[Chem. Pharm. Bull. 22(9)2014—2019(1974)]

UDC 547.892.04 : 547.558.04

Dibenzothiophenes and Related Compounds. IV.[1,2] Reactions of 5-Substituted 10,11-Dihydrodibenzo[*b*,*f*]thiepinium Salts with Aryllithiums

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(Received October 22, 1973)

5-Substituted 10,11-dihydrodibenzo[*b*,*f*]thiepinium salts were synthesized in order to elucidate the mechanism of reactions between acyclic triarylsulfonium salts and organolithiums.

The reaction of aryllithiums with 5-substituted 10,11-dihydrodibenzo[*b*,*f*]thiepinium salts has been investigated to get the results, as shown in Table I.

The mechanisms for the formation of all products of the runs in Table I have been clearly explained as shown in Chart 3.

We have made in the preceding reports[1] close studies on the mechanism for the formation of main products, such as ring-opening products or ligand-exchange ring-opening products, in the reactions of organolithiums with dibenzothiophenium and thioxanthenium salts (**1** and **2**) in order to elucidate the mechanism of reactions between acyclic triarylsulfonium salts and organolithiums. The results of these studies indicated that these reactions proceed by the collapse of preferred conformers, which are produced by the pseudorotation of pentacoordinated sulfur compounds present in the transition state. This explanation was acceptable in various aspects.

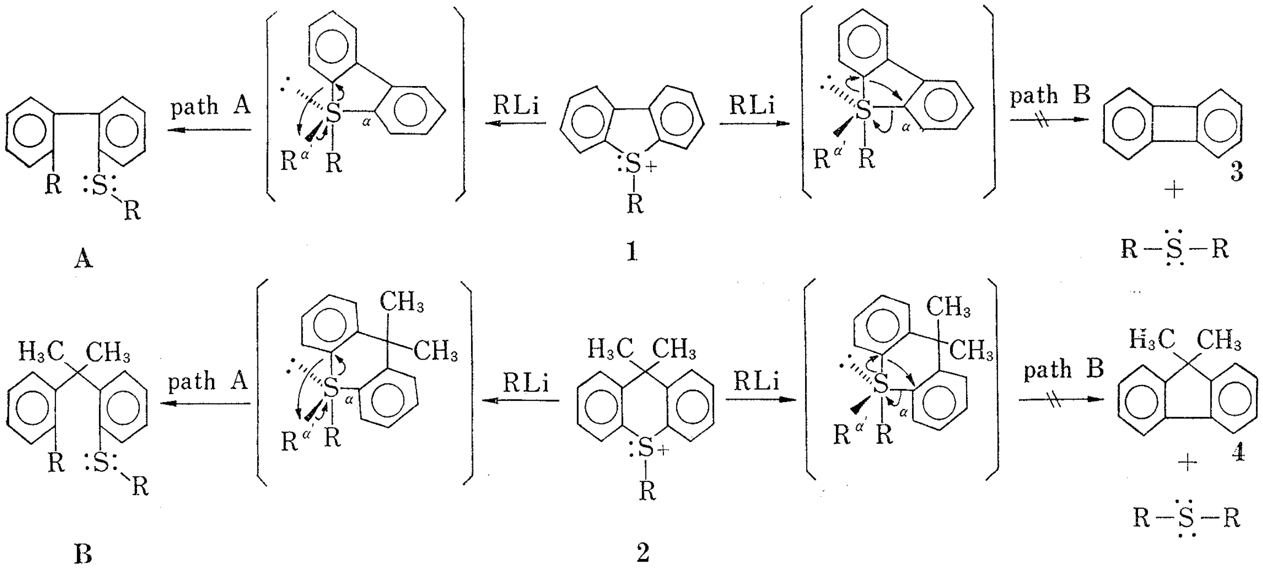

Chart 1

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[1] M. Hori, T. Kataoka, H. Shimizu, and M. Miyagaki, *Chemistry Lett.*, **1972**, 515. Part I—III: *Idem*, *Yakugaku Zasshi*, **93**, 476 (1973); *idem*, *Chem. Pharm. Bull.* (Tokyo), **21**, 1171, 2004 (1974).

[2] A part of this work was presented at the 93rd Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, April 5, 1973. Abstracts of papers, p. II—112 and also at VI International Symposium on Organic Sulphur Chemistry, Bangor (U.K.), July 4, 1974. Abstracts Book, B—18.

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

As shown in Chart 1, the above reactions, however, gave products **A** or **B** only. This result indicates that only path A was followed among various mechanisms of the collapse of pentacoordinated sulfur intermediate. Biphenylene (**3**) or 5,5-dimethylfluorene (**4**) and sulfides, which will be formed by path B, were not synthesized at all. Namely, both reactions will give products **A** or **B** if the apical C-S bond in the hetero-ring of the intermediate, cleaves and the reactions follow path A in which the anionic site of an apical phenyl group formed, attacks the α'-carbon of the equatorial ligand outside the hetero-ring. However, there remains some possibility that the anionic site described above attacks the α-carbon of the phenyl group, which is an equatorial ligand in the hetero-ring of the intermediate. Although the reactions follow path B in this case, the strain of **3** and the steric hindrance of **4** indicate that path B is hardly realized.

Therefore, the authors synthesized 5-substituted 10,11-dihydrodibenzo[*b*,*f*]thiepinium salts, which are the flexible cyclic compound most similar to acyclic triarylsulfonium salts and can produce strain-free and steric hindrance-free products through path B, in order to support the validity of the reaction mechanisms described above. The reactions of this salt with aryllithiums gave exactly the same results as expected. The details will be reported below.

Result and Discussion

Syntheses of 5-Substituted 10,11-Dihydrodibenzo[*b*,*f*]thiepinium Salts (9—11)

Jilek, *et al.*[4] have synthesized 10,11-dihydrodibenzo[*b*,*f*]thiepin (**7**), which is a precursor of 10,11-dihydrodibenzo[*b*,*f*]thiepin 5-oxide (**8**), by the Wolff-Kishner reduction of 10,11-dihydrodibenzo[*b*,*f*]thiepin-10-one (**5**) in a yield of 57%. This compound **7** was also synthesized by the authors with a good yield by the reduction of 10-chloro-10,11-dihydrodibenzo-[*b*,*f*]thiepin (**6**) with $LiAlH_4$. Compound **6** is obtained by the reduction of **5** with $LiAlH_4$ followed by the treatment with $SOCl_2$. The over-all yield of **7** from **5** showed 96.5%. Compound **7** was oxidized with 35% H_2O_2 to give **8** with a yield of 96.8%.

This compound **8** gave 5-phenyl-10,11-dihydrodibenzo[*b*,*f*]thiepinium bromide (**9**) on application of Grignard reaction by the use of conventional arylmagnesium halide. The yield was 21.4%. On the other hand, 5-(*p*-methoxyphenyl)- and 5-(*o*,*p*-dimethoxyphenyl)-10,11-dihydro[*b*,*f*]thiepinium perchlorates (**10** and **11**) were synthesized from **8** by the treatment with anisole and *m*-dimethoxybenzene, respectively, in the presence of 70% $HClO_4$. The yields were 64 and 61%, respectively. These compounds, **9**—**11**, were identified by elemental analysis as well as by infrared (IR) and nuclear magnetic resonance (NMR) spectra. Chart 2 shows the routes of synthesis of these.

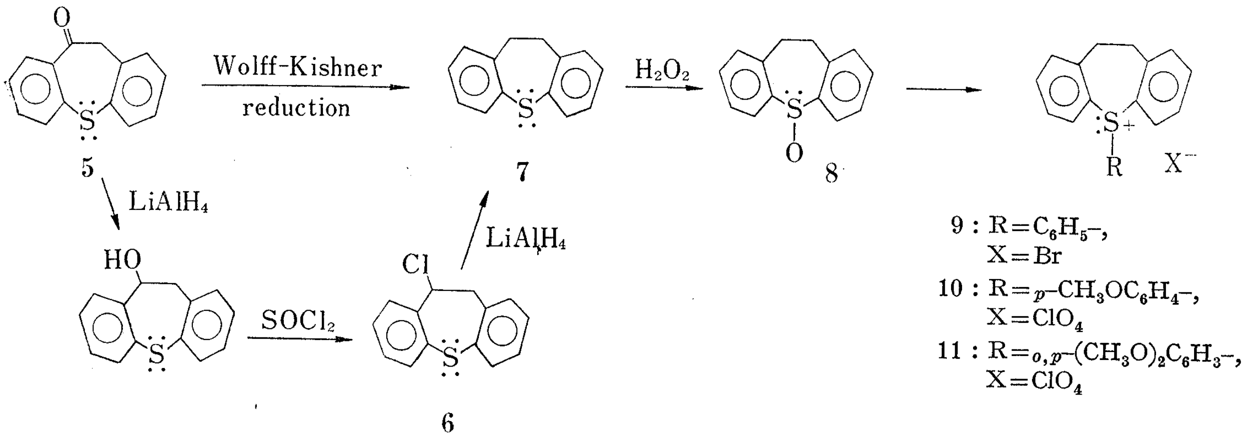

Chart 2

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[4] J.O. Jilek, V. Seidlova, E. Svatelz, M. Protiva, J. Pomykacelz, and Z. Sedivy, *Monatsh. Chem.*, **96**, 182 (1965).

Reactions of 5-Substituted 10,11-Dihydro[*b*,*f*]thiepinium Salts with Aryllithiums

All the title reactions were allowed to proceed between corresponding sulfonium salts and excess aryllithiums. The results are shown in Table I. All the reaction products were separated into various groups by thin-layer chromatography (TLC) on silica gel and then isolated and purified by recrystallization and other methods. The identification was made

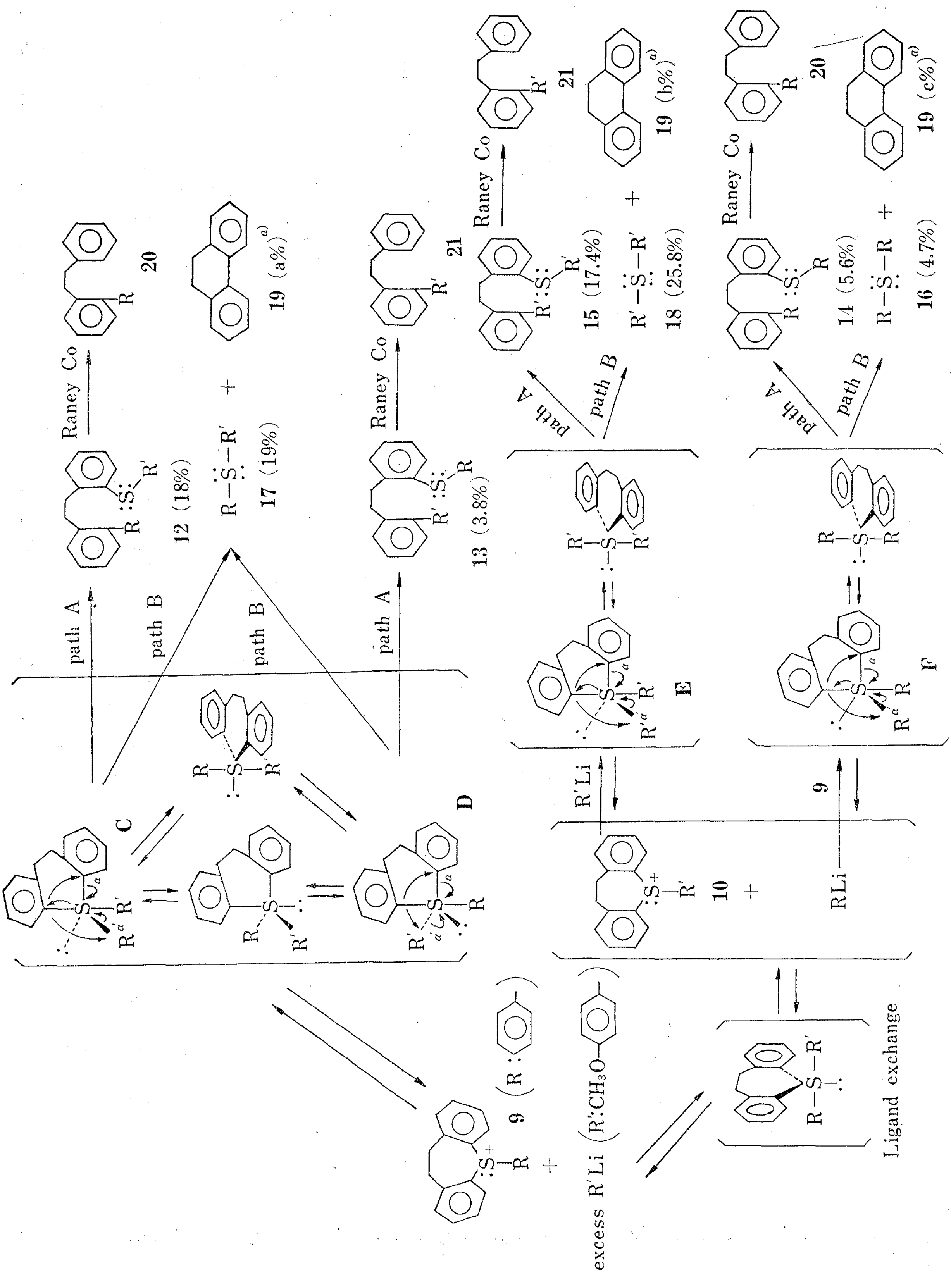


Chart 3 Mechanism for Formation of All Products of Run 1 in Table I

a) The total yield of **19** (a, b and c%) is 47.2%.

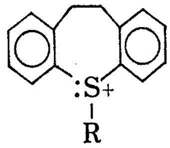
by the NMR, IR, and mass spectroscopic analyses, elemental analysis, and the analysis of retention time of gas–liquid chromatography (GLC) on 20% SE-30 column with phenetole as a standard. Ring-opening products, 1-(*o*-biphenylyl)-2-[*o*-(*p*-methoxyphenylthio)phenyl]ethane (**12**) and 1-(4′-methoxy-*o*-biphenylyl)-2-[*o*-(phenylthio)phenyl]ethane (**13**), and ligand-exchange ring-opening products, 1-(*o*-biphenylyl)-2-[*o*-(phenylthio)phenyl]ethane (**14**) and 1-(4′-methoxy-*o*-biphenylyl)-2-[*o*-(*p*-methoxyphenylthio)phenyl]ethane (**15**), were treated with W-7 Raney cobalt to give desulfurization products, 2-phenethylbiphenyl (**20**) and 4-methoxy-2′-phenetylbiphenyl (**21**), which were then identified by spectroscopic data and elemental analysis. Sulfides (**16**—**18**) were converted to corresponding crystalline sulfones by oxidation with H_2O_2 for identification.

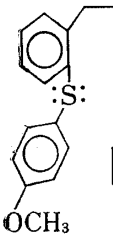
Mechanism for Formation of All Products on the Reactions between 5-Substituted 10,11-Dihydrodibenzo[*b*,*f*]thiepinium Salts and Aryllithiums

All the title reactions were followed carefully and closely with experimental means. The results are explained as shown in Chart 3 for the reaction of 5-phenyl-10,11-dihydrodibenzo-[*b*,*f*]thiepinium bromide (**9**) with *p*-methoxyphenyllithium.

Compound **9** couples with R′Li to form pentacoordinated intermediate (**C**) and its pseudorotational conformer (**D**). **C** and **D** give **12** and **13** with yields of 18 and 3.8%, respectively, through path A. At the same time, these give 19% of *p*-methoxyphenyl phenyl sulfide (**17**) and some of 9,10-dihydrophenanthrene (**19**) through path B. Compound **9** performs also ligand exchange with R′Li at 5-position phenyl group through the S_N2 type mechanism and gives **10** and RLi. Compound **10** couples with excess R′Li to form pentacoordinated sulfur compound (**E**). As in the case of **C**, **E** gives 17.4% of **15** through path A, and 25.8% of bis-(*p*-methoxyphenyl) sulfide (**18**) and some of **19** through path B. At the same time, **9** also couples with RLi newly formed by the ligand exchange mentioned above and gives **F**. Then 5.6% of **14** is formed by path A. 4.7% of **16** and some of **19** are formed by path B.

Table I. Reactions of 5-Substituted 10,11-Dihydrodibenzo[*b*,*f*]-thiepinium Salts with Aryllithiums

Run	No.	 :S+ R	R′–Li	Products (No. and yield (%))								RH
				Products by path-A				Product by path-B				
				12	13	14	15	16	17	18	19	
1	**9**	C_6H_5–	*p*-$CH_3OC_6H_4$–	18.0	3.8	5.6	17.4	4.7	19.0	25.8	47.2	*a*)
2	**10**	*p*-$CH_3OC_6H_4$–	C_6H_5–	10.6	2.2	18.6		33.6	31.6		66.0	*a*)
3	**9**	C_6H_5–	C_6H_5–			38.3		55.5			52.1	
4	**10**	*p*-$CH_3OC_6H_4$–	*p*-$CH_3OC_6H_4$–				33.6			60.1	64.0	
5	**11**	*o*,*p*-$(CH_3O)_2C_6H_3$–	C_6H_5–			38.0		54.3			57.7	*a*)



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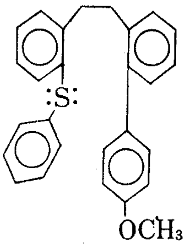

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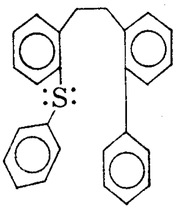

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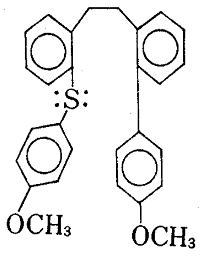

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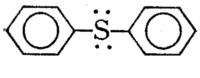

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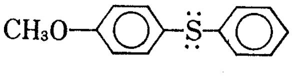

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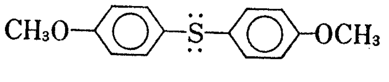

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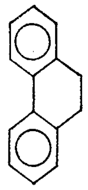

19

a) Were only detected by GLC.

The total yield of **19** obtained from **C-F** is 47.2%. This yield is almost equal to the total yield (49.5%) of sulfides simultaneously formed from **C-F**. This coincidence clearly indicates that **19** is the ring-contraction product by path B.

Runs 2—5 in Table I are also explained in a manner similar to the explanation of Run 1. Thus all the mechanisms of the reactions between sulfonium salts and organolithiums have been clarified by a series of reports presented by us.[1] We are now studying on the reactions between cyclic sulfonium salts and Grignard reagents as well as on the reactions of alkoxides and benzenethiolate in protic solvents. The mechanisms of these reactions are expected to be different from those of the reactions reported in this paper.

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 colomn with a thermal conductivity detector. Preparative thin-layer chromatography was carried out on silica gel (Wako Gel B-10) using solvent A: CH_2Cl_2–*n*-hexane (1: 4) and solvent B: CH_2Cl_2–*n*-hexane (1: 1). Fractions of preparative TLC were represented as Fraction I, Fraction II *etc.*; The *Rf* value decreased in this order. All identification of the compound has been done with respect to IR spectra, mixed melting point and GLC retention time.

10,11-Dihydrodibenzo[*b,f*]thiepin (7)——To a suspension of $LiAlH_4$ (6 g) in anhydrous ether (200 ml) a solution of 10-chloro-10,11-dihydrodibenzo[*b,f*]thiepin (**6**)[4] (35 g) in anhydrous ether (300 ml) was gradually added. After refluxing for 4 hr the reaction mixture was decomposed with water and acidified with dil. HCl and then extracted with ether. The extract was dried ($MgSO_4$) and evaporated. The residue was recrystallized from pet. ether to give colorless prisms (30 g, 99.5%), mp 47—50° (lit.[4] 50°).

10,11-Dihydrodibenzo[*b,f*]thiepin 5-Oxide (8)——A solution of **7** (2.4 g) in AcOH (60 ml) was oxidized by the use of 35% H_2O_2 (1.3 g) with stirring for 2 days at room temperature. The reaction mixture was poured into water and extracted with CH_2Cl_2. The extract was washed with 5% Na_2CO_3 and water, dried (K_2CO_3), and evaporated. The raw crystals (2.6 g) were recrystallized from ether as colorless prisms (2.50 g, 96.8%), mp 106°. *Anal.* Calcd. for $C_{14}H_{12}OS$: C, 73.67; H, 5.30. Found: C, 74.14; H, 5.55. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1030 (SO). NMR ($CDCl_3$) δ: 7.75—8.00 (2H, m, Ar-H), 7.08—7.50 (6H, m, Ar-H), 2.76—3.83 (4H, m, CH_2).

5-Phenyl-10,11-dihydrodibenzo[*b,f*]thiepinium Bromide (9)——A solution of phenylmagnesium bromide prepared from bromobenzene (9.1 g) and Mg (1.37 g) in the usual way. To the Grignard reagent thus prepared **8** (2.2 g) in benzene (100 ml) was added. After refluxing for 45 min the reaction mixture was cooled and decomposed with 25% HBr (25 ml). The benzene layer was separated and washed with 20 ml each of 25% HBr for several times. The washings were combined with the aqueous layer and extracted with CH_2Cl_2. The CH_2Cl_2 extract was dried ($MgSO_4$) and evaporated. Recrystallization of the residue from ether–CH_2Cl_2 gave colorless prisms (0.70 g, 21.4%), mp 210—220°. *Anal.* Calcd. for $C_{20}H_{17}SBr$: C, 65.03; H, 4.64. Found: C, 64.47; H, 4.94. NMR (DMSO-d_6) δ: 7.25—8.45 (13H, m, Ar-H), 2.48—2.64 (4H, m, CH_2).

5-(*p*-Methoxyphenyl)-10,11-dihydrodibenzo[*b,f*]thiepinium Perchlorate (10)——To a mixture of 70% $HClO_4$ (8 ml) and anisole (4.0 g) **8** (2.3 g) was gradually added. After stirring for 7 days, the reaction mixture was poured into water. The resulting precipitate was collected by filtration and rinsed with hot benzene. Recrystallization from MeOH gave colorless prisms (2.7 g, 64.0%), mp 172°. *Anal.* Calcd. for $C_{21}H_{19}O_5SCl$: C, 60.19; H, 4.57. Found: C, 60.26; H, 4.45. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1040—1140 (ClO_4^-). NMR (DMSO-d_6) δ: 7.17—8.30 (12H, m, Ar-H), 3.87 (3H, s, OCH_3), 2.47—2.60 (4H, m, CH_2).

5-(*o,p*-Dimethoxyphenyl)-10,11-dihydrodibenzo[*b,f*]thiepinium Perchlorate (11)——The mixture of 70% $HClO_4$ (8 ml), *m*-dimethoxybenzene (4 g), and **8** (2.3 g) was stirred for 7 days and poured into water. The resulting precipitate was collected by filtration and rinsed with hot benzene. Recrystallization from ether–CH_2Cl_2 gave colorless prisms (3.1 g, 61.5%), mp 164—165°. *Anal.* Calcd. for $C_{22}H_{21}O_6SCl$: C, 58.86; H, 4.71. Found: C, 58.79; H, 4.66. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1050—1150 (ClO_4^-). NMR ($CDCl_3$) δ: 7.45—8.00 (8H, m, Ar-H), 6.68—7.20 (3H, m, Ar-H), 3.90 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 3.03—3.78 (4H, m, CH_2).

Reaction of 9 with *p*-Methoxyphenyllithium (Run 1)——To an ethereal solution of 8 equivalents of *p*-methoxyphenyllithium **9** (1.80 g, 4.88 mmole) was added. After stirring for 8 hr the reaction mixture was decomposed with 5% HCl and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. The residual oil was separated into 5 fractions by preparative TLC using solvent A. Fraction I: An oily product which was obtained was a mixture of diphenyl sulfide (**16**) and 9,10-dihydrophenanthrene (**19**) by GLC analysis, oxidation and desulfurization reactions. Oxidation of the mixture (0.230 g) by the use of 35% H_2O_2 (1 g) yielded diphenyl sulfone (0.025 g, 4.7%). Desulfurization of the mixture (0.230 g) by the use of Raney cobalt prepared from 50% Co-Al alloy (20 g) yielded **19** (0.207 g, 47.2%) as a colorless oil. Fraction II: 1-(*o*-biphenylyl)-2-[*o*-(phenylthio)phenyl]ethane (**14**) (0.100 g, 5.6%), mp 66°, was obtained as colorless prisms by recrystallization from MeOH. *Anal.* Calcd. for $C_{26}H_{22}S$: C, 85.21; H, 6.05. Found: C, 85.05; H, 6.27. NMR (CCl_4) δ: 6.62—7.55 (18H, m, Ar-H), 7.86 (4H, s, CH_2). Mass Spectrum *m/e* (% of base peak): 366(M^+, 100), 201(16), 200(31), 199(92), 198(36), 197(97), 184(19), 168(19), 167(56), 166(53), 165(77), 152(35). Desulfurization of **14** (0.480 g) with Raney cobalt prepared from 50% Co-Al alloy (30 g) yielded 2-phenetylbiphenyl (**20**) (0.320 g) as a colorless oil. *Anal.* Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 93.25; H, 7.00. NMR (CCl_4) δ: 6.74—7.47 (14H, m, Ar-H), 2.53—2.96 (4H, m, CH_2). Fraction III: *p*-Methoxyphenyl phenyl sulfide (**17**) (0.318 g) was obtained as a colorless oil. Oxidation of **17** (0.318 g) with 35% H_2O_2 (1.0 g) gave 4-methoxyphenyl phenyl sulfone (0.230 g, 19.0%), mp 83—84° (lit.[5] 90—90.4°) as colorless leaflets by recrystallization from ether. *Anal.* Calcd. for $C_{13}H_{12}O_3S$: C, 62.90; H, 4.87. Found: C, 62.68; H, 4.91. IR ν_{max}^{KBr} cm^{-1}: 1315, 1150 (SO_2). NMR ($CDCl_3$) δ: 7.77—8.07 (2H, m, Ar-H), 7.83 (2H, d, J=9.0 Hz, Ar-H), 7.40—7.64 (3H, m, Ar-H), 6.99 (2H, d, J=9.0 Hz, Ar-H), 3.86 (3H, s, OCH_3). Fraction IV: A mixture (0.420 g, 21.8%) of 1-(*o*-biphenylyl)-2-[*o*-(*p*-methoxyphenylthio)phenyl]ethane (**12**) and 1-(4′-methoxy-*o*-biphenylyl)-2-[*o*-(phenylthio)phenyl]ethane (**13**) was obtained as a colorless oil. *Anal.* Calcd. for $C_{27}H_{24}OS$: C, 81.79; H, 6.10. Found: C, 81.52; H, 6.18. Mass Spectrum *m/e*: 396(M^+). Desulfurization of a mixture (0.350 g) of **12** and **13** was carried out with Raney cobalt prepared from 50% Co-Al alloy (30 g). Separation of the product by preparative TLC using pet. ether gave **20** (0.170 g) and 4-methoxy-2′-phenethylbiphenyl (**21**) (0.055 g). Fraction V: A mixture which was obtained was separated into 1-(4′-methoxy-*o*-biphenylyl)-2-[*o*-(*p*-methoxyphenylthio)phenyl]ethane (**15**) (0.355 g, 17.4%) and a mixture (0.435 g) of 4,4′-dimethoxybiphenyl and bis(*p*-methoxyphenyl) sulfide (**18**) by preparative TLC using pet. ether. Oxidation of the mixture (0.435 g) of 4,4′-dimethoxybiphenyl and **18** with 35% H_2O_2 (1.6 g) was conducted. Separation of the product by preparative TLC using solvent B gave bis(*p*-methoxyphenyl) sulfone (0.350 g, 25.8%) and 4,4′-dimethoxybiphenyl. Bis(*p*-methoxyphenyl) sulfone was recrystallized from ether to give colorless prisms mp 130° (lit.[6] 128°). *Anal.* Calcd. for $C_{14}H_{14}O_4S$: C, 60.43; H, 5.07. Found: C, 60.13; H, 5.18. NMR ($CDCl_3$) δ: 7.90 (4H, d, J=9.0 Hz, Ar-H), 6.99(4H, d, J=9.0 Hz, Ar-H), 3.87 (6H, s, OCH_3). Compound **15** was recrystallized from MeOH as colorless prisms, mp 78°. *Anal.* Calcd. for $C_{28}H_{26}O_2S$: C, 78.85; H, 6.14. Found: C, 78.73; H, 6.08. NMR (CCl_4) δ: 6.72—7.35 (16H, m, Ar-H), 3.80 (6H, s, OCH_3), 2.89 (4H, s, CH_2). Mass Spectrum *m/e* (% of base peak): 426(M^+, 93), 230(17), 229(85), 228(26), 227(96), 198(32), 197(100), 196 (20), 195(17), 166(25), 165(34), 152(22). Desulfurization of **15**: Desulfurization of an EtOH solution (50 ml) of **15** (0.190 g) with Raney cobalt prepared from 50% Co-Al alloy (20 g) resulted in the formation of **21** (0.140 g) as a colorless oil. *Anal.* Calcd. for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.07; H, 6.79. NMR (CCl_4) δ: 6.80—7.29 (13H, m, Ar-H), 3.85 (3H, s, OCH_2), 2.56—2.98 (4H, m, CH_2).

Reaction of 10 with Phenyllithium (Run 2)——Compound **10** (2.0 g, 4.77 mmole) was allowed to react with 8 equivalents of phenyllithium. The same treatment of the reaction mixture as mentioned above gave a raw reaction product. Separation by preparative TLC using solvent A afforded 4 fractions. Fraction I: A mixture (0.910 g) was obtained. Oxidation of the mixture (0.370 g) with 35% H_2O_2 (1 g) yielded diphenyl sulfone (0.140 g). Desulfurization of the mixture (0.540 g) with Raney cobalt gave **19** (0.330 g). Fraction II: **14** (0.325 g, 18.6%). Fraction III: Compound **17** (0.360 g, 31.6%) was obtained as a colorless oil and led to sulfone derivative (0.352 g) by oxidation with 35% H_2O_2. Fraction IV: A mixture (0.240 g, 12.8%) of **12** and **13** was obtained as a colorless oil. A part of the mixture (0.190 g) was desulfurized with Raney cobalt to give **20** (0.097 g) and **21** (0.002 g).

Reaction of 9 with Phenyllithium (Run 3)——Compound **9** (1.0 g, 2.71 mmole) was allowed to react with 8 equivalents of phenyllithium and the reaction mixture was treated as mentioned above. The resulting oily product was separated into 2 fractions by preparative TLC using pet. ether. Fraction I: A mixture (0.635 g) of biphenyl, **16** and **17**. Oxidation of the mixture (0.300 g) with 35% H_2O_2 yielded diphenyl sulfone (0.155 g). Desulfurization of the mixture (0.300 g) with Raney cobalt afforded **19** (0.120 g). Fraction II: **14** (0.380 g, 38.3%).

Reaction of 10 with *p*-Methoxyphenyllithium (Run 4)——Compound **10** (2.0 g, 4.78 mmole) was allowed to react with 8 equivalents of *p*-methoxyphenyllithium. A crude product was obtained in the same way as mentioned above. Separation by preparative TLC using pet. ether gave 3 fractions. Fraction I: **19** (0.550 g, 64.0%). Fraction II: A mixture (0.945 g) of 4,4′-dimethoxybiphenyl and **18** was obtained. Oxidation of the mixture (0.450 g) afforded bis(*p*-methoxyphenyl) sulfone (0.380 g). Fraction III: **15** (0.685 g, 33.6%).

Reaction of 11 with Phenyllithium (Run 5)——Compound **11** (2.00 g, 4.46 mmole) was allowed to react with 8 equivalents of phenyllithium. The raw product was obtained in the same manner as mentioned above. *m*-Dimethoxybenzene was detected by GLC analysis of the product. Separation by preparative TLC using pet. ether gave 2 fractions. Fraction I: A mixture (1.055 g) of biphenyl, **15**, and **19** was obtained. A part of the mixture (0.500 g) was oxidized with 35% H_2O_2 and resulted in diphenyl sulfone (0.250 g). Desulfurization of the mixture (0.500 g) with Raney cobalt gave **19** (0.220 g). Fraction II:,**14** (0.620 g, 38.0%).

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