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CHEMISTRY OF NITROSOIMINES. VIII.[1] REACTIONS OF 3-SUBSTITUTED 2-NITROSOIMINO-2,3-DIHYDROBENZOTHIAZOLES WITH ORGANOLITHIUMS

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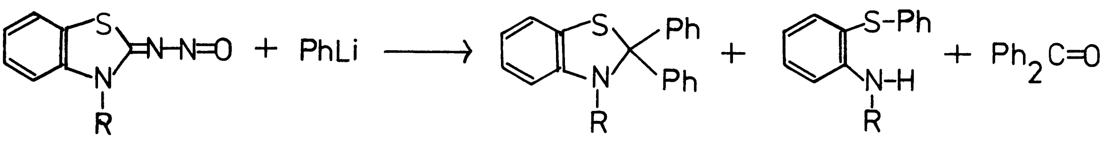
Reactions of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (1) with phenyllithium and n-butyllithium gave S, N-disubstituted *o*-aminothiophenol (3) as major product due to direct attack at the sulfur atom of benzothiazoline ring while that with benzyllithium gave 2,2-dibenzyl compound (2) and bis(N-substituted *o*-aminophenyl) disulfide (5). These results present a striking contrast to those with Grignard reagents.

Reactions of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (1) with Grignard reagents were shown to give different types of main products depending on the structure of Grignard reagents.[2] We report here some reactions of 1 with organolithiums, which are different from those of Grignard reagents in their main reaction paths.

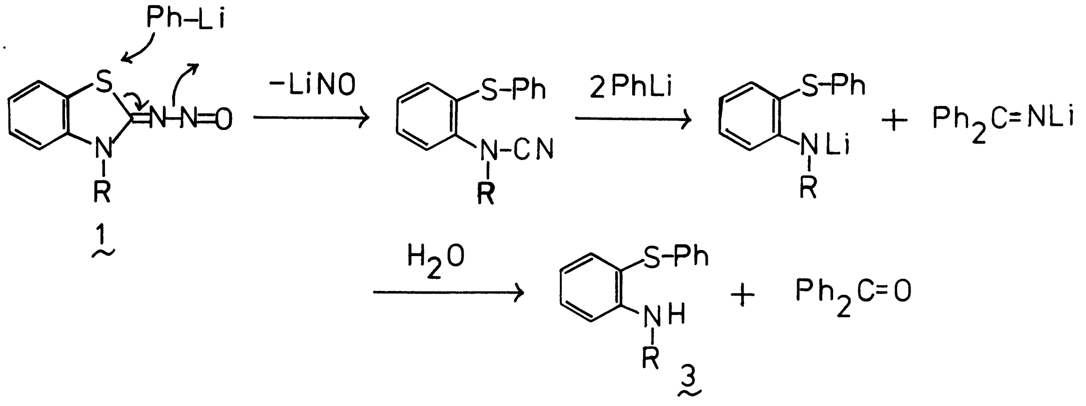
1a (20 mmol) was added portionwise to excess phenyllithium[3] (ca. 100 mmol) in ether at 0°C under nitrogen with stirring. The mixture was stirred for 60 min after the addition, and chromatographed on silica gel after usual work-up. A trace amount of 2a (mp 191.5-192.5°C)[2] was eluted with n-hexane and benzene (1:1). Monoacetyl derivative (4a; mp 107.0-107.5°C) of 3a was prepared in 80% yield by refluxing 3a in acetic anhydride for 1 hr.



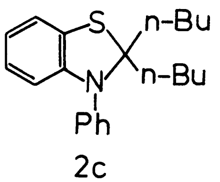
1 a) R=Ph; b) R=Me 2 3

Under the same conditions, 1b (25 mmol) and excess phenyllithium gave 2b (mp 142.0-143.0°C, trace), 3b (oil, 36%) and benzophenone (35%). Monoacetyl derivative (4b, oil) of 3b was also prepared in 68% yield.

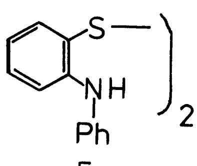
The formation of 3 can be ascribed to nucleophilic attack of phenyllithium to the sulfur atom of benzothiazoline ring followed by ring opening as shown below. The elimination of the cyano group from diphenylcyanamide by phenylmagnesium bromide supports the second step of the following scheme.[4)]



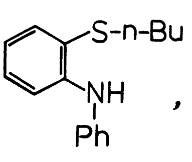
When n-butyllithium (68 mmol) in n-hexane was added to a suspension of 1a (19.2 mmol) in ether under nitrogen at 0°C, the following products, 2c (oil), 5a (oil), 3c (oil), and 6 (mp 112.0-113.0°C), were obtained by column chromatography on silica gel in 10, 3, 43, and 10% yields, respectively.



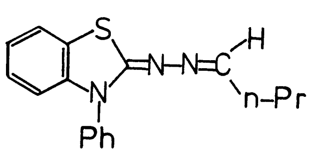
2c



5a



3c



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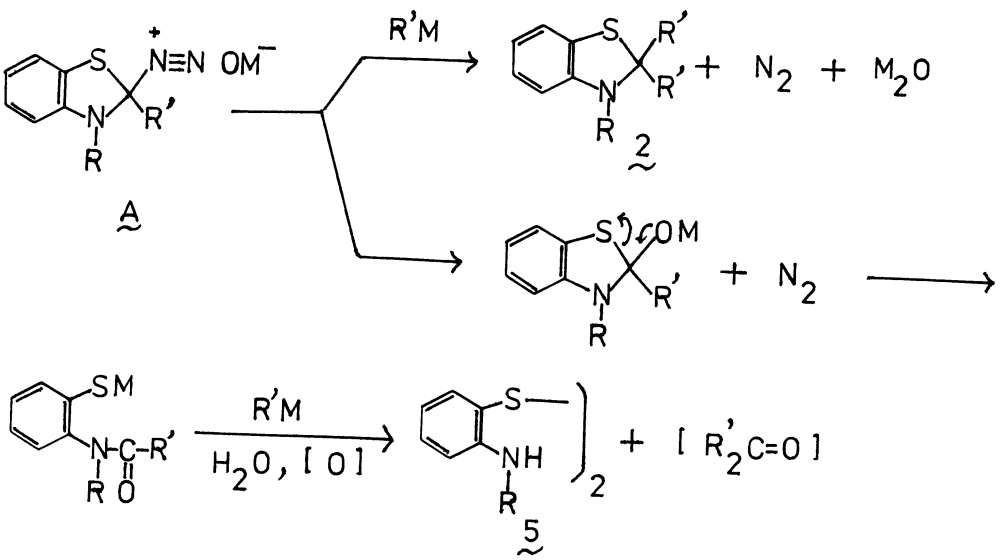
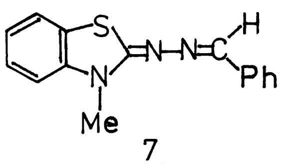
The formation of 2 and 6 can be explained by the same mechanism as that shown previously for the reaction of 1 with Grignard reagents.[2)]

The formation of bis(N-substituted o-aminophenyl) disulfide (5) is ascribable to the decomposition of the intermediate diazonium compound (A) because of the strong nucleophilicity of the counter ion (OM^-) from lithium reagents in contrast with that from Grignard reagents.



This process (attack on C-2) became the main path of the reaction when 1b and benzyllithium$^{5)}$ were allowed to react in tetrahydrofuran under the same conditions, yielding 2d (R=Me, R'=CH_2Ph; mp 86.5-87.5°C) and 5b (R=Me; mp 66.5-67.0°C) in 16 and 38%, respectively. Diacetyl derivative (mp 173.0-173.8°C) of 5b was obtained in 87% yield by refluxing 5b in acetic anhydride for 1 hr. Direct attack on the sulfur atom of benzothiazoline ring, which was the main path with phenyl- and n-butyllithiums, was observed neither in this case nor in reactions with Grignard reagents.

Although detailed mechanism is yet to be explored, it is worthwhile to mention, as a reference, that the products of the reaction of 1b with benzylmagnesium chloride in ether were 2d (8%),$^{6)}$ 7 (44%), and 8 (19%), where the main path was the attack on the nitroso group of 1b with benzylmagnesium chloride.$^{2)}$



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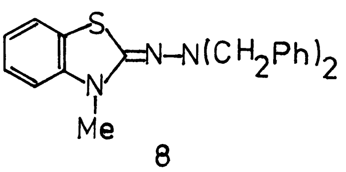

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2) K. Akiba, T. Kawamura, M. Hisaoka, and N. Inamoto, Chem. Lett., **1973**, 201.

3) R. G. Jones and H. Gilman, Org. Reactions, **4**, 339 (1951).

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6) In ref. 2, we reported that no **2d** was formed, but it has been found that **2d** is obtained in a small yield by later experiments.

7) **3a**, **4a** and **4b** gave correct elemental analyses and their structures were confirmed by MS, NMR and IR.
The structures of **2c**, **3b** and **3c** were supported by MS, NMR and IR.

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