LITHIATION OF FIVE-MEMBERED HETEROAROMATIC COMPOUNDS. THE 5-ALKOXYMETHYL- AND 5-ALKYLTHIOMETHYLISOXAZOLES.

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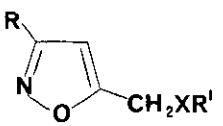

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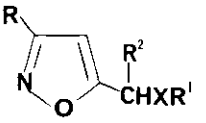

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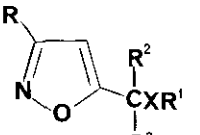

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Various methods for the preparation of 5-alkoxymethyl and 5-alkylthiomethylisoxazoles, 1, were studied and will be described. 1-Methoxypentan-2,4-dione with hydroxylamine gave a mixture of the isomeric 3-methyl-5-methoxymethylisoxazole, 1 ($R = R^1 = CH_3$; $X = O$) and 3-methoxymethyl-5-methylisoxazole, which was readily separated by utilizing the preferential reaction of 1 with n-butyllithium. Compounds of type 1 were readily converted to compounds of types 2 and 3, by sequential reaction with n-butyllithium and an appropriate reagent. Among the compounds thus prepared were thioacetals and mixed thioacetals, 2, α-alkoxy- and α-thioalkoxy acids, 2; ortho-thio esters and ortho-mixedthio esters, 3; α,α-dithioalkoxy acids and α-alkoxy-α-thioalkoxy acids, 3.