Chemistry of Nitrosoimines. XI.[1] Reactions of 3-Substituted 2-Nitrosoimino-2,3-dihydrobenzothiazoles with Benzyl and Allylic Grignard Reagents

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3-Substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (**1**) react with benzylmagnesium chloride to give 3-substituted 2,2-dibenzyl- (**2**), 2-*N'*-benzylidenehydrazono- (**3**) and 2-*N'*,*N'*-dibenzylhydrazono-2,3-dihydrobenzothiazoles (**4**). The main reaction (formation of **3** and **4**) occurrs on the nitroso group of **1**, which proceeds *via* 1,2-addition intermediate (**B**). Allylmagnesium bromide and cinnamylmagnesium chloride also react with 3-methyl derivative (**1a**) to afford 2-*N'*,*N'*-diallyl- and 2-*N'*-(1-phenyl-2-propenyl)hydrazono-3-methyl-2,3-dihydrobenzothiazoles, respectively.

In a previous paper,[1] it was shown that the major reaction of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (**1**) with aryl and *t*-butyl Grignard reagents occurs on the C-2 of the benzothiazoline ring (*path a*) and the minor one on the nitrogen of the nitroso group (*path b*). In order to clarify a correlation between structure of Grignard reagents and reaction center in **1** which has an ambident character,[2] reactions of **1** were carried out with benzyl, allyl and cinnamyl Grignard reagents, which are resonance-stabilized carbanions. Reactions of **1** with benzylmagnesium chloride, in particular, were investigated in detail.

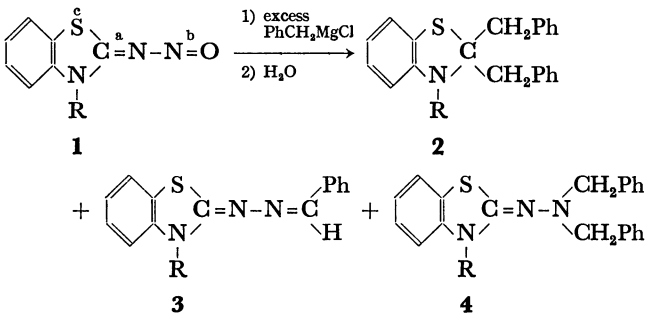
To an excess benzylmagnesium chloride in ether or tetrahydrofuran (THF) was added **1** under nitrogen. The reaction products were 2,2-dibenzyl- (**2**), 2-*N'*-benzylidenehydrazono- (**3**) and 2-*N'*,*N'*-dibenzylhydrazono-2,3-dihydrobenzothiazoles (**4**). The results are shown in Table 1.

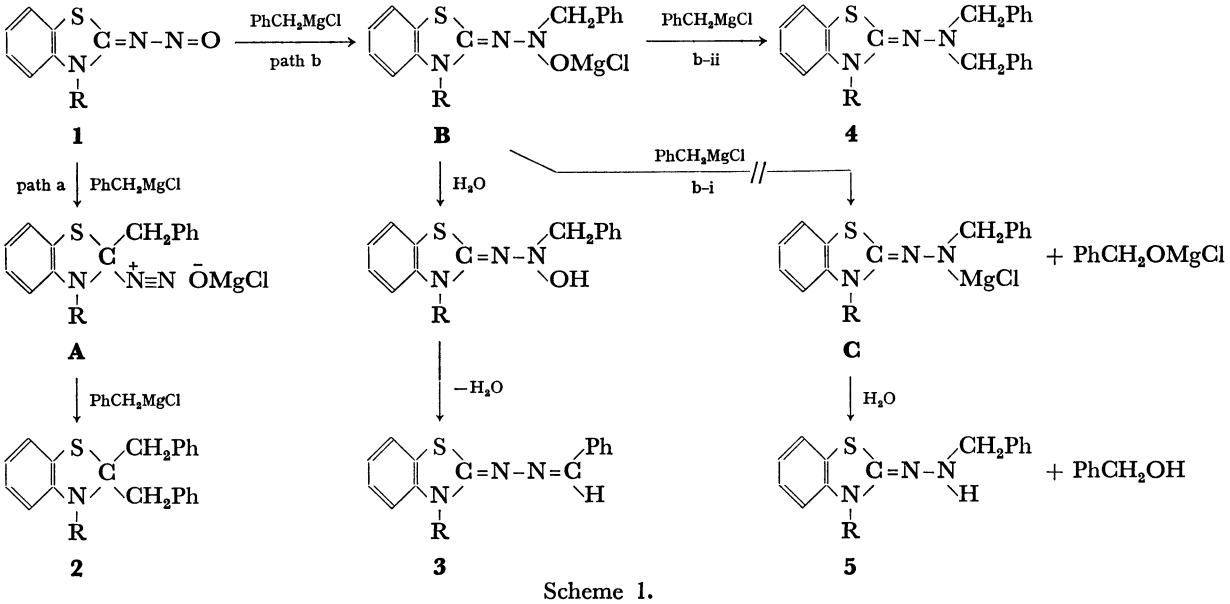
Table 1. Reaction products of **1** with excess (4 eqv.) benzylmagnesium chloride

Run	Reaction condition	Yield (%)		
		2	**3**	**4**
1[a]	**1a**, Et_2O, r.t. (4 hr)	8	44	19
2	**1a**, Et_2O, r.t. (4 hr) and then reflux (3 hr)	8	14	31
3	**1b**, Et_2O, r.t. (2.5 hr) and then reflux (1 hr)	4	9	25
4	**1c**, THF, r.t. (2.5 hr)	2	30	11
5[b]	**1a**, THF, r.t. (2.5 hr)	7	43	3

a) Neither $PhCH_2OH$ nor $PhCH_2Cl$ was detected by glc.
b) Reverse addition of Grignard reagent to a suspension of **1a** and $MgCl_2$. 2-*N'*-Benzylhydrazono-3-methyl-2,3-dihydrobenzothiazole (**5a**) was also isolated in 2% yield.

From a comparison of the result of run 2 with that of run 1 (Table 1), it is seen that the yield of **2a** remains unchanged by reflux of the solvent, but that of **3a** decreases, accompanied by the increase of **4a**, the total





Scheme 1.

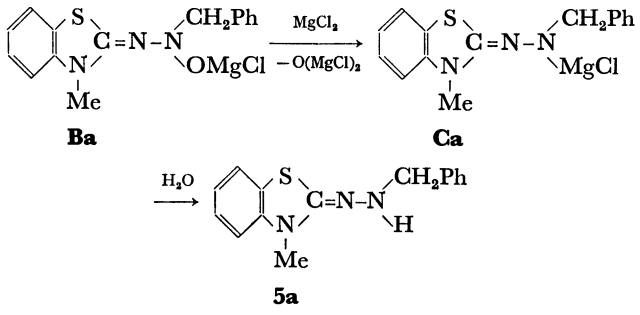
yield of **3a** and **4a** being almost the same as that of run 1. This suggests that **3a** and **4a** are produced through a common intermediate (**B**).

Similarly, 3-phenyl (**1b**, run 3) and 3-ethyl (**1c**, run 4) derivatives were allowed to react with excess benzylmagnesium chloride at room temperature. After 2.5 hr (run 3), the reaction mixture was refluxed to give a similar result to that of run 2. The result of run 4 was very similar to that of run 1.

From the results obtained in runs 1—4, paths of formation of **2**, **3** and **4** are proposed as shown in Scheme 1.

Nitrosoimines (**1**) react with benzylmagnesium chloride to produce initially 1,2- (**B**) and 1,4-addition intermediates (**A**).[1] Unsymmetric azines (**3**) and hydrazones (**4**) are formed *via* the common intermediates (**B**). Azines (**3**) are produced by the hydrolysis and dehydration of the intermediate (**B**). Two paths can be considered for the formation of **4** from **B**. One is the apparent exchange of the OMgCl group to give magnesium salt of hydrazones (**C**), which can proceed by Gilman's mechanism producing bibenzyl, Wieland's mechanism producing benzyl alcohol not being excluded *a priori*.[1] The other is the path along which a second Grignard reagent attacks directly on the nitrogen atom of the nitroso group to give **4** (*b-ii*). Two possibilities for the former path were ruled out since no benzyl alcohol could be detected in the reaction mixture by gas chromatography (glc) and no residual benzyl chloride was detected in the Grignard solution before use. The formation of **4** is accelerated by heating.

In the case of slow reverse addition of Grignard reagent to a suspension of **1a** and magnesium(II) chloride in THF (run 5), 2-*N'*-benzylhydrazono-3-methyl-2,3-dihydrobenzothiazole (**5a**) was also isolated in 2% yield together with **2a**, **3a** and **4a**. Thus, the path of formation of **5a** is explained as follows: the OMgCl-MgCl exchange between the 1,2-addition intermediate (**Ba**) and magnesium (II) chloride probably produces magnesium salt (**Ca**), which is hydrolyzed to produce **5a** (Scheme 2).

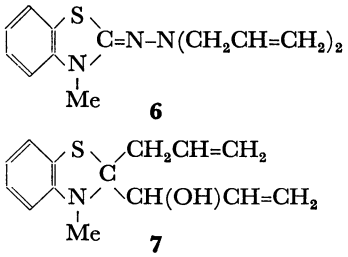


Ba **Ca** **5a**

Scheme 2.

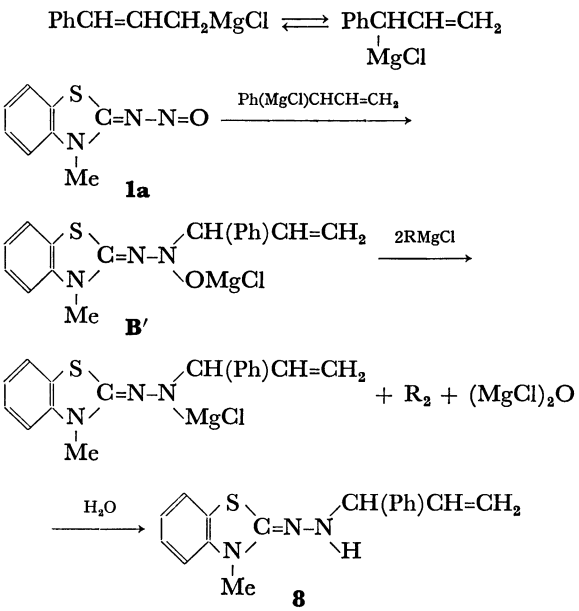
It is noteworthy that the benzyl protons of **2a** and **2c** appear as quartet whereas those of **2b** appear as singlet. The difference can be attributed to the presence of phenyl group in **2b**, although the exact reason is not clear.

Excess allylmagnesium bromide reacts with **1a** in ether at room temperature to give 2-*N'*,*N'*-diallylhydrazono-3-methyl-2,3-dihydrobenzothiazole (**6**) in 30% yield, together with an oily product, which is tentatively assigned as 2-allyl-2-(α-hydroxyallyl)-3-methyl-2,3-dihydrobenzothiazole (**7**, 27%) from spectral data. However, the mechanism of formation is obscure.



6 **7**

Excess cinnamylmagnesium chloride, which reacts easily with cinnamyl chloride to give a mixture of coupling products even without heating,[3] was allowed to react with **1a**, as soon as possible after the preparation. The isolated and identified products were found to be a mixture of 1,4-diphenyl- (main) and 1,6-diphenyl-1,5-hexadienes (minor) as coupling products and 3-methyl-2-*N'*-(1-phenyl-2-propenyl) hydrazono-2,3-dihydrobenzothiazole (**8**) in 8% yield. This result can be explained in terms of the equilibrium in the Grignard reagent and the apparent exchange between the OMgCl group of the addition product (**B**) and the MgCl group of Grignard reagent as shown in Scheme 3.



1a **B'** **8**

Scheme 3.

The main reaction of resonance-stabilized Grignard reagents such as benzyl, allyl, and cinnamylmagnesium halides with **1** occurs on the nitroso group (*path b*), accompanied by a minor reaction on the C-2 of the ring (*path a*). The results are in contrast with those reported for aryl- and *t*-butylmagnesium halides.[1] This can be explained as follows: resonance-stabilized Grignard reagents are not reactive enough to add on the C-2 and to cut off the entire conjugation between the benzothiazoline ring and the nitrosoimino group, whereas the latter type Grignard reagents are reactive enough. We should keep in mind the fact that C–C bond

formation is, in general, highly (or exclusively) favorable to C–N bond formation by Grignard reagents.[4]

Experimental

Materials. 3-Methyl (**1a**), 3-phenyl (**1b**) and 3-ethyl derivatives (**1c**) of 2-nitrosoimino-2,3-dihydrobenzothiazole were prepared by the reported methods: **1a**,[5] mp 143 °C (dec.); **1b**,[6] mp 140 °C (dec.); **1c**,[7] mp 143—144 °C (dec.). Cinnamyl chloride was prepared according to the method of Koch.[3]

In all cases, the reactions were carried out under nitrogen. MS spectra were measured at 70 eV.

Reaction of 3-Methyl-2-nitrosoimino-2,3-dihydrobenzothiazole (1a) with Benzylmagnesium Chloride in Ether at Room Temperature. To a stirred Grignard reagent prepared from magnesium (4.94 g, 0.20 mol) and benzyl chloride (12.99 g, 0.10 mol) in ether (100 ml) was added **1a** (4.83 g, 25.0 mmol) portionwise over a period of 1 hr at room temperature. Stirring was continued for 3 hr. The reaction mixture was treated with 20% aqueous solution of ammonium chloride, the resulting precipitates being filtered off and extracted with ether, benzene, and dichloromethane. The extracts and the ether layer of the filtrate were combined and washed with water and dried over anhydrous magnesium sulfate. After the solvents had been evaporated, the residue was chromatographed on silica gel. 2,2-Dibenzyl-3-methyl-2,3-dihydrobenzothiazole (**2a**, 0.63 g, 8%) was eluted with *n*-hexane–benzene (3: 2), mp 86.5—87.5 °C (from chloroform–ethanol). NMR ($CDCl_3$, 60 MHz): δ 2.90 (s, 3H, N–CH_3), 3.18 (AB q, J_{AB}=13 Hz, $\Delta\delta_{AB}$=20 Hz, 4H, 2PhCH_2), and 6.00—7.22 (m, 14H, Ar-H); MS: *m/e* (M^+, trace) and 240 (M^+-PhCH_2, 100%).

Found: C, 79.75; H, 6.44; N, 3.96%. Calcd for $C_{22}H_{21}NS$: C, 79.72; H, 6.39; N, 4.23%.

2-*N'*-Benzylidenehydrazono-3-methyl-2,3-dihydrobenzothiozole (**3a**, 3.06 g, 44%) was eluted with benzene and benzene–dichloromethane (1: 1) as pale yellow crystals, mp 162—163 °C (from benzene–ethanol).[5]

2-*N'*,*N'*-Dibenzylhydrazono-3-methyl-2,3-dihydrobenzothiazole (**4a**, 1.67 g, 19%) was eluted with benzene–dichloromethane (1: 1), mp 116.5—117.5 °C (from benzene–ethanol). IR (KBr): 1600 and 1580 cm^{-1}; NMR ($CDCl_3$): δ 3.31 (s, 3H, N–CH_3), 3.85 (s, 4H, 2PhCH_2), and 6.25—7.50 (m, 14H, Ar-H); MS: *m/e* 359 (M^+, 13%), 240 ($M^+-PhCH_2-N_2$, 50%), and 91 ($PhCH_2^+$, 100%).

Found: C, 73.61; H, 5.70; N, 11.95; S, 8.70%. Calcd for $C_{22}H_{21}N_3S$: C, 73.50; H, 5.88; N, 11.69; S, 8.92%.

Reaction of 1a with Benzylmagnesium Chloride in Ether at Room Temperature and Then with Reflux. To a stirred solution of Grignard reagent, prepared from magnesium (3.21 g, 0.13 mol) and benzyl chloride (8.60 g, 0.068 mol) in ether (80 ml), was added **1a** (3.24 g, 16.8 mmol) portionwise over a period of 1 hr at room temperature, stirring being continued for 3 hr. The reaction mixture was then refluxed for additional 3 hr. Compounds **2a**, **3a**, and **4a** were isolated in the amounts of 0.46 g (8%), 0.59 g (14%), and 1.90 g (31%), respectively.

Reaction of 2-Nitrosoimino-3-phenyl-2,3-dihydrobenzothiazole (1b) with Benzylmagnesium Chloride in Ether at Room Temperature and Then with Reflux. To a stirred Grignard solution prepared from magnesium (4.86 g, 0.20 mol) and benzyl chloride (12.71 g, 0.10 mol) in ether (100 ml) was added **1b** (5.20 g, 20.8 mmol) portionwise over a period of 0.5 hr at room temperature and stirring was continued for additional 2 hr. The reaction mixture was then refluxed for 1 hr. 2,2-Dibenzyl- (**2b**), 2-*N'*-benzylidenehydrazono- (**3b**), and 2-*N'*,*N'*-dibenzylhydrazono-3-phenyl-2,3-dihydrobenzothiazoles (**4b**) were eluted with *n*-hexane and *n*-hexane–benzene (1: 1), benzene–dichloromethane (1: 1), and benzene–dichloromethane (1: 1), respectively. All the products were recrystallized from chloroform–ethanol.

2b (0.33 g, 4%); mp 145.0—145.5 °C; NMR ($CDCl_3$): δ 3.20 (s, 4H, 2PhCH_2) and 6.25—7.50 (m, 19H, Ar-H); MS: *m/e* 393 (M^+, trace) and 302 (M^+-PhCH_2, 100%).

Found: C, 82.55; H, 5.77; N, 3.40; S, 8.18%. Calcd for $C_{27}H_{23}NS$: C, 82.40; H, 5.89; N, 3.56; S, 8.15%.

3b (0.64 g, 9%), pale yellow crystals; mp 124.5—125.0 °C; IR (KBr): 1605, 1575, and 1525 cm^{-1}; NMR ($CDCl_3$): δ 6.6—7.9 (m, 14H, Ar-H) and 8.25 (s, 1H, –N=CH–); MS: *m/e* 329 (M^+, 100%).

Found: C, 72.95; H, 4.58; N, 12.74; S, 9.73%. Calcd for $C_{20}H_{15}N_3S$: C, 72.92; H, 4.59; N, 12.76; S, 9.73%.

4b (2.18 g, 25%); mp 85.0—85.5 °C; IR (KBr): 1605, 1590, and 1575 cm^{-1}; NMR ($CDCl_3$): δ 3.81 (s, 4H, 2PhCH_2) and 6.32—7.60 (m, 19H, Ar-H); MS: *m/e* 421 (M^+, 13%), 302 (M^+-PhCH_2, 43%), and 91 ($PhCH_2^+$, 100%).

Found: C, 77.23; H, 5.78; N, 10.06; S, 7.71%. Calcd for $C_{27}H_{23}N_3S$: C, 76.93; H, 5.50; N, 9.97; S, 7.61%.

Reaction of 3-Ethyl-2-nitrosoimino-2,3-dihydrobenzothiazole (1c) with benzylmagnesium Chloride in Tetrahydrofuran (THF) at Room Temperature. To a stirred Grignard solution prepared from magnesium (4.84 g, 0.16 mol) and benzyl chloride (12.90 g, 0.10 mol) in THF (100 ml) was added **1c** (5.64 g, 27.2 mmol) portionwise over a period of 1 hr at room temperature, stirring being continued for 1.5 hr. 2,2-Dibenzyl-3-ethyl-2,3-dihydrobenzothiazole (**2c**, 0.37 g, 2%) was eluted with *n*-hexane–benzene (1: 1), mp 132—133 °C (from benzene–ethanol). NMR ($CDCl_3$): δ 1.20 (t, J=7 Hz, 3H, $C\underline{H}_3CH_2$), 3.24 (AB q, J_{AB}=14 Hz, $\Delta\delta_{AB}$=21 Hz, 4H, 2PhCH_2), 3.39 (q, J=7 Hz, 2H, $CH_3C\underline{H}_2$–N), and 5.95—7.45 (m, 14H, Ar-H); MS: *m/e* 345 (M^+, trace) and 254 (M^+-PhCH_2, 100%).

Found: C, 80.16; H, 6.69; N, 3.84; S, 9.21%. Calcd for $C_{23}H_{23}NS$: C, 79.96; H, 6.71; N, 4.05; S, 9.28%.

2-*N'*-Benzylidenehydrazono-3-ethyl-2,3-dihydrobenzothiazole (**3c**) was eluted with *n*-hexane–benzene (1: 1) and benzene as a yellow oil. The oil was rechromatographed on silica gel and eluted with *n*-hexane–benzene (2: 1 and 1: 1) and benzene to give an oil, 2.28 g (30%). The oil solidified to give yellow crystals (mp 51.0—52.2 °C (from *n*-hexane–benzene)) after being left to stand for several months. IR (KBr): 1610, 1570, and 1530 cm^{-1}; NMR ($CDCl_3$): δ 1.25 (t, J=7.5 Hz, 3H, $C\underline{H}_3CH_2$), 4.02 (q, J=7.5 Hz, 2H, $CH_3C\underline{H}_2$–N), 6.6—8.0 (m, 9H, Ar-H), and 8.39 (s, 1H, –N=CH–); MS: *m/e* 281 (M^+, 100%).

Found: C, 68.27; H, 5.09; N, 15.02%. Calcd for $C_{16}H_{15}N_3S$: C, 68.30; H, 5.37; N, 14.93%.

2-*N'*,*N'*-Dibenzylhydrazono-3-ethyl-2,3-dihydrobenzothiazole (**4c**) was eluted with benzene–dichloromethane (1: 1) as an oil. The oil was rechromatographed on silica gel and eluted with benzene and benzene–dichloromethane (1: 1) to give 1.19 g (11%) of **4c**, mp 108.5—109.0 °C (from chloroform–ethanol). IR (KBr): 1600 and 1580 cm^{-1}; NMR ($CDCl_3$): δ 1.10 (t, J=7 Hz, 3H, $C\underline{H}_3CH_2$), 3.86 (s, 4H, 2PhCH_2), 3.87 (q, J=7 Hz, 2H, $CH_3C\underline{H}_2$), and 6.57—7.58 (m, 14H, Ar-H); MS: *m/e* 373 (M^+, 12%), 254 ($M^+-PhCH_2-N_2$), and 91 ($PhCH_2^+$, 100%).

Found: C, 74.18; H, 6.18; N, 11.40; S, 8.60%. Calcd for $C_{23}H_{23}N_3S$: C, 73.96; H, 6.21; N, 11.25; S, 8.58%.

Reaction of 1a with Benzylmagnesium Chloride in THF at room Temperature in the Presence of Magnesium (II) Chloride (Reverse Addition of Grignard Reagent). A Grignard solution was prepared from magnesium (4.56 g, 0.19 mol) and benzyl chloride (11.93 g, 0.09 mol) in THF (100 ml) and transferred

to a dropping funnel through a Teflon tube fitted with glass wool in order to filter the unchanged magnesium under nitrogen. Seven-tenths of this solution, containing 66 mmol of benzylmagnesium chloride, was added dropwise to a suspension of **1a** (4.27 g, 22.1 mmol) and magnesium (II) chloride (0.25 g, 26 mmol) in THF (50 ml) over a period of 0.5 hr at room temperature with stirring, stirring being continued for 2 hr. Compounds **2a** (0.54 g, 7%), **3a** (2.53 g, 43%), and **4a** (0.22 g, 3%) were eluted with *n*-hexane–benzene (1: 1), benzene, and benzene–dichloromethane (1: 1), respectively. 2-*N'*-Benzylhydrazono-3-methyl-2,3-dihydrobenzothiazole (**5a**, 0.12 g, 2%) was also eluted with benzene–dichloromethane (1: 1), mp 143.5—144.5 °C (from chloroform–ethanol). IR (KBr): 3230 (NH), 1615 and 1580 cm^{-1}; NMR ($CDCl_3$): δ 3.07 (dd, $J_{vic}=7$ Hz, $J_{gem}=2.4$ Hz, 2H, $PhCH_2$), 3.30 (s, 3H, CH_3–N), 4.42 (t, $J_{vic}=7$ Hz, 1H, N–H), and 6.6—7.5 (m, 9H, Ar-H); MS: *m/e* 269 (M^+, 100%).

Reaction of ***1a*** *with Allylmagnesium Bromide.* To a stirred Grignard solution prepared from magnesium (11.00 g, 0.45 mol) and allyl bromide (18.43 g, 0.15 mol) in ether (150 ml) was added **1a** (4.38 g, 22.7 mmol) portionwise over a period of 1.5 hr at room temperature. Stirring was continued for 2.5 hr. 2-*N'*,*N'*-Diallylhydrazono-3-methyl-2,3-dihydrobenzothiazole (**6**) was eluted with benzene and recrystallized from *n*-hexane to give pure **6** (1.75 g, 30%), mp 50.5—51.5 °C. IR (KBr): 1610 and 1585 cm^{-1}; NMR ($CDCl_3$): δ 3.34 (d, $J_{CX}=6$ Hz, 4H, allylic-H_X), 3.38 (s, 3H, N–CH_3), 5.03 (dd, $J_{AC}=10$ Hz, $J_{AB}=2$ Hz, 2H, vinylic-H_A), 5.13 (dd, $J_{BC}=18$ Hz, $J_{AB}=2$ Hz, 2H, vinylic-H_B), 5.95 (dt, $J_{BC}=18$ Hz, $J_{AC}=10$ Hz, $J_{CX}=6$ Hz, 2H, vinylic-H_C), and 6.63—7.38 (m, 4H, Ar-H); MS: *m/e* 259 (M^+, 19%), 190 (M^+-CH_2CH-CH_2-N_2, 30%), and 41 ($CH_2=CHCH_2^+$, 100%).

Found: C, 64.79; H, 6.82; N, 16.16; S, 12.30%. Calcd for $C_{14}H_{17}N_3S$: C, 64.83; H, 6.61; N, 16.21; S, 12.36%.

Elution with dichloromethane gave crude 2-allyl-2-(α-hydroxyallyl)-3-methyl-2,3-dihydrobenzothiazole (**7**, 1.51 g, 27%) as an oil. Purification was difficult and no analytically pure sample was obtained. IR (neat): 3225 (OH), 1610, 1580, and 1470 cm^{-1}; NMR ($CDCl_3$): 2.33 (t, $J=6$ Hz, 2H, CH_2), 3.33 (s, 3H, N–Me), 3.62 (q, $J=6$ Hz, 1H, CH), 4.06 (s, 1H, OH), 4.86—5.37 (m, 4H, $2C\underline{H}_2$–CH), 5.50—6.22 (m, 2H, $2CH_2=C\underline{H}$), and 6.60—7.40 (m, 4H, Ar-H); MS: *m/e* 247 (M^+, 8.4%) and 218 ($M^+-HC=O$, 100%).

Reaction of ***1a*** *with Cinnamylmagnesium Chloride.* Cinnamylmagnesium chloride, prepared *in situ*, was allowed to react with **1a**. After a small amount of ethereal solution (100 ml) of cinnamyl chloride (15.10 g, 99 mmol) had been added to magnesium (7.67 g, 0.32 mol) covered with ether (15 ml) to start the reaction, **1a** (4.34 g, 22.4 mmol) was added with stirring. To this suspension, cooled with ice, was added the residual solution dropwise over a period of 8 hr. Stirring was continued for 0.5 hr after the addition. The reaction mixture was chromatographed on silica gel after usual work-up. A mixture (4.09 g, 21 mmol) of 1,4-diphenyl- (main) and 1,6-diphenyl-1,5-hexadienes (minor) was eluted with *n*-hexane and distilled to give an analytically pure sample, bp 160—162 °C/4 mmHg (lit,[3] 115 °C/0.005 mmHg).

Found: C, 92.46; H, 7.92%. Calcd for $C_{18}H_{18}$: C, 92.46; H, 7.84%.

3-Methyl-2-*N'*-(1-phenyl-2-propenyl) hydrazono-2,3-dihydrobenzothiazole (**8**), the only one identified product in this reaction, was eluted with dichloromethane–ether (1: 1) and ether, contaminated with a deep red oil, and recrystallized from ethanol to give 0.51 g (8%) of a pure sample, mp 103.5 °C. IR (KBr): 3225 (NH), 1620 and 1580 cm^{-1}: NMR ($CDCl_3$): δ 3.34 (s, 3H, CH_3–N), 4.2 (broad s, 1H, N–H), 4.9 (d, $J_{CX}=7$ Hz, 1H, allylic-H_X), 5.17 (dd, $J_{AC}=10$ Hz, $J_{AB}=2$ Hz, 1H, vinylic-H_A), 5.25 (dd, $J_{BC}=17$ Hz, $J_{AB}=2$ Hz, 1H, vinylic-H_B), 6.12 (sep, $J_{BC}=17$ Hz, $J_{AC}=10$ Hz, $J_{CX}=7$ Hz, 1H, vinylic-H_C), and 6.69—7.62 (m, 9H, Ar-H); MS: *m/e* 295 (M^+, 10%) and 178 ($M^+-CH_2CHCHPh$, 100%).

Found: C, 69.27; H, 5.67; N, 13.98; S, 10.87%. Calcd for $C_{17}H_{11}N_3S$: C, 69.12; H, 5.80; N, 14.22; S, 10.85%.

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