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TRITHIOCYCLOPROPENIUM ION AS A BUILDING BLOCK FOR NITROGEN HETEROCYCLE SYNTHESIS

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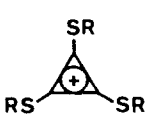
Abstract: A new methodology for heterocycle synthesis using trithiocyclopropenium salt as a building bock is described. Tris(*tert* -butylthio)cyclopropenium perchlorate (1) reacts with β-amino acids under basic conditions to give 1,2-dihydropyridines, where cyclopropenium salt serves as the three carbon homologator in heterocyclic ring formation. The selective syntheses of 1,5-benzodiazepines and benzimidazoles from 1 are also described. Reaction of 1 with *o*-phenylenediamines in dimethylformamide gives 1,5-benzodiazepines as a single product but in methanol benzimidazoles. The selective formation of 1,5-benzodiazepines and benzimidazoles could be accounted for by the solvent participation in the cyclization step.

So far chemistry of cyclopropenium ion has been investigated from the keen interest in peculiar properties due to the aromatic but highly strained ring structure.[3] Although recent papers[4] have reported the ring expansion reactions with some nucleophiles, its synthetic utility has not been extensively explored for lack of simple and efficient preparation method of cyclopropenium ions and of way to control the stability and reactivity. At present trithiocyclopropenium ions[5] are very easily prepared in large scale from tetrachlorocyclopropene and mercaptane by appling our strategy on one step synthesis of triaminocyclopropenium ion.[2c] Trithiocyclopropenium ion, for example, tris(*tert*-butylthio)cyclopropenium ion (1, the perchlorate form) is stable enough for handling and reactive for various nucleophiles at the appropriate condition. The trithiocyclopropenyl system (1) has D_{3h} symmetry with respect to the $C_3^+S_3$ and 1245-1260 cm^{-1} values of the asymmetric ring deformation mode (E') which correlates to the value of K_{C-C} (force constant for the C-C bond of the C_3 core).[6] The E' value for trithiocyclopropenium ion is smaller than those of other trisubstituted cyclopropenium ions (e.g. E': 1553 for Me_2N-, 1446 for CH_3-, 1441 for Ph-, 1321 for Cl-), indicating that the C-C bond of 1 should be weak compared with these cyclopropenium ions. The CNDO investigation[6] indicates that this bond weakening is due to the interaction between sulfur 3d orbitals and bent σ bonds of the C_3 ring. Reflected this feature of bonding in trithiocyclopropenium ion, the reaction of 1 with nucleophiles proceeds usually in the direction (2) of the ring opening to provide useful products. Since our finding on the ring expansion to pyrroles by the reaction of 1 with hexamethylphosphorous triamide,[1] we developed the new "one-pot" synthesis of pyrroles from 1 and amines under mild reaction conditions (eq 3). The reaction pathway is supposed to involve the initial nucleophilic attack of amine on the cyclopropenium ring, followed by the



ClO_4^- (R = tBu)

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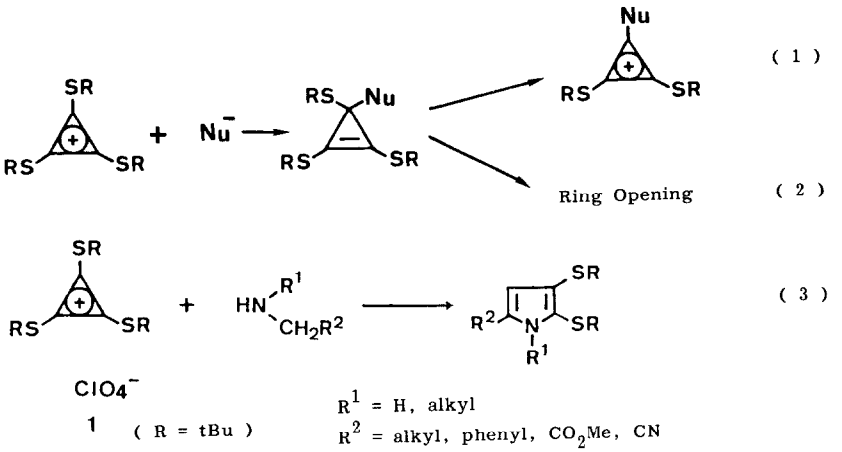
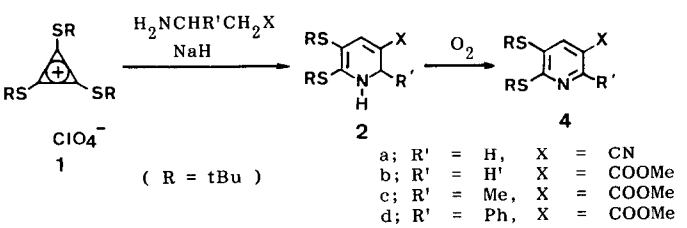


ring opening intermediate leading to the five membered ring formation. This strategy is quite different in concept from the other methodologies by the use of a three carbon fragment such as α-oxoketene dithioacetals[7,11], α-(aryl)-thiovinyl isocyanate,[8] and tosylmethyl isocyanate.[9] Furthermore, our method involves the one-step synthesis of the hitherto unknown class of heterocycles functionalized by sulfur atoms.[10,11]. Since the alkylthio group attached to the heterocycles ring can be replaced by other functional groups,[7,12] the trithiocyclopropenium salt is considered to be a very useful building block for heterocycle synthesis. This strategy for the five membered heterocycle synthesis might be extensively applied to six- and seven-membered heterocycle syntheses. In this paper, we present such methods for the synthesis of 2,3-bis(*tert*-butylthio)pyridines and of 2,3-bis(*tert*-butylthio)-1,5-benzodiazepines. Of special interest is that the exclusive formation of benzimidazoles was found in the reaction of 1 with *o*-phenylenediamines in methanol, in contrast to the formation of 1,5-benzodiazepines in dimethylformamide.

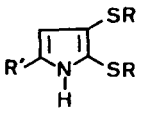
Results and Discussion

First, as the example of the ring expansion reaction of tris(*tert*-butylthio) cyclopropenium perchlorate (1) we describe the synthesis of pyridines by the reaction with β-amino acid derivatives. The reaction of 1 with β-aminopropionitrile in the presence of sodium hydride at 80°C gave 1,2-dihydro-3-cyano-5,6-bis(*tert*-butylthio)pyridine (2a) in 60% yield. The structure of 2a was established by the elemental analysis and spectral data. The ir spectrum revealed a strong band at 3400 cm^{-1} and a weak band at 2220 cm^{-1}, assigned to the N-H and C-N streching mode, respectively. Further evidence was obtained from the



^{1}H NMR spectrum, which showed a 2H doublet at δ 4.01 (J = 3.8 Hz) and a 1H broad doublet at δ 4.34, assigned to the methylene proton at C-2 of dihydropyridine ring and N-H proton, respectively.

It is reported that the anion of azapentadiene give rise to the electrocyclic ring closure to provide a five-membered heterocycle.[13] When the reaction of 1 with ethylamine or phenethylamine was carried out in the similar reaction condition, formation of dihydropyridine was not observed, but 2,3-bis(*tert*-butylthio)-5-methylpyrrole (3a) or 2,3-bis(*tert*-butylthio)-5-benzylpyrole (3b) was obtained in 69% or 65% yield. Accordingly, the presence of an electron-withdrawing substituent in β-position of alkylamine (β-carbonion formation) seems to be necessary for the dihydropyridine formation. Thus when reacted with β-amino acid derivatives as nucleophile the expected 1,2-dihydropyridines 2b-d were found to be produced.



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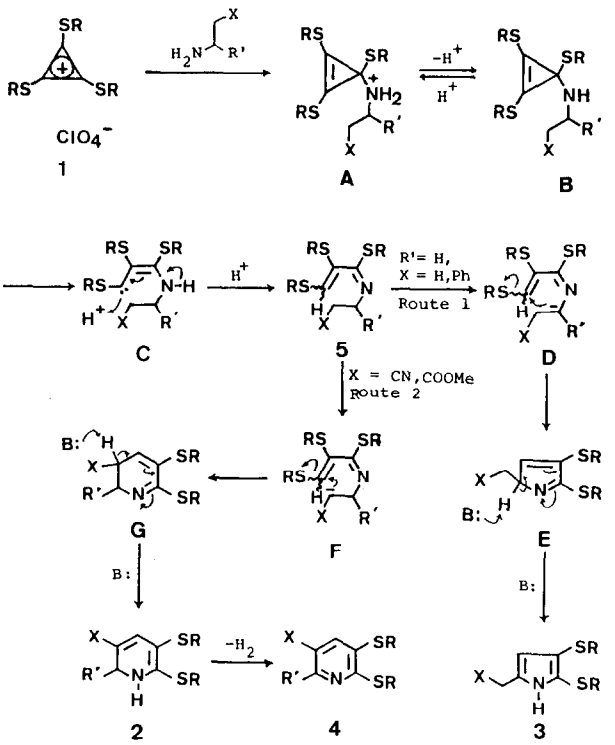
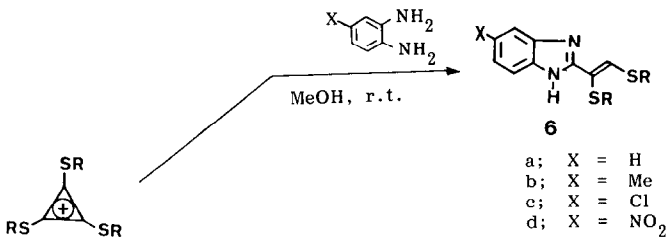
a; R' = CH_3
b; R' = CH_2Ph

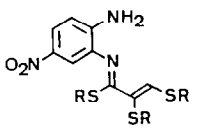
Dehydrogenation of these 1,2-dihydropyridines 2a-d occurs easily to give the corresponding pyridines 4a-d. For example, when the methylene chloride solution of 2a was allowed to stand overnight under contact with air, the quantitative dehydrogenation occurred to provide 2,3-bis(*tert*-butylthio)-5-cyanopyridine (4a), whose ^{1}H NMR spectrum showed charactaristic one hydrogen doublets at δ 7.74 and 8.57 (J = 2.0 Hz), respectively. However, for dihydropyridines, 2b-d, the formation of the corresponding pyridines 4b-d was not observed by contact with molecular oxygen (air), but by treatment with iodine in THF. A plausible pathway for the formation of 2 is shown in Scheme 1. The initial nucleophilic attack of the lone pair of the nitrogen and the subsequent deprotonation[14] afford B, which would be converted to the intermediate 5 by the further ring cleavage and subsequent protonation.[15] When R' is hydrogen or phenyl group, the proton abstraction of 5 should occur to afford D, since the α-proton of 5 is the most acidic one. Under the reaction conditions, the intermediate D may undergo an electrocyclic ring closure to give five-membered ring E, which leads to the formation of pyrrole 3 (Route 1). On the other hand, when R' is electron-withdrawing groups such as CN or COOMe, the proton abstraction of 5 should occur to give F, which might undergo a cyclization to afford the six-membered ring G. Under the basic conditions, the prototropy of G might occur to afford the more stable 1,2-dihydropyridine 2, which is dehydrogenated to produce the pyridine derivative, 4. In order to confirm the intermediate 5 to be an important intermediate in this reaction, an attempt to isolate the ring opening intermediate 5 was made. Thus, treatment of 1 with β-aminopropionitrile in methylene chloride at room temperature for 0.5h resulted in the quantitative formation of the intermediate 5a. Warming a mixture of 5a and sodium hydride as a base in DMF for 2h afforded 2a in 66% yield. It is therefore suggested that 5a is certainly the intermediate for the 1,2-dihydropyridine formation. This dihydropyridine ring formation is regarded as the six-membered ring construction by the combination of the three atoms fragment (C-C-N) of amine having an electron-withdrawing group at β-position and the three carbons of the C_3 ring of 1. If we use a four atoms fragment (e.g. N-C-C-N), a seven-membered heterocycle could be formed by the three carbon homologation of 1. However Eicher et al.,[4o] have reported that the reaction of 3-ethoxy-1,2-diphenylcyclopropenium ion with *o*-aminophenol and *o*-aminothiophenol does not afford the seven-membered heterocycle but the corresponding benzazole.

Scheme I



In their reactions, the cyclopropenium ion (C_3 ring) has served as the one carbon homologator in the heterocycle formation. We have examined which type of homologation leading to the heterocycle formation occurs in the reaction of 1 with *o*-phenylene diamines. When 1 was allowed to react with *o*-phenylene diamine in methanol at room temperature, (Z)-2-[1',2'-bis(*tert*-butylthio)vinyl]benzimidazole (6a) was obtained as a sole product in 77% yield. The structure of 6a was established from its analitical and spectral data.[16] Raney nickel treatment of 6a in ethanol afforded 2-ethylbenzimidazoles as the reductive desulfurization product. The reaction of 1 with various *p*-substituted *o*-phenylenediamines were also examined. When 1 was allowed to react with 3,4-diaminotoluene and *p*-chloro-*o*-phenylenediamine in methanol at room temperature the corresponding benzimidazole 6b, and 6c, was selectively produced respectively. However, *p*-nitro-*o*-phenylenediamine did not react with 1 at room temperature, but reacted in refluxing methanol to give 6d in 49% yield. Very interestingly, when 1 was reacted with *p*-nitro-*o*-phenylenediamine in DMF at room temperature, the single product could be isolated in 51% yield from the reaction mixture which was *tert*-butyl-2,3-bis(*tert*-butylthio)-N-(2'-amino-5'-nitrophenyl)iminothioarylate (7). Treatment of 7 with sodium hydride in DMF at -40°C did not afford the expected benzimidazole 6d but a new compound, 3,4-bis(*tert*-butylthio)-7-nitro-1,5-benzodiazepine (8e), was isolated in 51% yield. This finding led us to examine the reaction of 1 with *o*-phenylenediamines under the latter reaction conditions. Treatment of 1 with *o*-phenylenediamine in the presence of sodium

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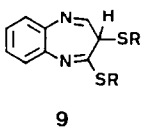
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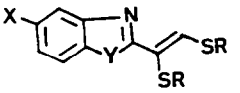
hydride in DMF at -40 °C afforded the corresponding benzodiazepine 8a in 52% yield. A similar ring expansion reaction was also found to occur in the absence of sodium hydride in DMF. The structure of 8a was established from the analitycal and spectral data. The ^{1}H NMR spectrum of 8a showed a broad doublet at δ 4.90 (1H, J = 7.0 Hz, exchangeable with D_2O) and a doublet at δ 6.10 (1H, J = 7.0 Hz) assinged to the N-H and olefinic protons, respectively. Raney nickel treatment of 8a in ethanol afforded 2,3,4,5-tetrahydro-1,5-benzodiazepine. The analogous reactions of 1 with 4-methyl-, 4,5-dimethyl-, and 4-chloro-*o*-phenylenediamines in DMF gave the corresponding benzodiazepines 8b-d. In spite of the quantitative formation of 8 under these reactions, the isolated yields were 41-73%, because the benzodiazepine 8 is prone to isomerize to the more thermodynamically stable form 9 in the purification procedure.[17] The speculative mechanism for the formations of 6 and 8 is shown in Scheme II. The initial nucleophilic attack of *o*-phenylenediamine on the cyclopropenium ring carbon and the subsequent deprotonation would provide the intermediate B, which undergoes the ring cleavege followed by protonation to give the allyl cation D. In methanol D might smoothly undergo cyclization, which involves the intramolecular nucleophilic attack on the carbon of allyl cation species, to result in the formation of benzimidazole 6. In contrast to the formation of 6, the iminothiolacrylate E could be formed by deprotonation of D in the basic DMF solvent. The intramolecular Michael addition of E should give benzodiazepine 8.

Actually, benzodiazepine 8e was obtained by the treatment of iminothiolacrylate 7 with sodium hydride in DMF, and no formation of benzimidazole was observed.

Finally the reaction of 1 with *o*-aminophenols in methanol gave the corresponding benzoxazoles 10a-d in good yields. Furthermore, benzothiazole 10e was also obtained by the reaction with *o*-aminothiophenol in 88% yield. However, the formation of benzoxazepine or benzothiazepine was not observed in DMF solvent.



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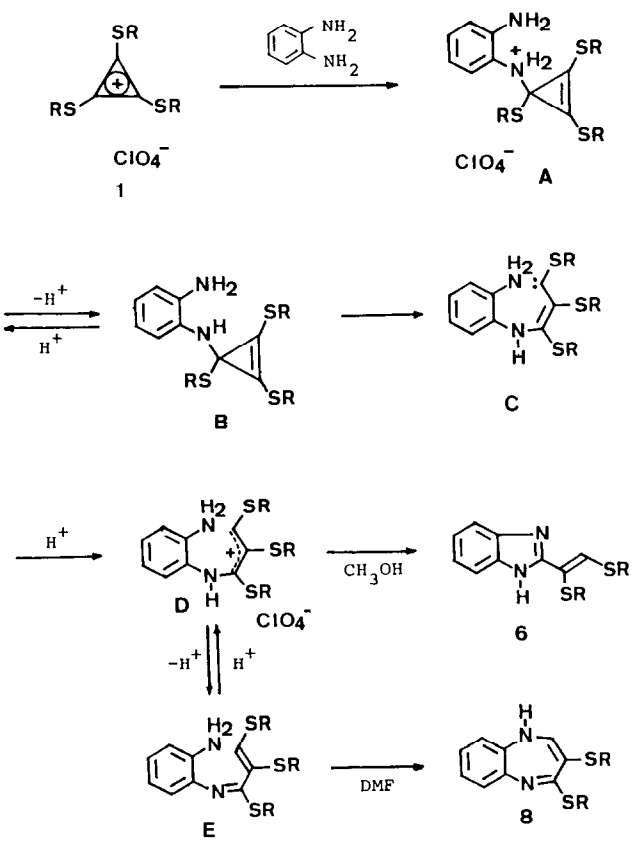
a; X = H, Y = O 96 %
b; X = Me, Y = O 97 %
c; X = Cl, Y = O 76 %
d; X = NO_2, Y = O 73 %
e; X = H, Y = S 88 %

In summary, trithiocyclopropenium salt 1 was found to be an useful building block for the five-, six- and seven-membered heterocycle synthesis. In most cases, 1 behaves as the three carbon homologator to result in the formation of pyridine and 1,5-benzodiazepine, but in some case, 1 behaves as the one carbon homologator to result in the formation of 1,3-benzazoles.

Scheme II



Experimental Section

Infrared spectra were obtained on a Hitachi grating ir spectrophotometer, Model 215. The ^{1}H NMR spectra were recorded on JEOL FX-60 or Varian HA-100D spectrometer, with tetramethylsilane as an internal reference. Mass spectra were measured with Hitachi RMU-6C or RMS-4 mass spectrometer, and the molecular ion (M^+) is indicated. Elemental analyses were carried out at the Elemental Analytical Center of Kyoto University. All melting points were determined on a Buchi capillary melting points apparatus and were uncorrected. Dry nitrogen or dry argon was used in reactions requiring an inert atmosphere. Anhydrous sodium sulfate was employed as drying agent in all reaction work-ups. Reactions were monitored by thin layer chromatography, using Kieselgel 60 F_{254} (Merck). Column chromatography was carried out on silica gel (Wakogel C-200).

Solvents were distilled prior to use: methylene chloride from $CaCl_2$, methanol from Mg, and THF from $LiAlH_4$. Anhydrous DMF was stored over sieves.

Tris-(*tert*-butylthio)cyclopropenium perchlorate (1). Our method to synthesize triaminocyclopropenium salt was applied to the synthesis of 1 with slight modification: A solution of tetrachlorocyclopropene (35 g, 0.2 mol) and *tert*-butylmercaptane (90 g, 1.0 mol) in methylene chloride (400 ml) was allowed to stand overnight at room temperature. To the reaction mixture was added 70% aqueous perchloric acid (50 ml) with vigorous stirring and ice cooling. After stirring for 2h at room temperature, the mixture was diluted with water (500 ml), washed with water (8 x 300 ml), dried and concentrated in vacuo. The crude 1 was deposited by addition of ether (60 ml) to the residual mixture. The crude salt was collected and recrystallized from methanol to give the pure salt 1 (60 g, 75%) as colorless solid: mp 156°C (lit.[5a] mp 156 °C).

Typical Procedure for Preparation of 1,2-Dihydropyridines from 1.

1,2-Dihydro-3-cyano-5,6-bis(*tert*-butylthio)pyridine (2a). To a solution of β-aminopropionitrile (0.0738 ml, 1.0 mmol) in DMF (20 ml) was added dropwise a solution of 1 (403 mg, 1.0 mmol) in DMF (10 ml) at room temperature. After the reaction mixture was stirred for 0.5h, sodium hydride (in 50% mineral oil, 144 mg, 3.0 mmol) was added and then the reaction mixture was heated at 80 °C for 1h. The resulting solution was poured into water (200 ml) containing small amount of NaCl, extracted with ether (50 ml)-hexane (50 ml), dried, and concentrated in vacuo. Purification by chromatography on silica gel eluting with ether-hexane (1:3) and recrystallization from hexane gave the pure 1,2-dihydropyridine 2A (169 mg, 60%) as yellow crystals: mp 71 °C dec.; IR (KBr) 3400, 2200 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.26 (9H, s, tert-butyl), 1.44 (9H, s, tert-butyl), 4.01 (2H, d, J = 3.8 Hz, methylene), 4.34 (1H, broad d, J = 3.8 Hz, N-H), 6.88 (1H, s, pyridine H-4); mass spectrum m/e 282 (M^+).

Anal. Calcd for $C_{14}H_{22}N_2S_2$: C, 59.53; H, 7.85; N, 9.92; S, 22.70. Found: C, 59.53; H, 7.74; N, 9.84; S, 22.47.

1,2-Dihydro-3-methoxycarbonyl-5,6-bis-(*tert*-butylthio)pyridine (2b). Purification by chromatography on silica gel eluting with ether-hexane (1:3) and recrystallization from hexane gave the pure 1,2-dihydropyridine 2b (227 mg, 72%) as pale yellow crystals: mp 83 °C dec.; ir (KBr) 3420, 1720 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.26 (9H, s, *tert*-butyl), 1.43 (9H, s, *tert*-butyl), 3.70 (3H, s, methyl), 4.14 (2H, d, J = 3.6 Hz, methylene), 4.38 (1H, broad d, J = 3.6 Hz, N-H), 7.69 (1H, s, pyridine H-4); mass spectrum m/e 315 (M^+).

Anal. Calcd for $C_{15}H_{25}NO_2S_2$: C, 57.10; H, 7.99; N, 4.44; S, 20.33. Found:

C, 57.00; H, 7.91; N, 4.16; S, 20.37.

1,2-Dihydro-2-methyl-3-methoxycarbonyl-5,6-bis(*tert*-butylthio)pyridine (2c) Purification by chromatography on silica gel eluting with ether-hexane (1:3) and recrystallization from hexane gave the pure 1,2-dihydropyridine 2c (178 mg, 54%) as pale yellow crystals: mp 90 °C dec.; ir (KBr) 3380, 1720 cm^{-1}; ^1H NMR (CCl_4) δ 1.19 (3H, d, J = 6.8 Hz, methyl), 1.28 (9H, s, *tert*-butyl), 1.48 (9H, s, *tert*-butyl), 3.74 (3H, s, O-methyl), 4.40-4.86 (1H, m, methylene), 7.17 (1H, s, pyridine H-4); mass spectrum m/e 329 (M^+).

Anal. Calcd for $C_{16}H_{27}NO_2S_2$: C, 58.32; H, 8.26; N, 4.25; S, 19.46. Found: C, 58.01; H, 8.10; N, 4.29; S, 19.66.

1,2-Dihydro-2-phenyl-3-methoxycarbonyl-5,6-bis(*tert*-butylthio)pyridine (2d). Purification by chromatography on silica gel eluting with ether-hexane (1:2) and recrystallization from hexane gave the pure 1,2-dihydropyridine 2d (215 mg, 55%) as pale yellow crystals: mp 129-130 °C dec.; ir (KBr) 3350, 1720 cm^{-1}; ^1H NMR (CCl_4) δ 1.15 (9H, s, *tert*-butyl), 1.30 (9H, s, *tert*-butyl), 3.70 (3H, s, methyl), 5.60 (1H, broad d, J = 3.8 Hz, N-H), 5.61 (1H, d, J = 3.8 Hz, methyne), 7.10-7.46 (5H, m, phenyl), 7.33 (1H, s, pyridine H-4): mass spectrum m/e 391 (M^+).

Anal. Calcd for $C_{21}H_{29}NO_2S_2$: C, 64.41; H, 7.46; N, 3.58; S, 16.38. Found: C, 64.33; H, 7.31; N, 3.66; S, 16.19.

2,3-bis(*tert*-butylthio)-5-benzylpyrrole (3b). To a solution of phenethylamine (121 mg, 1.0 mmol) in DMF (20 ml) was added dropwise a solution of 1 (403 mg, 1.0 mmol) in DMF (10 ml) at room temperature. After the reaction mixture was stirred for 0.5 h, sodium hydride (in 50% mineral oil, 144 mg, 3.0 mmol) was added and then the reaction mixture was heated at 80 °C for 1 h. The resulting solution was poured into water (200 ml) containing small amount of NaCl, extracted with ether (50 ml)-hexane (50 ml), dried, and concentrated in vacuo. The residue was chromatographed on silica gel eluting with methylene chloride-hexane (1:1) and recrystallization from hexane gave the pure pyrrole 3b (210 mg, 65%) as colorless crystals: mp 82 °C; ir (KBr) 3450 cm^{-1}: ^1H NMR (CCl_4) δ 1.19 (9H, s, *tert*-butyl), 1.23 (9H, s, *tert*-butyl) 3.92 (2H, s, $-CH_2Ph$), 6.09 (1H, d, J = 2.8 Hz, pyrrole H-4), 7.10-7.40 (5H, m, phenyl), 7.80 (1H, broad s, N-H): mass spectrum m/e 333 (M^+).

Anal. Calcd for $C_{19}H_{27}NS_2$: C, 69.41; H, 8.16; N, 4.20; S, 19.23. Found: C, 68.22; H, 8.41; N, 4.06; S, 19.21.

2,3-bis(*tert*-butylthio)-5-cyanopyridine (4a). A solution of dihydropyridine 2a (282 mg, 1.0 mmol) in methylene chloride (20 ml) was allowed to stand overnight at room temperature. The reaction mixture was concentrated to give the crude 4a (297 mg, 100%), which was purified by recrystallization from methanol to give the pure 4a as colorless crystals: mp 82 °C: ir (KBr) 2220 cm^{-1}; ^1H NMR (CCl_4) δ 1.36 (9H, s, *tert*-butyl), 1.58 (9H, s, *tert*-butyl),7.74 (1H, d, J = 2.0 Hz, pyridine H-4), 8.57 (1H, d, J = 2.0 Hz, pyridine H-6): mass spectrum m/e 280 (M^+).

Anal. Calcd for $C_{14}H_{20}N_2S_2$: C, 59.96; H, 7.19; N, 9.99; S, 22.87. Found: C, 59.95; H, 7.20; N, 9.96; S, 22.68.

General Procedure for Preparation of 6-substituted 2,3-bis(*tert*-butylthio)-5-methoxycarbonylpyridine (4b-d). A mixture of 2b-d (1.0 mmol) and iodine (253 mg, 1.0 mmol) in THF (20 ml) was allowed to stand for 2 h at room temperature. The

reaction mixture was poured into water (200 ml) containing small amount of sodium hydrogen sulfite, extracted with ether (50 ml)-hexane (50 ml), dried, and concentrated. The residue was chromatographed on silica gel eluting with methylene chloride-hexane (1:1) and recrystallization from methanol gave 4b-d as colorless crystals.

2,3-bis(*tert*-butylthio)-5-methoxycarbonylpyridine (4b). 100%; mp 73 °C: ir (KBr) 1720 cm^{-1}; ^1H NMR (CCl_4) δ 1.34 (9H, s, *tert*-butyl), 1.56 (9H, s, *tert*-butyl), 3.87 (3H, s, methyl), 8.02 (1H, d, J = 2.0 Hz pyridine H-4), 8.88 (1H, d, J = 2.0 Hz, pyridine H-6): mass spectrum m/e 313 (M^+).

Anal. Calcd for $C_{15}H_{23}NO_2S_2$: C, 57.47; H, 7.39; N, 4.47; S, 20.46. Found: C, 57.50; H, 7.40; N, 4.49; S, 20.22.

2,3-bis(*tert*-butylthio)-5-methoxycarbonyl-6-methyl-pyridine (4c). 100%; mp 81 °C: ir (KBr) 1712 cm^{-1}; ^1H NMR (CCl_4) δ 1,33 (9H, s, *tert*-butyl), 1.60 (9H, s, *tert*-butyl), 2.78 (3H, s, methyl), 3.85 (3H, s, O-methyl), 8.04 (1H, s, pyridine H-4): mass spectrum m/e 327 (M^+).

Anal. Calcd for $C_{16}H_{25}NO_2S_2$: C, 58.68; H, 7.69; N, 4.28; S, 19.58. Found: C, 58.49; H, 7.91; N, 4.03; S, 19.50.

2,3-bis(*tert*-butylthio)-5-methoxycarbonyl-6-phenyl-pyridine (4d). 100%; mp 101 °C: ir (KBr) 1703 cm^{-1}; ^1H NMR (CCl_4) δ 1.41 (9H, s, *tert*-butyl), 1.63 (9H, s, *tert*-butyl), 3.64 (3H, s, methyl), 7.28-7.68 (5H, m, phenyl), 7.80 (1H, s, pyridine H-4): mass spectrum m/e 389 (M^+).

Anal. Calcd for $C_{21}H_{27}NO_2S_2$: C, 64.74; H, 6.99; N, 3.60; S, 16.46. Found: C, 64.83; H, 7.00; N, 3.39; S, 16.05.

tert-Butyl 2,3-bis(*tert*-butylthio)-N-(2'-cyanoethyl)-iminothioacrylate (5a). To a solution of β-aminopropionitrile (140 mg, 2.0 mmol) in methylene chloride (20 ml) was added dropwise a solution of 1 (403 mg, 1.0 mmol) in methylene chloride (10 ml) at room temperature. After stirring for 1 h, the reaction mixture was washed with water (2 x 100 ml), dried, and concentrated. The residue was chromatographed on silica gel eluting with methylene chloride-hexane (1:1) and recrystallization from methanol gave the pure 5 (305 mg, 82%) as colorless crystals: mp 79 °C; ir (KBr) 2220 cm^{-1}; ^1H NMR (CCl_4) δ 1.40 (9H, s, *tert*-butyl), 1.45 (9H, s, *tert*-butyl), 1.55 (9H, s, *tert*-butyl), 2.60 (2H, t, J = 6.4 Hz, methylene), 3.76 (2H, t, J = 6.4 Hz, methylene), 7.30 (1H, s, olefinic); mass spectrum m/e 372 (M^+).

Anal. Calcd for $C_{18}H_{32}N_2S_3$: C, 58.01; H, 8.66; N, 7.52; S, 25.81. Found: C, 58.22; H, 8.88; N, 7.47; S, 25.66.

Typical Procedure for Preparation of Benzimidazoles from 1. (Z)-2-[1',2'-bis-(*tert*-butylthio)vinyl]benzimidazole (6a). To a solution of -phenylenediamine (208 mg, 2.0 mmol) in methanol (20 ml) was added dropwise a solution of 1 (403 mg, 1.0 mmol) in methanol (10 ml) at room temperature. After stirring for 2 h, the reaction mixture was poured into water (200 ml) containing small amount of NaCl, extracted with ether (50 ml)-hexane (50 ml), dried, and concentrated in vacuo. Purification by chromatography on silica gel eluting with methylene chloride-hexane (3:1) and recrystallization from methanol gave the pure 6a (245 mg, 77%) as colorless crystals: mp 251-252 °C; ir (KBr) 3200, 2960, 1540, 1450 cm^{-1}; ^1H NMR (CCl_4) δ 1.35 (9H, s, *tert*-butyl) 1.52 (9H, s, *tert*-butyl), 7.20-7.60 (4H, m, phenyl), 8.56 (1H, s, olefinic), 9.30 (1H, broad s, N-H); mass

spectrum m/e 320 (M^+).

Anal. Calcd for $C_{17}H_{24}N_2S_2$: C, 63.70; H, 7.55; N, 8.74; S, 20.01. Found: C, 63.52; H, 7.51; N, 8.52; S, 20.14.

(Z)-2-[1',2'-bis(*tert*-butylthio)vinyl]-5-methylbenzimidazole (6b). Purification by chromatography on silica gel eluting with ether-hexane (1:2) and recrystallization from methanol gave the pure 6b (225 mg, 68%) as colorless crystals: mp 223 °C; ir (KBr) 3200, 2970, 1540, 1460 cm^{-1}; ^1H NMR (CCl_4) δ 1.33 (9H, s, *tert*-butyl), 1.41 (9H, s, *tert*-butyl), 2.45 (3H, s, methyl), 7.02-7.52 (3H, m, phenyl), 8.24 (1H, s, olefinic), 9.40 (1H, broad s, N-H); mass spectrum m/e 334 (M^+).

Anal. Calcd for $C_{18}H_{26}N_2S_2$: C, 64.62; H, 7.83; N, 8.37; S, 19.17. Found: C, 64.65; H, 7.96; N, 8.12; S, 19.06.

(Z)-2-[1',2'-bis(*tert*-butylthio)vinyl]-5-chlorobenzimidazole (6c). Purification by chromatography on silica gel eluting with ether-hexane (1:2) and recrystallization from methanol gave the pure 6c (279 mg, 79%) as colorless crystals: mp 212-213 °C; ir (KBr) 3200, 2900, 1530, 1460 cm^{-1}; ^1H NMR (CCl_4) δ 1.37 (9H, s, *tert*-butyl), 1.56 (9H, s, *tert*-butyl), 7.23-7.70 (3H, m, phenyl), 8.65 (1H, s, olefinic), 10.90 (1H, broad s, N-H); mass spectrum m/e 354 (M^+).

Anal. Calcd for $C_{17}H_{23}N_2S_2Cl$: C, 57.52; H, 6.53; N, 7.89; S, 18.07. Found: C, 57.53; H, 6.33; N, 7.65; S, 17.95.

(Z)-2-[1',2'-bis(*tert*-butylthio)vinyl]-5-nitrobenzimidazole (6d). A mixture of 1 (403 mg, 1.0 mmol) and p-nitro-o-phenylenediamine (306 mg, 2.0 mmol) in methanol (20 ml) was heated at reflux for 4 h. The reaction mixture was poured into water (200 ml) containing small amount of NaCl, extracted with ether (50 ml)-hexane (50 ml), dried, and concentrated. The residue was chromatographed on silica gel eluting with ether-hexane (3:8) to give the benzimidazole 6d (177 mg, 49%), which was obtained by recrystallization from ethanol as orange crystals: mp 254-255 °C; ir (KBr) 3350, 2960, 1530, 1340 cm^{-1}; ^1H NMR (CCl_4) δ 1.33 (9H, s, *tert*-butyl), 1.47 (9H, s, *tert*-butyl), 7.40-8.58 (3H, m, phenyl), 8.65 (1H, s, olefinic), 10.90 (1H, broad s, N-H); mass spectrum m/e 365 (M^+).

Anal. Calcd for $C_{17}H_{23}N_3O_2S_2$: C, 55.86; H, 6.34; N, 11.50; S, 17.54. Found: C, 55.58; H, 6.74; N, 11.81; S, 17.30.

Isomerization of (Z)-2-[1',2'-bis(*tert*-butylthio)vinyl]benzimidazole (6a) to (E)-2-1',2'-bis(*tert*-butylthio)vinyl benzimidazole (6a'). A solution of 6a (320 mg, 1.0 mmol) and *p*-toluensulfonic acid (200 mg) in methylene chloride (20 ml) was allowed to stand for 7 days. The reaction mixture was washed with water (2 x 100 ml), dried, and concentrated in vacuo. The residue was chromatographed on silica gel eluting with ether-hexane (1:3) to give the trans isomer 6a', which was obtained by recrystallization from ethanol as colorless crystals: mp 186 °C; ir (KBr) 3200, 2980, 1550, 1460 cm^{-1}; ^1H NMR (CCl_4) δ 1.33 (9H, s, *tert*-butyl), 1.53 (9H, s, *tert*-butyl), 7.10-7.50 (4H, m, phenyl), 7.32 (1H, s, olefinic), 9.66 (1H, broad s, N-H); mass spectrum m/e 320 (M^+).

Anal. Calcd for $C_{17}H_{24}N_2S_2$: C, 63.70; H, 7.55; N, 8.74; S, 20.01. Found: C, 64.00; H, 7.81; N, 8.52; S, 20.04.

Reduction of (Z)-2-[1',2'-bis(*tert*-butylthio)vinyl]benzimidazole (6a) with Raney nickel. A suspension of 6a (320 mg, 1.0 mmol) in ethanol (20 ml) containing excess Raney Ni(W-7) was refluxed for 1 h. After filtration of

nickel, the filtrate was concentrated to give 2-ethylbenzimidazole (93 mg, 64%): mp 162-164 °C (lit.[18] 164-168 °C).

tert-Butyl-2,3-bis(*tert*-butylthio)-N-(2'-amino-5'-nitrophenyl)iminothiolacrylate (7). To a solution of *p*-nitro-*o*-phenylenediamine (306 mg, 2.0 mmol) in DMF (20 ml) was added dropwise a solution of 1 (403 mg, 1.0 mmol) in DMF (10 ml) at room temperature. After stirring for 2 h, the reaction mixture was poured into water (200 ml) containing small amount of NaCl, extracted with ether (50 ml)-hexane (50 ml), dried. and concentrated. The residue was chromatographed on silica gel eluting with ether-hexane (1:4) to give 7 (240 mg, 53%), which was obtained by recrystallization from methanol as dark purple crystals: mp 185 °C; ir (KBr) 3480, 3270, 1610, 1570, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (9H, s, tert-butyl), 1.40 (9H, s, *tert*-butyl), 1.59 (9H, s, *tert*-butyl), 4.50 (2H, broad s, N-H), 6.64 (1H, d, J = 9.0 Hz, phenyl H-6), 7.42 (1H, d, J = 3.0 Hz, phenyl H-3), 7.55 (1H, s, olefinic), 7.83 (1H, dd, J = 9.0 and 3.0 Hz, phenyl H-4); mass spectrum m/e 455 (M^+).

Anal. Calcd for $C_{21}H_{33}N_3O_2S_3$: C, 55.50; H, 7.50; N, 9.20; S, 21.06. Found: C, 55.23; H, 7.29; N, 9.19; S, 21.00.

Typical Procedure for Preparation of Benzodiazepines (8a-d) from 1. 1H-3,4-Bis(*tert*-butylthio)-1,5-benzodiazepine (8a). To a solution of *o*-phenylenediamine (208 mg, 2.0 mmol) in DMF (20 ml) was added dropwise a solution of 1 (403 mg, 1.0 mmol) in DMF (10 ml) at room temperature. After stirring for 2 h, the reaction mixture was poured into water (200 ml) containing small amount of NaCl, extracted with ether (50 ml)-hexane (50 ml), dried, and concentrated in vacuo. Purification by chromatography on silica gel eluting with ether-hexane (1:2) and recrystallization from methanol gave the pure 8a (200 mg, 63%) as pale yellow crystals: mp 136 °C; ir (KBr) 3220, 2960, 1610, 1470 cm^{-1}; ^1H NMR (CCl_4) δ 1.30 (9H, s, *tert*-butyl), 1.53 (9H, s, *tert*-butyl), 4.90 (1H, broad d, J = 7.0 Hz, N-H), 6.10 (1H, d, J = 7.0 Hz, benzodiazepine H-2), 6.30-7.10 (4H, m, phenyl); mass spectrum m/e 320 (M^+).

Anal. Calcd for $C_{17}H_{24}N_2S_2$: C, 63.70; H, 7.55; N, 8.74; S, 20.01. Found: C, 64.00; H, 7.67; N, 8.75; S, 19.81.

1H-3,4-Bis(*tert*-butylthio)-7 (or 8)-methyl-1,5-benzodiazepine (8b). Purification by chromatography on silica gel eluting with ether-hexane (1:2) and recrystallization from ethanol gave the pure 8b (264 mg, 74%) as pale yellow crystals: mp 142 °C; ir (KBr) 3300, 2950, 1600, 1460 cm^{-1}; ^1H NMR (CCl_4) δ 1.27 (9H, s, *tert*-butyl), 1.57 (9H, s, *tert*-butyl), 2.20 (3H, s, *tert*-butyl), 4.60 (1H, broad d, J = 7.0 Hz, N-H), 6.00 (1H, d, J = 7.0 Hz, benzodiazepine H-2), 6.10-6.80 (3H, m, phenyl); mass spectrum m/e 334 (M^+).

Anal. Calcd for $C_{18}H_{26}N_2S_2$: C, 64.62; H, 7.83; N, 8.38; S, 19.17. Found: C, 64.43; H, 7.95; N, 8.28; S, 19.06.

1H-3,4-Bis(*tert*-butylthio)-7,8-dimethyl-1,5-benzodiazepine (8c). Purification by chromatography on silica gel eluting with methylene chloridehexane (1:1) and recrystallization from methanol gave the pure 8c (231 mg, 66%) as pale yellow crystals: mp 158 °C; ir (KBr) 3350, 2950, 1600, 1480 cm^{-1}; ^1H NMR (CCl_4) δ 1.23 (9H, s, *tert*-butyl), 1.53 (9H, s, *tert*-butyl), 2.05 (3H, s, methyl), 2.10 (3H, s, methyl), 4.70 (1H, broad d, J = 7.0 Hz, N-H), 6.00 (1H, s, phenyl), 6.37 (1H, d, J = 7.0 Hz, benzodiazepine H-2), 6.60 (1H, s,

phenyl); mass spectrum m/e 348 (M^+).

Anal. Calcd for $C_{19}H_{28}N_2S_2$: C, 65.47; H, 8.10; N, 8.04; S, 18.40. Found: C, 65.18; H, 8.33; N, 8.06; S, 18.11.

1H-3,4-Bis(*tert*-butylthio)-7 (or 8)-chloro-1,5-benzodiazepine (8d). Purification by chromatography on silica gel eluting with eter-hexane (1:4) and recrystallization from methanol gave the pure 8d (146 mg, 41%) as yellow crystals: mp 160 °C; ir (KBr) 3300, 2940, 1600, 1450 cm^{-1}; ^1H NMR (CCl_4) δ 1.22 (9H, s, *tert*-butyl), 1.52 (9H, s, *tert*-butyl), 5.17 (1H, broad s, J = 7.2 Hz, N-H), 6.20 (1H, d, J = 7.2 Hz, benzodiazepine H-2), 6.30-6.70 (m, 3H, phenyl); mass spectrum m/e 354 (M^+).

Anal. Calcd for $C_{17}H_{23}ClN_2S_2$: C, 57.58; H, 6.55; N, 7.92; S, 18.12. Found: C, 57.66; H, 6.49; N, 7.88; S, 18.33.

1H-3,4-Bis(*tert*-butylthio)-7-nitro-1,5-benzodiazepine (8e). To a suspension of sodium hydride (in 50% mineral oil, 144 mg, 3.0 mmol) in DMF (20 ml) was added dropwise a solution of 7 (455 mg, 1.0 mmol) in DMF (10 ml) at -40 °C. After stirring for 2 h at -40 °C, the reaction mixture was poured into water (200 ml) containing small amount of NaCl, extracted with ether (50 ml) hexane (50 ml), dried, and concentrated in vacuo. The residue was chromatographed on silica gel eluting with ether-hexane (1:4) to give 8e (189 mg, 51%), which was obtained by recrystallization from carbon tetrachloride as purple crystals: mp 94-95 °C; ir (KBr) 3360, 2950, 1610, 1550 cm^{-1}; ^1H NMR (CCl_4) δ 1.26 (9H, s, *tert*-butyl), 1.56 (9H, s, *tert*-butyl), 5.27 (1H, broad d, J = 7.0 Hz, N-H), 6.44 (1H, d, J = 7.0 Hz, benzodiazepine H-2), 6.92 (1H, d, J = 9.0 Hz, phenyl), 7.28 (1H, d, J = 1.7 Hz, phenyl), 7.73 (1H, dd, J = 1.7 and 9.0 Hz, phenyl); mass spectrum m/e 365 (M^+).

Anal. Calcd for $C_{17}H_{23}N_3O_2S_2$: C, 55.86; H, 6.34; N, 11.50; S, 17.54. Found: C, 55.64; H, 6.57; N, 11.37; S, 17.24.

^1H NMR Spectrum Measurement of 3H-3,4-Bis(*tert*-butylthio)benzodiazepine (9). A solution of 8a (320 mg, 1.0 mmol) in carbon tetrachloride (0.4 ml) in ^1H NMR sample tube was allowed to stand overnight. The ^1H NMR spectrum showed at δ 1.28 (9H, s, *tert*-butyl), 1.51 (9H, s, *tert*-butyl), 3.25 (1H, d, J = 8.4 Hz, methyne), 7.25 (1H, d, olefinic), and 6.10-7.12 (1H, m, phenyl).

Reduction of 8a with Raney Nickel. A suspension of 8a (320 mg, 1.0 mmol) in ethanol (20 ml) containing excess Raney Ni(W-7) was refluxed for 1h. After filtration of nickel, the filtrate was concentrated to give 2,3,4,5-tetrahydro-1,5-benzodiazepine(100 mg, 68%): mp 103 °C (lit.[19] 103 °C).

Typical Procedure for Preparation of Benz-1,3-azoles (10a-e) from 1. (Z)-2-[1',2',-Bis(*tert*-butylthio)vinyl]benzoxazole (10a). To a solution of -aminophenol (198 mg, 2.0 mmol) in methanol (10 ml) at room temperature. After stirring for 2h, the reaction mixture was poured into water (200 ml) containing small amount of NaCl, extracted with erher (50 ml)-hexane (50ml), dried, and concentrated in vacuo. Purification by chromatography on silica gel eluting with methylene chloride-hexane (1:1) and recrystallization from methanol gave the pure 10a (308 mg, 96%) as colorless crystals: mp 85 °C; ir (KBr) 1550, 1250, 1180, 840 cm^{-1}; ^1H NMR (CCl_4) δ 1.31(9H, s, *tert*-butyl), 1.43 (9H, s, *tert*-butyl), 6.97-7.60 (4H, m, phenyl), 8.28(1H, s, olefinic); mass spectrum m/e 321 (M^+).

Anal. Calcd for $C_{17}H_{23}NOS_3$: C, 63.51; H, 7.21; N, 4.36; S, 19.95. Found: C, 63.77; H, 7.26; N, 4.27; S, 20.19.

(Z)-2-[1',2',-Bis(*tert*-butylthio)vinyl]-5-methylbenzoxazole(10b). Purification by chromatography on silica gel eluting with ether-hexane (1:3) and recrystallization from methanol gave the pure 10b (309 mg, 96%) as colorless crystals: mp 73 °C; ir (KBr) 2960, 1550, 1460, 1370, 1180 cm^{-1} ; ^1H NMR (CCl_4) δ 1.34 (9H, s, *tert*-butyl), 1.51(9H, s, *tert*-butyl), 2.46 (3H, S, methyl), 6.96-7.38 (3H, m, phenyl), 8.40 (1H, s, olefinic); mass spectrum m/e 335 (M^+). mass spectrum m/e 321 (M^+).

Anal. Calcd for $C_{18}H_{25}NOS_2$: C, 64.43; H, 7.51; N, 4.17; S, 19.11. Found: C, 64.40; H, 7.58; N, 4.05; S, 19.05.

(Z)-2-[1',2',-Bis(*tert*-butylthio)vinyl]-5-chlorobenzoxazole (10c). Purification by chromatography on silica gel eluting with methylene chloridehexane (1:1) and recrystallization from methanol gave the pure 10c (268 mg, 76%) as colorless crystals: mp 112 °C; ir (KBr) 2970, 1530, 1450, 1375, 1160 cm^{-1}; ^1H NMR (CCl_4) δ 1.34(9H, s, *tert*-butyl), 1,53 (9H, s, *tert*-butyl), 6.90-7.70 (3H, m, phenyl), 8.47 (1H, s, olefinic); mass spectrum m/e 355 (M^+).

Anal. Calcd for $C_{17}H_{22}ClNOS_2$: C, 57.36; H, 6.23; N, 3.94; S, 18.02. Found: C, 57.36; H, 6.36; N, 3.92; S, 18.27.

(Z)-2-[1',2',-Bis(*tert*-butylthio)vinyl]-5-nitorobenzoxazole (10d). Purification by chromatography on silica gel eluting with methylene chloride-hexane (1:3) and recrystallization from methanol gave the 10d (308 mg, 96%) as yellow crystals: mp 157°C; ir (KBr) 2970, 1520, 1440, 1350, 1170cm^{-1}; ^1H NMR (CCl_4) δ 1.37 (9H, s, *tert*-butyl), 1.56 (9H, s, *tert*-butyl), 7.66-7.88 (3H, m, phenyl), 8.70 (1H, s, olefinic); mass spectrum m/e 356 (M^+).

Anal. Calcd for $C_{17}H_{23}N_2O_3S_2$: C, 55.71; H, 6.05; N, 7.64; S, 17.50. Found: C, 55.55; H, 6.03; N, 7.39; S, 17.41.

(Z)-2-[1',2',-Bis(*tert*-butylthio)vinyl]benzthiazole (10e). Purifiction by chromatography on silica gel eluting with methylene chloridehexane (1:1) and recrystallization from methanol gave the pure 10e (297 mg, 88%) as colorless crystals: mp 129 °C; ir (KBr) 1507, 1100, 860 cm^{-1} ; ^1H NMR (CCl_4) δ 1.40(9H, s, *tert*-butyl), 1.53 (9H, s, *tert*-butyl), 7.17-7.98 (3H, m, phenyl), 8.45(1H, s, olefinic); mass spectrum m/e 337 (M^+).

Anal. Calcd for $C_{17}H_{23}NS_3$: C, 60.49; H, 6.87; N, 4.15; S, 28.50. Found: C, 60.66; H, 7.00; N, 4.01; S, 28.63.

Isomerization of (Z)-2-[1',2',-Bis(*tert*-butylthio)vinyl]benzoxazole (10a) to (E)-2-[1',2',-Di-(*tert*-butylthio)vinyl]benzoxazole (10a'). A mixture of 10a (320 mg, 10 mmol) and *p*-toluensulfonic acid (200 mg) in methylene chloride (20 ml) was allowed to stand for 5 days. The reaction mixture was washed with water (2 × 100ml), dried, and concentrated in vacuo. The residue was chromatographed on silica gel eluting with ether-hexane (1:4) to give the trans isomer 10a', which was obtained by recrystallization from methanol as colorless crystals: mp 110°C; ir (KBr) 1950, 1500, 1450, 1370, 1170cm^{-1} ; ^1H NMR (CCl_4) δ 1.28 (9H, s, *tert*-butyl), 1.47 (9H, s, *tert*-butyl), 7.18-7.76 (4H, m, phenyl), 7.58 (1H, s, olefinic); mass spectrum m/e 321 (M^+).

Anal. Calcd for $C_{17}H_{23}NOS_2$: C 63.51; H, 7.21; N, 4.36; S, 19.92. Found: C, 63.44; H, 7.36; N, 4.26; S, 19.95.

Reduction of 10a with Raney Nickel. A suspension of 10a (320 mg, 1.0 mmol) in ethanol(20 ml) containing excess Raney Ni(W-7) was heated at reflux for 1h.

After filtration of nickel, the filtrate was concentrated to give 2-ethylbenzoxazole (108 mg, 73%): mp 210 °C (lit.[20] 210 °C).

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