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Dibenzothiophenes and Related Compounds. VI.[1,2] Reactions of Cyclic Sulfonium Salts with Sodium Alkoxides and Benzenethiolate in Alcohols

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The reactions of 5-substituted dibenzothiophenium salts, having one or two substituents, with sodium alkoxides and benzenethiolate have been studied in the protic solvents.

The results in Table I showed that the 5-substituted dibenzothiophenium salts with alkoxide ions mostly proceed *via* aromatic bimolecular nucleophilic substitution and ligand exchange as shown in Chart 7.

It has been also found that the reactions of 5-substituted dibenzothiophenium salts with benzenethiolate ion support the validity of the mechanism proceed by the aromatic bimolecular nucleophilic substitution as shown in Table II.

The mechanisms of reactions were clarified by a series of reports by the present authors for the reactions between various organometallic compounds such as organolithiums and Grignard reagents and cyclic trivalent sulfur compounds, especially, 5-substituted dibenzothiophenium salts and related compounds. On the reactions between sulfonium salts and bases in protic solvents, however, little is known at present except the reports shown below.

Oae, *et al.*[4] reported that the reactions between acyclic triarylsulfonium salts and potassium hydroxide proceeds in ethanol through the nucleophilic attack of ethoxide ion against sulfur atom as shown in Chart 1 and that the reactions proceed in water *via* two processes involving nucleophilic attack of hydroxide ion on both aromatic carbon and sulfur atoms. On the other hand, McEwen, *et al.*[5] studied on the reactions between various alkoxide ions and triarylsulfonium salts in alcohols and claimed that these reactions are explained by competing free radical reactions shown in Chart 2 and aromatic bimolecular nucleophilic substitution reaction.

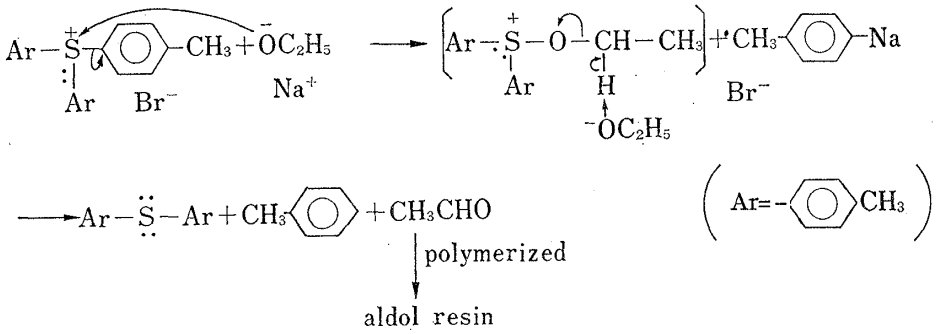
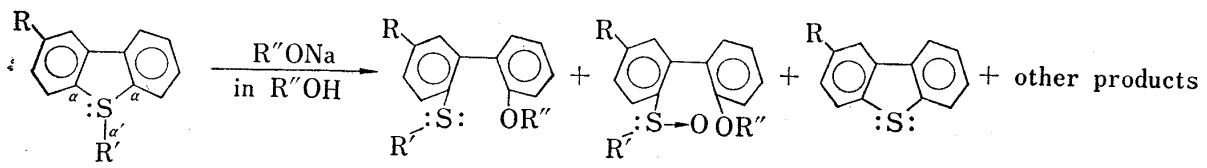


Chart 1. Mechanism of Nucleophilic Attack on Sulfur Atom[4]

1) Part V: M. Hori, T. Kataoka, H. Shimizu, and M. Miyagaki, *Chem. Pharm. Bull.* (Tokyo), 22, 2020 (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 and also at the 92nd Annual Meeting of the Pharmaceutical Society of Japan, Osaka, Apr. 7, 1972. Abstracts of Papers, p. II-38.
3) Location: *492–36, Mitahora, Gifu.*
4) S. Oae and Y.H. Khim, *Bull. Chem. Soc. Japan*, 42, 3528 (1969).
5) J.W. Knapizyk and W.E. McEwen, *J. Am. Chem. Soc.*, 91, 145 (1969).

TABLE I. Reactions of 5-Substituted Dibenzothiophenium Salts with Sodium Alkoxides in Alcohol



(A) 8—15 (B) 16—20 (C) 21—22

Run	Sulfonium salts No.	R	R′	Bases R″O–	Ring-opening products (A) No.	(A) Yield (%)	(B) No.	(B) Yield (%)	(C) No.	(C) Yield (%)	Other products yield (%)[a]
1	1	H	*p*-CH_3O C_6H_4–	CH_3O–	8	29.1	16	57.8	21	13.8	anisole (10.0), *p*-dimethoxybenzene (trace)
2	2	H	*m*-CH_3O C_6H_4–	CH_3O–	9	31.4	17	6.5	21	65.6	anisole (5.0), *m*-dimethoxybenzene (58.0)
3	3	H	C_6H_5–	CH_3O–	10	46.0	18	1.5	21	50.7	benzene, anisole (29.5)
4	4	H	*o*-CH_3O C_6H_4–	CH_3O–	11	17.3	19	39.8	21	41.6	anisole (31.8) *o*-dimethoxybenzene (3.4)
5	5	H	*o,p*-$(CH_3O)_2C_6H_3$–	CH_3O–	12	40.2	20	7.0	21	39.2	*m*-dimethoxybenzene (36.0)
6	6	H	CH_3–	CH_3O–					21	90.0	
7[b]	1	H	*p*-CH_3O C_6H_4–	CH_3O–	8	34.2	16	49.4	21	14.5	anisole (11.0)
8	7	CH_3O–	C_6H_5–	CH_3O–	13	44.9			22	49.4	*p*-dimethoxybenzene (trace) benzene, anisole
9	1	H	*p*-CH_3O C_6H_4–	$(CH_3)_2CHO$–	14	99.0			21	trace	anisole (trace), acetone (trace)
10	4	H	*o*-CH_3O C_6H_4–	$(CH_3)_2CHO$–	15	80.6			21	16.1	anisole (15.1) acetone

a) Were analysed by GLC.
b) reaction of **1** with KOH in CH_3OH

$Ar_3\overset{+}{S}\,\bar{O}CHR_2 \rightleftarrows Ar_3SOCHR_2 \rightleftarrows (Ar_3\dot{S}\ R_2CH\dot{O})$

$(Ar_3\dot{S}\ R_2CH\dot{O}) \longrightarrow Ar_3S + ArOCHR_2$

$(Ar_3\dot{S}\ R_2CH\dot{O}) \longrightarrow Ar_3S\cdot + R_2CHO\cdot$

$Ar_3S\cdot \longrightarrow Ar_2S + Ar\cdot$

$Ar\cdot + R_2CHOH \longrightarrow ArH + R_2\dot{C}OH$

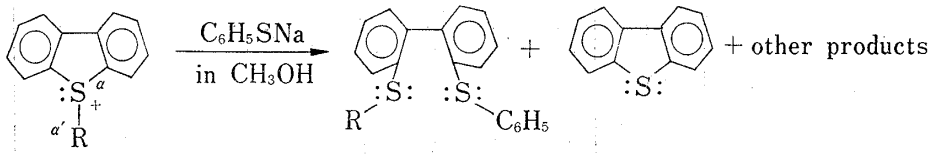
$R_2CHO\cdot + R_2CHOH \longrightarrow R_2CHOH + R_2\dot{C}OH$

$2R_2\dot{C}OH \longrightarrow RCOR + R_2CHOH$

Chart 2. Mechanism of Radical Reaction[5]

The present authors were interested in the reactions between bases and cyclic sulfonium salts, which are the closest in structure to acyclic triarylsulfonium salts, in the protic solvents, and experimented on the reactions of 5-phenyldibenzothiophenium salts, having one or two substituents, with alkoxide and benzenethiolate ions to elucidate the mechanism of the reactions mentioned above. The results are shown in Tables I and II.

Table II. Reactions of 5-Substituted Dibenzothiophenium Salts with Sodium Benzenethiolate in Methanol



Run	Sulfonium salts No.	R-	Ring-opening products No.	Yield (%)	21 Yield (%)	No.	Other products	Yield (%)
11	1	*p*-$CH_3OC_6H_4$-	33	36.2	36.2	37	*p*-$CH_3OC_6H_4$-S-C_6H_5	21.5
						1	starting compound	27.0
12	2	*m*-$CH_3OC_6H_4$-	34	14.7	83.8	38	*m*-$CH_3OC_6H_4$-S-C_6H_5	80.0
13	4	*o*-$CH_3OC_6H_4$-	35	20.0	51.6	39	*o*-$CH_3OC_6H_4$-S-C_6H_5	44.7
						40	5-(*o*-hydroxyphenyl)dibenzothiophenium bromide	28.0
14	5	*o,p*-$(CH_3O)_2C_6H_3$-	36	16.7	8.7	41	5-(*o*-hydroxy-*p*-methoxyphenyl)-dibenzothiophenium perchlorate	77.3

Discussions will be made on the mechanism of the title reactions and the effects of substituents in sulfonium salts on the reaction products.

Result and Discussion

All the reactions shown in Tables I and II were allowed to proceed in nitrogen atmosphere. One equivalent of sulfonium salts, **1**—**7**,[6] and 10 equivalents of sodium alkoxide or benzenethiolate were boiled in alcohol for 50—60 hours. The reaction products were identified by the method described in our preceding reports.[1]

I. Reactions between Cyclic Sulfonium Salts and Alkoxides in Alcohols. Aromatic Bimolecular Nucleophilic Substitution Reaction

Substituent Effect on the Title Reactions——The yield of ring-opening products in Runs 1—5 and 7 in Table I should be given by the sum of the yields of sulfide (A) and sulfoxides (B), because these sulfides (A) automatically give sulfoxide (B) if they are allowed to stand in ether (abstracting solvent) and because no sulfoxides (B) are formed if the treatments are quickly made in each run. Consequently, it was found that sulfides (A) give sulfoxides (B) by auto-oxidation by air as shown in Chart 3. The latter was identified by the comparison of a number of instrumental data with those of authentic samples obtained by the oxidation of the former with *m*-chloroperbenzoic acid.

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

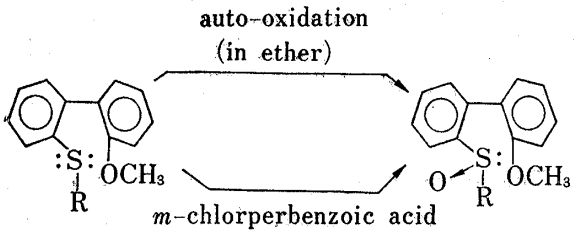


Chart 3

The comparison of the yields of various products clearly shows that Runs 1—3 are affected by the substituent at 5-position. In Run 1, the yield of 2-methoxy-2′-(*p*-methoxyphenylthio)-biphenyl (**8**) was 86.9%. This yield is much larger than that of *p*-dimethoxybenzene, which was found only as a trace. This large yield is attributable to the M-effect by the *p*-methoxy group of 5-(*p*-methoxyphenyl)dibenzothiophenium perchlorate (**1**). Namely, the electron density of α-carbon in the hetero-ring of **1** is smaller than that of the α′-carbon, which is present outside the hetero-ring. Therefore, the methoxide ion mainly gives **8**. On the other hand, the yield of 2-methoxy-2′-(*m*-methoxyphenylthio)biphenyl (**9**) is 37.9% in Run 2. This yield is smaller than that in Run 1, which is 86.9%. The yield of *m*-dimethoxybenzene is as large as 58% in Run 1. This yield is attributable to the I-effect by the *m*-methoxy group of 5-(*m*-methoxyphenyl)dibenzothiophenium bromide (**2**). Consequently, the electron density in α- and α′-carbon atoms of 5-phenyldibenzothiophenium bromide (**3**) in Run 3 is estimated to be intermediate between those of **1** in Run 1 and **2** in Run 2. Actually, the yields of anisole and 2-methoxy-2′-(phenylthio)biphenyl (**10**) obtained from Run 3 were 29.5% and 47.5%, respectively. These values are intermediate between those of anisoles and ring-opening products obtained from Run 1 and 2, respectively.

The effect of 5-position substituents of sulfonium salts, **1**—**7**, on the nucleophilic reactions is clearly noticed in Run 8. The methoxide ion easily reacts with the α-carbon in the benzene ring that lacks 2-methoxy group, because 2-methoxy-5-phenyldibenzothiophenium bromide (**7**) brings about some difference in the electron density in the two α-carbons in the hetero-ring. As shown in Chart 4, only a ring-opening product, 2,5′-dimethoxy-2′-(phenylthio)-biphenyl (**13**) was obtained though both the ring-opening products **13** and 2,5-dimethoxy-2′-(phenylthio)biphenyl (**23**) are expected to form from the reaction between **7** and sodium methoxide. Compound (**13**) was identified by the treatment of ring-opening products in Run 8 with W-7 Raney cobalt. Namely 2,3′-dimethoxybiphenyl (**24**) was obtained as a desulfurization product by this treatment. 2,5-Dimethoxybiphenyl (**25**), which is synthesized more easily than **24**, was synthesized as shown in Chart 5. Namely, the product, formed by the reaction between 2,5-dimethoxyphenylmagnesium bromide and cyclohexanone, was converted to 1-(2,5-dimethoxyphenyl)cyclohexene (**26**) by dehydration with sulfuric acid. Compound (**26**) was then treated with two

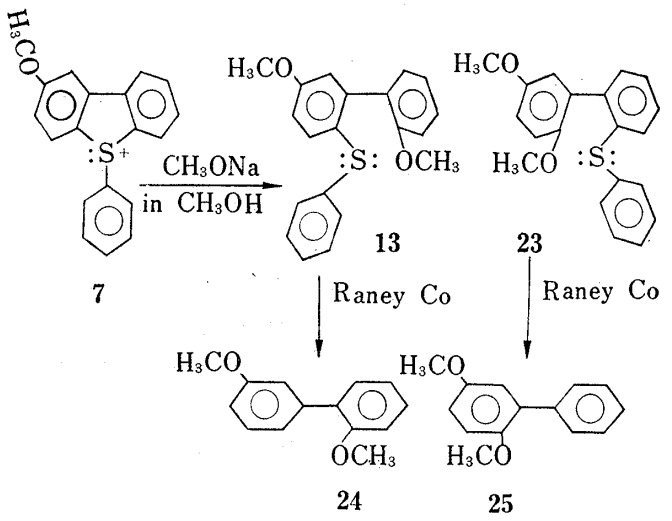


Chart 4

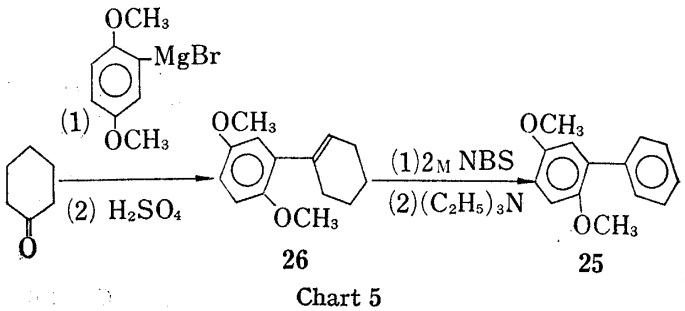


Chart 5

equivalents of N-bromosuccinimide (NBS) and then allowed to react with triethylamine to give **25**. It was found that **25** was completely different from the desulfurization product **24** of **13**. The ring-opening product, obtained from Run 8, was identified as **13**.

Ligand-Exchange Reaction

Runs 1—3 gave either anisole or benzene. Therefore, the ligand-exchange reaction on a trivalent sulfur atom is expected to proceed in a similar manner. The occurrence of this reaction is further supported by the results of Runs 4 and 5. With *o*-methoxy group of 5-(*o*-methoxyphenyl)dibenzothiophenium bromide (**4**) in Run 4 and *o*,*p*-dimethoxy groups of 5-(*o*,*p*-dimethoxyphenyl)dibenzothiophenium perchlorate (**5**) in Run 5, the reaction of methoxide ion with α- and α'-carbon will be retarded by the steric and electronic effects. Also, the starting materials **4** and **5** are easily converted to sulfonium salts, which are sterically more stable. Therefore, yields of ligand-exchange products increase. In fact, the yield of anisole and *m*-dimethoxybenzene, obtained by Runs 4 and 5, were 31.8 and 36%, respectively. McEwen, *et al.* and Oae, *et al.* explained the mechanism of formation of carbonyl compounds in all the runs by the radical reaction and the ligand-exchange reaction, respectively. In Runs 1—8 in the present report, carbonyl compounds are expected to form. However, the identification of carbonyl compounds were impossible when methoxide and ethoxide ions were used as bases in the title reaction. Acetone, which is formed by ligand exchange when isopropoxide ion is used as a base, is easily detected with gas-liquid chromatography (GLC).

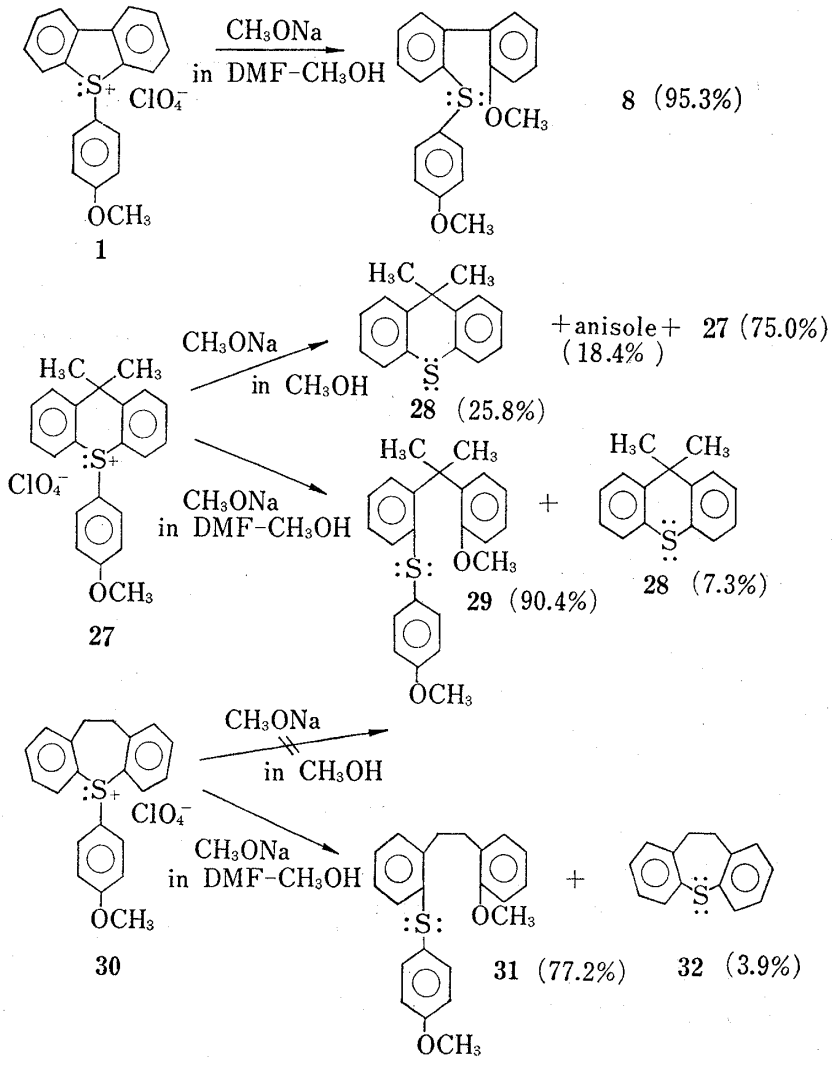


Chart 6

Actually, acetone was detected in Runs 9 and 10. Thus it is concluded that formaldehyde, which is a carbonyl compound, is formed in Runs 1—8.

Runs 9 and 10 gave much more ring-opening products and much less ligand-exchange products than Runs 1 and 4. This difference will be explained as follows: Isopropoxide ions are more bulky than methoxide ions. Also, the steric stability of the starting materials

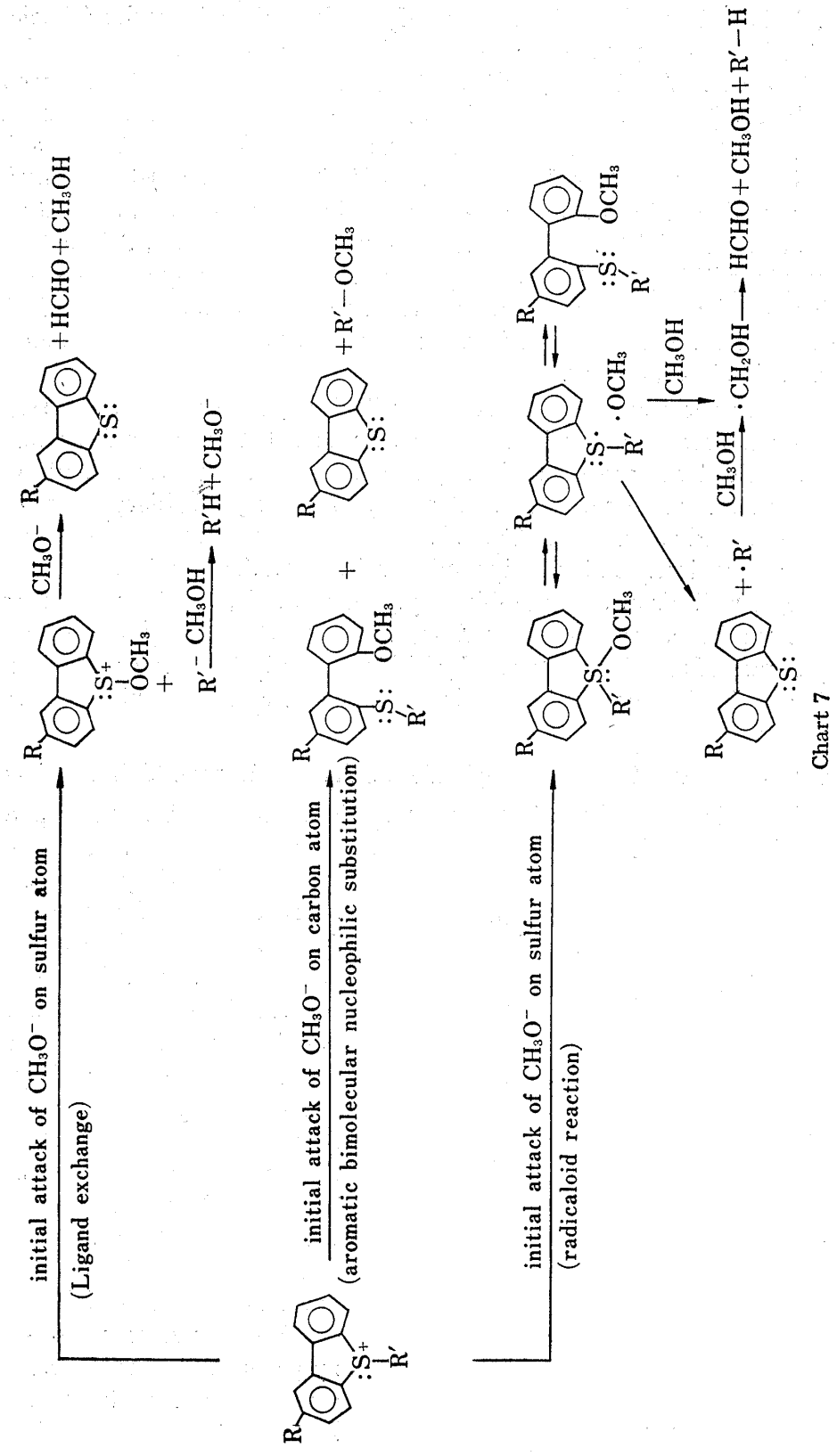


Chart 7

1 and **4** is about the same as that of 5-isopropoxydibenzothiophenium salt formed by ligand exchange.

The results of the reaction (Run 7) between **1** and potassium hydroxide was the same as that of Run 1. In Run 6, the proton-abstraction reaction of S^+–CH_3 of 5-methyldibenzothiophenium fluoroborate (**6**) predominantly proceeds because of the presence of the methoxide ion.

Effects of the Ring Strain in the Reactions of Cyclic Sulfonium Salts with Alkoxide Ions—— The strain in the hetero–ring in sulfonium salts of five–membered ring system also helps the title reaction to occur. As shown in Chart 6, 9,9-dimethyl-10-(*p*-methoxyphenyl)thioxanthenium perchlorate (**27**) of the six–membered ring system reacts with methoxide ion in methanol and gives 25.8% of 9,9-dimethylthioxanthene (**28**) and 18.4% of anisole. The starting material (**27**) is recovered by 75%. 5-(*p*-Methoxyphenyl)-10,11-dihydrodibenzo-[*b*,*f*]thiepinium perchlorate (**30**) of the seven–membered ring system allows almost quantitative recovery of the raw material **30**. However, ring–opening products, **8**, 2-(*o*-methoxyphenyl)-2-[*o*-(*p*-methoxyphenylthio)phenyl]propane (**29**), and 1-(*o*-methoxyphenyl)-2-[*o*-(*p*-methoxyphenylthio)phenyl]ethane (**31**) were obtained with high yields of 95.3, 90.4, and 77.2% when MeOH–DMF was used as a solvent in order to promote the reactivity of methoxide ion against these sulfonium salts, **1**, **27**, and **30**.

Examination on the experimental data described above shows that the title reactions mostly proceed *via* aromatic bimolecular nucleophilic substitution and ligand exchange. McEwen, *et al.* noticed the presence of biaryls in the reaction products and claimed that radicaloid reactions occur to some extent. Contrary to their results, biaryls were not detected at all in the present study as shown in Table I. Also the measurements of electron spin resonance (ESR) and chemically induced dynamic nuclear polarization (CIDNP) did not show the presence of free radicals at all and *o*-biphenylyl aryl sulfide, which are necessarily formed from radical intermediate, were not formed at all. However, it may not be safe to ignore the possibility of radical reactions proposed by McEwen, *et al.* The three possible mechanisms for the reaction of 5-substituted dibenzothiophenium salt and methoxide ion are shown in Chart 7.

II. Reaction of 5-Substituted Dibenzothiophenium Salts with Benznethiolate Ion in Methanol

Benzenethiolate ion was allowed to react with 5-substituted dibenzothiophenium salts and compared with methoxide ion. The results are shown in Table II. The reactions between acyclic triarylsulfonium salts and benzenethiolate ion were studied by Oae, *et al.*[4] and McEwen, *et al.*,[5] independently. In this case, both groups concluded that the reaction is aromatic bimolecular nucleophilic substitution.

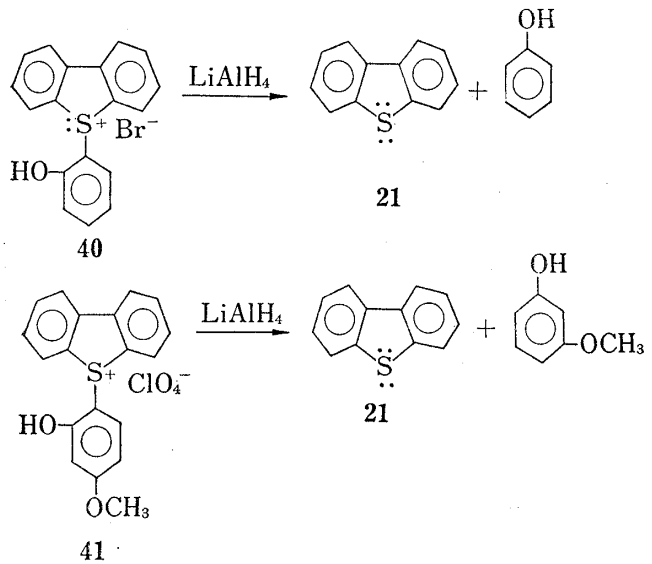


Chart 8.

The results obtained by the present authors on cyclic sulfonium salts also supported the validity of the mechanism proposed by them as shown in Table II. Run 12 shows higher reactivity than other runs. This high reactivity is attributable to the I-effect of *m*-methoxy group of **2**.

Demethylation of 5-(o-Methoxyphenyl)dibenzothiophenium Salts with Benzenethiolate Ion in Methanol——In Runs 11, 13, and 14 in Table II, sul-

fonium salt, used as a raw material, was recovered always. The reaction between 5-substituted dibenzothiophenium salts, **4** and **5**, which have a *o*-methoxy group in the 5-phenyl group, and benzenethiolate ion gave 5-(*o*-hydroxyphenyl)dibenzothiophenium bromide (**40**) and 5-(*o*-hydroxy-*p*-methoxyphenyl)-dibenzothiophenium perchlorate (**41**), respectively, in alcohol. Recently, Mirrington, *et al.*[7] reported that demethylation of aryl methyl ethers by ethanethiolate ion took place in DMF. In Runs 13 and 14, *o*-methoxy group only was preferentially demethylated. This is a particular example.

The structure of **40** and **41** was confirmed not only by spectral data and elemental analyses but also by the reduction by $LiAlH_4$ as shown in Chart 8, which gave phenol and *m*-methoxyphenol together with **21**.

Experimental

All melting points were uncorrected. IR spectra were measured on a JASCO Model IRA-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. Gas–liquid chromatography (GLC) was performed on JEOL 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 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 respects to IR spectra, mixed melting point and GLC retention time.

Reaction of 9-(*p*-Methoxyphenyl)dibenzothiophenium Perchlorate (1) with Sodium Methoxide in MeOH (Run 1)——To a solution of sodium methoxide prepared by dissolving Na (0.6 g, 25.5 mmole) in MeOH (40 ml) **1** (1.0 g, 2.56 mmole) was added under an N_2 stream. After boiling for 50 hr the reaction mixture was concentrated to one-half of its original volume, and then acidified with 5% HCl followed by extraction with ether. The extract was dried ($MgSO_4$) and evaporated. GLC analysis of the residual oil allowed determination of anisole (0.0277 g, 10.0%) and *p*-dimethoxybenzene (trace). Separation by preparative TLC using solvent A gave 3 fractions. Fraction I: Dibenzothiophene (**21**) (0.065 g, 13.8%). Fraction II: 2-Methoxy-2′-(*p*-methoxyphenylthio)biphenyl (**8**) (0.240 g, 29.1%) was obtained as colorless prisms, mp 86°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{20}H_{18}O_2S$: C, 74.52; H, 5.63. Found: C, 74.53; H, 5.82. NMR ($CDCl_3$) δ: 6.70—7.34 (12H, m, Ar-H), 3.76 (6H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 322(M^+, 100), 292 (16), 291(74), 276(21), 259(9), 247(5), 246(5), 215(6), 184(10), 181(8), 171(8), 168(18), 139(33). Fraction III: 2-Methoxy-2′-(*p*-methoxyphenylsulfinyl)biphenyl (**16**) (0.500 g, 57.8%) was obtained as colorless prisms, mp 104—106°, by recrystallization from ether. *Anal.* Calcd. for $C_{20}H_{18}O_3S$: C, 70.99; H, 5.36. Found: C, 71.09; H, 5.33.

Desulfurization of 8——To a suspension of W-7 Raney cobalt prepared from 50% Co-Al alloy (20 g) in EtOH (70 ml), **8** (0.6 g) was added. The reaction mixture was boiled for 12 hr and then cooled. The precipitate was filtered off and rinsed throughly with $CHCl_3$. The filtrate and $CHCl_3$ washings were combined and concentrated. To the residual oil dil. HCl was added and the mixture was extracted with ether. The extract was dried ($MgSO_4$) and evaporated. The residue was separated by preparative TLC using solvent A into 2 fractions, 2-methoxybiphenyl (0.205 g) as a colorless oil and the recovered compound **8** (0.235 g).

2-Methoxy-2′-(*p*-methoxyphenylsulfinyl)biphenyl (16)——To a solution of **8** (0.500 g, 1.55 mmole) in CH_2Cl_2 (20 ml) a solution of *m*-chloroperbenzoic acid (85%) (0.30 g) in CH_2Cl_2 (25 ml) was added at 0° with stirring. The reaction mixture was stirred for 17 hr at this temperature and for additional 10 hr at room temperature, and then added 10% Na_2CO_3. The organic layer was separated, washed with water, dried (K_2CO_3), and concentrated. The residue was recrystallized from ether to give colorless prisms (0.510 g, 97.2%), mp 104—105°. *Anal.* Calcd. for $C_{20}H_{18}O_3S$: C, 70.79; H, 5.36. Found: C, 71.04; H, 5.29. IR ν_{max}^{KBr} cm^{-1}: 1055(SO). NMR ($CDCl_3$) δ: 8.04—8.22 (2H, m, Ar-H), 6.65—7.73 (10H, m, Ar-H), 3.76 (3H, s, OCH_3), 3.65 (3H, broad s, OCH_3).

Reaction of 5-(*m*-Methoxyphenyl)dibenzothiophenium Bromide (2) with Sodium Methoxide in MeOH (Run 2)——To a solution of sodium methoxide prepared from Na (1.0 g, 43 mmole) and MeOH (60 ml) **2** (1.60 g, 4.31 mmole) was added under an N_2 stream. After boiling for 50 hr the reaction mixture was treated in the same way as Run 1. GLC analysis of the raw product allowed determination of anisole (0.023 g, 5.0%) and *m*-dimethoxybenzene (0.345 g, 58.0%). Separation by preparative TLC using solvent A gave 3 fractions. Fraction I: **21** (0.520 g, 65.5%). Fraction II: 2-Methoxy-2′-(*m*-methoxyphenylthio)biphenyl (**9**)

7) G.I. Fentrill and R.N. Mirrington, *Tetrahedron Letters*, **1970**, 1327.

(0.435 g, 31.4%) was obtained as colorless prisms, mp 68°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{20}H_{18}O_2S$: C, 74.52; H, 5.63. Found: C, 74.66; H, 5.55. NMR (CCl_4) δ: 6.48—7.50 (12H, m, Ar-H), 3.76 (6H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 322(M^+, 100), 292(21), 291(19), 276(23), 259(10), 258 (10), 184(13), 171(10), 168(27), 139(18). Fraction III: 2-Methoxy-2′-(*m*-methoxyphenylsulfinyl)biphenyl (17) (0.095 g, 6.5%) was obtained as colorless prisms, mp 135—137°, by recrystallization from ether. *Anal.* Calcd. for $C_{20}H_{18}O_3S$: C, 70.99; H, 5.36. Found: C, 70.76; H, 5.25.

2-Methoxy-2′-(*m*-methoxyphenylsulfinyl)biphenyl (17)——A solution of **9** (0.110 g, 0.342 mmole) in CH_2Cl_2 (4 ml) was oxidized by addition of a solution of *m*-chloroperbenzoic acid (85%) (0.069 g) in CH_2Cl_2 (5 ml) in the same way as that for **16**. The raw product was recrystallized from ether to give colorless prisms (0.085 g, 74%), mp 136—138°. *Anal.* Calcd. for $C_{20}H_{18}O_3S$: C, 70.99; H, 5.36. Found: C, 71.01; H, 5.43. IR ν_{max}^{KBr} cm^{-1}: 1030(SO). NMR ($CDCl_3$) δ: 7.98—8.14 (2H, m, Ar-H), 6.63—7.65 (10H, m, Ar-H), 3.67 (6Hm, s, OCH_3).

Reaction of 5-Phenyldibenzothiophenium Bromide (3) with Sodium Methoxide in MeOH (Run 3)——To a solution of sodium methoxide prepared from Na (1.01 g, 44 mmole) and MeOH (67 ml) **3** (1.50 g, 4.4 mmole) was added. The reaction mixture was worked up in the same manner as mentioned above. GLC analysis of the raw product allowed determination of benzene and anisole (0.140 g, 29.5%). Separation by preparative TLC using solvent A gave 3 fractions. Fraction I: **21** (0.410 g, 50.7%). Fraction II: 2-Methoxy-2′-(phenylthio)biphenyl (**10**) (0.590 g, 46.0%) was obtained as colorless prisms, mp 70°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{19}H_{16}OS$: C, 78.06; H, 5.52. Found: C, 78.28; H, 5.31. NMR ($CDCl_3$) δ: 6.87—7.50 (13H, m, Ar-H), 3.67 (3H, m, OCH_3). Fraction III: 2-Methoxy-2′-(phenylsulfinyl)biphenyl (**18**) (0.020 g, 1.5%) was obtained as colorless prisms, mp 112—113°, by recrystallization from ether.

2-Methoxy-2′-(phenylsulfinyl)biphenyl (18)——A solution of **10** (0.150 g, 0.514 mmole) in CH_2Cl_2 (6 ml) was oxidized with a solution of *m*-chloroperbenzoic acid (85%) (0.084 g) in CH_2Cl_2 (7 ml) in the same way as mentioned above. The crude product was recrystallized from ether to give colorless prisms (0.140 g, 88.5%), mp 113°. *Anal.* Calcd. for $C_{19}H_{16}O_2S$: C, 74.01; H, 5.23. Found: C, 74.18; H, 5.39. IR ν_{max}^{KBr} cm^{-1}: 1030(SO). NMR ($CDCl_3$) δ: 8.02—8.18 (2H, m, Ar-H), 6.65—7.72 (11H, m, Ar-H), 3.76 (3H, broad s, OCH_3).

Reaction of 5-(*o*-Methoxyphenyl)dibenzothiophenium Bromide (4) with Sodium Methoxide in MeOH (Run 4)——To a solution of sodium methoxide prepared from Na (0.50 g, 21.6 mmole) and MeOH (33 ml) **4** (0.80 g, 2.16 mmole) was added. The reaction mixture was worked up in the same manner as Run 1. GLC analysis of the raw product allowed determination of anisole (0.074 g, 31.8%) and *o*-dimethoxybenzene (0.0102 g, 3.4%). Separation by preparative TLC using solvent A gave 3 fractions. Fraction I: **21** (0.165 g, 41.6%). Fraction II: 2-Methoxy-2′-(*o*-methoxyphenylthio)biphenyl (**11**) (0.120 g, 17.3%) was obtained as colorless prisms, mp 113°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{20}H_{18}O_2S$: C, 74.52; H, 5.63. Found: C, 74.43; H, 5.70. NMR (CCl_4) δ: 6.65—7.60 (12H, m, Ar-H), 3.77 (3H, s, OCH_3), 3.72 (3H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 322(M^+, 100), 292(23), 291(83), 276(10), 259(7), 184(14), 181(10), 171(9), 168(20), 139(20). Fraction III: 2-Methoxy-2′-(*o*-methoxyphenylsulfinyl)biphenyl (**19**) (0.290 g, 39.8%) was obtained as colorless prisms, mp 162°, by recrystallization from ether. *Anal.* Calcd. for $C_{20}H_{18}O_3S$: C, 70.99; H, 5.36. Found: C, 71.08; H, 5.35.

2-Methoxy-2′-(*o*-methoxyphenylsulfinyl)biphenyl (19)——Compound (**11**) (0.150 g, 0.466 mmole) was oxidized with *m*-chloroperbenzoic acid (85%) (0.094 g) as mentioned above. The crude product was recrystallized from ether to give colorless oprisms (0.112 g, 71.3%), mp 163—164°. *Anal.* Calcd. for $C_{20}H_{18}O_3S$: C, 70.99; H, 5.36. Found: C, 70.84; H, 5.52. IR ν_{max}^{KBr} cm^{-1}: 1050(SO). NMR ($CDCl_3$) δ: 6.60—7.94 (12H, m, Ar-H), 3.79 (3H, m, OCH_3), 3.47 (3H, s, OCH_3).

Reaction of 5-(*o,p*-Dimethoxyphenyl)dibenzothiophenium Perchlorate (5) with Sodium Methoxide in MeOH (Run 5)——To a solution fo sodium methoxide prepared from Na (0.76 g, 33 momle) and MeOH (50 ml) **5** (1.40 g, 3.32 mmole) was added. The reaction mixture was worked up as mentioned above. GLC analysis of the raw product allowed determination of *m*-dimethoxybenzene (0.161 g, 35.0%). Separation by preparative TLC using solvent A gave 3 fractions. Fraction I: **21** (0.240 g, 39.2%). Fraction II: 2-(*o,p*-Dimethoxyphenylthio)-2′-methoxybiphenyl (**12**) (0.470 g, 40.2%) was obtained as colorless prisms, mp 91°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{21}H_{20}O_3S$: C, 71.58; H, 5.72. Found: C, 71.55; H, 5.76. NMR (CCl_4) δ: 6.81—7.52 (9H, m, Ar-H), 6.33—6.53 (12H, m, Ar-H), 3.80 (6H, s, OCH_3), 3.74 (3H, s, OCH_3). Mass spectrum *m/e* (% of base peak): 352(M^+, 100), 321(28.4). Fraction III: 2-(*o,p*-Dimethoxyphenylsulfinyl)-2′-methoxybiphenyl (**20**) (0.088 g, 7.0%) was obtained as colorless prisms, mp 148—150°, by recrystallization from ether. *Anal.* Calcd. for $C_{21}H_{20}O_4S$: C, 68.47; H, 5.47. Found: C, 58.51; H, 5.56.

2-(*o,p*-Dimethoxyphenylsulfinyl)-2′-methoxybiphenyl (20)——Compound (**12**) (0.120 g, 0.341 mmole) was oxidized with *m*-chloroperbenzoic acid (85%) (0.069 g) in the same way as mentioned above. The crude product was recrystallized from ether to give colorless pri sms (0.110 g, 87.7%), mp 149°. *Anal.* Calcd. for $C_{21}H_{20}O_4S$: C, 68.47; H, 5.47. Found: C, 68.27; H, 5.39. IR ν_{max}^{KBr} cm^{-1}: 1030(SO). NMR ($CDCl_3$) δ: 6.16—8.03 (11H, m, Ar-H), 3.77 (3H, s, OCH_3), 3.74 (3H, broad s, OCH_3), 3.45 (3H, s, OCH_3).

Reaction of 5-Methyldibenzothiophenium Fluoroborate (6) with Sodium Methoxide in MeOH (Run 6)——To a solution of sodium methoxide prepared from Na(1.2 g, 52.1 mmole) and MeOH (40 ml) **6** (1.45 g, 5.07 mmole) was added. The reaction mixture was treated as mentioned above. The reaction product was **21** (0.840 g, 90.0%).

Reaction of 1 with Potassium Hydroxide in MeOH (Run 7)——To a solution of KOH (1.50 g, 26.8 mmole) in MeOH (40 ml) **1** (1.00 g, 2.56 mmole) was added. The reaction mixture was treated as mentioned above. GLC analysis of the crude product allowed determination of anisole (0.029 g, 11.0%) and *p*-dimethoxybenzene (trace). Separation by preparative TLC using solvent A gave 3 fractions. Fraction I: **21** (0.075 g, 14.5%). Fraction II: **8** (0.310 g, 34.2%). Fraction III: **16** (0.470 g, 49.4%).

Reaction of 2-Methoxy-5-phenyldibenzothiophenium Bromide (7) with Sodium Methoxide in MeOH (Run 8)——To a solution of sodium methoxide prepared from Na (0.64 g, 27.8 mmole) and MeOH (40 ml) **7** (1.00 g, 2.7 mmole) was added. The reaction mixture was worked up as mentioned above. Benzene and anisole were detected by GLC analysis of the crude product. Separation by preparative TLC using solvent A gave 2 fractions. Fraction I: 2-Methoxydibenzothiophene (**22**) (0.285 g, 49.5%). Fraction II: 2,5′-Dimethoxy-2′-(phenylthio)biphenyl (**13**) (0.390 g, 44.9%) was obtained as colorless prisms, mp 106°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{20}H_{18}O_2S$: C, 74.52; H, 5.63. Found: C, 74.37; H, 5.70. NMR (CCl_4) δ: 6.61—7.50 (12H, m, Ar-H), 3.81 (3H, s, OCH_3), 3.61 (3H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 322(M^+, 100), 291(30), 276(10), 214(6), 198(11), 183((10), 171(7), 155(10), 77(6). Desulfurization of **13** (0.250 g) was conducted with Raney cobalt prepared from 50% Co-Al alloy (20 g). The reaction mixture was treated in the same way as mentioned before. Purification by preparative TLC using solvent A gave 2,3′-dimethoxybiphenyl (**24**) (0.160 g) as a colorless oil. *Anal.* Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.76; H, 6.67. NMR (CCl_4) δ: 6.65—7.36 (8H, m, Ar-H), 3.80 (3H, s, OCH_3), 3.77 (3H, s, OCH_3).

1-(2,5-Dimethoxyphenyl)cyclohexane (26)——An ethereal solution of 2,5-dimethoxyphenylmagnesium bromide was prepared from 2,5-dimethoxybromobenzene (26 g) and Mg (2.88 g). To the Grignard reagent thus prepared cyclohexanone (23.5 g) was added. After stirring for 2 hr, the reaction mixture was decomposed with 5% HCl and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. To the residual oil 20% H_2SO_4 (50 ml) was added. After refluxing for 2 hr, the reaction mixture was poured into water and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. The crude product was recrystallized from *n*-hexane to give colorless prisms (17 g, 65.4%), mp 42—43°. *Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.09; H, 8.36. NMR ($CDCl_3$) δ: 6.78 (3H, s, Ar-H), 5.81 (1H, m, C–CH), 3.80 (3H, s, OCH_3), 3.73 (3H, s, OCH_3), 2.00—2.54 (4H, m, CH_2), 1.57—1.90 (4H, m, CH_2).

2,5-Dimethoxybiphenyl (25)——A mixture of **26** (4.4 g), NBS (8.0 g), and a small amount og benzoyl peroxide in CCl_4 (88 ml) was refluxed for 12 hr. Resulting succinimide was filtered off. The filtrate was washed with 5% NaOH and water and then dried ($MgSO_4$). Evaporation of the solvent left crude bromide. Triethylamine (222 ml) was added to the bromide. The mixture was refluxed for 16 hr and then filtered. The filtrate was evaporated followed by addition of 5% HCl and extraction with ether. The extract was dried ($MgSO_4$) and evaporated. Purification of the residue was carried out by column chromatography on silica gel using solvent C to give a colorless oil (1.7 g, 39.1%). *Anal.* Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.76; H, 6.67. NMR (CCl_4) δ: 7.20—7.60 (5H, m, Ar-H), 3.79 (3H, s, OCH_3), 3.72 (3H, s, OCH_3).

Reaction of 1 with Sodium Isopropoxide in 2-Propanol (Run 9)——A solution of sodium isopropoxide was prepared by dissolving Na(0.5 g, 25.6 mmole) in 2-propanol (50 ml). To the alkoxide solution thus prepared **1** (1.0 g, 2.56 mmole) was added under an N_2 stream. The reaction mixture was refluxed for 60 hr. Acetone (trace) and anisole (trace) were detected by GLC analysis of the reaction mixture. The reaction mixture was treated in the same way as mentioned above. Separation by preparative TLC using solvent D gave 2 fractions. Fraction I: **21** (trace). Fraction II: 2-Isopropoxy-2′-(*p*-methoxyphenylthio)biphenyl (**14**) (0.887 g, 99.0%) was obtained as colorless prisms, mp 110°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{22}H_{22}O_2S$: C, 75.41; H, 6.33. Found: C, 75.70; H, 6.24. NMR ($CDCl_3$) δ: 7.27 (12H, m, Ar-H), 4.42 (1H, quintet, J=6.0 Hz, CH), 3.80 (3H, s, OCH_3), 1.23 (6H, d, J=6.0 Hz, CH_3). Mass Spectrum *m/e* (% of base peak): 350(M^+, 88), 308(100), 291(23), 260(13), 200(30), 172(18), 171(13), 169(18), 168(16), 140(18), 139(73).

Reaction of 4 with Sodium Isopropoxide in 2-Propanol (Run 10)——To a solution of sodium isopropoxide prepared from Na(0.62 g, 27 mmole) and 2-propanol (50 ml) **4** (1.0 g, 2.7 mmole) was added. The mixture was refluxed for 60 hr. Acetone was detected by GLC analysis of the reaction mixture. The mixture was treated as mentioned above. GLC analysis of the raw product allowed determination of anisole (0.0538 g, 15.1%). Separation by preparative TLC using solvent D gave 2 fractions. Fraction I: **21** (0.080 g, 16.1%). Fraction II: 2-Isopropoxy-2′-(*o*-methoxyphenylthio)biphenyl (**15**) (0.760 g, 80.6%) was obtained as colorless prisms, mp 102°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{22}H_{22}O_2S$: C, 75.41; H, 6.33. Found: C, 75.16; H, 6.14. NMR ($CDCl_3$) δ: 6.77—7.45 (12H, m, Ar-H), 4.40 (1H, quintet, J=6.0 Hz, CH), 3.78 (3H, s, OCH_3), 1.19 (6H, J=6.0 Hz, CH_3). Mass Spectrum *m/e* (% of base peak): 350(M^+, 78), 308(100), 291(22), 200(19), 172(11), 171(11), 169(34), 168(35), 140(28), 139(27).

Reaction of 9,9-Dimethyl-10-(*p*-methoxyphenyl)thioxanthenium Perchlorate (27) with Sodium Methoxide in MeOH——To a solution of sodium methoxide prepared from Na (0.53 g, 23 mmole) and MeOH (30 ml) **27** (1.0 g, 2.3 mmole) was added. After refluxing for 50 hr the reaction mixture was decomposed with 5% HCl. The precipitate newly formed was collected by filtration and dried. The filtrate was extracted with ether. Recrystallization of the precipitate from CH_2Cl_2–ether gave the recovery material **27** as colorless prisms (0.750 g, 75%), mp 197°. The ether extract was dried ($MgSO_4$) and evaporated. GLC analysis

of the residue allow determination of anisole (0.046 g, 18.4%). Purification by preparative TLC using *n*-hexane gave 9,9-dimethylthioxanthene (**28**) (0.130 g, 25.0%) as a colorless oil.

Reaction of 5-(*p*-Methoxyphenyl)-10,11-dihydrodibenzo[*b*,*f*]thiepinium Perchlorate (30) with Sodium Methoxide in MeOH——To a solution of sodium methoxide prepared from Na (0.55 g, 23.9 mmole) and MeOH (37 ml) **30** (1.0 g, 2.39 mmole) was added. After refluxing for 50 hr the reaction mixture was concentrated to one-half of original volume and acidified with 5% HCl. The precipitate newly formed was collected by filtration and dried. Recrystallization from CH_2Cl_2–ether gave **30** (0.960 g, 96.0%) as colorless prisms.

Reaction of 1 with Sodium Methoxide in DMF–MeOH——A solution of sodium methoxide was prepared by dissolving Na (0.6 g, 25.5 mmole) in MeOH (11 ml) and by addition of DMF (33 ml). To the alkoxide solution thus prepared **1** (1.0 g, 2.56 mmole) was added under an N_2 stream. After refluxing for 10 hr, the reaction mixture was concentrated under reduced pressure followed by acidification with 5% HCl and extraction with ether. The ether extract was dried ($MgSO_4$) and evaporated. Purification of the residue by preparative TLC using solvent A gave **8** (0.785 g, 95.3%) as colorless prisms.

Reaction of 27 with Sodium Methoxide in DMF–MeOH——A solution of sodium methoxide was prepared by dissolving Na (0.533 g, 23.2 mmole) in MeOH (10 ml) and by addition of DMF (30 ml). To the alkoxide solution thus prepared **27** (1.0 g, 2.31 mmole) was added under an N_2 stream. The reaction mixture was treated as mentioned above. The ether extract was dried ($MgSO_4$) and evaporated. Separation of the crude product by preparative TLC using solvent A gave 2 fractions. Fraction I: Compound (**28**) (0.038 g, 7.3%) was obtained as a colorless oil. Fraction II: 2-(*o*-Methoxyphenyl)-2-[*o*-(*p*-methoxyphenylthio)phenyl]-propane (**29**) (0.760 g, 90.4%) was obtained as colorless prisms, mp 69°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{23}H_{24}O_2S$: C, 75.80; H, 6.64. Found: C, 76.08; H, 6.68. NMR (CCl_4) δ: 6.57—7.57 (12H, m, Ar-H), 3.70 (3H, s, OCH_3), 3.26 (3H, s, OCH_3), 8.18 (6H, s, CH_3). Mass Spectrum *m/e* (% of base peak): 364(M^+, 100), 349(24), 333(10), 241(91), 165(18), 139(18).

Reaction of 30 with Sodium Methoxide in DMF–MeOH——To a solution of sodium methoxide prepared from Na (0.55 g, 23.9 mmole), MeOH (10 ml), and DMF (30 ml) **30** (1.0 g, 2.39 mmole) was added. The reaction mixture was treated as mentioned above. Separation of the crude product by preparative TLC using solvent A gave 2 fractions. Fraction I: 10,11-Dihydrodibenzo[*b*,*f*]thiepin (**32**) (0.020 g, 3.9%). Fraction II: 1-(*o*-Methoxyphenyl)-2-[*o*-(*p*-methoxypheylthio)phenyl]ethane (**31**) (0.645 g, 77.2%) was obtained as colorless prisms, mp 50°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{22}H_{22}O_2S$: C, 75.41; H, 6.33. Found: C, 75.64; H, 6.16. NMR (CCl_4) δ: 6.70—7.38 (12H, m, Ar-H), 3.82 (3H, s, OCH_3), 3.78 (3H, s, OCH_3), 2.96 (4H, s, CH_2). Mass Spectrum *m/e* (% of base peak): 350(M^+, 74), 229(55), 227(58), 214(13), 197(16), 121(100), 91(65).

Reaction of 1 with Sodium Benzenethiolate in MeOH (Run 11)—— To a solution of sodium benzenethiolate (3.40 g, 25.7 mmole) in MeOH (60 ml) **1** (1.00 g, 2.56 mmole) was added under an N_2 stream. After refluxing for 50 hr, the reaction mixture was poured into 5% HCl and extracted with ether and then $CHCl_3$. The ether and $CHCl_3$ extracts were dried ($MgSO_4$) and evaporated, separately. The residue from the $CHCl_3$ extract was recrystallized from $CHCl_3$–ether to give **1** (0.270 g, 27.0%). The residue from the ether extract was separated into 3 fractions by preparative TLC using solvent A. Fraction I: A mixture of **21** and diphenyl disulfide was obtained. It was reduced with excess $LiAlH_4$ in order to remove the disulfide and then **21** (0.170 g, 36.2%) was isolated. Fraction II: *p*-Methoxyphenyl phenyl sulfide (**36**) (0.118 g, 21.7%) was obtained as a colorless oil. NMR (CCl_4) δ: 7.35 (2H, d, J=9.0 Hz, Ar-H), 7.10 (5H, s, Ar-H), 6.78 (2H, d, J=9.0 Hz, Ar-H), 3.78 (3H, s, OCH_3). Mass Spectrum *m/e*: 216(M^+). Fraction III: 2-(*p*-Methoxyphenylthio)-2′-(phenylthio)biphenyl (**32**) (0.370 g, 36.2%) was obtained as colorless prisms, mp 104—105°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{25}H_{20}OS_2$: C, 74.99; H, 5.03. Found: C, 74.80; H, 5.02. Mass Spectrum *m/e* (% of base peak): 400(M^+, 8), 292(22), 291(99), 276(13), 262(23), 261(100), 260(20), 184 (67), 152(13), 139(36), 109(20). NMR (CCl_4) δ: 6.67—7.35 (17H, m, Ar-H), 3.76 (3H, s, OCH_3).

Reaction of 2 with Sodium Benzenethiolate in MeOH (Run 12)——To a solution of benzenethiolate (3.6 g, 27.7 mmole) in MeOH (60 ml) **2** (1.0 g, 2.7 mmole) was added. The reaction mixture was treated in the same way as Run 11. Separation of the crude product by preparative TLC using solvent A gave 3 fractions. Fraction I: A mixture of **21** and diphenyl disulfide was obtained. It was reduced with $LiAlH_4$ in order to remove the disulfide and then **21** (0.415 g, 83.8%) was isolated. Fraction II: *m*-Methoxyphenyl phenyl sulfide (**38**) (0.465 g, 80.0%) was obtained as a colorless oil. *Anal.* Calcd. for $C_{13}H_{12}OS$: C, 72.21; H, 5.59. Found: C, 72.09; H, 5.48. NMR (CCl_4) δ: 6.59—7.40 (9H, m, Ar-H), 3.73 (3H, s, OCH_3). Fraction III: 2-(*m*-Methoxyphenylthio)-2′-(phenylthio)biphenyl (**33**) (0.160 g, 14.7%) was obtained as a colorless oil. *Anal.* Calcd. for $C_{25}H_{20}OS_2$: C, 74.99; H, 5.03. Found: C, 74.85; H, 5.15. NMR (CCl_4) δ: 6.60—7.40 (17H, m, Ar-H), 3.65 (3H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 400(M^+, 15), 292(27), 192(95), 276(16), 262(27), 261(100), 184(38), 152(9), 139(13).

Reaction of 4 with Sodium Benzenethiolate in MeOH (Run 13)——To a solution of sodium benzenethiolate (3.6 g, 27.2 mmole) in MeOH (60 ml) **4** (1.00 g, 2.7 mmole) was added. After refluxing for 50 hr the reaction mixture was poured into 5% HBr and extracted with ether and $CHCl_3$. The ether and $CHCl_3$ extracts were dried ($MgSO_4$) and evaporated, separately. The residue obtained from the ether extract was separated into 3 fractions by preparative TLC using solvent A. Fraction I: A mixture of **21** and diphenyl disulfide was obtained. It was reduced with $LiAlH_4$ in order to remove the sulfide and then **21** (0.256 g, 51.6%) was iso-

lated. Fraction II: *o*-Methoxyphenyl phenyl sulfide (**39**) (0.260 g, 44.7%) was obtained as a colorless oil. *Anal.* Calcd. for $C_{13}H_{12}OS$: C, 72.21; H, 5.59. Found: C, 72.23; H, 5.64. NMR (CCl_4) δ: 6.65—7.35 (9H, m, Ar-H), 3.82 (3H, s, OCH_3). Fraction III: 2-(*o*-Methoxyphenylthio)-2′-(phenylthio)biphenyl (**34**) (0.216 g, 20.0%) was obtained as a colorless oil. *Anal.* Calcd. for $C_{25}H_{20}OS_2$: C, 74.99; H, 5.03. Found: C, 74.56; H, 5.15. NMR (CCl_4) δ: 6.65—7.35 (17H, m, Ar-H), 3.72 (3H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 400(M^+, 9), 292(20), 291(88), 276(8), 262(15), 261(100), 184(24), 152(4), 139(6). The solid obtained from the $CHCl_3$ extract was recrystallized from MeOH–ether to give 5-(*o*-hydroxyphenyl)dibenzothiophenium bromide (**40**) (0.269 g, 28.0%) as colorless prisms, mp 255—258° (decomp.). *Anal.* Calcd. for $C_{18}H_{13}OSBr$: C, 60.50; H, 3.67. Found: C, 60.35; H, 3.69. IR ν_{max}^{KBr} cm^{-1}: 3600—3200 (OH). NMR ($CDCl_3$–DMSO-d_6) δ: 6.75—8.48 (m, Ar-H).

Reduction of 40 with $LiAlH_4$——To a suspension of $LiAlH_4$ (0.5 g) in anhydrous ether (10 ml) **40** (0.20 g, 0.56 mmole) was added. After stirring for 5 hr at room temperature the reaction mixture was decomposed with dil. HCl and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. Separation of the residue by preparative TLC using pet. ether gave **21** (0.100 g, 97.1%) and phenol (0.050 g, 94.7%).

Reaction of 5 with Sodium Benzenethiolate in MeOH (Run 14)——To a solution of sodium benzenethiolate (3.1 g, 23.7 mmole) in MeOH (55 ml) **5** (1.00 g, 2.38 mmole) was added under an N_2 stream. After refluxing for 50 hr, the reaction mixture was poured into 5% HCl and extracted with ether and $CHCl_3$. The ether and $CHCl_3$ extracts were dried ($MgSO_4$) and evaporated, separately. The residue obtained from the ether extract was separated into 2 fractions by preparative TLC using solvent A. Fraction I: A mixture of **21** and diphenyl disulfide was obtained. It was reduced with $LiAlH_4$ as mentioned above and then **21** (0.05 g, 8.7%) was isolated. Fraction II: 2-(*o*,*p*-Dimethoxyphenylthio)-2′-(phenylthio)biphenyl (**35**) (0.170 g, 16.7%) was obtained as colorless prisms, mp 79°, by recrystallization from MeOH. *Anal.* Calcd. for $C_{26}H_{22}O_2S_2$: C, 72.54; H, 5.15. Found: C, 72.39; H, 5.27. NMR (CCl_4) δ: 6.65—7.50 (14H, m, Ar-H), 6.35—6.45 (2H, m, Ar-H), 3.76 (3H, s, OCH_3), 3.68 (3H, s, OCH_3). Mass Spectrum *m/e* (% of base peak): 430(M^+, 22), 322(25), 231 (100), 262(19), 261(87), 184(27), 152(4), 139(6). The solid obtained from the $CHCl_3$ extract was recrystallized from MeOH–ether to give 5-(*o*-hydroxy-*p*-methoxyphenyl)dibenzothiophenium perchlorate (**41**) (0.750 g, 77.3%) as colorless prisms, mp 215° (decomp.). *Anal.* Calcd. for $C_{19}H_{15}O_2SClO_4$: C, 56.09; H, 3.71. Found: C, 56.36; H, 3.68. IR ν_{max}^{KBr} cm^{-1}: 3600—3200 (OH), 1180—1020 (ClO_4^-). NMR (DMSO-d_6) δ: 6.56—8.60 (12H, m, Ar-H and OH), 3.81 (3H, s, OCH_3).

Reduction of 41 with $LiAlH_4$——To a suspension of $LiAlH_4$ (1.0 g) in anhydrous ether (20 ml) **41** (0.140 g, 0.98 mmole) was added. After stirring for 5 hr at room temperature, the reaction mixture was decomposed with dil. HCl and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. Separation by preparative TLC using pet. ether gave **21** (0.180 g, 100%) and *m*-methoxyphenol (0.120 g, 98.8%).