SYNTHESES AND REACTIONS OF HETEROCYCLIC IMINODITHIOCARBOXYLATE

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(Alkylthio)thiocarbonylimino-1-methyl-1,2-dihydropyridine derivatives (2a, b, c, d, e) were prepared by the reaction of 2-amino-1-methylpyridinium iodides (1a, b, c, d) with carbon disulfide and subsequent alkylation with dimethyl sulfate in the presence of sodium hydride in tetrahydrofuran in a good yield. Similarly, 1-methyl-4-(methylthio)thiocarbonylimino-1,4-dihydropyridine (2i), 1-methyl-2-(methylthio)thiocarbonyl-1,2-dihydrothiazole (2g), and 1-methyl-2-(methylthio)thiocarbonyl-1,2-dihydrobenzothiazole (2h) were also synthesized by the reaction of the corresponding 2-imino- and 4-imino-N-methylheterocyclic compounds with carbon disulfide.

Reaction of 2a - e with dimethyl acetylenedicarboxylate (DMAD) afforded 2 or 4-[1,2-bis(methoxycarbonyl)-2-thioxoethylidene]-1,2 or 1,4-dihydropyridine derivatives (6a, b, c, d), accompanied with extrusion of alkyl thiocyanate from 1,4-cycloadduct, spiro-1,3-thiazine derivatives. Further, reaction of 2i with DMAD (2 mol) gave cyclobuteno[1,2-b]azocine derivative (8). The reaction of 2h with DMAD affoded 4H-pyrrolo-2-spiro-2-(2,3-dihydrobenzothiazole) (9), accompanied with desulfrization.

2-[N-Bis(methylthio)methylene]amino-1-methylpyridinium and benzothiazolium iodides (10a, b), which were prepared by the alkylation of 2a and 2h with methyl iodide, reacted with nucleophilic reagents such as amines and active methylene compounds to yield the corresponding replacement products of one or two methylthio groups in a good yield.