Direct Synthesis of 2,2-Diaryl-3-methyl-2,3-dihydrobenzothiazoles from 3-Methyl-2,3-dihydrobenzothiazole-2-thione and Some Mechanistic Aspects

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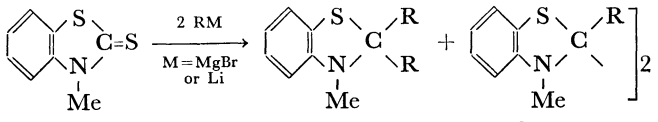
Rcactions of 3-methyl-2,3-dihydrobenzothiazole-2-thione (**1**) and 3-methyl-2-(methylthio)benzothiazolium iodide with Grignard reagents gave 2,2-disubstituted 3-methyl-2,3-dihydrobenzothiazole (**2**) as a major product as well as 2,2′-disubstituted 3,3′-dimethyl-2,2′,3,3′-tetrahydrobi(2-benzothiazolyl) (**3**). Reactions of **1** with organolithiums gave **2** as a major product. The results demonstrate that the formation of **3** is due to the presence of transition metals as an impurity in magnesium.

As previously reported,[1] reactions of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles with Grignard reagents have been shown to give 2,2,3-trisubstituted 2,3-dihydrobenzothiazoles as well as other types of products.

It is known that Grignard reagents and organolithiums can react with thiocarbonyl group at sulfur atom.[2] On the other hand, Beak *et al.*[3] have reported that phenyllithium attacks on carbon atom of the thiocarbonyl group on *N*,*N*-dimethylthiobenzamide. Thus, occurrence of C-2 attack with Grignard reagents is expected in 3-methyl-2,3-dihydrobenzothiazole-2-thione (**1**) among other possibilities. On the other hand, reactions of 3-methyl-2-(methylthio)benzothiazolium salt (**8**) with Grignard reagents can be expected to give also 2,2-disubstituted 2,3-dihydrobenzothiazoles. This paper describes synthesis of 2,2-disubstituted 3-methyl-2,3-dihydrobenzothiazoles (**2**) from **1**, **8**, and related compounds.

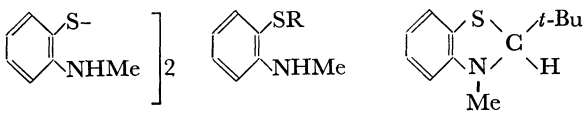
The reaction of 3-methyl-2,3-dihydrobenzothiazole-2-thione (**1**) with excess Grignard reagents in refluxing benzene for 1.5—4 h under nitrogen afforded 2,2-disubstituted 3-methyl-2,3-dihydrobenzothiazole (**2**) together with 2,2′-disubstituted 3,3′-dimethyl-2,2′,3,3′-tetrahydrobi(2-benzothiazolyl) (**3**) as a minor product.

The presence of unchanged magnesium did not affect considerably the product ratio of **2** to **3** (see Table 1).



1 **2** **3**

a: R=Ph, **b**:R=*p*-ClC$_6$H$_4$, **c**: R=*p*-MeC$_6$H$_4$
d: R=*p*-MeOC$_6$H$_4$, **e**: R=Et, **f**: R=Bu



4 **5** **a**: R=Et **b**: R=Ph **6**

The reaction of **1** with ethylmagnesium bromide gave also **2e** along with bis[*o*-(methylamino)phenyl] disulfide (**4**) and ethyl *o*-(methylamino)phenyl sulfide (**5a**). Refluxing of **1** with *t*-butylmagnesium bromide in benzene for 42 h gave 2-*t*-butyl-3-methyl-2,3-dihydrobenzothiazole (**6**) in 16% yield together with the recovered **1** (77%). Formation of the by-product (**3**) was encountered when phenyl and *p*-chlorophenyl Grignard reagents were employed.

Table 1. Reactions of **1** with Grignard reagents

R	**2** (%)	**3** (%)	Other (%)
Ph	**2a**, 67	**3a**, 23	
Ph[a]	**2a**, 60	**3a**, 19	
p-ClC$_6$H$_4$	**2b**, 58	**3b**, 21	
p-MeC$_6$H$_4$	**2c**, 84	—	
p-MeOC$_6$H$_4$	**2d**, 84	—	
Et[a]	**2e**, 54	—	**4**, 19: **5a**, trace
t-Bu	**6**, 16	—	recovered **1**, 77

a) In the presence of unchanged magnesium.

Table 2. Reactions of **1** with organolithiums

R	**2** (%)	Other (%)
Ph	**2a**, 42	**5b**, 19
Et	**2e**, 65	
Bu	**2f**, 58	**7**, 12

Reactions of **1** with organolithiums proceeded at room temperature and gave mainly **2**. The results are summarized in Table 2. In the cases of phenyl- and butyllithiums, **5b**[1,4] and 2-butylidene 3-methyl-2,3-dihydrobenzothiazole (**7**) were also isolated. The formation of **7** is explained by deprotonation of an intermediate (*A*) by butyllithium[5] as mentioned later.

Table 3 summarizes the results of reactions of **8** with Grignard reagents.

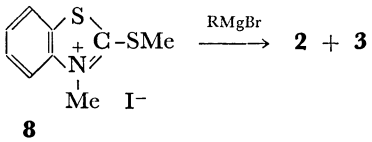


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Table 3. Reactions of **8** with Grignard reagents

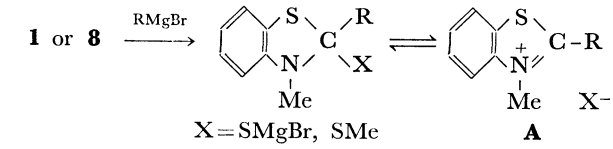
R	Condition	**2** (%)	**3** (%)	**2**/**3**
Ph	r.t., 1.5 h; then 80 °C, 0.5 h	**2a**, 54	**3a**, 25	2.1
Ph	r.t., 0.5 h; then 80 °C, 0.5 h[a]	**2a**, 48	**3a**, 37	1.3
p-MeC$_6$H$_4$	r.t., overnight	**2c**, 50	—	>10
p-MeC$_6$H$_4$	r.t., 0.5 h; then 80 °C, 0.5 h	**2c**, 43	**3c**, 28	1.5
p-ClC$_6$H$_4$	r.t., overnight	**2b**, 41	**3b**, 7	
p-MeOC$_6$H$_4$	r.t., overnight	**2d**, 85	—	

a) In the presence of unchanged magnesium.

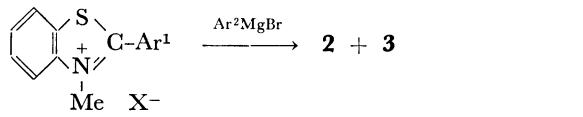
The results reveal that the *para*-methoxyphenyl Grignard reagent bearing an electron-donating group tends to give **2** preferentially, whereas electron-withdrawing groups attached to the aromatic ring of Grignard reagents and also higher temperature would stimulate producing the compound **3.**

In the case of *t*-butylmagnesium bromide, **6** was obtained in 31% yield. The salt (**8**) can react with the Grignard reagents at room temperature, but the yield of **2** was less than those with reaction of **1** because of heterogeniety of the system.

Formation of **2** in the reactions of **1** or **8** can be rationalized by assuming the intermediacy of benzothiazolium salt (**A**) as follows.



Dimerized products have also been obtained by the reaction of 3-methylbenzothiazolium,[6] 2-substituted 1,3-benzoxathiolium,[7] and 1,3-benzodithiolium salts[8] with Grignard reagents. Thereupon, reactions of 3-methyl-2-phenylbenzothiazolium iodide (**9a**) with aryl Grignard reagents were examined. The results are summarized in Table 4.



9: X=I
10: X=ClO_4
a: Ar^1=Ph
b: Ar^1=*p*-ClC_6H_4
c: Ar^1=*p*-$MeOC_6H_4$

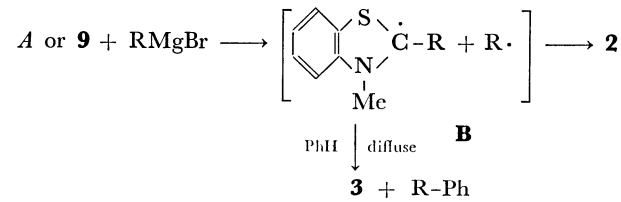
a: Ar^1=Ar^2=Ph
g: Ar^1=Ph, Ar^2=*p*-MeC_6H_4
h: Ar^1=*p*-ClC_6H_4, Ar^2=*p*-MeC_6H_4
i: Ar^1=*p*-$MeOC_6H_4$, Ar^2=*p*-MeC_6H_4

Table 4. Reactions of **9a** with aryl Grignard reagents

Ar^1	Ar^2	Condition	**2** (%)	**3a** (%)	**2/3a**
Ph	Ph	r.t., overnight	**2a**, 31	6	5.2
Ph	Ph	r.t., 0.5 h; then 60 °C, 0.5 h	**2a**, 39	51	0.76
Ph	*p*-MeC_6H_4	r.t., 0.5 h; then 60 °C, 0.5 h	**2g**, 43	31	1.4

The yield of **3** also increased at a higher temperature.

A possible pathway for the formation of **3** would involve reduction of the intermediate **A** or **9** with an Mg–$MgBr_2$ complex in the reaction mixture. In fact, **9a** could be reduced to **3a** with the Mg–$MgBr_2$ complex in refluxing benzene in almost quantitative yield. Another possibility is that one-electron transfer from the Grignard reagent to *A* or **9** would provide the radical intermediate (**B**), which may give **2**, **3**, and the corresponding biphenyl derivative.



Indeed, the formation of biphenyl (21% after correction) was observed, when **9a** was treated with phenylmagnesium bromide in refluxing benzene. The interesting results from *p*-tolylmagnesium bromide solutions prepared from two kinds of magnesium metals [reagent grade: Mg-1 and 99.9% purity: Mg-2], which were treated with **9** and **10** in refluxing benzene, are summarized in Table 5.

Table 5. Effect of purity of magnesium on reactions of **9** or **10** with *p*-tolylmagnesium bromide

Mg	**9** or **10**	**2** (%)	**3** (%)	*Bis-p-tolyl* (%) [a]
Mg-1	**9a**	**2g**, 39	**3a**, 28	20
	9b	**2h**, 76	**3b**, 15	5
	9d	**2i**, 63	**3d**, 20	16
	10c	**2i**, 39	**3d**, 42	14
Mg-2	**9a**	**2g**, 82	**3a**, trace	0
	10a	**2g**, 81	**3a**, trace	0
	10b	**2h**, 82	**3b**, trace	0
	10c	**2i**, 86	**3d**, 2	0
	10c [b]	**2i**, 9	**3d**, 41	55

a) After correction of blank experiment. b) In the presence of a microspatula of anhydrous cobalt(II) chloride.

The results clearly showed that the pure magnesium (Mg-2) provided **2** preferentially and bis-*p*-tolyl was not detected. However, **3** could be obtained as a major product together with a significant amount of bis-*p*-tolyl when the reaction of **10** was carried out in the presence of a small amount of cobalt(II) chloride.

The fact that **3** is always accompanied by a significant amount of bis-*p*-tolyl using Mg-1 or Mg-2 plus cobalt(II) chloride shows that these two products are formed catalyzed by some transition metals present in magnesium as an impurity. This is supported by the fact that *p*-methylbiphenyl was not detected in the reaction mixture by careful gas chromatographic analysis which means that free *p*-toyl radical was not generated during the reaction, thus, in turn, eliminating one-electron transfer mechanism.

In the reaction of **10a** with *p*-tolymagnesium bromide prepared from Mg-2, the presence of an excess magnesium showed no effect, indicating that the reduction of *A* or **9** with the Mg–$MgBr_2$ complex to give **3** does not take place under the reaction conditions using pure magnesium.

In order to prepare 2,2-diaryl derivatives of **2**, the present reaction of **1** with aryl Grignard reagents is recommended and magnesium of higher purity should be used for selective formation of **2** and for suppression of **3** as a by-product.

Experimental

3-Methyl-2,3-dihydrobenzothiazole-2-thione (***1***),[9] mp 92—94 °C (lit, 88—89 °C), 3-methyl-2-(methylthio)benzothiazolium

iodide (**8**),[10] mp 147—148 °C (lit, 148 °C (dec)), and 3-methyl-2-phenylbenzothiazolium iodide (**9a**),[11] mp 217—218 °C (lit, 218 °C (dec)), were prepared according to the reported methods.

*2-Aryl-3-methylbenzothiazolium Iodide (**9**).* *p*-Substituted benzaldehyde (80 mmol) was allowed to react with *o*-aminobenzenethiol (80 mmol) in ethanol (50 ml) for 1 h at 0 °C with stirring to afford 2-arylbenzothiazoline. The resulting thiazoline (60 mmol) was treated with dibenzoyl peroxide (60 mmol) in dichloromethane (250 ml) to give 2-arylbenzothiazole.[12] The benzothiazole (12 mmol) was heated with methyl iodide (40 mmol) at 100 °C in a sealed tube for 20 h to give 2-aryl-3-methylbenzothiazolium iodide (**9**) which was recrystallized from methanol; *p*-chloro derivative (**9b**), yield 80%, mp 253—256 °C (dec) (lit,[13] 224—225 °C) and *p*-methoxy derivative (**9d**), yield 87%, mp 197—198 °C (dec) (lit,[13] 199 °C).

*2-Aryl-3-methylbenzothiazolium Perchlorates (**10**).*[13] A solution of *o*-(methylamino)benzenethiol (69 mmol) and *p*-substituted benzoyl chloride (69 mmol) in benzene (60 ml) was stirred at room temperature for 0.1—1 h and then refluxed for 0.5 h. The resulting precipitates were collected; *p*-chloro chloride, mp 225 °C (dec) and *p*-methoxy chloride mp 191—196 °C (dec). To an aqueous solution of the chloride was added an excess amount of sodium perchlorate and the resulting precipitates were recrystallized from methanol; *p*-chloro (**10b**), yield 85%, mp 239—243 °C, and *p*-methoxy perchlorates (**10c**), yield 80%, mp 195.6—196.7 °C.

The following reactions were carried out under nitrogen.

*Reactions of 3-Methyl-2,3-dihydrobenzothiazole-2-thione (**1**) with Grignard Reagents. General Procedure.* An ethereal solution (20—30 ml) of the Grignard reagent (20—25 mmol), which was filtered through a glass filter, was added to a solution of **1** (905 mg, 5 mmol) in benzene (25—35 ml) and the mixture was refluxed for a time shown below. After addition of 10% aq ammonium chloride, the reaction mixture was extracted with dichloromethane, the extract was dried ($MgSO_4$), and the solvent was removed. The residue was submitted to dry column chromatography (DCC: SiO_2) to separate reaction products.

1) With Phenylmagnesium Bromide: The mixture was refluxed for 3 h. After addition of 10% aq sulfuric acid, evolved hydrogen sulfide was passe dthrough aq lead(II) acetate to give lead(II) sulfide (814 mg, 68%). Separation of the residue by DCC (CH_2Cl_2 : hexane=1 : 4) gave 3-methyl-2,2-diphenyl-2,3-dihydrobenzothiazole (**2a**; 1.021 g, 67%), mp 142—143 °C (from EtOH) (lit,[1a] 142—143 °C), and 3,3′-dimethyl-2,2′-diphenyl-2,2′,3,3′-tetrahydrobi(2-benzothiazolyl) (**3a**; 259 mg, 23%), mp 166—167 °C (from EtOH); NMR ($CDCl_3$): δ 2.24 (s, 6H) and 6.0—8.2 (m, 18H).

Found: C, 74.19; H, 5.26; N, 6.21%, Calcd for $C_{28}H_{24}N_2S_2$: C, 74.30; H, 5.34; N, 6.19%.

2) With p-Chlorophenylmagnesium Bromide: The mixture was refluxed for 4 h. Separation by DCC (CH_2Cl_2: hexane= 1 : 4) gave 2,2-di-*p*-chlorophenyl-3-methyl-2,3-dihydrobenzothiazole (**2b**; 1.079 g, 58%) and 2,2′-di-*p*-chlorophenyl-3,3′-dimethyl-2,2′,3,3′-tetrahydrobi(2-benzothiazolyl) (**3b**; 281 mg, 21%).

2b: did not solidify and was purified by molecular distillation; NMR ($CDCl_3$): δ 2.58 (s, 3H) and 6.3—7.5 (m, 12H).

Found: C, 64.76; H, 3.99; N, 3.63%. Calcd for $C_{20}H_{15}NCl_2S$: C, 64.52; H, 4.06; N, 3.70%.

3b: mp 203—204 °C (from PhH–EtOH); NMR ($CDCl_3$): δ 2.71 (s, 6H) and 6.0—8.1 (m, 16H).

Found: C, 64.33; H, 4.00; N, 5.37%. Calcd for $C_{28}H_{22}N_2Cl_2S_2$: C, 64.48; H, 4.25; N, 5.37%.

3) With p-Tolylmagnesium Bromide: The mixture was refluxed for 3 h. Separation by DCC (CCl_4) gave 3-methyl-2,2-di-*p*-tolyl-2,3-dihydrobenzothiazole (**2c**; 1.398 g, 84%), mp 143—144 °C (from EtOH) (lit,[1a] 141—141.5 °C).

4) With p-Methoxyphenylmagnesium Bromide: The mixture was refluxed for 1.5 h. Separation by DCC (CH_2Cl_2: hexane=1 : 1) gave 2,2-di-*p*-methoxyphenyl-3-methyl-2,3-dihydrobenzothiazole (**2d**; 1.532 g, 84%), mp 87—88 °C (from EtOH); NMR ($CDCl_3$): δ 2.61 (s, 3H), 3.85 (s, 6H), 6.3—7.2 (m, 4H), and 7.29 (ABq, $\Delta\delta$=32 Hz, J=9.5 Hz, 8H).

Found: C, 72.72; H, 5.86; N, 3.90%. Calcd for $C_{22}H_{21}NO_2S$: C, 72.70; H, 5.82; N, 3.85%.

5) With Ethylmagnesium Bromide: Filtration of the Grignard reagent was not carried out. The mixture was refluxed for 4 h. Separation by DCC (CH_2Cl_2 : hexane=1 : 4) and then preparative thin layer chromatography (PTLC) (SiO_2, CH_2Cl_2 : hexane=1 : 4) gave 2,2-diethyl-3-methyl-2,3-dihydrobenzothiazole (**2e**; 555 mg, 54%), bis[*o*-(methylamino)phenyl] disulfide (**4**; 133 mg, 19%), mp 66 °C (lit,[14] 64—68 °C), and ethyl *o*-(methylamino)phenyl sulfide (**5a**; 6 mg) (by IR and NMR[15]).

2e: oily material; NMR ($CDCl_3$): δ 0.95 (t, J=7.5 Hz, 6H), 1.3—2.2 (m, 4H), 2.70 (s, 3H), and 6.12—7.12 (m, 4H); MS: *m/e* 207 (M^+, 8%) and 178 (M^+ —Et, 100).

6) With t-Butylmagnesium Bromide: The mixture was refluxed for 42 h. Separation by DCC (CH_2Cl_2 : hexane= 1 : 4) gave recovered **1** (700 mg, 77%) and oily 2-*t*-butyl-3-methyl-2,3-dihydrobenzothiazole (**6**; 166 mg, 16%) (by NMR[1a]).

*Reaction of **1** with Organolithiums.* *1) With Phenyllithium*: Phenyllithium (40 mmol) in ether (30 ml) was added to **1** (905 mg, 5 mmol) in benzene (30 ml) and the mixture was stirred at room temperature for 15 min. After addition of 10% aq ammonium chloride and then usual work-up, the residue was submitted to DCC (SiO_2, CH_2Cl_2 : hexane= 1 : 4) and then PTLC (SiO_2, CH_2Cl_2 : hexane=1 : 4) to afford **2a** (635 mg, 42%) and oily *o*-(methylamino)phenyl sulfide (**5b**; 206 mg, 19%) (by IR and NMR[16]).

2) With Ethyllithium: To ethyllithium (20 mmol) in pentane (20 ml) was added **1** (905 mg, 5 mmol) in benzene (30 ml) and the mixture was stirred for 1 h. After usual work-up, **2e** (672 mg, 65%) was obtained by DCC (SiO_2, CH_2Cl_2 : hexane=1 : 4).

3) With Butyllithium: To butyllithium (50 mmol) in hexane (31 ml) was added **1** (1.812 g, 10 mmol) in benzene (30 ml) and the mixture was stirred for 1 h. After usual work-up, oily 2,2-dibutyl-3-methyl-2,3-dihydrobenzothiazole (**2f**; 1.536 g, 58%) (by IR and NMR[1c]) and oily 2-butylidene-3-methyl-2,3-dihydrobenzothiazole (**7**; 238 mg, 12%) were isolated by DCC (SiO_2, CH_2Cl_2 : hexane=1 : 1) and then PTLC (SiO_2, $CHCl_3$). **7** gradually changed to a solid on standing.

7: NMR ($CDCl_3$) : δ 0.6—1.9 (m, 7H), 3.01 (s, 3H), 4.65 (br s, 1H), and 6.9—7.4 (m, 4H); MS: *m/e* 205 (M^+, 100%) and 162 (M^+—Pr, 46).

*Reactions of 3-Methyl-2-(methylthio)benzothiazolium Iodide (**8**) with Grignard Reagents.* General procedure was almost the same as that for **1**.

1) With Phenylmagnesium Bromide: The mixture was stirred at room temperature for 1.5 h and then refluxed for 0.5 h. By DCC (CH_2Cl_2 : hexane=1 : 4), **2a** (818 mg, 54%) and **3a** (273 mg, 25%) were obtained.

2) With p-Chlorophenylmagnesium Bromide: The mixture was stirred overnight. By DCC (CH_2Cl_2 : hexane=1 : 4), **2b** (763 mg, 41%) and **3b** (86 mg, 7%) were obtained.

3) With p-*Tolylmagnesium Bromide*: The mixture was stirred overnight. By DCC (CCl_4), **2c** (823 mg, 50%) was obtained.

Similar reaction was carried out using **8** (808 mg, 2.5 mmol) and the Grignard reagent (10 mmol) under stirring for 0.5 h at room temperature and then refluxing for 0.5 h. **2c** (359 mg, 43%) and 3,3′-dimethyl-2,2′-di-*p*-tolyl-2,2′,3,3′-tetrahydrobi(2-benzothiazolyl) (**3c**: 166 mg, 28%), mp 163—165 °C (from EtOH); NMR (CCl_4): δ 2.29 (s, 6H), 2.94 (s, 6H), and 5.8—7.9 (m, 16H).

Found: C, 74.87; H, 5.86; N, 5.81%. Calcd for $C_{30}H_{28}N_2S_2$: C, 74.96; H, 5.87; N, 5.83%.

4) With p-*Methoxyphenylmagnesium Bromide*: The mixture was stirred overnight. By DCC (CH_2Cl_2: hexane=1 : 1), **2d** (1.515 g, 83%) was obtained.

5) *With* t-*Butylmagnesium Bromide*: The mixture was stirred overnight, and **6** (325 mg, 31%) was obtained by DCC (CH_2Cl_2 : hexane=1 : 4).

*Reactions of 3-Methyl-2-phenylbenzothiazolium Iodide (**9a**) with Grignard Reagents.* *1) With Phenylmagnesium Bromide*: Phenylmagnesium bromide (2 mmol) in ether (5 ml) was added to **9a** (353 mg, 1.0 mmol) in benzene (15 ml) and the mixture was stirred overnight. After usual work-up and PTLC (SiO_2, CCl_4), **2a** (93 mg, 31%), and **3a** (13 mg, 6%) were obtained.

Similar reaction was carried out using **9a** (883 mg, 2.5 mmol) and the Grignard reagent (5 mmol) under stirring at room temeperature for 0.5 h and then refluxing for 0.5 h, and **2a** (295 mg, 39%) and **3a** (289 mg, 51%) were obtained.

2) With p-*Tolylmagnesium Bromide*: *p*-Tolylmagnesium bromide (3 mmol) in ether (3 ml) was added to **9a** (353 mg, 1.0 mmol) in benzene (15 ml) and the mixture was stirred for 0.5 h and then refluxed for 0.5 h. After usual work-up and PTLC (SiO_2, CCl_4), 3-methyl-2-phenyl-2-*p*-tolyl-2,3-dihydrobenzothiazole (**2g**; 137 mg, 43%) and **3a** (70 mg, 31%) were obtained.

2g: mp 110.5—112.0 °C (from EtOH); NMR ($CDCl_3$); δ 2.30 (s, 3H), 2.52 (s, 3H), and 6.1—7.4 (m, 13H); MS; *m/e* 317 (M^+, 37%), 240 (100), and 226 (76).

Found: C, 79.46; H, 6.03; N, 4.33%. Calcd for $C_{21}H_{19}NS$: C, 79.45; H, 6.03; N, 4.41%.

*Reaction of **9a** with Mg–$MgBr_2$.* To a mixture of Mg and $MgBr_2$, prepared from magnesium (122 mg, 5 mmol) and 1,2-dibromoethane (470 mg, 2.5 mmol) in ether (10 ml), was added **9a** (883 mg, 2.5 mmol) in benzene (10 ml) and the mixture was stirred for 14 h and then refluxed for 1 h. After usual work-up, the residue was recrystallized from methanol to give **3a** (550 mg, 97%).

Determination of Biphenyl. An ethereal solution (10 ml) of phenylmagnesium bromide (8 mmol) was prepared. The Grignard solution (2.6 ml) and naphthalene as an internal standard were added to **9a** (353 mg, 1 mmol) in benzene (10 ml) and the mixture was refluxed for 49 min. Separately, the Grignard solution (2.6 ml), benzene (10 ml), and naphthalene were refluxed for 40 min. Based on gas chromatographic analysis (OV-1, 2m, 120 °C), the amount of biphenyl was 0.352 mmol and 0.142 mmol, respectively, indicating the net formation of biphenyl (0.210 mmol, 21%).

*Reactions of 2-Aryl-3-methylbenzothiazolium Salts (**9** or **10**) with* p-*Tolylmagnesium Bromide.* *General Procedure*: *p*-Tolylmagnesium bromide was prepared from magnesium (2.431 g, 0.1 mol) and *p*-bromotoluene (17.104 g, 0.1 mol) in ether (100 ml), using magnesium of reagent grade (Mg-1) and 99.9% magnesium (Mg-2), respectively, and filtered through glass wool.

To a suspension of **9** or **10** (2.5 mmol) in benzene (20 ml) was added the Grignard solution (5 mmol) at 78 °C and the mixture was heated as 76—80 °C for 1 h under stirring. A small aliquot was taken for gas chromatography. After addition of 1.5 M sulfuric acid, the reaction mixture was extracted with benzene, the extract was dired ($MgSO_4$), and evaporated. The residue was submitted to DCC (SiO_2, CH_2Cl_2: hexane=1 : 4; 1 : 1 for Mg-1 and **9c**). When the separation was incomplete, the yields were calculated based on the peak area of the NMR. The yields of bis-*p*-tolyl were determined by gas chromatography (OV-1, 120 °C) using biphenyl as an internal standard, and corrected by the amount produced after heating the Grignard solution in benzene without **9** or **10** under the same conditions. The results were listed in Table 5.

Physical data of new products are as follows.

2h: mp 145—146 °C (from MeOH–pentane); NMR ($CDCl_3$) : δ 2.27 (s, 3H), 2.51 (s, 3H), and 6.15—7.42 (m, 12H); MS : 353 (M^+ +2, 11%), 351 (M^+, 25), 262 (22), 260 (58), and 240 (100).

Found: C, 71.77; H, 5.19; N, 3.82%. Calcd for $C_{21}H_{18}NSCl$: C, 71.68; H, 5.16; N, 3.98%.

2i, mp 120.5—122.0 °C (from EtOH–pentane); NMR ($CDCl_3$): δ 2.33 (s, 3H), 2.59 (s, 3H), 3.75 (s, 3H), and 6.24—7.50 (m, 12H); MS : 347 (M^+, 46%), 256 (100), and 240 (92).

Found: C, 76.01; H, 6.19; N, 3.85%. Calcd for $C_{22}H_{21}NOS$: C, 76.05; H, 6.09; N, 4.03%.

3d: mp 182.0—183.5 °C (from MeOH–pentane); NMR ($CDCl_3$): δ 2.65 (s, 6H), 3.72 (s, 6H), and 5.90—7.95 (m, 16H); MS 512 (M^+, 0.8%), 256 (100), 241 (67), 226 (28), 198 (30), and 150 (16).

Found: C, 70.06; H, 5.54; N, 5.16%. Calcd for $C_{30}H_{28}N_2O_2S_2$: C, 70.28; H, 5.50, N, 5.46%.

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