,2-a]pyridines (9h, i, j, k). Ketene dithioacetals (1a: R^1=COOEt, 1g: R^1=COPh, 1f:R^1=CN, etc.) were reacted with substituted pyridinium N-imines(3g-m) having a electronattracting group on pyridine ring to yield only pyrazolo[1,5-a]pyridine derivatives(11h-r). Similarly, pyrazolo[1,5-a]quinoline (12) and pyrazolo[5,1-a]isoquinoline(13) derivatives were prepared from the corresponding N-imines(4,5) and 1a. Reaction of 2-[1-ethoxycarbonyl-2,2-bis(methylthio)ethenyl]isoquinolinium iodides (2a, b) with aromatic N-imine(3a) gave the corresponding imidazo[2,1-a]isoquinolines (10a, b). When 2a was reacted with isoqinolinium N-imine(5), a mixture of 10a and 13 was obtained.

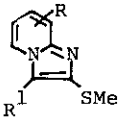
Reaction of ketene dithioacetals (1a, c, d, e, f) with various s-imines (6, 7, 8) was carried out to give imidazo[1,2-a]pyridine derivatives(9a, c, d, e, f, g) in quite low yields. However, these derivatives are available for the identification of compounds derived from 1 and 3.



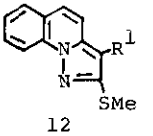
1a-i
R^1=COOEt, CN, COPh



2a, b
R=H, Me



9a-k



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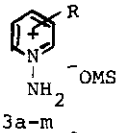
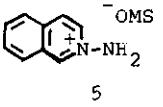


3a-m



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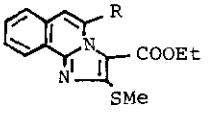
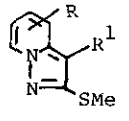
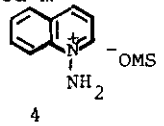


10a, b



11a-r



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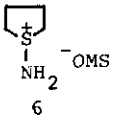

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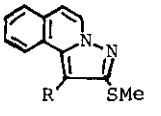

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