[Chem. Pharm. Bull.
22(9)2004—2013(1974)]

UDC 547.818.6.04 : 547.732.04

Dibenzothiophenes and Related Compounds. III.[1,2] Reactions of 10-Substituted 9,9-Dimethylthioxanthenium and 5-Substituted Dibenzothiophenium Salts with Organolithiums

Mikio Hori, Tadashi Kataoka, Hiroshi Shimizu,
and Michihiro Miyagaki

Gifu College of Pharmacy[3]

(Received October 22, 1973)

In order to elucidate the mechanism of the ligand-exchange reaction between sulfonium salt and organolithium, the reactions of organolithiums with 10-substituted 9,9-dimethylthioxanthenium salts and dibenzothiophenium salts having a bulky group at 5-position have been carried out to get the results, as shown in Tables I and II.

It has been proposed that the *S*N2 type mechanism is valid for the ligand exchange in the reactions described above.

In the preceding paper,[1] we reported that the reactions between 5-aryldibenzothiophenium salts and aryllithiums proceed through the nucleophilic attack on trivalent sulfur atoms to form ring-opening products, ligand-exchange ring-opening products and other products. The mechanism of ring-opening in these reactions was clearly explained by the pseudorotation of pentacoordinated sulfur intermediates.

Franzen, *et al.*[4] proposed before a mechanism, which includes the four-membered ring transition, for the ligand exchange in the reaction between aryllithiums and triarylsulfonium salts of the open chain system. However, Hellwinkel, *et al.*[5] estimated the presence of an *S*N2 type mechanism for the ligand exchange of tellurium compounds, which are homologous with sulfur compounds. According to Franzen's mechanism, the bond angle (θ of C-S-C) of the hetero-ring does not play an important role in the ligand exchange. However, a bond angle of $\theta=120°$ is important in the cyclic compounds such as dibenzothiophenium salts. Consequently, the sulfur-containing ring in a compound is apt to become planar[6] in the reaction between organolithiums and six-membered ring compounds, especially, 10-substituted 9,9-dimethylthioxanthenium salts, because of the steric hindrance. It is therefore expected that more ligand-exchange ring-opening products are formed than ring-opening products.

Based on these ideas, we examined the reactions between thioxanthenium salts and organolithiums and compared the results with those obtained with dibenzothiophenium salts investigated in the preceding study. It was thus found that the *S*N2 type mechanism is valid for the ligand-exchange reaction in agreement with our expectation.

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[1] Part II: M. Hori, T. Kataoka, H. Shimizu, and M. Miyagaki, *Chem. Pharm. Bull.* (Tokyo), **22**, 1711 (1974).

[2] A part of this work was presented at the 6th Symposium on Organic Sulfur Chemistry, Hamamatsu, Feb. 7, 1972. Abstracts of Papers, p. 5. 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] D. Hellwinkel and G. Fahrbach, *Chem. Ber.*, **101**, 574 (1968).

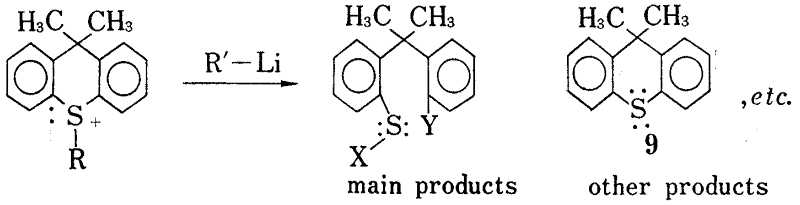
[6] K.K. Andersen, M. Cinquini, and N.E. Papanikolau, *J. Org. Chem.*, **35**, 706 (1970).

Result and Discussion

The Mechanism of the Formation of Ligand-Exchange Ring-Opening Products

Table I shows the results of reactions (Runs 1—7) between 10-substituted 9,9-dimethylthioxanthenium salts (**1**—**4**)[7] and organolithiums. The ligand-exchange ring-opening products (II) are 2-(4′-methoxy-*o*-biphenylyl)-2-[*o*-(*p*-methoxyphenylthio)phenyl]propane (**7**), 2-(*o*-biphenylyl)-2-[*o*-(phenylthio)phenyl]propane (**8**) in Runs 1, 2, and 3 as shown in Table I. The yield of II is larger than that of the corresponding ring-opening products (I). Especially, no I was formed by Run 3. These results are quite different from those of the reactions between 5-substituted dibenzothiophenium salts and aryllithiums reported

TABLE I. Reactions of 10-Substituted 9,9-Dimethylthioxanthenium Salts with Organolithiums



Run	Sulfonium salts No.	Sulfonium salts R–	Organolithiums R′–	Main products No.	Main products Type[a]	Main products X–	Main products Y–	Main products Yield (%)	Other products (Yield, %)
1	**1**	*p*-$\mathrm{CH_3OC_6H_4}$–	$\mathrm{C_6H_5}$–	**5**	I	*p*-$\mathrm{CH_3OC_6H_4}$–	$\mathrm{C_6H_5}$–	21.3	anisole[b]
				6	I	$\mathrm{C_6H_5}$–	*p*-$\mathrm{CH_3OC_6H_4}$–	3.0	**9** (trace)
				7	II	*p*-$\mathrm{CH_3OC_6H_4}$–	*p*-$\mathrm{CH_3OC_6H_4}$–	5.0	4-methoxybiphenyl (trace)[b]
				8	II	$\mathrm{C_6H_5}$–	$\mathrm{C_6H_5}$	64.0	
2	**2**	$\mathrm{C_6H_5}$–	*p*-$\mathrm{CH_3OC_6H_4}$–	**5**	I	*p*-$\mathrm{CH_3OC_6H_4}$–	$\mathrm{C_6H_5}$	13.4	**9** (9.0)
				6	I	$\mathrm{C_6H_5}$–	*p*-$\mathrm{CH_3OC_6H_4}$–	2.0	4-methoxybiphenyl (trace)[b]
				7	II	*p*-$\mathrm{CH_3OC_6H_4}$–	*p*-$\mathrm{CH_3OC_6H_4}$–	59.0	
				8	II	$\mathrm{C_6H_5}$–	$\mathrm{C_6H_5}$–	1.0	
3	**3**	*o*,*p*-$\mathrm{(CH_3O)_2C_6H_3}$–	$\mathrm{C_6H_5}$–	**8**	II	$\mathrm{C_6H_5}$–	$\mathrm{C_6H_5}$–	84.0	**9** (17.9) *m*-dimethoxybenzene (67.1)[b]
4	**2**	$\mathrm{C_6H_5}$–	$\mathrm{C_6H_5}$–	**8**	I II	$\mathrm{C_6H_5}$–	$\mathrm{C_6H_5}$–	81.8	**9** (11.4)
5	**4**	$\mathrm{CH_3}$–	$\mathrm{C_6H_5}$–						**9** (28.6), **10** (18.7), **4** (31.4), polymethylene[c]
6	**2**	$\mathrm{C_6H_5}$–	$\mathrm{CH_3}$–						**9** (92.5), polymethylene[c]
7	**1**	*p*-$\mathrm{CH_3OC_6H_5}$–	$\mathrm{CH_3}$–						**9** (83.6), anisole (89.5))[b] 4-methylanisole (trace)[b]

a) (I): ring-opening products, (II): ligand-exchange ring-opening products
b) They were afforded by a ligand-exchange reaction.
c) It was not analysed.

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

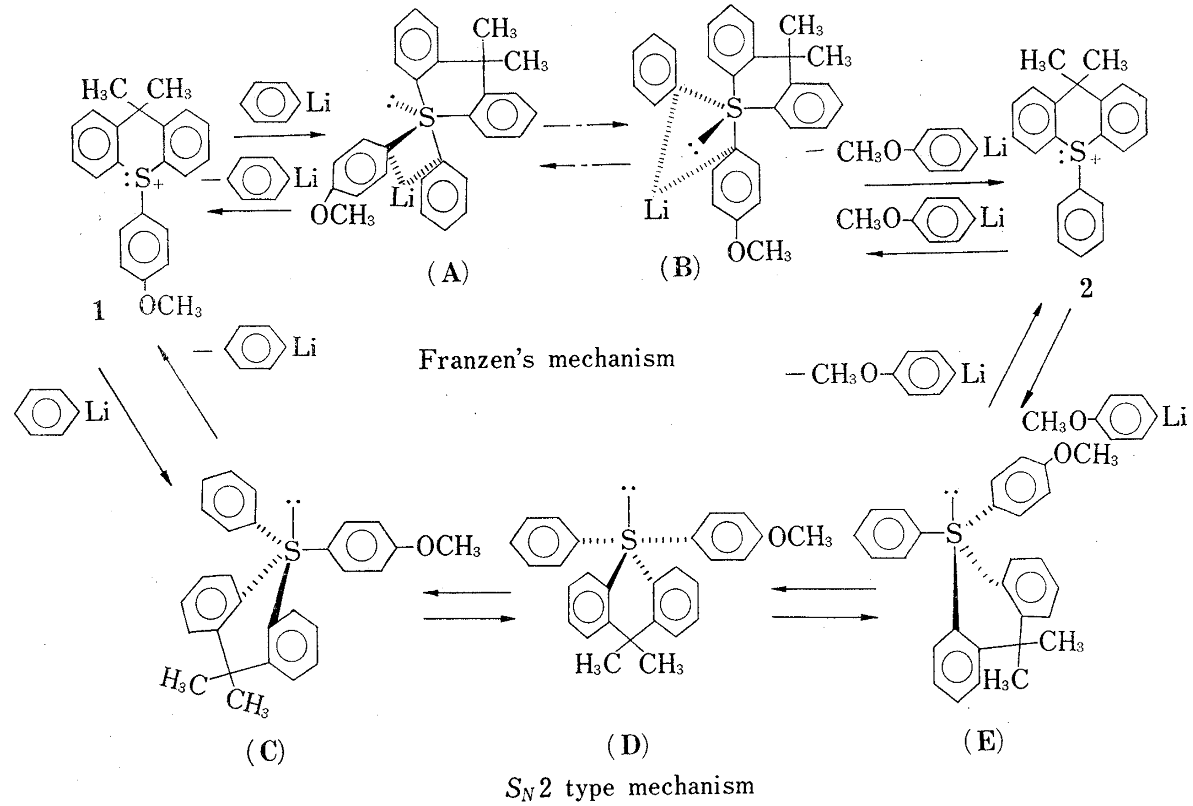


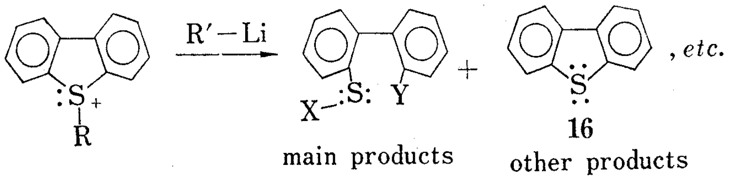
Chart 1. Ligand-Exchange Mechanism

before.1) Ligand exchange mechanisms described above will be applied to Runs 1 and 2. The ligand exchange from 10-(*p*-methoxyphenyl)-9,9-dimethylthioxanthenium perchlorate (**1**) to 9,9-dimethyl-10-phenylthioxanthenium perchlorate (**2**) will be explained by Franzen's mechanism as follows: **1** is attacked by phenyllithium from the apical position (a-position). Pentacoordinated sulfur compound (**A**) thus formed gives pseudorotational conformer (**B**) and then *p*-methoxyphenyllithium is eliminated from the a-position in **B** to form **2**. The process from **2** to **1** can be explained just by the reverse of the above process. According to the S_N2 type mechanism, phenyllithium attacks the positive sulfur atom in **1** from the opposite direction to the *p*-methoxyphenyl group and gives **2** through the intermediates (**C**, **D**, and **E**). The ring inversion of thioxanthene, which easily takes place, suggests the formation of **D** followed by the occurrence of ligand exchange, which supports the results shown in Table I.

The authors planned following experimental investigations in order to confirm the validity of the S_N2 type mechanism for the ligand-exchange reaction mentioned above: (1) The reaction between 5-substituted dibenzothiophenium salts and aryllithiums mainly gave I accompanied by the formation of II as a by-product, as reported in the preceding report. However, ligand exchange in the reactions between 5-substituted dibenzothiophenium salts and aryllithiums can also be assumed to proceed by the S_N2 type mechanism. Ideal pentacoordinate trigonal bipyramidal geometry requires θ of C-S-C in hetero-ring$=90°$ for a ring-opening reaction to occur. The angle of the hetero-ring of the reaction intermediate in the transition state approach $\theta=120°$ by the introduction of the bulky group at 5-position of dibenzothiophenium salt. This approach favors the ligand-exchange reaction to occur. The resulting ligand-exchange reaction will result in the formation of ligand-exchange ring-opening product (II) as a main product. This is as in the case of thioxanthenium salts. (2) The ligand equilibration in the ligand-exchange reaction results in the generation of a 5-substituted dibenzothiophenium salt, which is stereochemically relaxed, and an organolithium, which is more stable than the starting organolithium. They then generate pentacoordinated sulfur compound by coupling between them.

Thus, carrying out the reaction of organolithiums with dibenzothiophenium salts having a bulky group at 5-position, expected results as shown in Table II have been obtained. The results of Runs 8 and 9 shown in Table II indicate that the yield of 2-(phenylthio)-*o*-terphenyl (**19**) is larger than that of the corresponding ring-opening products (I) and that the ligand exchange reaction precedes the ring-opening reaction.

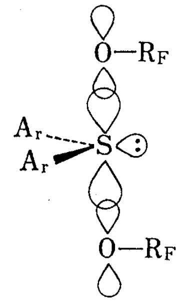
Table II. Reactions of 5-Substituted Dibenzothiophenium Salts with Organolithiums



Run	Sulfonium salts No.	Sulfonium salts R–	Organolithiums R′–	Main products No.	Main products Type[a]	Main products X–	Main products Y–	Yield (%)	Other products (Yield, %)
8	**11**	o-$CH_3OC_6H_4$–	C_6H_5–	**17**	I	o-$CH_3OC_6H_4$–	C_6H_5–	5.7	anisole[b]
				18	I	C_6H_5–	o-$CH_3OC_6H_4$–	12.1	**16** (trace)
				19	II	C_6H_5–	C_6H_5	65.9	
9	**12**	o,p-$(CH_3O)_2C_6H_3$–	C_6H_5–	**20**	I	o,p-$(CH_3O)_2$-C_6H_3–	C_6H_5–	10.6	m-dimethoxybenzene[b]
				21	I	C_6H_5–	o,p-$(CH_3O)_2$-C_6H_3–	3.8	
				19	II	C_6H_5–	C_6H_5–	78.9	**16** (trace)
10	**13**	C_6H_5–	o-$CH_3OC_6H_4$–	**17**	I	o-$CH_3OC_6H_4$–	C_6H_5–	23.5	**16** (trace)
				18	I	C_6H_5–	o-$CH_3OC_6H_4$–	67.3	
11	**13**	C_6H_5–	o,p-$(CH_3O)_2$-C_6H_3–	**20**	I	o,p-$(CH_3O)_2$-C_6H_3–	C_6H_5–	66.7	**16** (trace)
				21	I	C_6H_5–	o,p-$(CH_3O)_2$-C_6H_3–	24.0	
12	**14**	CH_3	C_6H_5–	**22**	I	CH_3	C_6H_5–	37.4	**16** (40.0) polymethylene
13	**13**	C_6H_5–	CH_3–	**22**	I	CH_3–	C_6H_5–	34.0	**16** (41.2), benzene,[b]
				19	II	C_6H_5–	C_6H_5–	14.2	toluene, phenol,[b]
				23	II	CH_3–	CH_3–	2.6	polymethylene, ethane[c]
14	**15**	C_2H_5–	C_6H_5–	**24**	I	C_2H_5–	C_6H_5–	45.0	**16** (49.6), polyethylene[c]

[a] (I): ring-opening products, (II): ligand-exchange ring-opening products
[b] They were afforded by a ligand-exchange reaction.
[c] It was not analysed.

On the other hand, the progress of the ligand exchange is affected by the size of the organolithium and the stability of the organolithium newly formed by the ligand exchange even in the compounds of the six-membered ring system. This effect is clearly noticed in the results of Runs 5—7 in Table I and Runs 12—14 in Table II. The ring-opening products of Runs 12 and 14 are 2-(methylthio)-*o*-terphenyl (**22**) and 2-(ethylthio)-*o*-terphenyl (**24**) as a sole product, respectively. However, **22** and the ligand-exchange ring-opening products (**19** and 2-methyl-2′-(methylthio)biphenyl (**23**)) were obtained in Run 13. The ligand-exchange is the most remarkable in Run 3 in Table I and Run 9 in Table II. The leaving group of the former is much larger than the attacking group. Moreover, ligand exchange easily takes place in the six-membered system. Therefore, ring-opening product (I) was not obtained at all. Only **8** was formed.



$R_F = C(CF_3)_2C_6H_5$

Fig. 1. Molecular Orbital Representation of a Sulfurane

As described above, the *S*N2 mechanism is a satisfactory explanation for the ligand-exchange reaction. The structure of the compound shown below also supports the validity of the *S*N2 mechanism in the ligand exchange reaction. This compound was synthesized recently by Martin, *et al.* who confirmed its structure by the X-ray analysis.[8]

The Mechanism of the Formation of Ring-Opening Products

The formation of the ring-opening products (I) in Runs 1 and 2 in Table I is explained by the mechanism shown in Chart 2. In Run 1, **1** is attacked by the phenyl anion (C_6H_5Li) from the a-position and gives pentacoordinated sulfur compound **(F)**. **F** cleaves the apical C-S bond in its six-membered hetero-ring to give an anionic site, which in turn attacks an α-carbon of the *p*-methoxyphenyl group at the equatorial position (e-position). Thus a ring-opening product, 2-(4′-methoxy-*o*-biphenylyl)-2-[*o*-(phenylthio)phenyl]propane **(6)** is formed. **F** also repeats the pseudorotation to form a conformer **(H)**, which is preferred for the ring-

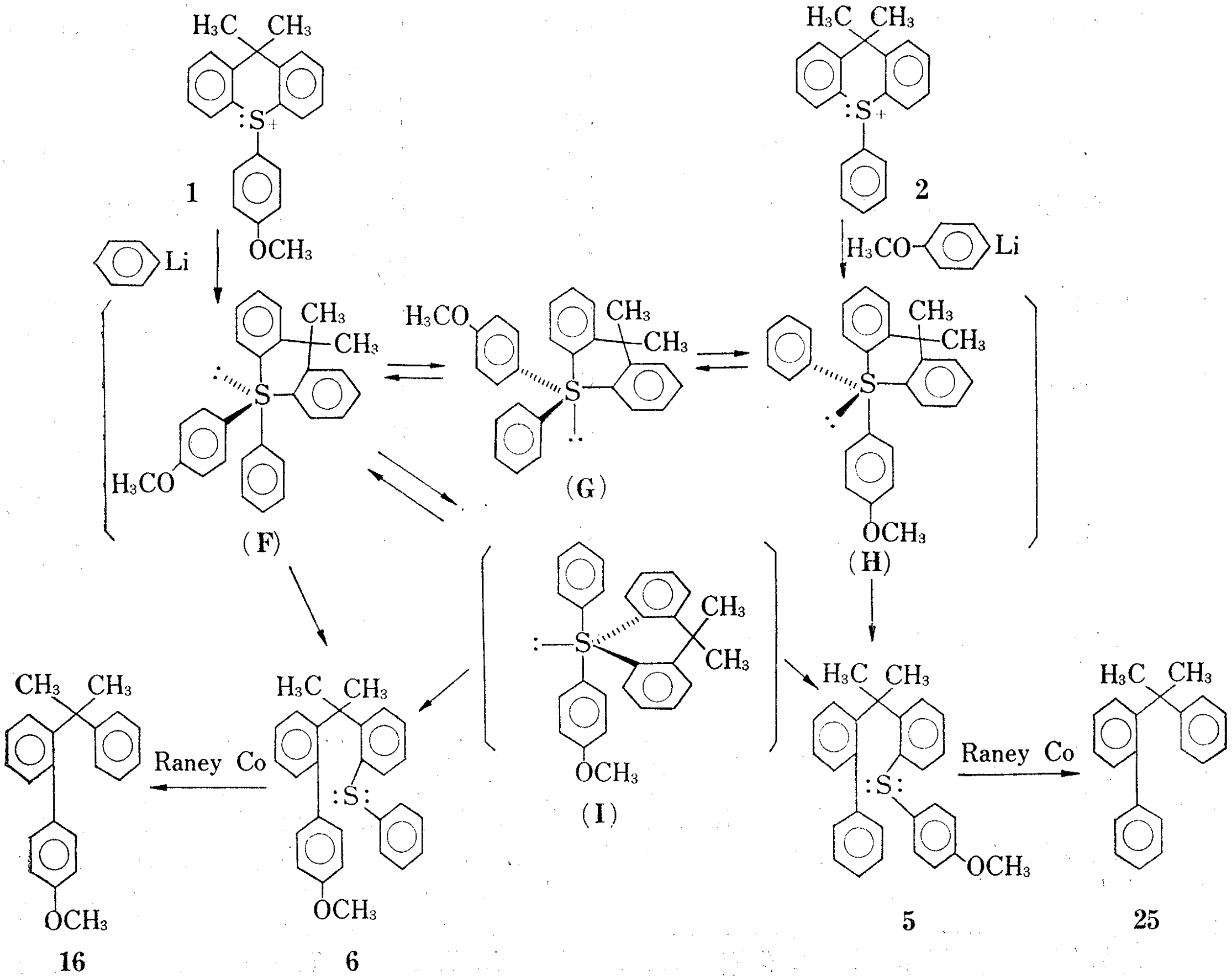


Chart 2. Mechanism for Formation of Ring-Opening Products

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[8] R.J. Arhart and J.C. Martin, *J. Am. Chem. Soc.*, **94**, 4997 (1972); I.C. Paul, J.C. Martin, and E.F. Perozzi, *ibid.*, **94**, 5010 (1972).

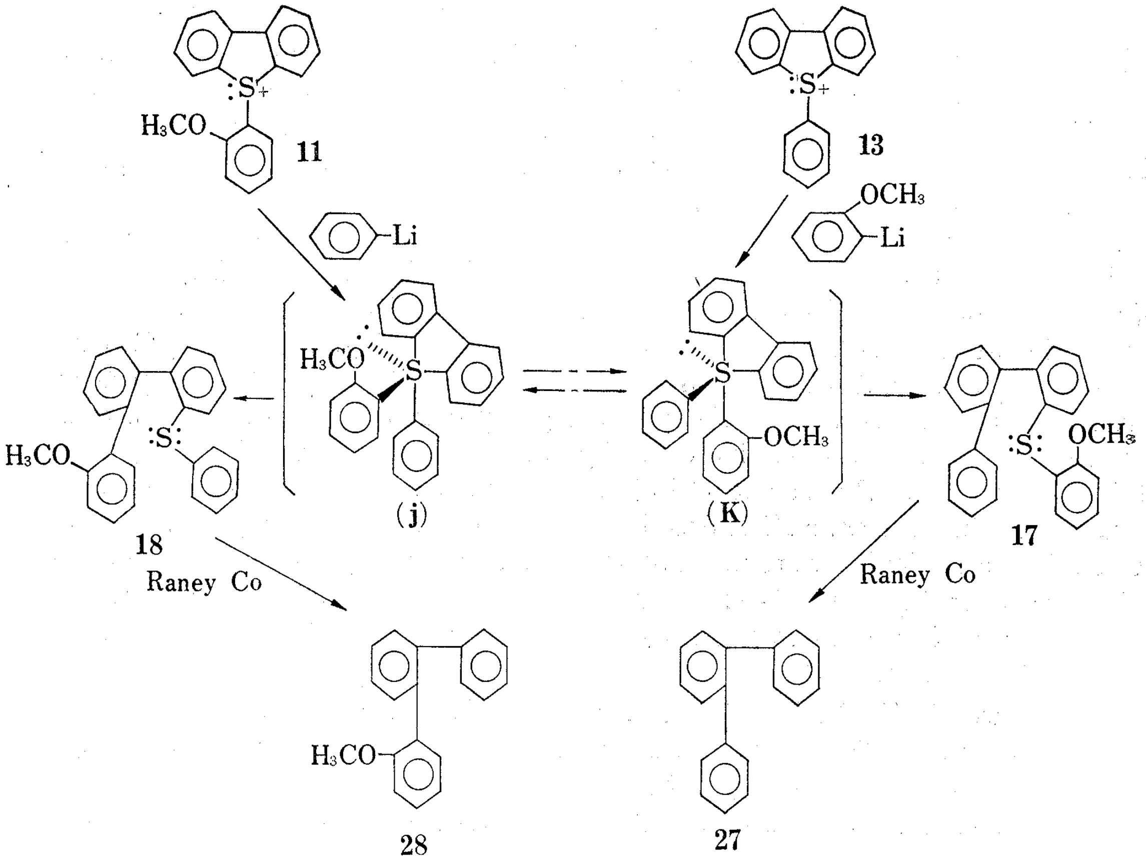

Chart 3

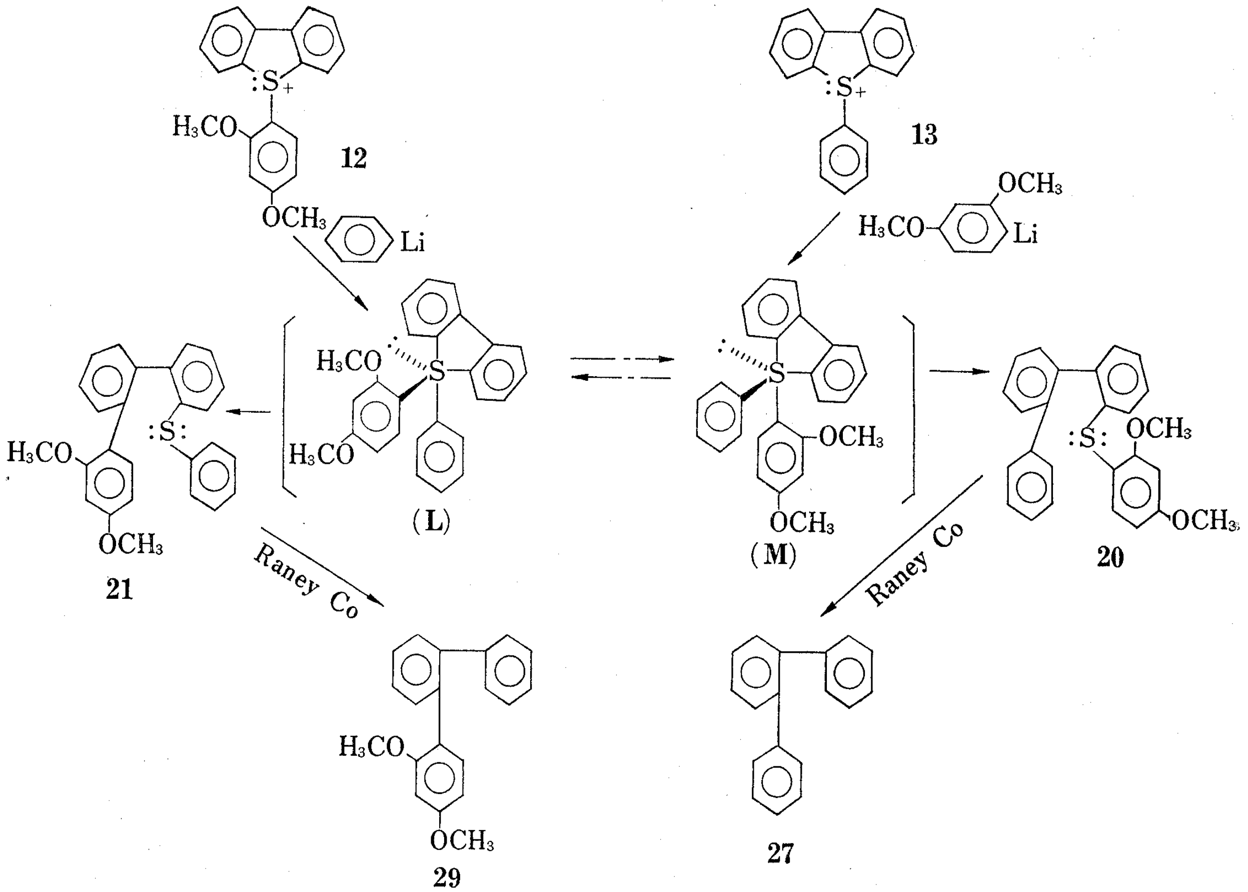

Chart 4

opening reaction, through a conformer (**G**). **H** gives 2-(*o*-biphenylyl)-2-[*o*-(*p*-methoxyphenylthio)phenyl]propane (**5**) by the ring opening like **F**. Run 2 also gives **5** and **6** by the same mechanism as that of Run 1. Compounds **5** and **6** are possibly formed from conformer (**I**), also. The reason why the yield of **5** is several times that of **6** is that the reaction intermediates of Runs 1 and 2 mainly form preferred conformer (**H**) by the pseudorotation and give products **5** and **6** through the same conformer.

Now mention will be made on the ring-opening products of the two pairs of corresponding reactions. Runs 8 and 10 give 2-(*o*-methoxyphenylthio)-*o*-terphenyl (**17**) and 2-methoxy-2″-(phenylthio)-*o*-terphenyl (**18**), respectively, whereas Runs 9 and 11 give 2,4-dimethoxy-2″-(phenylthio)-*o*-terphenyl (**21**) and 2-(*o*,*p*-dimethoxyphenylthio)-*o*-terphenyl (**20**), respectively. The result of Runs 8 and 10 in Chart 3 often gives ring-opening products through the preferred conformer (*J*), in which an *o*-methoxyphenyl group occupies the e-position because of the steric hindrance and the inductive effect by the methoxy group. Therefore, more **18** was obtained than **17**. In Runs 9 and 11 in Chart 4, the electronic effect of the *p*-methoxy group affected more than the *ortho* effect described above on the ring-opening reaction. As a result of this effect, an anionic site resulted by the cleavage of an apical C-S bond in a hetero-ring of the conformer (**L**) must attack weakly the *o*,*p*-dimethoxyphenyl group. Consequently, the preferred conformation to the ring-opening is conformer (**M**). The formation of more **20** than **21** is thus explained.

It is noticed in Tables I and II that other products such as 9,9-dimethylthioxanthene (**9**), dibenzothiophene (**16**), alkylbenzenes and biaryls are formed by the coupling between the ligands outside the hetero-ring in the pentacoordinated sulfur intermediates, respectively. And also organolithium attacks on the alkyl group of **4**, **14** or **15** to form carbene which turns out to polyalkane.

Although the mechanism of the reactions between sulfonium salts and organolithiums was clearly explained, it is also possible to form ring-contraction products such as sulfides and 5,5-dimethylfluorene or biphenylene, which are formed by the coupling between the ligands in the hetero-ring of pentacoordinated sulfur intermediates in the title reaction. However, such compounds were not formed at all. This result gives some doubt on the reliability of the conclusion given above. Therefore, the authors are now studying on the reaction between aryllithiums and 5-substituted 9,10-dihydrodibenzo[*b*,*f*]thiepinium salts. The result of this study is expected to further support the conclusion of the present report. The results will be reported in the following paper.

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 GEOL Model 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: ether–pet. ether (1: 8) and solvent C: ether–pet. ether (1: 5). Fractions of preparative TLC were represented as Fraction I, Fraction II, *etc.*; The *Rf* value decreased in this order. All identification of the compounds has been done with respect to IR spectra, mixed melting point and GLC retention time.

Reaction of 10-(*p*-Methoxyphenyl)-9,9-dimethylthioxanthenium Perchlorate (1) with Phenyllithium (Run 1)——To an ethereal solution of 8 equivalents of phenyllithium 1 (1.00 g, 2.31 mmole) was gradually added at room temperature under an N_2 stream. After stirring for 8 hr the reaction mixture was quenched with 5% HCl and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. Anisole was detected by GLC analysis of the residual oil. Separation by preparative TLC using solvent A afforded 5 fractions. Fraction I: Biphenyl and 9,9-dimethylthioxanthene (**9**) were detected by GLC analysis. Fraction II: 2-*o*-Biphenyl-2-[*o*-(phenylthio)phenyl]propane (**8**) (0.560 g, 64%) was obtained as colorless prisms, mp 109°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{27}H_{24}S$: C, 85.23; H, 6.36. Found: C, 85.37;

H, 6.42. NMR (CCl_4) δ: 6.35—7.55 (18H, m, Ar-H), 1.72 (6H, s, CH_3). Mass Spectrum *m/e* (% of base peak): 380(M^+, 100), 287(20), 271(6), 241(7), 211(16), 179(20), 178(13), 165(11), 144(10), 118(10), 117(7). Desulfurization of **8**: The W-7 Raney cobalt catalyst was prepared from 50% Co-Al alloy (10 g) by the method of Bardger, *et al.*[9] A mixture of **8** (0.3 g) and Raney cobalt catalyst thus prepared in EtOH (40 ml) was refluxed for 12 hr. The cooled reaction mixture was filtered and the catalyst was washed thoroughly with $CHCl_3$. The washings were combined with the filtrate and evaporated under reduced pressure. After addition of 5% HCl (100 ml) to the residue, the mixture was extracted with ether, dried ($MgSO_4$), and evaporated. Separation by preparative TLC using solvent A yielded 2-(*o*-biphenylyl)-2-phenylpropane (**25**) (0.135 g) and the recovered material **8** (0.110 g). Compound **25** was recrystallized from MeOH to give colorless prisms, mp 51—53°. *Anal.* Calcd. for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.74; H, 7.58. NMR (CCl_4) δ: 6.37—7.68 (14H, m, Ar-H), 1.52 (6H, s, CH_3). Fraction III: 4-Methoxybiphenyl (trace). Fraction IV: A mixture of 2-(*o*-biphenylyl)-2-[*o*-(*p*-methoxyphenylthio)phenyl]propane (**5**) and 2-(4′-methoxy-*o*-biphenylyl)-2-[*o*-(phenylthio)phenyl]propane (**6**) was obtained as a colorless oil (0.230 g, 24.3%). *Anal.* Calcd. for $C_{28}H_{26}OS$: C, 81.92; H, 6.38. Found: C, 82.19; H, 6.54. Mass Spectrum *m/e*: 410 (M^+). NMR (CCl_4) δ: 6.60—7.56 (m, Ar-H), 3.72 (s, OCH_3), 3.65 (s, OCH_3), 1.73 (s, CH_3). The intensity ratio of the peaks at δ 3.72 to 3.65 was 7.1 to 1. Desulfurization of a mixture of **5** and **6**: The mixture (0.410 g) of **5** and **6** was desulfurized using Raney cobalt prepared from 50% Co-Al alloy (20 g) by refluxing for 15 hr. After the same treatment as mentioned above separation by TLC using solvent A yielded the following products: **25** (0.06 g), 2-phenyl-2-(4′-methoxy-*o*-biphenyl)propane (**26**) (0.04 g), and **5** (0.24 g). Compound **26** was recrystallized from MeOH as colorless prisms, mp 80—81°. *Anal.* Calcd. for $C_{22}H_{22}O$: C, 87.37; H, 7.33. Found: C, 87.45; H, 7.45. NMR (CCl_4) δ: 6.65—7.67 (8H, m, Ar-H), 6.38 (5H, s, Ar-H), 3.70 (3H, s, OCH_3), 1.52 (3H, s, CH_3). Compound **5** was recrystallized from MeOH as colorless prisms, mp 105°. NMR (CCl_4) δ: 6.64—7.60 (17H, m, Ar-H), 3.74 (3H, s, OCH_3), 1.72 (6H, s, CH_3). Mass Spectrum *m/e* (% of base peak): 410(M^+, 100), 396(15), 395(48), 288(15), 287(59), 272(15), 271(18), 241(21), 179(12), 178(20), 165(18), 149(40), 117(18). Not **26** but **25** was obtained even when desulfurization of the recovered material **5** was allowed to react again. Fraction V: 2-(4′-Methoxy-*o*-biphenylyl)-2-[*o*-(*p*-methoxyphenylthio)phenyl]propane (**7**) (0.047 g, 5.0%) was obtained as colorless prisms, mp 110°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{29}H_{28}O_2S$: C, 79.07; H, 6.41. Found: C, 79.21; H, 6.67. NMR (CCl_4) δ: 6.30—7.58 (16H, m, Ar-H), 3.74(3H, s, OCH_3), 3.68(3H, s, OCH_3), 1.72(6H, s, CH_3). Mass Spectrum *m/e* (% of base peak): 440(M^+, 100), 426(7), 425(15), 318(5), 317(20), 287(5), 271(17), 241(17). Desulfurization of **7** gave only **26**.

Reaction of 9,9-Dimethyl-10-phenylthioxanthenium Perchlorate (2) with *p*-Methoxyphenyllithium (Run 2)——Compound **2** (1.4 g, 3.48 mmole) was allowed to react with 8 equivalents of *p*-methoxyphenyllithium in ether. The reaction mixture was worked up in the same manner as Run 1. Separation by preparative TLC using solvent A afforded 6 fractions. Fraction I: **9** (0.070 g, 9.0%). Fraction II: **8** (0.013 g, 1.0%). Fraction III: 4-Methoxybiphenyl (trace). Fraction IV: A mixture (0.220 g, 15.4%) contained **5** and **6** was a 6.7:1 ratio by NMR assay. Fraction V: 4,4′-Dimethoxybiphenyl, mp 171—172°. Fraction VI: **7** (0.900 g, 59.0%).

Reaction of 10-(*o,p*-Dimethoxyphenyl)-9,9-dimethylthioxanthenium Perchlorate (3) with Phenyllithium (Run 3)——Compound **3** (1.00 g, 2.16 mmole) was allowed to react with 8 equivalents of phenyllithium in ether. GLC analysis of the raw product allowed determination of *m*-dimethoxybenzene (0.200 g, 67.1%). Separation by preparative TLC using pet. ether afforded 2 fractions. Fraction I: A mixture of biphenyl and **9** was obtained and oxidized with 35% H_2O_2 (1.0 g) yielded 9,9-dimethylthioxanthene 10,10-dioxide (0.100 g), mp 163—165°, which corresponds to 17.9% of **9**. Fraction II: **8** (0.690 g, 84.0%).

Reaction of 2 with Phenyllithium (Run 4)——Compound **2** (1.50 g, 3.72 mmole) was allowed to react with 8 equivalents of phenyllithium in ether. The reaction mixture was worked up as mentioned above. Separation by preparative TLC using pet. ether gave 2 fractions. Fraction I: A mixture of biphenyl and **9** was obtained and oxidized with 35% H_2O_2 yielded 9,9-dimethylthioxanthene 10,10-dioxide (0.11 g), which corresponds to 11.4% of **9**. Fraction II: **8** (1.116 g, 81.8%).

Reaction of 9,9-Dimethyl-10-methylthioxanthenium Perchlorate (4) with Phenyllithium (Run 5)——To 8 equivalents of phenyllithium in ether, **4** (1.50 g, 4.42 mmole) was added at room temperature under an N_2 stream. After stirring for 4 days, the reaction mixture was quenched with 5% HCl. The resulting precipitate was collected by filtration and recrystallized from CH_2Cl_2-ether to give the unreacted material **4** (0.470 g, 31.4%). The filtrate was extracted with ether. The extract was dried ($MgSO_4$) and evaporated. Separation by preparative TLC using pet. ether afforded 2 fractions. Fraction I: A mixture of biphenyl and **9** was obtained. Oxidation of the mixture with H_2O_2 yielded 9,9-dimethylthioxanthene 10,10-dioxide (0.326 g), which corresponds to 28.6% of **9**. Fraction II: 9,9-Dimethylthioxanthene 10-oxide (**10**) (0.200 g, 18.7%).

Reaction of 2 with Methyllithium (Run 6)——Compound **2** (1.50 g, 3.72 mmole) was allowed to react with 8 equivalents of methyllithium and separation by preparative TLC of the product using pet. ether yielded **9** (0.770 g, 92.5%).

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9) G.M. Bardger, N. Kowanko, and W.H.F. Sasse, *J. Chem. Soc.*, **1959**, 440.

Reaction of 1 with Methyllithium (Run 7)——Compound **1** (1.40 g, 3.24 mmole) was allowed to react with 8 equivalents of methyllithium in ether. The reaction mixture was treated as mentioned above. GLC analysis allowed determination of anisole (0.320 g, 89.5%) and 4-methylanisole (trace). Separation by preparative TLC using pet. ether yielded **9** (0.610 g, 83.6%).

Reaction of 5-(*o*-Methoxyphenyl)dibenzothiophenium Bromide (11) with Phenyllithium (Run 8)——Compound **11** (1.50 g, 4.05 mmole) was allowed to react with 8 equivalents of phenyllithium in ether in the same way as Run 1. Anisole was detected by GLC analysis of the residual oil which was formed. Separation by preparative TLC using solvent A afforded 3 fractions. Fraction I: Biphenyl and dibenzothiophene (**16**) (trace) were detected by GLC analysis. Fraction II: 2-(Phenylthio)-*o*-terphenyl (**19**) (0.900 g, 65.9%) was obtained as colorless prisms, mp 88° (lit.[10] 89—90°), by recrystallization from MeOH. Fraction III: A mixture of 2-(*o*-methoxyphenylthio)-*o*-terphenyl (**17**) and 2-methoxy-2″-(phenylthio)-*o*-terphenyl (**18**) was obtained. Compound **18** was separated from the other component **17** by preparative TLC using solvent B, and was recrystallized from MeOH as colorless prisms (0.180 g, 12.1%), mp 81°. *Anal.* Calcd. for $C_{25}H_{20}OS$: C, 81.50; H, 5.47. Found: C, 81.61; H, 5.62. NMR (CCl_4) δ: 6.50—7.38 (17H, m, Ar-H), 3.50 (3H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 368(M^+, 100), 260(16), 259(48), 245(14), 244(36), 229(13), 228(34), 227(41), 226(22), 216(20), 215(38), 189(11), 184(11). Desulfurization of **18** (0.700 g) was conducted with Raney cobalt prepared from 50% Al-Co alloy (20 g). Separation of the desulfurization product by preparative TLC using solvent A yielded 2-methoxy-*o*-terphenyl (**28**) (0.410 g) as a colorless oil and the unchanged material **18** (0.050 g). The following analytical and spectral properties were exhibited by **28**. *Anal.* Calcd. for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.40; H, 6.33. NMR (CCl_4) δ: 7.39—6.48 (13H, m, Ar-H), 3.32 (3H, s, OCH_3). Compound **17** (0.085 g, 5.7%) was recrystallized from MeOH as colorless prisms, mp 152°. *Anal.* Calcd. for $C_{25}H_{20}OS$: C, 81.50; H, 5.47. Found: C, 81.32; H, 5.68. NMR (CCl_4) δ: 6.68—7.37 (17H, m, Ar-H), 3.70 (3H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 368(M^+, 100), 261(19), 259(13), 258(13), 230(19), 229(87), 228(69), 227(23), 202(11), 184(10). Desulfurization of **17** (0.300 g) was carried out using Raney cobalt. Separation by preparative TLC using pet. ether gave *o*-terphenyl (**27**) (0.010 g) and the unchanged material **17** (0.270 g).

Reaction of 5-(*o*,*p*-Dimethoxyphenyl)dibenzothiophenium Perchlorate (12) with Phenyllithium (Run 9)——Compound **12** (1.50 g, 3.58 mmole) was allowed to react with 8 equivalents of phenyllithium in ether in the same way as Run 1. *m*-Dimethoxybenzene was detected by GLC analysis of the crude product. Separation by preparative TLC using solvent A afforded 3 fractions. Fraction I: Biphenyl and **16** (trace) were detected by GLC analysis. Fraction II: **19** (0.710 g, 78.9%). Fraction III: A mixture obtained from this fraction was subdivided into 2-(*o*,*p*-dimethoxyphenylthio)-*o*-terphenyl (**20**) and 2,4-dimethoxy-2″-(phenylthio)-*o*-terphenyl (**21**) by preparative TLC using solvent C. Compound **21** (0.05 g, 3.8%) was isolated as a colorless oil. *Anal.* Calcd. for $C_{26}H_{22}OS$: C, 78.37; H, 5.57. Found: C, 78.15; H, 5.62. NMR (CCl_4) δ: 6.81—7.21 (14H, m, Ar-H), 6.11—6.27 (2H, m, Ar-H), 3.68 (3H, s, OCH_3), 3.48 (3H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 398(M^+, 71), 290(23), 289(100), 274(20), 259(12), 258(35), 257(10), 245(8), 242(10), 231(11), 214(17), 202(20). Desulfurization of **21** (0.300 g) was carried out using Raney cobalt as mentioned above and separation by preparative TLC using solvent A gave 2,4-dimethoxy-*o*-terphenyl (**29**) (0.080 g) and the recovered material **21** (0.170 g). Compound **29** was recrystallized from MeOH as colorless prisms, mp 99—100°. *Anal.* Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.84; H, 6.45. NMR (CCl_4) δ: 6.88—7.34 (10H, m, Ar-H), 3.74 (3H, s, OCH_3), 3.31 (3H, s, OCH_3). Compound **20** (0.140 g, 10.6%), which is the other component of Fraction III, was recrystallized from MeOH as colorless prisms, mp 87°. *Anal.* Calcd. for $C_{26}H_{22}O_2S$: C, 78.37; H, 5.57. Found: C, 78.41; H, 5.31. NMR (CCl_4) δ: 6.25—7.32 (16H, m, Ar-H), 3.72 (3H, s, OCH_3), 3.67 (3H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 398(M^+, 100), 261(6), 260(15), 259(8), 258(8), 230(8), 229(30), 228(26), 227(10), 226(13), 202(8), 170(16). Desulfurization of **20** (1.00 g) was conducted using Raney cobalt in the same way as mentioned above, and separation of the product by preparative TLC using pet. ether afforded **27** (0.070 g) and the unchanged material **20** (0.770 g).

Reaction of 5-Phenyldibenzothiophenium Bromide (13) with *o*-Methoxyphenyllithium (Run 10)——Compound 13 (1.50 g, 4.40 mmole) was allowed to react with 8 equivalents of *o*-methoxyphenyllithium in ether and the reaction mixture was worked up as Run 1. Separation by preparative TLC using solvent A gave 2 fractions. Fraction I: **16** (trace). Fraction II: A mixture obtained from this fraction was subdivided into 2 components, **17** (0.380 g, 23.5%) and **18** (1.09 g, 67.3%) by preparative TLC using solvent B.

Reaction of 13 with 2,4-Dimethoxyphenyllithium (Run 11)——Compound **13** (0.90 g, 2.64 mmole) was allowed to react with 8 equivalents of 2,4-dimethoxyphenyllithium in ether and the mixture was treated as mentioned above. Separation of the product by preparative TLC using solvent A afforded 2 fractions. Fraction I: **16** (trace). Fraction II: A mixture obtained from this fraction was subdivided into **20** (0.700 g, 66.7%) and **21** (0.250 g, 24.0%) by preparative TLC using solvent C.

Reaction of 5-Methyldibenzothiophenium Fluoroborate (14) with Phenyllithium (Run 12)——Compound **14** (1.50 g, 5.25 mmole) was allowed to react with 8 equivalents of phenyllithium in ether as mentioned above. The decomposed reaction mixture was filtered in order to collect a precipitate, which was polymethylene

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[10] R.W. LaRochelle and B.M. Trost, *J. Am. Chem. Soc.*, 93, 6077 (1971).

(0.034 g) as colorless powders, mp 119—125° (lit.4) 120—123°). IR ν_{max}^{KBr} cm^{-1}: 2920, 2860, 1465, 710. The filtrate was extracted with ether. The ether extract was dried and evaporated. Separation of the residue by preparative TLC using pet. ether gave 2 fractions. Fraction I: A mixture obtained from this fraction was subdivided into biphenyl and **16** (0.396 g, 40.0%) by column chromatography on alumina using pet. ether. Fraction II: 2-(Methylthio)-*o*-terphenyl (**22**) (0.540 g, 37.4%) was obtained as colorless prisms, mp 58°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{19}H_{16}S$: C, 82.58; H, 5.84. Found: C, 82.42; H, 5.84. NMR (CCl_4) δ: 6.90—7.46 (13H, m, Ar-H), 2.24 (3H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 276 (M^+, 74), 261(12), 260(9), 259(7), 258(9), 230(21), 229(100), 228(47), 227(9), 224(14), 184(16). Desulfurization of **22** (0.5 g) was carried out using Raney cobalt as mentioned above. and separation by preparative TLC of the product using pet. ether afforded *o*-terphenyl (**27**) (0.080 g) and the unchanged material **22** (0.390 g).

Reaction of 13 with Methyllithium (Run 13)——Compound **13** (1.35 g, 3.96 mmole) was allowed to react with 8 equivalents of methyllithium in ether and worked up in the same manner as mentioned above. A slight amount of polymethylene was isolated by filtration of a water-insoluble material. Benzene, toluene, and phenol were detected by GLC analysis of the raw product. Separation by preparative TLC using pet. ether afforded 4 fractions. Fraction I: **16** (0.30 g, 41.2%). Fraction II: 2-Methyl-2′-(methylthio)biphenyl (**23**) (0.022 g, 2.6%) was obtained as colorless prisms, mp 52°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{14}H_{14}S$: C, 78.48; H, 6.59. Found: C, 78.72; H, 6.47. NMR (CCl_4) δ: 6.97—7.30 (8H, m, Ar-H), 2.27 (3H, s, SCH_3), 2.07 (3H, s, CH_3). Mass Spectrum *m/e* (% of base peak): 214(M^+, 100), 200(26), 199(95), 198(10), 197(20), 185(30), 184(99), 166(44), 165(60), 152(20), 149(18). Fraction III: **19** (0.190 g, 14.2%). Fraction IV: **22** (0.310 g, 34.0%).

Reaction of 5-Ethyldibenzothiophenium Perchlorate (15) with Phenyllithium (Run 14)——Compound **15** (1.20 g, 3.84 mmole) was allowed to react with 8 equivalents of phenyllithium in ether and treated as mentioned above. Separation by preparative TLC using pet. ether afforded 2 fractions. Fraction I: A mixture obtained from this fraction was subdivided into 2 components, biphenyl and **16** (0.36 g, 49.6%). Fraction II: 2-(Ethylthio)-*o*-terphenyl (**24**) (0.50 g, 45.0%) was obtained as a colorless oil. *Anal.* Calcd. for $C_{20}H_{18}S$: C, 82.73; H, 6.25. Found: C, 82.45; H, 6.23. NMR (CCl_3) δ: 6.88—7.37 (13H, m, Ar-H), 2.68 (2H, q, $J=7.0$ Hz, CH_2), 1.17 (3H, t, $J=7.0$ Hz, CH_3). Mass Spectrum *m/e* (% of base peak): 290(M^+, 100), 261(16), 260(8), 259(5), 258(6), 230(5), 229(20), 228(17), 227(3), 226(6), 185(6), 184(12). Desulfurization of **24** in the same manner as mentioned above gave **27** and the unchanged material **24**.