

REACTIONS OF TRIFLUOROACETONITRILE YLIDES WITH ELECTRON-DEFICIENT
OLEFINS AND ACETYLENES

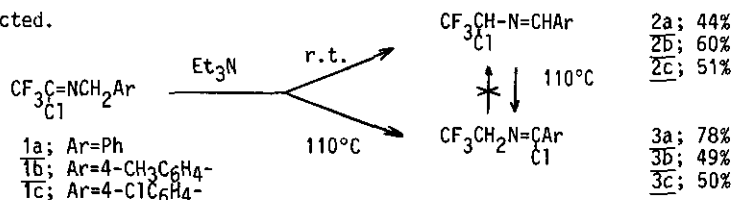
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As a part of research on applications of the fluorinated 1,3-dipolar compounds as building blocks of the heterocyclic compounds with fluorine groups, we now report the behavior of trifluoroacetimidoyl chlorides 1, the precursors of trifluoroacetonitrile ylides, in the presence of triethylamine, and their reactions with electron-deficient olefins and acetylenes which give trifluoromethylpyrrolines and -pyrroles.

The imidoyl chlorides 1 were prepared by chlorination of the corresponding trifluoroacetamides with phosphorus pentachloride in moderate yields.

Treatment of the imidoyl chlorides 1a-c with triethylamine in toluene at room temperature for 20 h gave the proton-shifted chlorides 2a-c in good yields which could be isolated by distillation and stored under the nitrogen atmosphere. On the other hand, refluxing of 1a-c in toluene resulted in the formation of the benzimidoyl chlorides 3a-c which were also obtained from the isolated 2 under the similar conditions. The reverse conversion from 3 to 2, however, could not be detected.



The reaction of the chloride 1a with an excess of methyl acrylate at room temperature for 7 days in the presence of triethylamine yielded 34% of 4-methoxycarbonyl-5-phenyl-2-trifluoromethyl-Δ¹-pyrroline (4a). The similar reaction with phenyl acrylate gave the corresponding pyrroline 4b in 29% yield. In contrast to acrylates, the reaction with acrylonitrile was more complicated and gave 5 in 20% yield which may be obtained from the addition of the proton-shifted pyrroline 6 to another molecule of acrylonitrile. Similarly, the results of the reactions of 1 with dimethyl maleate, fumarate, dimethyl acetylenedicarboxylate and methyl propiolate are also presented.

