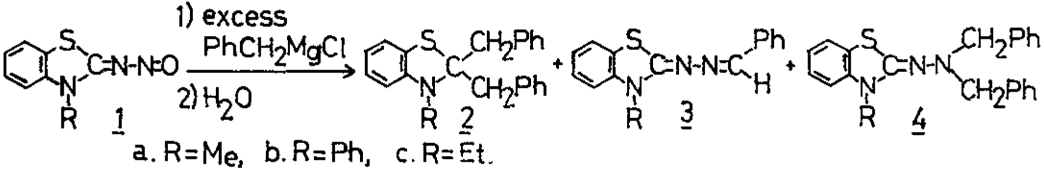
REACTIONS OF 3-SUBSTITUTED 2-NITROSOIMINO-2,3-DIHYDROBENZOTHIAZOLES WITH GRIGNARD REAGENTS AND ORGANOLITHIUMS

Motoyuki Hisaoka, Kin-ya Akiba, and Naoki Inamoto

Department of Chemistry, Faculty of Science, The University of Tokyo,

Hongo, Bunkyo-ku, Tokyo, 113.

3-Substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (1) reacted with excess benzylmagnesium chloride to give 3-substituted 2,2-dibenzyl- (2), 2-N'-benzylidenehydrazono- (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).



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.