

## Dibenzothiepin Derivatives and Related Compounds. II.<sup>1)</sup> A Novel Cyclization Reaction of 6-Chloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepins<sup>2)</sup>

MIKIO HORI, TADASHI KATAOKA, HIROSHI SHIMIZU, and KAZUHIRO ONOGI

*Gifu College of Pharmacy*<sup>3)</sup>

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By the reaction of 11-chloro-11-phenyl- (II) and 11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (III) with NCS 6,11-dichloro- (I) and 6-chloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (XV) were prepared, respectively. The compound (I) reacted with water or aqueous ammonia to afford a new heterocyclic compound, 6,11-epoxy-(V) or 6,11-epimino-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (VIII), respectively. On heating in proper solvent, I or XV underwent a novel cyclization to form a bridged compound (IX, XIII or XIV). The radical mechanism for the new cyclization was proposed.

**Keywords**—6,11-dihydrodibenzo[*b,e*]thiepin derivative; thermal cyclization reaction; bridged compound; epoxy compound; epimino compound

The chemistry of thiepins has become of interest in recent years. In the previous paper, as part of a study on the chemistry of 6,11-dihydrodibenzo[*b,e*]thiepin derivatives, the synthesis of 11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin-11-ylum salts and their novel dehydrocyclization reaction were reported.<sup>1)</sup>

We wish to report here the preparation of 6-chloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepins, their reactions with some nucleophiles and their novel cyclization to the corresponding bridged compounds.

### Preparation of 6,11-Dichloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (I) and Its Reaction with Some Nucleophiles

By the treatment of 11-chloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (II)<sup>1)</sup> with N-chlorosuccinimide (NCS)<sup>4)</sup> in CCl<sub>4</sub> or benzene for 4 hr, 6,11-dichloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (I) was prepared. Although I was moderately stable in CCl<sub>4</sub> or benzene solution, it was unstable to be isolated. The preparation of I from the reaction of 11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (III) with 2 eq of NCS was unsuccessful, namely, the NMR spectrum of the reaction mixture revealed the decomposition of the thiepin ring. The structural assignment of I was mainly based on the NMR spectroscopic data which showed a singlet signal of C<sub>6</sub>-H at  $\delta$  5.81 in CCl<sub>4</sub>.

The compound, I reacted with some nucleophiles as shown in Chart 1. The treatment of I with MeOH-Et<sub>3</sub>N afforded nearly 3:2 mixture of two isomers of 6,11-dimethoxy-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (IV) which could be separated nicely by recrystallization from benzene-*n*-hexane. One isomer is colorless prisms having mp 148–150° and the other isomer is colorless prisms having mp 143–144°. They are assumed to be *cis* and *trans* configurational isomers due to the methoxyl groups at 6- and 11-positions of IV by comparison

1) Part I: M. Hori, T. Kataoka, H. Shimizu, and K. Onogi, *Yakugaku Zasshi*, **98**, (1978), in press.

2) A part of this work was presented at a) the 5th Congress of Heterocyclic Chemistry, Gifu, Nov., 1972, Abstracts of Papers p.81: b) the 97th Annual Meeting of Pharmaceutical Society of Japan, Tokyo, Apr., 1977, Abstracts of Papers p. 7.

3) Location: 5-6-1, *Mitahora-Higashi*, Gifu 502, Japan.

4) D.L. Tuleen and R.H. Bennett, *J. Heterocycl. Chem.*, **6**, 115 (1969); D.L. Tuleen and T.B. Stephens, *J. Org. Chem.*, **34**, 31 (1969).

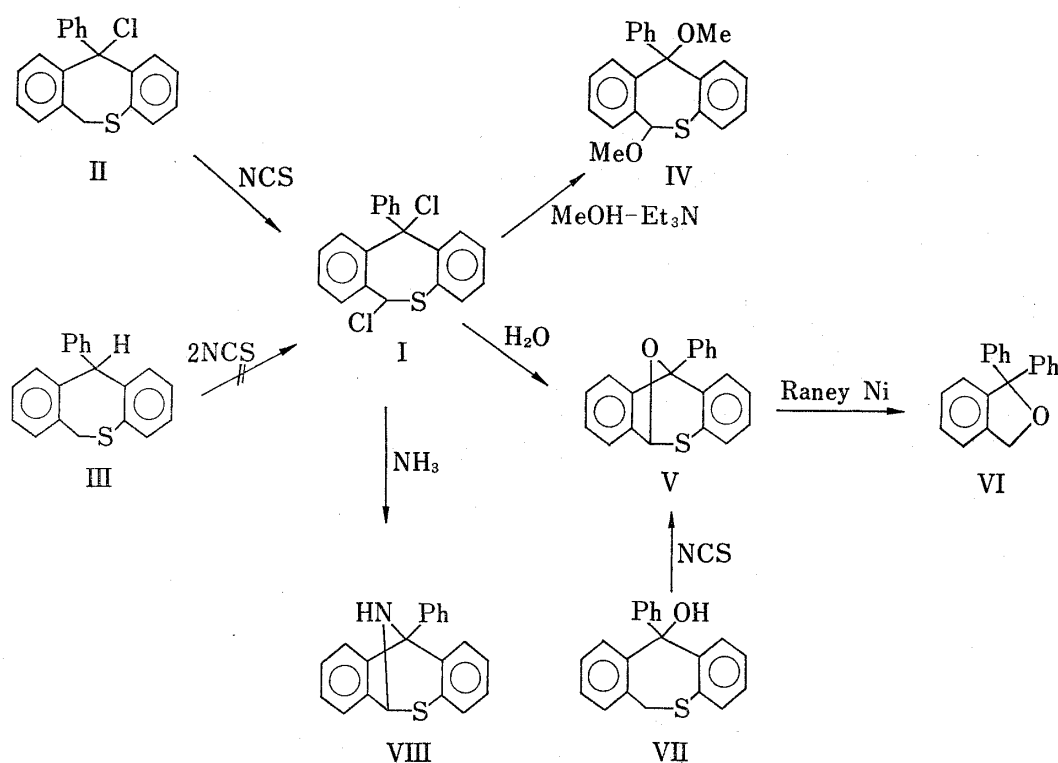


Chart 1

of their NMR spectra. Refluxing a CCl<sub>4</sub> solution of I with water for 2 hr gave 6,11-epoxy-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (V) as colorless prisms having mp 141–142.5° in 55.2% yield. The structure of V was determined by the spectroscopic and analytical data, and also chemically confirmed by desulfurization reaction using Raney Ni (W-7) to yield 1,1-diphenyl-1,3-dihydroisobenzofuran (VI). Epoxy compound (V) was also obtained from the reaction of 11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin-11-ol (VII) and NCS. By the treatment of I with aqueous ammonia, an expected 6,11-epimino-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (VIII) was yielded in 98% yield.

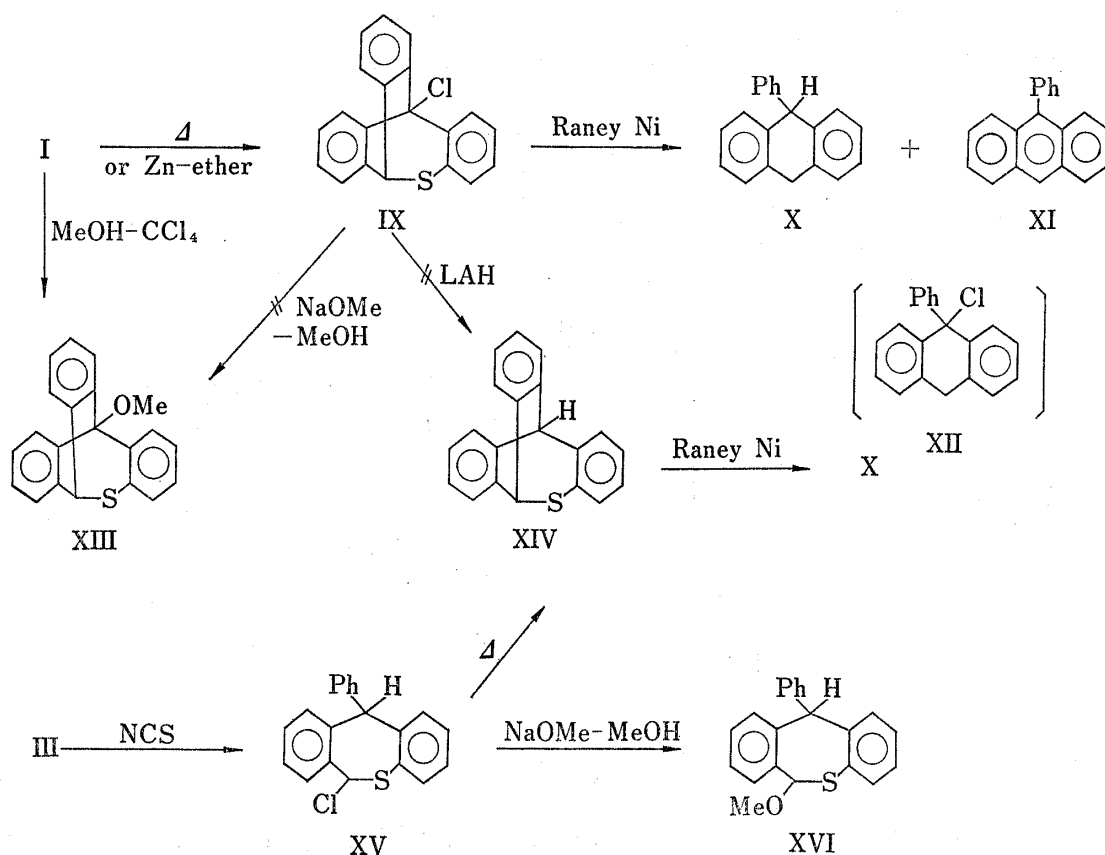
#### Novel Cyclization Reaction of 6-Chloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepins

A CCl<sub>4</sub> solution of I was concentrated *in vacuo* to give a yellow oil, which became dark, and then yellow with the evolution of hydrogen chloride on exposure to air. The resulting yellow solid was heated further at 150° for 30 min to afford colorless prisms in 75.5% yield. The NMR spectrum possessed a singlet (1H) at  $\delta$  4.91, a multiplet (9H) at  $\delta$  6.65–7.55, a multiplet (2H) at  $\delta$  7.83–8.17, and a multiplet (1H) at  $\delta$  8.17–8.45. The mass spectrum showed a molecular ion at *m/e* 321. In order to elucidate the structure of the compound, desulfurization reaction using Raney Ni (W-7) in EtOH was carried out yielding a mixture of 9,10-dihydro-9-phenylanthracene (X)<sup>5)</sup> and 9-phenylanthracene (XI)<sup>5,6)</sup> in a ratio of 1:1. Thus, the structure of the compound was assigned to 6,11-(*o*-benzeno)-11-chloro-6,11-dihydrodibenzo[*b,e*]thiepin (IX). The bridged compound (IX) did not react with nucleophiles such as LiAlH<sub>4</sub>, sodium methoxide and so on. This chemical inertness of chlorine atom of IX may be due to the fact that it is attached to the bridgehead carbon. Therefore, the formation of X may be explained by initial desulfurization of IX followed by reductive dechlorination of the resulting XII.

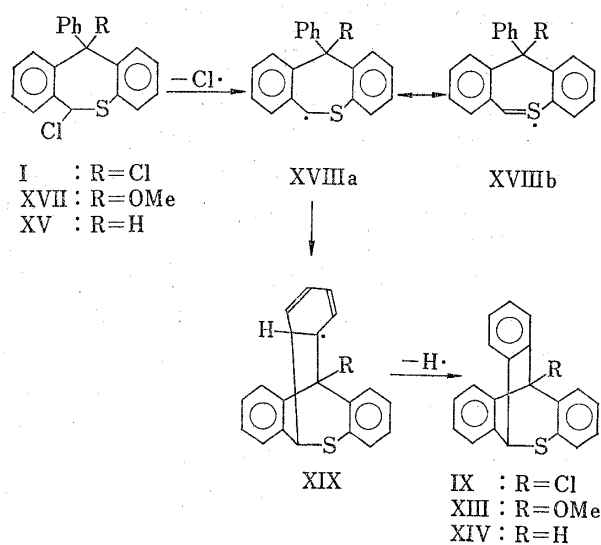
Although 6,11-(*o*-benzeno)-11-methoxy-6,11-dihydrodibenzo[*b,e*]thiepin (XIII) was not obtained from the reaction of IX with sodium methoxide, I reacted with boiling MeOH to

5) M.P. Cava, M. J. Mitchell, and A.A. Deana, *J. Org. Chem.*, **25**, 1481 (1960).

6) E. Clar and D.G. Stewart, *J. Am. Chem. Soc.*, **74**, 6235 (1952).



give the bridged compound, XIII. This result is explained by the assumption that the replacement of chlorine atom by methoxide anion occurred in preference to cyclization. Bridged compound (IX) was also formed under the conditions of the Gomberg reaction<sup>7)</sup> which is well known as a radical reaction. Namely, when a solution of I in  $\text{CCl}_4$  and dry ether was refluxed in the presence of zinc dust, IX was obtained in 34.2% yield.



The similar cyclization reaction occurred when 6-chloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (XV) was heated. Compound XV was prepared by stirring III with an equimolecular amount of NCS in  $\text{CCl}_4$  at room temperature for 4 hr, and it was found to be stable at room temperature in contrast with an unstable nature of I. Compound XV reacted with sodium methoxide in MeOH to give 6-methoxy-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (XVI) in 36% yield. On heating at  $180^\circ$  for 1 hr, XV changed to 6,11-(*o*-benzeno)-6,11-dihydrodibenzo[*b,e*]thiepin (XIV) in 51.2% yield with the evolution of hydrogen chloride. The desulfurization reaction of XIV using Raney Ni (W-7) afforded 9-phenyl-9,10-dihydroanthracene (X).

7) M. Gomberg, *J. Am. Chem. Soc.*, **22**, 757. (1900); M. Hori, T. Kataoka, H. Shimizu and C.-F. Hsü, *Chem. Lett.*, 1973, 391.

From the fact that the above cyclization reaction also occurred under the conditions of the Gomberg reaction as described in the formation of IX from I, and the deep color characteristic of radical was observed during the reaction, we propose the radical mechanism for the thermal cyclization reaction of 6-chloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin derivatives to bridged compounds as shown in Chart 3. A chlorine radical is ejected from 6-chloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin derivative (I, XVII or XV) and the resulting thiepinyl radical (XVIII), which is stabilized by resonance with the adjacent sulfur atom, subsequently attacks the *ortho*-position of the phenyl group at the C-11-position to form a second radical intermediate (XIX) which aromatizes with the loss of a hydrogen radical to give the corresponding bridged compound (IX, XIII or XIV).

### Experimental

Melting points were taken on a Yanagimoto micromelting point apparatus and are uncorrected. Infrared spectra were determined on a JASCO Model IRA-1. Nuclear magnetic resonance (NMR) spectra were determined on a Hitachi R-20B spectrometer and chemical shifts are given in parts per million relative to tetramethylsilane as an internal standard. Mass spectra were taken on a Hitachi RMU-6E spectrometer at an ionizing voltage of 70 eV.

**6,11-Dichloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (I)**—To a solution of 11-chloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (II)<sup>1)</sup> (1.61 g) in CCl<sub>4</sub> (20 ml) *N*-chlorosuccinimide (NCS) (0.67 g) was added in one portion and then the mixture was stirred for 4 hr at room temperature. The precipitated succinimide was removed by filtration to give the CCl<sub>4</sub> solution of I. NMR (CCl<sub>4</sub>)  $\delta$ : 5.81 (1H, s, C<sub>6</sub>-H), 6.89—7.54 (1H, m, ArH), 7.59—7.84 (1H, ArH), 8.10—8.50 (1H, m, ArH).

**Reaction of I with MeOH in the Presence of Et<sub>3</sub>N**—To a solution of I prepared from II (3.23 g) and NCS (1.34 g) in CCl<sub>4</sub> (40 ml) a solution of Et<sub>3</sub>N (3 ml) in MeOH (30 ml) was added and the mixture was refluxed for 2 hr. After cooling, the reaction mixture was washed with water, dried over MgSO<sub>4</sub> and evaporated to give 6,11-dimethoxy-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (IV) (3.47 g, 99.6%) which was found to be a mixture of two isomers in a ratio of 3:2 by NMR spectrum. The mixture was recrystallized from benzene-*n*-hexane to give one isomer as colorless prisms, mp 148—150°. *Anal.* Calcd. for C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>S: C, 75.83; H, 5.79. Found: C, 75.66; H, 5.77. IR  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 1070, 1100 (C—O). NMR (CDCl<sub>3</sub>)  $\delta$ : 3.06 (3H, s, C<sub>11</sub>-OCH<sub>3</sub>), 3.54 (3H, s, C<sub>6</sub>-OCH<sub>3</sub>), 5.51 (1H, s, C<sub>6</sub>-H), 7.00—7.78 (13H, m, ArH). MS *m/e*: 348 (M<sup>+</sup>). The filtrate was concentrated and the residue was recrystallized from MeOH-benzene to give the other isomer as colorless prisms, mp 143—144°. *Anal.* Calcd. for C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>S: C, 75.83; H, 5.79. Found: C, 75.92; H, 5.82. IR  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 1050, 1075 (C—O). NMR (CDCl<sub>3</sub>)  $\delta$ : 3.06 (3H, s, C<sub>11</sub>-OCH<sub>3</sub>), 3.31 (3H, s, C<sub>6</sub>-OCH<sub>3</sub>), 5.21 (1H, s, C<sub>6</sub>-H), 7.12—8.04 (13H, m, ArH). MS *m/e*: 348 (M<sup>+</sup>).

**Hydrolysis of I**—To a solution of I prepared from II (1.61 g) and NCS (0.67 g) in CCl<sub>4</sub> (20 ml) water (20 ml) was added and the mixture was refluxed for 2 hr. After cooling, the reaction mixture was extracted with CCl<sub>4</sub>. The extract was washed with water, and dried over MgSO<sub>4</sub>. The solvent was evaporated to afford 1.34 g of a crude oil which was recrystallized from EtOH to give 6,11-epoxy-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (V) as colorless prisms (0.84 g, 55.2%), mp 141—142.5°. *Anal.* Calcd. for C<sub>20</sub>H<sub>14</sub>O<sub>2</sub>S: C, 79.45; H, 4.67. Found: C, 79.49; H, 4.64. IR  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 1000 (C—O). NMR (CDCl<sub>3</sub>)  $\delta$ : 6.55 (1H, s, C<sub>6</sub>-H), 6.82—7.13 (4H, m, ArH), 7.20—7.60 (7H, m, ArH), 7.60—7.85 (2H, m, ArH). MS *m/e*: 302 (M<sup>+</sup>).

**Desulfurization of V**—To Raney Ni (W-7) (4g) prepared from 20% NaOH (32 ml) and Raney alloy (8 g) a solution of V (1.51 g) in absolute EtOH (50 ml) was added. After the mixture had been stirred under reflux for 3 hr, the reaction mixture was filtered during hot and the filtrate was allowed to stand overnight to precipitate 1,1-diphenyl-1,3-dihydroisobenzofuran (VI) as colorless prisms (0.46 g, 33.8%), mp 100—101° which was further recrystallized from EtOH to give an analytical sample as colorless prisms, mp 103—104°. *Anal.* Calcd. for C<sub>20</sub>H<sub>16</sub>O: C, 88.20; H, 5.92. Found: C, 88.16; H, 5.94. IR  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 1025 (C—O). NMR (CDCl<sub>3</sub>)  $\delta$ : 5.15 (2H, s, CH<sub>2</sub>), 7.08—7.52 (14H, m, ArH).

**Reaction of 11-Phenyl-6,11-dihydrodibenzo[*b,e*]thiepin-11-ol (VII)<sup>1)</sup> with NCS**—A mixture of VII (12.18 g) and NCS (5.34 g) in CH<sub>2</sub>Cl<sub>2</sub> (160 ml) was stirred for 3 hr at room temperature. To this reaction mixture Et<sub>3</sub>N (20 ml) was added and stirred for 30 min. The solvent was evaporated *in vacuo* and the residue was extracted with ether to separate off the ether insoluble material.

The ether extract was washed with water, 2% HCl, water, 10% K<sub>2</sub>CO<sub>3</sub> and water successively, dried over MgSO<sub>4</sub> and evaporated. The residue was recrystallized from EtOH to give V as colorless needles (10.97 g, 91%), mp 142—144° which on admixture with the sample obtained by hydrolysis of I showed no depression in melting point. *Anal.* Calcd. for C<sub>20</sub>H<sub>14</sub>O<sub>2</sub>S: C, 79.45; H, 4.67. Found: C, 79.26; H, 4.68.

**Ammonolysis of I**—To a solution of I prepared from II (3.23 g) and NCS (1.34 g) in CCl<sub>4</sub> (40 ml) 28% aqueous ammonia (50 ml) was added and the mixture was stirred for 1 hr at room temperature and refluxed for 2 hr. The cooled reaction mixture was extracted with CCl<sub>4</sub> and the extract was washed with water and dried over MgSO<sub>4</sub>. The solvent was removed and the resulting oil was chromatographed on

silica gel using  $\text{CH}_2\text{Cl}_2$  as the eluent to provide 6,11-epimino-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (VIII) as colorless powder (2.95 g, 98%), mp 65–66°. *Anal.* Calcd. for  $\text{C}_{20}\text{H}_{15}\text{NS}$ : C, 79.69; H, 5.02. Found: C, 79.84; H, 5.23. IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 3350, 3200 (NH). NMR ( $\text{CCl}_4$ )  $\delta$ : 2.12 (1H, br. s, NH), 5.62 (1H, s,  $\text{C}_6\text{-H}$ ), 6.77–7.73 (13H, m, ArH).

**Thermolysis of I**—A solution of I prepared from II (3.23 g) and NCS (1.34 g) in  $\text{CCl}_4$  (40 ml) was concentrated under reduced pressure on a steam bath. The yellow oil resulted turned black then yellow and crystallized with the evolution of hydrogen chloride. The yellow solid was further heated to 150° for 30 min and extracted with  $\text{CHCl}_3$ . The extract was washed with water, dried over  $\text{MgSO}_4$  and evaporated. The residual solid was recrystallized from benzene-*n*-hexane to give 6,11-(*o*-benzeno)-11-chloro-6,11-dihydrodibenzo[*b,e*]thiepin (IX) as colorless prisms (2.42 g, 75.5%), mp 240–242°. *Anal.* Calcd. for  $\text{C}_{20}\text{H}_{13}\text{ClS}$ : C, 74.87; H, 4.08; Cl, 11.05; S, 9.99. Found: C, 74.95; H, 4.18; Cl, 11.15; S, 9.82. NMR ( $\text{CDCl}_3$ )  $\delta$ : 4.91 (1H, s,  $\text{C}_6\text{-H}$ ), 6.65–7.75 (9H, m, ArH), 7.83–8.17 (2H, m, ArH), 8.17–8.45 (1H, m, ArH). MS *m/e*: 321 ( $\text{M}^+$ ).

**Desulfurization of IX**—Raney Ni (W-7) (4 g) prepared from 20% NaOH (32 ml) and Raney alloy (8 g) was added to a solution of IX (1.60 g) in absolute EtOH (50 ml) and the mixture was refluxed with stirring for 3 hr. The reaction mixture was filtered during hot and the filtrate was concentrated. NMR spectrum of the resulting solid (1.15 g, 90.4%) showed that it was a mixture of 9,10-dihydro-9-phenylanthracene (X) and 9-phenylanthracene (XI) in a ratio of 1:1. A part of the solid was recrystallized from *n*-hexane to give X as colorless prisms, mp 80.5–82° (reported<sup>5</sup>) mp 86–87°. *Anal.* Calcd. for  $\text{C}_{20}\text{H}_{16}$ : C, 93.71; H, 6.29. Found: C, 93.55; H, 6.41. NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.92 (2H, s,  $\text{CH}_2$ ), 5.18 (1H, s,  $\text{C}_9\text{-H}$ ), 6.90–7.35 (13H, m, ArH). MS *m/e*: 256 ( $\text{M}^+$ ) and XI as colorless prisms, mp 151–152° (reported<sup>5</sup>) 154–156°. *Anal.* Calcd. for  $\text{C}_{20}\text{H}_{14}$ : C, 94.45; H, 5.55. Found: C, 94.45; H, 5.64. NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.04–8.20 (13H, m, ArH), 8.47 (1H, s,  $\text{C}_{10}\text{-H}$ ). MS *m/e*: 254 ( $\text{M}^+$ ). UV  $\lambda_{\text{max}}^{\text{MeOH}}$  nm: 255, 336, 346, 364, 384.

**Reaction of I with Zinc Dust in Ether (Gomberg Reaction)**—To a suspension of zinc dust in dry ether a solution of I prepared from II (1.61 g) and NCS (0.67 g) in  $\text{CCl}_4$  (20 ml) was added and the mixture was stirred at room temperature for 4 hr under a nitrogen stream. Zinc dust was removed by filtration and the filtrate was concentrated. The residue was chromatographed on alumina using benzene as the eluent and recrystallized from benzene-pet. ether to afford IX as colorless prisms (0.55 g, 34.2%), mp 237–240°. This compound was identified by the comparison of the IR and NMR spectra with those of an authentic sample which was provided by thermolysis of I.

**Methanolysis of I**—Absolute MeOH (40 ml) was added to a solution of I prepared from II (3.23 g) and NCS (1.34 g) in  $\text{CCl}_4$  (60 ml). The mixture was stirred at room temperature for 1 hr and refluxed for 2 hr. After water was added, the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The extract was washed with water, dried over  $\text{MgSO}_4$  and evaporated. The residual oil was chromatographed on silica gel using ether-*n*-hexane as the eluent and the resulting solid was recrystallized from benzene-*n*-hexane to afford 6,11-(*o*-benzeno)-11-methoxy-6,11-dihydrodibenzo[*b,e*]thiepin (XIII) as colorless prisms (0.53 g, 16.7%), mp 185–187°. *Anal.* Calcd. for  $\text{C}_{21}\text{H}_{16}\text{OS}$ : C, 79.71; H, 5.10. Found: C, 79.67; H, 5.22. IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 1050 (C–O). NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.44 (3H, s,  $\text{OCH}_3$ ), 4.92 (1H, s,  $\text{C}_6\text{-H}$ ), 6.62–7.68 (11H, m, ArH), 8.02–8.22 (1H, m, ArH).

**6-Chloro-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (XV)**—NCS (0.67 g) was added to a solution of 11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (III) (1.44 g) in  $\text{CCl}_4$  (30 ml) with stirring and the mixture was stirred at room temperature for 4 hr. The reaction mixture was cooled with ice for 1 hr, and the precipitated succinimide was removed by filtration. The filtrate was concentrated to give XV as a yellow oil in quantitative yield. NMR ( $\text{CCl}_4$ )  $\delta$ : 5.41 (1H, s,  $\text{C}_{11}\text{-H}$ ), 6.18 (1H, s,  $\text{C}_6\text{-H}$ ), 6.75–7.68 (13H, m, ArH).

**Reaction of XV with NaOMe in MeOH**—A solution of XV which was prepared from III (1.44 g) and NCS (0.67 g) in  $\text{CCl}_4$  (30 ml) as described above was added dropwise to a solution of NaOMe (2 g) in MeOH (40 ml). After stirring for 1 hr, the reaction mixture was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$ . The extract was washed with water, dried over  $\text{MgSO}_4$  and evaporated. The residue was recrystallized from nitromethane to give 6-methoxy-11-phenyl-6,11-dihydrodibenzo[*b,e*]thiepin (XVI) as colorless prisms (0.57 g, 36%), mp 121–122°. *Anal.* Calcd. for  $\text{C}_{21}\text{H}_{18}\text{OS}$ : C, 79.20; H, 5.70. Found: C, 79.30; H, 5.67. IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 1080 (C–O), NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.35 (3H, s,  $\text{OCH}_3$ ), 5.45 (1H, br. s,  $\text{C}_{11}\text{-H}$ ), 5.53 (1H, s,  $\text{C}_6\text{-H}$ ), 6.87–7.65 (13H, m, ArH).

**Thermolysis of XV**—A benzene solution of XV was prepared from III (4.47 g) and NCS (2.07 g) in benzene (100 ml) as described above. The solvent was removed under reduced pressure, and the residue was heated at 180° for 1 hr. After cooling, the resulting solid was purified by recrystallization from EtOAc two times to afford 6,11-(*o*-benzeno)-6,11-dihydrodibenzo[*b,e*]thiepin (XIV) as colorless prisms (2.27 g, 51.2%), mp 217–218°. *Anal.* Calcd. for  $\text{C}_{20}\text{H}_{14}\text{S}$ : C, 73.88; H, 4.93; S, 11.09. Found: C, 83.72; H, 4.97; S, 11.04. NMR ( $\text{CDCl}_3$ )  $\delta$ : 4.82 (2H, s,  $\text{C}_{11\text{ and }6\text{-H}}$ ), 6.62–7.54 (12H, m, ArH). In the NMR spectrum of XIV in  $\text{CDCl}_3$ -DMSO- $d_6$  the signal at  $\delta$  4.82 was separated into two signals which appeared at  $\delta$  5.01 and 5.14. MS *m/e*: 286 ( $\text{M}^+$ ).

**Desulfurization of XIV**—A mixture of XIV (1.63 g) and Raney Ni (W-7) (4 g) in absolute EtOH (50 ml) was heated under reflux with stirring for 3 hr. The hot reaction mixture was filtered and the filtrate was concentrated. The residue was recrystallized from *n*-hexane to give X as colorless prisms (0.79 g, 54.7%), mp 81–82°. It was identified by the comparison of the IR and NMR spectra with those of an authentic sample.