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

Kin-ya Akiba, Kiyofumi Ishikawa, and Naoki Inamoto*
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113, Japan

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.

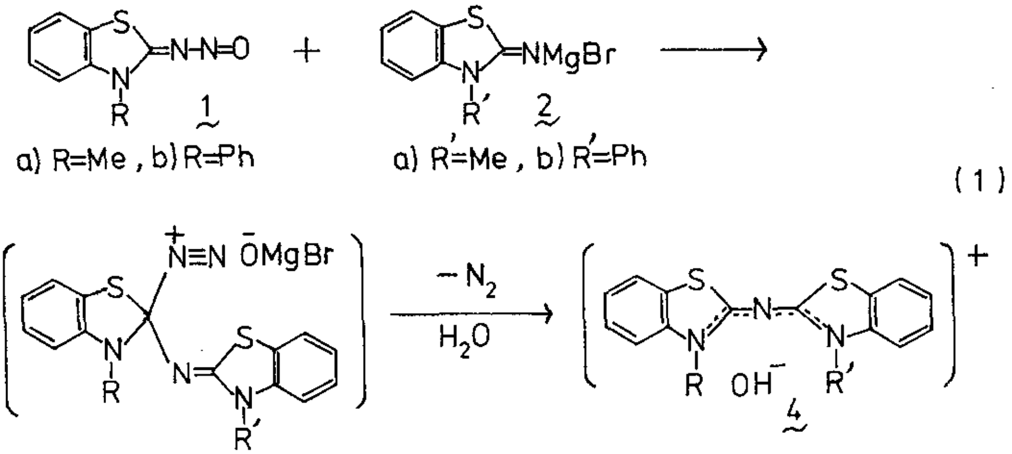
We reported previously that lithium aluminum hydride[2] and several Grignard reagents[3] reacted with 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (**1**) at both nitrogen of nitroso group and C-2 of the ring.

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 was stirred for additional 4h and the solvent was removed in vacuo. After water (100 ml) was added to the residue, the resulting precipitates were filtered and washed with 10% aqueous acetic acid and then recrystallized from ethanol to give azamethinecyanine hydroxide (4a, mp 319.2-320.0°, 8.5 mmol). The aqueous filtrate was extracted with dichloromethane to recover 3a (4.5 mmol).

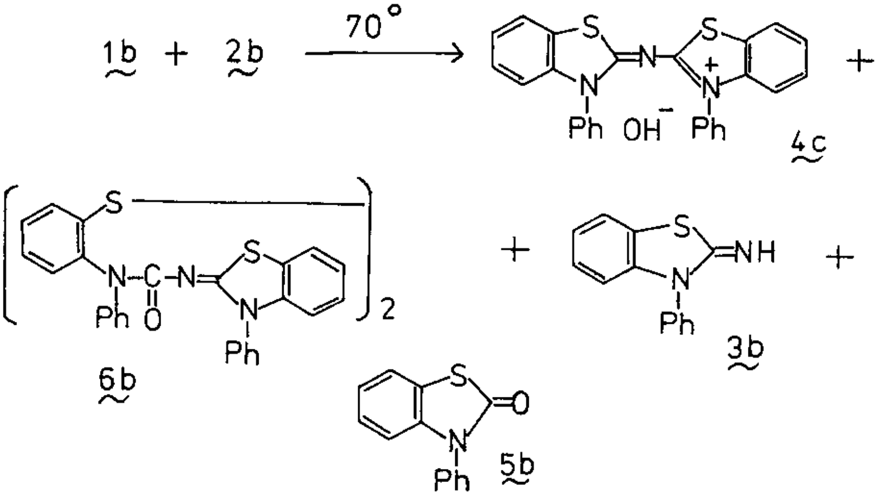
Similar reaction of 1b (10 mmol) and 2a (15 mmol) (run 2) gave 4b (mp 245.0-246.5°, 7.1 mmol) together with 3b (1.8 mmol) and 3-phenyl-2,3-dihydrobenzothiazol-2-one (5b, 0.4 mmol).

The scheme of the main reaction is shown below.



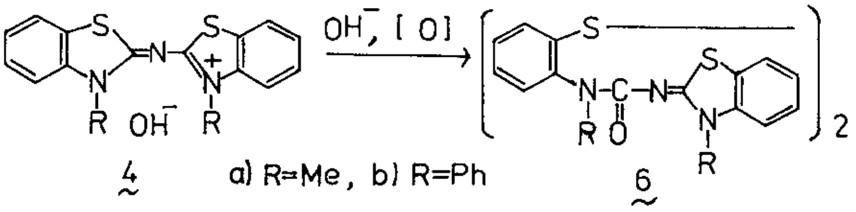
(1)

As the solubility of 2b in THF was small, 1b (10 mmol) and 2b (15 mmol) were allowed to react at 60-70° (run 3). Chromatography of the reaction products on silica gel gave 4c (mp 301.0-302.0°, 3.7 mmol), disulfide (6b, mp 231.0-232.0°, 0.66 mmol), 3b (4.2 mmol), and 5b (1.3 mmol).



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.



(2)

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]

Transnitrosation[5] 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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