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Dibenzothiophenes and Related Compounds. V.[1,2] Reactions of 5-Substituted Dibenzothiophenium Salts with Organometallic Reagents

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In order to compare the mechanisms of reactions of sulfonium salts with organolithiums and Grignard reagents, the reactions between 5-substituted dibenzothiophenium salts and methyllithium, methylmagnesium halides, and phenylmagnesium halides have been investigated to get a large difference as shown in Tables I and II, respectively.

The reactions of 5-substituted dibenzothiophenium salts with methyllithium gave ring-opening products (I) as main products in Table I, whereas the reactions of those with methylmagnesium iodide gave no I or only little. Instead, these reactions gave ring-opening products (III) as main products in Table II.

The mechanisms of the formation of the products of the runs in Table I and II have been explained as shown in Chart 2 and Chart 4, respectively.

Franzen, *et al.*[4] studied on the reactions between triarylsulfonium salts and alkyllithiums as examples of the reactions between sulfonium salts and organolithium and proposed a ligand exchange mechanism. We also reported on the reactions between cyclic sulfonium salts, such as 5-substituted dibenzothiophenium and 10-substituted 9,9-dimethylthioxanthenium salts, and organolithiums.[1]

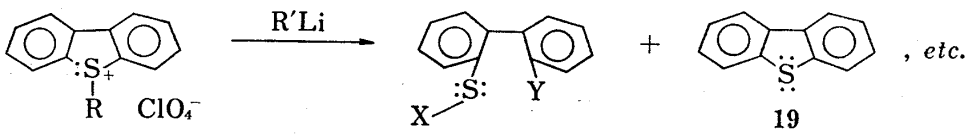
However, little has been studied so far on the mechanism of reactions between sulfonium salt and Grignard reagents. We performed a series of experiments on the reaction between 5-substituted dibenzothiophenium salts and methyllithium, methylmagnesium halides, and phenylmagnesium halides in order to compare the mechanisms of reactions of sulfonium salts with organolithiums and Grignard reagents. An interesting difference was found between the results.

Result and Discussion

All the reactions of 5-substituted dibenzothiophenium salts,[5] such as 5-(*p*-methoxyphenyl)- (**1**), 5-(*o*-methoxyphenyl)- (**2**), 5-(*m*-methoxyphenyl)- (**3**), 5-phenyl- (**4**), and 5-methyldibenzothiophenium salt (**5**) with excess organolithiums and Grignard reagents were made to proceed at room temperature in ether under nitrogen atmosphere. The reaction products were identified by the methods in our preceding reports.[1] Tables I and II show the results of both reactions. A large difference is noticed between the results shown in Tables I and II. At first, Runs 1—4 in Table I gave ring-opening products (I), such as 4-methoxy-2″-(methylthio)-*o*-terphenyl (**6**), 2-methoxy-2″-(methylthio)-*o*-terphenyl (**9**), 3-methoxy-2″-(methylthio)-*o*-terphenyl (**11**), and 2-(methylthio)-*o*-terphenyl (**13**) as main products, whereas Runs 7—11 in Table II gave no I or only little. Instead, Runs 7—11 gave 2-(*p*-methoxyphenylthio)-2′-

1) Part IV: M. Hori, T. Kataoka, H. Shimizu, M. Miyagaki, and M. Murase, *Chem. Pharm. Bull.* (Tokyo), **22**, 2014 (1974).
2) A part of this work was presented at the 6th Symposium on Organosulfur Chemistry, Hamamatsu, Feb. 7, 1972, Abstracts of Papers, p. 5.
3) Location: *492–36, Mitahora, Gifu.*
4) V. Franzen and C. Mertz, *Ann. Chem.*, **643**, 24 (1961).
5) M. Hori, T. Kataoka, H. Shimizu, and M. Miyagaki, *Yakugaku Zasshi*, **93**, 476 (1973).

TABLE I. Reactions of 5-Substituted Dibenzothiophenium Salts with Organolithiums

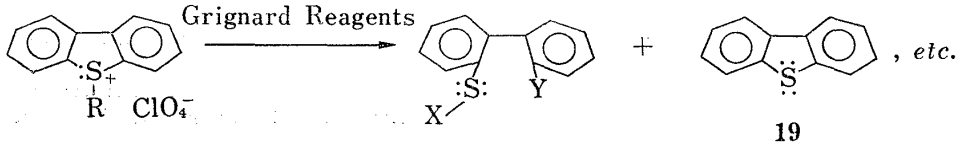


main products other products

Run	Substituents			Main products					Other products	
	No.	R–	R'–	No.	Type[a]	X–	Y–	Yield (%)	**19**, Yield (%)	Yield (%)
1	**1**	*p*-CH_3O C_6H_4–	CH_3–	**6**	I	CH_3–	*p*-CH_3O C_6H_4–	25.5	42.4	anisole (26.0)[b]
				7	II	*p*-CH_3O C_6H_4–	*p*-CH_3O C_6H_4–	13.0		*p*-methylanisole (trace)
				8	II	CH_3–	CH_3–	3.6		
2	**2**	*o*-CH_3O C_6H_4–	CH_3–	**9**	I	CH_3–	*o*-CH_3O C_6H_4–	7.7	84.0	anisole (81.7)[b]
				10	II	*o*-CH_3O C_6H_4–	*o*-CH_3O C_6H_4–	0.6		*o*-methylanisole (3.2)
				8	II	CH_3–	CH_3–	7.0		
3	**3**	*m*-CH_3O C_6H_4–	CH_3–	**11**	I	CH_3–	*m*-CH_3O C_6H_4–	24.3	44.0	anisole (14.0)[b]
				12	II	*m*-CH_3O C_6H_4–	*m*-CH_3O C_6H_4–	21.0		*m*-methylanisole (3.4)
				8	II	CH_3–	CH_3–	3.0		
4[c]	**4**	C_6H_5–	CH_3–	**13**	I	CH_3–	C_6H_5–	34.0	41.2	benzene[b]
				14	II	C_6H_5–	C_6H_5–	14.2		phenol[b]
				8	II	CH_3–	CH_3–	2.6		toluene, polymethylene(trace)
5[c]	**5**	CH_3–	C_6H_5–	**8**	I	CH_3–	C_6H_5–	37.4	40.0	polymethylene
6	**5**	CH_3–	CH_3–	**8**	I II	CH_3–	CH_3–	6.3	83.0	*d*)

a) I: ring-opening products, II: ligand-exchange ring-opening products
b) were afforded by ligand-exchange reaction
c) lit. 6)
d) The analysis of ethane was not determined.

TABLE II. Reactions of 5-Substituted Dibenzothiophenium Salts with Grignard Reagents



19

main products other products

Run	Sulfonium salts No.	Sulfonium salts R–	Grignard reagents	Main products No.	Main products Type[a]	Main products X–	Main products Y–	Main products Yield (%)	Other products 19 Yield (%)	Other products Yield (%)
7	**1**	*p*-CH_3O C_6H_4–	CH_3MgI	**15**	III	*p*-CH_3O C_6H_4–	CH_3–	2.1	1.0	anisole **20** (87.5) **1** (8.0)
8[b]	**1**	*p*-CH_3O C_6H_4–	CH_3MgI	**15**	III	*p*-CH_3O C_6H_4–	CH_3–	67.0	26.5	anisole (11)
				7	II	*p*-CH_3O C_6H_4–	*p*-CH_3O C_6H_4–	1.5		*p*-methylanisole (10) 4,4′-dimethoxybiphenyl (trace)
9	**2**	*o*-CH_3O C_6H_4–	CH_3MgI	**16**	III	*o*-CH_3O C_6H_4–	CH_3–	37.2	51.0	anisole (67)
				10	II	*o*-CH_3O C_6H_4–	*o*-CH_3O C_6H_4–	2.2		*o*-methylanisole (5.7)
				9	I	CH_3–	*o*-CH_3O C_6H_4–	1.6		
10	**3**	*m*-CH_3O C_6H_4–	CH_3MgI	**17**	III	*m*-CH_3O C_6H_4–	CH_3–	57.0	35.0	anisole (6.3)
				12	II	*m*-CH_3O C_6H_4–	*m*-CH_3O C_6H_4–	1.0		*m*-methylanisole (19.6)
				11	I	CH_3–	*m*-CH_3O C_6H_4–	0.8		3,3′-dimethoxybiphenyl (trace)
11	**4**	C_6H_5–	CH_3MgI	**18**	III	C_6H_5–	CH_3–	58.7	27.2	benzene, polymethylene (trace)
				14	II	C_6H_5–	C_6H_5–	1.0		phenol, toluene,
				13	I	CH_3–	C_6H_5–	trace		biphenyl
12	**5**	CH_3–	CH_3MgI						99.0	*c*)
13	**4**	C_6H_5–	CH_3MgBr	**18**	III	C_6H_5–	CH_3–	44.5	43.2	benzene, phenol,
				14	II	C_6H_5–	C_6H_5–	3.7		toluene, biphenyl
14	**1**	*p*-CH_3O C_6H_4–	C_6H_5MgI						4.3	**20** (56.0)
15[b]	**1**	*p*-CH_3O C_6H_4–	C_6H_5MgI						65.0	4-methoxybiphenyl (2.1)
16	**5**	CH_3–	C_6H_5MgI						62.0	toluene

a) I and III: ring-opening products, II: ligand-exchange ring-opening products

b) Were boiled.

c) The analysis of ethane was not determined.

methylbiphenyl (**15**), 2-(*o*-methoxyphenylthio)-2′-methylbiphenyl (**16**), 2-(*m*-methoxyphenylthio)-2′-methylbiphenyl (**17**), and 2-(phenylthio)-2′-methylbiphenyl (**18**) as main products. These are ring-opening products (III), in which the substituents X and Y are just opposite to those in **6**, **9**, **11**, and **13**. Secondly, the yields of ligand-exchange ring-opening products (II) in Tables I and II were larger in Runs 1—4 than in Runs 7—11. Also, no large difference is noticed in the yields of methylanisoles (R-Me) in Runs 1—3, but considerable difference is noticed in the yields in Runs 7—10. The latter reactions are possibly affected by the electronic and steric effects of the substituents at 5-position in **1**—**3**. Of these, the yield of R-Me in Run 10 was 19.6%, and was larger than any of the other reactions.

Mechanisms of Reactions between 5-Substituted Dibenzothiophenium Salts and Methyllithium

Ring-opening products having methylthio group were obtained in all the runs shown in Table I. This result clearly shows that the reactions of **1**—**4** with methyllithium give products (I) through pentacoordinated sulfur intermediates (**A**—**D**) as shown in Chart 1. Also, only **6**, **9**, **11**, and **13** were obtained as products (I) in all the runs, respectively. This result suggests that products (I) were given from conformer (**A**) only, in which methyl and aryl groups occupy the apical position and equatorial position, respectively, because of the bulky effect. This mechanism of Chart 1 is also strongly supported by the result that the reaction (Run 5) between **5** and aryllithium gave **13** only as a main product.

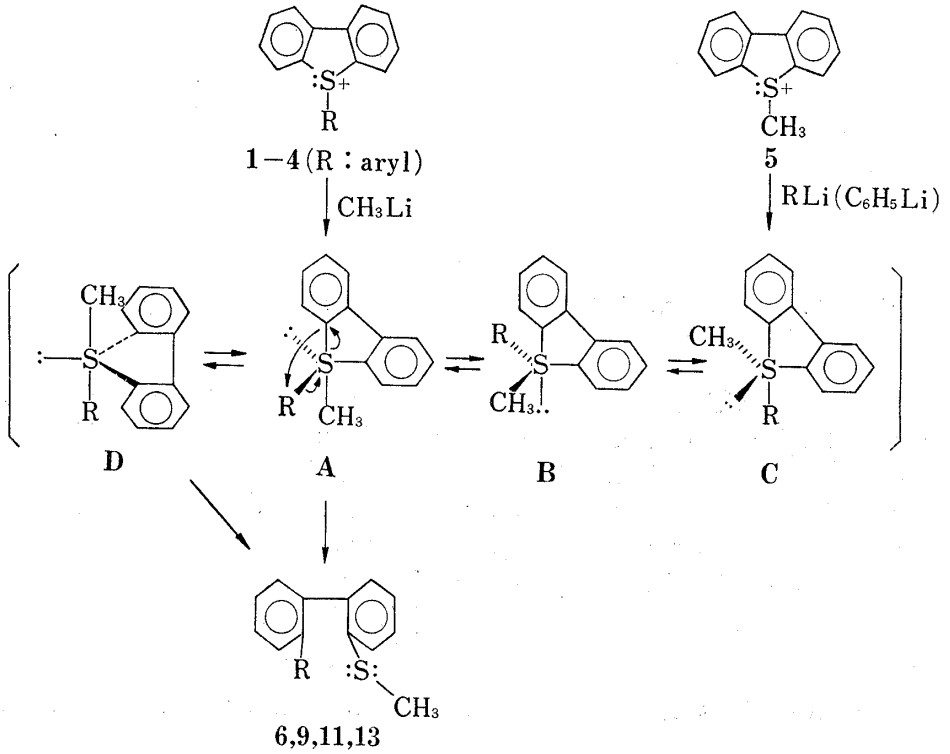


Chart 1. Mechanism for Formation of Ring-Opening Products

Thus all the mechanisms of formation of all the products in Table I were satisfactorily elucidated as shown in Chart 2, in which Run 4 described in our previous report[6] was examined in further detail. According to path A, **4** couples with methyllithium to form conformer (**E**), which gives ring-opening product **13**, dibenzothiophene (**19**) and toluene. According to path B, **4** performs ligand exchange with methyllithium to give phenyllithium and **5**. Phenyllithium will partly form benzene, and the rest will contribute to paths C and D. The

6) M. Hori, T. Kataoka, H. Shimizu, and M. Miyagaki, *Chem. Pharm. Bull.* (Tokyo), 22, 2004 (1974).

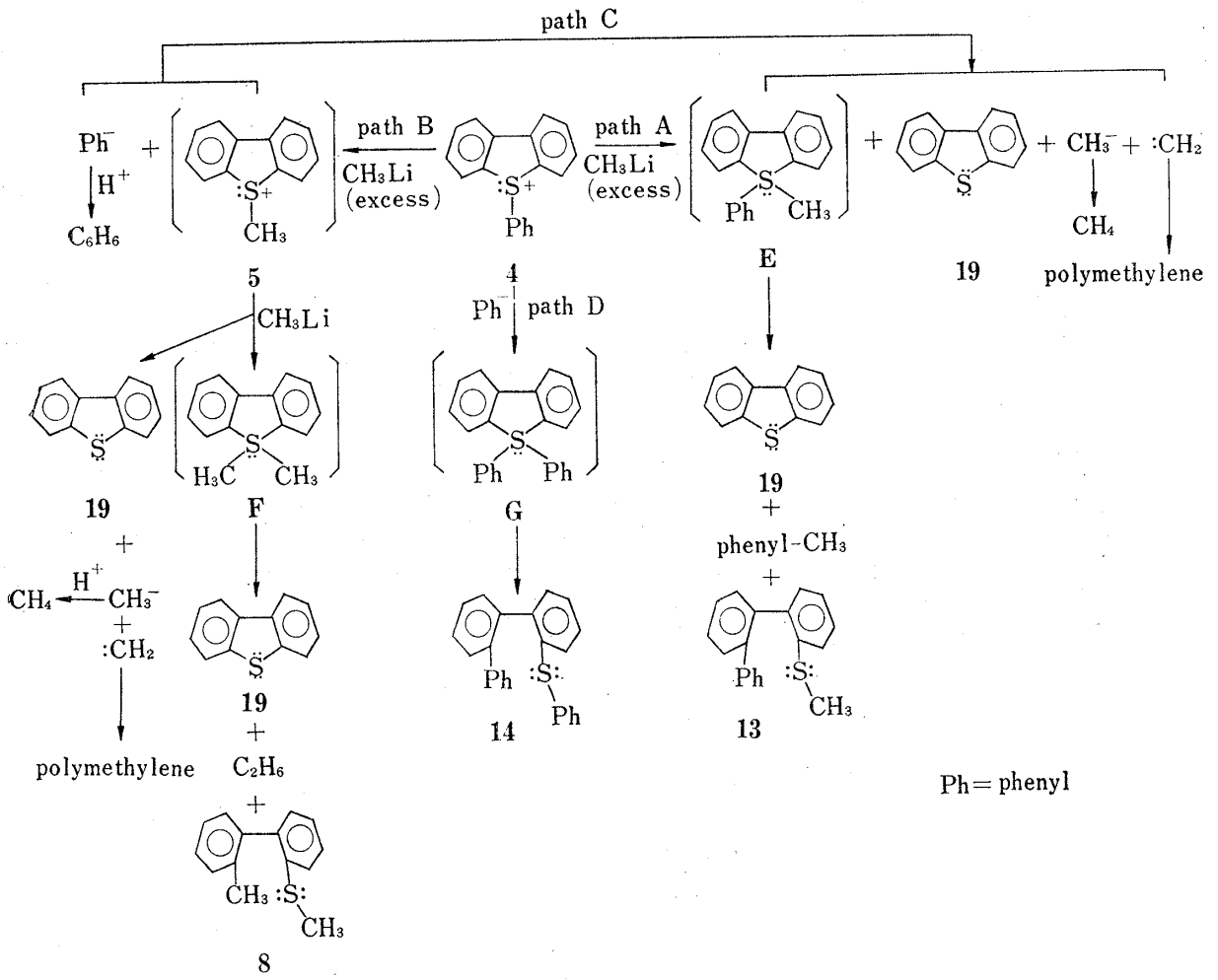


Chart 2. Mechanism of Reactions between 5-Phenyldibenzothiophenium Salt (**4**) and Methyllithium

latter, **5**, either couples with methyllithium to form conformer (**F**), which in turn gives 2-methyl-2′-(methylthio)biphenyl (**8**), which is a ligand–exchange ring–opening product (II), **19**, and ethane or loses a proton in S^+–CH_3 by the abstracting effect of methyllithium to form **19** and carbene, which is a precurser of polymethylene. In path C, phenyllithium either couples at 5-position to form conformer (**E**), which in turn gives **19**, toluene, and **13**, or abstracts a proton from S^+–CH_3 in **5** to give **19** and polymethylene. According to path D, **4** couples with phenyllithium to form conformer (**G**), which in turn gives 2-(phenylthio)-*o*-terphenyl (**14**) of ligand–exchange ring–opening product (II).

Mechanism of the Reactions between 5-Substituted Dibenzothiophenium Salts and Grignard Reagents

Comparison of the results shown in Tables I and II indicates that the possible mechanisms of the reactions between 5-substituted dibenzothiophenium salts and methylmagnesium halides are the radicaloid reaction and the nucleophilic substitution on the aromatic carbon. McEwen, *et al.*[7] explained the reaction between triarylsulfoniums salts and sodium alkoxides by a radicaloid reaction. Their explanation was applied to the reactions (Runs 7—11) between **1**—**4** and methylmagnesium iodide as shown in Chart 3. However, the contribution of this mechanism to the title reactions will be small because of the following reasons: Firstly, the results of measurements of electron spin resonance (ESR) and chemically induced dynamic

7) J.W. Knapczyk and W.E. McEwen, *J. Am. Chem. Soc.*, **91**, 145 (1969).

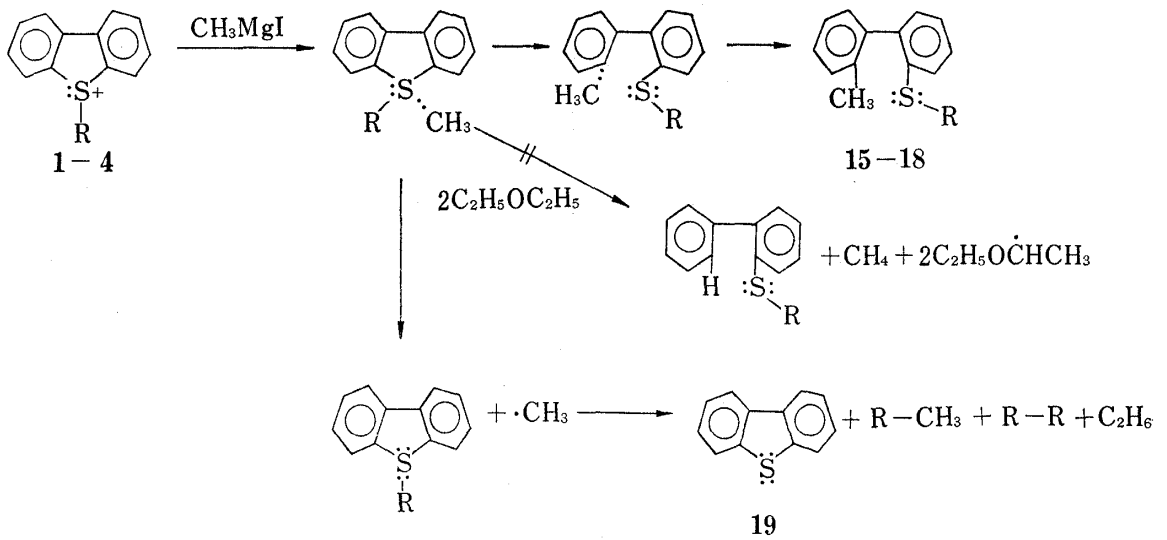


Chart 3. Mechanism of Radicaloid Reactions between 5-R-dibenzothiophenium Salts and Methylmagnesium Iodide

nuclear polarization (CIDNP) on these reactions do not show the presence of free radicals at all. Secondly, *o*-biphenylyl aryl sulfides, which are necessarily formed from radical intermediate, were not formed at all. The radical mechanism is not supported by the yields of the products (**15—18**) formed by the reaction between methylmagnesium iodide and **1—4**, having different substituents. However, it will not be safe to ignore the validity of the mechanism.

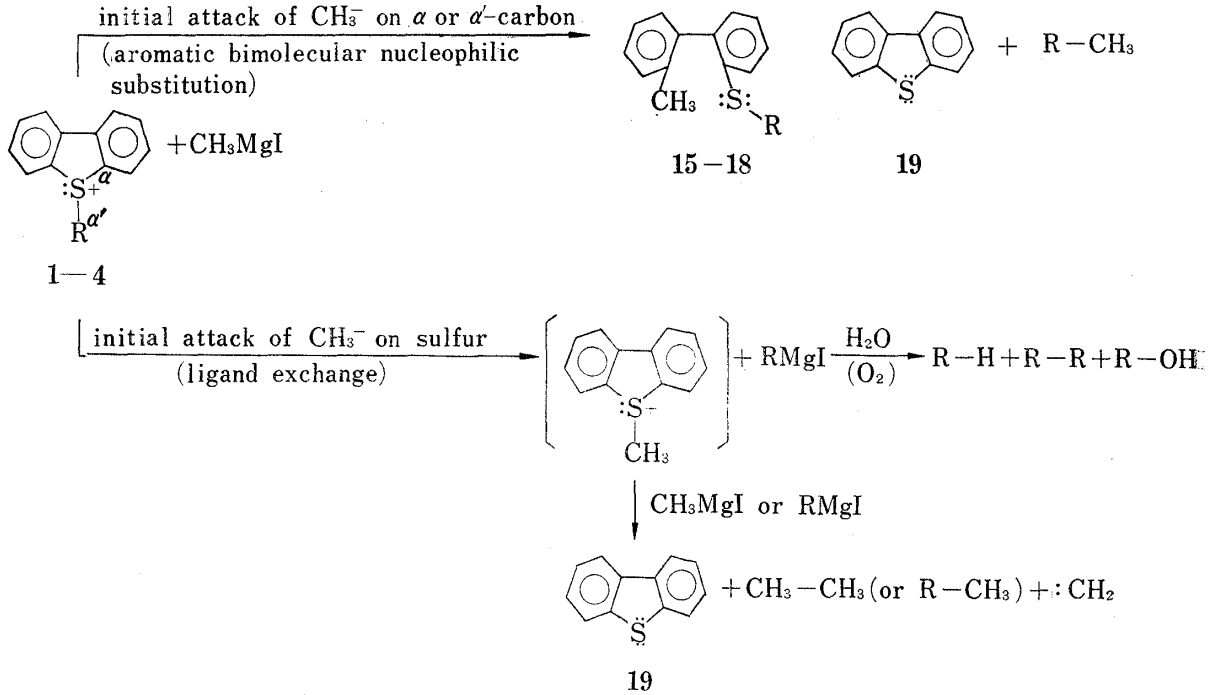


Chart 4. Mechanism of Reactions between 5-R-dibenzothiophenium Salts and Methylmagnesium Iodide

According to the mechanism of aromatic bimolecular nucleophilic substitution, methylmagnesium iodide attacks the α- and α′-carbon in the hetero-ring of **1—4** to give **15—18** of ring-opening products (III), **19**, and R-CH_3 as shown in Chart 4. This mechanism satisfactorily explains the experimental data. In the runs in Table II, Run 10 gave more R-CH_3 (19.6%) than any of the runs in Table II. This result also supports the mechanism, because

the electron density in α'-carbon outside the hetero-ring of **3** is small by the presence of electron-attracting *m*-methoxy group and easily attacked by methylmagnesium iodide. This mechanism is further supported by the results of comparison of the reactions of **2** having large ortho effect due to the presence of a methoxy group with methyllithium and methylmagnesium iodide. In Run 2 in Table I, the trivalent sulfur of **2** gives **9** through pentacoordinated sulfur intermediate compound with methyllithium. However, in Run 9 of Table II, it is reasonable to understand that **16** was formed by the nucleophilic attack of α-carbon in the hetero-ring of **2** by methylmagnesium iodide. It was also found that the yield of **9** (7.7%) was smaller than that of **16** (33%). This difference is clearly attributable to the difference in steric hindrance of the reaction intermediates.

Other products in Table II, such as **19**, R-H, R-R, R-OH, CH_3-CH_3, R-CH_3, and polymethylene were presumably formed as shown in Chart 4. As much as anisole as 67% was formed by Run 9. This yield is attributable, just as the yield 81% in Run 2, to the ligand-exchange reaction, which took place more extensively than other runs because of the necessity to reduce the steric hindrance by *o*-methoxyphenyl group.

On the other hand, some of the Runs 9—11 in Table II gave traces of **9**, **11**, and **13**, which are ring-opening products (I). Thus, it is concluded that the reaction between Grignard reagents and **1**—**4** partly proceed through the formation of pentacoordinated sulfur intermediate, but most of the reaction proceeds by the mechanism of aromatic bimolecular nucleophilic substitution.

However, in the present report, no explanation was proposed on the mechanism of formation of ligand-exchange ring-opening products (II), such as 4-methoxy-2″-(*p*-methoxyphenylthio)-*o*-terphenyl (**7**), 2-methoxy-2″-(*o*-methoxyphenylthio)-*o*-terphenyl (**10**), 3-methoxy 2″-(*m*-methoxyphenylthio)-*o*-terphenyl (**12**), and 2-(phenylthio)-*o*-terphenyl (**14**) in all the runs in Table II. Because, the reaction between **1** and phenylmagnesium iodide (Runs 14—15 in Table II) gave neither ring-opening products (I and III) nor ligand-exchange ring-opening products (II), but gave **19** and a small amount of 4-methoxybiphenyl only.

Generally speaking, Grignard reagents are more bulky and more complex in structure than organolithiums. In Runs 7 and 14, recovery of the starting materials and the formation of 5-(*p*-methoxyphenyl)dibenzothiophenium iodide (**20**) took place. In **20**, ClO_4^- and Br^-, which are ate anion of **1**, were substituted by I^-. These results indicate that the rate of reactions of Grignard reagents to sulfonium salts are slower than those of organolithiums. Consequently, it will be hard to explain the Grignard reactions with **1**—**5** by simple mechanisms.

Experimental

All melting points were uncorrected. Infrared (IR) spectra were measured on a JASCO Model IRA-1. Nuclear magnetic resonance (NMR) spectra were measured on a Hitachi R-20B spectrometer with tetramethylsilane as an internal standard. Mass spectra were measured on a Hitachi RMU-6E spectrometer at an ionizing voltage of 70 eV. Gas-liquid chromatography (GLC) was performed on JEOL JGC-1100 by 20% SE-30 on a Chromosorb W column with a thermal conductivity detector and for quantitative analysis phenetole was used as an internal standard. Preparative thin-layer chromatography (TLC) was carried out on silica gel (Wako Gel B-10) using solvent A: CH_2Cl_2-*n*-hexane (1:4), solvent B: CH_2Cl_2-*n*-hexane (1:3), solvent C: CH_2Cl_2-acetone (3:2) and solvent D: pet. ether-ether (10:1). Fractions of preparative TLC were represented as Fraction I, Fraction II, *etc.*; The *Rf* value decreased in this order. All identification of the compound has been done with respect to IR spectra, mixed melting point and GLC retention time.

Reaction of 5-(*p*-Methoxyphenyl)dibenzothiophenium Perchlorate (1) with Methyllithium (Run 1)—To an ethereal solution of 8 equivalents of methyllithium 1[5] (1.50 g, 3.84 mmole) was added under N_2 at room temperature. After stirring for 8 hr, the reaction mixture was decomposed with 5% HCl and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. GLC analysis of the raw product allowed determination of anisole (0.106 g, 26.0%) and *p*-dimethoxybenzene (trace). Separation by preparative TLC using *n*-hexane gave 3 fractions. Fraction I: Dibenzothiophene (**19**) (0.30 g, 42.4%). Fraction II: 2-Methyl-2′-(methylthio)biphenyl (**8**) (0.03g, 3.6%) was obtained as colorless prisms, mp 52°,[6] by recrystallization from MeOH. Fraction III: A mixture of 4-methoxy-2″-(methylthio)-*o*-terphenyl (**6**)

and 4-methoxy-2″-(*p*-methoxyphenylthio)-*o*-terphenyl (**7**) which was obtained from this fraction was subdivided into 2 components by preparative TLC using solvent A. Compound (**6**) (0.300 g, 25.5%) was recrystallized from MeOH as colorless prisms, mp 77°. *Anal.* Calcd. for $C_{20}H_{18}OS$: C, 78.41; H, 5.92. Found: C, 77.96; H, 5.98. NMR ($CDCl_3$) δ: 6.60—7.45 (12H, m, Ar-H), 3.70 (3H, s, OCH_3), 2.26 (3H, s, SCH_3). Mass Spectrum *m/e* (% of base peak): 306(M^+. 100), 291(14), 276(17), 260(23), 259(63), 258(26), 245(20), 244(32), 229 (14), 228(29), 227(40), 226(14), 216(26), 215(43), 189(14), 184(15), 149(26). Compounds (**7**) (0.200 g, 13.0%) was obtained as a colorless oil.

Desulfurization of 6——To a suspension of Raney cobalt prepared from 50% Co-Al alloy (20 g) in EtOH (50 ml) **6** (0.790 g) was added. The mixture was refluxed for 12 hr and then cooled. The catalyst was filtered off and rinsed with $CHCl_3$. The filtrate and rinsings were combined and evaporated under reduced pressure. After addition of dil. HCl to the residue, the resulting mixture was dried ($MgSO_4$) and evaporated. Separation of the residue by preparative TLC using solvent B gave 4-methoxy-*o*-terphenyl (0.240 g), which was recrystallized from *n*-hexane as colorless plates, mp 62° (lit.[8] 61.5—62.5°) and the recovered material (**6**) (0.470 g).

Reaction of 5-(*o*-Methoxyphenyl)dibenzothiophenium Bromide (2) with Methyllithium (Run 2)——Compound 2[5] (1.50 g, 4.05 mmole) was allowed to react with 8 equivalents of methyllithium as mentioned above. GLC analysis of the raw product allowed determination of anisole (0.357 g, 81.7%) and *o*-dimethoxybenzene (0.016 g, 3.2%). Separation by preparative TLC using solvent A afforded 4 fractions. Fraction I: **19** (0.625 g, 84.0%). Fraction II: **8** (0.060 g, 7.0%). Fracfon III: 2-Methoxy-2″-(methylthio)-*o*-terphenyl (**9**) (0.095 g, 7.7%) was obtained as colorless prisms, mp 105°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{20}H_{18}OS$: C, 78.41; H, 5.92. Found: C, 78.36; H, 6.04. NMR (CCl_4) δ: 6.50—7.30 (12H, m, Ar-H), 3.51 (3H, s, OCH_3), 2.25 (3H, s, SCH_3). Mass Spectrum *m/e* (% of base peak): 306(M^+, 100), 291(5), 276 (22), 275(27), 260(17), 259(50), 258(31), 245(16), 244(32), 229(13), 228(29), 227(28), 226(18), 216(20), 215(31), 189(12), 184(14). Fraction IV: 2-Methoxy-2″-(*o*-methoxyphenylthio)-*o*-terphenyl (**10**) (0.010 g, 0.6%) was obtained as a colorless oil. *Anal.* Calcd. for $C_{26}H_{22}O_2S$: C, 78.37; H, 5.57. Found: C, 78.19; H, 5.66. NMR (CCl_4) δ: 6.50—7.80 (16H, m, Ar-H), 3.74 (3H, s, OCH_3), 3.55 (3H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 398(M^+, 100), 260(11), 259(32), 258(16), 254 (11), 244(21), 229(9), 228(18), 227(26), 226(14), 216(12), 215(22).

Reaction of 5-(*m*-Methoxyphenyl)dibenzothiophenium Bromide (3) with Methyllithium (Run 3)——Compound (3)[5] (1.50 g, 4.05 mmole) was allowed to react with 8 equivalents of methyllithium. GLC analysis of the raw product allowed determination of anisole (0.061 g, 14.0%) and *m*-dimethoxybenzene (0.017 g, 3.4%). Separation by preparative TLC using solvent A gave 4 fractions. Fraction I: **19** (0.325 g, 44.0%). Fraction II: **8** (0.025 g, 3.0%). Fraction III: 3-Methoxy-2″-(methylthio)-*o*-terphenyl (**11**) (0.300 g, 24.3%) was obtained as colorless prisms, mp 62—64°, by recrystallization from MeOH. NMR (CCl_4)δ: 6.50—7.38 (12H, m, Ar-H), 3.51 (3H, s, OCH_3), 2.25 (3H, s, SCH_3). Mass Spectrum *m/e* (% of base peak): 306(M^+, 21), 260(25), 259(100), 258(15), 245(12), 244(25), 229(7), 228(22), 227(38), 226(15), 216(15), 215(25), 189(7), 184(8). *Anal.* Calcd. for $C_{29}H_{18}OS$: C, 78.41; H, 5.92. Found: C, 78.23; H, 6.19. Fraction IV: 3-Methoxy-2″-(*m*-methoxyphenylthio)-*o*-terphenyl (**12**) (0.330 g, 21.0%) was obtained.

Reaction of 5-Methyldibenzothiophenium Fluoroborate (5) with Methyllithium (Run 6)——Compound (**5**)[5] (1.50 g, 5.24 mmole) was allowed to react with methyllithium as mentioned above. Separation by preparative TLC using *n*-hexane gave 2 fractions. Fraction I: **19** (0.800 g, 83.0%). FractionII: 2-Methyl-2′-(methylthio)biphenyl (**8**) (0.070 g, 6.3%).

Reaction of 1 with Methylmagnesium Iodide (Runs 7 and 8)——a) Compound (**1**) (1.50 g, 3.84 mmole) was added to an ethereal solution of methylmagnesium iodide prepared from methyl iodide (5.5 g) and Mg (1.0) at room temperature under an N_2 stream. The sulfonium salt was dissolved and then the reaction mixture became turbid. After stirring for 15 hr, the reaction was quenched with 5% HCl and extracted with ether. The extract was dried ($MgSO_4$). An insoluble material was collected by filtration and separated by chromatography on silica gel using solvent C into 5-(*p*-methoxyphenyl)dibenzothiophenium iodide (**20**) (1.40 g, 87.5% and the recovered material **1** (0.12 g, 8.0%). From the ether extract **19** (0.0077 g, 1.0%) and 2-(*p*-methoxyphenylthio)-2″-methylbiphenyl (**15**) (0.025 g, 2.1%) were obtained. b) Compound (**1**) (2.0 g, 5.02 mmole) was allowed to react with methylmagnesium iodide prepared from methyl iodide (7.5 g) and Mg (1.3 g). The reaction mixture was refluxed until the turbidity disappered (for about 20 hr) and then treated as method a). GLC analysis of the raw product allowed determination of anisole (0.061 g, 11.0%) and *p*-methylanisole (0.062 g, 1.00%). Separation by preparative TLC using solvent D gave 3 fractions. Fraction I: **19** (0.250 g, 26.5%). Fraction II: A mixture obtained from this fraction was subdivided by preparative TLC using solvent A into 2-(*p*-methoxyphenylthio)-2′-methylbiphenyl (**15**) (1.05 g, 67.0%) and 4,4′-dimethoxybiphenyl (0.04 g). Recrystallization of **15** from MeOH gave colorless prisms, mp 102°. *Anal.* Calcd. for $C_{20}H_{18}OS$: C, 78.41; H, 5.92. Found: C, 78.20; H, 6.11. NMR ($CDCl_3$) δ: 6.71—7.50 (12H, m, Ar-H), 3.73 (3H, s, OCH_3), 2.17 (3H, s, CH_3). Mass Spectrum *m/e* (% of base peak): 306(M^+, 100), 291(48), 197(62), 184(20), 166(24), 165(52), 152(20), 141(24), 139(20). 4,4′-Dimethoxybiphenyl

8) T. Sato, S. Shimada, and K. Hata, *Bull. Chem. Soc. Japan*, **42**, 766 (1969).

was melted at 171—172° (lit.[9] 171—172°). Fraction III: 4-Methoxy-2″-(*p*-methoxyphenylthio)-*o*-terphenyl (**7**) (0.03 g, 1.5%) was obtained.

Desulfurization of 15——To a suspension of Raney cobalt prepared from 50% Co-Al alloy (20 g) in EtOH (30 ml) **15** (0.50 g) was added. After refluxing for 12 hr the reaction mixture was treated in the same way as compound (**6**). Separation of the raw product by preparative TLC using *n*-hexane afforded 2-methylbiphenyl (0.05 g) and the recovered material **15** (0.385 g).

Reaction of 2 with Methylmagnesium Iodide (Run 9)——Reaction of **2** (1.5 g, 4.05 mmole) and methylmagnesium iodide prepared from CH_3I (5.8 g) and Mg (0.97 g) was carried out in the same way as mentioned above. The reaction mixture was stirred until the precipitate formed was dissolved (for about 24 hr). GLC analysis of the raw product allowed determination of anisole (0.292 g, 67.0%) and *o*-methylanisole (0.025 g, 5.0%). Separation by preparative TLC using solvent A gave 4 fractions. Fraction I: **19** (0.380 g, 51.0%). Fraction II: 2-(*o*-Methoxyphenylthio)-2′-methylbiphenyl (**16**) (0.460 g, 37.2%) was obtained as a colorless oil. *Anal.* Calcd. for $C_{20}H_{18}OS$: C, 78.41; H, 5.92. Found: C, 78.42; H, 6.14. NMR (CCl_4) δ: 6.64—7.50 (12H, m, Ar-H), 3.68 (3H, s, OCH_3), 2.15 (3H, s, CH_3). Mass Spectrum *m/e* (% of base peak): 306(M^+, 100), 291(40), 276(18), 259(6), 258(10), 199(8), 198 (22), 197(46), 185(8), 184(13), 167(20), 166(26), 165(45), 152(13), 139(8). Fraction III: 2-Methoxy-2″-(methylthio)-*o*-terphenyl (**9**) (0.02 g, 1.6%). Fraction IV: 2-Methoxy-2-(*o*-methoxyphenylthio)-*o*-terphenyl (**10**) (0.035 g, 2.2%).

Reaction of 3 with Methylmagnesium Iodide (Run 10)——Reaction of **3** (1.50 g, 4.05 mmole) with methylmagnesium iodide prepared from methyl iodide (5.8 g) and Mg (0.97 g) was carried out as mentioned above. GLC analysis of the raw product allowed determination of anisole (0.028 g, 6.3%) and *m*-methylanisole (0.097 g, 19.6%). Separation by preparative TLC using solvent A gave 5 fractions. Fraction I: **19** (0.260 g, 35.0%). Fraction II: 2-(*m*-Methoxyphenylthio)-2′-methylbiphenyl (**17**) (0.70 g, 57.0%) was obtained as a colorless oil. *Anal.* Calcd. for $C_{20}H_{18}OS$: C, 78.41; H, 5.92. Found: C, 78.24; H, 5.89. NMR (CCl_4) δ: 6.55—7.30 (12H, m, Ar-H), 3.68 (3H, s, OCH_3), 2.10 (3H, s, CH_3). Mass Spectrum *m/e* (% of base peak): 306(M^+, 100), 291(29), 276(15), 259(11), 258(12), 199(11), 198(14), 197(32), 185(23), 184(23), 167(14), 166(35), 165(88), 152(18), 139(11), 122(46). Fraction III: **11** (0.01 g, 0.8%). Fraction IV: **12** (0.015 g, 1.0%).

Reaction of 4 with Methylmagnesium Iodide (Run 11)——Compound (**4**) (1.50 g, 4.4 mmole) was allowed to react with methylmagnesium iodide prepared from methyl iodide (6.25 g) and Mg (1.1 g). The reaction mixture was treated in the same way as mentioned above. Benzene, toluene, phenol and biphenyl were detected by GLC analysis. Separation by preparative TLC using *n*-hexane gave 5 fractions. Fraction I: **19** (0.220 g, 27.2%). Fraction II: 2-Methyl-2′-(phenylthio)biphenyl (**18**) (0.710 g, 58.7%) was obtained as a colorless oil. *Anal.* Calcd. for $C_{19}H_{16}S$: C, 82.58; H, 5.84. Found: C, 82.49; H, 6.05. NMR (CCl_4) δ: 6.98—7.25 (13H, m, Ar-H), 2.10 (3H, s, CH_3). Mass Spectrum *m/e* (% of base peak): 276(M^+, 100), 261 (60), 199(8), 198(6), 197(15), 185(11), 184(23), 167(10), 166(30), 165(50), 152(13), 149(10), 139(8). Fraction III: 2-(Methylthio)-*o*-terphenyl (**13**) (0.02 g, 1.6%). Fraction IV: **14** (0.015 g, 1.0%). Fraction V: Polymethylene (trace).

Reaction of 5 with Methylmagnesium Iodide (Run 12)——Compound (**5**) was allowed to react with methylmagnesium iodide prepared from methyl iodide (5.0 g) and Mg (0.91 g). After refluxing for 5 hr the reaction mixture was decomposed with 5% HCl and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on alumina to give **19** (0.63 g, 99.0%).

Reaction of 4 with Methylmagnesium Bromide (Run 13)——Compound (**4**) (1.50 g, 4.4 mmole) was allowed to react with methylmagnesium bromide prepared from methyl bromide (4.2 g) and Mg (1.05 g). The reaction mixture was treated in the same way as mentioned above. Benzene, toluene, phenol and biphenyl were detected by GLC analysis. Separation by preparative TLC using *n*-hexane gave 3 fractions. Fraction I: **19** (0.350 g, 43.2%). Fraction II: **18** (0.540 g). Fraction III: **19** (0.055 g, 3.7%).

Reaction of 1 with Phenylmagnesium Iodide (Runs 14 and 15)——a) Compound (**1**) (1.0 g, 2.56 mmole) was added to an ethereal solution of phenylmagnesium iodide prepared from iodobenzene (5.2 g) and Mg (0.62 g). The reaction mixture was refluxed for 12 hr. A precipitate newly formed did not dissolved. After decomposition of the mixture with 5% HCl the resulting precipitate was collected by filtration and the filtrate was extracted with ether. The precipitate was 5-(*p*-methoxyphenyl)dibenzothiophenium iodide (**20**) (0.587 g), mp 243°. The residue from the ether extract was purified by column chromatography on alumina using pet. ether to give **19** (0.02 g, 4.3%). b) Compound (**1**) (1.0 g, 2.56 mmole) was allowed to react with phenylmagnesium iodide until a precipitate newly formed was dissolved (for 30 hr). After decomposition of the reaction mixture it was extracted with ether. No ring-opening products were detected by GLC analysis of the raw product. Separation by column chromatography on alumina using pet. ether gave 3 fractions. Fraction I: A mixture obtained from this fraction was separated into its components, biphenyl and **16** (0.306 g, 65.0%) by column chromatography on alumina using pet. ether. Fraction II: *p*-Terphenyl (trace). Fraction III: 4-Methoxybiphenyl (0.01 g), mp 87° (lit.[10] 89°).

5-(*p*-Methoxyphenyl)dibenzothiophenium Iodide (20)——To a solution of **1** (0.3 g) in $CHCl_3$ (50 ml) a solu-

9) J.H. Gardner and P. Borstrom, *J. Am. Chem. Soc.*, **51**, 3375 (1929).
10) J. Ellos, J.W. Haworth, and R.H. Hey, *J. Chem. Soc.*, **1940**, 1284.

tion of tetraphenylphosphonium iodide (0.434 g) in $CHCl_3$ (10 ml) was added. The mixture was stirred for 1 hr. The resulting tetraphenylphosphonium perchlorate (0.266 g) was filtered off and the filtrate was evaporated. The residual solid was rinsed with ether and recrystallized from MeOH as colorless prisms (0.12 g), mp 240—244°. *Anal.* Calcd. for $C_{19}H_{15}OSI$: C, 54.41; H, 3.62. Found: C, 54.55; H, 3.60. NMR (DMSO-d_6) δ: 8.32—8.60 (4H, m, Ar-H), 7.52—8.10 (6H, m, Ar-H), 7.10—7.20 (2H, m, Ar-H), 3.82 (3H, s, OCH_3).

Reaction of 5 with Phenylmagnesium Iodide (Run 16)——Compound (5) (2.0 g, 7 mmole) was allowed to react with phenylmagnesium iodide prepared from iodobenzene (14.2 g) and Mg (1.70 g). The reaction mixture was refluxed for 5 hr and decomposed with 5% HCl and then extracted with ether. The extract was dried ($MgSO_4$) and evaporated. The residue was separated into biphenyl and **19** (0.794 g, 62.0%) by preparative TLC using solvent A and by column chromatography on alumina using pet. ether.