REACTIONS OF 3-SUBSTITUTED 2-NITROSOIMINO-2,3-DIHYDROBENZOTHIAZOLES WITH GRIGNARD REAGENTS AND ORGANOLITHIUMS

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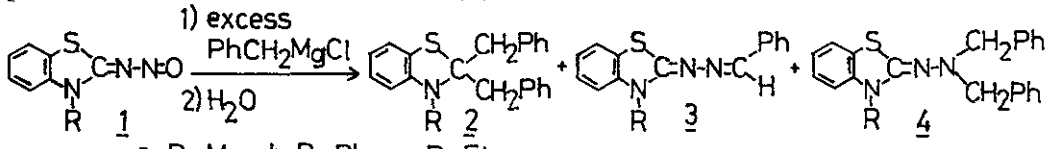
3-Substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (1) reacted with excess benzylmagnesium chloride to give 3-substituted 2,2-dibenzyl- (2), 2-N'-benzylidene-hydrazono- (3), 2-N',N'-dibenzylhydrazono-2,3-dihydrobenzothiazoles (4). Main reaction (formation of 3 and 4) occurred on the nitroso group of 1, which was shown to proceed via the same intermediate (A).



a. R=Me, b. R=Ph, c. R=Et.

On the other hand, phenylmagnesium bromide reacted with 1b to produce 2,2,3-triphenyl- (8b, 48%), 3-phenyl-2-N'-phenylhydrazono-2,3-dihydrobenzothiazoles (10b, 17%) and small amount of bis(N-phenyl-o-aminophenyl) disulfide (9b). Mesitylmagnesium bromide reacted with 1a to give 2-mesityl- (11a, 46%), 2-N'-mesitylhydrazono-3-methyl-2,3-dihydrobenzothiazoles (13a, 18%) and 3-methyl-2-benzothiazolone(12a, 10%). tert-Butylmagnesium chloride reacted with 1 to give similar products to mesitylmagnesium bromide. These reactions occurred mainly on C-2 of benzothiazoline ring.

The main reaction path of organolithiums (phenyl- and n-butyllithium) with 1 was the attack on the sulfur of benzothiazoline ring, different from that of the corresponding Grignard reagents.

1 reacted with excess phenyllithium to give mainly N,S-disubstituted o-aminothiophenols (21) and almost the same amount of benzophenone. A trace of 3-substituted 2,2-diphenyl-2,3-dihydrobenzothiazoles (8) were also obtained.

1a reacted with excess benzyllithium to afford 2a and 9a.

These apparent differences of reactivity of Grignard reagents and organolithiums with 1 are discussed in relation to the unique character of 1 and also to organometallics used.