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Chemistry of Nitrosoimines. X.[1] Reactions of 3-Substituted 2-Nitrosoimino-2,3,-dihydrobenzothiazoles with Aryl and *t*-Butyl Grignard Reagents

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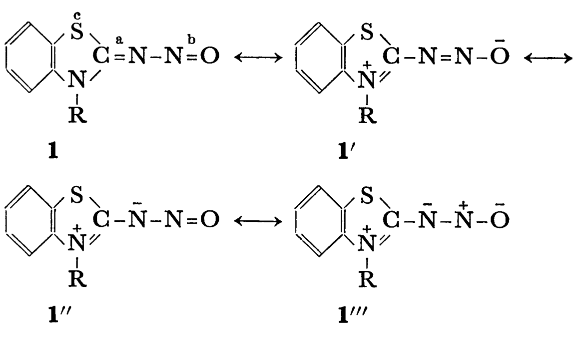
3-Substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (**1**) react with arylmagnesium bromide to give 3-substituted 2,2-diaryl-2,3-dihydrobenzothiazoles as the major product and 2-*N'*-arylhydrazono-2,3-dihydrobenzothiazoles as a minor product. **1** reacts also with *t*-butylmagnesium chloride to give 3-substituted 2-*t*-butyl- and 2-*N'*-*t*-butylhydrazono-2,3-dihydrobenzothiazoles and 2,3-dihydrobenzothiazol-2-one. Reaction of **1** with mesitylmagnesium bromide gave a similar result to that with *t*-butylmagnesium chloride.

Simple nitrosoimines are thermally unstable and apt to decompose unimolecularly to the corresponding carbonyl compounds and nitrogen. Sterically hindered nitrosoimines have been prepared as rather unstable compounds, some of their reactions being reported.[2] Resonance-stabilized nitrosoimines were found to be considerably unstable. 2-Nitroso-1,1,3,3-tetraphenyl guanidine is the only one compound which gave correct elemental analysis.[3]

On the other hand, nitrosoimines are known to be stable when the nitrosoimino group is contained in heterocycles such as benzothiazole, 1,2,4-thiadiazole,[4] and 1,3,4-thiadiazole.[5]

We have chosen 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazole (**1**) as a model and investigated reactions of **1** with nucleophiles such as Grignard reagents,[6] lithium aluminum hydride,[1,7] organolithiums,[8] and Grignard type and lithium reagents of 3-substituted 2-imino-2,3-dihydrobenzothiazoles.[9] Preliminary results have been interpreted to be due to large contribution of an ambident character to **1**.

We recently obtained direct evidence for the contribution of ambident structures (**1'**, **1''** and **1'''**) to the ground state of **1** by UV[3] and ESCA study.[10a]

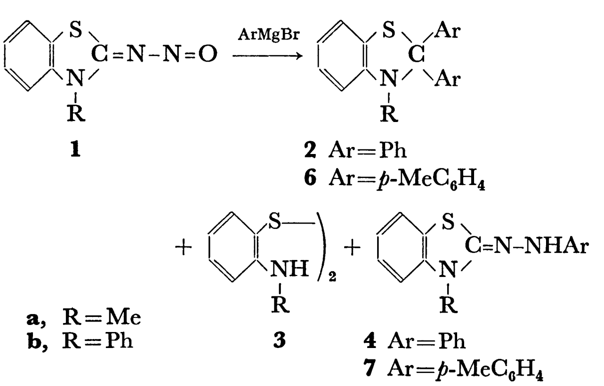


a, R=Me, **b**, R=Ph, **c**, R=Et

The result suggests that **1** has three possible reactive centers for nucleophiles, *i.e.*, the C-2 position of the ring (a), the nitrogen atom of the nitroso group (b), and the sulfur atom of the ring (c). We investigated the reactions of **1** with Grignard reagents and organolithiums.

From an investigation on the chemistry of nitrosoimines to prepare and investigate the nature of the nitrosoimino group, a new functionality, studies were turned to reactions of nucleophiles toward ambident cation (**1**). In this connection, it is necessary to mention the extensive studies on cyclic azosulfones by Hünig.[10b] He mainly studied the oxidative coupling of azosulfones with active methylenes and phenols, paying attention to the ambident nature of quaternary salts of azosulfones. A couple of reactions of 2-azido-3-ethylbenzothiazolium ions with nucleophiles have recently been interpreted by means of HSAB principle as the nucleophilic addition of bases to ambident aromatic cations.[10c] This paper describes the reactions of **1** with arylmagnesium and *t*-butylmagnesium halides.

Excess phenylmagnesium bromide reacted with 2-nitrosoimino-3-phenyl-2,3-dihydrobenzothiazole (**1b**) in ether at 0 °C under nitrogen to give 2,2,3-triphenyl-2,3-dihydrobenzothiazole (**2b**, 48%), a small amount of bis(*o*-anilinophenyl) disulfide (**3b**) and 3-phenyl-2-*N'*-phenylhydrazono-2,3-dihydrobenzothiazole (**4b**, 17%).



2 Ar=Ph
6 Ar=p-MeC$_6$H$_4$

a, R=Me
b, R=Ph

4 Ar=Ph
7 Ar=p-MeC$_6$H$_4$

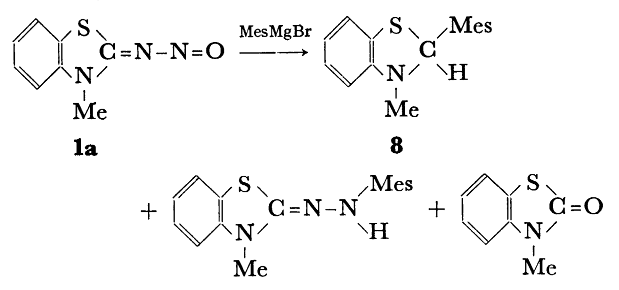
The structures of **2b** and **4b** were confirmed by elemental analyses, NMR, IR and MS. The structure of **3b** was confirmed by comparing the spectral data with those of an authentic sample[11] prepared from 3-phenyl-2,3-dihydrobenzothiazol-2-one (**5b**) and potassium hydroxide.

A similar reaction with 3-methyl derivative (**1a**) gave the corresponding **2a** (22%), **3a** (5%), and **4a** (*ca.* 15%), but **4a** could not be sufficiently purified for elemental analysis.

p-Tolylmagnesium bromide reacted with **1a** to afford 3-methyl-2,2-bis(*p*-tolyl)-2,3-dihydrobenzothiazole (**6a**, 66%) and 3-methyl-2-*N'*-*p*-tolylhydrazono-2,3-dihydrobenzothiazole (**7a**, 12%), and with **1b** to give the corresponding **6b** (50%) and **7b** (8%).

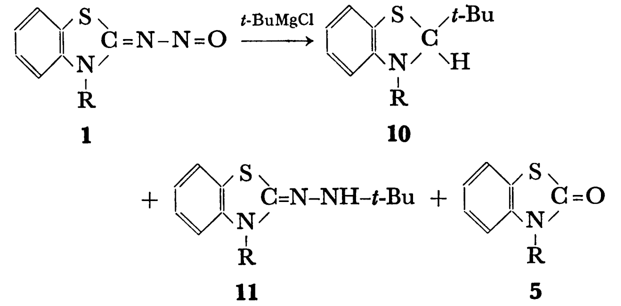
Reactions of **1a** were also carried out, but separation of the reaction products was unsuccessful. In particular, fractions containing mainly *N'*-arylhydrazono type compounds were unstable in the atmosphere, gradually producing a purple red tar.

Mesitylmagnesium bromide reacted with **1a** in a similar manner to give 2-mesityl- (**8**, 46%) and 2-*N'*-mesitylhydrazono-3-methyl-2,3-dihydrobenzothiazoles (**9**, 18%), and 3-methyl-2,3-dihydrobenzothiazol-2-one (**5a**, 10%).



1a **8** **9** **5a**

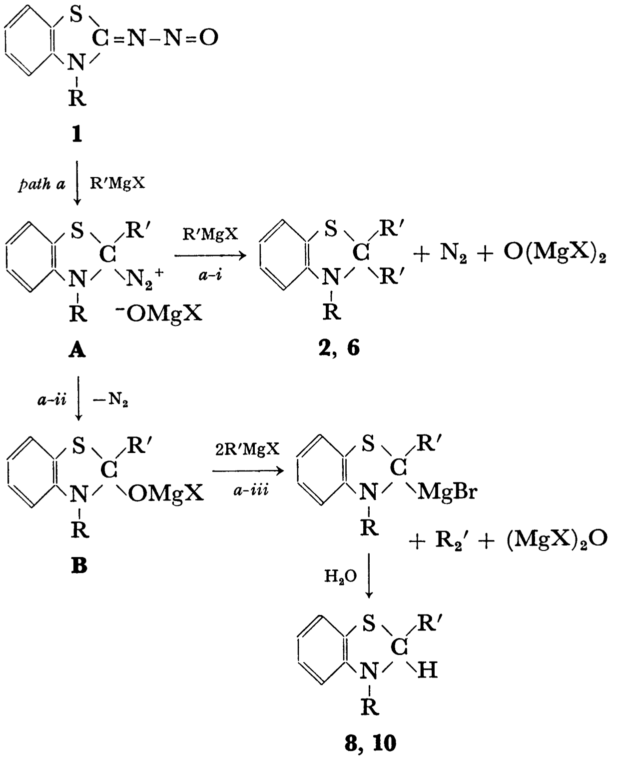
The formation of 2-monosubstituted compound (**8**) is in contrast to that of 2,2-disubstituted compounds (**2** and **6**) in the case of phenyl and *p*-tolyl Grignard reagents. The difference is attributable to the difference of the bulkiness of Grignard reagents. It was found that the reaction of **1** with *t*-butylmagnesium chloride gives the corresponding 3-substituted 2-*t*-butyl- (**10**), 2-*N'*-*t*-butylhydrazono-2,3-dihydrobenzothiazoles (**11**) and 3-substituted 2,3-dihydrobenzothiazol-2-one (**5**). The result is given below.



1 **10** **11** **5**

	10(%)	**11**(%)	**5**(%)
1a	39	8	13
1b	50	15	22

2,2-Diaryl (**2** and **6**), 2-mesityl (**8**) and 2-*t*-butyl (**10**) derivatives are considered to be formed *via* the common 1,4-addition intermediate between **1** and Grignard reagent, a diazonium salt (**A**), which reacts with Grignard reagent to give 2,2-disubstituted derivatives (*path a-i*) or loses nitrogen to give magnesium bromide 2-mesitly (or *t*-butyl)-2,3-dihydrobenzothiazol-2-yl oxide (**B**). The formation of **8** and **10** is explained below (*path a-ii, a-iii*).



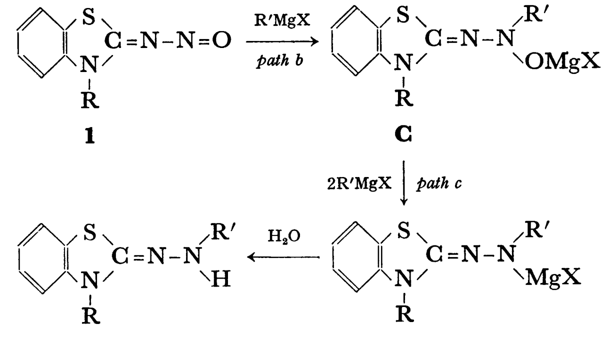
1 **A** **2, 6** **B** **8, 10**

The fate of **A** seems to depend on the bulkiness of Grignard reagents. Bulky Grignard reagents such as mesityl and *t*-butyl prefer the latter path (*path a-ii*).

The *path a-ii* was supported by the fact that the evolved gas was only nitrogen in the reaction of **1b** with *t*-butylmagnesium chloride, the amount (76%) being nearly equal to the sum (72%) of the amounts of **10** and **5b**.

N'-Substituted hydrazono derivatives (**4**, **7**, **9**, and **11**) are considered to be produced as follows.

1 first reacts with Grignard reagent to give 1,2-addition intermediate (**C**), **C** then reacting with excess Grignard reagents to give **D**.



1 **C** **4, 7, 9, 11** **D**

p-Cresol (4 mmol) was actually obtained in the reaction of **1b** (24 mmol) with *p*-tolylmagnesium bromide (100 ml). This seems to support OMgX-MgX exchange for *path c* producing R'OMgX as Wieland and Roseeu reported for the reaction of nitrosobenzene with phenylmagnesium bromide.[12]

However, their postulate was not substantiated by Gilman, who found that the following should be the case,[13] this being now accepted.

$$Ph_2NOMgBr + 2\,PhMgBr \longrightarrow Ph_2NMgBr + Ph_2 + (MgBr)_2O$$

This type of reaction is sensitive to the structure of both reagents. However, no systematic investigation has been carried out. We prefer Gilman's postulate. This can also be the case for *path a-iii*, although exact mechanism may be more complex.

The mechanism of formation of **3** will be discussed in a succeeding paper.[14]

Thiazolones (**5**) are formal products in the thermal decomposition of **1**, but **1** is completely stable under the reaction conditions. The reason why **5** is produced in considerable amount in the reaction with bulky Grignard reagents is obscure.

We see that aryl and *t*-butyl Grignard reagents react at positions a (major) producing diazonium salt (**A**) as an intermediate and at b (minor) producing hydroxylamine type intermediate (**C**).

Experimental

All the melting and boiling points are uncorrected. NMR spectra were recorded with Hitachi R-20B and R-24 spectrometers (60 MHz) using TMS as an internal standard. IR spectra were taken with a Hitachi EPI-G2 spectrometer. MS were measured with a Hitachi RMU-6L mass spectrometer at 70 eV.

Materials. 3-Methyl- (**1a**, mp 143 °C (dec.))[15] and 3-phenyl-2-nitrosoimino-2,3-dihydrobenzothiazoles (**1b**, mp 140 °C (dec.))[16] were prepared by reported methods. Mesityl bromide was prepared by the bromination of mesitylene,[17] bp 80—85 °C/6 mmHg.

All the reactions were carried out under nitrogen except the one for the determination of evolved gas (argon).

Reaction of 2-Nitrosoimino-3-phenyl-2,3-dihydrobenzothiazole (1b) with Phenylmagnesium Bromide. To a stirred solution of Grignard reagent prepared from magnesium turnings (3.60 g, 0.15 mol) and bromobenzene (23.55 g, 0.15 mol) in anhydrous ether (150 ml), was added **1b** (7.61 g, 30 mmol) portionwise over a period of 1 hr at 0 °C. The reaction took place immediately with vigorous evolution of gas, stirring being continued for 3 hr. The reaction mixture was treated with saturated aqueous ammonium chloride and the resulting precipitates were filtered off. The precipitates were extracted with ether (100 ml × 2) and benzene (100 ml). The extracts and ether layer of the filtrate were combined and dried over anhydrous magnesium sulfate. The solvent was evaporated in a vacuum and the residue was chromatographed on silica gel. 2,2,3-Triphenyl-2,3-dihydrobenzothiazole (**2b**, 5.25 g, 48%) was eluted with benzene and recrystallized from benzene–ethanol (1: 1) as yellowish crystals, mp 191.5—192.5 °C; MS: *m/e* 365 (M^+, 23%) and 288 (M^+-Ph, 100%).

Found: C, 82.35; H, 5.36; N, 3.79; S, 8.64%. Calcd for $C_{25}H_{19}NS$: C, 82.17; H, 5.24; N, 3.84; S, 8.76%.

A small amount of bis(*o*-anilinophenyl) disulfide (**3b**) was eluted with benzene as a yellow oil. The structure was confirmed by comparison with the spectral data of an authentic sample[11] prepared from 3-phenyl-2,3-dihydrobenzothiazol-2-one (**5b**) and potassium hydroxide in ethanol. 3-Phenyl-2-*N'*-phenylhydrazono-2,3-dihydrobenzothiazole (**4b**, 1.57 g, 17%) was eluted with dichloromethane–chloroform (1: 1) and recrystallized from benzene–ethanol (1: 1), mp 157—158 °C; IR (KBr): 3230 (NH), 1595, and 1585 cm^{-1}; NMR(CDCl$_3$): δ 3.45 (broad s, 1H, N–H) and 6.70—7.65 (m, 15H, Ar-H); MS: *m/e* 317 (M^+, 100%) and 225 (M^+-PhNH, 41%).

Found: C, 71.92; H, 4.77; N, 13.31; S, 9.80%. Calcd for $C_{19}H_{15}N_3S$: C, 71.91; H, 4.76; N, 13.24; S, 10.08%.

Reaction of 3-Methyl-2-nitrosoimino-2,3-dihydrobenzothiazole (1a) with Phenylmagnesium Bromide. To a stirred Grignard solution prepared from magnesium (3.63 g, 149 mmol) and bromobenzene (23.26 g, 148 mmol) in ether (100 ml) was added **1a** (4.80 g, 24.3 mmol) portionwise over a period of 2.5 hr at 0 °C and the mixture was stirred for 13.5 hr. After a similar work-up, 3-methyl-2,2-diphenyl-2,3-dihydrobenzothiazole (**2a**, 1.63 g, 22%) was eluted with *n*-hexane, mp 142—143 °C (from CHCl$_3$); NMR (CDCl$_3$): δ 2.59 (s, 3H, N–Me) and 6.12—7.63 (m, 14H, Ar-H); MS: *m/e* 303 (M^+, 16%) and 226 (M^+-Ph, 100%).

Found: C, 79.37; H, 5.37; N, 4.64; S, 10.43%. Calcd for $C_{20}H_{17}NS$: C, 79.17; H, 5.65; N, 4.62; S, 10.57%.

Bis(*o*-methylaminophenyl) disulfide (**3a**, 0.657 g, 5%) was eluted with *n*-hexane–benzene (1: 1) as yellow crystals, mp 66.5—67.0 °C (from chloroform–ethanol) (lit,[18] 64—68 °C).

A fraction corresponding to 3-methyl-2-*N'*-phenylhydrazono-2,3-dihydrobenzothiazole (**4a**, 1.0 g, 15%) was obtained, **4a** decomposing slowly during the course of isolation.

Reaction of 1a with p-*Tolylmagnesium Bromide.* To a stirred Grignard solution prepared from magnesium (4.80 g, 0.20 mol) and *p*-bromotoluene (34.20 g, 0.20 mol) in ether (150 ml) was added **1a** (7.72 g, 40 mmol) portionwise at 0 °C and the mixture was stirred for 1 hr. After a similar work-up 3-methyl-2,2-bis(*p*-tolyl)-2,3-dihydrobenzothiazole (**6a**, 8.8 g, 66%) was eluted with benzene as yellowish crystals, mp 141.0—141.5 °C (from benzene–methanol (1: 1)); NMR (CDCl$_3$): δ 2.35 (s, 6H, 2 Me), 2.65 (s, 3H, Me), and 6.7—7.5 (m, 12H, Ar-H).

Found: C, 79.72; H, 6.16; N, 3.92; S, 9.59%. Calcd for $C_{22}H_{21}NS$: C, 79.73; H, 6.39; N, 4.23; S, 9.66%.

Red brown tarry material (2.45 g) was eluted with chloroform–ether (7: 1) and crystallized partly on standing, mp 155.0—156.5 °C. The compound was assigned as 2-*N'*-*p*-tolylhydrazono-3-methyl-2,3-dihydrobenzothiazole (**7a**) by comparison of its IR data with those of **4b** and **7b**. IR (KBr): 3350 (NH), 1610 (C=N), 1595, and 1590 cm^{-1}.

Reaction of 1b with p-*Tolylmagnesium Bromide.* To a stirred Grignard solution prepared from magnesium (2.51 g, 0.10 mol) and *p*-bromotoluene (17.13 g, 0.10 mol) in ether (100 ml) was added **1b** (6.14 g, 24 mmol) portionwise at room temperature and the mixture was stirred for 2 hr. After a similar work-up, extraction with 20% aqueous sodium hydroxide gave *p*-cresol (0.43 g, 4 mmol), whose spectral data were in agreement with those of an authentic sample. The residue was chromatographed on silica gel. Elution with *n*-hexane–benzene (1: 1) gave a mixture of bi-*p*-tolyl and 3-phenyl-2,2-bis(*p*-tolyl)-2,3-dihydrobenzothiazole (**6b**), but separation of the mixture was very difficult. The yield of **6b** was estimated to be 4.7 g (50%) by its NMR spectrum, and the structure was determined by the following data; NMR (CDCl$_3$): δ 2.56 (s, 6H, 2 Me) and 6.15—7.20 (m, 19H, Ar-H).

Elution with benzene–dichloromethane (1: 1) gave a reddish purple tarry material (1.48 g), which was treated with dry column chromatography (silica gel) to give 3-phenyl-2-*N'*-*p*-tolylhydrazono-2,3-dihydrobenzothiazole (**7b**, 0.672 g, 8%), mp 186.5—187.5 °C (from chloroform–ethanol); IR (KBr): 3270 (NH), 1610, 1590, and 1580 cm^{-1}; NMR (CDCl$_3$): δ 2.23 (s, 3H, Me) and 6.30—7.53 (m, 13H, Ar-H) (N-H signal was obscure); MS: *m/e* 331 (M^+, 100%). Compound **7b** was unstable in solvents.

Found: C, 72.35; H, 5.18; N, 12.72%. Calcd for $C_{20}H_{17}N_3S$: C, 72.48; H, 5.14; N, 12.68%.

Reaction of 1a with Mesitylmagnesium Bromide. To a stirred Grignard solution prepared from magnesium (4.8 g, 0.20 mol) and mesityl bromide (39.8 g, 0.20 mol) in ether (150 ml) was added **1a** (7.72 g, 40 mmol) portionwise and the mixture was treated and chromatographed in the usual way. Elution with benzene with 2-mesityl-3-methyl-2,3-dihydrobenzothiazole (**8**, 4.9 g, 46%) as yellowish crystals, mp 222.0—223.5 °C (from ethanol); NMR (CDCl$_3$): δ 2.1 (s, 3H, Me), 2.3 (s, 6H, 2 Me), 3.2 (s, 3H, Me), 5.0 (s, 1H, CH), and 6.7—7.4 (m, 6H, Ar-H).

Found: C, 75.62; H, 6.90; N, 5.18; S, 12.01%. Calcd for $C_{17}H_{19}NS$: C, 75.81; H, 7.11; N, 5.20; S, 11.88%.

Elution with dichloromethane gave 3-methyl-2,3-dihydrobenzothiazol-2-one (**5a**, 0.64 g, 10%), mp 74—75 °C (75—

76 °C,[11] 76 °C[15]). Elution with dichloromethane–chloroform (1: 1) gave 2-*N*′-mesitylhydrazono-3-methyl-2,3-dihydrobenzothiazole (**9**, 2.1 g, 18%), mp 152.0—154.5 °C; IR (KBr): 3310 (NH), 1610, and 1590 cm^{-1}. IR supports structure **9**.

*Reaction of **1b** with* t*-Butylmagnesium Chloride.* To a stirred solution of Grignard reagent prepared from magnesium (3.60 g, 0.15 mol) and *t*-butyl chloride (13.50 g, 0.146 mol) in ether (150 ml), was added **1b** (7.71 g, 30 mmol) portionwise over a period of 1 hr at 0 °C. Stirring was continued for 3 hr. 2-*t*-Butyl-3-phenyl-2,3-dihydrobenzothiazole (**10b**, 3.70 g, 50%) was eluted with benzene, mp 61—62 °C (from ethanol); NMR ($CDCl_3$): δ 1.00 (s, 9H, Me_3C), 5.10 (s, 1H, $>$C–H), and 6.85—7.25 (m, 9H, Ar-H); MS: *m*/*e* 279 (M^+, 8.9%) and 212 (M^+-t-Bu, 100%).

Found: C, 75.81; H, 7.11; N, 5.20; S, 11.88%. Calcd for $C_{17}H_{19}NS$: C, 76.02; H, 7.15; N, 5.20; S, 11.60%.

3-Phenyl-2,3-dihydrobenzothiazol-2-one (**5b**, 1.48 g, 22%) was eluted with benzene–dichloromethane (1: 3), mp 78—79 °C (from *n*-hexane) (lit,[16] 75—76 °C). 2-*N*′-*t*-Butylhydrazono-3-phenyl-2,3-dihydrobenzothiazole (**11b**, 1.33 g, 15%) was eluted with dichloromethane, mp 161—162 °C (from ethanol); IR (KBr): 3230 (NH), 1615, 1590, and 1580 cm^{-1}; NMR ($CDCl_3$): δ 1.10 (s, 9H, Me_3C), 3.05 (broad s, 1H, N–H), and 6.7—7.6 (m, 9H, Ar-H); MS: *m*/*e* 297 (M^+, 88%) and 282 (M^+-Me, 100%).

Found: C, 68.38; H, 6.22; N, 14.06; S, 10.99%. Calcd for $C_{17}H_{19}N_3S$: C, 68.66; H, 6.44; N, 14.13; S, 10.76%.

*Reaction of **1a** with* t*-Butylmagnesium Chloride (Reverse Addition Method).* *t*-Butylmagnesium chloride free of excess magnesium, prepared from magnesium (2.59 g, 0.106 mol) and *t*-butyl chloride (8.06 g, 87.1 mmol) in ether (100 ml), was added dropwise over a period of 1 hr at 0 °C with stirring to a suspension of **1a** (3.00 g, 15.5 mmol) in ether (50 ml). Stirring was continued for 1 hr. The reaction mixture was chromatographed on silica gel after the usual work-up. 2-*t*-Butyl-3-methyl-2,3-dihydrobenzothiazole (**10a**, 1.05 g, 39%) was eluted with *n*-hexane–benzene (1: 1) as an oil. The structure was confirmed by the following NMR data: NMR ($CDCl_3$): δ 0.93 (s, 9H, Me_3C), 2.99 (s, 3H, N–Me), 4.62 (s, 1H, $>$C–H), and 6.35—7.46 (m, 4H, Ar-H).

3-Methyl-2,3-dihydrobenzothiazol-2-one (**5a**, 0.346 g, 13%) was eluted with benzene, mp 76.0—76.5 °C (lit,[15] 76 °C). 2-*N*′-*t*-Butylhydrazono-3-methyl-2,3-dihydrobenzothiazole (**11a**, 0.307 g, 8%) was eluted with benzene–dichloromethane (1: 1) and chloroform as an oil. The structure was confirmed by the following spectral data: IR (KBr): 3220 (NH), 1630 and 1580 cm^{-1}: NMR ($CDCl_3$): δ 1.19 (s, 9H, Me_3C), 2.76 (broad s, 1H, N–H), 3.44 (s, 3H, N–Me), and 6.7—7.9 (m, 4H, Ar-H). By addition of D_2O, a broad singlet at δ 2.76 disappeared.

Determination of the Evolved Gas. *t*-Butylmagnesium chloride was prepared from magnesium (0.43 g, 18 mmol) and *t*-butyl chloride (1.67 g, 18 mmol) in ether (50 ml) under argon. In a closed system, **1b** (0.92 g, 3.6 mmol) was added to the above solution at 0 °C under stirring. The amount of evolved gas was 61.5 ml (76%). The gas was found to be pure nitrogen by MS. No dinitrogen oxide (*m*/*e* 44) was detected.

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