

FLUORIDE- OR ALKOXIDE-INDUCED REACTION OF 1-(TRIMETHYLSILYL)-
METHYLAZOLES WITH CARBONYL COMPOUNDS

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Fluoride- or alkoxide-induced desilylation of 1-(trimethylsilyl)methylazoles (1a-e) in the presence of carbonyl compounds was explored and the reactivities of the azolymethylanions (2a-e) obtained from these reactions are reported. Also, in connection with the reactivity of 1-(trimethylsilyl)methyl-1,2,4-triazole (1d), desilylation of 1-bis(trimethylsilyl)methyl-1,2,4-triazole (3d) was investigated.

Reactions of 1d with carbonyl compounds were carried out in the presence of cesium fluoride (CsF) catalyst or tetrabutylammonium fluoride (TBAF). For example, the CsF-catalyzed reaction of 1d with benzophenone (4) and subsequent hydrolysis gave 1,1-diphenyl-2-(1,2,4-triazol-1-yl)-1-ethanol (5d, 52%) and diphenyl(1-methyl-1,2,4-triazol-5-yl)methanol (6d, 28%). However, when TBAF was used, 21% of 5d and 46% of 6d were obtained. These results can probably be explained as follows. Desilylations of 1d by these fluorides generate the common anion 2d. The anion 2d generated by CsF mainly reacts as a nucleophile with 4 to give 5d as the main product. However, the naked anion 2d generated by TBAF mainly reacts as a base to pull off the proton at the 5 position of 1d and gives the corresponding anion which adds to 4 and yields 6d as the main product of the subsequent desilylation. Analogous reactions of 1a, b, c and e with carbonyl compounds using fluoride or alkoxide were studied. Also TBAF-catalyzed desilylation of 3d generated 7d which upon selective nucleophilic addition to carbonyl compounds and subsequent elimination gave 1-vinyl-1,2,4-triazoles 8d in good yields.

