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Dibenzothiepin Derivatives and Related Compounds. V.[1] Reactions of 6,11-Dihydrodibenzo[*b*,*e*]thiepin 5-Oxides with $SbCl_5$ and Perchloric Acid[2]

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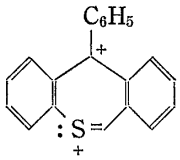
Reactions of sulfides with $SbCl_5$ or perchloric acid were examined. Sulfoxides having no α-hydrogens produced very stable 1:1 adducts of them and $SbCl_5$. On the other hand, sulfoxides having α-hydrogens formed the intermediates of sulfonium or carbonium ion. In the reactions of benzyl phenyl sulfoxide (**12**) and 11-phenyl-6,11-dihydrodibenzo-[*b*,*e*]thiepin 5-oxide (**21a**) the intermediates reacted with MeONa to give sulfides substituted by a methoxy group at α-position.

A novel transannular reaction and an intramolecular 1,2-rearrangement of the intermediate were found in the reaction of 11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin-11-ol 5-oxide (**26**) or 11-methoxy-11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin 5-oxide (**34**). The bridged sulfonium intermediate (**32**) was isolated in good yield from the reaction of **26** or **34** with perchloric acid. The mechanism of the reactions was discussed.

Keywords——transannular reaction; bridged sulfonium salt; intramolecular 1,2-rearrangement; Stevens type rearrangement; 6,11-dihydrodibenzothiepin 5-oxides; sulfoxide-$SbCl_5$ adducts

In the previous paper, the reactivities of 6,11-dihydrodibenzo[*b*,*e*]thiepin derivatives were reported.[1,4–6] The authors have been interested in the synthesis of 11-phenyldibenzo[*b*,*e*]-thiepinium dication (**1**). During the course of the investigation on the reaction of 6,11-dihydrodibenzo[*b*,*e*]thiepin 5-oxides with $SbCl_5$ or perchloric acid, we unexpectedly found a novel transannular reaction and an intramolecular 1,2-rearrangement of the product.



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This paper deals with the transannular reaction and the rearrangement together with the reactions of some sulfoxides with $SbCl_5$ or perchloric acid.

Reactions of Sulfoxides and $SbCl_5$

It is known that mercaptans, sulfides and disulfides react with $SbCl_5$ to give very unstable sulfonium salts.[7] However, the reactions of sulfoxides and $SbCl_5$ have not been reported yet, so the reaction was carried out and was classified into two categories according as the sulfoxides have or do not have α-hydrogens adjacent to the S–O group.

Diphenyl sulfoxide (**2**), dibenzothiophene 5-oxide (**3**), 10,11-dihydro- (**4**) and 10,11-dimethyldibenzo[*b*,*f*]thiepin 5-oxide (**5**) were chosen as the compounds having no α-hydrogen and allowed to react with 2—3 eq of $SbCl_5$ for 2 hr. The reactions afforded the stable yellow products (**6**—**9**) and their analytical data showed that they were 1:1 adducts of sulfoxides and $SbCl_5$, respectively. In their IR spectra a new band due to the Sb-Cl bond appeared at

1) Part IV: M. Hori, T. Kataoka, H. Shimizu, and K. Onogi, *Yakugaku Zasshi*, **98**, in press (1978).
2) A part of this work was presented at the 91st Annual Meeting of Pharmaceutical Society of Japan, April, 1971, Fukuoka and the 5th Congress of Heterocyclic Chemistry, November, 1972, Gifu.
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4) M. Hori, T. Kataoka, H. Shimizu, and K. Onogi, *Yakugaku Zasshi*, **98**, 1189 (1978).
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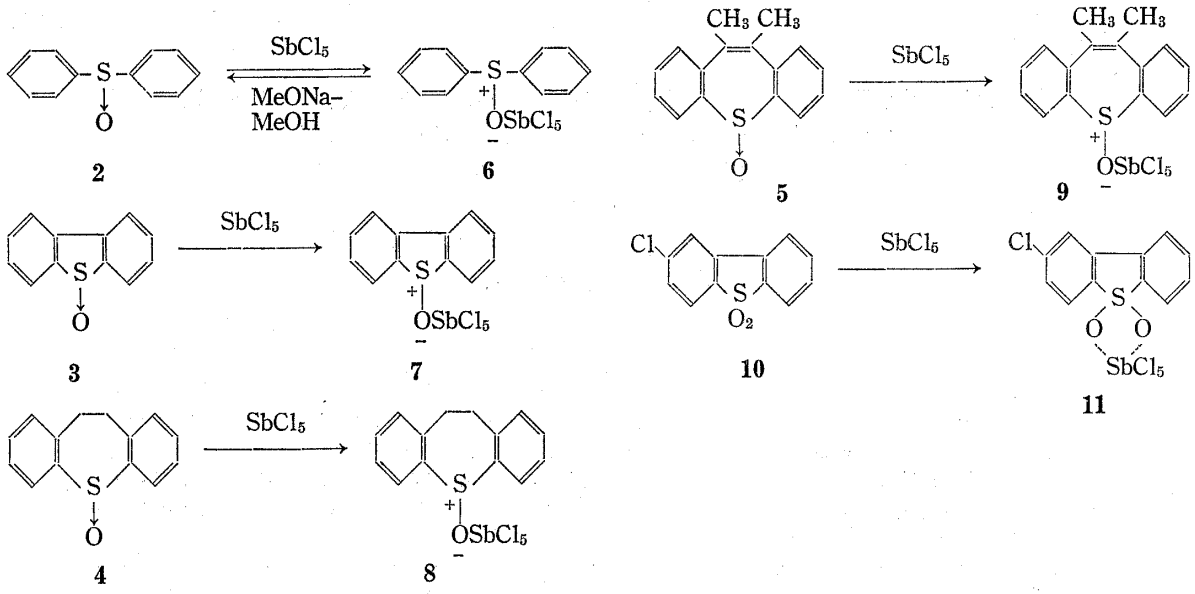


Chart 1

340 cm^{-1} [8] and a characteristic absorption band of sulfoxides at 1030 cm^{-1} shifted downfield by 150—200 cm^{-1}. Their NMR spectra showed the same appearance as those of the original sulfoxides except for the downfield shift of the whole absorption. Additionally the reaction of the compound **6** with MeONa gave the corresponding original sulfoxide (**2**). These data confirmed that the compounds (**6**—**9**) were the adducts of the sulfoxides and $SbCl_5$, in which the oxygen atom of the sulfoxide and $SbCl_5$ formed a coordinate bond.

In order to compare the reactivity of the sulfoxides and the sulfones against $SbCl_5$ 2-chlorodibenzothiophene 5,5-dioxide (**10**) was allowed to react under the same conditions as the sulfoxides. The 1:1 adduct of **10** and $SbCl_5$ was obtained as a yellow powder in 43.9% yield. Its IR spectrum exhibited a new strong absorption at 850 cm^{-1} and no absorption bands at 1305 and 1170 cm^{-1} due to the SO_2 group. This finding showed the SO_2 group and $SbCl_5$ bound each other. However, **11** was hydroscopic and very unstable compared with **7** synthesized from **3**. The difference is attributable to the difference of the mode of bonding between sulfoxides and sulfones.

On the other hand, benzyl phenyl sulfoxide (**12**) which has the partial structure of 6,11-dihydrodibenzo[*b*,*e*]thiepin 5-oxides was chosen as the sulfoxide having α-hydrogens and allowed to react with $SbCl_5$ under the same conditions as mentioned above. The authors could not isolate the products but obtained the deep red solution only. Decomposition of the solution with MeONa–MeOH afforded some products such as benzyl phenyl sulfide (**16**, 11.4%), α-meth-

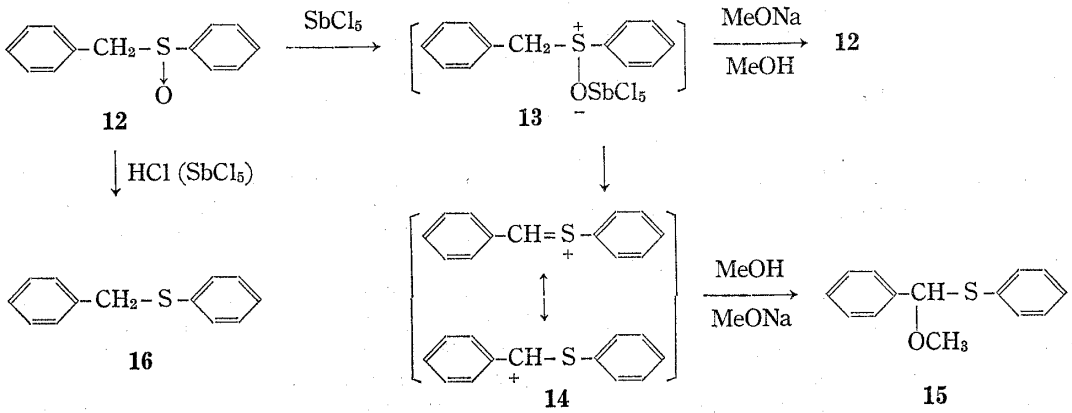


Chart 2

oxybenzyl phenyl sulfide (**15**, 16.2%) and **12** (49.0%). The reaction may progress by way of the following mechanism. The compound **12**, on the reaction with $SbCl_5$, gave the adduct **13** which was decomposed by MeONa to give **12**. Carbonium ion intermediate (**14**) was formed from **13** and reacted with MeONa to afford **15**. HCl formed from $SbCl_5$ reduced **12** into the sulfide **16**. The result of this reaction showed that a carbonium ion intermediate such as **14** was formed by the reaction of the sulfoxide having α-hydrogen and $SbCl_5$ and suggested that it might be possible to synthesize the dication **1** from the cyclic sulfoxides having α-hydrogens.

Reactions of 6,11-Dihydrodibenzo[*b*,*e*]thiepin-11-one 5-Oxide (17) and 11-Phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin 5-Oxides (21a and 21b) with $SbCl_5$

The authors began with the reactions of **17** and **21** with $SbCl_5$ for the synthetic approach to **1**. When **17** was treated with an excess of $SbCl_5$ in $MeNO_2$ overnight, a yellow product (**18**), mp 122—123° (dec.), $C_{14}H_{10}Cl_5O_2SSb$ was obtained in 57.4% yield. In its IR spectrum an absorption of the carbonyl group at 1645 cm^{-1} appeared in the same place, but an absorption of the S–O group shifted to 875 cm^{-1}. This showed that **18** was not a dicationic compound (**19**), but a 1:1 adduct of **17** and $SbCl_5$, in which $SbCl_5$ bound to the S–O moiety. In addition, the reaction of **18** with MeOH containing water afforded **17** almost quantitatively. 11-Phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin (**20**), on oxidation with equimolecular amount of H_2O_2, gave two kinds of sulfoxides (**21a** and **21b**). Product **21a**, $C_{20}H_{16}OS$, mp 226—228°, exhibited an absorption band at 1020 cm^{-1} due to the S–O group in the IR spectrum and a pair of doublet at δ 4.79 and 3.95 (J=13 Hz) ascribable to the CH_2 group at C_6 position in the NMR spectrum. Product **21b**, $C_{20}H_{16}OS$, mp 140—141° exhibited an absorption band at 1040 cm^{-1} in its IR spectrum and a pair of doublet at δ 4.27 and 3.97 (J=13 Hz) due to the CH_2 group at C_6 position in its NMR spectrum. Oxidation of the compounds, **21a** and **21b** with H_2O_2 afforded the same sulfone (**22**). These data showed **21a** and **21b** are the isomers, but the stereostructure of these two isomers were not able to be determined. The reaction of **21a** with $SbCl_5$ in CH_2Cl_2 at an ice-bath temperature gave only a dark red solution though many attempts to isolate the product were carried out. The solution was treated with

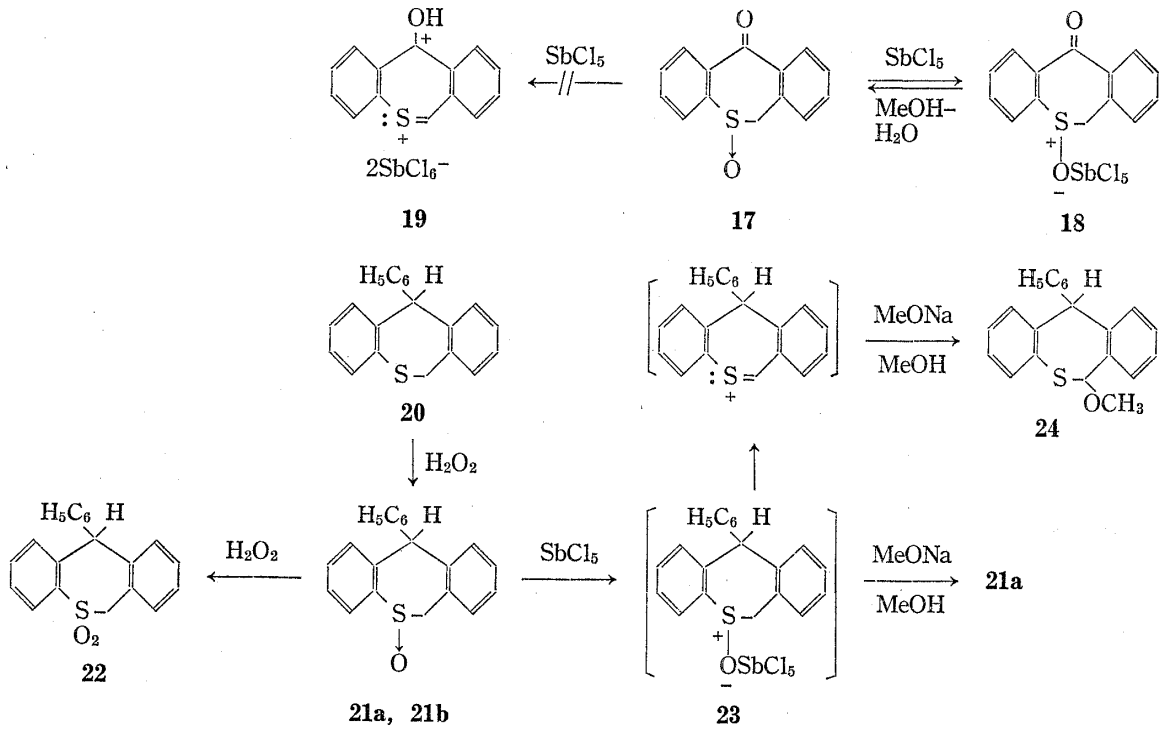


Chart 3

MeONa in MeOH. Separation of the products by column chromatography on alumina gave 6-methoxy-11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin (**24**), mp 124.5—126° as colorless prisms in 18.9% yield and **21a**, mp 225—227° in 22.5% yield. The reaction may progress *via* an intermediate (**23**) by the same mechanism as that of **12**, but in this case a product **20** could not be isolated. The compound **24** was identified by comparison of the melting point, IR and NMR spectra with an authentic sample synthesized by alternative route.[1)]

Reactions of 11-Phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin-11-ol 5-Oxide (25) and 11-Methoxy-11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin 5-Oxide (34) with $SbCl_5$ and Perchloric Acid

As **1** could not be isolated from the reaction of **21a** and $SbCl_5$ another attempt was made to synthesize **1** from **26** or **34** which were more active than **21a** against $SbCl_5$ or perchloric acid. Oxidation of 11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin-11-ol (**25**) and 11-methoxy-11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin (**33**) with an equimolecular amount of H_2O_2 gave **26**, mp 235—237°, colorless needles (38.0%) and **34**, mp 154—155°, colorless prisms (74.1%), respectively. Compounds, **26** and **34** reacted with 4 eq of $SbCl_5$ at room temperature for 3 hr to give a dark green solution but not to afford the precipitate. Treatment of the solution with MeONa–MeOH or MeOH–Et_3N gave an unexpected product, 6,11-epoxy-11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin (**31**) in 97.2% or 88.2% yield, respectively. Structural identification of **31** was made by comparison with the melting point and IR spectrum of the authentic sample. On the other hand, reactions of **26** and **34** with perchloric acid in CH_2Cl_2 at room temperature for 2 hr formed a dark green solution and then afforded colorless prisms, mp 219—221° (dec.), $C_{20}H_{15}ClO_5S$. Its spectral data were: IR (KBr) cm^{-1}: 1120, 1070 (ClO_4^-). NMR (CF_3CO_2H) δ: 8.51—8.12 (1H, m, ArH), 4.35 (1H, d, J=18 Hz, C_6–H). In addition, the product reacted with bases such as Et_3N and *n*-butylamine at room temperature or with

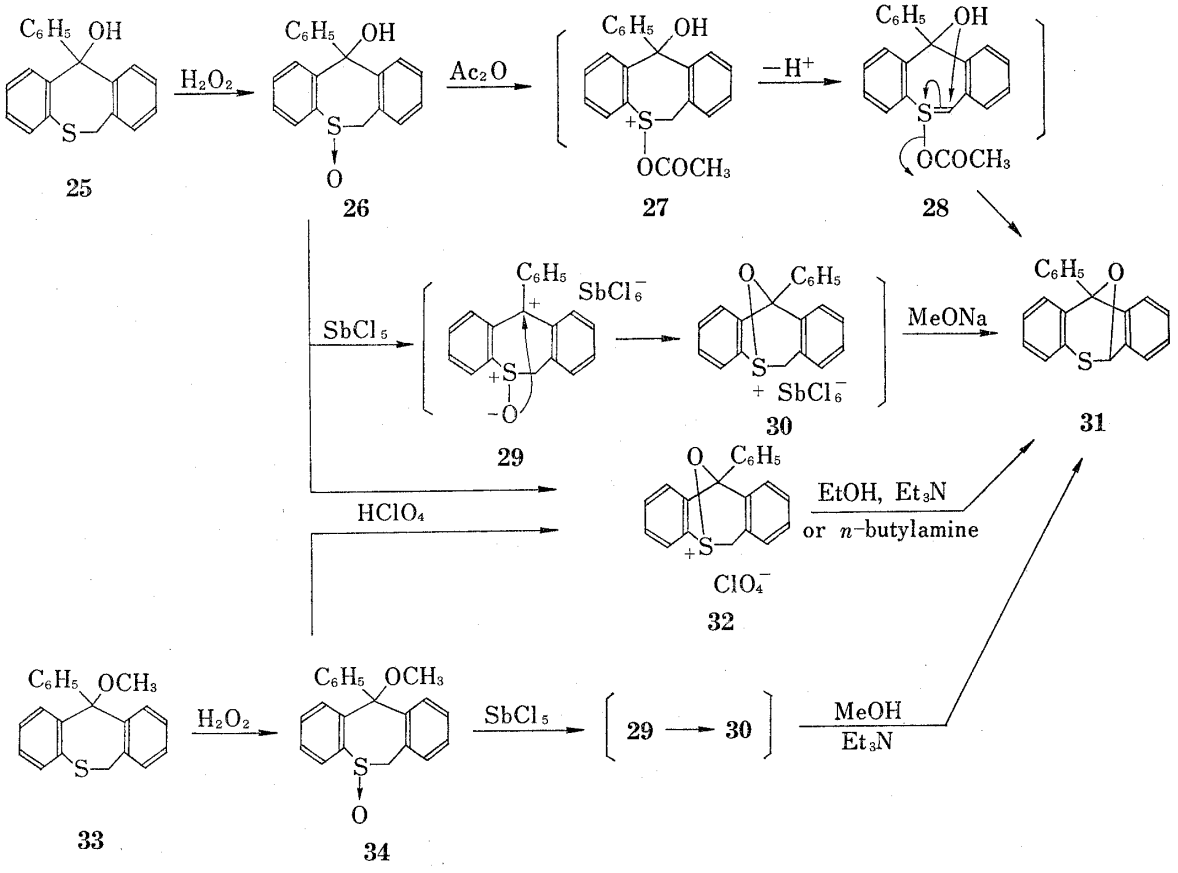
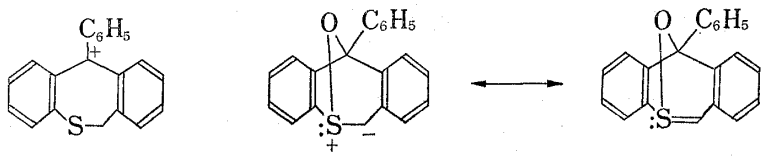


Chart 4

hot EtOH to give **31** almost quantitatively or in 80.2% yield, respectively. From these data it was determined to be 5,11-epoxy-11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepinium perchlorate (**32**).

The mechanism of this reaction may progress as follows. Compounds **26** and **34** reacted with $SbCl_5$ or perchloric acid to form a dark green solution which was very similar to that of 11-phenyl-6,11-dihydrobenzo[*b*,*e*]thiepin-11-ylium cation (**35**). Therefore, it could be presumed that a cation **29** was first formed by the removal of a hydroxy or a methoxy group at C_{11} position and the oxygen atom of the S–O group attacked nucleophilically at C_{11} position to produce the bridged sulfonium salt (**30**). Leonard *et al.* have reported the similar transannular reaction of seven or eight-membered cyclic keto sulfoxides,[9] but in his case the products were very unstable. The transannular product (**30**) was readily depronated and generated the intermediate **36** which could be stabilized by the ylene-ylide resonance and easily underwent



35 : X=ClO_4^-, BF_4^-, $SbCl_6^-$ **36**

the intramolecular 1,2-shift to give **31**. On the rearrangement of **30** the intermolecular rearrangement products which have methoxy, ethoxy or *n*-butylamino group could not be detected. The results of these experiments showed the rearrangement was not the Pummerer type reaction but the Stevens type reaction. Additionally the reaction of **26** and acetic anhydride was carried out with expectation of the Pummerer reaction in the same way as 6,11-dihydrodibenzo[*b*,*e*]thiepin 5-oxides.[10] However, an unexpected product **31** was obtained in 72.5% yield. The reaction mechanism could be estimated as given below by considering that the reaction between **24** and acetic anhydride did not proceed under the same conditions. Acetic anhydride attacked the S–O group to form the intermediate **27** which was converted into another intermediate **28** by deprotonation. In the intermediate **28** an attack on C_6 position by the hydroxy group at C_{11} position was preferable to that by acetate anion and resulted in the formation of **31**. Therefore, the oxygen atom of the epoxy bridge was derived from the hydroxy group at C_{11} position. The result of this reaction was different from that of **26** or **34** with $SbCl_5$ or perchloric acid.

Application of the transannular reaction described above to the synthesis of drugs will be reported in a succeeding paper.

Experimental[11]

Reaction of Diphenyl Sulfoxide (2) and $SbCl_5$——A solution of **2** (4.37 g) in $MeNO_2$ (30 ml) was added dropwise to a solution of $SbCl_5$ (7.97 g) in $MeNO_2$ (10 ml) with stirring at room temperature. After the reaction mixture was stirred for 2 hr, a precipitate was collected by filtration and dried. Diphenyl sulfoxide–$SbCl_5$ adduct (**6**) was obtained as pale yellow prisms (7.29 g, 70.4%), mp 143—145°. *Anal.* Calcd. for $C_{12}H_{10}Cl_5OSSb$: C, 28.75; H, 2.02. Found: C, 28.76; H, 2.00. IR ν_{max}^{KBr} cm^{-1}: 860 (S–O–$SbCl_5$), 340 (Sb–Cl). NMR ($CDCl_3$) δ: 8.07—7.56 (10H, m, ArH).

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10) K. Sindelar and M. Protiva, *Collect. Czech. Chem. Commun.*, **35**, 3328 (1970).
11) Melting points were uncorrected. IR spectra were recorded with a JASCO Model IRA-1. NMR spectra were measured by Hitachi R-20B spectrometer and chemical shifts were given in ppm relative to tetramethylsilane as an internal standard.

Reaction of 6 with MeONa in MeOH——To a solution of MeONa (1.08 g) in dry MeOH (50 ml) was added **6** (2.01 g) in dry CH_2Cl_2 (15 ml). After stirring the reaction mixture for 2 hr at room temperature water was added to it and it was extracted with CH_2Cl_2. The extract was washed with water, dried ($MgSO_4$) and evaporated. The residue was recrystallized from ether–pet. ether to give **2** (0.71 g, 80.7%) as colorless prisms, mp 66—68°. This sample was identified with an authentic sample by admixture and by comparison of their IR spectra.

Reaction of Dibenzothiophene 5-Oxide (3) and $SbCl_5$——To a solution of **3** (0.60 g) in $MeNO_2$ (5 ml) was added dropwise a solution of $SbCl_5$ (1.59 g) in $MeNO_2$ (5 ml). After stirring the reaction mixture for 2 hr at room temperature a yellow precipitate was filtered, washed with $MeNO_2$ and dried. Dibenzothiophene 5-oxide–$SbCl_5$ adduct (**7**) was given as yellow powder (1.32 g, 88.3%), mp 241—243°, (dec.). *Anal.* Calcd. for $C_{12}H_8Cl_5OSSb$: C, 28.86; H, 1.61. Found: C, 29.13; H, 1.63. IR ν_{max}^{KBr} cm^{-1}: 855, 830 (S–O–$SbCl_5$), 342 (Sb–Cl).

Reaction of 10,11-Dihydrodibenzo[*b*,*f*]thiepin 5-Oxide (4) and $SbCl_5$——A solution of **4** (1.14 g) in $MeNO_2$ (6 ml) was treated with $SbCl_5$ (2.06 g) in $MeNO_2$ (4 ml) for 2 hr at room temperature. A precipitate was collected, washed with $MeNO_2$ and dried (P_2O_5) under reduced pressure. The adduct of **4** and $SbCl_5$ (**8**) was given as yellow powder (1.86 g, 70.6%), mp 180—182° (dec.). A part of it was recrystallized from $CHCl_3$ to give yellow prisms, mp 188—190° (dec.). *Anal.* Calcd. for $C_{14}H_{12}Cl_5OSSb$: C, 31.88; H, 2.29. Found: C, 31.68; H, 2.29. IR ν_{max}^{KBr} cm^{-1}: 830 (S–O–$SbCl_5$), 342 (Sb–Cl). NMR ($CDCl_3$) δ: 8.33—8.02 (2H, m, ArH), 7.82—7.32 (6H, m, ArH), 3.58 (4H, s, CH_2).

Reaction of 10,11-Dimethyldibenzo[*b*,*f*]thiepin 5-Oxide (5) and $SbCl_5$——An adduct of **5** and $SbCl_5$ was prepared from **5** (0.51 g) and $SbCl_5$ (1.36 g) in a similar manner as above. The product **9** was recrystallized from $CHCl_3$ as yellow prisms (0.95 g, 85.5%), mp 192—193° (dec.). *Anal.* Calcd. for $C_{16}H_{14}Cl_5OSSb$: C, 34.73; H, 2.55. Found: C, 34.67; H, 2.60. IR ν_{max}^{KBr} cm^{-1}: 900 (S–OSbCl_5). NMR ($CDCl_3$) δ: 8.22—7.90 (2H, m, ArH), 7.87—7.50 (6H, m, ArH), 2.48 (6H, s, CH_3).

Reaction of 2-Chlorodibenzothiophene 5,5-Dioxide (10) and $SbCl_5$——An adduct (**11**) was prepared from **10** (0.66 g) and $SbCl_5$ (2.58 g) in a similar manner as above. The product **11** was isolated as yellow powder (0.63 g, 43.9%), mp>300° (dec.). *Anal.* Calcd. for $C_{12}H_7Cl_6O_2SSb$: C, 26.21; H, 1.28. Found: C, 25.88; H, 1.32. IR ν_{max}^{KBr} cm^{-1}: 850 (SO_2–$SbCl_5$), 340 (Sb–Cl).

Reaction of Benzyl Phenyl Sulfoxide (12) and $SbCl_5$——To a solution of $SbCl_5$ (12.15 g) in dry CH_2Cl_2 (20 ml) was added **12** (4.33 g) in dry CH_2Cl_2 (80 ml). The reaction mixture was stirred at room temperature for 3 hr, poured into a solution of MeONa (20 g) in dry MeOH (200 ml) and extracted with CH_2Cl_2. The extract was washed with water, dried ($MgSO_4$) and evaporated. The residue was separated by column chromatography on silica gel. Benzyl phenyl sulfide (**16**) (0.45 g, 11.4%) and α-methoxybenzyl phenyl sulfide (**15**) (0.28 g, 6.2%) were obtained from the pet. ether eluate. From the CH_2Cl_2 fraction **12** (2.12 g, 49.0%) was obtained. These three compounds were identified with authentic samples by comparison of their IR spectra, respectively.

Reaction of 6,11-Dihydrodibenzo[*b*,*e*]thiepin-11-one 5-Oxide (17) and $SbCl_5$——To a solution of **17** (1.21 g) in $MeNO_2$ (10 ml) was added $SbCl_5$ (2.13 g) and the reaction mixture was stirred at room temperature overnight. An adduct **18** was obtained by filtration and recrystallized from $CHCl_3$ as yellow prisms (1.55 g, 57.4%), mp 122—123° (dec.). *Anal.* Calcd. for $C_{14}H_{10}Cl_5O_2SSb$: C, 31.06; H, 1.87. Found: C, 31.25; H, 1.19. IR ν_{max}^{KBr} cm^{-1}: 1645 (CO), 875 (S–O–$SbCl_5$).

Decomposition of 18 by Methanolic Water——MeOH (20 ml) was added to a solution of **18** (1.55 g) in CH_2Cl_2 (20 ml) and the mixture was stirred at room temperature for 2 hr. Water was added to the mixture and it was extracted with CH_2Cl_2. The extract was washed with water, dried ($MgSO_4$) and evaporated. Recrystallization of the residue from EtOH gave **17** as colorless prisms (0.69 g, 99.7%), mp 102—104°. The sample was identical with an authentic sample in all respects.

11-Phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin 5-Oxide (21)——A solution of 11-phenyl-6,11-dihydrodibenzo-[*b*,*e*]thiepin (**20**)[5] (5.77 g) in CH_2Cl_2 (120 ml) was oxidized with 35% H_2O_2 (1.94 g) in AcOH (40 ml). The reaction mixture was stirred at room temperature for 48 hr and water was added to it. The aqueous solution was extracted with CH_2Cl_2. The extract was washed with water, dried ($MgSO_4$) and evaporated. The residue was recrystallized from EtOH to give colorless prisms (**21a**) (2.50 g, 41.1%), mp 226—228°. *Anal.* Calcd. for $C_{20}H_{16}OS$: C, 78.90; H, 5.30. Found: C, 78.66; H, 5.34. IR ν_{max}^{KBr} cm^{-1}: 1020 (S–O). NMR ($CDCl_3$) δ: 8.15—7.80 (1H, m, ArH), 8.72—7.06 (10H, m, ArH), 7.06—6.70 (2H, m, ArH), 5.42 (1H, s, C_{11}–H), 4.79 (1H, d, J=13Hz, C_6–H), 3.95 (1H, d, J=13 Hz, C_6–H). The residue obtained from the filtrate was recrystallized from ether and then a mixture of benzene–hexane to afford colorless prisms (**21b**) (2.06 g, 33.9%), mp 140—141°. *Anal.* Calcd. for $C_{20}H_{16}OS$: C, 78.90; F, 5.30. Found: C, 78.68; H, 5.23. IR ν_{max}^{KBr} cm^{-1}: 1040 (S–O). NMR ($CDCl_3$) δ: 8.26—7.75 (1H, m, ArH), 7.65—6.99 (10H, m, ArH), 6.99—6.65 (2H, m, ArH), 5.42 (1H, s, C_{11}–H), 4.27 (1H, d, J=13 Hz, C_6–H), 3.97 (1H, d, J=13 Hz, C_6–H).

Oxidation of 21——a) To a solution of **21a** (0.61 g) in CH_2Cl_2 (10 ml) was added 35% H_2O_2 (1.00 g) in AcOH (30 ml) and the mixture was stirred at room temperature for 48 hr. Water was added to the mixture and it was extracted with CH_2Cl_2. The extract was washed with water, dried ($MgSO_4$) and evaporated. The residue was recrystallized from EtOH to give 11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin 5,5-dioxide (**22**) as colorless prisms (0.57 g, 89.5%), mp 249—251°. *Anal.* Calcd. for $C_{20}H_{16}O_2S$: C, 74.97; H, 5.03.

Found: C, 74.84; H, 5.16. IR ν_{max}^{KBr} cm^{-1}: 1310, 1165, 1135 (SO_2). NMR ($CDCl_3$) δ: 8.32—7.88 (1H, m, ArH), 7.06—6.64 (2H, m, ArH), 5.46 (1H, s, C_{11}–H), 4.60 (1H, d, J=15 Hz, C_6–H), 3.95 (1H, d, J=15 Hz, C_6–H).

b) A solution of **21b** (0.30 g) in CH_2Cl_2 (5 ml) was oxidized with 35% H_2O_2 (0.50 g) in AcOH (15 ml) in the same way as oxidation of **21a**. The product (**22**) was recrystallized from EtOH to give colorless prisms (0.26 g, 80.9%), mp 247—249°, which was identical with the sample obtained from oxidation of **21a** by admixture and by comparison of their IR spectra.

Reaction of 21a and $SbCl_5$——A solution of $SbCl_5$ (5.86 g) in CH_2Cl_2 (10 ml) was added at an ice-bath temperature to a solution of **21a** (1.19 g) in CH_2Cl_2 (20 ml). After stirring for 30 min the mixture was poured into a large excess of MeOH containing MeONa and then water was added to it. The aqueous solution was extracted with CH_2Cl_2. The extract was washed with water, dried ($MgSO_4$) and evaporated. The residual oil was purified by column chromatography on alumina. Recrystallization of the material eluted by CH_2Cl_2–hexane (1: 2) afforded 6-methoxy-11-phenyl-6,11-dihydro[*b*,*e*]thiepin (**24**) as colorless prisms (0.24 g, 18.9%), mp 124.5—126°. *Anal.* Calcd. for $C_{21}H_{18}OS$: C, 79.20; H, 5.70. Found: C, 79.32; H, 5.89. This sample was identified with an authentic sample[1] synthesized from 6-chloro-11-phenyl-6,11-dihydrodibenzo[*b*,*e*]-thiepin. From the CH_2Cl_2 fraction **21a** was obtained as colorless prisms, (0.27 g, 22.5%), mp 225—227°, which was identical with an authentic sample by comparison of mixed melting point and their IR spectra.

11-Phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin-11-ol 5-Oxide (**26**)——To a solution of 11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin-11-ol (**25**)[5] (12.18 g) in CH_2Cl_2 (250 ml) was added 35% H_2O_2 (3.89 g) in AcOH (125 ml) and after stirring for 72 hr water was added to the reaction mixture. The product was extracted with CH_2Cl_2, washed with water, dried and evaporated. The residue was dissolved in ether and allowed to stand overnight to give a colorless solid. Recrystallization from EtOH gave colorless needles (4.87 g, 38.0%). mp 235—237°. *Anal.* Calcd. for $C_{20}H_{16}O_2S$: C, 74.96; H, 5.03. Found: C, 74.76; H, 4.99. IR ν_{max}^{KBr} cm^{-1}: 3260 (OH), 1000 (S–O). NMR ($CDCl_3$) δ: 8.26—7.96 (2H, m, ArH), 7.64—6.93 (1H, m, ArH), 4.23 (1H, d, J=15 Hz, C_6–H), 3.77 (1H, d, J=15 Hz, C_6–H), 2.82—2.65 (1H, broad s, OH).

11-Methoxy-11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin 5-Oxide (**34**)——A solution of 11-methoxy-11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin (**33**)[5] (9.59 g) in CH_2Cl_2 (70 ml) was oxidized with 35% H_2O_2 (2.93 g) in AcOH (30 ml) as the same way as mentioned above. The raw product (7.45 g) was recrystallized from MeOH to give colorless prisms (6.27 g, 62.3%), mp 154—155°. *Anal.* Calcd. for $C_{21}H_{18}O_2S$: C, 75.41; H, 5.43. Found: C, 75.41; H, 5.45. IR ν_{max}^{KBr} cm^{-1}: 1070 (C–O), 1025 (S–O). NMR ($CDCl_3$) δ: 8.14—7.76 (3H, m, ArH), 7.67—6.96 (10H, m, ArH), 6.92 (3H, s, OCH_3), 4.45 (1H, d, J=16 Hz, C_6–H), 3.78 (1H, d, J=16 Hz, C_6–H).

Reaction of 26 and $SbCl_5$——To a solution of **26** (1.60 g) in dry CH_2Cl_2 (50 ml) was added a solution of $SbCl_5$ (5.25 g) in dry CH_2Cl_2 (10 ml). After stirring at room temperature for 3 hr the mixture was poured into MeOH (100 ml) containing MeONa (10 g) and refluxed for 30 min. Water was added to the mixture and it was extracted with CH_2Cl_2. The extract was washed with water, dried and evaporated. The residue was purified by column chromatography on alumina using CH_2Cl_2 as a solvent. 6,11-Epoxy-11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepin (**31**) was recrystallized from EtOH as colorless prisms (1.47 g, 97.2%), mp 143—144°. The sample was identical with an authentic sample[6] by comparison of their melting points and IR spectra.

Reaction of 34 and $SbCl_5$——To a solution of **34** (1.67 g) in CH_2Cl_2 (20 ml) was added a solution of $SbCl_5$ (4.98 g) in CH_2Cl_2 (20 ml) and the reaction mixture was stirred for 3 hr at room temperature. To the mixture was added a solution of Et_3N (10 ml) in dry MeOH (50 ml) and then water. The aqueous solution was extracted with CH_2Cl_2. The extract was washed with water, dried and evaporated. The residue was purified by column chromatography on alumina. A CH_2Cl_2 fraction gave **31** which was recrystallized from EtOH to afford colorless prisms (1.33 g, 88.2%), mp 141.5—143°. The sample was identical with a sample from the reaction of **26** and $SbCl_5$.

Reaction of 34 and Perchloric Acid——To a solution of **4** (2.91 g) in CH_2Cl_2 (80 ml) was added dropwise 70% $HClO_4$ (5 ml). After the reaction mixture was stirred for 2 hr at room temperature, the aqueous layer was removed and the CH_2Cl_2 layer was washed with water, dried and evaporated. 5,11-Epoxy-11-phenyl-6,11-dihydrodibenzo[*b*,*e*]thiepinium perchlorate (**32**) was recrystallized from CH_2Cl_2–pet. ether as colorless prisms (3.10 g, 86.4%), mp 219—221° (dec.). *Anal.* Calcd. for $C_{20}H_{15}ClO_5S$: C, 59.61; H, 3.75. Found: C, 59.61; H, 3.69. IR ν_{max}^{KBr} cm^{-1}: 1140, 1110, 1070 (ClO_4^-). NMR (CF_3CO_2H) δ: 8.51—8.12 (1H, m, ArH), 8.12—7.12 (12H, m, ArH), 5.43 (1H, d, J=18 Hz, C_6–H), 4.35 (1H, d, J=18 Hz, C_6–H).

Reaction of 26 and Perchloric Acid——A solution of **26** (0.64 g) in CH_2Cl_2 (40 ml) was allowed to react with 70% perchloric acid (2 ml) for 0.5 hr at room temperature. After the aqueous layer was separated, the CH_2Cl_2 layer was washed with water and concentrated. The residue was recrystallized from CH_2Cl_2–pet. ether to give **32** as colorless prisms (0.85 g, 100%), mp 217—220° (dec.). The sample was identified with the sample synthesized from **34** and perchloric acid.

Rearrangement of 32 to 31——a) A solution of **32** (0.40 g) in dry CH_2Cl_2 (20 ml) was treated with Et_3N (1 ml) for 30 min at room temperature. Water was added to the mixture and it was extracted with CH_2Cl_2. The extract was dried and evaporated to give **31** as colorless powder (0.28 g, 93.4%) which was identified with an authentic sample obtained from **26** and $SbCl_5$.

b) A solution of **32** (0.28 g) in CH_2Cl_2 (10 ml) was allowed to react with *n*-butylamine (0.26 g) for 30 min at room temperature. The reaction mixture was washed with water, dried and evaporated. The residual powder was recrystallized from EtOH to afford **31** as colorless prisms (0.20 g, 97.4%), mp 142—144°, which was identified with the sample obtained from a).

c) Compound **32** (0.84 g) was dissolved in hot EtOH and allowed to stand overnight. The precipitate was collected by filtration. The product **31** was obtained as colorless prisms (0.50 g, 80.2%), mp 141—142.5°.

Reaction of 26 and Acetic Anhydride——A mixture of **26** (1.28 g) and acetic anhydride (30 ml) was refluxed with stirring for 3 hr. The cooled solution was evaporated under reduced pressure to give the yellow oil. After purification of the oil **38** was obtained as colorless prisms (0.88 g, 72.5%) and identified with an authentic sample.