

SYNTHESES OF PHENYLTRIFLUOROMETHYLACETYLENES
AND THEIR 1,3-DIPOLAR REACTION

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Hexafluorobutyne-2, or bis(trifluoromethyl)acetylene, is a very interesting species of high reactivity. It reacts as a good dipolarophile or dienophile and it is a good starting material for many trifluoromethyl compounds. Thus, we want to examine a monotrifluoromethylated acetylenes, but a convenient method for the synthesis of such compounds was not known. To solve this problem, we examined the intramolecular Wittig reaction of trifluoroacetylphosphonium benzylides and found it very useful. p-Substituted benzyl halides reacted with triphenylphosphine. The phosphonium salts were treated with a suitable base and then trifluoroacetic anhydride to give the trifluoroacetyl ylides. The ylides were thermolyzed under vacuum. Fairly good yields of phenyltrifluoromethylacetylenes were obtained.

These acetylenes reacted with excess of diazomethane to give N-methyltrifluoromethylphenylpyrazoles. In this case, the reactivity of the acetylenes are rather low than hexafluorobutyne-2. The carbon atom of diazomethane added to the carbon substituted with the trifluoromethyl group preferentially. This is a short cut for trifluoromethylated pyrazoles.

A Similar reaction with phenylazide provided a simple method for trifluoromethyltriazole derivatives.

