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Dibenzothiophenes and Related Compounds. II.[1,2] Reactions of 5-Substituted Dibenzothiophenium Salts with Organolithiums

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The reactions of 5-substituted dibenzothiophenium salts with aryllithiums have been found to yield ring-opening products (I), ligand-exchange ring-opening products (II) and other products, as shown in Table I. The formation of these compounds supports the assumption of the pseudorotation of pentacoordinated sulfur intermediates in these reactions.

Many reports have been published so far on the reactions between organolithiums and open chain compounds such as triphenylsulfonium salt and diarylsulfoxides. However, some differences are found among the reaction conditions and the results of these reports. Franzen, *et al.*[4] assumed the formation of tetravalent sulfur compound as an intermediate of the reaction between triphenylsulfonium bromide and *n*-butyllithium and confirmed that a ligand-exchange reaction takes place. Andersen, *et al.*[5] reported that the reaction between ditolyl sulfoxide and tolyllithium gives sulfonium salt followed by the formation of a benzyne intermediate. On the other hand, Oae, *et al.*[6] reported that the reactions between tritolylsulfonium bromide and phenyllithium proceed through two mechanistic routes, *i.e.*, one involving the nucleophilic attack of phenyl anion on the sulfur atom and the other, involving the benzyne route. Very recently, Trost, *et al.*[7] studied on the reaction between triphenylsulfonium salt and phenyl-, vinyl-, allyl-, and *t*-butyllithiums and assumed tetravalent sulfur compounds as reaction intermediates. They also discussed on the mechanism of the reaction.

Following five mechanisms are possible as mechanistic routes of the reaction between triarylsulfonium salt and organolithiums. However, the analysis of the reaction mechanism is very difficult because such sulfonium salts easily perform ligand-exchange reactions with organolithiums and make the reaction very complex.

We are interested from the mechanistic view point, in the nucleophilic reactions of the trivalent sulfur present not in the open chains but in cyclic sulfonium salts. The plane of the hetero-ring and the bond angle in cyclic sulfonium salts are different from those of open chain compounds. Therefore, one of the three C–S$^+$ bonds of the former will be preferentially cleaved. In the case of the former, it is easy to discriminate the ligand-exchange ring-opening product of the reaction of organolithium and sulfonium salt newly formed by the ligand–

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[1] Part I: M. Hori, T. Kataoka, H. Shimizu, and M. Miyagaki, *Yakugaku Zasshi*, **93**, 476 (1973).

[2] A part of this work was presented at the 91st Annual Meeting of the Pharmaceutical Society of Japan, Fukuoka, April 9, 1971. Abstracts of Papers, p. 690. M. Hori, T. Kataoka, H. Shimizu, and M. Miyagaki, *Chemistry Lett.*, **1972**, 515.

[3] Location: *492-36, Mitahora, Gifu.*

[4] V. Franzen and C. Mertz, *Ann. Chem.*, **643**, 24 (1961).

[5] K.K. Andersen, S.A. Yeager, and N.B. Prynircioglu, *Tetrahedron Letters*, **1970**, 2485.

[6] Y.H. Khim and S. Oae, *Bull. Chem. Soc. Japan*, **42**, 1968 (1969).

[7] B.M. Trost, R.W. LaRochelle, and R.C. Atkins, *J. Am. Chem. Soc.*, **91**, 2175 (1969); R.W. LaRochelle and B.M. Trost, *ibid.*, **93**, 6077 (1971) have systematically reported reactions of organolithiums with triarylsulfonium salts. In the report they have also described about the reactions of 5-phenyldibenzothiophenium salt with phenyllithium and vinyllithium, but their reaction conditions were different from ours, because ligand-exchange ring-opening products (II in Table I) have not been reported.

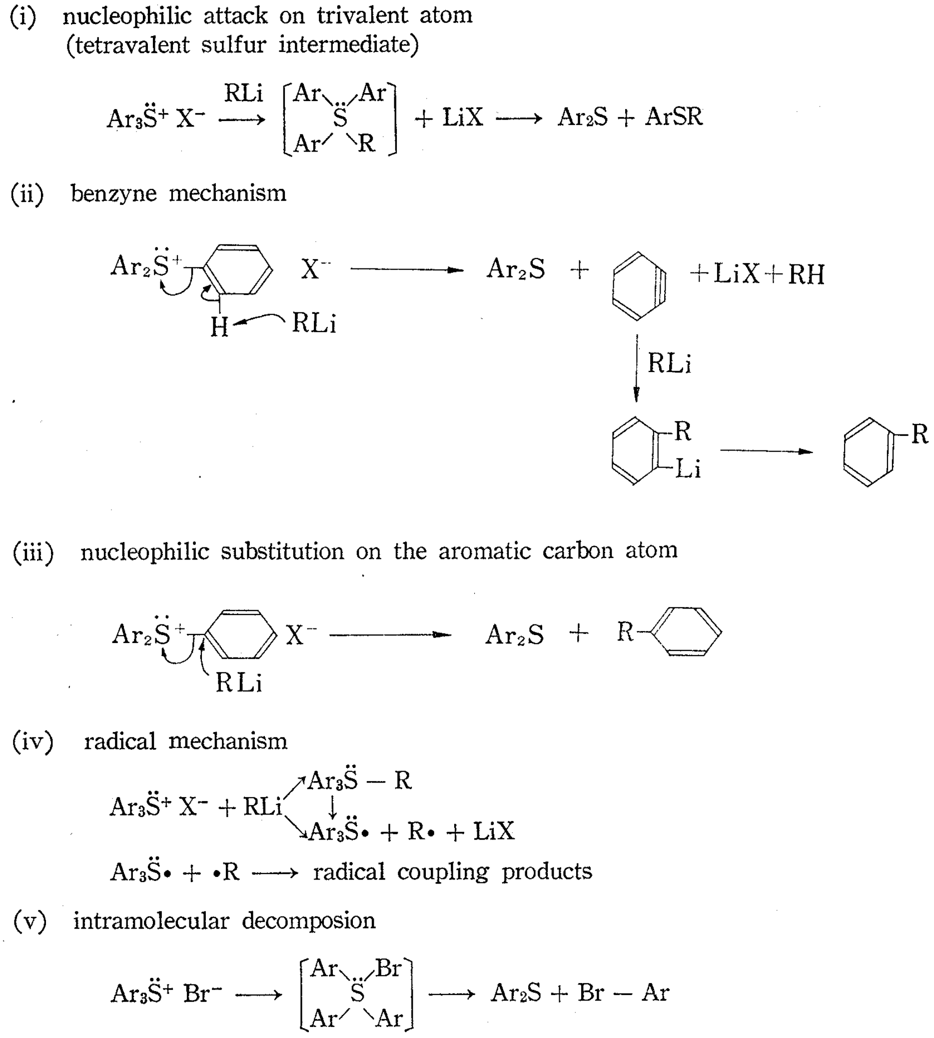


Chart 1

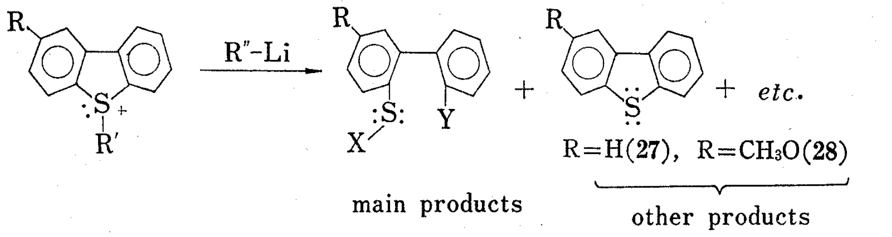
exchange reaction from the ring-opening products obtained by the reaction between organolithium and the sulfonium salt, which is a starting material. This is one of the merits of the former. Therefore, we chose 5-substituted dibenzothiophenium salts[1] as the cyclic compound most similar to triarylsulfonium salts. Reports will be made below on the reaction between aryllithiums and the 5-substituted dibenzothiophenium salts.

Result and Discussion

All the title reactions were allowed to proceed at room temperature in ether under nitrogen atmosphere. One equivalent of sulfonium salt was made to react with eight equivalents of aryllithium. The reaction gave ring-opening products (I) and ligand-exchange ring-opening products (II) as main products (**11**—**25**) and dibenzothiophenes (**27**—**28**) and aromatic hydrocarbons as minor products.

These reaction products were isolated by recrystallization from a suitable solvent after thin-layer chromatography (TLC) on silica gel. Aromatic hydrocarbons such as anisole were analyzed by gas-liquid chromatography (GLC) on a 20% SE-30 column with phenetole as a standard. They were identified by means of GLC retention time, nuclear magnetic resonance (NMR), infrared (IR), mass spectroscopic analysis, and elemental analysis. Furthermore, the main desulfurization products such as *o*-terphenyl obtained by the use of W-7 Raney cobalt and its derivatives were identified by comparing their spectroscopic data or GLC retention time with those of the authentic samples. The results of these are shown in Table I.

Table I. Reactions of 5-Substituted Dibenzothiophenium Salts with Aryllithiums



Run	No.	Sulfonium salt		Aryllithium	No.	Main products				Yield (%)	Other products
		R	R′	R″-		Type[a]	R	X-	Y-		Yield (%)
1	**1**	H	p-$CH_3OC_6H_4$-	C_6H_5-	**11**	I	H	p-$CH_3OC_6H_4$-	C_6H_5-	74.4	anisole(trace)[b]
					12	I	H	C_6H_5-	p-$CH_3OC_6H_4$-	6.6	**27** (trace)[c]
					13	II	H	C_6H_5-	C_6H_5-	4.0	
1[d]	**1**	H	p-$CH_3OC_6H_4$-	C_6H_5-	**11**	I	H	p-$CH_3OC_6H_4$-	C_6H_5-	79.5	anisole(trace)[b]
					12	I	H	C_6H_5-	p-$CH_3OC_6H_4$-	6.5	**27** (trace)[c]
					13	II	H	C_6H_5-	C_6H_5-	2.6	
					14	II	H	p-$CH_3OC_6H_4$-	p-$CH_3OC_6H_4$-	1.6	
2	**2**	H	C_6H_5-	p-$CH_3OC_6H_4$-	**11**	I	H	p-$CH_3OC_6H_4$-	C_6H_5-	69.0	**27** (trace)[c]
					12	I	H	C_6H_5-	p-$CH_3OC_6H_4$-	6.0	
					13	II	H	C_6H_5-	C_6H_5-	4.0	
					14	II	H	p-$CH_3OC_6H_4$-	p-$CH_3OC_6H_4$-	15.5	
3	**3**	H	m-$CH_3OC_6H_4$-	C_6H_5-	**15**	I	H	m-$CH_3OC_6H_4$-	C_6H_5-	26.0	anisole(trace)[b]
					16	I	H	C_6H_5-	m-$CH_3OC_6H_4$-	36.4	**27** (trace)[c]
					17	II	H	m-$CH_3OC_6H_4$-	m-$CH_3OC_6H_4$-	6.0	
					13	II	H	C_6H_5-	C_6H_5-	26.4	
4	**2**	H	C_6H_5-	C_6H_5-	**13**	I II	H	C_6H_5-	C_6H_5-	72.0	**27** (trace)[c]
5	**2**	H	C_6H_5-	p-$(CH_3)_2NC_6H_4$-	**18**	I	H	p-$(CH_3)_2NC_6H_4$-	C_6H_5-	60.0	**27** (trace)[c]
					19	II	H	p-$(CH_3)_2NC_6H_4$-	p-$(CH_3)_2NC_6H_4$-	29.5	
					13	II	H	C_6H_5-	C_6H_5-	5.4	
6	**4**	H	p-FC_6H_4-	C_6H_5-	**20**	I	H	C_6H_5-	p-FC_6H_4-	8.0	oils
					13	II	H	C_6H_5-	C_6H_5-	27.0	**27** (trace)[c]
7	**5**	H	p-ClC_6H_4-	C_6H_5-	**21**	I	H	C_6H_5-	p-ClC_6H_4-	30.0	oils
					13	II	H	C_6H_5-	C_6H_5-	24.4	**27** (trace)[c]
8	**10**	CH_3O	C_6H_5-	C_6H_5-	**22**	I II	CH_3O	C_6H_5-	C_6H_5-	93.5	**28** (7.9)
9	**10**	CH_3O	C_6H_5-	p-$CH_3OC_6H_4$-	**23**	I	CH_3O	p-$CH_3OC_6H_4$-	C_6H_5-	58.0	**28** (1.4)
					24	I	CH_3O	C_6H_5-	p-$CH_3OC_6H_4$-	6.2	4-methoxybiphenyl(1.5)
					25	II	CH_3O	p-$CH_3OC_6H_4$-	p-$CH_3OC_6H_4$-	30.6	
					22	II	CH_3O	C_6H_5-	C_6H_5-	1.8	

a) (I): ring-opening products, (II): ligand-exchange ring-opening products
b) Was afforded by a ligand exchange reaction.
c) Quantitative analysis of biphenyl derivatives (trace) is impossible because excess organolithium is used.
d) 1 equivalent of **1** was treated with 1 equivalent of phenyllithium.

Comparison of products shown in Table I denies the mechanisms of ii—v and strongly suggests the mechanism of i. Mechanisms ii and v are unacceptable because *m*-terphenyl and its derivatives were not formed by the reaction between W-7 Raney cobalt and any of the products; bromobenzene derivatives such as *p*-bromoanisole were not formed by the reaction between 5-(*p*-methoxyphenyl)dibenzothiophenium bromide and phenyllithium in Run 1. Mechanism iv is denied by the results of the extensive work by Trost, *et al.*[7] and by Run 4 of the present work because all the reaction products were simple products. Also no electron spin resonance (ESR) spectra of free radicals were observed in all the runs. Mechanism iii is also unacceptable because no significant difference was found between the yields of 2-(*p*-

methoxyphenylthio)-*o*-terphenyl (**11**) and 4-methoxy-2″-(phenylthio)-*o*-terphenyl (**12**) of ring-opening products (I) in Runs 1 and 2. If title reactions were to proceed according to Mechanism iii, main product in Run 1 must be **11**, and that of Run 2 must be **12**. The results of Runs 5 and 9 cannot be explained by Mechanism iii.

By the ligand-exchange or ligand-coupling reaction, Mechanism i would give tetravalent sulfur intermediate. If the ligand definition includes a lone pair residing in a valence orbital, tetravalent sulfur can be considered as pentacoordinated sulfur which possesses a trigonal bipyramidal geometry with sp^3d hybrid orbitals in the sulfur atom.[7,8] We introduced an assumption of pseudorotation[9] into the pentacoordinated sulfur intermediate and successfully elucidated the process of the title reaction as will be described below. This concept has been closely studied with the chemistry of phosphorus,[10] selenium,[11] tellurium,[12] and arsenic.[13] In the case of sulfur compounds, the concept was examined by Mislow, *et al.*[8] and Cram, *et al.*[14] only on the compounds having an optically active center.

If the pentacoordinated sulfur intermediate gives the reaction products through the pseudorotation by analogy to phosphorane chemistry, following must be assumed: Assumption (1) Both the Muetterties rule and the bulky effect of ligand hold. (2) The five-membered ring in equatorial-apical orientation requires that $\theta=90°$. (3) Attacking and eliminating groups involve apical positions. (4) The lone pair occupies the most electronegative equatorial orbital.

The formation mechanism of ring-opening products (I) in Runs 1 and 2 are shown below. In Chart 2, a trivalent sulfur is attacked by phenyllithium from the apical position (a-position) under Assumption 3 and gives pentacoordinated sulfur intermediate (**A**). The C-S bond in the ring, which occupies the a-position, is preferentially cleaved to give an anionic site because the five-membered hetero-ring in **A** is strained. The anionic site thus formed nucleophilically attacks the α-carbon of *p*-methoxyphenyl group, which occupies the equatorial position (e-position), and opens the ring. Thus **12** is formed from **A** through these processes. It is also possible that the anionic site attacks the α-carbon of the phenyl group in the hetero-ring, which occupies the e-position. However, the expected product is biphenylene, which is rarely formed. Therefore, it is concluded that such an attack does not occur. **A** also forms **11** because it opens the C-S bond, which occupies the a-position in the hetero-ring, after forming conformer (**C**) through an unstable conformer (**B**) of **A**. The yield of **11** is larger than that of **12**. This difference in the yields is attributable to the preferential attack of the phenyl group whose electron density of α-carbon is less than that of the *p*-methoxyphenyl group, which occupies the e-position. When a five-membered ring in a compound occupies equatorial-equatorial orientation ($\theta=120°$), the compound is also a pseudorotational conformer (**D**) which possibly forms **11** and **12**. However, consideration on the C-S-C bond angle in the hetero-ring indicates that **D** is a hardly formed conformer under Assumption 2. On the other hand, it will be reasonable to apply the explanation for Run 1 to Run 2. In the case of the reaction between 5-(*m*-methoxyphenyl)dibenzothiophenium salt (**3**) and phenyllithium (Run 3), the electron density of the α-carbon of *m*-methoxyphenyl group in pseudorotational conformers is smaller than that of the α-carbon of the phenyl group because of the electron-

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8) R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **91**, 5644 (1969).

9) For reviews on pseudorotation, E.L. Muetterties and R.A. Shunn, *Quart. Rev.* (London), **20**, 245 (1966); M. Kumada, *Kagaku* (Kyoto), **25**, 957, 1086 (1970).

10) D. Hellwinkell, *Chem. Ber.*, **99**, 3628, 3642, 3650, 3608 (1966); D.W. Allen and I.T. Millar, *J. Chem. Soc.*, **1969**, 252; D. Gorenstein and F.H. Westheimer, *J. Am. Chem. Soc.*, **92**, 643 (1970).

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13) D. Hellwinkell and G. Kilthau, *Chem. Ber.*, **101**, 121 (1968).

14) D.J. Cram, J. Day, D.R. Rayner, D.A. von Schriltz, D.J. Duchamp, and D.C. Garwood, *J. Am. Chem. Soc.*, **92**, 7369 (1970).

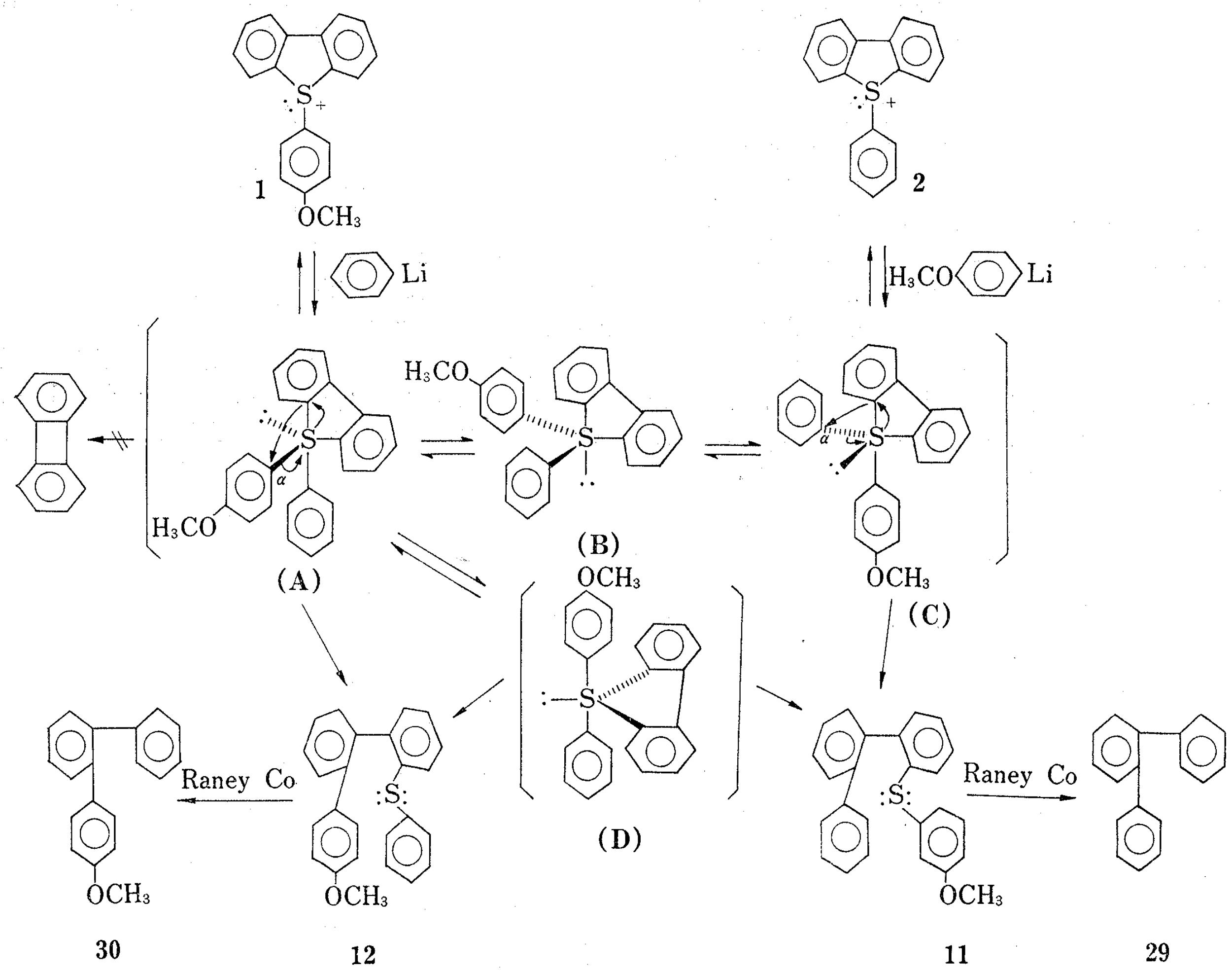

Chart 2. Formation Mechanism of Ring-Opening Product

attracting effect of the methoxy group. Consequently, Run 3 gives more 3-methoxy-2″-(phenylthio)-*o*-terphenyl (**16**) than 2-(*m*-methoxyphenylthio)-*o*-terphenyl (**15**).

Such an electronic effect of substituent groups was more marked in the reaction (Runs 8 and 9) between 2-methoxy-5-phenyldibenzothiophenium salt (**10**) and aryllithiums. Compound (**10**), used in Runs 8 and 9 was synthesized as shown in Chart 3. 2-Bromodibenzothiophene[15] was oxydized by H_2O_2 to form 2-bromodibenzothiophene 5,5-dioxide (**6**), in which the bromo group at 2 position was activated. By the condensation of **6** and $NaOCH_3$, 2-

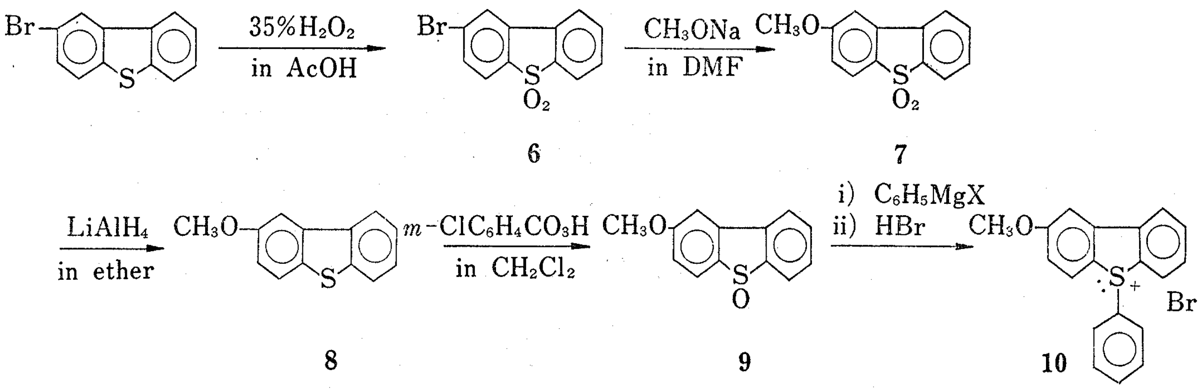

Chart 3

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15) N.M. Cullinana, C.G. Davies, and G.I. Davies, *J. Chem. Soc.*, **1936**, 1435.

methoxydibenzothiophene 5,5-dioxide (**7**) was formed. Compound (**7**) was then reduced with $LiAlH_4$ to give 2-methoxydibenzothiophene (**8**). Compound **8** was further led to **10** by the conventional method.[1)]

The main product of Run 8 was 5-methoxy-2-(phenylthio)-*o*-terphenyl (**22**) only. No 5′-methoxy-2-(phenylthio)-*o*-terphenyl (**26**) was formed. It is reasonable to consider that Run 8 proceeds through conformer (**F**) rather than through pseudorotational conformer (**E**) as shown in Chart 4. 5-Methoxy-2-(*p*-methoxyphenylthio)-*o*-terphenyl (**23**) and 5,4″-dimethoxy-2-(phenylthio)-*o*-terphenyl (**24**), which are the main products of Run 9, are formed from the pseudorotational conformers (**H** and **G**) as shown in Chart 5. The yield of the former is larger than that of the latter. The results of Runs 8 and 9 are explained as those of Run 1. In the case of the reaction between 5-(*p*-halophenyl)dibenzothiophenium salts (**4** and **5**) and phenyllithium, as in Runs 6 and 7, the reaction products further react with phenyllithium, and the reaction such as the benzyne reaction takes place. As a result of this reaction, the yields of the main products decrease.

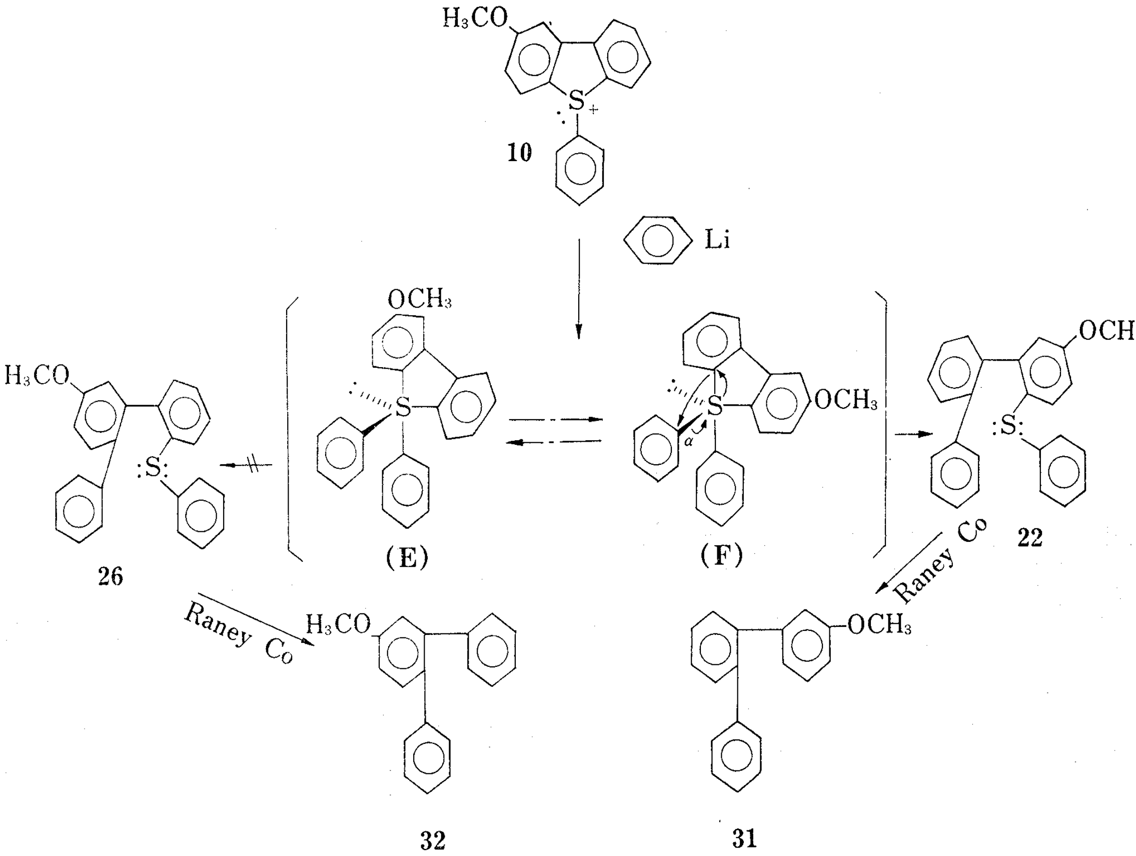


Chart 4

On the other hand, ligand–exchange ring–opening products (II) in Table I, for example, 2-(phenylthio)-*o*-terphenyl (**13**), 4-methoxy-2″-(*p*-methoxyphenylthio)-*o*-terphenyl (**14**), 3-methoxy-2″-(*m*-methoxyphenylthio)-*o*-terphenyl (**17**), 4-dimethylamino-2″-(*p*-dimethylaminophenylthio)-*o*-terphenyl (**19**), 5,4″-dimethoxy-2-(*p*-methoxyphenylthio)-*o*-terphenyl (**25**), and **22** were obtained by all the runs. These products were possibly formed from sulfonium salts, which performed ligand–exchange reaction with excess aryllithium and then performed ligand–coupling reaction to give pentacoordinated sulfur intermediate. The pentacoordinated sulfur intermediate gave those compounds after ring–opening reactions.

Franzen has claimed that the four–membered ring transition is valid for ligand exchange in the reaction between triarylsulfonium salt and alkyllithium. However, the ligand exchange is better explained by the S_N2 type mechanism.

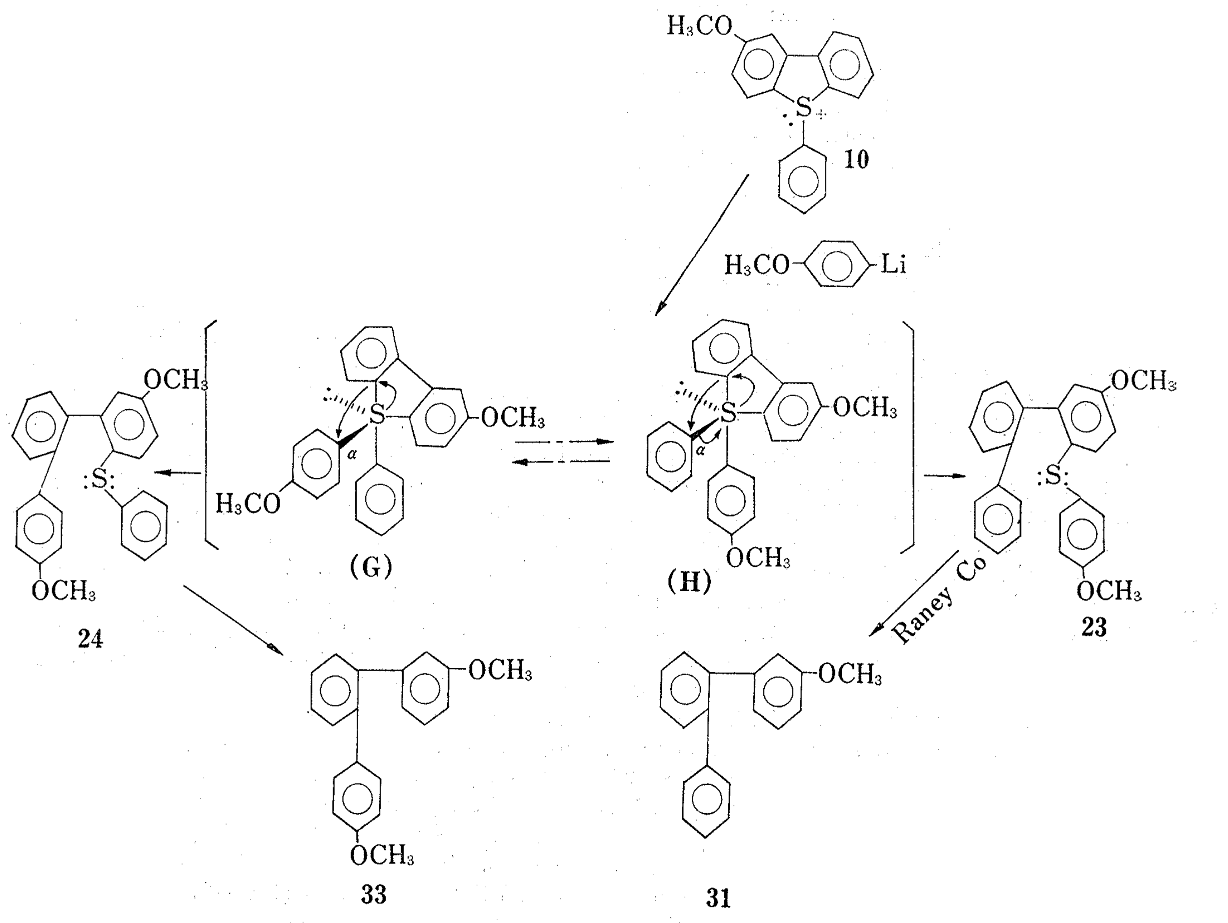


Chart 5

On the ligand exchange mechanism mentioned above, we are now examining the reactions between organometallic reagents with dibenzothiophenium salts having a bulky group at 5-position and a compound of six-membered ring system. The results will be reported in the following report.

Experimental

All melting points were uncorrected. IR spectra were measured on a JASCO model IR A-1. 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. GLC was performed on JEOL model JGC-1100 by 20% SE-30 on a Chromosorb W column with a thermal conductivity detector. Preparative TLC was carried out on silica gel (Wako Gel B-10). Fractions of preparative TLC were represented as Fraction I, Fraction II, *etc.*; The *Rf* value decreased in this order.

2-Bromodibenzothiophene 5,5-Dioxide (6)——To a solution of 2-bromodibenzothiophene[15] (5 g, 19 mmole) in AcOH (150 ml) 35% H_2O_2 (20 g) was added. After refluxing for 5 hr, the reaction mixture was poured into water. The resulting precipitate was collected, rinsed with water, and dried. Recrystallization from CH_2Cl_2–benzene gave colorless needles (5.6 g, 96.4%), mp 266—267°. *Anal.* Calcd. for $C_{12}H_7O_2SBr$: C, 48.82; H, 2.39. Found: C, 48.71; H, 2.17. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1305, 1165 (SO_2).

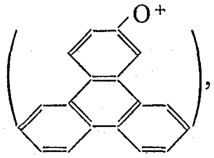
2-Methoxydibenzothiophene 5,5-Dioxide (7)——To a solution of **6** (2 g, 6.8 mmole) in DMF (80 ml) a solution of CH_3ONa prepared from Na (0.3 g) and anhydrous MeOH (10 ml) was added. The reaction mixture was refluxed for 6 hr and removal of the solvent was followed by addition of 5% HCl. The mixture was extracted with $CHCl_3$. The extract was washed with water and dried ($MgSO_4$). Evaporation of the solvent left the solid, which was recrystallized from benzene as colorless needles (1.6 g, 95.6%), mp 248—249°. *Anal.* Calcd. for $C_{13}H_{10}O_3S$: C, 63.41; H, 4.09. Found: C, 63.32; H, 4.20. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1295, 1165 (SO_2). NMR (DMSO-d_6) δ: 7.10—8.35 (7H, m, Ar–H), 3.98 (3H, s, OCH_3).

2-Methoxydibenzothiophene (8)——To a suspension of $LiAlH_4$ (2.0 g, 53 mmole) in anhydrous ether (300 ml) **7** (6.0 g, 24 mmole) was added. After refluxing for 6 hr, the reaction mixture was decomposed with water and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. The resulting residue was recrystallized from ether–*n*-hexane as colorless prisms (4.2 g, 80.8%), mp 54—55°. *Anal.* Calcd. for

$C_{13}H_{10}OS$: C, 72.89; H, 4.71. Found: C, 72.87; H, 4.55. NMR (CCl_4) δ: 6.90—8.10 (7H, m, Ar–H), 3.89 (3H, s, OCH_3).

2-Methoxydibenzothiophene 5-Oxide (9)——To a solution of **8** (2.3 g) in CH_2Cl_2 (120 ml) a solution of *m*-chloroperbenzoic acid (85%) (2.2 g) in CH_2Cl_2 (150 ml) was added. After stirring for 2 days at 0°, the mixture was washed with 5% Na_2CO_3 and then with water, dried (K_2CO_3) and evaporated. Recrystallization from ether gave colorless prisms (2.3 g, 93.1%), mp 136°. *Anal.* Calcd. for $C_{13}H_{10}O_2S$: C, 67.82; H, 4.38. Found: C, 67.96; H, 4.53. IR ν_{max}^{KBr} cm^{-1}: 1060 (SO). NMR ($CDCl_3$) δ: 6.88—8.05 (7H, m, Ar–H), 3.92 (3H, s, OCH_3).

2-Methoxy-5-phenyldibenzothiophenium Bromide (10)——A solution of phenylmagnesium bromide in benzene (100 ml) was prepared from bromobenzene (6.2 g) and Mg (0.94 g). A benzene solution (100 ml) of **9** (1.5 g) was added to the Grignard reagent thus prepared. After refluxing for 30 min the reaction mixture was decomposed with 25% HBr (30 ml). The benzene layer was washed with 50 ml each of 25% HBr for several times. The washings were combined with the aqueous layer and extracted with CH_2Cl_2. The extract was dried ($MgSO_4$) and evaporated. Recrystallization of the residue from CH_2Cl_2–ether gave colorless prisms (1.96 g, 81%), mp 269°. *Anal.* Calcd. for $C_{19}H_{15}OSBr$: C, 61.45; H, 4.07. Found: C, 61.23; H, 4.28. NMR (DMSO-d_6) δ: 7.26—8.70 (12H, m, Ar–H), 4.04 (3H, m, OCH_3).

Reaction of 5-(*p*-Methoxyphenyl)dibenzothiophenium Bromide (1) with Phenyllithium (Run 1)——To an ethereal solution of phenyllithium (86.4 mmole) **1** (4.0 g, 10.8 mmole) was gradually added at room temperature under an N_2 stream. After stirring for 5 hr the reaction mixture was decomposed with 5% HCl and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. The aqueous layer was also extracted with $CHCl_3$ in order to recover **1** and the $CHCl_3$ extract was dried ($MgSO_4$). But no substance was obtained from the $CHCl_3$ extract. Anisole (trace) was detected by GLC analysis of the residual oil from the ether extract. The oil was treated as follows: Separation by preparative TLC using CH_2Cl_2–*n*-hexane (1: 4) gave 3 fractions. Fraction I: Biphenyl and dibenzothiophene (**27**) (trace) were detected by GLC analysis. Fraction II: 2-(Phenylthio)-*o*-terphenyl (**13**) (0.145 g, 4.0 %), mp 88° (lit.[7] 89—90°). *Anal.* Calcd. for $C_{24}H_{18}S$: C, 85.18; H, 5.36. Found: C, 85.26; H, 5.59. NMR (CCl_4) δ: 6.96—7.45 (m, Ar–H). Mass Spectrum *m/e*: 338 (M^+), 229 ($M^+-C_6H_5S$), 228 ($M^+-CH_3OC_6H_5S$, triphenylene). Desulfurization of **13**: The W-7 Raney cobalt catalyst was prepared from Co–Al alloy (20 g) by the method of Badger.[16] A mixture of **13** (0.60 g, 1.77 mmole) and Raney cobalt catalyst thus prepared in EtOH (60 ml) was refluxed for 13 hr. The catalyst was filtered and washed with $CHCl_3$. The $CHCl_3$ washings were combined with the filtrate and removal of the solvent was followed by addition of 5% HCl (100 ml). The mixture was extracted with ether. The extract was dried ($MgSO_4$) and evaporated. Only *o*-terphenyl (**29**) was detected by GLC analysis of the residual oil. Separation by preparative TLC using pet. ether gave **29** (0.4 g, 98.4%), mp 56°, as colorless prisms by recrystallization from MeOH. Compound (**29**) was identified by the comparison of IR spectrum and melting point with those of an authentic sample. Fraction III: This fraction gave colorless crystals (3.20 g, 81.0%), mp 125—127°. The gas chromatogram showed only one peak, but NMR and mass spectral data showed this fraction to be a mixture of 2-(*p*-methoxyphenylthio)-*o*-terphenyl (**11**) and 4-methoxy-2″-(phenylthio)-*o*-terphenyl (**12**). This fact was confirmed by desulfurization of the mixture. *Anal.* Calcd. for $C_{25}H_{20}OS$: C, 81.50; H, 5.47. Found: C, 81.81; H, 5.65. NMR ($CDCl_3$) δ: 6.70—7.50 (m, Ar–H), 3.75 (s, OCH_3), 3.71 (s, OCH_3). The intensity ratio of the peaks at δ 3.75 to 3.71 was 11.2 to 1. Mass Spectrum *m/e*: 368 (M^+), 259 ($M^+-C_6H_5S$), 229 ($M^+-H_3COC_6H_4S$). Desulfurization of the mixture of **11** and **12**: An EtOH solution (70 ml) of the mixture (0.85 g, 2.3 mmole) was desulfurized with Raney cobalt catalyst prepared from 50% Co–Al alloy (20 g) by refluxing for 12 hr. The reaction mixture was treated as mentioned above. The gas chromatogram of the desulfurization product showed three peaks. Separation by preparative TLC using pet. ether–CH_2Cl_2 (10: 1) gave 3 compounds, **29** (0.185 g), 4-methoxy-*o*-terphenyl (**30**) (0.045 g), and **11** (0.42 g). Compound **30** was recrystallized from *n*-hexane as colorless plates, mp 62° (lit.[17] 61.5—62.5°). Compound **11** was recrystallized from MeOH as colorless prisms, mp 132°. *Anal.* Calcd. for $C_{25}H_{20}OS$: C, 81.50; H, 5.47. Found: C, 81.25; H, 5.60. Mass spectrum *m/e*: 368 (M^+), 229 ($M^+-H_3COC_6H_4S$), 228 ($M^+-H_3COC_6H_4SH$, triphenylene). Desulfurization of **11** with Raney cobalt gave only **29**. Isolation of **12**: The mixture of **11** and **12** was washed with pet. ether, and chromatography of the washings on silica gel resulted in the isolation of **12** (trace), which was recrystallized from MeOH as colorless prisms, mp 42°. Mass Spectrum *m/e*: 368 (M^+), 259 ($M^+-C_6H_5S$), 258 ($M^+-C_6H_5SH$, 10-methoxytriphenylene), 244 , 228, 227.

Reaction of 1 with Equimolecular Quantities of Phenyllithium (Run 1[d])——To a suspension of **1** (0.9 g, 2.42 mmole) in anhydrous ether (2 ml) 1.20N phenyllithium (2 ml) was added. The reaction mixture was

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16) G.N. Badger, N. Kowanko, and W.H.F. Sasse, *J. Chem. Soc.*, **1959**, 440.
17) T. Sato, S. Shimada, and K. Hata, *Bull. Chem. Soc. Japan*, **42**, 766 (1969).

worked up as mentioned above. Anisole was detected by GLC analysis of the raw product. Treatment of the crude product by preparative TLC using CH_2Cl_2–*n*-hexane (1:4) gave 4 fractions. Fraction I: Biphenyl and **27** (trace) were detected by GLC analysis. Fraction II: **13** (0.0214 g, 2.6%). Fraction III: A mixture of **11** and **12** (0.767 g, 86.0%) was obtained. The ratio of **11**/**12**=12.3 was determined by measuring the peak areas of OCH_3 groups in the NMR spectrum. Desulfurization of this fraction (0.8 g) with Raney cobalt resulted in the formation of **29** (0.16 g), **30** (0.04 g), and **11** (0.435 g). Fraction IV: 4-Methoxy-2″-(*p*-methoxyphenylthio)-*o*-terphenyl (**14**) (0.0155 g, 1.6%) was obtained as a colorless oil. *Anal.* Calcd. for $C_{26}H_{22}O_2S$: C, 78.37; H, 5.57. Found: C, 78.52; H, 5.81. NMR (CCl_4) δ: 6.53—7.35 (16H, m, Ar–H), 3.73 (3H, s, OCH_3), 3.70 (3H, m, OCH_3). Mass Spectrum *m/e*: 398 (M^+), 259 ($M^+-H_3COC_6H_4S$), 258, 244, 228, 227.

Reaction of 5-Phenyldibenzothiophenium Bromide (2) **with *p*-Methoxyphenyllithium (Run 2)**——Compound 2 (1.3 g, 3.82 mmole) was allowed to react with 8 equivalents of *p*-methoxyphenyllithium in the same conditions as mentioned above. Separation of the oily crude product by preparative TLC using CH_2Cl_2–*n*-hexane (1: 4) gave 5 fractions. Fraction I: Compound **27** (trace) was detected by GLC analysis. Fraction II: **13** (0.052 g, 4.0%). Fraction III: The mixture (1.04 g, 75.0%) contained **11** and **12** was a 11.6: 1 ratio by NMR assay. Desulfurization of this fraction (0.85 g) by Raney cobalt resulted in the formation of **29** (0.202 g), **30** (0.044 g), and **11** (0.40 g). Fraction IV: 4,4′-Dimethoxybiphenyl (0.15 g) was obtained as colorless plates, mp 171—172° (lit.[18] 171—172°) by recrystallization from MeOH. Fraction V: **14** (0.24 g, 15.5%).

Reaction of 5-(*m*-Methoxyphenyl)dibenzothiophenium Bromide (3) **with Phenyllithium (Run 3)**——Compound 3 (1.50 g, 4.05 mmole) was allowed to react with 8 equivalents of phenyllithium in the same conditions as Run 1. Anisole was detected by GLC analysis of the crude product. Separation by preparative TLC using pet. ether gave 4 fractions. Fraction I: Compound **27** (trace) was detected by GLC analysis. Fraction II: **13** (0.36 g, 26.4%). Fraction III: A mixture of 2-(*m*-methoxyphenylthio)-*o*-terphenyl (**15**) and 3-methoxy-2″-(phenylthio)-*o*-terphenyl (**16**) was obtained as a colorless oil (0.93 g, 62.4%). *Anal.* Calcd. for $C_{25}H_{20}OS$: C, 81.50; H, 5.47. Found: C, 81.63; H, 5.70. The gas chromatogram of this fraction showed only one peak, but mass and NMR spectral data and the result of desulfurization indicated that **15** and **16** were present. Mass Spectrum *m/e*: 368 (M^+), 259 ($M^+-C_6H_5S$), 258, 244, 229 ($M^+-H_3COC_6H_4S$), 228, 227. NMR (CCl_4) δ: 6.50—7.38 (m, Ar–H), 3.65 (s, OCH_3), 3.50 (s, OCH_3). The intensity of OCH_3 groups at δ 3.65 and 3.50 was 2 and 3, respectively. Desulfurization of the mixture (0.7 g) was carried out with Raney cobalt, and separation of the product by preparative TLC afforded **29** (0.13 g), 3-methoxy-*o*-terphenyl (**31**) (0.22 g), and the unreacted starting material (0.145 g). NMR analysis showed the recovered oil to be a mixture of **15** and **16** (1: 1). Compound **31** was recrystallized from *n*-hexane as colorless prisms, mp 39.5°. *Anal.* Calcd. for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.86; H, 6.37. NMR (CCl_4) δ: 7.34 (4H, s, Ar–H), 7.14 (5H, s, Ar–H), 6.52—7.10 (4H, m, Ar–H), 3.53 (3H, s, OCH_3). Fraction IV: 3-Methoxy-2″-(*m*-methoxyphenylthio)-*o*-terphenyl (**17**) was obtained as a colorless oil (0.095 g, 6.0%). *Anal.* Calcd. for $C_{26}H_{22}O_2S$: C, 78.37; H, 5.57. Found: C, 78.61; H, 5.52. NMR (CCl_4) δ: 6.50—7.38 (16H, m, Ar–H), 3.66 (3H, s, OCH_3), 3.50 (3H, s, OCH_3). Mass Spectrum *m/e*: 398 (M^+), 259, 258, 244, 228, 227.

Reaction of 2 with Phenyllithium (Run 4)——Compound 2 (1.5 g, 4.4 mmole) was allowed to react with 8 equivalents of phenyllithium under the same conditions as Run 1. Separation by preparative TLC using pet. ether gave biphenyl, **27** (trace), and **13** (1.07 g, 72.0%).

Reaction of 2 with *p*-Dimethylaminophenyllithium (Run 5)——Compound **2** (1.5 g, 4.4 mmole) was allowed to react with 8 equivalents of dimethylaminophenyllithium in the same conditions as Run **1**. Separation by column chromatography on alumina using pet. ether gave 4 fractions. Fraction I: **13** (0.08 g, 5.4%). Fraction II: 4,4′-Bis(dimethylamino)biphenyl, mp 197° (lit.[19] 198°). Fraction III: 2-(*p*-Dimethylaminophenylthio)-*o*-terphenyl (**18**) (1.01 g, 60.0%) was obtained as colorless plates, mp 113°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{26}H_{23}NS$: C, 81.86; H, 6.08; N, 3.67. Found: C, 81.79; H, 6.15; N, 3.67. Mass Spectrum *m/e*: 381 (M^+), 229 ($M^+ -(CH_3)_2NC_6H_4S$), 228. NMR ($CDCl_3$) δ: 6.66—7.50 (17H, m, Ar–H), 2.95 (6H, s, CH_3). Desulfurization of **18** with Raney cobalt resulted in the formation of **29**, which was identified by the comparison of GLC retention time and IR spectrum with those of an authentic sample. Fraction IV: 4-Dimethylamino-2″-(*p*-dimethylaminophenylthio)-*o*-terphenyl (**19**) (0.55 g, 29.5%) was obtained as colorless prisms, mp 190°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{28}H_{28}N_2S$: C, 79.21; H, 6.65; N, 6.60. Found: C, 79.63; H, 6.65; N, 6.30. NMR ($CDCl_3$) δ: 6.47—7.45 (16H, m, Ar–H), 2.96 (6H, s, CH_3), 2.90 (6H, s, CH_3). Mass Spectrum *m/e*: 424 (M^+), 381 ($M^+ -NC_2H_5$), 273, 272 ($M^+ -(CH_3)_2NC_6H_4S$), 271 ($M^+ -(CH_3)_2NC_6H_4SH$, 10-dimethylaminotriphenylene).

Reaction of 5-(*p*-Fluorophenyl)dibenzothiophenium Bromide (4) **with Phenyllithium (Run 6)**——Compound **4** (0.9 g, 2.51 mmole) was allowed to react with 8 equivalents of phenyllithium under the same conditions as Run **1**. The reaction mixture was worked up in the same way as before. Preparative TLC using pet. ether gave 3 fractions. Fraction I: Biphenyl and **27** (trace) were detected by GLC analysis. Fraction

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[18] J.H. Gardner and P. Borgstrom, *J. Am. Chem. Soc.*, **51**, 3375 (1929).

[19] J.P. Morizur and R. Palland, *Compt. Rend.*, **255**, 711 (1962).

II: 4-Fluoro-2″-(phenylthio)-*o*-terphenyl (**20**) (0.072 g, 8.0%) was obtained as colorless prisms, mp 92°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{24}H_{17}SF$: C, 80.86; H, 4.81. Found: C, 80.66; H, 5.07. NMR (CCl_4) δ: 6.64—7.35 (17H, m, Ar–H). Mass Spectrum *m/e*: 356 (M^+), 247 ($M^+ - C_6H_5S$), 246 ($M^+ - C_6H_5SH$, 10-fluorotriphenylene), 228, 227. Fraction III: Compound **13** (0.23 g, 27.0%) and an unknown oil (0.42 g) were obtained.

Reaction of 5-(*p*-Chlorophenyl)dibenzothiophenium Bromide (5) with Phenyllithium (Run 7)——Reaction between **5** (1.0 g, 2.67 mmole) and 8 equivalents of phenyllithium was conducted under the same conditions as Run 1. Separation by preparative TLC using pet. ether gave 3 fractions. Fraction I: Biphenyl and **27** (trace) were detected by GLC analysis. Fraction II: 4-Chloro-2″-(phenylthio)-*o*-terphenyl (**21**) (0.30 g, 30.05), mp 101°, was obtained by recrystallization from MeOH. *Anal.* Calcd. for $C_{24}H_{17}SCl$: C, 77.30; H, 4.59. Found: C, 77.49; H, 4.60. Fraction III: Compound **13** (0.22 g, 24.4%) and an unknown oil (0.2 g) were obtained.

Reaction of 2-Methoxy-5-phenyldibenzothiophenium Bromide (10) with Phenyllithium (Run 8)——Compound (**10**) (1.1 g, 2.97 mmole) was allowed to react with 8 equivalents of phenyllithium as mentioned above. Separation by preparative TLC using pet. ether gave 3 fractions. Fraction I: Biphenyl. Fraction II: 2-Methoxydibenzothiophene (**28**) (0.050 g, 7.9%). Fraction III: 5-Methoxy-2-phenyl-*o*-terphenyl (**22**) (1.02 g, 93.5%) was obtained as colorless prisms, mp 95—96°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{25}H_{20}OS$: C, 81.50; H, 5.47. Found: C, 81.38; H, 5.71. NMR (CCl_4) δ: 6.60—7.36 (17H, m, Ar–H), 3.62 (3H, s, OCH_3). Mass Spectrum *m/e*: 368 (M^+), 259 ($M^+ - C_6H_5S$), 258 ($M^+ - C_6H_5SH$, 3-methyltriphenylene), 228, 227. Desulfurization of **22** with Raney cobalt resulted in the formation of **31**, which was identified by the comparison of IR and NMR spectra and GLC retention time with those of an authentic sample.

Reaction of 10 with *p*-Methoxyphenyllithium (Run 9)——Compound (**10**) (1.7 g, 4.58 mmole) was allowed to react with 8 equivalents of *p*-methoxyphenyllithium as Run 1. Separation by preparative TLC using CH_2Cl_2–*n*-hexane (3:1) gave 6 fractions. Fraction I: 4-Methoxybiphenyl (0.013 g, 1.5%), mp 87° (lit.[20] 89°), was obtained by recrystallization from MeOH. Fraction II: **28** (0.01 g, 1.4%). Fraction III: **22** (0.03 g, 1.8%). Fraction IV: 4,4′-Dimethoxybiphenyl (0.2 g). Fraction V: A mixture of 5-methoxy-2-(*p*-methoxyphenylthio)-*o*-terphenyl (**23**) and 5,4″-dimethoxy-2-(phenylthio)-*o*-terphenyl (**24**) (1.170 g, 64.2%) was obtained as a colorless oil. *Anal.* Calcd. for $C_{26}H_{22}OS$: C, 78.37; H, 5.57. Found: C, 78.54; H, 5.53. NMR (CCl_4) δ: 6.54—7.34 (m, Ar–H), 3.73 (s, OCH_3), 3.60 (s, OCH_3). Desulfurization of the mixture of **23** and **24** (0.58 g) was carried out with Raney cobalt, and separation by preparative TLC using CH_2Cl_2–*n*-hexane (1:4) afforded **31** (0.337 g) and 3,4″-dimethoxy-*o*-terphenyl (**33**). Compound **33** was a colorless oil. *Anal.* Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.68; H, 6.07. NMR (CCl_4) δ: 6.59—7.34 (12H, m, Ar–H), 3.74 (3H, s, OCH_3), 3.60 (3H, s, OCH_3). Fraction VI: 5,4″-Dimethoxy-2-(*p*-methoxyphenylthio)-*o*-terphenyl (**25**) (0.60 g, 30.6%) was obtained as colorless prisms, mp 118°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{27}H_{24}O_3S$: C, 75.68; H, 5.65. Found: C, 75.64; H, 5.74. NMR (CCl_4) δ: 6.55—7.38 (15H, m, Ar–H), 3.76 (6H, s, OCH_3), 3.65 (3H, s, OCH_3). Mass Spectrum *m/e*: 428 (M^+), 289 ($M^+ - H_3COC_6H_4S$), 288 ($M^+ - H_3COC_6H_4SH$, 3,10-dimethoxytriphenylene).

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20) J. Elks, J.W. Haworth, and D.H. Hey, *J. Chem. Soc.*, **1940**, 1284.