

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:  $R^1 = \text{COOEt}$ , 1g:  $R^1 = \text{COPh}$ , 1f:  $R^1 = \text{CN}$ , 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-f). 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 isoquinolinium 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.

