

CHEMISTRY OF NITROSOIMINES. VII.¹ REACTIONS OF 3-SUBSTITUTED
2-NITROSOIMINO-2,3-DIHYDROBENZOTHAZOLES WITH GRIGNARD AND
LITHIUM REAGENTS OF THE CORRESPONDING 2-IMINO COMPOUNDS

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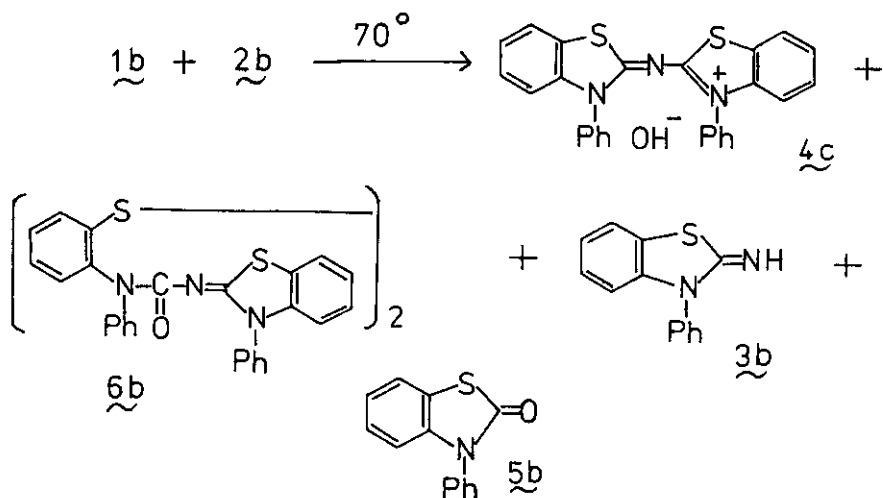
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Reactions of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles with Grignard and lithium reagents of the corresponding 2-imino compounds gave azamethinecyanine hydroxides and their hydrolysis products, respectively, in high yields.

We reported previously that lithium aluminum hydride² and several Grignard reagents³ reacted with 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (1) at both nitrogen of nitroso group and C-2 of the ring.

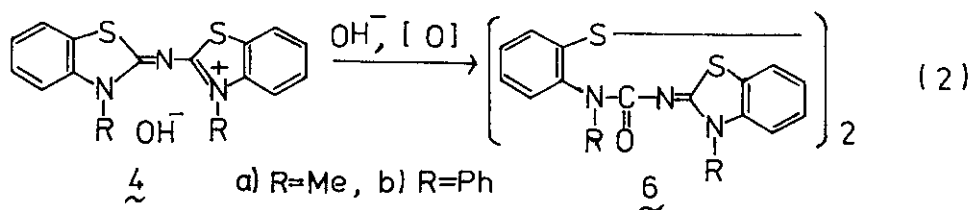
Now we report here the reactions of Grignard and lithium reagents of 3-substituted 2-imino-2,3-dihydrobenzothiazole (3) on 1, which seemingly reacted almost exclusively at C-2 of 1. A typical example is shown below.

To a Grignard reagent (2, 15 mmol) of 3a in tetrahydrofuran (THF) (150 ml), 1a (10 mmol) was added portionwise at room temperature with stirring under nitrogen (run 1). The solution



Then, the reaction of 1a (10.5 mmol) with lithium compound (13 mmol) of 3a was carried out in THF (150 ml) at 0 ° (run 4). After filtration of the resulting precipitates (4a), chromatography of the filtrate afforded 4a (1.0 mmol) and 6a (mp 253.0-253.5°, 8.2 mmol). Thus, in the case of lithium compound, the ring opened product (6) was mainly obtained.

The formation of 6b in run 3 and 6a in run 4 is ascribed to the hydrolysis of the corresponding 4. This was shown by separate hydrolysis of 4a and 4b with aqueous sodium hydroxide in ethanol, which afforded 6a and 6b in 84 and 78%, respectively.



The result of hydrolysis of 4 is in contrast with that of a triazacyanine which afforded the corresponding 2-iminothiazoline (3) and thiazol-2-one (5).⁴

Transnitrosation⁵ of the nitroso group of 1 to the metalated imino group of 2 should be competing with Eq. (1), and we have obtained such evidences in run 2 (formation of 3b) and also in the reaction of 1a with 2b, and details are under investigation. However, this selective and facile reaction of the nitrosoimines can be used as a synthetic method of azamethinecyanines.⁶

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