PREPARATIONS OF 3-TRIFLUOROMETHYLPYRAZOLINES AND PYRAZOLES FROM N-ARYLTRIFLUOROMETHYLNITRILIMINES

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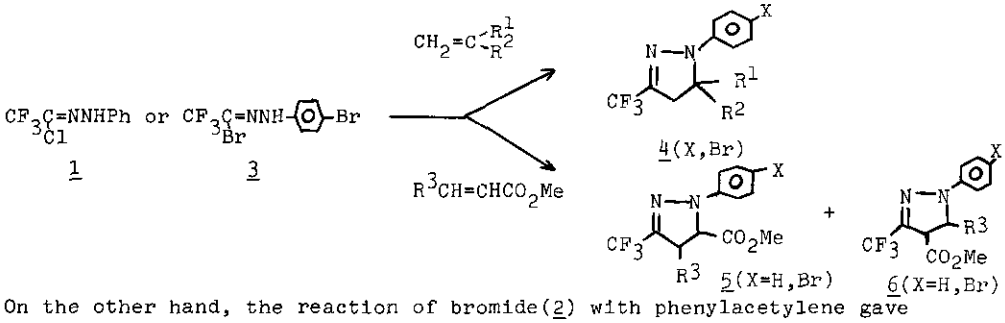
The heterocyclic compounds bearing fluorine atom or trifluoromethyl group have received current interest because of their pharmacological activity. On the other hand, it is well known that 1,3-dipolar compounds are useful to prepare various heterocyclic compounds. In this connection, we prepared trifluoromethylnitrilimine which reacted with olefins and acetylenes to give 3-trifluoromethylpyrazolines and pyrazoles, respectively.

N-Phenyltrifluoroacethydrazidoylchloride(1) and bromide(2), the precursors of N-phenyltrifluoromethylnitrilimine, were obtained by the reactions of trifluoroacetaldehyde phenylhydrazone with N-chlorosuccinimide and N-bromosuccinimide, respectively. The similar reaction with 2 equiv. of bromine gave N-p-bromophenyltrifluoroacethydrazidoylbromide(3).

Halides(1) and (3) reacted with 1-substituted and 1,1-disubstituted olefins in the presence of triethylamine to afford only 3-trifluoromethylpyrazolines(4). The similar reactions with β-substituted methyl acrylates, however, gave rather complicating results: that is, the reactions with methyl crotonate gave exclusively (5), whereas those with methyl cinnamate provided (5) together with the isomers(6).



On the other hand, the reaction of bromide(2) with phenylacetylene gave 3-trifluoromethylpyrazole(7) and its isomeric substituted product(8).